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*Biomass – a source of chemicals and energy
for sustainable development*

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EDITORIAL

A SPECIAL ISSUE DEDICATED TO

BIOMASS – A SOURCE OF CHEMICAL AND ENERGY FOR SUSTAINABLE DEVELOPMENT

In the top 25 major questions concerning science over the next quarter century, the following question is on 24th place: **"What could replace cheep oil-and when?"** At present, less than 10% of the chemicals and raw materials offered by the chemical industry are generated from biomass.

At the European level it was proposed that 20% of the overall energy consumption by 2020 should covered by renewable energy sources and that 10% of the road transport should run on biofuels. In this context, it seems that biomass will play an important part.

That is why the *Editorial Board of Environmental Engineering and Management Journal* decided to publish a special issue dedicated to the following subject: **Biomass – a source of chemical and energy for sustainable development.** As a consequence this special issue gathered papers which demonstrate that biomass could represent a valuable solution to solve the problem of energy and raw materials for chemical industry and not only. At the same time, a new philosophy could lead to the new opportunities to assure an increasing compatibility between biomass processing and environmental protection according to the concept of green chemistry.

Having in mind that in 2030, 90% of energy consumption will be based on fossil resources, the use of biomass for energy can be one way to reduce the ever-increasing emissions of carbon dioxide, one of the main gases responsible for global warming.

Biomass for energy uses and chemical production presents the following important advantages:

- it is mainly an indigenous source and therefore reduces dependency on energy imports and increase security supply;
- like the other renewable, it has an enormous potential for job creation predominantly in agriculture and forestry and in small and medium sized enterprises;
- technologies for renewable energy carriers of European industry offer promising business opportunities, because world energy consumption is expected to grow;
- in many industries biomass is a by-product of industrial processes, so its utilization solves both a waste and energy problems.

Moral responsibility for future generation forces the industrial nations to aspire to sustainability. In the long term, sustainability cannot rely on finite resources and biomass as renewable raw material could correspond to this concept. All these aspects are demonstrated in the papers published in this special issue. Thus, some of papers present the possibilities to obtain energy and chemicals from biomass using thermochemical, biochemical and chemical ways.

The option for one of them depends on the accessibility of raw material and the efficiency calculated as a function of its characteristics (humidity content, chemical composition and applied technology).

Some applications refer to the utilization of wastes resulted from industry by direct combustion of them or in the mixture with fossil fuels in the cogeneration of energy. There also presented some case studies in Romania, Latvia and Hungary. Biofuels can be obtained by methanization of different wastes resulted from industry. In this case an important role is played by the composition of wastes and microorganisms used for fermentation.

It is important to mention that the application of biotechnological processes which are environmentally friendly allow us to obtain valuable products and their utilization in bioremediation.

Different aspects are developed in this field, such as: immobilization of bacteria, utilization of biomass or compost resulted from it to remove some toxic metal ions.

Very interesting are the aspects concerning cultivation of plants having capacity to synthesize compounds with biological properties for phytotherapy.

Biomass or by products resulted from industry could represent valuable resource to obtain different chemicals (e.g. biocides), and composites.

Therefore, biomass production and its use bring additional environmental and social benefits.

Correctly managed biomass is a sustainable fuel that can deliver a significant reduction in net carbon emissions when compared with fossil fuels. Biomass fuels generate lower levels of such atmospheric pollutants as sulphur dioxide that contributes to "acid rains".

At the same time, by renewable capacity, biomass could provide an important resource for compounds which can be used in a closed cycle due to their compatibility with the environment.

The possibility to include biomass among other solutions to solve the crisis of energy and raw materials is sustained by huge volume resulted by biosynthesis and which is estimated to be of 150.10^9 t/year at world level.

Valentin I. Popa
Guest Editor

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BIOMASS – A SOURCE OF CHEMICALS AND ENERGY FOR SUSTAINABLE DEVELOPMENT

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Abstract

Nowadays, energetic utilization of biomass, biotechnology attracts a big attention not only from the environmental point of view but also have a social, political and economical impact. According to the Directive 2003/30/EC of the European Parliament and the European Council the emission of greenhouse gases can be reduced by 49% using bioethanol produced by a manufacturing process based on corn, instead of crude oil based fuels. Moreover in Hungary from 1st of July 2007 only gasoline with at least 4.4% bioethanol content is commercialized. In this article, some concrete examples of successful developments and/or implementation of biomass projects in Hungary are given such as: production friendly raw synthetic material at "Nitrokémia" chemical plant, manufacture of bioethanol by "Hungrana" and "Győr Distillery" companies, bio-ethyl-tert-buthyl-ether production by MOL Pls. Danube Refinery, research on new generation of biofuels.
The main advantages and disadvantages as well motivations for further research and development of Hungarian bio-industrial and bio-consumer sectors are discussed.

Keywords: agrorefinery, biorefinary, biofuels, environmental friendly materials, Hungarian bio-industries

1. Hungarian developments of biomass projects

Recently, the utilization of the renewable energy sources can hardly reach a ratio of 3.6%. Simultaneously, renewable energy sources get more and more important role in the national energy-policy. By the year of 2010, 3.6% of electric power and 6-7% of the total energy is planned to come from renewable resources. This requires the energetic utilization of biomass in the first place. Previously, the use of mainly primer-biomasses (wood and agricultural waste from agricultural areas) was typical.

During the first phase, in 1980s, there were large improvements in the Hungarian wood processing and agricultural plants. A total capacity of 100 MW heat power had been established, based on burning solid biofuels (wood waste, agricultural residuals). In the second period of program development, improvements began to be made in public heat supply system. Woodchip-based small and medium scale heat plants were built, with a total capacity of 40 MW. In the past 5 years, there was no significant development in heat production. Furthermore - because of the special economical conditions of public heat supply - the profitableness of wood-chip based heat power has been decreasing.

As a result of the changes occurred in the Hungarian wood industry and agricultural plants, some biomass-based heat power plants were closed.

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At the same time, a most meaningful development has begun in electric power production on wood base. Between 2003 and 2005, three of the former coal-based power plants had been changed over to wood-chips. Their total capacity is 100 MW.

The waste heat generated in the process of power production is used in public heat supply. The fuel-demand of the tree power plants is about 800 000 t/year energy-wood. By the building of these plants, Hungary made a large step ahead in the "green" development of the national energy-sector.

In the next period, large improvements are expected. With regard to the EU-regulation on renewable sources, the right valuation of biomass-based energy production and its correct recognition (as a way of contribution to proper land use, rural development, new places of work, etc.) may be realised in the near future in Hungary. In the developments advised by the scientists, the utilization of secondary and tertiary biomasses is also included.

The results of analyses show that Hungary has a large potential of biomass, which can be even enlarged by growing energy plants (wood and other agricultural products). Besides, there is a major potential of secondary and tertiary biomass sources. The role of the technologies by which waste problems can be also solved (e.g. biogas production from waste biomass), is also expected to grow. The recently available biomass would be enough to reach the ratio of 12% of it in the domestic energy supply. In the long term, even the ratio of 17-20% seems to be realistic (Marosvölgyi and Vityi, 2004).

2. Agriculture for industry: the agrorefinery

Hungarian agriculture can increase its output in industrial feedstock in two ways, by:
1. The promotion of existing agro-feedstock, mostly by improving the quality and decreasing the costs. However, this, in general, will not lead to any breakthrough, but may only result in a slow growth of the markets.
2. The development of completely novel kinds of feedstocks, including the required infrastructure.

Usually a crop, „as it is ", will not be applicable for industrial use. Industry is only interested in a certain part, or in a chemical or physical component of the crop, which therefore has to be processed in the agrorefinery. The different „fractions" produced by the agrorefinery are to be sold to various industries, or partially recycled to agriculture, as cattle feed or as organic fertilizer.

The feedstock prepared for industrial application may be chemicals (bulk chemicals like oils, carbohydrates, rubber and gums and fine chemicals like essential oils and intermediates for chemical specialties, pharmaceuticals, pesticides and special polymers) or physicals (like fibres for textile, papermaking pulp, as a major reinforcement element in „wood extenders", like fibreboard, building materials etc., or as a filter in rubber, plastics, adhesives and printing ink).

Biopolymers for industrial programmes have been developed by the University of Pannonia.

Depending on its „function", the agrorefinery may apply simple mechanical and physical processes and may operate on a large scale. Occasionally, the first phase of the processing may begin with mobile total harvesting units, pretreating the crop in the field, separating fractions of interest like crude juices, fibrous fractions etc., which can be transported efficiently to regional plants for further processing. The agrorefinery has to fill the gap between agriculture and the agroindustrial production chains.

The new Hungarian bio-based economy is being established under the following criteria: use of renewable bio-resources (mostly cereals), eco-efficient (bio)-processes and eco-industrial clusters. The latter ones, as the Integrated Regional Bio-refinery, will provide the basis for state, provincial and municipal governments which, together with the industrial and research communities, will stimulate innovation at a local level using local biomass feedstocks and capabilities. These clusters link local research organizations headed by the University of Pannonia in the Transdanubian Region of Hungary, they will provide the infrastructure for the development of bio-products consortia focusing on eco-efficient processing of biomass into an array of value-added bio-products, as a refinery does with petroleum. Special interest should be put in the Transdanubian region regarding the use of glycerol and lactic acid as platform chemicals from which many types of products could be obtained (glycerol esters, ethers and glycerol-carbonates, etc.). Additional (mostly SMEs) companies would co-locate to take advantage of cost savings and synergies with companies and research organizations already in the cluster. As a result, it would be easier for companies in the cluster to attract investment because of improved access to services, technology and opportunities for strategic alliances.

An integrated regional biorefinery model on "lactic acid platform" is under development by the University of Pannonia and the Basque Country Universities for the region using 200 000 t/year grain of wheat as feedstocks.

3. Implementation of biotechnology at "Nitrokémia" Chemical Plant

"Nitrokémia" industrial complex situated near to Lake Balaton was one of the most important Hungarian chemical plants in the last century. Nowadays the main strategy of the Nitrokemia, *Closed Share Company, by Hungary,* is the implementation of environmentally safe industrial technologies such as biorefinery. The biorefinery project aims at the manufacture of lactic acid, environmentally friendly raw synthetic material, obtained from bio-processing of national agricultural crops, for lactic ester solvents production with utilization of all technology by-products.

3.1. Advantages of the biotechnology

- bio-products are environmental friendly materials;
- wrapping material made from poly-lactic acid can be recycled;
- poly-lactic based materials are suitable for full substitution of existing wrapping materials made from PET, polyethylene, polystyrene;
- residues of the non-recycled wrapping material decompose into CO_2 and H_2O under ambient condition; the degradation time is about 3-4 months under composting conditions;
- the energy consumption for production of lactic acid is at least by 30 % lower than that one for production of concurrent synthetic materials;
- poly-lactic based solvents can replace existing toxic hydrocarbon solvents by non-toxic ones.
- the products can be utilized for biogas production and as a fertilizer for agricultural utilization.

3.2. Short description of applied biotechnology

The starch suspension for usage in saccharification is produced with wet separation of the gluten in flour processing unit connected to the mill. The bran obtained from milling of corn is utilized as an energy source. The glucose is produced with a help of lactic acid bacterium after the saccharification and the dissolution process of the starch suspension in the presence of enzyme. The lactic acid fermentation of glucose is achieved by ammonium hydroxide neutralization. The ammonium lactate solution of high purity is obtained by applied several stages separation method including micro-, ultra-, nano-filtration. The collected bacteria after filtration, dissolved proteins, oligosaccharides and other non recyclable by-products are used for biogas production. The three-stage evaporator is applied for concentration of filtrated ammonium-lactate solution. It should be mentioned that the concentrated ammonium-lactate itself is already a market product. The addition of butanol to the concentrated ammonium-lactate produces the butyl-lactate. The obtained solution is purified by the distillation process or could be converted to ethyl-lactate by esterification.

High purity lactic acid solution is generated by hydrolysis of butyl-lactate.

It is worth to mention that the polymer manufacturing is planned to produce up to 20 000 t/year biodegradable poly-lactic acid and the polymerization technology as well as whole polymer manufacture is ready for implementation.

Moreover, the water treatment facilities, the cooling system, bran remained from milling process and all liquid wastes for utilization in biogas production as well as the power facility for generating biogas are additional units of the biorefinery plant. The dehydrated sludge or bio-manure is another product of the biogas plant which can be used in the agriculture.

The chosen technology combines the advantages of existing processes. The technology developed allows establishing cost-effective production and can be used easily for further improvement of plant structure.

4. Production and utilisation of bioethanol in Hungary

In Hungary bioethanol is produced by two enterprises, the HUNGRANA Co. Ltd. (Szabadegyháza) and the Győr Distillery Co. Ltd. At the second one, 27-30 thousand tons of food quality alcohol is produced a year.

Direct and indirect impact of the development program (Balatonfűzfő)
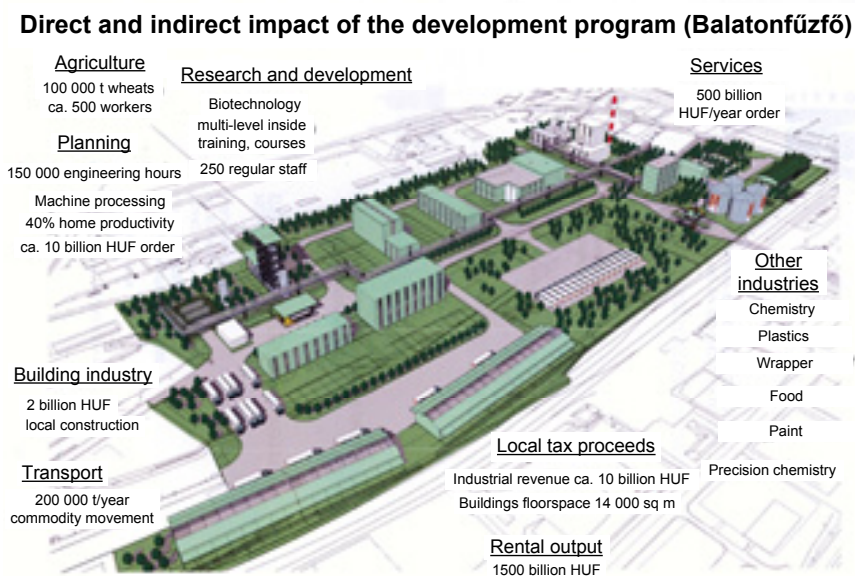
Fig. 1. The planned biorefinery plant in Balatonfűzfő

The Hungrana Co. Ltd., which is owned by the British Eaststarch and the Austrian Agrana-team in 50-50% ownership, produces principally starch, isosugar and alcohols from corn. The corn processing capacity of the plant, which was enlarged, updated and delivered in the summer of 2008, is more than 1 million t/year. From a part of this amount of corn, 135 thousands tons of bioethanol is produced. The rest of the products is mainly the starch (to food and packaging industry and to the production of corrugated paper) and the isosugar (that is the natural sweetening agent of soft drinks, milk and fruit products). From the corn cooking oil, from the high fibre and protein containing part of the corn forage can be produced. The Hungrana Co. Ltd. has the biggest isosugar quota of the European Union (27%, 220 thousand t/year).

One of the most important environmental programmes of the European Union is the reduction of the rate of consumption of fossil fuels. One of the possible solutions is the utilisation of bioethanol in transportation, which is dehydrated alcohol, produced from renewable organic material. The biggest environmental advantage of biofuels is that burning them does not result in extra carbon dioxide because during the reproduction of the plant it is consumed. Considering vehicles with average consumption and the complete process of alcohol production, by the utilization of bioethanol, the global carbon-dioxide emission can be reduced by 50% compared to the use of fossil fuels.

According to the operative European and Hungarian standards, bioethanol can be blended into the gasoline. One alternative (MSZ EN 228:2004) is the blending of low quantity alcohol, the other one is (MSZ CWA 15293) the E85 fuel, which approximately contains 85 % of bioethanol and 15 percent of gasoline.

In Hungary from the 1st of July 2007 only gasoline with at least 4.4% bioethanol content is commercialised (In case of lower bioethanol content extra excise tax has to be paid). The bioethanol can be blended stand-alone or as a component part of molecule (e.g. bio-ethyl-tert-buthyl-ether). From the middle of 2005 the MOL Plc. Danube Refinery (Százhalombatta) produces 55 thousand tons of the latter.

According to the directive 2003/30/EC of the European Parliament and of the European Council the emission of greenhouse gases (GHG) can be reduced by 49% by using bioethanol produced by manufacturing process based on corn, instead of crude oil based fuels. The 49% is a basic value accepted by the EU, but by means of the favourable Hungarian agricultural facility and the front-rank manufacturing process of the Hungrana Co. Plc., the company in Szabadegyháza could realise more favourable GHG-savings, than the average value of 56% of the similar European plants. By the utilisation of 135 thousands tons of bioethanol produced, and the replacement of gasoline with the same energy content, the carbon dioxide emission of Hungary would be lower by some 150 thousand ton per annum.

4.1. Bio-ethyl-tert-buthyl-ether

In Hungary, Bio-ethyl-tert-buthyl-ether is produced at MOL Plc. Danube Refinery from the middle of the year 2005. The plant (55 thousands t/year capacity) had been established by the conversion of a former methyl-tert-buthyl-ether plant. The synthesis is carried out on acidic ion exchange resin catalyst under mild reaction conditions (<100°C, near atmospheric pressure), the feedstock is bioethanol and isobutylene from the C_4-fraction of the fluid catalytic cracking (FCC). Table 1 contains the properties of the bio-ETBE, of the ethanol and of an average gasoline.

The main performance advantages of bio-ETBE are:

- increase of octane number
- internal source of oxygen
- less soluble in water than ethanol
- emission reducing effect

Table 1. Properties of the bio-ETBE, of the ethanol and of an average gasoline

Property	*Gasoline*	*Bio-ETBE*	*Bioethanol*
Molecular mass, g/mol	-	102.18	46.07
Density (20°C), g/cm^3	0.73-0.77	0.747	0.7893
Boiling point, °C	30-220	71.7	78.5
Reid vapour pressure (37,8°C), kPa	45-60	27.6	16.2
Stoichiometric air-fuel mass ratio	14.7	12.1	8.97
Research octane number	88-98	118	111
Motor octane number	80-88	102	92
Energy content, MJ/kg	42-44	36.2	27.7
Evaporation heat, kJ/kg	349	321	839
Solubility in water (20°C), %	-	2.0	in every ratio
Mass ratio of biocomponent, %	-	45.1	100

5. Production and utilisation of fuels from vegetable oil derivatives

In Hungary, there is near 200 thousand tons of fatty acid methyl ester (FAME, biodiesel) production capacity per annum. There are two small plants (<10.000 t/year), one middle plant in Bábolna (>15.000 t/year), and a 150.000 tons/year capacity plant operates in Komárom. Their feedstock is sunflower oil, rapeseed oil, used frying oils and fats, and triglycerides from some other sources. In every plant the alcoholysis (transesterification) is carried out on alkaline catalyst. Approximately 80% of the production is blended into diesel gas oil at the MOL Plc.

The biodiesel plant in Komárom was established by Rossi Biofuels Plc. The MOL Plc. has 25% share of the plant, the other 75% is owned by the Austrian ROSSI Beteiligungs GmbH. The cost of the investment is 40 million Euros. Estimated by MOL, vehicles using (approximately 5v/v%) biodiesels (produced from renewable energy sources) containing fuels emit to the atmosphere 200 thousand tons less CO_2 than vehicles using conventional diesel fuel.

In Hungary, from the 1st of January 2008 diesel fuel has to contain at least 4.4v/v% biodiesel, otherwise extra excise tax has to be paid.

6. Research and development of new generation biofuels

To eliminate the numerous disadvantages (high installation cost, unfavourable properties in use (Tables 2 and 3), not unequivocally positive energy balance related to whole life cycle, insecurity of feedstock, etc.) of conventional biofuels (bioethanol produced from "sugar plants" and cereals, fatty acid methyl esters which are transesterified vegetable oils, called biodiesel), the recognition, the research and development and the adaptation of a new generation of biofuels is needed.

Table 4 summarised an arbitrary classification of biofuels (DOE, 2004; Hancsók, 2005; Hancsók et al., 2005a,b; Hancsók et al., 2006b) according to chronology of recognition, production or rather probable introduction of these. The four generations delineated, the system of short, middle and long term economical producible and usable biofuels are represented on Fig. 2, it shows, that all known fuels can be produced from biomass (Hancsók , 2005).

According to the previous facts the EU has developed and found naturally step by step the expectations related to the production and utilisation of biofuels (Table 5).

In Hungary bioethanol production based on conventional feedstock, and also on lignocelluloses could play an important role in the future, because there is 6-8 million t/year cereal crops.

Table 2. The main disadvantageous properties of bioethanol and gasoline/ bioethanol mixtures

- Lower heat value related to mass,
- Higher consumption in case of working with pure ethanol, and worse mechanical efficiency,
- High hydrocarbon emission, due to evaporation
- Cold start problems in case of working with pure ethanol (low vapour pressure, high evaporation heat),
- Higher ethane, ethylene and acetaldehyde but lower formaldehyde emission,
- Poor lubricating properties (abrasions, surplus lubricant additives),
- Corrosion (iron, steel, zinc etc., more corrosion inhibitor needed),
- In gasoline/ethanol mixtures the presence of water cause phase stability problems,
- Attacks gaskets (elastomers), plastics,
- Fuel tank has to be made of special material,
- Requirement of higher degree of dopping (for example because of sulphate deposits, corrosion, low lubricating ability).

Table 3. The main disadvantageous properties of biodiesels

- For producing NOME significant amount of fossil energy is needed (for example methanol synthesis, heat and electrical energy), and there is significant emission during their production,
- High iodine number (high unsaturated content, poor heat and oxidation stability),
- High water content (biological degradation, corrosion),
- Sensibility at hydrolysis (corrosion),
- Negative effect of phosphorus content on three-way catalyst,
- Methanol content (poison),
- Higher fuel consumption (~10-15%),
- Higher CFPP and viscosity (cold start and spray problems),
- Can not be used in smog danger area because of the high NO_X- and acrolein emission
- In case of commercial vehicles extra costs (motor oil, filter, inactivation of used oil) due to the shorter oil change period; these are valid in case of passenger cars and buses, but only in a small compass; the long, undisturbed service is guaranteed with only proper composition of motor oil
- FAME-resistant fuel piping and gaskets have to be used,
- Higher pressure is needed in the fuel system,
- Storage problems after 5 months,
- Because of the penetration smell of exhaust gas in commercial vehicles additional oxidant catalyst has to be produced in (extra cost) and/or flavour is needed,
- To reduce the disadvantageous properties of FAME-s surplus additive is definitely needed (for examples: flow improvers, oxidation inhibitors),
- Because of the significantly higher production cost, relevant subsidies (for example tax allowance) are needed

Table 4. Classification of biofuels according to chronology of recognition and their introduction

First	*Second*	*Third*	*Fourth*
Generation			
- bioethanol - vegetable oils - biodiesels - blends of previous and petroleum-based fuels	- biocomponent as molecular consituents (bio-ETBE) - bio gas oils (hydroisomerised vegetable oils) - bioethanol from lignocelluloses - biobutanol - biomethane (biogas) - etc.	- higher (>C_2) bioalcohols - biogasoline and bio gas oil (hydrocracking of biooils produced by biomass pyrolysis - biofuels from bio synthesis gas - bioparaffins from carbohydrates - biodimethyl-ether - etc.	- biohydrogen - biomethanol - bio electric current (indirectly for fuel cells) - etc.

FAME: Fatty acid methyl esters (MSZ EN 14214/2004)
F.-T.:Fischer-Tropsch
*High isoparaffin containing gasoline, diesel, baseoil, etc.
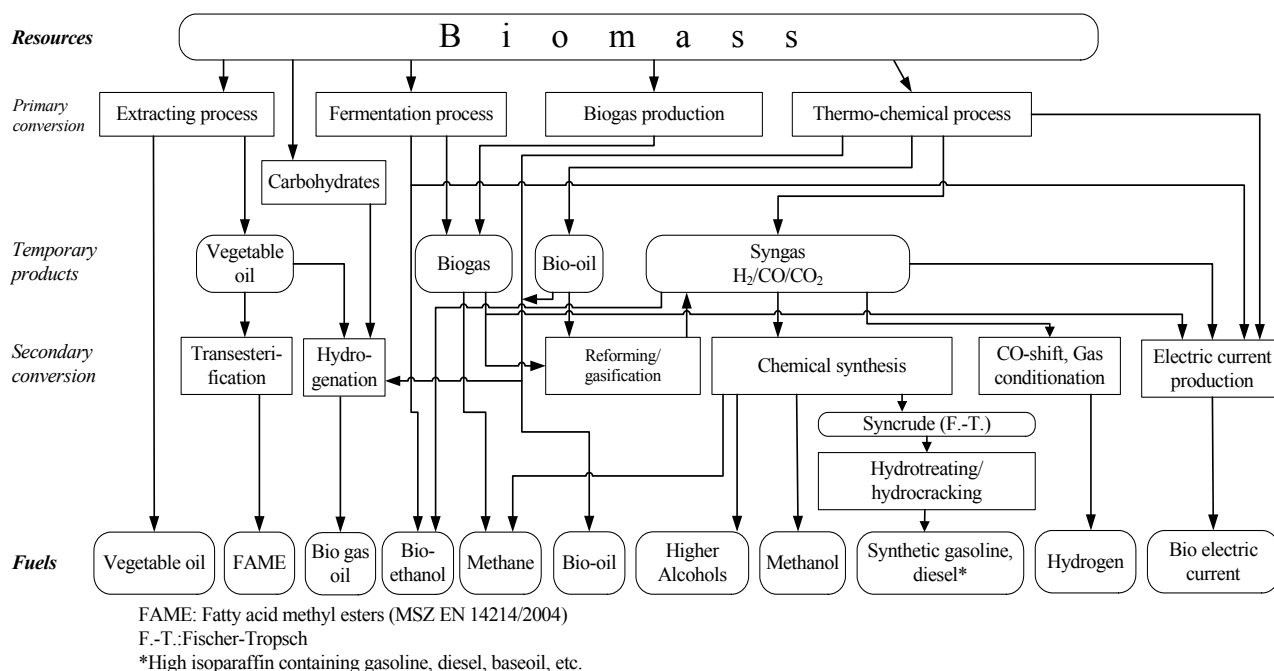
Fig. 2. Production possibilities of motor fuels from biomass

Table 5. Changes of the European Union's directions, expectations related to biofuels

Directives	*Main directions, expectations*
Directive 2003/30/EC	Up to 2005 2.0 %, to 2010 5.75% biofuel content proposed, relative to energy content
COM (2006) 34 „EU startegy for biofuels"	Second generation biofuels (for examples bioethanol from lignocelluloses, synthetic liquid fuels: bio gas oil, BtL) research-development, utilisation
COM(2006) 848 „Renewable energy road map"	Up to 2020 in the EU countries average biofuels ratio have to be at least 10 %

Regarding the oilseeds the case is different. After satisfying the domestic frying oil demand, there are approximately 300-400 thousand t/year of vegetable oil which can be used for other goal.

There are also 40-60 thousand t/year of used frying oil and fat, in addition significant quantity of triglyceride containing feedstock from other sources (e.g. slaughterhouse's adiposes). The high feedstock price of vegetable oils, the expensive processing and conversion of other cheap feedstock into FAME, the disadvantageous properties of the utilisation of biodiesels lead our attention to recognise more valuable (than biodiesel) products with better performance properties, and work out new processes to produce them.

Rsearch and development activities were based on system approach recognition, accordingly the most favourable fuels of Diesel engines are n-paraffins having high cetane number (Fig. 3.).

At the same time flow properties of n-paraffins having high carbon number are bad. (The C_{17} and

higher carbon number hydrocarbons are solids at 20°C and ambient pressure (Table 6).

The iso-derivatives of these n-paraffins have lower freezing-point by 15-30°C, although their cetane numbers are lower by 10-20 units. So that at the University of Pannonia, at the Department of Hydrocarbon and Coal Processing, the main aim of our research and development activity was to produce mixtures of n- and i-paraffins from vegetable oil and/or triglycerides, which have high cetane number (>75-90) and good cold flow properties (CFPP value: from -10 to -20°C).

The new product was named bio gas oil (Hancsók et al., 2006a, Hancsók et al., 2007a, b).

The definition of bio gas oil is: a mixture of iso- and n-paraffins, which is produced by catalytic hydrogenation from triglyceride containing renewable sources (vegetable oils, used frying oil, fats, slaughterhouse's adipose etc.). Fig. 4 demonstrates the reactions taking place under the catalytic hydrogenation of triglycerides, which have been determined in our experiments (Hancsók, 2007; Krár et al., 2007; Krár and Hancsók, 2007).

Table 7 summarises the main properties of the product mixture (bio gas oils), in comparison of the winter grade diesel fuel, and of an average biodiesel.
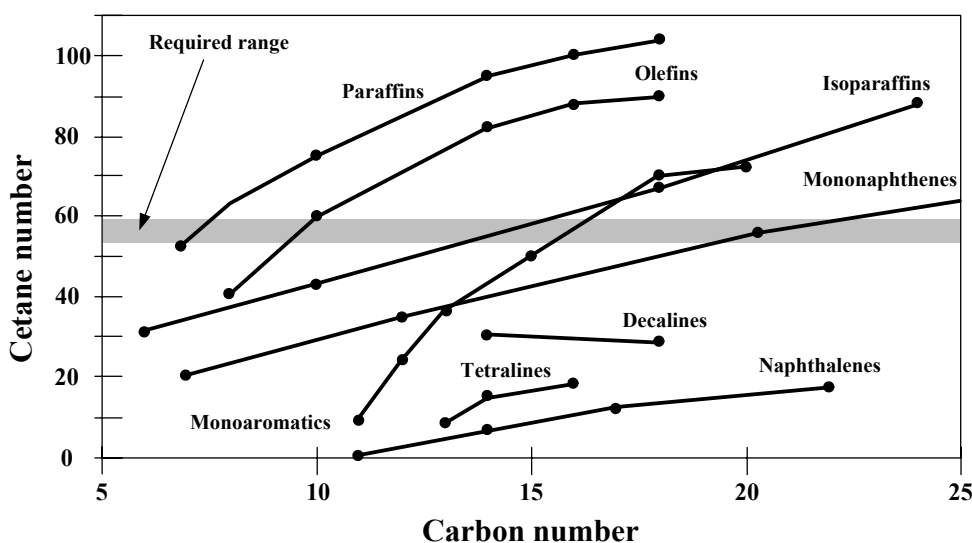
Fig. 3. Changing of the cetane number of different compound types in function of carbon number

Table 6. Some properties of open chained paraffins

Carbon number	Branch	Boiling point, °C	Freezing point, °C
12	-	216	-10
12	2-methyl	211	-46
12	5-methyl	206	-70
13	-	235	-5
13	2-methyl	230	-26
13	5-methyl	227	-69
16	-	287	18
16	2-methyl	281	-10
16	5-methyl	273	-31
18	-	317	28
18	2-methyl	308	6
18	5-methyl	307	-20
20	-	342	37
20	2-methyl	334	18
20	5-methyl	335	-7
24	-	388	51
24	2-methyl	383	39
24	5-methyl	380	18
24	2,4-dimethyl	-	10
24	2,4,6-trimethyl	-	-7
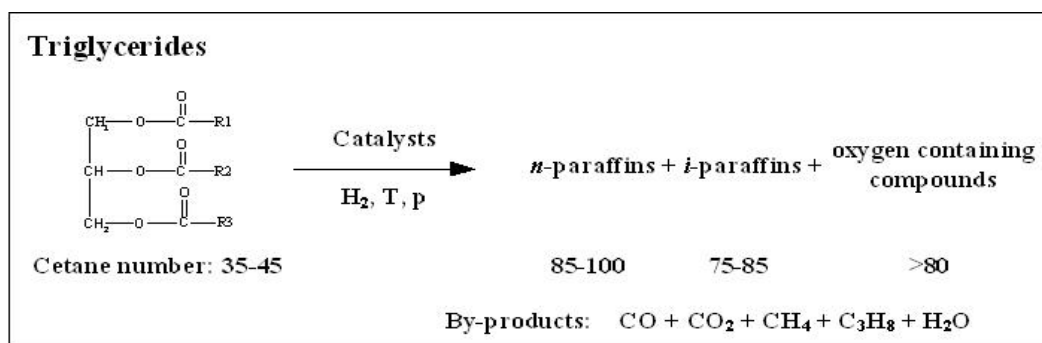
Fig. 4. The reactions taking place under the catalytic hydrogenation of triglycerides

Table 7. Properties of bio gas oil, Diesel fuel and biodiesel

Property	Bio gas oil	MSZ EN 590:2004 diesel fuel (winter grade)	MSZ EN 14214:2004 biodiesel (winter grade)
Density, g/cm^3	0.775-0.785	0.820-0.845	0.860-0.900
Viscosity 40°C-on, mm^2/s	2.9-3.5	2.00-4.50	c.a. 4.5
Cetane number	75-85[a]	min. 51	c.a. 51
Destillation properties			
10%, °C	c.a. 260-270	c.a. 200	c.a. 340
90%, °C	c.a. 295-300	c.a. 350	c.a. 355
Cold filter plugging point, °C	c.a. (-15)-(-35)[b]	< -20[c]	< -20[c]
Heat value, MJ/kg	c.a. 44	c.a. 43	c.a. 38
Heat value, MJ/dm^3	c.a. 34	c.a. 36	c.a. 34
Poliaromatic content, %	0	max. 11	0
Oxygen content, %	0-1	0	kb. 11
Sulphur content, mg/kg	< 1	< 10	< 10
Estimated total life cycle CO_2 emission, kg CO_2/kg	0.9-1.8	3.6-3.8	1.3-2.2

(a: blending cetane number; b: without additives; c: with additives)

The data demonstrate well the numerous advantageous properties of bio gas oils (high cetane number: 75-85, high energy content: approx. 44 MJ/kg, aromatic content: 0; sulphur content <1 mg/kg, CFPP: -15 (-) -30°C, etc.).

To realise the research and development project (the whole innovation chain), the MOL Plc. supported by the NORT (National Office for Research and Technology) established a consortium (2006 December). Members of this consortium are:

- MOL Plc. (Head of consortium)
- OLAJTERV Plc.
- KITE Agricultural Service and Trade Co.
- Biodiesel Ltd.

University of Pannonia, Faculty of Engineering, Institute of Chemical and Process Engineering, Department of Hydrocarbon and Coal Processing

Chemical Research Centre of the Hungarian Academy of Sciences

Hungarian Institute of Agricultural Engineering Department of Mechanization of Plant Production

Regional Innovation Centre of Veszprém Public Utility Company

7. Synthetic bio gas oils

Beside bio gas oils, synthetic bio gas oils have to be mentioned as well. These could be produced from bio synthetic gas of biomass origin. The bio synthetic gas is extracted from bio origin feedstock (including waste) by some different gasification technologies (Hancsók, 2004; Tippe, 2005; Sentenac, 2003). From this cleaned mixture of gas, the product mixture containing also bio gas oil is produced by Fischer-Tropsch synthesis. Fig. 5 contains the summarised block scheme (Hancsók et al., 2005a).

Fig. 6 demonstrates the product yields of a plant which process heavy residue (>360°C) by also isomerisation hydrocracking compared to that of an average European oil refinery. Meanwhile the main properties of synthetic gas oil can be found in Table 8. Based on the foregoing data it could be stated, that bio gas oil could be produced in better quality and higher yield from synthetic gas than from crude oil. This is very important because of the growing demand of middle distillate and of the strict quality expectations (free of sulphur and of aromatic compounds, high cetane number, clean burn etc.).
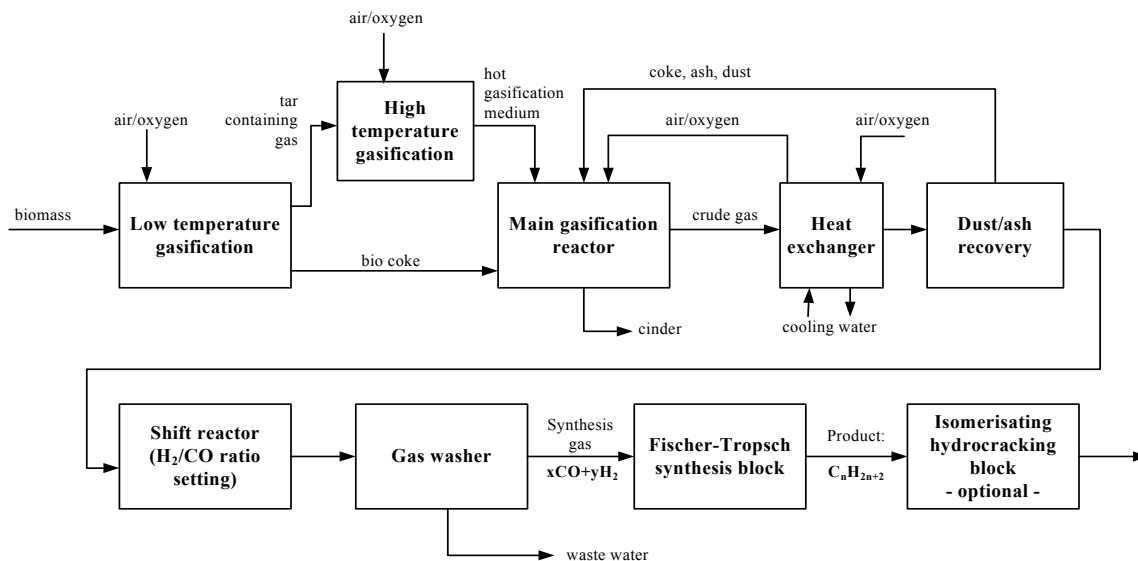
Fig. 5. Block scheme of the Carbo-V® process and of the hydrocarbon synthesis
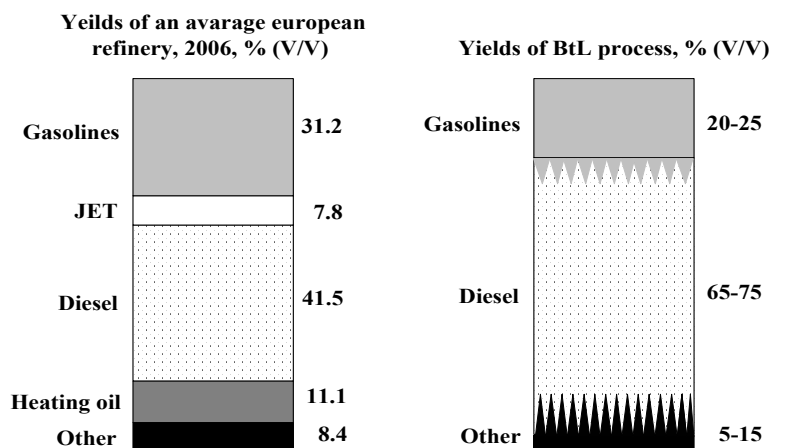
Fig. 6. Comparing the product yields from crude oil and of BtL technology

Table 7. The main properties of synthetic bio gas oil and of crude oil origin diesel fuel

Property	Synthetic bio gas oil *	Bio gas oil	MSZ EN 590:2004 diesel fuel (winter grade)	MSZ EN 14214:2004 biodiesel (winter grade)
Density, kg/m^3	770-785	0.775-0.785	0.820-0.845	0.860-0.900
Viscosity at 40°C, mm^2/s	2.4-4.5	2.9-3.5	2.00-4.50	c.a. 4.5
Cetane number	73-81	75-85**	min. 51	c.a. 51
Distillation properties				
10%, °C	c.a. 209	c.a. 260-270	c.a. 200	c.a. 340
90%, °C	c.a. 331	c.a. 295-300	c.a. 350	c.a. 355
Cloud point, °C	c.a. 0-(-25)	c.a. (-15)- (-35)	< -20	< -5
Heat value, MJ/kg	c.a. 43	c.a. 44	c.a. 43	c.a. 38
Heat value, MJ/dm3	c.a. 34	c.a. 34	c.a. 36	c.a. 34
Poliaromatic content, %	0	0	max. 11	0
Oxygen content, %	0	0-1	0	c.a. 11
Sulphur content, mg/kg	< 10	< 1	< 10	< 10

* gas oil by Fischer-Tropsch synthesis (synthetic crude oil from different origin, synthetic gas) and isomerisation hydrocracking;
** blending cetane number

In Diesel engines, because of numerous performance disadvantage and high installation cost of the first generation biofuels (vegetable oils, biodiesels) it is needed to produce and apply more valuable new generation products with better quality. In short and middle term the spread of bio gas oils (mixture of n- and i-paraffins produced from triglycerides by catalytic hydrogenation) and of synthetic bio gas oils (mixture of n- and i-paraffins produced from bio synthetic gas) is expected. Performance properties of these are significantly more favourable (cetane number: 70-85, CFPP without additives: -10°C (-) -35°C, free of sulphur, nitrogen and olefin, higher energy content, etc.) compared to those properties of first generation vegetable oils and their derivatives. In a refinery the production cost of the bio gas oil is not higher than the production cost of biodiesel, considering its value and net cost it is uniquely competitive with diesel fuel, moreover…! Nowadays the production cost of synthetic bio gas oil exceeds the production cost of others, but around 2015-2020 it would be competitive in a further stage of development.

In case of biofuels, there are different possibilities according to geological regions and nations. Everybody has to make decision considering his own national interest to import the feedstock of fuels or insure oneself at least part of proper feedstock. In Hungary 16 million tons of grains have been grown in an average year, approximately half of it is used in food industry. In case of the rest 8 million t/year, we have to take the decision to what ratio is it economical to export or to produce biofuels. In case of growing of oilseeds, the main problem is that a remarkable quantity of non-food rapeseed oil and used frying oil is exported. After satisfying the total demand of Hungarian food industry, there is approximately 400-500 thousand t/year of oilseed available.

Keeping the principles, that while elaborating development programmes, special attention must be paid for the initiation of home and foreign contractors being interested in this subject and we judge necessary to elaborate a national agro-energetical developing programme because of the importance of developing tasks. Central state support must be assured, too, for professional basement of developments containing state tasks. It is important to bring together environmental-, land-, economical-, agro-, energy-and employment political conceptions. Organizing national agro-energetical coordination is important for coordinating works of state bodies interested in realizing prospective developing tasks, research and developing institutes, industrial, agricultural enterprises and contractors.

Evaluating home results and international developing trends of agriculture originated renewing energy-carrier production, agrotechnical possibilities and technical-economical conditions, the next comprehensive conclusions have to be made:

Looking at natural endowments, potential stocks of Hungary and evaluation of their practical use, biomass can be considered as the most important energy-resource in Hungary;

The country's fire-wood production is 0.32MtOE (Million ton of oil equivalent), which can be increased to 0.7MtOE with energetically use of timber industrial and forestry byproducts, with energetic forests plantation to 1.5MtOE;

Recently 0.1MtOE agricultural byproducts are used for thermoenergetical purposes, which can be increased to 1.0- 1.5 MtOE by proper technologies;

Renewing potential energy-resource produced by anaerobic fermentation of animal water manure and other wastes is significant (0.3-0.5MtOE), complex technologies serving environmental protection and energy-generation purposes need development;

Further potential liquid bioenergy carrier producing ability is about 0.5-1.0MtOE of agro-sectors depending on the size of areas given for that purpose;

Future potential energy generating ability of agro-sectors is 3.0-4.0MtOE without any deleterious effect on food-supply and conditions of soils;

Energetically use of agricultural and forestry byproducts in 10-15% measure does not endanger the organic content and structure of soil;

Energetically use of biomass, plantation of energetic forests and energetic plant production significantly repairs the energetic factors micro- and macro regions;

Technologies for economical use of biomass firing are available, however the technical-economical effectiveness of energy producing and conversion technologies need improvement;

Biomass based fuel production, producing and processing methods, producing technologies and their profitability need further technological development;

Economically operating water manure and waste-water treatment technologies serving environmental protection purposes are to be developed in connection with biogas production direction;

Biomass energy-carrier production extension is reasonable for improving environmental factors and extending application of renewing energy-resources;

For evaluation of biomass energy-resource efficiency, considering economical effect of environmental factors new methods would be required;

While strategic evaluation of biomass originated energy-resource production and utilization, consideration of rational leasehold and employment in the county has got special role;

Technological and economical substantiates of biomass originated energy-carrier production representing the same order as crude oil production, requires significant central developing resources;

Elaboration of this extremely complicated ecological - biological - technical - economical tasks

can be realized only within the frame of a national agro-energetically strategic R+D programme, while certain processes, application of equipment and investments can be done only if we know the exact local endowments in detail and we have evaluation and analysis of it. EU-FP-7 seems to be a powerful tool for the development.

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INTEGRATED STUDIES ON THE BEHAVIOUR OF PERSISTENT POLLUTANTS AND RISKS ASSOCIATED WITH THEIR PRESENCE IN THE ENVIRONMENT

PERSENVIR - Research Grant no. 132 / 2007 of Idei Programe PNCDI-II, Project ID _595

The research project is conceived within the PNCDI-Ideas Program, being an exploratory research project oriented through generation of knowledge for enhancing the contribution of Romanian scientific research to establishment of a solid base of applicative research and technological development by innovatory ideas and by formation of highly qualified researcher. At the same time, the international excellence and visibility are considered by approaching some advanced researches that are interdisciplinary and complex in a field where Romania has a research potential and where o series of results that are comparable to that from European Union were achieved.

Project objectives:

Main objective:

The project aims to contribute to a deep understanding of the environmental behaviour and effects of persistent pollutants (PCs), through elaboration and performing of experiments in the view of development of quantitative relationships and models on their fate, transport and behaviour and on the remediation alternatives of environmental components affected by pollution. The research as well as information on the ways to evaluate the risks associated with the impacts induced in the environment by PCs presence in various environmental matrices will combine both analytical methods and multivariate modeling. Based on experimental and calculated data, methods for various pollutants characterization and ranking will be developed, which facilitate the risk assessment process as well as the decisional process for risk management and remediation of the environmental components affected by the contamination with persistent pollutants.

Specific objectives:

- examine physical, chemical, and biological processes resulting in the migration of persistent pollutants through the individual environmental compartments
- describe chemical, physical, and biological parameters affecting the mobility of PCs in the environment,
- describe and possibly explain observed spatial patterns and temporal trends in the fluxes, concentrations, and relative compositions of various persistent contaminants
- evaluate the relative importance of degradation, sediment burial, export in the atmosphere and outflow to various environmental matrices, bioavailability of PCs in soils and waters and implications for risk assessment
- assess environmental impacts and risks that gather, integrate, and evaluate site-specific information regarding:
  1. environmental fate and transport of contaminants
  2. modes of action of each contaminant under evaluation (effects information)
  3. contaminant uptake by biota from the environment and subsequent movement through food webs
  4. responses of the ecological resources under evaluation to the contaminant exposure

Under this context, the project proposes a coherent, conceptual framework for integrated environmental risk assessment and management, generated by the presence of persistent pollutants (persistent contaminants, PCs) able to compare, evaluate and develop a set of methods and indicators to represent the links between source and exposure, for use in the assessment procedure, based on scientific concepts and methods. They are devoted to improve the use made of the data and knowledge that is already in force in order to obtain more integrated assessments of risks and impacts. These advances will be brought together, in order to identify and fill key gaps in the existing knowledge and methodologies, and develop the tools needed to make them operational. In this context, three key gaps are addressed:

- data and knowledge are spread across disciplines, through different networks and in different databases – tools, methods and collaborative research are needed to bring together and link these different areas of data and knowledge more effectively to inform integrated assessments;
- in many areas, a large gap between science and policy remains – methods are needed to bridge this gap by translating the science that exists into information that is of direct relevance to policy;
- in specific contexts, there are key gaps in data or knowledge that break the continuity of current understanding.

Project description/activities
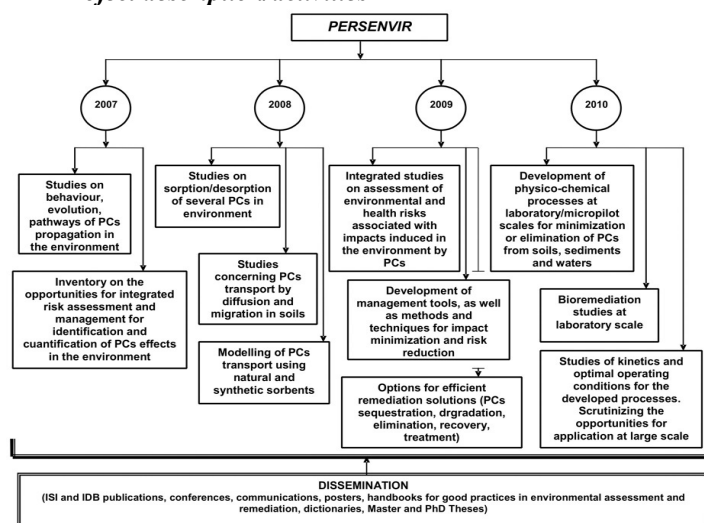
For more information on the *PERSENVIR* Project, please visit: http://persenvir.xhost.ro

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EQUILIBRIUM STUDY OF Pb(II) AND Hg(II) SORPTION FROM AQUEOUS SOLUTIONS BY MOSS PEAT

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Abstract

The sorption of Pb(II) and Hg(II) ions from aqueous solutions by moss peat (from Poiana Stampei, Romania) was studied in a batch system. The data obtained from experiments of a single-component sorption were analyzed using Langmuir and Freundlich models. The Langmuir equation describe sorption isotherm of Pb(II) and Hg(II) with high correlation coefficients, and better than Freundlich model. According to the Langmuir model, the maximum uptake capacities of moss peat for Pb(II) and Hg(II) were obtained as 117.58 mg/g and 81.97 mg/g, respectively. The effect of temperature on the Pb(II) and Hg(II) sorption process onto moss peat was also investigated, and various thermodynamic parameters, such as ΔG, ΔH, ΔS and E_a have been calculated.

Keywords: equilibrium study, lead(II), mercury(II), moss peat, sorption

1. Introduction

Aqueous heavy metal pollution represents an important environmental problem due to their toxic effects and accumulation throughout the food chain. Heavy metals contaminants exist in aqueous wastewaters of many industries, such as metal plating facilities, mining operations and tanneries (Gogate and Pandit, 2004; Paterson, 1985, Srivastava et al., 1999). Among heavy metals, lead(II) and mercury(II) have high prior for removal from aqueous environments (Londrigan et al., 1990). The conventional methods for the removal of these heavy metals from wastewaters include chemical precipitation, membrane separation, ion exchange, adsorption and biosorption (Babel and Krniavan, 2003; Kumar, 2006; Rusten et al., 1997). But, these processes are not economically feasible even for small-scale industries, due to huge capital investment.

Adsorption of pollutants on solid adsorbents is an effective method used for heavy metals removal from aqueous solutions, in special when the adsorbent used is not very expensive (Babel and Krniavan, 2003; Bailey et al., 1999). Thus, natural materials that are available in large quantities or certain waste products from industrial or agricultural operations may have potential as inexpensive sorbents. The moss peat is one example of such low-cost sorbents which can be utilized for the heavy metals removal from aqueous solutions (Brown et al., 2000; Coupal and Spiff, 1999).

In generally, the moss peat is considered a complex natural organic material, resulted from partial degradation of vegetables, in water and in absence of oxygen (Syrovetnik, 2005). Even the moss peat cannot be included into biomass materials category, due mainly to the long time required for its formation, the interaction way with heavy metals from aqueous solutions is similar, with those observed in case of biomass materials. This similarity is determined by the major constituents, such as lignin, cellulose, humic substances, which are present both in moss peat and in biomass (Ho et al., 1996, Horsfall and Spiff, 2005).

Because of these constituents, the moss peat contains in its structure different polar functional groups (ex. –COOH, –OH, –NH₂ etc.), which bind metal ions from aqueous solutions. In addition, the

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moss peat is an inexpensive available material which can be used as an alternative sorbent from removing of heavy metals.

In this paper, the sorption of lead(II) and mercury(II) ions from aqueous solutions by moss peat (from Poiana Stampei, Romania) was studied in a batch system. The data obtained from experiments of a single-component sorption were analyzed using Langmuir and Freundlich isotherm models.

The effect of temperature on the Pb(II) and Hg(II) sorption process by moss peat was also investigated. The thermodynamic parameters (ΔG, ΔH, ΔS, E_a), calculated from experimental results, show that the sorption process is spontaneous and endothermic. These suggest that the chemical interactions play an important role in controlling the sorption rate.

2. Experimental

2.1. Materials

The experiments were carried out using moss peat drawing at 0.5-1.0 m depth, from Poiana Stampei, Romania. The moss peat was dried in air for 4 hours, at 90 ± 2 °C, and then was grounded and sieved until the granulation less than 1-2 mm was obtained.

All chemical reagents were of analytical degree and were used without further purifications. The stock solutions of lead(II) and mercury(II), contains around 2000 mg M(II)/L, were prepared by metal nitrate (Reactivul Bucharest) dissolving in twice distilled water, following by solution standardization (Dean, 1995). The working solutions were obtained by diluting the stock solutions with twice distilled water. The initial pH values (pH 6.0) of working solutions were obtained using acetate buffer (CH_3COOH/CH_3COONa) in case of lead(II), and hexamethylene-tetraamine buffer (HMT / HNO_3) in case of mercury(II).

2.2. Methods

A volume of 25 mL of metal ion solution (lead(II) and mercury(II)) with varying initial metal ion concentration of 40 – 525 mg/L was added on cca 0.125 g of moss peat, in a 150 mL conical flask. The initial solution pH was obtained by adding 5.0 mL of certain buffer (pH 6.0) and was measured with a Radelkis OK-281 pH/ion-meter equipped with a combined glass electrode. A serried of such conical flasks was then intermittent shaken in a water bath at temperature of 5, 25 and 55 °C, respectively.

After shaking the flasks for 4 hours, the phases were separated by filtration, and the Pb(II) and Hg(II) concentrations in filtrate were spectrophotometrically determined (Table 1), using a calibration curve.

Table 1. The analytical characteristics of spectrophotometrical methods used for Pb(II) and Hg(II) analysis
(Flaska and Barnard, 1976; Popa and Moldovan, 1969)

	Pb(II)	*Hg(II)*
Reagent	4-(2-pyridyl-azo)-resorcinol	Methyl-tymol-blue
Linearity domain	0 – 3.0 mg/L	0 – 4.0 mg/L
λ_{max}	530 nm	610 nm
Reference	Blank solution	Distilled water

3. Theory and data evaluation

The amount of metal ion adsorbed by the moss peat at each temperature was calculated using Eq. (1):

$$q = \frac{(c_0 - c) \cdot V}{m} \qquad (1)$$

where: q – amount of metal ion adsorbed per unit mass of moss peat (mg/g), at equilibrium; c_0, c – initial and residual concentration of metal ion in solution, respectively (measured in mg/L); V – volume of initial metal ion solution used (L); m – mass of dry moss peat (g).

Two models were used to describe the experimental sorption isotherms: Langmuir model and the Freundlich model (Cochrane et al., 2006; Ho et al., 2002; Nadeem et al., 2006). The Langmuir equation was chosen for to estimation of maximum adsorption capacity, corresponding to moss peat surface saturation. The liniarized form of Langmuir equation, after rearrangement is (Eq. 2):

$$\frac{c}{q} = \frac{1}{q_0 \cdot K_L} + \frac{c}{q_0} \qquad (2)$$

where: K_L is a constant related to the adsorption/desorption energy (L/mg), and q_0 is the maximum adsorption upon complete saturation of the moss peat surface (mg/g). These constants were determined by plotting c/q against c.

The Freundlich model was chosen to estimate the adsorption intensity of the metal ion towards moss peat, and the linear form is represented by Eq. (3):

$$lg\, q = lg\, K_F + \frac{1}{n} lg\, c \qquad (3)$$

where: K_F – Freundlich constant, is an indicator of the sorption capacity; n – constant that characterizes the affinity of the metal ion towards the moss peat. A plot of $lg\, q$ in function of $lg\, c$, yielding a straight line indicated the confirmation of the Freundlich adsorption isotherm. The Freundlich constants, K_F and n, can be determined from the intercept and slope, respectively.

In these systems, the free Gibbs energy change (ΔG) is the driving force and the fundamental criteria of spontaneity. As is known, the processes occur spontaneously, at a given temperature if ΔG is a negative quantity. The free energy of the sorption process was calculated from the Langmuir constant using Eq. (4):

$$\Delta G = -RT \ln K_L \qquad (4)$$

where: R is the universal gas constant, 8.314 J/mol K; T is absolute temperature, K.

The other thermodynamic parameters, such as enthalpy change (ΔH) and entropy change (ΔS) may be determined from the slope of linear dependence $\ln K_L$ against $1/T$, and using Eq. (5):

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad (5)$$

The activation energy (E_a) was obtained from the slope of plot $\ln (1-\theta)$ against $1/T$, where the surface coverage (θ) was calculated from the relation (6):

$$\theta = \left(1 - \frac{c}{c_0} \right) \qquad (6)$$

where: c, c_0 are the initial and residual concentration of metal ion in solution, respectively (mg/L).

4. Results and discussion

4.1. Effect of temperature

The effect of temperature on the Pb(II) and Hg(II) sorption from aqueous solutions by moss peat was studied by varying the temperature between 5 and 55 °C. The results presented in Fig. 1a and 1b showed that the sorption of metal ions by moss peat increase with the increase of temperature.

This is because with the increasing of temperature, the attractive forces between moss peat surface and metal ions are stronger and the sorption increase. This behaviour is typical for the adsorption of most metal ions from their solutions onto natural materials (Chong and Volesky, 1995; Ho et al., 1996).

The temperature increase was observed to be in two stages, with exception of Pb(II) adsorption at lower temperature, when three stages are observed. The sorption equilibrium occurs rapidly at lower metal ion concentration, for all studied temperatures and becomes relatively constant at higher concentrations. The equilibrium concentration was obtained at 37 mg/L for Pb(II) and 49 mg/L for Hg(II), and are not significant different from a temperature to other. This indicate that increasing of the metal concentration above the equilibriums concentration of 37 – 49 mg/L may not have any

significant increasing in the sorption of metal ions by moss peat.

(a)

(b)
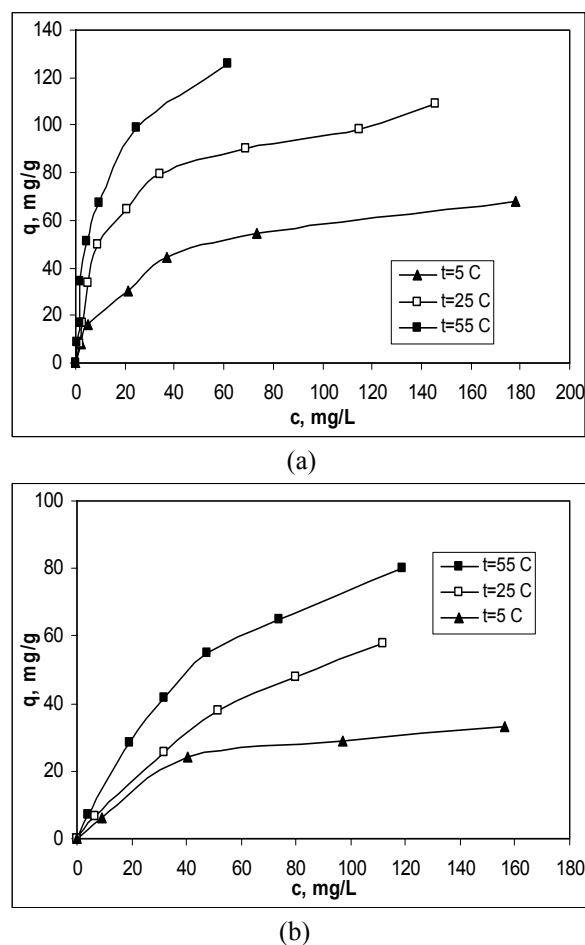
Fig. 1. Effect of temperature on the adsorption on to moss peat: (a) – Pb(II); (b) – Hg(II)

At high temperature, the thickness of the boundary layer increase, due to the increased tendency of the metal to interact with the moss peat surface, which result in an increase in sorption as temperature increases (Do, 1998). The increase in the adsorption with increasing of temperature suggest strong adsorption interactions (ionic or / and covalent) between functional groups of moss peat surface and the metal ion, which support the chemo-sorption.

In order to estimate the adsorption capacities, at various temperatures, the experimental data were fitted into equilibrium isotherm models Freundlich and Langmuir. The liniarized profile of Freundlich and Langmuir sorption isotherms of Pb(II) and Hg(II) onto moss peat, are presented in Figs. 2 and 3. The values of K_F, n, q_0 and K_L, calculated from the intercept and slope of the linear plots and the correlation coefficients (R^2), at each temperature, are summarized in Tables 2 and 3.

The values of correlation coefficients indicate that the Pb(II) and Hg(II) sorption data are very well represented by the Langmuir model ($R^2 >$

0.98), in case of Freundlich model, these have lower values.
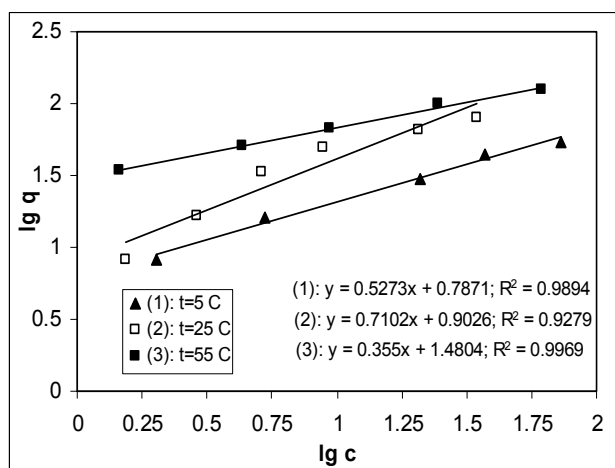
(a)
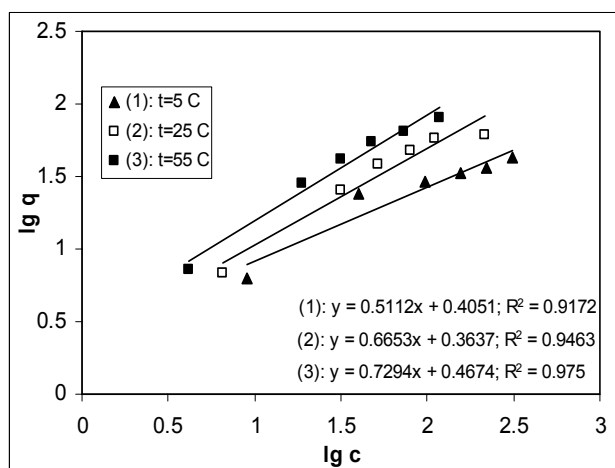
(b)

Fig. 2. Freundlich isotherm plots for the adsorption onto moss peat: (a) – Pb(II); (b) – Hg(II).

The Freundlich constant, n, which estimate the adsorption intensity of the metal ion on the moss peat surface, is higher than 1 for both metal ions at all studied temperatures, indicating the favourable sorption even at higher metal ion concentrations.

In addition, the values of this constant are higher in case of Pb(II) than in case of Hg(II) sorption onto moss peat, and increase with the increasing of temperature.

This suggest that the free Pb^{2+} ions (predominant specie of Pb(II) at pH 6.0) have a higher affinity for superficial functional groups of moss peat than HgO^+ (predominant specie of Hg(II) at pH 6.0) (EpH-web diagrams, 2008).

But, because the experimental values of n, obtained in case of Pb(II) and Hg(II) sorption by moss peat have the same order of magnitude, suggest that the retention of metal ions from aqueous solutions probably take place, in the first moments, by ionic interactions. The values of K_F, which is a measure of the adsorption degree, increase with the increase of temperature.
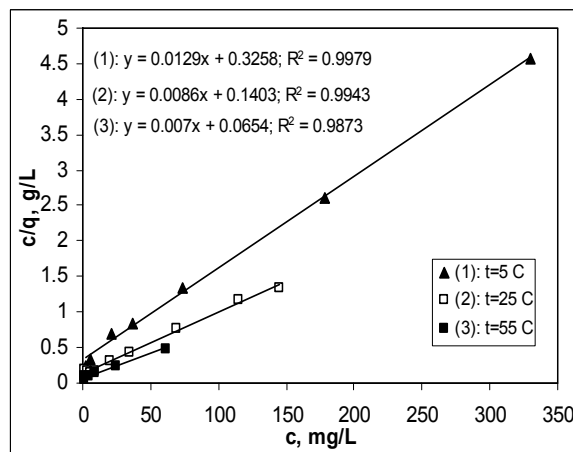
(a)
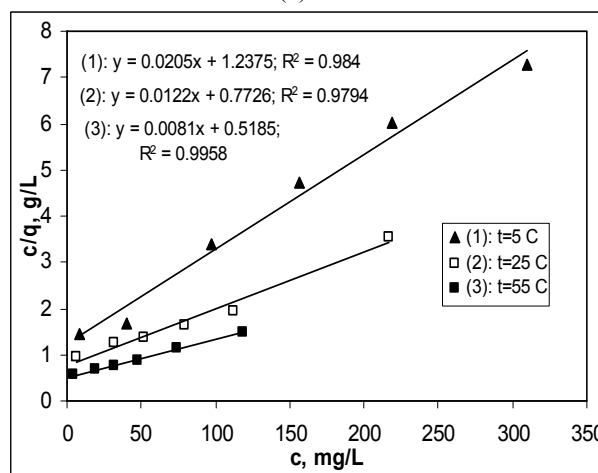
(b)

Fig. 3. Langmuir isotherm plots for the adsorption onto moss peat: (a) – Pb(II); (b) – Hg(II).

Table 2. The values of constants from Freundlich model for Pb(II) and Hg(II) sorption by moss peat, at studied temperatures

t, °C	Pb(II)			Hg(II)		
	R^2	n	K_F, mg L$^{1/n}$/g mg$^{1/n}$	R^2	n	K_F, mg L$^{1/n}$/g mg$^{1/n}$
5	0.9894	1.411	6.136	0.9172	1.372	2.310
25	0.9279	1.905	7.991	0.9463	1.506	2.541
55	0.9969	2.823	30.227	0.9750	1.966	2.933

Table 3. The values of constants from Langmuir model for Pb(II) and Hg(II) sorption by moss peat, at studied temperatures

t, °C	Pb(II)			Hg(II)		
	R^2	q_0, mg/g	K_L, L/mg	R^2	q_0, mg/g	K_L, L/mg
5	0.9979	77.523	0.040	0.9840	48.782	0.010
25	0.9943	117.582	0.061	0.9794	81.975	0.015
55	0.9873	142.854	0.110	0.9958	123.451	0.016

The higher K_F values at higher temperature indicate that more sorption would be expected at these temperatures, and this variation is more pronounced in case of Pb(II) sorption by moss peat than in case of Hg(II).

The most probable temperature of adsorption was further evaluated by the Langmuir model. The Langmuir maximum adsorption capacity (q_0, mg/g), and the Langmuir constants (K_L, L/mg) at the studied temperatures were obtained from the dependences given in Fig. 3. The constants values as show in Table 3 indicate that the optimal temperature of adsorption in utilizing moss peat for the removal of Pb(II) and Hg(II) from aqueous solutions is 55°C.

By comparison of experimental values of K_L constants, obtained for Pb(II) and for Hg(II), it can be observed that on the sorbent surface is not a single sites type. Two or more sites with different affinity may be involved in metal ions sorption onto moss peat. On the other hand, the values of q_0 and K_L increase with the increasing of temperature, showing that the adsorption capacity and intensity of adsorption are enhanced at higher temperatures.

4.1. Thermodynamic parameters of sorption process

The thermodynamic treatment of the sorption experimental results shows that ΔG values were negative at all temperatures investigated, for both metal ions. The negative values of ΔG (Table 4) indicate the spontaneous nature of Pb(II) and Hg(II) adsorption by moss peat.

According to the studied from literature, a ΔG value up to -15 kJ/mol are connected with the physical interactions between sorption sites and metal ion (physical adsorption), while a ΔG values more negative than -30 kJ/mol involve charge transfer from sorbent surface to the metal ion to form a coordination bond (chemical adsorption) (Chong and Volesky, 1995; Ho et al., 1996). The ΔG values obtained in this study for both metal ions, are higher than -15 kJ/mol, but lower than -30 kJ/mol, indicating that in the sorption mechanism the chemical

interactions (both ionic and covalent) have the predominant role in the controlling sorption rate.

The values of ΔH and ΔS were obtained from the slope of plots $ln\ K_L$ vs $1/T$ (Fig. 4) and from Eq. (5), and are presented in Table 4. The positive values of ΔH for Pb(II) and Hg(II) on to moss peat further confirm the endothermic nature of the adsorption process. The positive values of ΔS (Table 4) show that the freedom of metal ions is not too restricted at the moss peat surface.
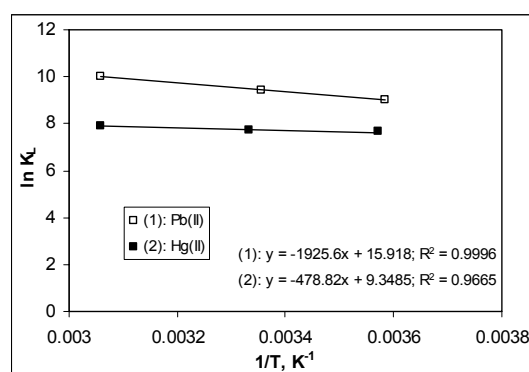
Fig. 4. Plot $ln\ K_L$ against $1/T$ for Pb(II) and Hg(II) sorption on moss peat

In order to further support the assertion that chemical adsorption is the predominant mechanism, the values of activation energy (E_a, kJ/mol) were estimated from experimental data. According with the modified Arrhenius equation, the plot of $ln\ (1-\theta)$ against $1/T$ gave a linear plot with slope of E_a/R, as it is shown in Fig. 5.

The E_a values calculated from the slope of plot were found to be 79.57 kJ/mol and 140.79 kJ/mol for Pb(II) and Hg(II) respectively. The positive values of E_a indicate that the higher temperature favours the metal ion removal by adsorption onto moss peat. On the other hand, the high values of E_a suggest that the metal ion adsorption is chemical controlled process.

Table 4. The thermodynamic parameters for the Pb(II) and Hg(II) adsorption onto moss peat.

t, °C	Pb(II)				Hg(II)			
	ΔG, kJ/mol	ΔH, kJ/mol	ΔS, J/mol K	E_a, kJ/mol	ΔG, kJ/mol	ΔH, kJ/mol	ΔS, J/mol K	E_a, kJ/mol
5	-20.92		132.33		-17.81		113.53	
25	-23.39	16.00	131.58	79.57	-19.26	13.98	110.80	140.79
55	-27.00		131.50		-21.46		108.34	
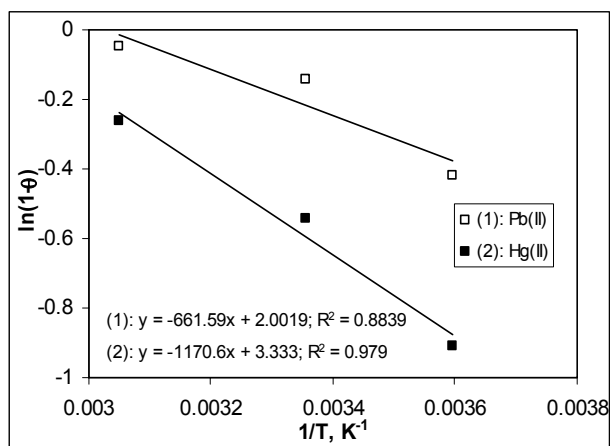
Fig. 5. The dependence *ln(1-θ)* against *1/T* for Pb(II) and Hg(II) sorption on moss peat

5. Conclusions

The experimental results presented in this study clearly establish that the sorption of Pb(II) and Hg(II) onto moss peat is favoured at higher solutions temperatures. The studied temperature range (5 - 55°C) is favourable for the solubility of chemicals in wastewater treatment systems and will also enhance the adsorption rates. The equilibrium data agrees with the Langmuir isotherm. The sorption capacity of Pb(II) is higher than Hg(II), probable because to the nature of predominant species which are present in aqueous solutions with pH = 6.0 (Pb^{2+}, in case of Pb(II) and HgO^+, in case of Hg(II)). However, there is no significant difference in the sorption intensity of the moss peat towards the two metal ions. The values of thermodynamic parameters (*ΔG, ΔH* and *ΔS*) indicate that the sorption process is spontaneous for all studied temperatures and endothermic. The activation energy further support higher solution temperatures and the obtained values indicate that the metal ion adsorption is chemical controlled process.

Acknowledgements

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WOOD-BASED EPOXY RESINS AND THE RAMIE FIBER REINFORCED COMPOSITES

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Abstract

Wood-based epoxy resin was synthesized from resorcinol-liquefied wood. First, wood components were depolymerized and liquefied by reaction with resorcinol. The resorcinol-liquefied wood with plenty of hydroxyl groups could be considered as a precursor for synthesizing wood-based epoxy resin. Namely, the phenolic-OH groups of the liquefied wood reacted with epichlorohydrine under alkali condition. By the glycidyl etherification, epoxy functionality was introduced to the liquefied wood. The wood-based epoxy resin was cured with 4, 4'- diamino diphenyl sulphone (DDS) and the thermal and mechanical properties were evaluated. The flexural modulus and strength of the cured wood-based epoxy resin were comparable to those of the petroleum-based bisphenol-A type epoxy resin (diglycidyl ether of bisphenol-A: DGEBA). The mechanical and adhesive properties of the wood-based epoxy resins suited well for matrix resins of fiber reinforced composites. Therefore, biomass composites consist of ramie fibers and the wood-based epoxy resin were fabricated. The flexural modulus and strength of the biomass composites were equivalent to those of the same fiber reinforced bisphenol-A type epoxy composites.

Keywords: biomass, composites, fibers, modulus, resins, strength

1. Introduction

It is essential that industrial systems respect anti-global warming restriction. An effective use of plant biomass should be an ideal replacement for fossil fuel resource. Moreover, in contrast to fossil fuel resources, plant biomass is a renewable resource, which is another advantage. Therefore, much effort has been devoted to utilizing disposed biomass as a valuable resource for polymers and chemicals.

The liquefaction of wood in the presence of phenols or alcohols had been intensively studied by Lin et al. (1994, 1997), Pu and Shiraishi (1993a, 1993b, 1994), Yao et al., (1993). The liquefied wood has a high reactivity due to the large amount of phenolic-OH groups and alcoholic-OH groups. Using these functional groups, liquefied wood could be converted to phenolic resins and polyurethane forms (Lin et al., 1995a, 1995b; Maldas and Shiraishi, 1996; Yao et al., 1995). Liquefied wood would have further potential and may be used as a resource for other valuable biomass-based materials.

The epoxy resin family has good mechanical and adhesive performances, and is widely used in various fields, such as adhesives, coatings and matrix resins of composites. The first objective of this study is to synthesize wood-based epoxy resins using the liquefied wood as the precursor of the resin. The second objective is to fabricate biomass composites consist of the wood-based epoxy as matrix resin and plant fibers as reinforcements, and to evaluate the mechanical properties.

2. Experimental

2.1. Materials

The wood sample used was 20-80 mesh powder from German spruce (*Picea abies*). Resorcinol, epichlorohydrine, and all other chemicals for liquefaction of wood and synthesis of wood-based epoxy resins were of reagent grade and were used without further purification.

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A mixture of diglycidyl ether of bisphenol-A oligomers (Ep828:Ep1001=7:3 in mass ratio, produced by Japan Epoxy Resin Inc.) was used as a reference epoxy resin. The epoxy resins were cured with a stoichiometric amount of 4,4'-diamino diphenyl sulphone (DDS).

2.2. Synthesis of wood-based epoxy resins

2.2.1 Liquefaction of wood

Wood-based epoxy resins were attained via the following two steps. The first step was the liquefaction of the wood, and the second step was the synthesis of epoxy resins from the liquefied wood.

The wood was liquefied with resorcinol at 250°C in a pressure-proof reaction tube (TVS-1 type, Taiatsu Glass Industry Inc.) made of SUS-316 stainless steel (Pu and Shiraishi,1993a, b). The resorcinol / wood ratio was 1.

In order to quantify the insoluble residue in the liquefaction process, the black liquid after the liquefied treatment was diluted 20 times with 1,4-dioxane, and filtered with a glass-fiber filter (Toyo GA-100: 1μm particle-retainable). After drying in an oven at 80°C, the dioxane-insoluble residue was weighed. The amounts of the residue are expressed as mass percents on the basis of the wood samples used.

The hydroxyl value of the liquefied wood is defined as the amount (milligrams) of potassium hydroxide equivalent to the acetic anhydride consumed in the acetylation of 1 g of liquefied wood sample and was determined according to JIS K0070.

2.2.2 Glycidyl etherification of liquefied wood

The route for the synthesis of wood-based epoxy resins was basically same as the general synthesis method for commercially available epoxy resins. Namely, the liquefied wood with phenolic-OH groups and epichlorohydrine were put into a glass flask and the temperature was raised to 100°C while stirring. The amount of epichlorohydrine was set as the molar ratio of epichlorohydrine for resorcinol in the liquefied wood was 10, which means the epichlorohydrine was put in the reaction system excessively. Next, 50 w/w% sodium hydroxide (NaOH) aqueous-solution, corresponding to two times in molar ratio compared to phenolic-OH groups in resorcinol, was slowly added to the composition using a dropping funnel while stirring. The flask was kept at the same temperature for 2.5 hours in total to achieve the addition reaction of epichlorohydrine and the ring formation of epoxy groups.

The reacted products were diluted ten times with acetone, and salts as by-products were filtered out with a filter paper made of glass-fiber (Toyo GA-100: 1 μm particle-retainable). The acetone and non-reacted excess epichlorohydrine in the filtered resin solution were evaporated using a rotary evaporator at 80°C under reduced pressure.

Then, the wood-based epoxy resins remained in the flask of the evaporator.

The epoxy equivalent of synthesized resin was determined according to JIS K7236, from which the epoxy index (epoxide equivalent / kg resin) was calculated.

2.3. Gel permeation chromatography

The molecular mass distributions of the liquefied wood and the synthesized wood-based epoxy resins were determined using gel permeation chromatography (GPC, PU-2080 HPLC system using JASCO-Borwin-GPC program), equipped with columns, Shodex KF-802 and KF-803. Tetrahydrofuran (THF) was used as the solvent. The average molecular mass was calibrated by mono-dispersed polystyrene standards.

2.4. FT-IR analyses

Infrared absorption spectra (IR) of the samples were measured using an FT-IR 4100 spectrometer (JASCO Corporation) by the KBr-pellet method or the liquid thin layer method.

2.5. Curing of resins

In order to prepare cured resin specimens, mixtures of epoxy resin and DDS were first heated to 80°C to lower the viscosity of the resin compositions, making it easier for the DDS particles to disperse. Then, the resin compositions were held at 60°C under a vacuum to de-gas. The resin compositions were poured into preheated silicone-coated molds and cured at 130°C for 3 hours then at 140°C for 3 hours. Test specimens were processed from the 2 mm thick cured plaques.

2.6. Dynamic mechanical analyses

The temperature dependencies of the viscoelastic properties (storage modulus: E' and mechanical loss tangent: tanδ) of the cured resins were evaluated by dynamic mechanical analyses (DMA) in the bending mode using a dynamic frequency of 1Hz. The instrument used was a DMS6100 (Seiko Instruments, Inc.). Cured resin specimens with a length of 50 mm, a width of 10 mm, and a thickness of 2 mm were machined from 2 mm-thick cured plaques. The samples were tested over a temperature range between -100°C and 180°C with a heating rate of 2°C/minute. The glass transition temperatures (Tg) was defined as the temperature where the tangent line of E' in the glassy region and the tangent line of E' in the transition region intersect.

2.7. Flexural tests for cured resins and composites

The flexural tests for the cured resins and the composites were performed in the three point bending (3PB) mode with a strain rate of 5 mm/min at 25°C.

Specimens with a length of 80 mm, a width of 10 mm, and a thickness of 2 mm were machined from 2mm-thick cured plaques.

2.8. Fabrication of ramie fiber reinforced wood-based epoxy composites

First, uncured resin films composed of mixtures of epoxy resin and DDS were coated on release papers. Additionally, ramie fiber fabrics were cut into 90 mm squares. Each cut fabric was placed between two resin films and pressed to make a fiber / resin prepreg. Next, the prepregs were laid on top of each other and pre-compacted in a nylon-bag sheet under vacuum pressure. The pre-compacted prepregs were placed in a hot-press machine and cured. The curing condition for the composites was at 130°C for 3 hours and 140°C for 3 hours under 10MPa pressure. Test specimens were cut with a diamond saw from the cured composites.

2.9. Scanning electron microscopy observation

The fractured surfaces of the biomass composites after flexural tests were observed using a scanning electron microscope (SEM) "KEYENCE VE-7800". The samples were mounted on brass stubs and were coated with a thin layer of gold using an ion sputter coater "JFC- 1100E" made by JEOL, Japan.

3. Results

3.1. Synthesis of wood-based epoxy resins

Wood powder was liquefied by the reaction with resorcinol. The black, high viscous liquid was considered as a precursor of the wood-based epoxy resin, because the reacted compounds included considerable amount of hydroxyl groups as the reactive sites originated from the wood and the resorcinol.

Fig. 1 shows the relationship between the amount of the insoluble residue and the reaction time for liquefaction. About 1.5 - 2 hours reaction gave the minimum value on the insoluble residue. More than 2 hours reaction resulted in increased insoluble residue, which would indicate that re-condensation of components from degraded wood (polysaccharide and lignin) had occurred (Pu and Shiraishi, 1993a; Yao et al., 1993).

Next, wood-based epoxy resins were synthesized. Fig. 2 shows the synthesized resin after reaction between the liquefied wood (liquefaction time: 1.5 hours) and epichlorohydrine. The resin was in a viscous liquid state at room temperature, which suited for a matrix resin of fiber reinforced composites.

Fig. 3 shows the relationship between the hydroxyl value of the liquefied wood and the heating time at 250°C for the liquefaction with resorcinol. The hydroxyl value became reduced as the heating time was extended, probably due to heat

decomposition and recondensation of the molecular structure (Lora and Wayman, 1978; Pu and Shiraishi, 1993a).
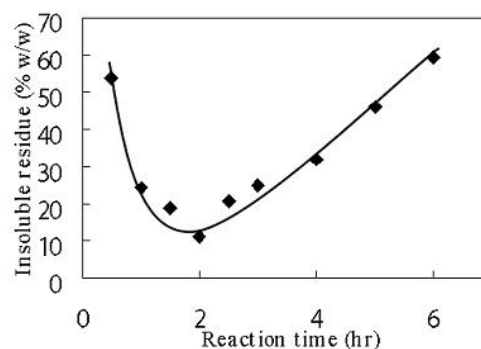
Fig. 1. Insoluble residue (%w/w) generated in the process of liquefaction of wood with resorcinol
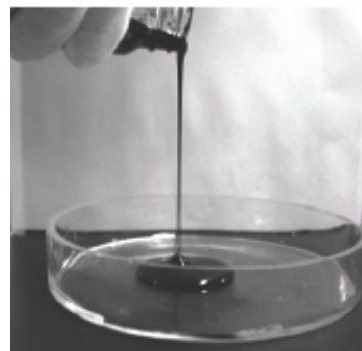
Fig. 2. Liquefied wood-based resin after reaction with epichlorohydrine
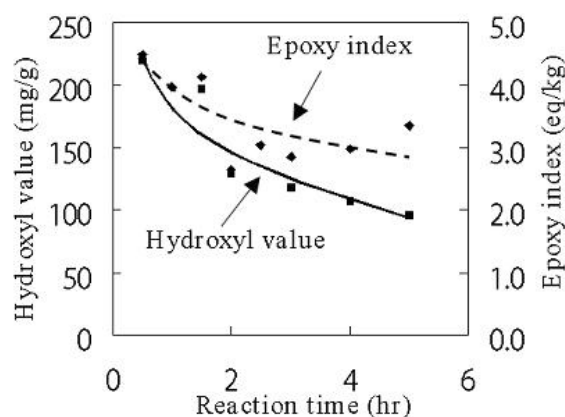
Fig. 3. Relationship between the hydroxyl value of the liquefied wood and the reaction time at 250°C for the wood-liquefaction (resorcinol / wood ratio = 1), and epoxy index of the resin synthesized from the liquefied wood

Fig. 3 also shows the epoxy index of the epoxy resin synthesized from the corresponding liquefied wood. The epoxy index became also reduced as the heating time was extended. The synthesis route of the wood-based epoxy resins appeared to be glycidyl etherification for the

phenolic-OH groups. The epoxy functionality shown as the epoxy index would depend on the concentration of phenolic-OH groups in liquefied wood as the precursors.

Fig. 4 shows the IR spectra of the wood, the resorcinol liquefied wood and the liquefied wood-based resin. The peak of 910 cm^{-1} in spectra shows vibration of the epoxy groups, which indicates the wood-based resin possesses epoxy functionality.
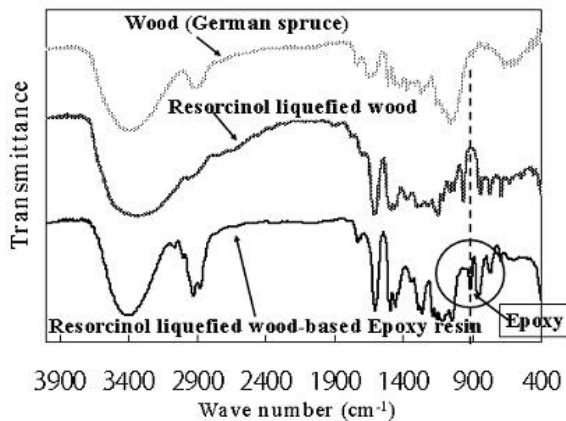
Fig. 4. IR spectra of wood, resorcinol-liquefied wood, and the liquefied wood-based epoxy resin, (liquefaction time = 1.5 hours, resorcinol / wood ratio = 1)

Fig. 5 shows the results of gel permeation chromatography (GPC) for the liquefied wood and for the synthesized resin from the liquefied wood. Namely, the molecular mass of the products, before-and-after the reaction with epichlorohydrine was determined. From the chromatography, the number average molecular mass (Mn) of the liquefied wood was calculated as about 500 by polystyrene standards calibration. This indicated that the polymeric wood components, cellulose, hemicelluloses and lignin, decomposed to a great extent at 250°C. The de-polymerization would have transformed the solid-state wood into the liquid-state material.
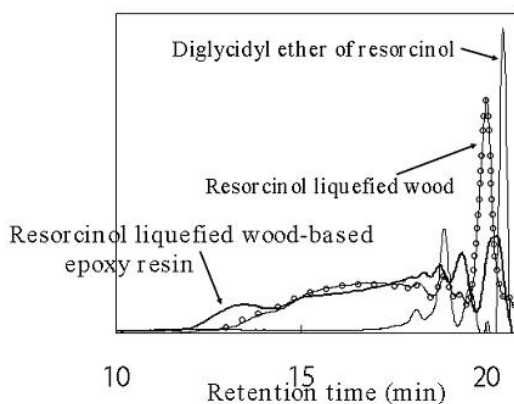
Fig. 5. Gel permeation chromatography (GPC) of the liquefied wood, the synthesized epoxy resin from the liquefied wood, (liquefaction time = 1.5 hours, resorcinol / wood ratio = 1) and that of diglycidyl ether of resorcinol as a reference material

If the liquefied wood reacts with epichlorohydrie, the molecular mass should increase. The distribution of retention time of the synthesized resin was faster than that of the liquefied wood. The Mn of the resin (about 600) became higher than that of the liquefied wood before reaction with epichlorohydrine (about 500). Moreover, the Mn of the resin (about 600) were obviously higher than that of diglycidyl ether of resorcinol (Mn = 390).

All the data of the epoxy index by the titration in Fig. 3, the IR spectra in Fig. 4, and the GPC in Fig. 5 suggest that glycidyl etherification reaction for the phenolic-OH groups of resorcinol-liquefied wood was achieved and the wood-based epoxy resins were synthesized.

3.2. Viscoelastic properties of cured wood-based epoxy resins

Fig. 6 shows the dynamic viscoelastic properties of the wood-based epoxy resins cured with DDS. The cured wood-based epoxy resins showed high stiffness at room temperature and a clear rubbery plateau after the Tg. The storage modulus of elasticity of the resorcinol-liquefied wood-based epoxy resin at 25°C was higher than that of the bisphenol-A type epoxy resin. And the rubbery plateau indicates that a crosslink network structure was definitely formed. The Tg of the resorcinol-liquefied wood-based epoxy resin was lower than that of the bisphenol-A type epoxy resin. The broad Tg region would mean there is a diversity of crosslink structures in the cured resin, which suggests that the glycidyl etherified wood components co-reacted, and were incorporated into the crosslink structures.
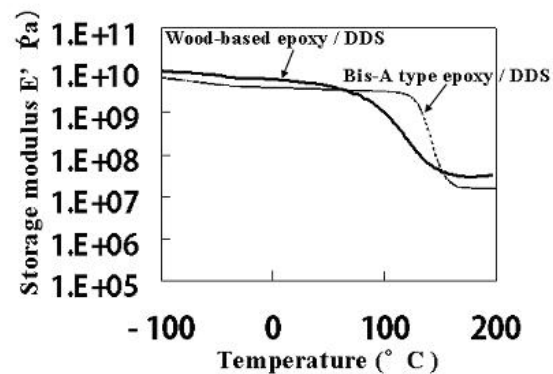
Fig. 6. Dynamic viscoelastic properties of the resorcinol-liquefied wood-based epoxy resin (resorcinol / wood ratio = 1) and the bisphenol-A type epoxy resin (Both were cured with DDS)

3.3. Flexural properties of cured wood-based epoxy resins

Fig. 7 shows the flexural properties (the flexural modulus of elasticity and the flexural strength) of the cured resorcinol-liquefied wood-based epoxy resin at room temperature, in comparison with the bisphenol-A type epoxy resin. The cured wood-based epoxy resin indicated higher flexural

modulus than the petroleum-based bisphenol-A type epoxy resin. The flexural strength of the wood based epoxy resin was almost equivalent to that of the bisphenol-A type epoxy resin. The high stiffness of the wood-based epoxy resin is an attractive property for a matrix resin of fiber reinforced composites.
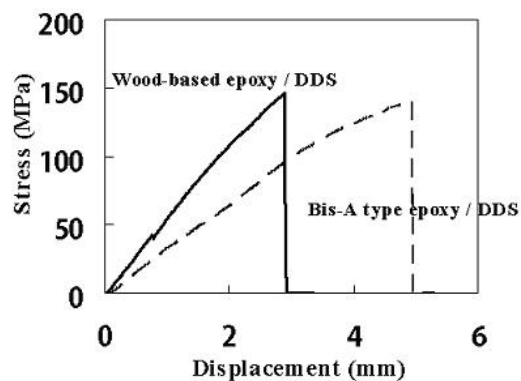
Fig. 7. Flexural stress – displacement behavior of resorcinol-liquefied wood-based epoxy resins and that of the bisphenol-A type epoxy resin. Both were cured with DDS

3.4. Potential of wood-based epoxy resins as matrix resins for biomass composites

In order to find a suitable application for the wood-based epoxy resin, a natural plant fiber reinforced composites consisting of ramie fibers and the wood-based epoxy matrix resin were fabricated, as shown in Fig. 8. Flexural properties of the ramie fibers reinforced wood-based epoxy composites and the same fiber reinforced bisphenol-A type epoxy composites as reference materials were evaluated, as shown in Fig. 9.

The flexural modulus of elasticity (stiffness) and the strength of composites increased with increasing the content of ramie fibers in both composites (Fig. 9), and the stiffness and the strength of the wood-based epoxy composites were equivalent to those of the bisphenol-A type epoxy composites.

The fracture surfaces of the composites were observed using SEM, as shown in Fig. 10. The observed fiber pull-out phenomenon in the fracture surfaces of the composites is a kind of index of the adhesiveness between the fibers and the matrix resin. Namely, the length of exposed ramie fibers which were pulled out from the fracture surfaces of wood-based epoxy composites was shorter than that of bisphenol-A type epoxy composites.

This suggests that the wood-based epoxy resin has better adhesion to ramie fibers than bisphenol-A type epoxy resin. In the high magnified scale in Fig. 11 also, the surfaces of the ramie fibers were covered well with the wood-based epoxy resin in the composites, and the wood-based resin showed better adhesion to the ramie fibers than the bisphenol-A type epoxy resin.

The wood-based epoxy resin includes molecules from cellulose and lignin that would have similar chemical structures to the components of the ramie fibers. That would be one of the reasons to explain the good adhesive property between the wood-based epoxy resin and the biomass fibers.

Fig. 8. Ramie fibers fabric (left) and the ramie fiber reinforced resorcinol-liquefied wood-based epoxy composite (right)
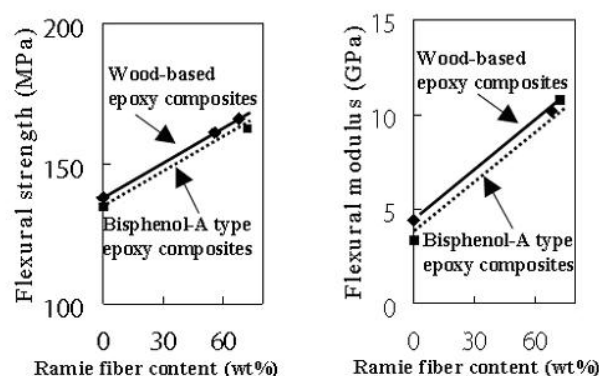
Fig. 9. Flexural strengths and moduli of the biomass composites made from the resorcinol liquefied wood-based epoxy resin and ramie fibers, compared with bisphenol-A type epoxy composites

4. Conclusions

(1) Wood-based epoxy resins were synthesized from resorcinol-liquefied wood biomass.

(2) The DDS cured wood-based epoxy resin indicated higher flexural modulus than the petroleum-based bisphenol-A type epoxy resin at room temperature. The flexural strength of the wood based epoxy resin was almost equivalent to that of the bisphenol-A type epoxy resin.

Fig. 10. Scanning electron micrographs of the fractured surfaces of the ramie fiber reinforced epoxy composites (left: resorcinol-liquefied wood-based epoxy composite, right: bisphenol-A type epoxy composite)
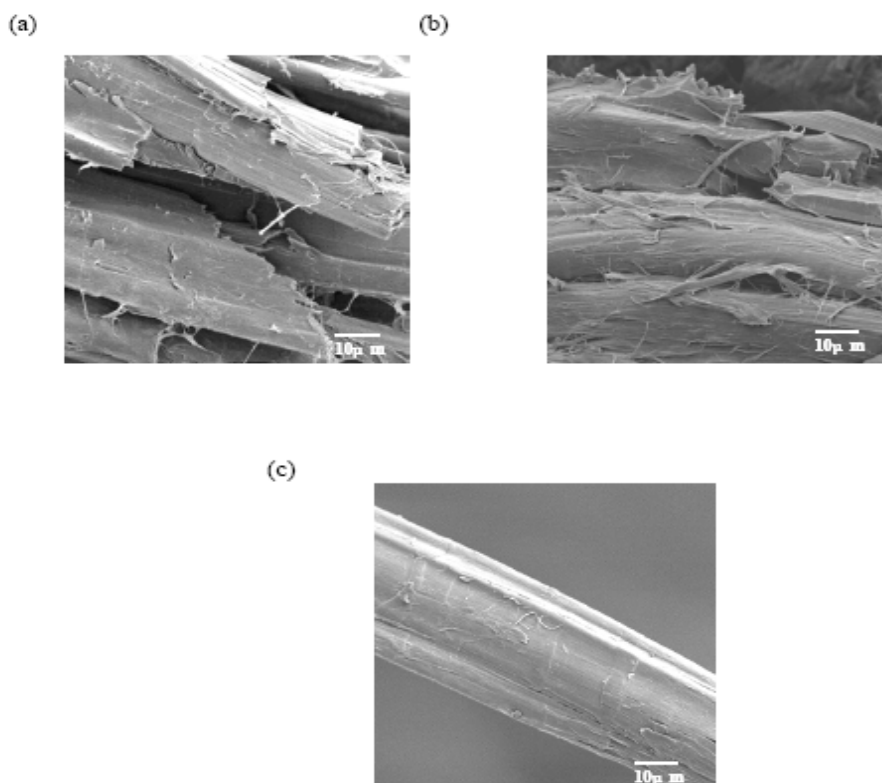
Fig. 11. Scanning electron micrographs of the fractured surfaces of the ramie fiber reinforced epoxy composites: (a) resorcinol-liquefied wood-based epoxy composite, (b) bisphenol-A type epoxy composite, and (c) ramie fiber itself

(3) The wood-based epoxy resins showed good adhesive property to ramie fibers. The high stiffness and the good adhesive property of the wood-based epoxy resin indicate their high potential as matrix resins for biomass-based green composites.

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INFRASTRUCTURE DEVELOPMENT OF QUALITY CONTROL FOR ENVIRONMENTAL FACTORS LABORATORY IN ORDER TO ESTIMATE, CHARACTERIZE AND RECOVERY RENEWABLE AND RECYCLE RESOURCES, USING CHEMICAL AND BIOCHEMICAL PROCESSES
MEDRES LAB, Research Grant no. 94 /2007 (PNCDI II)

The aim of the project is infrastructure development and capacity extension of an analysis and control of environmental factors laboratory in order to estimate, characterize and upgrade renewable and recycled resources, the first regional laboratory specialized in the recovery of this resources using chemical and biochemical processes.

The data provided by the Romanian Accreditation Association (www.renar.ro) shows a deficiency at national level of a specialized laboratory equipped for complex biochemical modifications of these types of resources taking into account environmental protection.

This project has two major objectives:
- **Upgrading** the Environmental Quality Control Laboratory, part of the Faculty of Chemical Engineering and Environmental Protection, which in the 8 years of activity had realized numerous partnerships with different universities, economic agents, research institutes and non-governmental organizations. Using all the available means, the laboratory ensure the logistics for environment components (water, air, soil) quality control, aside with information and education for specialized staff.
- **Development** of new possibilities to evaluate renewable and recycled resources. The uses of the new directions are in agreement with the current researches, the requirements of the industry and the actual European trends. Currently, the renewable and recycled resources are used as rough material for chemical and energetic supplies and the tendency is to substitute conventional initial materials. Based on this information, the recycling of the secondary products can fulfill the sustainable development conditions, becoming the centre of a close functional system compatible with the environment. In the same time, the laboratory will make use of the present knowledge in upgrading secondary products and the development of new processing methods of different resources or special rough materials used for obtaining biopolymers, biofules, proteins and natural regulators substances. The preservation of environment will be assured by special attentions to recycling, closing the circuits and the following of the duration of life function the use of the products. All these problems will open new possibilities for collaboration and to strengthen relationship with industry and research institutes, founding the premise for competitive approach in different domains and also for technological transfers. The laboratory endowment will anticipate the equipment acquisition necessary to enlarge the offered services and will contribute to testing and certification of special products obtained by biotechnological processes. The project will carry on **four activities**: equipement acquisitions, materials, soft and calculation technologies, applicative and pre-competitive (testing, verifications, measurements, analysis) research activities, dissemination and project management activities. The project will accomplish training activities, audit and certification ISO 17025 of the laboratory and the initialization of the proceeding of RENAR acreditation.

The **general objective** is represented by **the development of the material base for research in the field of sustainable and incorporate management of resources.**
The specific objectives are:
- **Development of existing infrastructure** of the Environmental Factors Quality Controls Regional Laboratory, through acquirement of performing equipments in order to reinforce the public private partnership in the region.
- **Accomplish of material base** necessary to build a new research direction of renewable and recycled resources, using the already existing structure.

- **Development of research capacities** in order to participate as work packages or European programs (such as FP 7) coordinators.
- **Disseminations of relevant results** for the national and international scientific communities, governmental organizations specialized in renewable resources management (Agriculture and Forestry Departments, Environment Protection Agencies, local and regional authorities) and civil society.

Implementation of MEDRES laboratory will lead to the following **estimative results**:
- Development of C-D activities and approach of new domains/sub domains of scientific researches, in agreement with the European trends in renewable and recycled resources.
- The quality increase and diversification of the educational act, upgrading of faculties laboratories for practical applications.
- Better accessibility of Romanian research in European programs C-D (there is a partnership proposal in FP 7 - BIOAROMATICS)
- Extensive and new research services for industrial units, especially for measurements, testing, trials and certifications.

Regarding the **stipulated benefits**, taking into account the present tendencies and personnel experiences, it is highly possible that in the next period new opportunities will be develop for resources diversification and increase the treatment possibilities using biorefinery technologies. In this way, renewable and recycled resources are use to obtain chemical products with/or energetic value. These activities in the north east development area will be **correlated with future programs**, having in mind the good use of agricultural areas, supplementation of the forestry zone necessary for providing additional renewable resources. "Gheorghe Asachi" Technical University will have an important role in the excellence centre SUSTENPOL INNOVATION (SUSTINOV) from Piatra Neamt, used to promote the concept of sustainable development. Beside the excellence centre, this laboratory proposed in this project will allow the **promotions of new technologies and activities**, having a positive role in setting up **new working positions** in this area with a high rate of unemployment. The approach of new research programs using the created C-D base will permit the increase of the research capacities of the personnel with the involvement of young researchers (PhD students and postdoctoral researches). The possible risks of this project are related with the difficulties in finding partners and the implementation of developed technologies and products. These risks can be preventive and diminish by the involvement of TECHNOLOGICAL PLATFORM FOR FOREST BASED SECTOR –FTP and the existing excellence centre.

The **estimate profit** is the integration of excellence centers in international CD networks, as well as the expansion of the possible applications in the various regions of Romania. The implementation of this project will allow the access to CDI infrastructure, necessary to obtain new products within the "green chemistry" concept. The created infrastructure will permit specialized and certified services for the business medium and the possibilities of financial support for PhD and postdoctoral fellowships. **Potentials beneficiary** are partners universities thanks to their integration in a CD network regarding the Resources Management, specialized organizations from MEDRES laboratory geographical area, members of national and international networks related with Resources Management, Romanian civil society, researches, PhD students.

For more information on the **Medres Lab Project**, please visit *http://medres_lab.cs.tuiasi.ro* and contact *iwolf@ch.tuiasi.ro*

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STUDIES ON THE INTERACTION BETWEEN BIRCH VENEER AND COMPOUNDS WITH BIOCIDE POTENTIAL ACTION

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Abstract

This paper discusses the results of study concerning the interaction between the birch veneer and some compounds with biocide potential action are presented. With this end in view the samples of veneer were immersed in solutions with a concentration of 5% of the following products: unmodified straw lignin or modified through hydroxymethylation, furan resin and tannins dissolved in 0.1 N ammonia solution. To make a comparison, the same combined treatments were applied, using ammonia solutions of some copper compounds ($CuCl_2$ and copper-ammonia solution) and the above mentioned organic compounds to obtain *in situ* their complexes. The stability of the treatments was followed through successive elution with distilled water of the impregnated samples. The toxicity of the extracts was followed by germination tests of tomato seeds. The obtained results highlighted that the stability of the treatments are in agreement with the nature's products, the functionality and the complex forming degree, that determine their interaction with the veneer.

Keywords: biocides, birch, copper compounds veneer, furan resins, lignin, tannin

1. Introduction

Frequent utilization of wood in different fields and its reduced stability on the action of environment factors infer using chemical compounds for protection against biological agents attack. Dimensional instability of wood is a consequence of its hygroscopicity and absorption or desorption capacity of water vapors from atmosphere take place as to establish a permanent equilibrium between its humidity and that of the environment.

An excessive increase in humidity and temperature influence significantly the biological stability of wood. To increase the biostability of wood, diverse chemical treatments based on its chemical modification or impregnation are recommended (Malutan et al., 2008), and these determine the modification of wood properties because, sometimes new materials could be obtained.

The evaluation of the effects of wood treatments, carried out by specific procedures of bioprotection can be evidenced through separate and successive stages according to the degree of wood chemical modification, physico-mechanical properties

and durability (Dumitrescu et al., 1997; Ungureanu et al., 2008). In this respect, there are various possibilities given by a large variety of products used for wood treatment, but most of them are characterized by high toxicity (Popa et al.,1993, 2007). That is why the finding solutions based on the properties of natural compounds is now in progress. From this point of view, lignins and polyphenols have shown an increased interest and the elucidation of their action mechanism will allow to create bioprotection systems which could substitute or supplement the products used at present. (Malutan et al., 2007; Popa et al., 2007; Rowell, 1984, 2005).

At the same time the possibilities to obtain some bioprotection agents soluble in water and compatible with the environment are analyzed by a number of researchers. This paper presents a study on the interaction between birch veneer and different products with potential biocide action (lignin and its derivatives, tannin and furan resins) obtained from renewable resource, as well as with copper compounds, as a possible combination of two categories of biostabilization agents. At the same time, the efficiency of the treatment is analyzed

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regarding its stability in the elution conditions in the presence of water, and the eluted products after different periods of time are evaluated for their toxicity, using tests on the germination of tomato seeds.

2. Experimental

2.1. Materials

In this study the following materials have been used:
- birch veneer samples with the dimensions (1x10) cm and the equilibrium relative humidity of 7.00%;
- unmodified straw lignin from Granit Recherche Development (Switzerland) and straw lignin modified through hydroxymethylation (Popa et al., 2007).
- unmodified and hydroxymethylated Pb 1000 (commercial product based on lignin)
- copper chloride;
- tetraaminocopper hydroxide (cuproxam);
- ammonia solution 0.1N;
- furan resins - from Trans Furan Chemicals (Belgium);
- tannin- from Tanin Svenica, Slovenia;

2.2. Methods

Using the veneer samples and the mentioned products dissolved in ammonia solution 0.1 N, at a concentration of 5 %, the following treatments have been applied:

a) the immersion of the samples in solutions for 5 minutes followed by their drying;

b) the immersion of the samples in solutions of the copper compounds, drying them and then treating with ammonia solutions of lignin and its derivatives followed by drying.

Then the impregnated and thermally treated samples were immersed successively in distilled water for 24, 48, 72 and 96 hours, and the elution liquids were collected after each interval of time. These samples were characterized in terms of their absorption by UV spectroscopy at 280 nm and toxicity. The absorption in UV was determined using the spectrometer V-55 Jasco, NO, CO 2951930. The evaluation of toxicity degrees was carried out by germination of tomato seeds. Thus in Petri dishes with the diameter of 10 cm a filter paper support was introduced along with 10 mL of aqueous extract. Then, 10 seeds of tomato were introduced and the percentage of germinated seeds was determined after 96 hours. As reference sample distilled water has been used.

3. Results and discussion

At present there are sustained preoccupations to find new solutions to increase the resistance of wooden products through acceptable methods from the environment point of view. It is well known that the compounds of secondary metabolism - lignin and polyphenols - are included in the defense mechanism developed by plants against the pathogens and nonpathogen microorganisms.

On the other hand the mentioned compounds could result as industrial by-products of chemical wood processing or from the technologies of biomass refining. At the same time, this renewable source of raw material was proved convenient for obtaining some derivatives with increased functionality, or some important products such as furan resins. The application of compounds based on copper in wood protection due to their antifungal properties has also been known and used for a long time. These facts were prominent in a first stage of the study of the interaction of birch veneer with some products based on modified and unmodified lignin, polyphenols (tannins) and furan resins along with copper compounds.

The possibility of complexes forming *in situ* between organic compounds and copper ions was also taken into account. The samples of veneer treated in the above mentioned conditions were analysed to establish the retention degree of bioprotection agents. With this aim, the samples were exposed to a successive extraction by distilled water for different durations (Figs. 1-3) and the mass losses were determined.

The data presented in Fig. 1 are obtained in the case of the birch veneer treated with lignin, its hydroxymethylated derivative and their complex with copper. From the analysis of these results one can identify an increased affinity of veneers for modified lignin through hydroxymethylation reaction, as well a high stability at the treatment by extraction with distilled water. At the same time preliminary impregnation of wood with solution of copper ions assure, as it was expected, a high retention degree and stability of applied treatment.

This fact is determined by the presence of functional groups in the wooden substrate, and also of those introduced into lignin, offering thus a good condition for complex forming with copper ions and therefore a better fixation of them on used support.

In case when the product Pb1000 and its derivative are used it can be noticed that the last one is better retained on the surface of veneer (Fig. 2) due to its increased functionality. Moreover this fact is confirmed by high stability of the complex with cooper of the hydroxymethylated derivative.

The data obtained concerning furan resin and tannins are presented in Fig. 3. In this case we observed a reduced affinity against wood, as compared with lignin and its derivative. The complex forming of tannins with copper ions is favorable for the interaction with substrate, a situation similar to that reported in literature (Yamaguchi et al., 2001).

The extracts separated by water were investigated by UV spectroscopy and it was observed that there exist a correlation between absorption and degrees of retention.
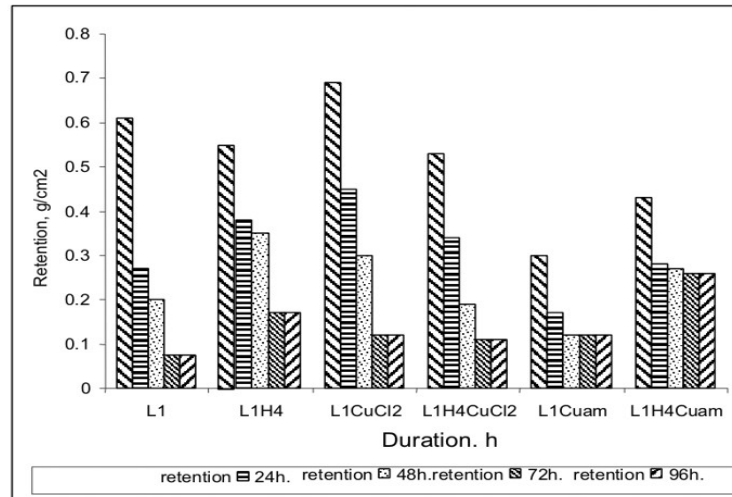
Fig. 1. Variation of retention of lignin (L1), hydroxymethylated lignin (L1H4) and their complexes with copper ions (L1CuCl$_2$, L1H4CuCl$_2$, L1Cuam and L1H4Cuam) by birch veneer as a function of elution degree after extraction with distilled water for different durations
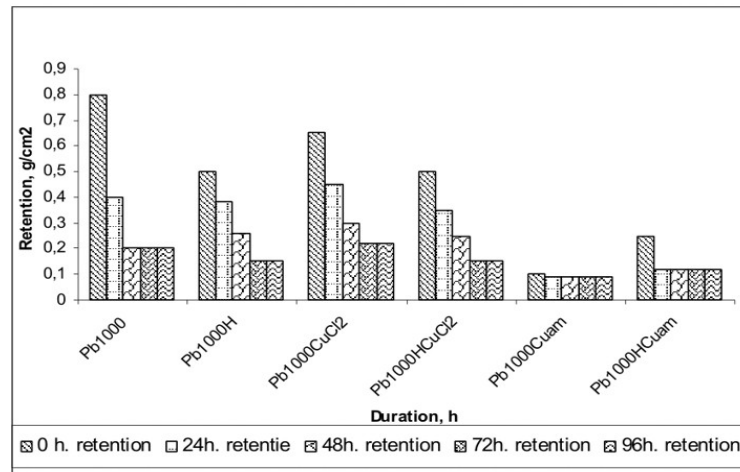
Fig.2. Variation of retention of Pb1000 nonmodified and modified through hydroxymethylation reaction (Pb1000H) and their complexes with copper ions (Pb1000CuCl2, Pb1000Cuam, Pb1000HCuCl2, Pb1000Hcuam) as a function of elution degree
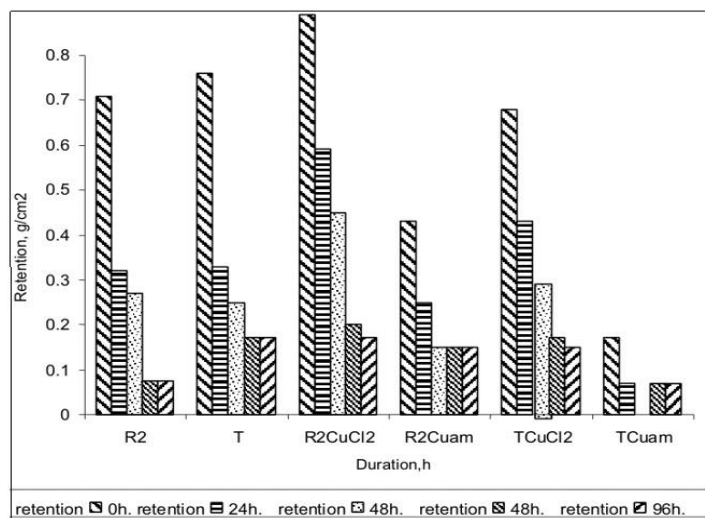
Fig. 3. Variation of retention of furan resin (R2) and tannins (T) and their complex with copper ions (R2CuCl2, R2Cuam, T CuCl2, T Cuam) depending on the elution duration

Thus, the values of absorption intensity are more reduced when the degree of retention is increased. At the same time, most of the products taken into consideration were eluted within the first 24 hours (Figs. 4 -6). The complex forming capacity of the studied products with copper ions assured a high stability degree of the treatment. The increasing the elution duration over 24 hours didn't remove important quantities of the compounds with biocide potential action and the values of the absorption intensities of extracts were relatively constant.

Taking into account that the veneer protected with the studied products will come into contact with the environment and it will be exposed to the interaction with water, which removes part of the used compounds, it was then necessary to obtain information concerning the toxicity of leachates. With this and in view, the elution liquids resulted after successive immersions of wood samples in water were tested from the point of view of the toxicity in the germination experiments of tomato seeds (Figs. 7-9). The data obtained in this study point out that the toxicity of the extracts was different depending on the compound or complex used, and that toxicity effect diminished with the decrease of the concentration (increase of elution time) and these are not to be considered as relevant.
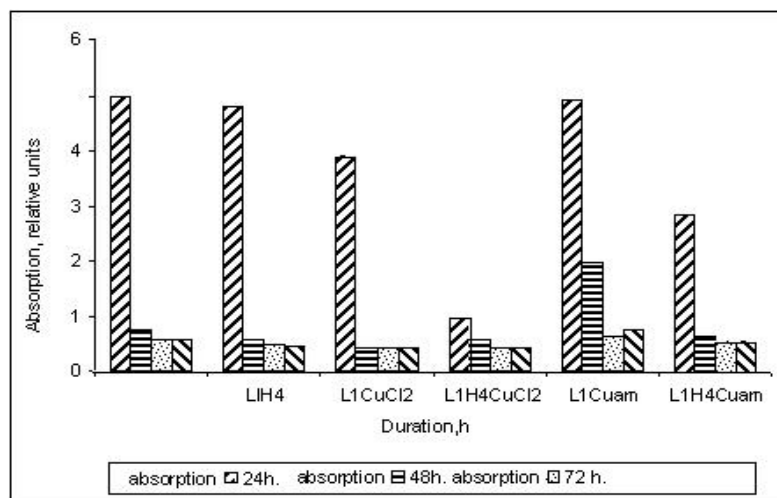
Fig. 4. Variation of absorption intensity in UV of leachates depending on elution time for the samples treated with L1, L1H4, L_1CuCl_2, $L_1H_4 CuCl_2$, L_1Cuam, $L_1H_4 Cuam$
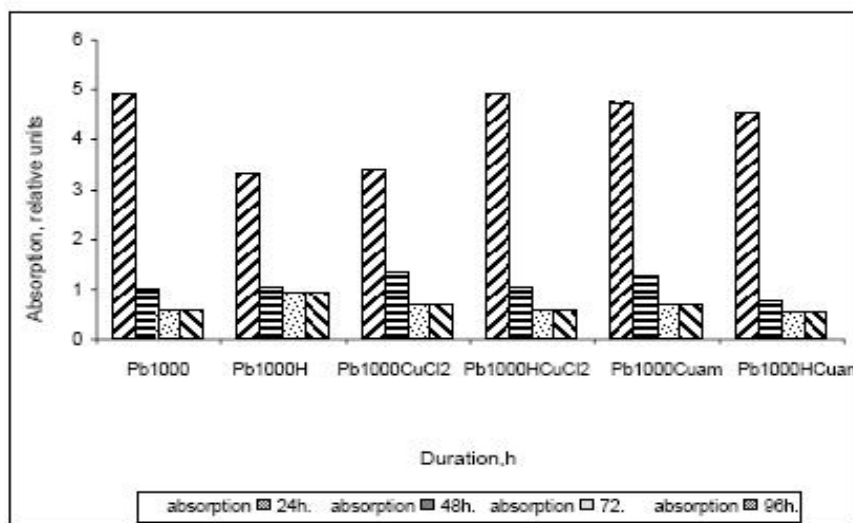
Fig. 5. Variation of absorption intensity in UV of leachates depending on elution time for the samples treated with Pb1000, Pb1000H, Pb1000CuCl2, $Pb1000H CuCl_2$, $Pb1000Cuam$, Pb1000HCuam
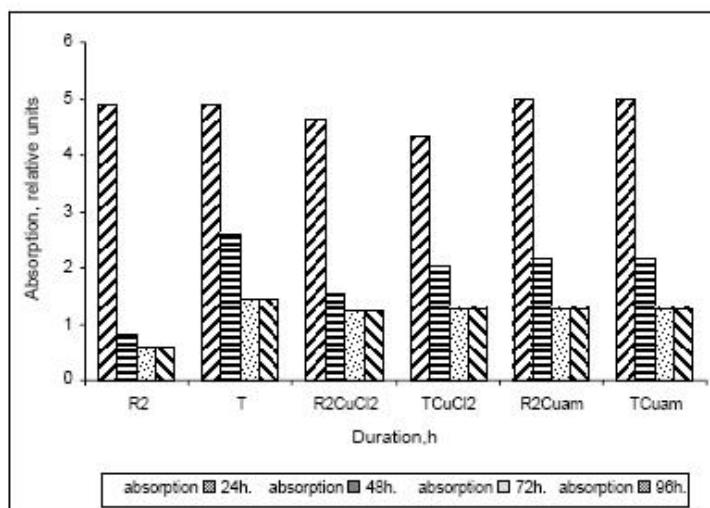
Fig. 6. Variation of absorption intensity in UV of leachates depending on elution time for the samples treated with R2, T, R2CuCl2, TCuCl$_2$, R$_2$Cuam, TCuam.
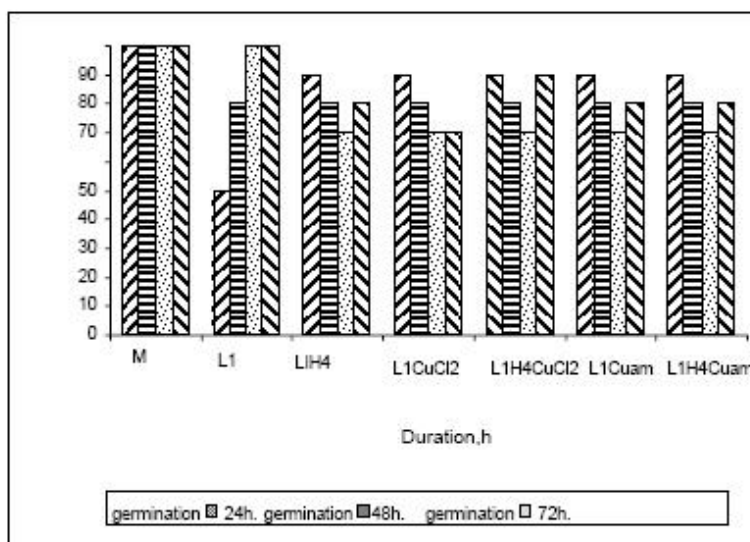
Fig.7. The evolution of germination degree of tomato seeds in the presence of leachates resulted after the elution of the veneer treated with L$_1$, L$_1$H$_4$, L$_1$CuCl$_2$, L$_1$H$_4$ CuCl$_2$, L$_1$Cuam, L$_1$H$_4$ Cuam

The information obtained in this study will be completed with biodegradability tests of birch veneer treated with the studied compounds which could have a biocide potential action.

4. Conclusions

A study concerning the interaction between birch veneers was carried out using a series of products, which could have a biocide potential action, such as unmodified and modified lignin by hydroxymethylation, furan resin and tannins, along with their complex obtained *in situ* using the CuCl$_2$ and copper ammonia solution.

The stability of the treatments was followed by successive elution with water of wooden substrate impregnated with mentioned compounds. It can be concluded that the retention degree is influenced by the nature of products, their functionality and the complex forming capacity.

UV spectroscopy led us to the conclusion that there exists a direct correlation between the absorption of extracts and the retention degree. A significant removal of treating agents was found within the first 24 hours, and that no important losses could be identified. The capacity of tomato seeds germination in the presence of solutions resulted after successive extraction with water of birch veneer treated with products with biocide potential activity didn't reveal major toxic effects. Therefore, we consider that there is a premise to obtain some environmentally friendly biocide agents.
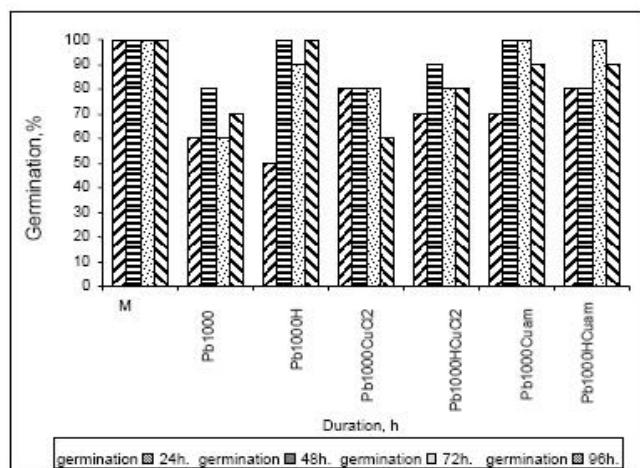
Fig. 8. The evolution of germination degree of tomato seeds in the presence of leachates resulted after the elution of veneer treated with Pb1000, Pb1000H, Pb1000E₂ Pb1000CuCl₂, Pb1000HCuCl₂, Pb1000E₂CuCl₂, Pb1000Cuam, Pb1000HCuam, Pb1000E₂ Cuam
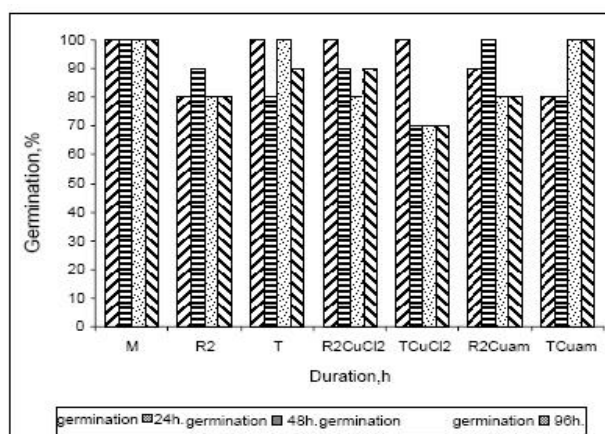
Fig. 9. The evolution of germination degree of tomato seeds in the presence of leachates resulted after the elution of veneer treated with R2, T, R₂CuCl₂, TCuCl₂, R₂Cuam, TCuam

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EFFECT OF METHANOGENIC INHIBITORS, INOCULA TYPE, AND TEMPERATURE ON BIOHYDROGEN PRODUCTION FROM FOOD COMPONENTS

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Abstract

Dark fermentation hydrogen production from a mixture of food components using two different methods of methanogenic inhibition (autoclaving and BES) and three different temperatures (37, 60, and 70 ºC) was examined in batch assays for two different mixed anaerobic cultures - one suspended sludge (S) obtained from an anaerobic digester and one granular sludge (G) obtained from a brewery wastewater treatment plant. In general, BES-inhibition of sludge was more robust when compared against heat-treated inoculum. Also, hydrogen, VFA, and sCOD production were affected by increases in temperature although the effects were less severe for G than for S. In addition, differences in individual VFAs were observed between the two inocula. S produced more acetate as a percentage of VFA_{TOTAL} compared to G. Conversely, G produced more butyrate compared to S. Differences in the microbial communities were likely responsible for the diverse behaviour of the two inocula.

Keywords: biohydrogen, fermentation, food waste, mixed cultures

1. Introduction

The rise in global pollution and diminishing reserves of fossil fuels has lead to an increase in investment and research into alternative fuel technologies. Hydrogen may be an ideal candidate as an alternative fuel because it is CO_2-neutral and it has the highest energy per mass content of fuels (Boyles, 1984; Kotay and Das, 2007). A wide range of biological technologies can be used to produce hydrogen including photolysis and fermentation. However, rates of hydrogen production from photolysis are less than those from fermentation (Das and Veziroglu, 2001; Levin et al., 2004).

Biohydrogen production from municipal solid waste has been well studied (Lay et al., 1999; Liu et al., 2006; Ueno et al., 2007; Valdez-Vazquez et al., 2005; Valdez-Vazquez et al., 2006). Even though municipal solid waste is comprised of 20-65% kitchen waste (Tchobanoglous et al., 1993), there have only been a few studies concerning hydrogen production from food waste. Okamoto et al. (2000) observed hydrogen production when individual food components such as carrots, cabbage, and rice were used as the substrates (Okamoto et al., 2000). The inoculum used for these experiments was heat treated anaerobic digester sludge. Shin et al., (2004) observed hydrogen production batch reactors using a mesophilic and thermophilic inocula from laboratory scale acidogenic reactor incubated at 37 or 55 ºC (Shin et al., 2004). Hydrogen production has also been observed from semicontinuous reactors using inocula from anaerobic digesters (Shin and Youn, 2005; Kim et al., 2008) or a pilot scale acidogenic reactor (Li et al., 2008). Kim et al. (2008) also used heat treatment to supress methanogenic activity.

Previous studies carried out with other substrates have shown that the different methods to inhibit methanogens can affect hydrogen production (Cheong and Hansen, 2006; Kraemer and Bagley, 2007; Oh et al., 2003; Valdez-Vazquez et al., 2006; Zhu and Béland, 2006). In addition, different inocula

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sources and temperature can affect the amount of hydrogen produced (Danko et al., 2008; Lay et al., 1999; Li and Fang, 2007; Lin et al., 2006; Shin et al., 2004; Valdez-Vazquez et al., 2006; Van Ginkel et al., 2001; Yu et al., 2002).

There are conflicting reports in the literature as to effects of temperature on hydrogen production. Several studies have shown that hydrogen yields and rates increase as the temperature increases (Lin and Chang 2004; Morimoto et al., 2004; Valdez-Vazquez et al., 2005; Yu et al., 2002). However, increasing temperature can also have detrimental effects on hydrogen production and rates (Lin et al. 2008; Valdez-Vazquez et al. 2006). Lin et al (2008) showed that even increases of just 5 ºC can impact hydrogen production and rates by as much as 25% (Lin et al., 2008). The work presented herein examines the effect of different methanogenic inhibitors and temperature on hydrogen production for two different anaerobic mixed cultures.

2. Experimental

2.1. Inoculum

A granular sludge and suspended sludge were used in this study. The granular sludge (G) was obtained from an upflow anaerobic sludge blanket reactor treating brewery wastewater located in Oporto, Portugal. The suspended sludge (S) was obtained from a wastewater treatment anaerobic digester supplemented with fat near Coimbra, Portugal.

Prior to use, G was first filtered using a 0.2 mm sieve. Sludge retained on top of the sieve was used as the G inoculum for batch reactors. S was prepared by centrifuging (5,000 rpm), washing in media, and centrifuging (5,000 rpm). Two different methods were used to inhibit methanogenic activity in both G and S: heat treatment by autoclaving (30 min) and bromoethanesulfonate (BES) (25 mM).

2.2. Batch experiments

Batch experiments were performed in 125 mL serum bottles with 20 mL liquid volume containing media, food components, and inoculum. The media contained a bicarbonate buffer with micro- and macro-nutirents as previously described (Abreu et al., 2007; Zehnder et al., 1980). The initial pH of the batch experiments was adjusted to 6.5 by flushing the headspace of each batch reactor with 100% CO_2 for several minutes. The initial amount of biomass used in batch experiments was approximately 10 g/L VS.

The substrate used for these experiments was simulated food waste. The composition of the food waste was prepared by mixing pork lard, cabbage, chicken breast, and potato flakes to simulate lipids, cellulose, protein, and carbohydrates, respectively. Previous research has shown that this simulated food waste adequately represents a real restaurant waste

(Neves et al., 2008). The composition of the food waste was manipulated in order to achieve an equal amount of COD for each component of the food waste. This corresponded to 4 g COD/L of each component or a total of 16 g COD/L for the four components in each batch reactor.

The characteristics of the food components are as previously described (Neves et al., 2008). The amount of food components used in the batch experiments are presented in Table 1.

Table 1. Range of the mass (in grams) used for each food component used in the batch experiments

Food Component	*Range (g)**
Fat (Lipids)	0.04 – 0.08
Chicken (Protein)	0.24 – 0-28
Cabbage (Carbohydrates)	1.35 – 1.60
Potato (Cellulose)	0.06 – 0.09

* mass of raw waste expressed in grams of wet mass

Batch cultures were incubated at three different temperatures: 37 ºC (± 2 ºC), 60 ºC (± 2 ºC), and 70 ºC (± 2 ºC). Experiments at each temperature were performed in triplicate.

2.3. Analytical methods

The biogas content of the batch reactors were monitored for hydrogen and methane production using a Hayesep Q column (80/100 mesh) and a Porapak Q (180 to 100 mesh), respectively, with thermal conductivity detector as previously described (Danko et al. 2008). Gas pressure was released using the Owen method (Owen et al., 1979) using a 20 or 50 mL glass syringe.

Production of volatile fatty acids (formate, acetate, propionate, *n*- and *i*-butyrate, valerate) and ethanol were determined using high pressure liquid chromatography (Jasco, Japan) using a Chrompack column (6.5 x 30 mm²) with 0.7 mL/min sulfuric acid (0.005 mM) as the mobile phase. Detection was accomplished using a UV (210 nm) or refractive index detector (ethanol). The column temperature was set at 60 ºC.

Hydrogen production potential and rates were determined using the Modified Gompertz equation (Eq. 1) (Lay et al., 1999; Zwietering et al., 1990):

$$H(t) = P\,exp\left\{-exp\left[\frac{R_m e}{P}(\lambda - t) + I\right]\right\} \quad (1)$$

where:
$H(t)$ is the cumulative hydrogen production (mL)
P is the hydrogen production potential (mL),
R_m is the maximum hydrogen production rate (mL/hr)
λ is the duration of the lag phase (hr)
t is time (hr),
e is approximately 2.718.

3. Results and discussion

Hydrogen production occurred for both inoculum but there were differences in the amounts depending on the temperature or type of methanogenic inhibition (Fig. 1). Methane production was not detected in any of the batch experiments.

The Modified Gompertz equation was used to calculate the values for the maximum hydrogen production rate, hydrogen production potential, and duration of the lag phase for all batch reactors. In addition, the R^2 values listed are the ranges of the values obtained for modelling the individual triplicate bottles. The results are shown in Table 2.

BES-inhibited G and S produced in general more hydrogen at higher production potentials with smaller lag times when compared against heat treatment.

There was little difference in hydrogen production between BES and heat treatment for G at mesophilic temperatures (average difference of 1.9 mL H_2). However, the differences in the amounts of hydrogen production for heat and BES treatments were larger at thermophilic (8.3 mL H_2) and hyperthermophilic temperatures (3.1 mL H_2) for G.

The largest difference between the BES-inhibited biomass and the heat treated biomass was observed with the S inocula at 37 ºC where the hydrogen production by BES inhibition was three times larger than for the autoclaved inoculum.

Differences were also observed for hydrogen production rates and lag times. In general, BES inhibited biomass had higher production rates and smaller lag times when compared against heat treatment. The largest average difference in lag time (~ 66 hours) was observed for S at thermophilic temperatures.
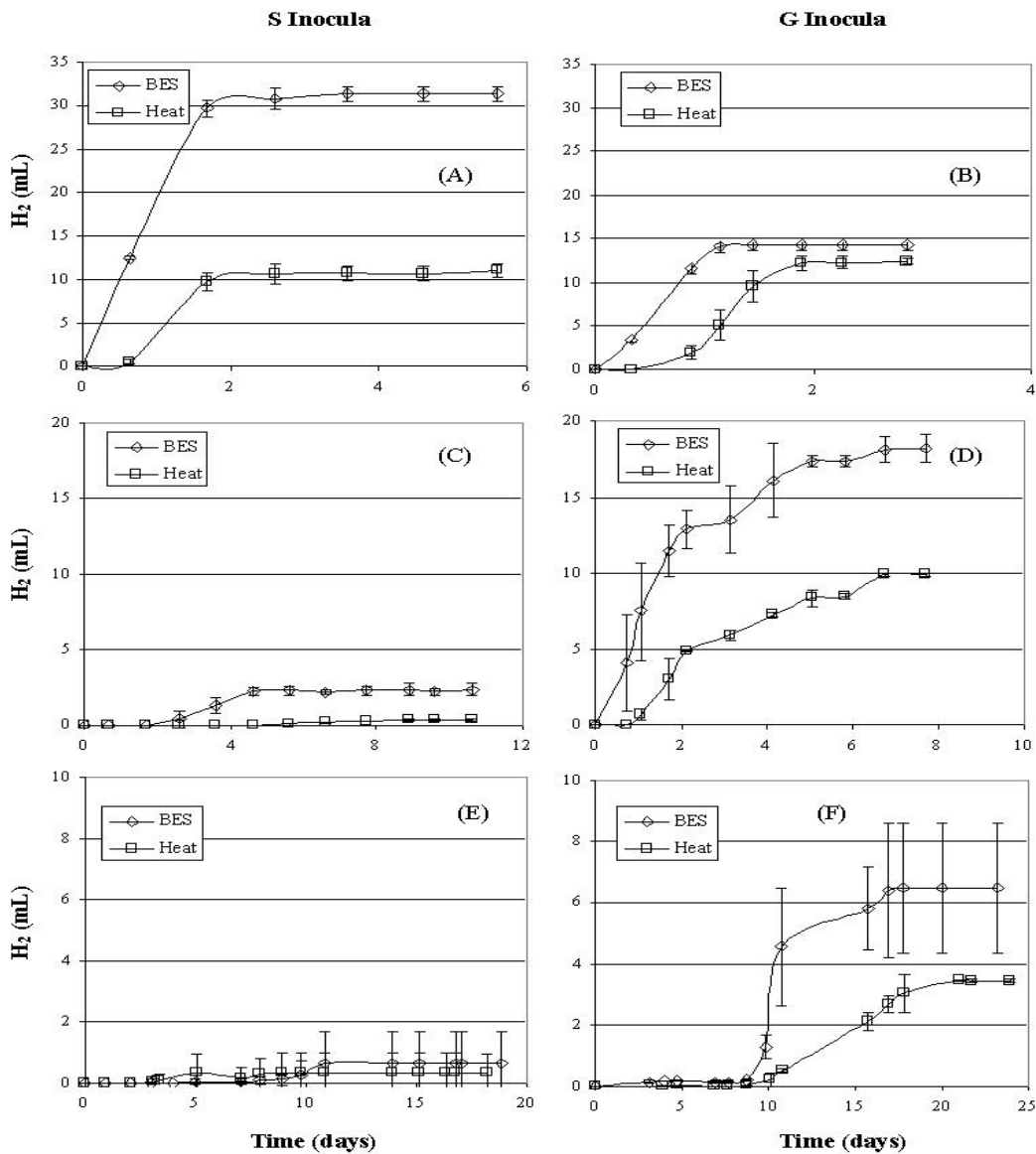
Fig. 1. Biohydrogen production from the S (Panels A, C, and E) and G (Panels B, D, and F) inocula at different temperatures and inhibition. The temperatures for the batch experiments were the following: 37 ºC for A and B, 60 ºC for C and D, and 70 ºC for E and F. Error bars represent one standard deviation of triplicate bottles.

Table 2. Modified Gompertz equation parameters for the two different sludges and two different methanogenic inhibitors where P = the hydrogen production potential, R_m = maximum hydrogen production rate, and λ = lag phase. The R^2 values listed are the range of the values obtained for modelling the individual triplicate bottles

Type of Inocula	Temperature (ºC)	Inhibition Treatment	P (mL)	R_m (mL/hr)	λ (hr)	R^2
S	37	Heat	11.23±0.15	0.64±0.23	14.96±1.82	0.9953-0.9980
		BES	31.39±0.87	1.99±1.08	9.01±2.67	0.9999-0.9999
G	37	Heat	12.51±0.39	0.73±0.14	20.21±1.40	0.9750-0.9949
		BES	14.38±0.54	0.86±0.06	4.30±0.52	0.9315-0.9989
S	60	Heat	0.38±0.12	0.01±0.00	128.80±21.96	0.9942-0.9969
		BES	2.29±0.29	0.09±0.06	63.39±22.83	0.9999-0.9999
G	60	Heat	9.65±0.03	0.11±0.01	16.02±6.19	0.9809-0.9896
		BES	16.98±0.99	0.35±0.11	3.64±1.65	0.9300-0.9976
S	70	Heat	ND*	ND	ND	ND
		BES	ND	ND	ND	ND
G	70	Heat	3.72±0.00	0.02±0.00	242.69±19.08	0.9993-0.9999
		BES	6.63±1.98	0.16±0.09	227.05±2.15	0.9933-0.9977

*ND means not determined

Previous studies have also indicated that heat treatment can be detrimental to hydrogen production when compared to other methods (Cheong and Hansen, 2006; Valdez-Vazquez et al., 2006; Zhu and Béland, 2006). G and S also showed significant differences for the effects of temperature. G was more robust with the effect of temperature for both BES and autoclaved biomass. Hydrogen production increased when the temperature was increased from 37 ºC to 60 ºC for BES inhibited sludge. However, hydrogen production potential decreased as the temperature increased from mesophilic to thermophilic temperatures.

As temperatures were increased a further 10 ºC from 60 ºC to 70 ºC, hydrogen production decreased approximately 55%. Similar results were observed when temperatures were increased from 50 to 55 ºC, although, hydrogen production and rates decreased only 25% (Lin et al., 2008).

For the S inocula, hydrogen production, potentials, and lag times were adversely affected as temperatures increased. Maximum hydrogen production for S was observed at 37 ºC (approximately 31 mL H_2) for BES-inhibition and decreased dramatically at 60 ºC (3 mL H_2). The amount of hydrogen produced from autoclaved S also decreased from 10 mL at 37 ºC to approximately 0.4 mL H_2 for 60 ºC. Hydrogen production was sporadic at hyperthermophilic conditions (70 ºC) as only one batch reactor (out of three) for each inhibition treatment produced hydrogen and therefore values for hydrogen production, potentials, and lag times were not determined for this experiment. Previous studies have shown that temperature can have a detrimental effect on hydrogen production (Lin et al., 2008; Valdez-Vazquez et al., 2006). This may be attributed to differences in microbial communities (Lin et al., 2008; Valdez-Vazquez et al., 2006).

The high degree of correlation between the data and the model for both inocula suggested that the Modified Gompertz Equation adequately described the data.

Results for the amount of sCOD, VFA, and ethanol production are shown in Table 3. Similar results on the effects of temperature and the type of methanogenic inhibition were observed with the amount of soluble COD (sCOD) and total VFA (VFA_{TOTAL}) that was produced for the G and S inocula. BES inhibited sludge produced on average more sCOD and VFA_{TOTAL} than the autoclaved sludge. In addition, the S inoculum was more adversely affected by the increases in temperature than was G, as was previously mentioned. For example, at 37 ºC, BES and autoclaved S inoculum produced 11600 and 6500 mg/L sCOD and 5800 and 3900 mg/L VFA_{TOTAL}, respectively. However, as the temperatures increased to 60 and 70 ºC, the amount of sCOD and VFA_{TOTAL} produced decreased significantly to levels less than 5400 mg/L and 2300 mg/L, respectively.

Also, the amount of sCOD and VFA_{TOTAL} produced was related to the amount of hydrogen that was generated. For example, the amount of sCOD and VFA_{TOTAL} was low ($\leq$ 5500 mg/L and 2600 mg/L, respectively) when H_2 production was less than 6.5 mL. An increase in VFA_{TOTAL} was observed by Shin et al. (2004) when temperatures increased from mesophilic to thermophilic temperatures (Shin et al., 2004). However, Valdez-Vasquez et al. (2005) observed a decrease in VFA_{TOTAL} under the same temperature conditions (Valdez-Vazquez et al., 2006). Possible differences between the two studies may be attributed to differences in the microbial communities.

Similarities and differences were also observed between S and G for individual VFAs. Formate and ethanol were generally the lowest percentage (as VFA_{TOTAL}) for both inoculum regardless of temperature. Propionate had the next highest percentage (average between 5 and 15% of VFA_{TOTAL}) but there were differences between the inocula. S inoculum produced HPr percentages generally above 10% (with the exception being autoclaved S at 37 ºC) while G was observed to produced HPr at values < 9% of VFA_{TOTAL}.

Table 3. Production of sCOD, H$_2$, and VFA during fermentation with two different inocula and two types of methanogenic inhibitors with food components

Type of Inocula	Temperature (ºC)	Inhibition Treatment	H$_2$ (mL)	sCOD (mg/L)	VFA$_{TOTAL}$ (mg/L)	HFo (%)[a]	HAc (%)	HPr (%)	HBu (%)	EtOH (%)	HAc+HBu (%)
S	37	Heat	11.1±0.9	6 500	3 900	1.5%	33.1%	12.6%	52.5%	1.4%	85.6%
		BES	31.4±0.8	11 600	5 800	1.1%	36.1%	9.1%	52.9%	1.3%	89.0%
G	37	Heat	12.4±0.4	7 200	3 500	4.8%	20.2%	8.6%	63.0%	3.5%	83.2%
		BES	14.2±0.5	12 900	4 500	2.4%	26.6%	8.9%	58.7%	3.9%	85.3%
S	60	Heat	0.4±0.1	4 200	700	4.3%	35.7%	15.1%	41.3%	2.0%	77.0%
		BES	2.4±0.4	5 400	2 300	0.8%	27.7%	13.5%	56.1%	1.9%	83.8%
G	60	Heat	9.9±0.2	8 500	4 300	4.8%	26.4%	4.9%	57.9%	4.8%	84.3%
		BES	18.2±1.0	14 200	5 800	4.0%	27.7%	8.6%	55.8%	3.7%	83.5%
S	70	Heat	0.4±0.6	4 100	700	10.1%	46.2%	12.0%	30.9%	2.0%	77.1%
		BES	0.6±1.1	4 700	900	2.3%	42.8%	14.1%	44.6%	1.8%	87.4%
G	70	Heat	3.4±0.1	4 300	1 900	1.6%	16.1%	5.4%	74.0%	2.7%	90.1%
		BES	6.5±2.1	5 500	2 600	1.7%	22.9%	8.1%	63.1%	2.6%	86.0%

[a]Percentage of VFA$_{TOTAL}$

HFu, HAc, HPr HBu, EtOH stand for formate, acetate, propionate, butyrate, and ethanol, respectively.

The two largest amounts of VFA were from acetate and butyrate. This suggests that hydrogen is being produced *via* butyrate-acetate fermentation (Noike and Mizuno, 2000; Fang and Liu, 2002). The percentage of HAc and HBu was calculated to be between approximately 77 and 90% of VFA$_{TOTAL}$ for both inocula. However, the percentage of acetate (as VFA$_{TOTAL}$) was generally higher in S compared to G. Conversely, S was also observed to have a lower percentage of HBu compared to G over the three temperature values. Differences in metabolic products at different temperatures have also been observed previously and may have been caused by different microbial communities (Lin et al. 2008; Shin et al. 2004).

4. Conclusions

The effect of methanogenic inhibitors, inoculum type, and temperature on biohydrogen production using food components was examined. In general, BES-inhibited sludge produced more hydrogen with higher rates and smaller lag times than heat treated suspended (S) and granular (G) inoculum. In addition, G was less sensitive to the effects of temperature as hydrogen production was observed for all three temperatures (37, 60, and 70 ºC) used with the maximum hydrogen production observed at 60 ºC. S was severely affected by temperature as hydrogen, sCOD, and VFA$_{TOTAL}$ production all dramatically decreased as temperatures increased. Differences were also observed in individual VFAs. Differences in the microbial communities were likely responsible for the diverse behaviour of the two inocula.

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ENERGY FROM BIOMASS IN PULP AND PAPER MILLS

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Abstract

Pulp and paper mills generate various quantities of energy-rich biomass as wastes, depending on technological level, pulp and paper grades and wood quality. These wastes are produced in all stages of the process: wood preparation, pulp and paper manufacture, chemical recovery, recycled paper processing, waste water treatment. Energy recovery from wastes of different origin has become a generally accepted alternative to their disposal. Pulp and paper industry expresses an interest in adapting and integrating advanced biomass energy conversion technologies into its mill operations. Industrial adoption of these new technologies has the potential for higher efficiency, lower capital cost, and safer operation than conventional operations that burn fossil fuels for energy. Incineration with energy recovery has the advantage of hygienic disposal, volume reduction, and the recovery of thermal energy by means of steam or super heated water that can be used for heating and power generation.

The paper reviews the current state and tendencies in using as a fuel of solid wastes generated in pulp and paper mills. A description of biomass-derived wastes regarding their opportunity to be used for energy recovery is presented. The heating properties of wood wastes, rejects from recycled paper processing, paper sludge, and low-quality recovered paper grades are discussed. Some aspects of emission of greenhouse gases (GHG) are also presented.

Key words: air emissions, biomass incineration, environment, pulp and paper, solid wastes

1. Introduction

According to the requirements of the Kyoto Protocol, the European Union must accomplish over the period 2008-2012 an overall greenhouse gas emission reduction by 8% compared with the 1990 levels, A realistic option is represented by substitution of typical fossil fuels with low-carbon fuels for energy production purposes. Energy recovery from wastes of different origin, e.g. industrial or agricultural, has become moreover a generally accepted alternative to their disposal or incineration. Waste-to-energy is gaining more and more attention as landfill costs and environmental concern increase and, at the same time, space available for landfilling waste is diminishing, especially in densely populated areas. Along with landfill, CO_2 and CH_4 emissions, potential groundwater pollution, the reduction of space available for landfilling has led to policy and legislation to increase the recycling and reuse of wastes. Legislation under preparation in the EU will prohibit landfilling of energy-containing waste.

Biomass is defined as any organic material derived from plants. Biomass is produced through photosynthesis as plants convert the sun's energy into chemical energy. The chemical energy in biomass can be extracted through combustion to produce energy that can be used as heat or power. Sustainable managed biomass resources are considered green because they are renewable and do not contribute to global warming. Carbon dioxide generated from the combustion of biomass is consumed as plants re-grow, so that as long as the resource is sustainable managed (for example, through replanting), the net contribution of carbon dioxide to the atmosphere is zero. Biomass represents an attractive source both for energy recovery and for valuable chemicals obtaining, (Popa and Volf, 2008).

Pulp and paper industry's role in the national bio-energy production is significant in many European countries. In 2004 the bio-energy accounted for 638.8 PJ (15.3 Mtoe) in pulp and paper industry in Europe, which represents 50% of the total energy consumption in pulp and paper industry. Pulp and paper industry accounts on average 27% of bio-energy use in these countries and 23% of total bio-energy use in EU countries. Renewable energy share in pulp and paper industry has increased from 45.5 % (1996) to 54.5 % (2006), (CEPI, 2007). Pulp and paper industry is an energy-intensive but energy-efficient industry. Energy can represent up to 40% of

manufacturing costs. Many pulp and paper mills generate more than half of their energy needs from biomass fuels recovered from solid waste and process streams (Table 1). Energy-rich biomass, derived from black liquor, wood chips, bark, sawdust, rejects, sludge, is the result of atmospheric carbon dioxide amassed by trees during growth and transformed into organic carbon substances. Carbon dioxide emissions from biomass combustion are not counted in the GHG inventory.

Table 1. Shares of energy carriers in total energy consumption in the member countries of the Confederation of European Paper Industry, (CEPI, 2007).

Fossil and non-fossil fuels	Share, %
Biomass (black liquor is included)	50
Gas	34
Oil	9
Coal	5
Other fossil	1
Other	1

2. Biomass in pulp and paper industry

Biomass resources include agricultural residues, wood wastes from forestry and industry, residues from food and paper industries, municipal green wastes, sewage sludge, dedicated energy crops such as short-rotation (3-15 years), coppice (eucalyptus, poplar, willow), grasses, sugar crops (sugar cane, beet, sorghum), starch-containing crops (corn, wheat) and oil crops (soy, sunflower, oilseed rape). Organic wastes and residues have been the major biomass sources so far, but green energy is gaining importance and market share in the last decade. With re-planting, biomass combustion is a carbon-neutral process as the CO_2 emitted has previously been absorbed by the plants. Residues and wastes are mostly used for heat and power generation. Sugar, starch and oil crops are primarily used for fuel production.

The pulp and paper industry has adapted and integrated advanced biomass energy conversion technologies. Industrial adoption of these new technologies has the potential for higher efficiency, lower capital cost, and safer operation than conventional operations that burn fossil fuels (Bowyer and all, 2005). A list o biomass generated in pulp and paper industry is presented in Table 2. The characteristics of typical fuels are listed in Table 3.

Black liquor is the most important biomass fuel in a kraft pulp mill. Black liquor contains around 50 % from wood substance as dissolved organic fraction. Typical higher heating values for black liquor lie between 13,000 and 15,500 kJ/kg of solid black liquor, depending on wood species and pulp yield. Burning of black liquor in a special recovery boiler generates around 4 tones of steam per tone of pulp. By processing of steam in a back-pressure turbine, a high quantity of electricity is produced. Recovery boiler covers the steam and electrical

energy consumption of the pulp mill (Adams and Frederik, 1988).

Elemental composition of black liquor solids and typical values for heating value are presented in Table 4 (Krotscheck and Sixta, 2006).

Table 2. Biomass wastes in pulp and paper industry.

Type of biomass	Sources of biomass wastes
Black liquor	Chemical pulp manufacture (kraft process)
Bark and wood residues	Chemical and semi-chemical pulp processes and mechanical pulp manufacture
Rejects of screening and cleaning processes	Chemical pulp production; recycled paper processing; paper stock preparing
Mechanical-chemical sludge	White water treatment and effluent treatment
Biological sludge	Biological effluent treatment
Deinking sludge	De-inking of recycled paper
Mixed sludge	Different sources

3. Wood wastes as a fuel

The source of wood wastes in a pulp mill is the preparation of pulpwood. The wood wastes generate in a pulp mill are: sawdust coming from the slasher deck, bark falling from the debarking drum, pins and fines from chip screening, wood residue from wood-yard. The characteristics of wood wastes are as follows:
- wood wastes consist of particles with various dimensions and shapes (from sawdust to log butts);
- moisture content of wood wastes is high and time depending;
- heating value of wood wastes is highly influenced by their moisture content;
- generation of wood wastes in the pulp mill is time-depending

Bark represents up to 300 kg/t of pulp and shares 60-90 % from wood wastes in a pulp mill (Gavrilescu, 2004). Its properties are:
- bark particles are very different regarding their dimensions (1 to 100 mm or larger) and shapes;
- bark moisture content is high and depends on debarking method: dry debarking leads to 40-50 % bark moisture while semi-wet debarking leads to 70-80 % bark humidity;
- bark particles are rigid and brittle;
- bark can absorb water easily, which is difficult to eliminate;
- ash content of bark is much higher than of wood;
- heat of combustion is around 20,000 kJ/kg (dry basis); the moisture drastically reduces heating value of bark.

Pins and fines are generated at the logs chipping: The percentage of pins and fines in chips depends on: pulpwood quality, short-or long-wood receiving, wood species, chipper performance.

Table 3. Comparison of typical fuel properties, (Clarke and Guidotti, 1995)

Heat value and components		*Bark*	*Mech.& biological sludge*	*Deinking sludge*	*Peat*	*Coal*
Heat value – as received, kJ/Kg, (at average moisture)		5900 (60%)	4200 (63%)	2800 (58%)	9200 (50%)	24000 (12%)
Ash (dry basis),%		3	20	50	5	14
Elemental analysis (dry basis), %	C	50.6	33.7	19.0	57.1	71.6
	H	5.9	4.4	2.4	6.2	4.9
	S	-	0.3	0.05	0.2	0.6
	N	0.5	0.7	1.0	1.9	1.9
	O	40.2	41.2	27.4	29.6	7.0

Table 4. Chemical analysis and heating values of black liquor solids

Component, % on dry solids	*Wood species*	
	Hardwood	*Softwood*
C	33.5	37.0
H	3.7	3.9
N	0.1	0.1
O	35.8	34.0
S	4.4	3.7
Na	19.9	19.2
K	1.5	1.5
Cl	0.5	0.5
Higher heating value, MJ/Kg	13.2	15.1

Pins and fines represent 50-100 kg/t o.d. pulp and their main characteristics are:
- pins are small wood pieces, while fines contains both wood and bark particles;
- bark content ranged between 20-50 %;
- particles dimension is optimum for firing;
- moisture level (40-50 %) of this fraction allow to their combustion without dewatering

Wood wastes generated in a pulp mill are listed in Table 5.

Table 5. Wood wastes generated in a pulp mill

Wood wastes	Quantity, kg/t of o.d. pulp
1. Sawdust coming from the slasher deck	10-30 kg/ t of pulp
2. Bark falling from the debarking drum	100-300 kg/t of pulp
3. Pins and fines from chip screening	50-100 kg/ t of pulp
4. Wood waste from wood yard	0-20 kg/t of pulp
Total:	160 – 450 kg/ t of pulp

The most common way to use wood residues is to burn it for heat (Huhtinen, 2000). The economic importance of the wood wastes depends both on its heating value and moisture content. High moisture content is detrimental in two ways (Lyngfelt and Leckner, 1999):

- reduces the available heat of wood wastes;
- reduces boiler efficiency, because heat energy is lost in vaporizing the moisture in wood and bark.

The influence of spruce bark moisture on the available heat is presented in Table 6.

Table 6. Available heat versus moisture content for spruce bark

*Moisture content (percent)**	*Available heat, kJ/kg*
0	20, 000
10	16, 300
30	12, 000
50	8, 100
70	4, 400

*most furnaces operate poorly if moisture content exceeds 50 %

In order to burning, wood wastes must be screened to remove oversized pieces, and pressing or dried, (if necessary) to reduce their moisture content at minimum as possible, 50 % or lower. Wood-waste is a medium heating value fuel, the average heating value being 20,000 kJ/kg (dry basis). The acceptable lower limit of the heating value ranges from 7,500-8,000 kJ/Kg corresponding to around 50 % wood-waste moisture, (EBIPPC, 2001; Koch, 1985). In order to enhance the boiler efficiency, fossil fuels (coal, oil, natural gas) are co-fired with wood wastes. The ratio of fossil fuel/wood wastes of 30/70 (heat input basis) is considered as acceptable. Wood-waste burning allows obtaining 0.8-2.0 t steam (1.2 MPa)/t of o.d. pulp, depending on wood losses at pulpwood preparation and boiler performance (Fogelholm, 2000). Solid residues from wood waste combustion are ash and incompletely combusted carbon. Combustion of hogged fuel generates 40-100 kg ash/t of pulp (Koch, 1985). The ash content of the wood, bark and wood wastes are listed in Table 7 and the emissions from combustion of hogged fuel are presented in Table 8 (Gavrilescu, 2005).

Table 7. Ash content of wood and bark

Material	*Ash content (percent)*
Wood	0.7-2.0
Bark	4-6
Wood wastes (as hogged fuel[*])	5-8

[*]sand and dirt are included

Rejects are generated during chemical pulp treatment and recycled paper processing. The two categories substantially differ regarding their properties and use in the pulp and paper mill. Rejects generated at chemical pulp treatment are represented by "knots" (coarse screening of pulp) and rejects (fine screening of pulp), (Kostinen, 2000; Ljokkoi, 2000). "Knots" is a general term that includes: true knots from wood, uncooked chips and bark particles. Knots represent 2-6 % on unscreened pulp or 25-70 Kg/t of pulp and their characteristics are:

- various size (5 to 50 mm) and shape;
- knots are dense and rigid;
- knots are impregnated with black liquor moisture content 70-80%)

This fraction may also contain small rocks, metal pieces, wires etc.

Table 8. Emissions from combustion of hogged fuel, mass percent (example)[*]

Gases		Particulate matter
Nitrogen	65	Inorganic fly ash
Carbon dioxide	8	Fixed carbon
Oxygen	11	Traces of salts and
Water vapor	12	metals
96-98 % of total		
--		
Carbon mono-oxide	0.1	2-3 % of total
Unburned hydrocarbons 0.005		
Sulfur dioxide 0.01		
Oxides of nitrogen 0.005		

[*]no fossil fuels are used

Knots processing methods are: knots cooking (in a separate digester) or mixing them with fresh chips; knots refining (when the knots are free from black liquor); knots burning (after mixing with wood wastes); knots landfilling. Burning of knots is not a common method for their processing in a pulp mill. Fine screening rejects contain fiber bundles and the common practice is refining and subsequent screening. In some cases, fine rejects are separated from circuit and mixed with knots.

4. Rejects from recycled paper processing

Depending on the final product, the reject rate varies from 5 % e.g. for used corrugated containers to 25 % and even more for waste graphical papers. Based on a final rejects dryness of 60 %, their amount lies from 83 kg to 416 kg per ton of paper. Reject is non-homogeneous. The two major categories are coarse and fine rejects. Coarse reject has its origin in recovered paper pulping and de-trashing, as well as coarse screening. Fine reject comes from process stages like cleaning, fine screening and from the approach flow.

There are heavy coarse rejects like metal of all kind, shape and size; stones, not disintegrated paper or wet strength paper, wires, etc. Light coarse rejects consist from fiber bundles, plastics pieces, foils, polystyrene, etc.

Fine rejects differentiate into light and heavy weight. Heavy fine rejects mainly consist from sand, glass, staples and other metallic office waste, discharged from cleaners, as well as from the heavy junk traps of combined screening/cleaning equipment. Light fine rejects from slot screening or light weight cleaning contain fiber broke, spin-ups, stickies, wax, filler etc. Low-organic content rejects (non-combustible heavy rejects) are landfiled.

The portion of the reject which is suitable for incineration (light coarse rejects) has to be discharged at the highest possible dryness, accompanied by the highest possible caloric value (> 11 MJ/Kg). It might be even necessary to apply a drying process in order to achieve the above-mentioned limit of the calorific value. Furthermore, the particle size of the rejects has to meet the requirements of the available incineration technology. The content of organic contaminants in the non-burnable, inorganic fraction has to be limited to a minimum, in order to allow disposal, (Ronga and Brauer, 2004).

The rejects from the pulping of recycled paper contain large quantities of plastics that range between 20 and 60 Kg/t depending on recycled paper grade. Plastics are "engineered" materials made by combining polymers with additives that build its desired properties such as mechanical resistance, flexibility, extruding/molding capacity, flame resistance, color, etc. Most polymers contain carbon and hydrogen only and their combustion products are carbon dioxide and water vapor. Some polymers contain chlorine or nitrogen and their combustion products include hydrochloric acid or hydrogen cyanide, respectively. Plastics are valuable fuel regarding available heat, as is shown in Table 9.

Table 9. Available heat and air consumption at combustion of plastics

Waste component	Available heat, kJ/kg	Air consumption, kg air/kg waste
Cellulosic fibers	16,000	4
Polyethylene	44,000	16
Polystyrene	38,000	13
Polyurethane	26,000	9
Polyvinylchloride	23,000	8

Combustion of plastics is a complex process and it is highly pollutant. During combination of oxygen with plastics carbon is converted to carbon dioxide, hydrogen to water, sulfur to sulfur dioxide, nitrogen to cyanides or molecular nitrogen, and chlorine to hydrochloric acid. Since most plastics are composed of carbon and hydrogen, the majority of the gases produced are carbon dioxide and water vapor. However, plastics and almost all other fuels are never burned under ideal conditions and products of incomplete combustion (PICs) may be formed that

are toxic to humans or harmful to the environment. PICs are formed because of inadequate oxygen concentration and temperatures in all areas of the furnace.

If there is inadequate mixing, complete combustion may not occur and materials are removed from the furnace and cool before they are converted into their most stable products. The PICs resulting from plastics combustion are mostly hydrocarbons, having the characteristics of the monomers from which they are made (Lyons and Kerstetter, 1990)

5. Paper sludge as a fuel

The option to use paper sludge as a bio-waste fuel for energy production has been recently considered in many European countries. The organic fraction in paper sludge is renewable, and therefore it does not contribute to net CO_2 emissions. A few mills incinerate paper sludge in their boilers as "hog" fuel. This practice is not widespread, because the heating value is very low (Table 3) and the high moisture of the sludge affects its ability to burn efficiently. To enhance the heating value, the sludge is mixed with dryer waste materials (such as wood residue). Fluidized bed combustion is an emerging technology that works particularly well with the wet sludge produced by de-inking mills. In this process, air is bubbled through a bed of inert material (usually sand or limestone), which greatly improves the combustion process. This technology also produces fewer sulfur dioxide and nitrous oxide emissions than do conventional hog boilers. Burning sludge is advantageous because the landfill volume required for ash disposal is about 25 percent of that required for sludge. In addition, boiler ash from de-inking sludge incineration is sometimes used as an aggregate in cement and concrete.

Sludge ash concentrates heavy metals, however, and if their concentration arises hazardous levels, the ash requires special handling, (Shin et al., 2005; Usherson, 1992). Every tone of recovered fiber generates up to 200 kg (dry weight) of sludge of different types and up to 400 kg (dry weight) of rejects and sludge, Table 10 shows the amount of rejects and sludge depending on the recovered paper grades and paper produced (Scott et al., 1995).

De-inking sludge consist of printing inks (black and colored pigments), fillers and coating pigments, fibers, fiber fines, and adhesive components. More than 55 % of the solids removed by flotation are inorganic compounds. They are primarily fillers and coating pigments such as clay and calcium carbonate. The proportion of cellulosic fiber is low. The heating value depends on the ash content and is 4.7–8.6 GJ/t of dry substance, (Hamm, 2006). The sulfur, fluorine, chlorine, bromine, and iodine contents are low and for this reason, no costly flue gas purification systems are necessary when incinerating de-inking sludge. Compared with sludge from biological effluent treatment plants, the nitrogen and phosphorus contents are very low. This is something that requires consideration when using de-inking sludge for composting and agricultural and land application purposes. The level of heavy metals in sludge of recovered paper processing is generally low. Sludge of de-inking plants contains less contamination than those of municipal wastewater treatment. The concentration of cadmium and mercury is especially insignificant and sometimes even below the detection limit of the test method applied (atomic absorption spectrometry). Only the concentration of copper has the same order of magnitude as that of municipal sewage sludge. The copper content of deinking sludge is primarily due to blue pigments of printing inks which contain phthalocyano- compounds (Kiphann, 2001).

Table 10. Amount of rejects and sludge depending on the recovered paper grades and paper produced

Paper grade	Recovered paper grade	Wastes (% by dry mass)				
		Total	*Rejects*		*Sludges*	
		Rejects and sludges	*Heavy-mass and coarse*	*Light-mass and fine*	*Flotation de-inking*	*White water clarification*
Graphic paper	News, magazines	15-20	1-2	3-5	8-13	3-5
	High grades	10-25	< 1	≤ 3	7-16	1-5
Sanitary paper	News, magazines, office paper, medium grades	27-45	1-2	3-5	8-13	15-25
Market DIP	Office paper	32-46	< 1	4-5	12-15	15-25
Liner, fluting	Old corrugated containers, Kraft papers	4-9	1-2	3-6	-	0-1
Board	Sorted mixed recovered paper, Old corrugated containers	4-9	1-2	3-6	-	0-1

Halogenated organic compounds such as polychlorinated biphenyls (PCB), polychlorinated dibenzodioxins (PCDD), and polychlorinated dibenzofurans (PCDF) are found in the flue gas. The PCB concentration is below 0.3 mg/kg dry solids (0.3 ppm) and PCDD/PCDF concentrations of de inking sludge show a similar pattern of decline. Due to the change from elemental chlorine bleaching of chemical pulp to oxygen delignification and chlorine dioxide bleaching, the PCDD/PCDF contents of deinking sludge have been decreasing significantly.

Today, PCDD/PCDF concentrations of de inking sludge are 25–60 ng I-TE/kg dry solids (I-TE - International toxicity equivalent). PCDD/PCDF concentrations are not significantly higher than the average contents of PCDD/PCDF in municipal sewage sludge. As a result of modifications of the bleaching sequences in chemical pulping, dioxin formation does not occur in most pulp producing countries. Consequently, dioxin discharges from recovered paper processing mills are already low and will decrease further (Hamm, 2006).

Regarding dewatering capacity, a distinction has to be made between de-inking sludge and the primary (chemical) and secondary (biological) sludge of the waste water treatment. This sludge contains ink particles, adhesives from the converting processes, mineral fillers such as clay, calcium carbonate, and some cellulosic fibers. The dewatering capacity of de-inked sludge is low. By contrast, the sludge from paper mill waste-water treatment plants, which contains higher percent of cellulosic fibers is much easier to dewater than de-inking sludge. It can be stated that the higher the fiber content, the higher the dry substance content that can then be obtained through dewatering. Sludge handling methods are available for all types of sludge produced by the common effluent treatment processes. De-inking sludge is usually handled mixed with the effluent sludge. Maximum mechanical dewatering of sludge prior to incineration is essential, (EEA, 2006).

Due to its low heating value, sludge must be co-fired with fuels having higher heating value, as bark and wood residues, see Table 3. Problems of sludge utilization for co-firing with bark have been reported as (Usherson, 1992):
- low heating value of all types of sludge which limits the ratio of sludge at boiler feeding;
- too much water in the sludge gives difficulties in keeping the boiler load;
- too big amount of sludge at boiler feeding may sinter in the fuel bed or in the ash handling system;
- limitation in capacity of ash handling systems;
- increasing environmental problems associated with sludge combustion due to the presence of toxic metals.

All types of sludge contain toxic trace metals (Pb, Cd, Cu, Zn, Hg) in various quantities. The behavior of toxic trace metals in de-inking and biological sludge, has been found to be strongly affected by metal interactions with the solid substrate

in the furnace (mostly with the Al/Si structure) which acted as a limit to their vaporization. It was observed that, during fluidized bed incineration of sludge from biological treatment, the ash was formed of loosely agglomerated particles and solid fused spheres. Cd and Pb encapsulation within a Si-Al-Ca based glassy structure was also observed. Paper sludge is also characterized by high chlorine content, which will be partly retained in the fly ash as condensed alkali chlorides, the rest forming HCl to a high extent. Ash-forming constituents of paper sludge influence chlorine enrichment in fine fly ash. Kaolin enhances HCl release in the flue gas, while calcium carbonate enhances chlorine capture on the coarse fly ash fraction (Coda, 2004).

6. Recovered paper as a fuel

With the continuing increase of world paper consumption, more and more waste paper of poor or unknown quality is entering in the solid wastes circuit. Sources of waste paper fibers (secondary fibers) are as follows: mixed (varied paper quality, boxboard cuttings and mill wrappings); news (old newspapers, over-issue news, and ground wood and container plant cuttings); pulp substitutes (grades of white colored kraft, white and semi-bleached sheets/cuttings, tab cards, trims and unprinted grades); purchased de-inked (de-inked white and colored ledger, computer printout, ground wood, coated book and bleached sulfate sheet and cuttings); other (lightweight coated grades). For this part of the waste paper stream, a better solution (other than fiber recovery) is its incineration. Although these residues are still largely dumped on landfill sites, a trend towards thermal processing is considered.

Mixed recycled paper represents a valuable source of energy for several reasons: it is easy to separate from the waste stream; it is relatively homogeneous and mostly free from metals, putrescibles and other noncombustible materials; it requires minimum processing to be converted into densified form of energy suitable for direct combustion; its heating value is fairly high; it has a low sulfur content, and low nitrogen oxides (NO_x) emissions. One tone of wastepaper combusted as fuel will produce 9.8 GJ of thermal energy (Porteous, 2007). Table 11 shows the calorific values of some paper grades.

Table 11. Calorific values of some paper grades

Paper grade	Mean gross calorific value, kJ/kg (dry basis)
Newspaper	17,600
Kraft and cardboard	16,100
Boxboard	16,000
Tissue	15,200
Office paper	14,700

The moisture content of mixed paper waste lies between 6-28 % by mass. If the moisture content

do not exceeds 20 %, heating values of mixed paper waste samples do not show big differences. Moisture contents exceeding 30 % lead to low heating value for mixed paper waste and must also be detrimental for shredding and for pelletizing of mixed paper waste.

During paper combustion all carbon in the organics is converted to carbon dioxide, with a trace amount of carbon monoxide. Hydrogen is converted into water vapor, and all chlorine is converted into hydrogen chloride, HCl, and chlorine gas, Cl_2. Sulfur is converted to sulfur dioxide, SO_2 and sulfur trioxide, SO_3. Nitrogen is converted into nitrogen oxides such as nitrogen monoxide, NO, or nitrogen dioxide, NO_2, and nitrogen gas, N_2. Organics are decomposed into lower molecular mass species at high temperature in the flame zone. When some of these smaller species meet with oxygen and hydroxyl radicals, some combustion intermediates such as aldehydes, ketones, alcohols, and acids are formed. In incomplete combustion, further oxidation of these intermediates is hindered due to flame quenching by cold air, water, or by a cold surface, or lack of additional oxygen. Therefore these intermediates are emitted from the flame zone as PICs (Lyons and Kerstetter, 1990).

Typical emissions that can be expected from the combustion of mixed paper waste are particulates, carbon dioxide, carbon monoxide, water, oxygen, nitrogen, oxides of sulfur, oxides of nitrogen, ammonia, hydrocarbons as hexane or methane, aldehydes as formaldehyde, and organic acids as acetic acid. Primary air pollution concern is with emission of particulate matter rather than gases and odors. A big portion of particulate emission arises from the carry-over of mineral matter introduced with paper waste.

The quantity of particulate emissions from an incinerator depends on the waste composition and the design and operation of the incinerator. Mixed paper waste, like all solid wastes and fuels, has substantial ash content. Some amount of the fly ash may settle in the bottom of the furnace or in other sections.

Settlement reduces the emission rate depending on the settling rate which is related to the size and mass of fly ash particles, flue gas properties, and residence time in the furnace. The ash content of paper waste is a major factor influencing the particulate emission rates, and the amount of ash carried over generally ranges between 10-20 % of the total, (Lyons and Kerstetter, 1990).

Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste includes the limit values for incineration plant emissions (EC Directive, 2000). They concern heavy metals, dioxins and furans, carbon monoxide (CO), dust, total organic carbon (TOC), hydrogen chloride (HCl), hydrogen fluoride (HF), sulfur dioxide (SO_2), nitrogen monoxide (NO) and nitrogen dioxide (NO_2). The limits are listed in Table 12.

7. Greenhouse gas emissions

The Kyoto Protocol set very ambitious targets for reducing energy consumption and emission of greenhouse gases (GHG). Emissions included in the inventory were as follows:
- carbon dioxide emission from fossil fuel combustion that includes those from production processes, as well as from the use of company-owned vehicles and from other equipments producing CO_2. Emissions are estimated using widely-accepted emission factors, which are based on the carbon content of the fuel;
- methane and nitrous oxide emissions from combustion processes, which are estimated using emission factors. Emissions of CH_4 and N_2O are usually very small compared to those of CO_2, and some inventory protocols do not address such emissions;
- greenhouse gas emissions from mill landfills and wastes water treatment plants, which are estimated using mill-generated data, and are consistent with methods suggested by the Intergovernmental Panel on Climate Change (IPCC).

Table 12. Air emission limit values at solid waste incineration, (EC Directive, 2000**).**

Pollutant	*Concentration,* mg/Nm^3 *at 11 % oxygen*
Total dust	10
VOC as C	10
HCl	10
HF	1
SO_x	50
NO_x	200
Cd	0.05
Hg	0.05
Heavy metals, total	0.5

In 2001, the International Council of Forest and Paper Associations (ICFPA) began a project to develop an international methodology for estimating GHG emissions. The calculation tools were recognized by governments as well as by domestic and international organizations, establishing protocols and developing calculation techniques as the appropriate tools for calculating GHG emissions for pulp and paper mills, (ICFPA, 2002; NCASI, 2005). Although emission of CO_2 from biomass burning is almost excluded from GHG inventories, methane (CH_4) and nitrous oxide (N_2O) from biomass burning are included. If a company has reliable site-specific data allowing it to estimate CH_4 and N_2O emissions from biomass combustion, it should use this data. Otherwise, it will be necessary to use the most appropriate emission factors available. Unfortunately, there are little data on CH_4 and N_2O emissions from biomass boilers and recovery furnaces (Table 13).

The table summarizes the available information on methane and nitrous oxide emissions from biomass-burning boilers. The variability in the data reflects the many different types and ages of boilers, diversity of operating conditions, control equipment and fuel characteristics.

Where an emission factor description shown in Table 13 matches the conditions at a mill, the company may want to select that emission factor for estimating mill emission.

In many cases, however, because of the ranges in emission factors and the limited ability to match emission factors to boiler design, operating conditions and fuels at this time, it is reasonable to use the average emission factors shown in Table 13.

Table 13. Emission factors for CH_4 and N_2O from biomass combustion, (NCASI, 2002, NCASI, 2005)

Combustion unit	Emission factor description	CH_4 kg/TJ	N_2O kg/TJ
Wood wastes fired boilers	Wood, wood wastes	30	4
	Uncontrolled emissions from wood-fired stoker boilers	15	-
	Average from wood residue combustion	9.5[a]	5.9[a]
	Average from circulating fluidized bed boilers (CFB) burning peat or bark	4	8.8
	Average from bubbling fluidized bed boilers (BFB) burning peat or bark	2[b]	< 2
	Pre-1980 wood residue-fired stoker boilers sampled ahead of control devices	8.2[a]	-
	Pre-1980 wood residue-fired stoker boilers sampled after wet scruber	2.7[a]	-
	Wood fired boilers	41[c]	3.1[c]
	Wood as fuel	24[c]	3.4[c]
	Wood waste	30	5
	Average emission factor for wood waste	12	4
	Data dispersion of emission factors	1-40	1.4-75
Recovery furnaces	Recovery furnaces	< 1	< 1
	Recovery furnaces-black liquor	2.5[d]	-
	Black liquor	30	5
	Average emission factor for black liquor	2.5	2.0
	Data dispersion of emission factors	1-17.7	1-21.4

a) - converted from GCV to NCV assuming a 5% difference, GCV - gross calorific value, NCV - net calorific value, NCV=0.95xGCV; b) - excludes one very high number associated with low oxygen-high carbon monoxide conditions; c) - based on the heat content of 20 GJ/t dry solids, d) - based on the liquor heat content of 13.3 GJ/t dry solids

The most severe air pollution problems are usually associated with black liquor burning. Recovery boiler is a potential source of sulfur dioxide, but the emission level is generally below the accepted level. The major sources of TRS emission are digester blow and relief gases and multiple effect evaporation plant. Over the last two decades, evaporator and recovery boiler manufacturers have improved their designs to achieve higher solids liquor for firing and better mixing within the combustion zone. These improvements provide to reduce TRS emissions (Tarnawski, 2004).

Relatively little attention has been directed toward the control of nitrogen oxides, which are by-products of high-temperature combustion processes. However, both NO and NO_2 are known to have a photochemical impact on the atmosphere. Fortunately, with respect to recovery boilers and lime kilns, it appears that the formation of nitrogen oxides can be adequately controlled by operating these combustion units with a minimum flame temperature and limited excess air.

The development of fluidized-bed combustion technology seems to have very good perspectives for using low-quality fuel such as bark and other wood wastes. This kind of biomass has a relatively low content of sulfur (< 0.1%), and SO_2 emission during its combustion is much lower than in the case of coal combustion (IPCC, 2006; Matthes, 2004).

At the present, the use of biomass as a fuel, replacing fossil fuels, was demonstrated to be technically feasible and economically attractive. Benefits are gained from the reduction of plant fuel cost although the high capital costs involved. Of course, the economics of biomass energy generation should become more attractive as traditional fuel prices should increase. Other benefits are the pollutant emission reduction and the fuel self-sufficiency in self-generating fuel. The encouraging results obtained in pulp and paper mills can motivate other industries to consider the scenario of using biomass for energy.

8. Conclusions

1. In pulp and paper industry energy-rich biomass is represented by pulping liquors, wood wastes, sludge and rejects. Many pulp and paper mills produce more than half of their energy needs from biomass fuels recovered from solid wastes. Carbon dioxide emission from biomass combustion is not counted in the GHG inventory.

2. Black liquor is the most important biomass fuel in a kraft pulp mill. Black liquor contains around 50 % from wood substance. Burning of black liquor in a special recovery boiler covers the steam and electrical energy consumption of the pulp mill.

3. Wood wastes are the second biomass fuel as importance in a pulp mill. Combined wood waste and sludge generated at the mill are insufficient for

combustion demand, because of low heating value resulting from their high moisture and ash content. In order to enhance the boiler efficiency, fossil fuels (coal, oil, natural gas) are co-fired with wood wastes.

4. Rejects from recycled paper processing contain large quantity of combustible materials as plastics and cellulosic fibers. Plastics that contain only carbon, hydrogen, and oxygen are unlikely to present an environmental risk if they are burned in small quantities in well designed combustors. These types of plastics include polyethylene, polypropylene, and polystyrene. Plastics that contain halogenated compounds such as polyvinylchloride or teflon are best kept out of combustors unless there are adequate pollution control devices to handle the acid compounds that are formed.

5. The use of paper sludge as a bio-waste fuel for energy production has been recently considered in several pulp and paper mills. Due to its low heating value, sludge must be co-fired with fuels having higher heating value, as bark and wood residues. Sludge co-firing is not widespread, because its heating value is very low and the high moisture of the sludge affects its capacity to burn efficiently.

6. Low-quality recycled paper represents a valuable source of energy for many reasons: it is easy to separate from the waste stream; it is relatively homogeneous and mostly free from noncombustible materials; it requires minimum processing to be incinerated; its heating value is fairly high; it has low sulfur content, and low nitrogen oxides emissions. Pulp and paper mills show an increased interest in this topic.

7. GHG emissions from biomass incineration contain carbon dioxide, CO_2, methane, CH_4 and nitrous oxide, N_2O. The last two are usually very small compared to CO_2, and some inventory protocols do not include them. Emissions are estimated by using widely accepted factors which are based on the carbon content of the fuel. Other important gas emissions in the pulp and paper industry include SO_2, H_2S, NOx, TRS and CO, generated in lime kiln and recovery boiler. Bark combustion produces SO_2, NO_2 and CO in small quantities.

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PHYTOREMEDIATION: THE APPLICATION OF VERMICOMPOST TO REMOVE ZINC, CADMIUM, COPPER, NICKEL AND LEAD BY SUNFLOWER PLANT

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Abstract

A greenhouse experiment was conducted to determine the phytotoxic effect of heavy metals such as Cd, Cu, Ni, Pb and Zn on the growth of Sunflower (*Helianthus annuus*): on the seed germination, root/shoot growth and uptake of metals in soil-vermicompost media. The selected metals were dosed at various concentrations ranging from 0, 5, 10, 20, 40 and 50 ppm separately in soil - vermicompost media (3:1) in pot experiment. The seed germination, root and shoot growth were found significantly affected by these metals at higher concentration of 40 and 50 ppm. However, the lower concentration of heavy metals ranging from 5 to 20 ppm doses were observed to be stimulating the root and shoot length and increase biomass of the sunflower plant. Sunflower was able to germinate and grow efficiently at all Zn concentration evaluated in this study. The research study of the sunflower indicates the heavy metal uptake at the concentrations 5, 10, 20, 40 and 50 ppm. Sunflower is a very fast-growing industrial oil crop with a high biomass producing plant to be used for phytoremediation (uptake) of toxic metals (Cu, Zn, Pb, Hg, As, Cd, Ni) from soil in heavily contaminated areas. Vermicompost can be used to remediate metals –contaminated sites because it binds metals and increase uptake by providing nutrients such as sodium, magnesium, iron, zinc, manganese and copper which can serve as a natural fertilizer giving high yield of biomass and microbial consortium helped the overall growth of the sunflower plant. The use of vermicompost amended soil would be effective to remediate the heavy metals from contaminated environment.

Keywords: heavy metals, *Helianthus annuus,* phytotoxicity, remediation uptake

1. Introduction

Heavy metal toxicity and the danger of their bioaccumulation in the food chain represent one of the major environmental and health problems of our modern society. Primary sources of pollution is from the burning of fossil fuels, mining and melting of metallic ferous ores, municipal wastes, fertilizers, pesticides, and sewage sludge (Peng et al., 2006; Xiong, 1998). The most common heavy metal contaminants are: Cadmium (Cd), Chromium (Cr), Copper (Cu), Mercury (Hg), Lead (Pb), Nickel (Ni) and Zinc (Zn) (Lasat et al., 2001; USEPA, 1997).

The term heavy metals refers to metals and metalloids having densities greater than 5 g cm^{-3} and is usually associated with pollution and toxicity although some of these elements (essential metals) are required by organisms at low concentrations (Adriano, 2001). For example, zinc (Zn) is the component of a variety of enzymes (dehydrogenases, proteinases, peptidases) but is also involved in the metabolism of carbohydrates, proteins, phosphate, auxins, in RNA and ribosome formation in plants Mengel and Kirkby, 1982). Copper (Cu) contributes to several physiological processes in plants (photosynthesis, respiration, carbohydrate distribution, nitrogen and cell wall metabolism, seed production) including disease resistance (Kabata-Pendias and Pendias, 2001).

However, at high concentrations, these metals exhibit toxic effects on cells (Baker & Walker, 1989). On the contrary, cadmium (Cd) is not involved in any known biological processes (nonessential metal) and may be quite toxic as it is accumulated by organisms (Peng et al., 2006; Suziki et al., 2001). It is known to disturb enzyme activities, to inhibit the DNA-mediated transformation in microorganisms, to interfere in the symbiosis between microbes and

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plants, as well as to increase plant predisposition to fungal invasion (Kabata-Pendias and Pendias, 2001).

The soil has been traditionally the site for disposal for most of the heavy metal wastes which needs to be treated. Currently, conventional remediation methods of heavy metal contaminated soils include electrokinetical treatment, chemical oxidation or reduction, leaching, solidification, vitrification, excavation, and off-site treatment. These clean up processes of heavy metal pollution are expensive and environmentally destructive (Aboulroos, et al., 2006; Bio-Wise, 2003).

Unlike organic compounds, metals cannot be degraded, and their cleanup requires their immobilization and toxicity reduction or removal. In recent years, scientists and engineers have started to generate cost effective technologies which includes use of microorganisms/ biomass or live plants for cleaning of polluted areas (Qui et al., 2006; Kuzovkina et al, 2004). Phytoremediation is an emerging technology, which should be considered for remediation of contaminated sites because of its cost effectiveness, aesthetic advantages and long term applicability (Boonyapookana et al., 2005; Su and Wong, 2004). This technology can be defined as the efficient use of plants to remove, detoxify or immobilize environmental contaminants in a growth matrix (Soil, Water or Sediments) through the natural, biological, chemical or physical activities and processes of the plants (Ciura et al., 2005). It is best applied at the sites with shallow contamination of organic, nutrient or metal pollutants that are amenable to one of the five applications: Phytotransformation, Rhizosphere Bioremediation, Phytostabilization, Phytoextraction, Rhizofiltration (Schnoor, 1997; Yang et al., 2005).

Phytoextraction (uptake) is the use of living green plants in order to remove inorganic contaminants, primarily metals, from polluted soils and concentrate them into roots and easily harvestable shoots (Lasat, 2002; Tang et al., 2003). Phytoremediation can be used to remove not only metals (e.g. Ag, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Zn) but also radionuclides (e.g. ^{90}Sr, ^{137}Cs, ^{239}Pu, ^{234}U, ^{238}U) and certain organic compounds (Andrade et al., 2002). Plants have shown the capacity to withstand relatively high concentration of contaminants without toxic effects. Some of the heavy metals at low doses are essential micronutrients for plants, but in higher doses, may cause metabolic disorder and growth inhabitation for most of the plant species (Sinha, 2005). Researchers have observed that some plant species are endemic to metallic-ferrous soil and can tolerate greater than the used amount of heavy metal or other compounds (Peralta et al, 2000). Plants such as Indian mustard (*Brassica juncea*), Corn (*Zea mays L.*) or sunflower (*Helianthus annuus* L.) show high tolerance to heavy metals and therefore, are used in phytoremediation studies (Pilon-Smits, 2005; Schmidt, 2003; Tang et al., 2003). The plant material may be used for non-food purposes; alternatively, it can be burned followed by recycling

of the metals or as disposal in a landfill (Angel and Linacre, 2005; Bennett et al., 2003). In the present study we examine the potential of sunflower plant for phytoremediation (uptake) of heavy metals which is reported to be the fast-growing deep-rooted industrial (Prasad, 2004) oil crop with a high biomass (Zhuang, 2005) producing plant species to remove heavy metals such as zinc or copper as well as several radionuclides from contaminated environment (Nehnevajova et al., 2005). Ximenez-Embun et al. (2001) also states that sunflower plant is effective in removing Pb, Cr, Zn, Cd and Ni.

The uptake efficiency of the plant depends on soil type, plant species and conditions. Soil receiving repeated application of chemical fertilizers, fungicides, and pesticides have exhibited high concentrations of extractable heavy metals and subsequently resulted in increased heavy metal concentrations (Arthur et al., 2005). It has been observed that prolonged use and lavish application of chemical fertilizers reduce land productivity and crops become dependent on periodic inputs of the chemical fertilizers. The factories manufacturing fertilizers are continuously polluting the air, land and water with the price of the fertilizers increasing every year (Maharashtra Nature Park Socity, 2003). The addition of these fertilizers, however, can also inhibit the uptake of some major metal contaminants, such as Pb, due to metal precipitation as pyromorphite and chloropyromorphite (Chaney et al., 2000). Natural chelating action of plants or microbial origin seem more promising than synthetic chemical chelating agent, since chemical chelating agents have additional toxicity to plants, thus they may increase the uptake of metals but decrease plant growth thus proving to be of limited benefit (Malik et al., 2000).

Phytoremediation has gained popularity with government agencies and industry in the past 10 years. This popularity is based in part on the relatively low cost of phytoremediation. Currently, $6-8 billion per year is spent for environmental cleanup in the United States, and $25-50 billion per year worldwide (Pilon- Smits, 2005). This plant based technique is essentially an agronomic approach and its success depends ultimately on agronomic practices applied at the site. Biological processes such as composting followed by vermin-composting to convert vegetable waste (as valuable nutrient source) in agriculturally useful organic fertilizer would be of great benefit. The composting followed by vermin-composting of vegetable waste with earthworm (*Eisenia foetida*) develops in to a natural fertilizer (Maharashtra Nature Park Bulletin, 2003). The vermicompost contain high nutrient value, increases fertility of soil and maintains soil health (Suthar et al., 2005). Application of compost and vermin-compost in contaminated soil improves soil fertility and physical properties as well as helps in successful approach to phytoremediation which has been demonstrated by Zheljazkov and Warman (2004). It also enhances quality of growing plants and increased biomass which could suggest that more metal can be

taken up from the contaminated growth media and the tolerance to the metal toxicity is improved (Tang et al., 2003). The use of vermin-compost developed from vegetable waste by vermin-culture biotechnology with soil would provide natural environment for phytoremediation (Elcock and Martens, 1995).

The presented work deals with the application of vermin-compost developed from vegetable waste in soil contaminated with heavy metals for phytoremediation studies. The objectives of this study is to determine the effects of heavy metals on seed germination, plant growth and examine their uptake by sunflower in soil-vermicompost media.

2. Experimental

2.1. Soil sampling, processing, and characterization

Soil was collected from a depth of about 0-15 cm along the banks of Surya River, Palghar (located 100 km away from Mumbai). Stones and plant tissues were carefully removed from the soil prior to drying process under laboratory condition. The soil was screened through 2 mm stainless steel sieve, and stored in a plastic bag at room temperature until use. Concentrations of Pb, Zn, Cu, Ni, and Cd were measured by atomic absorption spectrophotometer (APHA, 1998). The physicochemical parameters were measured by standard methods (Table1). Soil texture was determined by the hydrometer method. The moisture content of soil was calculated by the mass difference before and after drying at 105 ^{0}C to a constant mass. The pH and electrical conductivity (EC) were measured after 20 min of vigorous mixing samples at 1: 2.5 : : solid : deionized water ratio using digital meters [Elico, Model LI-120] with a combination pH electrode and a 1-cm platinum conductivity cell respectively. Total nitrogen and total phosphorus were determined according to the standard methods of the American Public Health Association (1998). Cation exchange capacity was determined after extraction with ammonium acetate at pH 7.0, and the organic carbon was determined by using Walkley–Black method (Jackson, 1973).

2.2. Vermi-composting development

The vermin-compost was produced from vegetable waste (cabbage, french bean, cauliflower, lady finger, spinach, carrot, and radish) collected from the vegetable market. In the process dry leaves, coconut fibers and fresh grasses having high lignin content were taken with the vegetable waste in appropriate quantity. About ½ Kg of exotic varieties of earthworms (*Eisenia foetida*) was spread on bedding materials. Everyday, 200 to 300 g of vegetable waste collected from market was supplied for a period of two and half months as a source of food for the earthworms.

The physicochemical parameters were measured during vermin-composting as described in soil analysis. After two and half month, vermicompost was collected, air dried, sieved (2-mm) and a portion of it was taken for nutrient analysis in order to prove its potency as biofertilizer. The nutrients in dried sample of vermin-compost was digested with concentrated nitric acid and 30% hydrogen peroxide and then determined by an atomic absorption spectrophotometer [AAS, Perkin Elmer] (APHA, 1998).

2.3. Greenhouse experiments

Green house pot culture experiments were conducted to study the effect of heavy metals viz Cd, Ni, Cu, Pb, and Zn on seed germination, root growth, shoot growth and phytoremediation (uptake) by sunflower. The ratio 3:1 of alluvial soil and vermi-compost were used as media. Nutrient and trace elements concentrations in the vermin-compost are presented in table 2. This soil–vermin-compost media was then amended with the heavy metals: Cd as Cd (NO$_3$).4H$_2$O; Cu as CuSO$_4$.5H$_2$O; Ni as Ni (NO$_3$) $_2$; Pb as Pb (NO$_3$) $_2$ and Zn as Zn (NO$_3$) $_2$.6H$_2$O. The concentrations of each heavy metal used in this study were 0, 5, 10, 20, 40 and 50 ppm. Sunflower seeds were obtained from seed supplier Ratanshi Agro-Hortitech (Byculla, Mumbai). Seeds were immersed in 3% (v/v) of formaldehyde for 5 minutes and washed with distilled water several times to avoid fungal contamination. The soil-vermi-compost media contaminated/amended with the heavy metal was used as potting media. To determine the effect of heavy metals; 30 seeds of uniform size were placed in every Petri dish (the lids were left partially open until 3 days after the germination) for study of seed germination. The Petri dish were kept in the dark and observed for germination. The seeds were considered germinated with the emergence of radicles. Small plastic pots/glasses were used for studying shoot and root growth. Ten plants were grown in 2 Kg capacity plastic pots for phytoremediation study. Soil-moisture content was adjusted regularly by mass to about 60% of water-holding capacity with deionized water.

To prevent loss of nutrients and trace elements out of the pots, plastic trays were placed under each pot and the leachets collected were put back in the respective pots. Each treatment of plant consisted of three replicate for statistical purpose. The seeds were set under 12/12 hrs light/dark cycle and temperatures of 30^{0}C during the day and 27^{0}C during the night. The average relative humidity was recorded to be 75%. The seedlings were harvested after two weeks; germination rate and shoot/root length were recorded. For the phytoremediation study plants were harvested after 10 weeks. The plants were then separated into roots and shoots. The plant samples were washed with distilled water and dried in an oven at 70°C for 3 days, and the dry mass of biomass was determined, after which these samples were stored in the brown paper bags. The samples

were considered for analysis of metal content digested with concentrated nitric acid and 30% hydrogen peroxide and then the heavy metal content was determined by an atomic absorption spectrophotometer [AAS, Perkin Elmer] (APHA, 1998).

2.4. Statistical analysis

Each treatment for % seed germination, plant root/ shoot growth and uptake consisted of three replicate for statistical purpose. The data presented for each treatment in this study is represented as mean of samples with standard deviation (X + S.D.) calculated by standard statistical methods (Mahajan, 1997).

3. Results and discussion

3.1. Soil analysis

After selecting the probable site, soil was collected and subjected to extensive analysis of various physicochemical parameters, which influence root establishment in soil (Table 1).
Soil, texture, which was found to be sandy loam, had profound effect upon the properties of soil including its water supplying power, rate of water intake, aeration, fertility and ease of tillage. The pH was 7.2, which lies within the recommended value for proper growth and efficient uptake of nutrients and compounds from soil. The percentage of organic matter and nitrogen were found to be 0.80 and 0.05 respectively. Macronutrients including metals were also present in substantial amount. Further to augment the existing native state of soil, it was spiked with vermin-compost, which gives all the nutrients conducive to plant growth for phytoremediation studies. There was no history of heavy metal (Cd, Ni, and Pb) contamination found in the soil collected.

3.2. Vermi-composting analysis

The vermin-compost developed was characterized and found to have high concentration of nutrients such as Zn, Cu, Mg, Fe, and Mn (Table 2). This vermin-compost developed by the vermin-culture biotechnology was then used as a natural fertilizer for phytoremediation studies of heavy metals. Several researchers have demonstrated that earthworm castings (vermicompost) have excellent aeration, porosity, structure, drainage, and moisture-holding capacity. The vermin-compost is a rich source of beneficial microorganisms and nutrients (Paul, 2000) and is used as a soil conditioner or fertilizer (Hattenschwile and Gaser, 2005; Rock and Martnes, 1995). Increase in crop yield, soil nutrients status and nutrients uptake was reported due to application of vermicompost (Roberts et al., 2007; Singh and Sharma, 2003). Experimental work has shown that earthworm activity enhances tree seedling growth associated with enhanced soil organic matter,

improved nutrition (including NO^{3-}, NH^{4+}, and Ca^{2+}), and increased mycorrhizal colonization (Welke and Parkinson, 2003).

Table 1. Physicochemical properties of experimental soil. †

Soil parameters	Values	S.D.
Clay %	25.9	+1.8
Silt %	21.7	+2.5
Sand %	50.4	+2.8
pH	7.2	+0.1
Organic matter %	0.80	+0.1
Nitrogen %	0.05	+0.02
C EC* c mol/ 100 g soil	11.27	+0.76
EC‡ dS⁻¹	1.1	+ 0.1
Potassium mg/kg	22.73	+2.63
WHC** %	62	+4.0
Moisture Content %	34	+1.8
Heavy metals ppm		
Cu	3.6	± 0 .5
Cd	ND	
Ni	ND	
Pb	ND	
Zn	12	± 1.5

† Values are averages of three replicates ± S.D.
* Cation exchange capacity
‡ Electrical conductivity.
**Water Holding Capacity

Yield of a tropical leguminous woody shrub, *Leucaena leucocephala*, in amended Pb–Zn mine tailings has been found to be increased by 10 to 30% in the presence of burrowing earthworms (*Pheretima spp.*) (Ma et al., 2003). The consecutive effect of organic treatment on the sunflower root yield caused a considerable growth of root system mass (in comparison with the mineral treatment) in the objects where vermin-compost with added cardboard (by over 28%) and straw (by over 21%) was applied (Gondek and Filipek-Mazur, 2003).

Table 2. Chemical and nutrient status of vermin-compost†

Parameters	Values	S.D.
pH	6.8	+0.173
EC‡ dS m⁻¹	10.55	+0.01
Total C %	13.5	+0.7
Total N %	1.33	+0.015
Available P %	0.47	+0.09
Sodium mg /100g	354.68	+9.44
Magnesium mg/100g	832.48	+22.48
Iron mg/100g	746.26	+23.39
Zinc mg/100g	16.19	+0.55
Manganese mg/100g	53.86	+2.84
Copper mg/100g	5.16	+0.36

† Values are averages of three replicates ± S.D.
‡ Electrical conductivity.

The earthworms increased available forms of N and P in soil, increased metal bioavailability, and raised metal uptake into plants by 16 to 53%. Some evidence indicates that earthworms increase metal bioavailability in relatively low-level metal-

contaminated soils with higher organic matter contents (Rida, 1996). This agrees with results of experiments in which the addition of exogenous humic acid to soil has been shown to increase plant-available metals (Halim et al., 2003).

3.3. Effect of heavy metals on seed germination

The present research demonstrated a concentration dependent inhibition of the seed germination with regards to alfalfa species (Table 3). The results of this study indicated that Cd, Ni and Pb at 5 ppm levels had very low toxic effects on seed germination while copper at the same doses increased seed germination. The most toxic metals for seed germination were Cd, Cu, Ni and Pb at 10, 20, 40 and 50 ppm levels. Delayed germination was also observed in all cases at higher i.e 40 and 50 ppm concentrations.

The resulting rank order of toxicity for metals on seed germination was Cd > Cu > Ni > Pb >Zn. However, seed germination increased at all Zn concentrations. Metal removal from contaminated media started at first stage of the germination process when the seed absorbed water and therefore large quantities of metal ions. Once accumulated, ions enter into the root, where they can be stored or exported to the shoot *via* the transpiration stream (Ximenez-Embun et al., 2001). Claire and coworkers (1991) obtained similar results in a study using nickel and other heavy metals on cabbage, lettuce, millet, radish, turnip, and wheat. The heavy metals (Cd and Ni) at higher concentration inhibit the seed germination and growth of sunflower plant (Khan and Moheman, 2006). The failure of the treated seeds of sunflower to germinate at the high concentrations of the applied CdCl$_2$ may be consequence of retarded water uptake, inhibited cell divisions and enlargements in the embryo and or an overall decrease in metabolic activity relevant to these steps. The blockage of any one of the phases may inhibit the germination process. (Shaddad et al., 1989). In this respect, Bazzaz et al. (1974) demonstrated that interference with stomatal function is a primary mode of action of cadmium and several other heavy metals.

3.4. Effect of heavy metals on root growth

The doses of 5 ppm and 10 ppm of Cd, Ni, Pb and Cu promoted the root growth of the plants. The heavy metals Cu, Ni and Pb at 20 ppm level further increased the root growth over the control root size. However, at the same dose Cd reduced the root growth. Cadmium, nickel, copper and lead significantly reduced root size at 40 and 50 ppm dosages. All the Zn concentrations increased the root length than the control root length of sunflower plants. Increase in the heavy metal concentration in the soil-vermin-compost media caused root length decrease with stunt growth of roots (Table 3). Root toxicity symptom included browning, reduced number of roots hair, and growth. In comparison to

the control treatment without heavy metals (Cd, Pb, Cu, and Ni), plant roots were healthy and normal.

The color of the roots receiving higher heavy metals treatment (40 and 50 ppm) except Zn, changed gradually over time from creamy white color to dark brown, an indication of intense suberification. There was reduction in the formation of secondary roots and number of root hairs by cadmium ion at 40 and 50 ppm. Plants treated at lower concentrations were not significantly affected by the metals. All zinc, concentrations showed increase in root growth. Lateral roots were observed in almost all treated samples of Zn, Cd, Cu, Pb and Ni demonstrated concentration dependant inhibition of root growth at higher ppms. One of the explanations for roots to be more responsive to toxic metals in environment might be that roots were the specialized absorptive organs so that they were affected earlier and subjected to accumulation of more heavy metals than any of the other organs This could also be the main reason that root length was usually used as a measure for determining heavy metal- tolerant ability of plant (Xiong 1998).

Nandkumar et al. (1995) demonstrated that root growth of Pb treated sunflower plants was retarded compared to the controls. Boonyapookana et al. (2005) found similar results using *H. annuus* in Pb contaminated soil (2.5mM). According to Chaignon and Hinsinger (2003), higher concentrations of copper can inhibit root growth before shoot growth and can accumulate in the roots without any significant increase in its content of the aerial parts. Previous studies have demonstrated that growth of *T. caerulescens* roots was essentially unaffected by 20 ppm concentration of cadmium relative to the control cultures without cadmium (Boominathan and Doran, 2003). Root density and the depth of rooting are particularly significant in the context of phytoremediation. Shaddad et al., (1989) reported a depressed root elongation in *Zea mays* seedlings in the presence of cadmium.

3.5. Effect of heavy metals on shoot growth

The heavy metals Cd, Cu, Ni, and Pb showed increased shoot growth at 5 and 10 ppm levels. At the 20 ppm concentration Cd reduction was noticed in shoot length against the further increase in shoot length of sunflower plants at 20 ppm of Cu, Pb and Ni contaminations. When the concentration of these metals was increased to 40 and 50 ppm dose, significant reduction in the shoot size of the plants was found as compared to the control plants. All plants grown in the media contaminated with Zn showed increase in the shoot growth than the plants grown in media without Zn contamination. All the plants appeared to be healthy and the shoot growth of the plant was stimulated by a concentration of 5, 10, and 20 ppm by the heavy metals (Table 3).

Table 3. Seed germination, root and shoot length of sunflower after two weeks of exposure to heavy metals†

Metal	Dose (ppm)	Germination rate (%)	Root length (cm)	Shoot length (cm)
Cd	0	70 ± 4	9.1 ± 0.50	7.5 ± 0.7
	5	65 ± 4	9.7 ± 0.6	18.1 ± 0.8
	10	60 ± 3	10.5 ± 0.71	20.3 ± 0.82
	20	53 ± 3	8.5 ± 0.31	16.2 ± 0.27
	40	46 ± 6	7.1 ± 0.43	12.6 ± 0.65
	50	40 ± 5	5.8 ± 0.88	10.01 ± 0.74
Cu	5	75 ± 5	10 ± 0.86	17.8 ± 1.88
	10	63 ± 4	11.3 ± 0.91	18.3 ± 0.76
	20	60 ± 7	13.8 ± 0.61	19.5 ± 1.38
	40	55 ± 3.05	8.7 ± 0.2	16.7 ± 1.18
	50	50 ± 6	8.3 ± 0.5	14.4 ± 1.28
Ni	5	66 ± 4	9.8 ± 0.68	17.2 ± 1.39
	10	63 ± 4	10.7 ± 1.58	19.2 ± 0.9
	20	56 ± 3	12.3 ± 1.5	20.2 ± 3.1
	40	48 ± 5	8.4 ± 0.5	17.3 ± 1.7
	50	43 ± 2	7.2 ± 0.62	14.3 ± 1.3
Pb	5	70 ± 7	10.64 ± 1.54	18.3 ± 1.5
	10	57 ± 5.5	11.45 ± 1.15	19.4 ± 1.4
	20	56 ± 3.05	13.2 ± 1.4	20 ± 1.5
	40	60 ± 4	8.6 ± 0.5	14.5 ± 1.19
	50	46 ± 4	7.9 ± 1.2	16.2 ± 1.35
Zn	5	74 ± 5.56	11.9 ± 1.69	18.5 ± 2.29
	10	76 ± 7	14.3 ± 1.52	19.7 ± 1.4
	20	84 ± 5	15.1 ± 1.3	21.6 ± 2.04
	40	92 ± 7.37	15.8 ± 0.81	22.8 ± 2..25
	50	94 ± 4	17.3 ± 1.47	24.7 ± 2.2

† Values are averages of three replicates ± S.D.

These results indicate that low concentrations of Cd, Cu, Ni, and Pb have micronutrient action effects on the sunflower plants. However, at 40 and 50 ppm gradual reduction of the shoot growth was observed as compared to control shoot growth. These symptoms were more common in case of cadmium treatments.

No signs of toxicity from the high levels of Zn were observed in the shoot. All zinc concentrations showed positive effects and shoot growth efficiently. The Pb treated sunflower (*Helianthous annuus*) plants at higher concentrations showed stunted growth and reduced leaf expansion (Nandkumar et al., 1995). Christodoulakis and Margaris (1996) demonstrated that the sludge from sewage treatment products (domestic activities) increased leaf area in sunflower. Ormrod et al. (1986) noted that nickel caused stunted and deformed growth of shoot with symptoms of chlorosis. Wenger et al. (2003) reported that the critical toxicity level of Cu in the shoots of crop plants is greater than 20 to 30 mg kg⁻¹. These data corresponded with those of Oncel et al. (2000), who found that Cd reduces chlorophyll a and b in wheat. Chatterjee and Chatterjee (2000) determined that Cu significantly decreased the water potential and Fe concentration in cauliflower.

The influence of relatively higher amounts of Cu, Zn, Pb, Ni, Cr and Cd in wheat cv. Vergina resulted in depressed shoot growth (Athar and Ahmad, 2002). Stunted growth and visual toxicity symptom of cadmium in shoot of sunflower plant was demonstrated by Singh (2006).

3.6. Effect of heavy metals on plant biomass

The biomass results after 10 weeks of experiments indicated that the mean plant biomass of sunflower showed increasing tendency as the concentrations increased from 5 to 10 to 20 ppm for Cd, Cu, Ni and Pb (Table 4). Biomass decreased gradually as the concentration of Cd, Cu, Pb and Ni in the soil- vermicompost media increased to 40 and 50 ppm. The biomass yield affected by the higher ppm levels of Cd caused reduction in the plant biomass. There was a significant positive effect seen in all Zn concentrations and increase in biomass yield as compared to control ones. Kayser (2001) demonstrated that *Helianthus annuus* produced the largest biomass as compared to *B. juncea* and *S. viminalis* in Zn and Cd contaminated soil. Boonyapookana et al. (2005) have studied that the plant biomass of *H. annuus* in Pb contaminated

nutrient media declined with increasing concentration. Higher doses of heavy metal can affect physiology, reduced plant growth and dry biomass yield (Grifferty and Barrington, 2000; Roy et al., 2005).

Similar findings were evaluated with sunflower in artificially contaminated soil with heavy metals (Zn, Cd, Pb and Cu), Herrero et al., (2003) reported that part of the plant with greatest biomass was the shoot (50% of total mass) and the biomass decreased proportionally to the contamination level. Nwosu, et al. (1995) observed that the mean plant biomass decreased in both lettuce and radish, as the concentration of Cd and Pb in soil increased. Grifferty and Barrington (2000) showed that the increased Zn concentration from 25 to 50 mg/kg had a significantly positive effect on dry biomass yield. The application of Tobacco plant in metal uptake by high biomass-producing plants was mentioned by

Wenger et al. (2003). Higher levels of organic matter (882.30g/ kg) and nutrients content in the compost had beneficial influence on soil chemical and biochemical properties and plant growth, thus increasing biomass yields (Yang et al., 2005). The plant biomass may be incinerated either to reduce volume, recover energy, disposed off using appropriate techniques or recycled to recover valuable metals (Angel and Linacre, 2005).

Nehnevajova et al., (2005) noted that *Helianthus annuus* accumulated relatively very low amounts of heavy metals in flowers and sunflower seed and sunflower oil may be used for technical lubricants or energy production. The fertilization with vermin-composts and untreated tannery sludge caused a statistically proved increase in the sunflower shoot yield as compared with the mineral treatment (Gondek and Filipek-Mazur, 2003).

Table 4. Biomass of sunflower after 10 weeks of growth in heavy metals enriched soil-vermi-compost media †

Metal	*Dose (ppm)*	*Root Dry Weight (g)*	*Shoot Dry Weight (g)*
Cd	0	1.510 ± 0.108	2.450 ± 0.138
	5	1.680 ± 0.17	2.490 ± 0.37
	10	1.832 ± 0.124	2.570 ± 0.47
	20	2.01 ± 0.64	2.712 ± 0.293
	40	1.332 ± 0.068	1.906 ± 0.268
	50	0.815 ± 0.08	1.371 ± 0.163
Cu	5	1.619 ± 0.092	2.503 ± 0.114
	10	1.862 ± 0.139	2.735 ± 0.155
	20	2.216 ± 0.109	2.929 ± 0.314
	40	1.753 ± 0.234	2.309 ± 0.134
	50	1.390 ± 0.105	1.962 ± 0.178
Ni	5	1.524 ± 0.065	2.60 ± 0.119
	10	1.786 ± 0.176	2.852 ± 0.178
	20	1.800 ± 0.15	3.115 ± 0.085
	40	1.453 ± 0.138	2.219 ± 0.219
	50	1.208 ± 0.027	2.005 ± 0.1
Pb	5	1.550 ± 0.127	2.508 ± 0.127
	10	1.792 ± 0.158	2.705 ± 0.144
	20	1.850 ± 0.061	2.923 ± 0.143
	40	1.453 ± 0.052	2.5 ± 0.14
	50	1.181 ± 0.095	2.012 ± 0.123
Zn	5	1.712 ± 0.112	2.523 ± 0.121
	10	1.928 ± 0.118	2.824 ± 0.145
	20	2.317 ± 0.212	3.072 ± 0.138
	40	2.507 ± 0.097	3.281 ± 0.199
	50	2.601 ± 0.151	3.402 ± 0.122

† Values are averages of three replicates $\pm$ S.D.

3.7. Heavy metal uptake by plant tissue

The mean uptake of all five metals by sunflower plants increased as the concentration of these metals in the soil- vermin-composting media increased (Table 5). In this plant the heavy metals, Cu, Cd , Ni and Zn were taken up by shoot and root both; where Pb concentration was found to be higher in roots. The heavy metals were untaken by the sunflower plants in the following order: Zn>

Cu>Cd>Ni>Pb. Several studies have demonstrated that the metal concentration in the plant tissue is a function of the heavy metals content in the growing environment (Cui et al., 2004; Grifferty and Barrington, 2000). Uptake is largely influenced by the availability of metals, which is in turn determined by both external (soil-associated) and internal (plant associated) factors. The roots preferentially explored metals in the contaminated area. The exploration of polluted soil inclusions by the roots was associated

with higher extraction of metals. Many plant species or ecotypes associated with heavy-metal enriched soils accumulate metals in the shoots. These plants can be used to clean up metal-contaminated sites by extracting metals from soil and concentrating them in aboveground biomass (Peng et al., 2006).

The metal-enriched biomass can be harvested using standard agricultural methods and smelted to recover the metals. Plant growing in metal contaminated environment can accumulate toxic metal ions and efficiently compartmentalize these into various plant parts. Several studies indicated that the partitioning of heavy metals at the whole plant level could broadly be divided into three categories. For instance, Chaney and Giordano classified Mn, Zn, Cd, B, Mo and Se as elements, which were readily translocated to the plant shoots; Ni, Co and Cu, were intermediate, and Cr, Pb and Hg were translocated to the lowest extent (Alloway, 1995).

Some species, such as cabbage (*Brassica oleracea L.*), lettuce (*Latuca sativa L.*) and tobacco (*Nicotiana tabacum L.*), accumulate high levels of Cd in leaves rather than in roots and increases or decreases the bioavailability of metal ions. In plants Cd damages the light harvesting complex II and photosystems II, and I, which are active in photosynthesis. Total chlorophyll content is decreased by Cd treatment, and nonphotochemical quenching is increased in *Brassica napus*. Probably Cd also interferes with movement of K^+, Ca^{2+} and abscisic acid in guard cells, while inhibiting stomal opening

(Shaw, 1995). The root of Indian mustard are found to be effective in the removal of Cd, Cr, Cu, Ni, Pb, and Zn, and sunflower can remove Pb, U, Cs,-137 and Sr-90 from hydroponic solutions (Lone et al., 2008).

Tang et al. (2003) reported the increase in uptake of copper by Indian mustard and sunflower plant. Nehnevajova et al., (2005) investigated that the highest metal concentration was found in leaves (shoot) of commercial cultivars of sunflower plants grown on metals-contaminated soil.

Among the cultivated crops rape and sunflower revealed higher cadmium concentrations in their shoots than in the roots.

Significantly more copper was found in grains and straw of oat treated with vermin-compost than in the objects where mineral fertilizers were used (Gondek and Filipek-Mazur, 2003). UNEP (2002) mentioned the application of sunflower plantation for phytoremediation in Silesia, Poland where heavy metals were directly applied on the top soil by dispenser designed at the Institute for Ecology of Industrial Areas-Katowice, Poland.

Studies done in sunflower plant showed that the maximum concentration of Pb was found in root and leaf (shoot) was the major organ of Zn accumulation (Herrero et al., 2003). At a Department of Energy site in Ashtabula, Ohio, sunflower plants were used to help clear uranium from surface water and groundwater.

Table 5. Metal concentration in roots and shoots and uptake (compared to control treatmet).†

Metal	Dose (ppm)	Roots Metal uptake (ppm)	Shoots Metal uptake (ppm)
Cd	5	0.619 ± 0.019	1.105 ± 0.057
	10	1.602 ± 0.087	2.349 ± 0.174
	20	2.105 ± 0.057	4.816 ± 0.108
	40	4.168 ± 0.040	9.021 ± 0.162
	50	5.211 ± 0.129	11.527 ± 0.131
Cu	5	0.908 ± 0.048	1.613 ± 0.087
	10	1.327 ± 0.045	2.719 ± 0.039
	20	2.685 ± 0.054	5.276 ± 0.074
	40	5.029 ± 0.073	10.781 ± 0.088
	50	6.078 ± 0.074	13.162 ± 0.153
Ni	5	0.517 ± 0.048	1.318 ± 0.042
	10	1.275 ± 0.074	2.152 ± 0.024
	20	2.316 ± 0.045	4.701 ± 0.074
	40	3.961 ± 0.257	8.138 ± 0.125
	50	4.673 ± 0.092	12.152 ± 0.145
Pb	5	0.724 ± 0.031	0.287 ± 0.027
	10	1.001 ± 0.097	0.602 ± 0.049
	20	2.862 ± 0.061	0.975 ± 0.074
	40	4.784 ± 0.171	1.364 ± 0.076
	50	6.052 ± 0.119	1.961 ± 0.064
Zn	5	1.253 ± 0.045	2.972 ± 0.07
	10	2.014 ± 0.084	5.162 ± 0.099
	20	5.132 ± 0.063	9.084 ± 0.083
	40	8.019 ± 0.083	16.327 ± 0.212
	50	9.205 ± 0.166	20.815 ± 0.314

† Values are averages of three replicates $\pm$ S.D.

The same technique was used in a pond within a kilometer of the Chernobyl nuclear generating plant in the Ukraine where an explosion and fire in 1986 caused the world's most serious nuclear accident spreading radioactive contamination across much of Europe (Wikimedia Foundation, Inc 2006).

The trial with uranium-contaminated water was carried out at U concentrations of 100-400ppb. Roots of a selected sunflower cultivar (*Helianthus annuus L.*) caused the uranium solution concentration to decline by 95% within the first 24 hours. A similar approach was used to evaluate the use of plants to treat water contaminated with cesium and strontium in the Ukraine. A natural pond with a surface area of about 75 square meters (m^2) near the village of Yanov was selected as a site for a rhizofiltration field trial. Radionuclide concentrations in the basin were approximately 80 Bq/L for cesium-137 and 1200Bq/L for strontium-90 as a result of the 1986 release by the nearby Chernobyl nuclear reactor. Radionuclide uptakes studied were carried out directly in the contaminated pond. After 4 to 8 weeks of hydroponic growth in the pond, sunflower plants were harvested dried, and the radionuclide concentration measured. The plant tissue concentrations of cesium-137 reached 6.4 x 10 5 Bq per kilogram (dry mass) and 2.5 x 10 6 Bq of strontium-90 per kilogram dry mass (Ensley et al., 1997). The phytoavailable lead is usually very low due to its strong association with organic matter, Fe-Mn oxides, clays and precipitation as carbonates, hydroxides, and phosphates (Shen et al., 2002). The uptake of Pb by 5.6 +1.3 mg in shoot and 61.6 +3.3 mg in root of sunflower plant has been investigated by Nandkumar et al. (1995). Boonyapookana et al. (2005) showed that 80- 87% of the total Pb uptake was localized in plant roots of *H. annuus* with only 13-20% translocated to the aboveground parts (shoot) after the fourth week of studies. He also reported that very low concentration of the Pb is translocated to aerial plant tissues. The X-ray map of root tissue of sunflower revealed the spots of Pb, forming patterns of concentric circles inside the stele, more precisely in the central region of vascular bundles. These spots were also visible on the surface of root epidermis, in the parenchyma cells of the cortical region and outside the endodermis. When Pb enters the plant root, it immediately comes in contact with high phosphate concentrations, relatively high pH, and high carbonate-bicarbonate concentrations in the intercellular spaces. Pb precipitates out of solution in the form of phosphates or carbonates that can be seen in electron micrographs of roots. Plant roots contain inclusion bodies of these forms of Pb in the tissue, reduce Pb translocation in plants.

Plants use photosynthetic energy to extract ions from the soil and concentrate them in their biomass, according to nutritional requirements (Kramer and Chardonnens, 2001). The essential elements (Cu and Zn) are required in low concentrations and hence are known as trace elements or micronutrients, whereas nonessential elements (Cd, Ni, and Pb) are phytotoxic (Gerard et al., 2000). Zn is relatively mobile in soils and is the most abundant metal in root and shoot of contaminated plants as it is in soils. This metal is necessary as a minor nutrient and it is known that plants have special zinc transporters to absorb this metal (Zhu et al., 1999). However, an excessive accumulation of this element in living tissues leads to toxicity symptoms.

In this experiment, shoot is the major organ of heavy metals accumulation (except Pb). Cu is the second most abundant element in contaminated plants and in soils. When the contamination increased, a significantly higher content of copper was found in shoots than roots. Cadmium also is considered to be mobile in soils but is present in much smaller concentrations than Zn (Zhu et al., 1999). Higher Cd concentrations are generally observed in plants grown on soil subjected to the metal-processing industry, sludge application, and long-term fertilization, with up to 70 mg Cd kg $^{-1}$ DM in lettuce (Gerard et al., 2000). Moreover, many studies have demonstrated that Cd taken up by plants accumulates at higher concentrations in the roots than in the leaves (Boominathan and Doran, 2003). Alloway (1995) reported that *Alyssum* species which are naturally adapted to serpentine soils can accumulate over 2% Ni. The uptake by some plants has been confirmed for Cd (up to 0.2% Cd in shoot dry biomass), Ni (up to 3.8% Ni in shoot dry biomass) and Zn (up to 4% Zn in shoot dry biomass) by Kramer and Chardonnens (2001). The application of peat and manure in contaminated soil increased Cu, Zn, and Ni accumulation by wheat (Schmidt, 2003).

Organic matter in soil could effectively increase the activity of metals in soil and improve metal mobility and distribution in soil. The application of natural fertilizer (compost and vermin-compost) in soils has helped in increase in metal mobility through the formation of soluble metal-organic complexes (Yang et al., 2005). In addition, exudation of organic compounds by plant roots, such as organic acids, influence ion solubility and uptake (Klassen et al., 2000) through their effects on microbial activity, rhizosphere physical properties, and root-growth dynamics.(Yang et al., 2005).

Plant root exudation is of particular importance due to their metal chelating/complex forming properties for the mobilization of mineral nutrients and heavy metals (Jauert et al., 2002).

4. Conclusions

This research work deals with phytoremediation of heavy metals by sunflower in the soil - Vermin-compost media. The phytoremediation techniques for the heavy metal management proves to be very effective as its cost is approximately one tenth that of conventional soil cleansing procedures, and in some cases, the plant material can be further

utilized to recoup the cost of the operation or even turn a profit. Another advantage of phytoremediation is that it leaves the soil fertile and has less adverse environmental effects as compared to conventional procedures.

The research finding shown that the low doses of heavy metals applied stimulated the root and shoot elongation of sunflower plants. At higher concentrations i.e. 40 and 50 ppm of Cd, Cu, Ni and Pb significantly reduced the ability to germinate. However, the plants were able to germinate and grow efficiently at any Zn concentration evaluated in this study. The study shows that heavy metals were efficiently up taken at all concentrations using high biomass producing plant *Helianthus annuus* grown in vermicompost media and the uptake was increased along the increasing concentrations in soil.

The sunflower seed and sunflower oil may be used for technical lubricants or energy production and metal-enriched biomass can be harvested using standard agricultural methods and smelted to recover the metals.

The present technology will help to remediate the higher concentrations of metals by the application of vermin-compost as a natural fertilizer in soil. This technology will be applicable at the site to remediate the heavy metals. Thus, an increase in the plant resistance to heavy metal toxicity (Zn, Cu, Ni, Pb and Cd) seems possible by means of addition of nutrient (vermincompost) supply.

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BIOMASS – AN IMPORTANT RENEWABLE SOURCE OF ENERGY IN ROMANIA

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Abstract

At the beginning of 3rd century the humankind finds at a crossroads. Daily, people assist at miracles, live in a time of change, both in economical and rational areas. Energy demand is expected to increase steadily over the next couple of decades, as income levels and economic output expand, especially in the new democratic states after '90th.
Renewable energy resources represent a new opportunity in Romania, with less participation in the market than those forums outside of the country borders, but with developing perspectives in the future. In present in Romania it doesn't exist a very well established renewable resources industry, but only small scale projects or developing pilot projects of some developing institutes or small companies could be mentioned. Energy renewable resources capitalization could contribute to achieve some strategic objectives regarding increasing security of energy supplying by diversifying energy resources and reducing of imports, and for a sustainable developing of energetic sector and environment protection. Renewable energy resources from biomass could be o good solution for heating in rural zones. Biomass potential in Romania is expecting to increase in 2005-2010 trough re-forestations with various trees species and short term re-afforestation. In this paper the advantages of using biomass for energetical purposes and the technological level achieved by conversion processes of biomass in energetical products are presented.

Keywords: biomass, conversion, environment, renewable resources, sustainable development

1. Introduction

The interest in using renewable energy resources increases more and more in the past decades. Because the known fossil resources (oil, natural gasses and others) are considered almost exhausted, the only chance of human kind for the near future remains the renewable resources. Even if governments adopt dynamic policies to conserve energy, the demand continues to increase.

Energy problems are today so acute at the international level that it is no longer possible to satisfy the world's constantly growing needs by continuing to exploit, as before, too limited a range of resources. This growth of energy demand must be increasingly satisfied by diversified energy resources, including sustainable and renewable sources (Tripsa, 2006; Buzdugan and Tripsa, 2006; Gavrilescu and Chisti, 2005).

Another phenomenon, which threats the whole humankind is the climate change and global warming of Earth due to greenhouse effect, determined by increasing the content of the so named greenhouse gases (CO_2, CH_4, NO_x) in the upper layers of atmosphere. Earth global warming determines the appearence of some dangerous meteorological phenomenons: hurricanes, tornados, higher and unexpected floods, El Niňo phenomenon

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of which dimension is higher every passing year, giving rise of huge damages, agricultural fields emptiness on higher altitudes.

Biomass resources include wood and wood wastes, agricultural crops and their waste byproducts, municipal solid waste, animal wastes, waste from food processing, aquatic plants and algae (Gavrilescu and Chisti, 2005;Demirbas, 2001).

Biomass is the plant material derived from the reaction between CO_2 in the air, water and sunlight, *via* photosynthesis, to produce carbohydrates that form the building blocks of biomass. Typically photosynthesis converts less than 1% of the available sunlight to stored, chemical energy. The solar energy driving photosynthesis is stored in the chemical bonds of the structural components of biomass. If biomass is efficiently processed, either chemically or biologically, by extracting the energy stored in the chemical bonds and the subsequent 'energy' product combined with oxygen, the carbon is oxidized to produce CO_2 and water. The process is cyclic, as the CO_2 is then available to produce new biomass (Fig. 1) (McKendry, 2001).

Biomass is being used as a source of primary energy all over the world since ancient times. The use of biomass to produce energy is only one form of renewable energy that can be utilized to reduce the impact of energy production and use on the global environment, in contrast to fossil fuels.

As with any energy rears limitation on the use and applicability source there are limitation on the use and applicability of biomass and it must compete not only with fossil fuels but with other renewable energy sources such as wind, solar and wave power (McKendry, 2002a, b).

Energy sources will play an important role in the world's future. They have been grouped into three categories: fossil fuels (coal, petroleum and natural gas), renewable sources and nuclear sources (Demirbas, 2000a, b; Parikka, 2004).

Biomass is used to meet a variety of energy needs, including generating electricity, heating homes, fueling vehicles and providing process heat for industrial facilities. It can be converted into useful forms of energy using a number of different processes (McKendry, 2001, 2002a).

2. Resources of biomass

Biomass differs from other alternative energy sources in that the resource is variable, and it can be converted to energy through many conversion processes. Biomass resources can be divided into four general categories:

Wastes: agricultural production wastes, agricultural processing wastes, crop residues, mill wood wastes, urban wood wastes, and urban organic wastes;

Forest products: wood, logging residues, trees, shrubs and wood residues, sawdust, bark etc. from forest clearings;

Energy crops: short rotation woody crops, herbaceous woody crops, grasses, starch crops (corn, wheat and barley), sugar crops (cane and beet), forage crops (grasses, alfalfa and clover), oilseed crops (soybean, sunflower, safflower);

Aquatic plants: algae, water weeds, water hyacinth, reed and rushes.

Biomass contributes about 12% of today's world primary energy supply, while in many developing countries, its contribution ranges from 40% to 50% (Buzdugan and Tripsa, 2006). World production of biomass is estimated at 146 billion metric tons a year, mostly wild plant growth. Some farm crops and trees can produce up to 20 metric tons per acre of biomass a year. Types of algae and grasses may produce 50 metric tons per year (Demirbas, 2001). Conversion of biomass to energy is undertaken using two main process technologies: thermo-chemical and bio-chemical/biological.
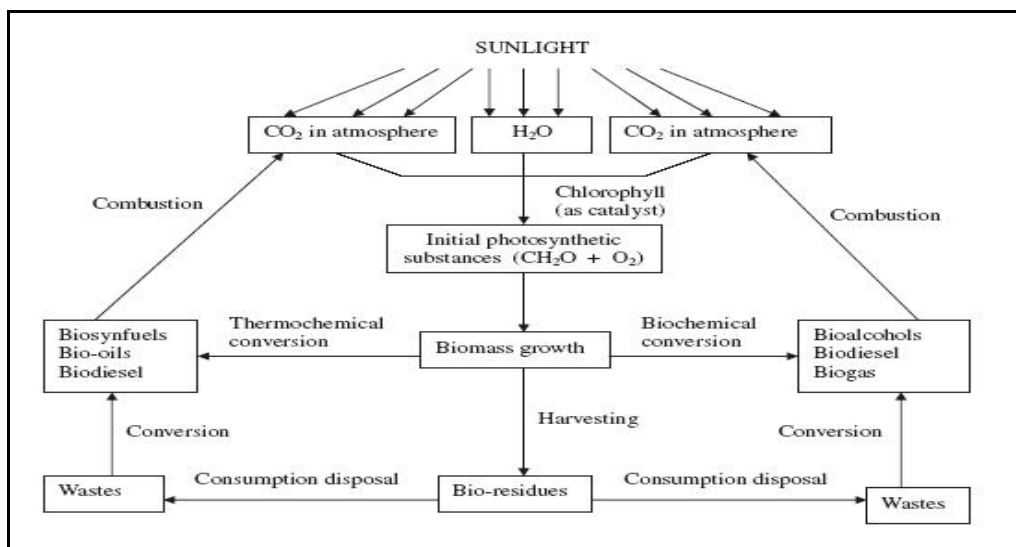
Fig 1. Main steps of biomass technology

3. Energetic potential of biomass in Romania

Romania has a considerable energetic potential of biomass, evaluated at 7594 tap/year (318×10^9 MJ/an) representing almost 19% from the total primary energy resources in the year 2004. This potential leads to the following biomass fuel category:
- wood wastes from woods and wood for fire, 1175×10^3 tap/an (49.2 PJ/an)**;**
- sawdust and others wood wastes, 487×10^3 tap (20.4 PJ/an)**;**
- agricultural wastes, resulting from cereals, corn, vine residues, 4799×10^3 tap (200.9 PJ/an)**;**
- biogas, 588×10^3 tap/an;
- urban and household wastes 545×10^3 tap/an.

Wood for fire and agricultural wastes represent almost 80% from the total biomass quantity, while wood wastes coming from industrial processes, almost 6.5%.

The heat resulted from biomass burning holds various\ percentages in primary resources balance, in respect with the type of wastes or final destination (Buzdugan and Tripsa, 2006).

Biogas was used in past in large quantities. Nowadays, biomass is used only for heating, spontaneous burning for cooking and hot water preparing. House heating is on the second place of using biomass. Almost 95% of used biomass nowadays is fire wood and agricultural wastes, the rest being represented by wastes coming from wood processing. Production capacity of wood saws is 3.3 Math, while in other industry fields is 4.7MW.

Market potential for biomass conversion is very large, but funding and subventions are necessary for developing this field. Direct burning in stoves and roasters for burning, cooking and preparing hot water represents almost 95% from the total used biomass, with a total capacity of 4.8 kW. The feed is manually and has efficiency between 15% and 50%. Burning in steam generators and industrial applications represents almost 5% from the total amount of used biomass (Jefferson, 2006).

Biomass usages can be classified in the following market segments:
- replacing a part of fossil fuels from urban heating installations (wood splints)
- using biomass as substituent of fossil fuel (wood splints and logs as industrial fuel from steam generators and hot water boilers) instead of oil;
- improving the usage of biomass for urban heating in small towns and villages, located near resources, where the population doesn't have access to gas network distribution;
- usage of straws and other agricultural wastes in generators for biomass burning to heat the isolated farms or small villages ;
- maximum priority is using biomass for thermal purposes and to replace the oil.

Biomass conversion could be the best and cheapest method for urban heating in Romania.

4. Conversion of biomass

Biomass can be converted into useful forms of energy using a number of different processes. Factors that influence the choice of conversion process are: the type and quantity of biomass feedstock, the desired form of the energy, i.e. end-use requirements, environmental standards, economic conditions, and project specific factors. In many situations the form in which the energy is required determines the process route followed by the available types and quantities of biomass (Demirbas, 2001; Gavrilescu and Christi, 2005) (Fig. 2). The conversion technologies to utilize biomass can be classified into four basic categories (, 2001):
- direct combustion;
- thermochemical processes;
- biochemical processes;
- agrochemical processes.

Biomass can be converted into three main products: two related to energy – power/heat generation and transportation fuels – and one as a chemical feedstock (McKendry, 2001).

Fig.2. Main biomass conversion processes

4.1. Thermo-chemical conversion

Thermo-chemical biomass conversion does include a number of possible roots to produce useful fuels and chemicals from the initial biomass feedstock (Overend, 2002).
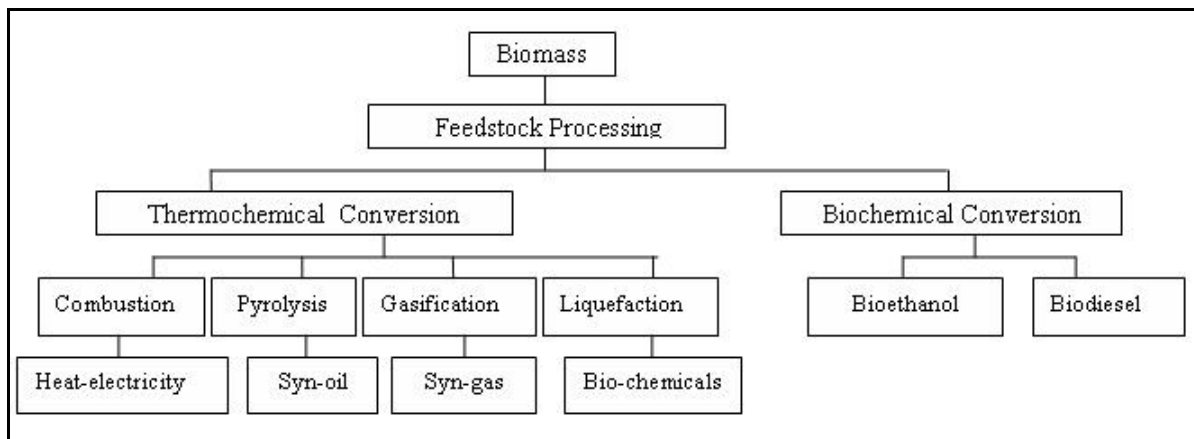
Thermo-chemical processing of biomass and wastes offers a number of ways to produce energy and if this is applicable, a potential attractive method is provided to avoid waste accumulation. In addition to obtain heat from biomass, wastes can be converted into a mixture of gases, liquids and carbon char (Fig. 3) (Jackson and Löfsedt, 1998). The proportions of the various products are dependent upon the feedstock, temperature and pressure of the reaction, the time spent in the reaction zone, and the heating rate.
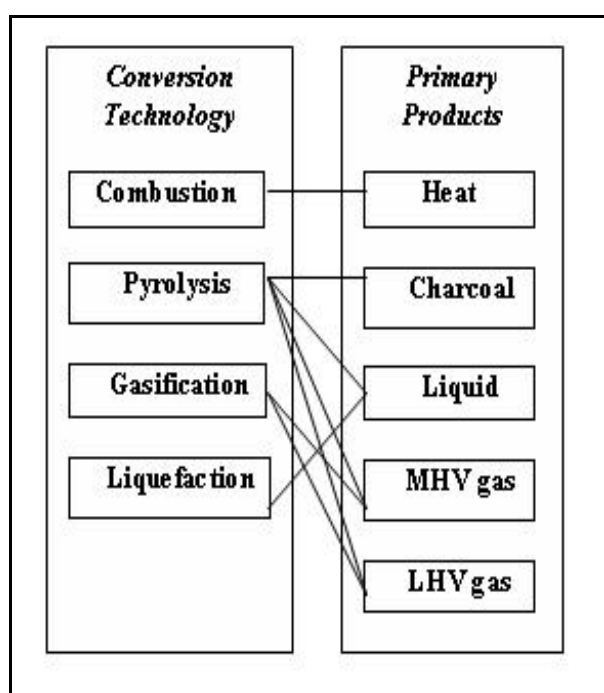
Fig. 3. Thermochemical conversion processes and primary products

Large industrial scale furnaces and boilers have been developed for burning bark, wood, wood wastes, black liquor from pulping operations, food industry wastes and municipal solid wastes. The high moisture content and variable composition of many biomass sources makes them difficult to achieve the same cost-benefit as fossil fuel furnaces in smaller units, but larger units can be very efficient, nearly matching the performance of fossil fuel furnaces.

Along with combustion of biomass and waste, a well-known technology, the major areas of current research focus appear to be pyrolysis and gasification. However, combustion technologies are simple and their dominant role among technologies currently in use would be mentioned.

4.1.1. Combustion

Direct combustion is a thermo-chemical conversion process type that utilizes as major biomass feedstock wood, agricultural wast, municipal solid and residential waste to produce fuels for heat, steams or electricity. In general combustion models of biomass can be classified as macroscopic or microscopic. The macroscopic properties of biomass are given with for macroscopic analysis, such as ultimate analysis, heating value, moisture content, particle size, bulk density, and ash fusion temperature. Properties for microscopic analysis include thermal, chemical kinetic and mineral data (Ragland et al., 1991; Demirbas, 2004). Physical property values vary greatly and properties such as density, porosity, and internal surface area are related to biomass grades whereas bulk density, particle size, and shape distribution are related to fuel preparation methods (Demirbas, 2004).

Combustion is widely used on various scales to convert biomass energy to heat and/or electricity with the help of a steam cycle (stoves, boilers and power plants) (Demirbas, 2000a).

The advantages of co-firing are apparent: the overall electrical efficiency is high due to the economies of scale of the existing plant (usually around 40%) and investment costs are low up to negligible when high-quality fuels as pellets are used. Also, directly avoided emissions are high due to direct replacement of coal. Combined with the fact that many coal-fired power plants in operation are fully depreciated, this makes co-firing usually a very attractive Green House Gases mitigation option. In addition, biomass firing leads to lowering sulfur and other emissions (Faaij, 1999).

Combustion of biomass produces hot gases at temperatures around 800–1000 ^{0}C. It is possible to burn any type of biomass but in practice combustion is feasible only for biomass with moisture content lower than 50%, unless the biomass is pre-dried. High moisture content biomass is better suited in the case of biological conversion processes.

4.1.2. Pyrolysis

Pyrolysis is defined as the thermal destruction of organic materials in the absence of oxygen, or partially combusted in a limited oxygen supply, to produce a hydrocarbon rich gas mixture, an oil-like liquid and a carbon rich solid residue (Demirbas, 2000c, d). Pyrolysis converts biomass at temperatures around 500^{0}C, in the absence of oxygen, to liquid (bio-oil), gaseous and solid (charcoal) fractions. The process can be adjusted to favor charcoal, pyrolytic oil, gas, or methanol production with a 95.5% fuel-to-feed efficiency. Pyrolysis can be used for the production of bio-oil if flash pyrolysis processes are used and are currently at pilot stage (Fig. 4) (EUREC, 1996). The bio-oil can be used in engines and turbines and its use as a feedstock for refineries is also being considered (McKendry, 2001, 2002a).
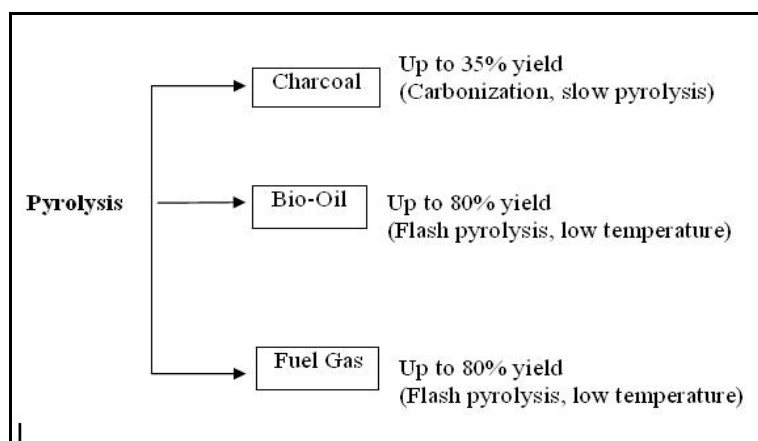
Fig. 4. Pyrolysis process

Bio-oil contains about 40 wt% of oxygen and is corrosive and acid. The crude oil can also be upgraded (e.g. *via* hydrogenation) in order to reduce the oxygen content. But upgrading comes with both economic and energy penalties (Faaij, 2002; Radlein, 1998).

Some problems in the conversion process and use of the oil need to be overcome; these include poor thermal stability and corrosiveness of the oil. Upgrading by lowering the oxygen content and removing alkalis by means of hydrogenation and catalytic cracking of the oil may be required for certain applications (Demirbas, 2000a, b). Pyrolysis of wood has been studied as a zonal process (Demirbas, 2004). Thermal degradation properties of hemicelluloses, cellulose and lignin can be hierarchized as follows (Chum and Overend, 2001):

Thermal degradation of hemicelluloses - of cellulose - of lignin

Pyrolysis of biomass is thermal decomposition of the fuel. As with coal, pyrolysis is a relatively slow chemical reaction occurring at low temperatures. The reaction mechanisms of biomass pyrolysis are complex but can be defined in five stages for wood (Demirbas, 2000a; Demirbas 2004):

- Moisture and some volatile loss.
- Breakdown of hemicelluloses; emission of CO and CO_2.
- Exothermic reaction causing the woody biomass temperature to rise from 525 to 625 K; emission of methane, hydrogen and ethane.
- External energy is now required to continue the process.
- Complete decomposition occurs.

4.1.3. Gasification

Gasification is a form of pyrolysis, carried out at high temperatures in order to optimize the gas production. The resulting gas, known as synthesis gas, is a mixture of carbon monoxide, hydrogen and methane, together with carbon dioxide and nitrogen. Biomass gasification technologies have historically been based upon partial oxidation or partial combustion principles, resulting in the production of a hot, dirty, low calorific value gas that must be directly ducted into boilers or dryers. In addition to limiting applications and often compounding environmental problems, these technologies are an inefficient source of usable energy.

Biomass gasification is the latest generation of biomass energy conversion processes, and is being used to improve the efficiency, and to reduce the investment costs of biomass electricity generation through the use gas turbine technology. High efficiencies (up to about 50%) are achievable using combined-cycle gas turbine systems, where waste gases from the gas turbine are recovered to produce steam to be used in a steam turbine. Economic studies show that biomass suffocation plants can be as economical as conventional coal-fired plants (Demirbas, 2004; Toft and Bridgwater, 1996).

Practically, gasification is the conversion of biomass into a combustible gas mixture by partial oxidation at high temperatures, typically in the range 800–900 ^{0}C. The low calorific value gas produced (about 4–6 MJ/N m^3) can be burnt directly or used as a fuel for gas engines and gas turbines (LRZ, 1993; N.R.I. 1996). The produced gas can be used as a feedstock (syn-gas) in the production of chemicals (e.g. methanol) (McKendry, 2001). The gas is very costly to be stored or transported due to its the low energy density so it has to be locally used.

The gasification of coal is well known, and has a history back to year 1800. The oil-shortage of World War II imposed an introduction of almost a million gas producers to fuel cars, trucks and busses. One major advantage of gasification is the wide range of biomass resources available, ranging from agricultural crops, and dedicated energy crops to residues and organic wastes. The feedstock might have a highly various quality, but still the produced gas is can be standardized and transformed in a homogeneous product. This makes possible to choose

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the feedstock that is the most available and economic at all times (Adam, 2006). The precise composition of the gas from a reactor depends on the type of biomass used, the temperature, and the reaction rate.

Gasification technology has been used quite successfully for direct heat applications, as a sophisticated gas cleaning system is not required. Thermo-chemical gasification involves decomposition and devolatilization reactions that may be represented as:

$$C_aH_\beta O_? + yO_2 + zN_2 + wH_2O + dh\ ? \qquad + x_6CH_4 + x_7C\mu Hp + x_8O_2 + x_9N_2$$

$$x_1C + x_2H_2 + x_3H_2O + x_4CO + x_5CO_2$$
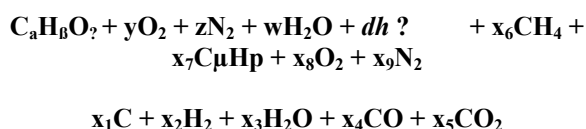
In the above presented equation, $C_aH_\beta O_?$ represents biomass, and y, z and w are molar numbers of oxidant. Air (oxygen, nitrogen, and water vapor), oxygen, steam or a mixture of these may be used in this partial oxidation. On the output side of the equation, x_1, x_2, x_3, etc., are molar numbers of char, hydrogen, carbon monoxide, carbon dioxide, methane, higher hydrocarbons (tar vapors), traces of unreacted oxygen, and nitrogen produced by these reactions. Theoretical, zN_2 should be equivalent to x_9N_2 (i.e., the nitrogen in the air remains inert). The heat requirements (*dh*) for the reaction to occur may be supplied either by *in situ* combustion of part of the biomass or heat applied from an external source. Note that by replacing air in the reaction with pure oxygen, all nitrogen is removed from the mass reaction equation (UN, 1996; Jackson and Löfsedt, 1998).

Air gasification produces a low heating value gas (4-7 MJ/Nm³), while oxygen gasification produces a medium heating value gas (10-18 MJ/Nm³). Although air gasification produces a low heating value, it is the more widely used gasification technology. It avoids the cost and hazard of oxygen production and usage, as well as the complexity and cost of multiple reactors.

The product, consisting of char (carbon), H_2, H_2O, CO, CO_2, CH_4, and $C_\mu H_p$ (with O_2 and N_2), is a relatively low energy density combustible gas which may be burned directly for space heating or drying, or which may be used in a boiler to produce steam and/or electricity or (after some cleaning to remove entrained char) in an internal combustion engine .

For power generation, the down draft gas producer has been found to be most suitable, as it is capable of producing clean gas. The main problem in biomass gasification for power generation is the cleaning of gas so that it as to be free of impurities before entering the engine. The development of a gas cleaning system is as important as that of the development of a gas producer (Toft and Bridgwater, 1996).

4.1.4. Liquefaction

Liquefaction is the conversion of biomass into a stable liquid hydrocarbon using low temperatures and high hydrogen pressures (WSL, 1993).

The process produces a marketable liquid product. The interest in liquefaction is low because the reactors and fuel feeding systems are more complex and more expensive than for pyrolysis processes. A generalized conceptual flow sheet for liquefaction is shown in Fig .5.

Concerning the catalytic effect of alkali hydroxides and carbonates, there has been little description about that a catalyst plays in liquefaction with some exceptions (Demirbas, 2001).

4.2. Bio-chemical conversion

Biochemical conversion is the process by which biomass is converted into gas (CO_2/CH_4), waste (compost or fertilizer) and water (water or C_2H_5OH) by using microorganisms.
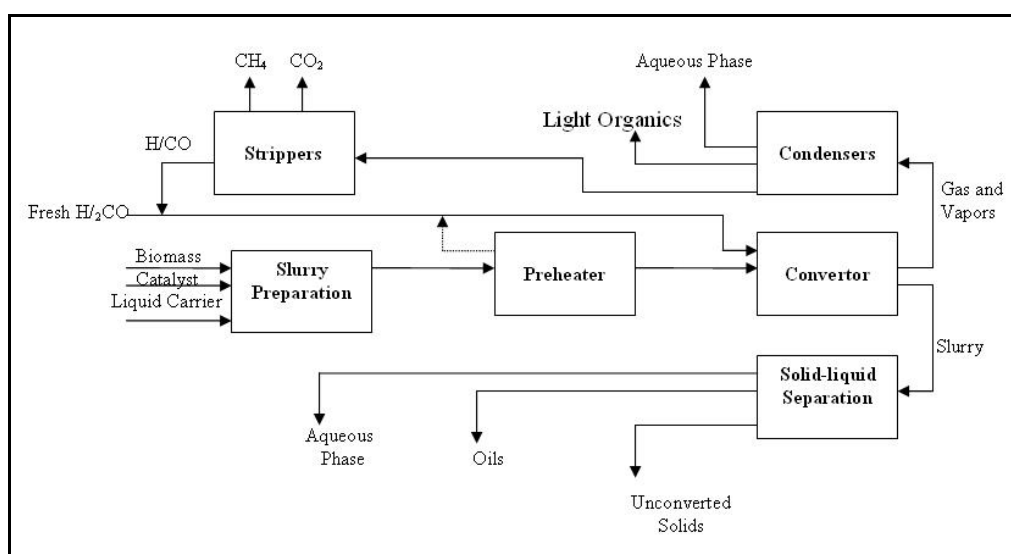

Fig. 5. Flow sheet for biomass liquefaction

The biochemical processes refer mainly to (1) aerobic fermentation which produces compost, carbon dioxide and water, (2) anaerobic fermentation which produces fertilizer and gas (CH_4/CO_2) and (3) alcoholic fermentation which produces ethanol (C_2H_5OH), carbon dioxide (CO_2) and waste.

Biochemical procedures, non-pollution methods, characterized by low energy consumption, have been studied by specialists mainly with regard to biogas, ethyl alcohol, compost and protein obtaining. But, the world-wide application of such procedures has not gone beyond preliminary experiments on a pilot scale, with few industrial results or as stations of producing biogas and compost, placed according to specific and local responsibilities (Demirbas, 2000a, c).

Biochemical systems are among the most promising, environmentally sustainable alternatives for reducing atmospheric carbon dioxide (CO_2) levels. Biomass can act as a reservoir of carbon or as a direct substitution for fossil fuels with no net contribution to atmospheric CO_2 if produced and used sustainable (Kücük, 1995).

The sun is the energy source on which all terrestrial life is based. The energy of solar radiation is the driving force of the biological cycle. Only about 0.1% of the energy received by the earth from the sun enters into photosynthetic production of organic matter. Roughly 150-200 billion tons of dry organic matter is estimated to be produced annually in the world as vegetation in forests, grasslands, marshes, oceans, estuaries, lakes, rivers, tundras etc.

Approximately half of the energy tied up in photosynthesis is involved in plant respiration. Biochemical conversion methods are inverse photosynthesis. This action can be converted inversely by using some microorganisms (Demirbas, 1998).

4.2.1. Anaerobic digestion

Anaerobic digestion is the decomposition of biomass through bacterial action in the absence of oxygen. It is essentially a fermentation process and produces a mixed gas output of methane and carbon dioxide. The product generated by the decay, in the absence of air, of sewage or animal waste is known as biogas.

Biogas is most commonly produced by using animal manure mixed with water which is stirred and warned inside an airtight container, known as a digester. Digesters range in size from around $1m^3$ for a small household unit to as large as $2000\ m^3$ for a large commercial plant (Ramage and Scurlock, 1996). The biogas produced can be burnt directly for cooking and space heating, or used as fuel in internal combustion engines to generate electricity.

Methane gas produced in landfill sites eventually escapes into the atmosphere. However, the landfill gas can be extracted from existing landfill sites by inserting perforated pipes into the landfill. In this way, the gas will travel through the pipes under natural pressure for use as an energy source, rather than simply escaping into the atmosphere to contribute to greenhouse gas emissions (Demirbas, 2001; Gavrilescu and Macoveanu, 1999). The gas composition is 65-70% methane, 35-30% carbon dioxide and negligible traces of other gases (e.g. H_2S and H_2) and is saturated with water. The gas has an approximate heating value of about 26 MJ/m^3 (Demirbas, 2000d).

The biomass is converted by bacteria in an anaerobic environment, producing a gas with an energy content of about 20–40% of the lower heating value of the feedstock. Anaerobic digestion is a commercially proven technology and is widely used for treating high moisture content organic wastes (80–90%). Biogas can be used directly in spark ignition gas engines and gas turbines and can be upgraded to higher quality i.e. natural gas quality, by the removal of CO_2.

Used as a fuel in spark ignition gas engines to produce electricity only, the overall conversion efficiency from biomass to electricity is about 10–16%. As with any power generation system using an internal combustion engine as the prime mover, waste heat from the engine oil and water-cooling systems and the exhaust could be recovered using a combined heat and power system. A typical flow sheet for processing biomass using anaerobic digestion is shown in Fig.6.

Anaerobic fermentation, where the waste is kept without oxygen for approximately 2-8 weeks around 310 K, not only solves the pollution problem but also produces energy and organic fertilizer from a renewable source. Animal waste has created a major waste disposal problem and is becoming more acute because greater numbers of animals are being raised on concentrated feedstocks.

4.2.2. Alcoholic fermentation

Ethanol can be produced from certain biomass materials which contain sugars, starch or cellulose. The best known source of ethanol is sugar cane, but other materials can be used, including wheat and other cereals, sugar beet, Jerusalem artichoke and wood. The choice of biomass is important as feedstock costs typically make up 55-80 % of the final alcohol selling price (W.E.C., 1994). Starch based biomass is usually cheaper than sugar based materials but requires additional processing. Similarly, cellulose materials, such as wood and straw, are readily available but require expensive preparation.

Ethanol is usually produced by fermentation. Typically, sugars are extracted from the biomass crop by crushing, mixed with water and yeast and kept warm in fermenters. The yeast breaks down the sugar and converts it to methanol. A distillation process is required to remove the water and other impurities in the diluted alcohol product (10-15% ethanol).
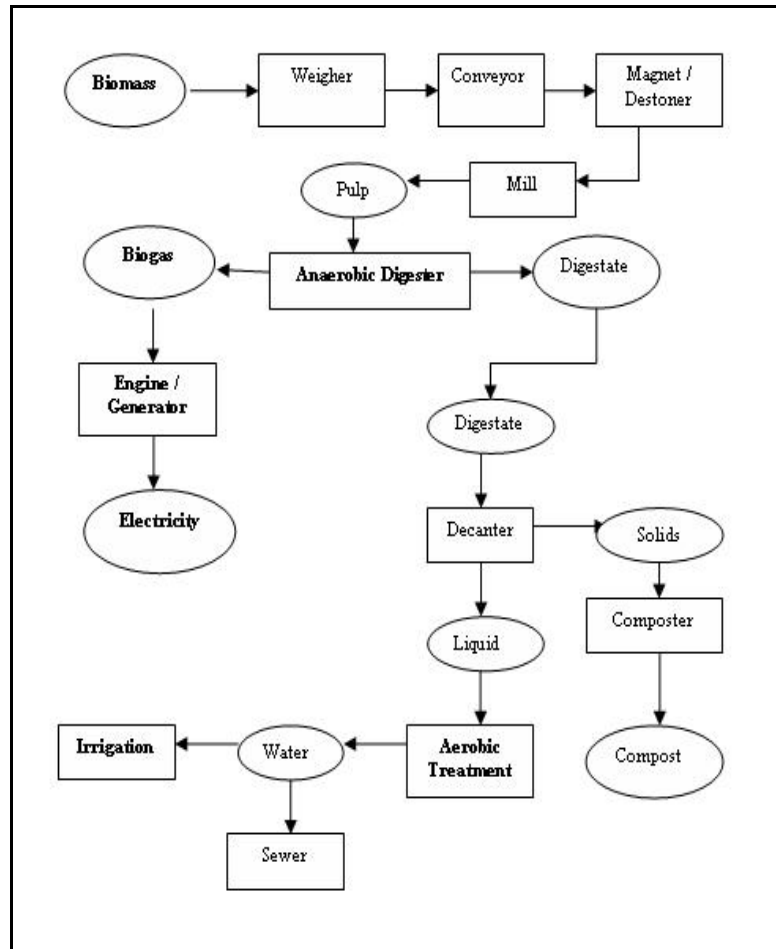
Fig. 6. Flow sheet for anaerobic digestion of biomass

The concentrated ethanol (95% by volume with a single step distillation process) is drawn off and condensed to a liquid form.

Ethanol can be used as a supplement or substitute for gasoline in cars. Brazil has a successful industrial scale ethanol project which produces ethanol from sugar cane for blending with gasoline. Some vehicle adaptations are required for full gasoline substitution.

Crop residues are often used to supply the external heat required for the process. There is a significant energy loss in the distillation stage, particularly the complex secondary distillation process required to achieve ethanol concentrations of 99% or better. This may be acceptable, however, due to the convenience of the liquid fuel and relatively low cost and maturity of the technology (Demirbas, 2001).

5. Benefits of biomass utilization

Biomass is a renewable, potentially sustainable and relatively environmentally benign source of energy. If it is grown and utilized on a sustainable basis, biomass is carbon dioxide neutral. Thus, the substitution of fossil fuels for energy production using biomass will result in a net reduction in greenhouse gas emissions and the replacement of a non-renewable energy source. Many large power producers in industrialized countries are looking for biomass as a means of meeting greenhouse gas reduction targets (Demirbas, 2001). The natural decomposition of biomass produces methane, which is about twenty times more active as a greenhouse gas than carbon dioxide (Demirbas, 2000a, b).

There is, therefore, an additional greenhouse gas emission in burning biogas, landfill gas and biomass residues to produce carbon dioxide.

Biomass fuels have negligible sulfur content and, therefore, do not contribute to sulfur dioxide emissions, which cause acid rain. The combustion of biomass produces less ash than coal combustion, and the ash produced can be used as a soil additive on farm targets.

Biomass is a domestic resource, which is not subject to world price fluctuations or the supply uncertainties of imported fuels. In developing countries in particular, the use of liquid biofuels, such as biodiesel and ethanol, reduces the economic pressures of importing petroleum products.

Perennial energy crops (grasses and trees) have lower environmental impacts than conventional agricultural crops.

6. Environmental impacts of biomass energy

As with all forms of energy production, biomass energy systems raise some environmental issues that must be addressed. In biomass energy projects, issues such as air pollution, impacts on forests and impacts due to crop cultivation must be addressed on a case by case basis. Unlike other non-renewable forms of energy, biomass energy can be produced and consumed in a sustainable fashion, and there is no net contribution of carbon dioxide to global warming. One example is a closed loop system in which carbon dioxide will be taken up by new plant growth at the same rate that it is released by using the harvested biomass for fuel. (Jefferson, 2006; Robu et al., 2005) Such bioenergy crops would have little or no net contribution to atmospheric carbon dioxide as a greenhouse gas. On the other hand, when fossil fuels are burned, carbon is released that has been stored underground for millions of years, making a net contribution to atmospheric greenhouse gases. Therefore, if managed carefully, biomass energy can have significant environmental advantages over the use of fossil fuels. An appropriate level of biomass energy use can have less environmental impacts than our current means of energy production (Demirbas, 2001).

7. Conclusions

This brief introduction regarding the usage of biomass as a renewable energy resource for preventing the natural and antropogenic disasters disclose the importance of biomass for the environment and humankind existence.

Multiple changes adaptation and choosing the right way represents probably the essence of survival, and having in mind the hopes of humankind for a better understanding and knowledge of living systems, for satisfying the increasing needs of humankind, for preserving and protecting the environment, the usage of biomass as a renewable energy resource remains an efficient way of solving the social-economical problems of this millennium beginning society.

Therefore, it must be underlined the beneficial effect of regenerating energies not only regarding the environment protection, but also in economical and social domain. Thus, increasing the air quality, energetic security, but also the percentage of labour force who work and developing the business frame are key-objectives that can be achieve trough renewable energy promotion.

Biomass could be recommended as the main renewable source energy in Romania.

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INTEGRATION OF BIOREFINERY CLUSTERS TOWARDS ZERO EMISSIONS

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Abstract

Depletion of world recourses, increasing pollution, and climate change make us shift from linear economy to system economy – an economy of technologies integrated to reach a non-polluting zero emissions production system. Transition to renewable resources requires replacement the present crude oil refinery by biomass refinery. Along with conventional biomass refinery technologies bioengineering and nano-technologies become significant players of systems in the design of clusters of integrated biorefinery technologies. The authors consider a number of case-studies of biomass conversion into value-added chemicals and sources of energy, the steam explosion autohydrolysis (SEA) in particular. Modelling of the SEA processes is represented by a preliminary analysis of energy flows. The eMergy (energy memory) approach is applied to assess environmental impacts and sustainability.

Keywords: zero emissions, biomass, biorefinery, systems design

1. Introduction

The UN University/ Institute of Advanced Studies (UNU/IAS) Zero Emissions concept (Pauli, 1998; Gravitis, 1999; Gravitis and Della Senta, 2001; Gravitis et al., 2004; Gravitis, 2007) has the following objectives:

- to emphasizes shift from the traditional linear industrial model in which wastes are considered the norm, to integrated technologies systems utilizing everything;
- to introduce sustainable cycles as found in nature;
- to prescribe reorganization of industries into clusters the wastes of one complying with input requirements of another and the integrated whole producing no waste of any kind.

Zero emission means shift from "cradle to grave" (LCA) to "cradle to cradle".

Biorefinery, according to the Laboratory of Biomass Eco-Efficient Conversion of the Latvian State Institute of Wood Chemistry (LSIWC/LBE-EC) (Gravitis et al., 1997; Gravitis et al., 2001; Gravitis, 2006; Gravitis, 2008), is a cluster of integrated technologies converting biomass into transportation fuels, power, chemicals, and advanced materials within the zero emissions framework and comprises two platforms: Energy and Chemicals & Materials (Fig.1).

The biorefinery concept is an analogue of today's petroleum refineries producing multiple fuels and products from petroleum. By combining chemistry, biotechnology, engineering and systems approach, biorefineries could produce food, feed, fertilizers, industrial chemicals, fuels, and power from biomass.

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Many of the biorefinery ideas overlap with the ideas and approaches of green chemistry (Gravitis, 2006).

As was defined by Kamm and Kamm (2004), „Biorefineries combine the necessary technologies between biological raw materials and industrial intermediates and final products". The principal goal in the development of biorefineries is defined as (biomass) feedstock-mix + process-mix ∗ product-mix".

Chemicals &Materials Platform
Furfural
Levoglucosan
Fibres
Biodegradable polymers
Nano-materials

Biomass

Energy Platform
Biomass co-firing with coal
Bio-diesel
Bio-ethanol
Charcoal
....
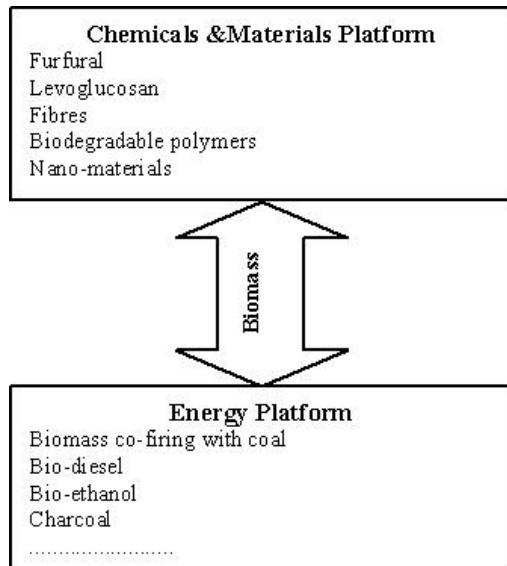
Fig. 1. Platforms of the LSIWC/LBE-EC biorefinery concept

Advancement of up-to-date and efficient technological implementations of biomass conversion becomes particularly vital as the deposits of non-renewable resources are being used up (Fig. 2) the products of photosynthesis becoming the only available source of organic fuels and chemicals.

2.1. Steam explosion pre-treatment. First, second, and third generation feedstock for bio-fuels

The main idea of Zero Emission is zero wastes and clustering of industries. *Steam explosion auto-hydrolysis* (SEA) can serve as a seed for dispersed but integrated clusters comprising fine chemical industry, paper industry, building industry, food industry, pharmaceutical industry, fuel industry, biotechnology, and farming.

Efficient pre-treatment technologies and new uses of lignocellulosic biomass are needed for future bio-refineries. SEA being one of the most prospective pre-treatment technologies facilitates separation of the lignocellulosic biomass components in a single course of action providing the source for biofuels, chemicals, and nano-materials.

SEA (steam explosion, steam explosion pulping, steam cracking) principally is a simple technique (Gravitis, 1987; Gravitis et al., 2001). The biomass is treated with saturated steam at pressures up to 4 MPa. The treatment time varies from some seconds to some minutes.

Under conditions of severe competition for the carriers of captured solar energy limited by the terrestrial annual total of 56 Gt fixed carbon (Potter, 1999) efficient and sustainable consumption of the unique resource is extremely important for the future bio-refineries required to replace the present petrochemical factories.

2. Case studies

After being held at high pressure, within a split second, the biomass is decompressed (exploded) to ambient pressure. Empirically result of SEA is determined by severity parameter R_o expressed as (Heitz et al., 1991):
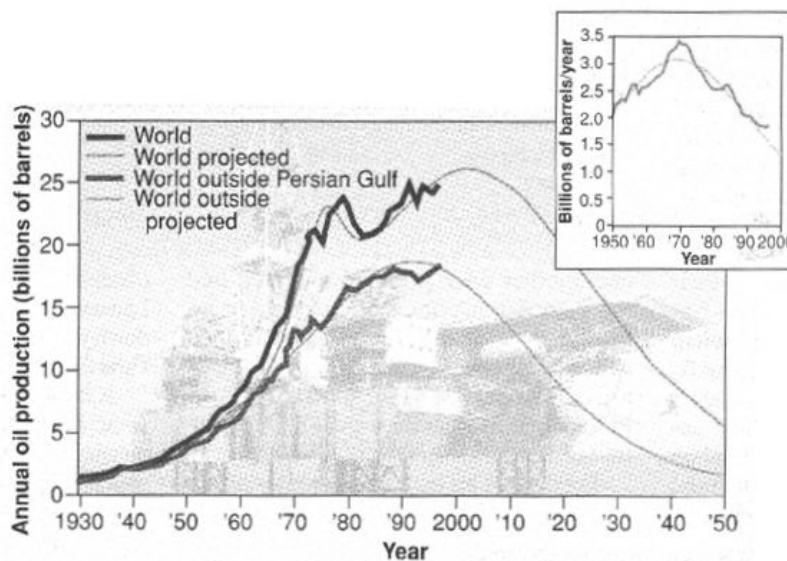
Fig. 2. Predicted peaks in the world oil production
(Right top - Hubbert King predicted oil peak in the U.S. upper states (Kerr, 1998))

$$R_o = t * exp\ [(T-100)/\ 14.75] \qquad (1)$$

where duration of exposure to high pressure (t, minutes) and temperature (T, ^oC) express the SEA severity against the base temperature $T_{base} = 100\ ^oC$. Similar SEA results may be achieved with different combinations of t and T. However, there is a contribution from other factors such as moisture content of the sample, size of particles etc.

The principal block scheme of SEA is shown in Fig.3.
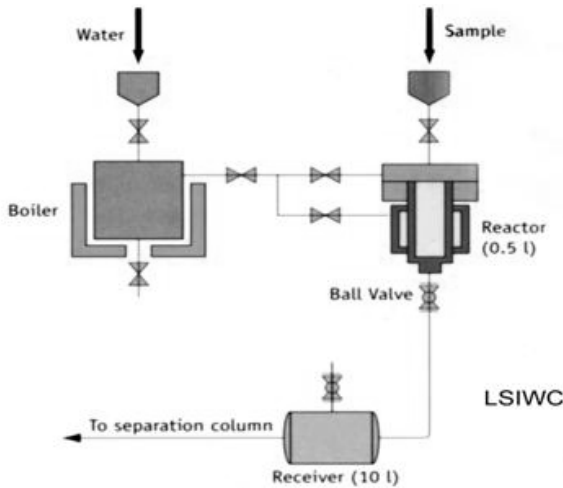
Fig. 3. Steam explosion unit

Of a number of chemical and physical processes occurring during the SEA treatment, two are most important:

- the functional groups are cut off during the process and thereby acid molecules are formed in the system (for example, acetic groups of hemicelluloses form acetic acid). These newly formed acids act as catalysts of hydrolysis (auto-hydrolysis);
- after sudden release of the pressure at the end of the SEA process, the difference of pressure in the tissues of the material and surroundings blasts the material providing an effective defibration of wood or other biomass.

Since the lignocellulosic material, under conditions of steam explosion, can provide "self-sufficient" chemical and physical transformation (Kokorevics et al., 1999) both the processes, hydrolysis and defibration, can be achieved without any additional reagents (except steam). Further fractionation (Gravitis, 1996) of the biomass products after SEA is rather simple (Fig. 4).

The main problem is optimizing fractionation technologies including vacuum evaporation, microfiltration, ultrafiltration, reverse osmosis etc., after the SEA treatment.

All SEA products have a variety of applications (Gravitis, 1996). Hemicelluloses (Fig. 5), during the SEA can be hydrolysed to sugars – xylose, mannose, arabinose, etc. and used as molasses, the substrate for fodder yeast or bio-ethanol. The xylose sugar can be hydrogenated to xylitol (sweetener) and can also be dehydrogenated to furfural – an excellent feedstock for chemical processing.
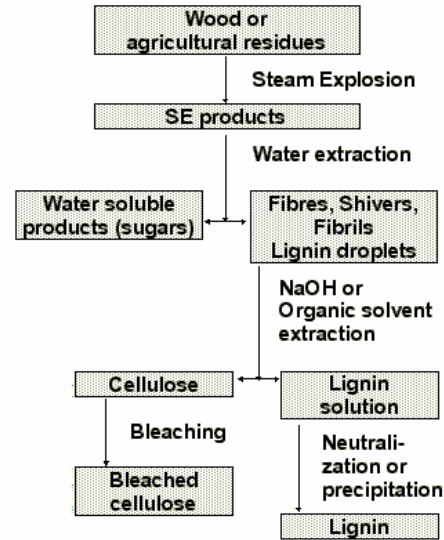
Fig. 4. Fractionation of steam exploded biomass. (Gravitis, 1996)
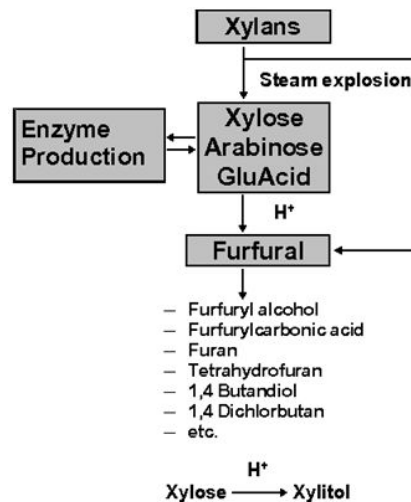
Fig. 5. SEA treatment products from hemicelluloses (Gravitis, 1996)

Lignin (Fig. 6) can be used as binder to plywood, fibreboards and particle boards. Lignin is also used as a component in coatings and foams. Lignin and its modification serve as dispersants, slow-release fertilizers, sorbents, carbon fibres, insecticides, and plant hormones. Commercial potential of many lignin derivatives showing good properties is still unclear. Lignin obtained by conventional technologies containing sulphur is often burned and used as a heat source. The SEA lignin is sulphur-free and chemically reactive. During the SEA

treatment lignin coalescing in spheres of diameter to some micrometers on the surface of cellulose fibres promotes enzymatic attack on cellulose.

Cellulose (Fig. 7) can be hydrolyzed to glucose and oligosugars. The enzymatic isomerization of glucose to fructose is well established. Glucose can be fermented to acids, alcohols, polyols and ketones. Derivatives of cellulose serve as animal fodder, substrate for microorganisms and mushrooms, super-high swollen gels, liquid crystals etc. Microcrystalline cellulose is used in paper industry and in food and pharmaceutical industries. The SEA produces cellulose micro-fibrils. It looks perspective to use homogeneously dispersed cellulose fibrils in a polymer matrix of nano-composite structures (nano-technology). Finally, cellulose fibres are a fundamental resource for paper industry.
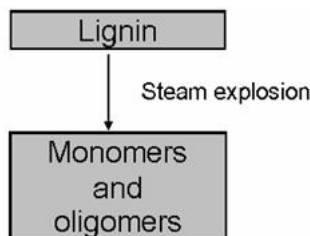
Fig. 6. Application of lignin from SEA pulp (Gravitis, 1996)

In addition, the SEA technology is flexible in the meaning of satisfying the demand of tree-free pulping ("tree-free paper"). Extensive deforestation requires that fibre materials are not produced from wood but from sugar cane bagasse, bamboo, straw, kenaf and others.

Rudolf Diesel and Henry Ford were the first to demonstrate the use of bio-fuels from a variety of crops. Now only biodiesel and bio-ethanol are industrial products. However, the feedstock for bio-fuel is food crops the products being called first-generation bio-fuels. The main criticism against first generation bio-fuels is the use of arable land, driving up food prices, and small effect on reducing emissions of greenhouse gases (GHG) ("food versus fuel" controversy).

The challenge is to shift from first generation bio-fuels to second generation bio-fuels the feedstock of which is non-food lignocellulosic materials (straw, wood waste, etc.). The main problem of deriving bio-ethanol from cellulose and hemicelluloses is separating lignin from

lignocellulosic carbohydrate polymers, and SEA is an excellent method important for material science and energy.
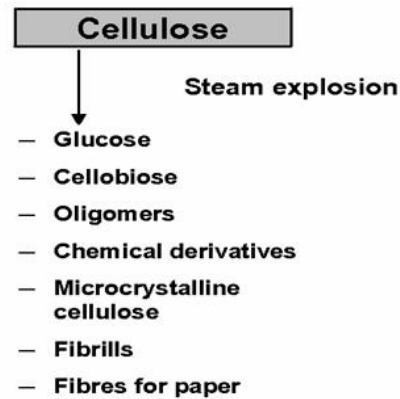
Fig. 7. SEA treated cellulose products and application (Gravitis, 1996)

The most recent is the idea of third-generation bio-fuels. According to Carere (Carere et al., 2008), "consolidated bio processing (CBP) is a system in which cellulose production, substrate hydrolysis, and fermentation are accomplished in a single-step process by cellulolytic microorganisms. CBP offers potential for reducing production costs of bio-fuel due to a simpler feedstock processing, lower energy inputs, and higher conversion efficiencies than separate processes of hydrolysis and fermentation, and is an economically attractive near-term goal for "third-generation" bio-fuel production". Separation of lignin and pre-treatment by the SEA technology will be essential also in case of introducing the process of third-generation bio-fuels.

2. 2. Steam explosion energy evaluation

Presently a simple model (Fig. 8) of the main energy flow has been used to assess the energy costs and environmental impacts (Gravitis and Abolins, 2007; Abolins and Gravitis, 2007). The energy consumed in the process depends on the moisture content in the raw material. A critical moisture amount H_c beyond which heating of the moisture requires more energy than heating the waterless part of biomass to the operation temperature could be defined by the ratio:

$$H_c = C_b \, \Delta T / \, (C_b \, \Delta T + \Delta h) \qquad (2)$$

where:
C_b is specific heat of dry biomass;
ΔT – the difference between the operation temperature and the initial temperature;
Δh – difference between the enthalpy of water and steam.

Sustainability of the SEA technology may be considered in two aspects: environmental impacts of a technology on the global system (particularly the biosphere) and physical sustainability of the

technological process itself mainly dependent on availability of the necessary resources.

Steam explosion auto-hydrolysis
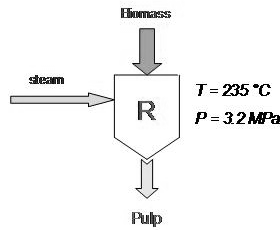
Fig. 8. Model of the steam explosion system (R – reactor)

The eMergy (energy memory) approach offered by Odum (1996) based on the energy of solar radiation as the primary source of all other resources and products providing a general basis common for environment, resources, and other components has been applied to estimate the SEA pre-treatment technology (Abolins and Gravitis, 2007). For the model calculations including the basic energy flow and the source material are made under assumptions of sustainable consumption of naturally grown wood, 20 % of energy being supplied by hydroelectric power plants and 80 % – by thermoelectric power plants, and any energy or other costs for simplicity being neglected.

Defining sustainability S of the process by the ratio of renewable eMergy R (biomass and hydroelectricity) to the total of renewable and non-renewable (thermoelectricity) eMergy NR:

$$S = R / (R + NR) \qquad (3)$$

The value of S being zero if $R = 0$ means that only non-renewable resources are used and the process is not sustainable. If $NR = 0$, then $S = 1$ (or 100 %) indicating condition of a completely sustainable process. Within the simplified model discussed here S equally refers to the environment and the SEA process itself since the major impact on the environment is due to release of carbon dioxide by thermoelectric power plants.

The SEA process can be made completely self-sufficient providing the necessary energy by burning biomass. Defining the net efficiency F of the process by the ratio of energy necessary per unit bio-mass E_0 to energy $E > E_0$ actually spent per unit mass:

$$F = E_0 / E \qquad (4)$$

the latter from (4) may be expressed as:

$$E = E_0 / F \qquad (5)$$

If E_c is combustion heat of the biomass used to provide the energy for SEA treatment, the ratio E_c/E is the number N of biomass units that can be processed at the expense of burning one biomass unit. From Eq. (5) it may be expressed as:

$$N = E_c / E = E_c \cdot F / E_0 = F / (E_0 / E_c). \qquad (6)$$

Eq. (6) does not specify the kind of biomass used to supply the energy. It is valid under condition that E_0 refers to the biomass undergoing the treatment while E_c – to the biomass used to fuel the process. If the same kind of biomass is used as fuel, the E / E_c ratio determines the amount of biomass available for treatment or the yield:

$$Y = 1 / (1 + E / E_c) \qquad (7)$$

2.3. Wood cell wall structure – the opportunity to obtain nano-materials by steam explosion

Nanotechnology as the study of wood cell structures with dimensions of 1-100 nm or larger (microstructures) is a promising field of research and industrial application. Cellulose consists of microscopic fibril nanostructures (whiskers) of high stiffness and strength. The nanostructures of lignin are less clear.

Relationship between structure, function, and properties is the key issue of developing new materials. Recently the shape of lignin particles lacking some exact molecular formula has been determined by ultra-small angle synchrotron X-ray scattering (USAXS) (Vainio et al., 2004).

The TEM (Kallavus and Gravitis, 1995), SAXS and USAXS (Vainio et al., 2004) experiments have revealed size-dependent properties of nano-particles obtained by SEA from new cell wall modifications. Studies of nano-cell structure and dynamics of natural plant walls would reveal diverse opportunities for natural nano-composites and nano-technologies of synthetic intermediates and substrates to imitate the nature by chemical processes (Gravitis, 2006).

2.4. Design of integrated technology clusters

System design is the first step integrating technologies. Clustered technologies should have maximum throughput and minimum waste. The unsolved problem of Zero Emissions is connecting technologies in an optimized network.

Fig. 9 shows the general strategy of integrating technologies (Gravitis, 2003) designed by the LSIWC/LBE-EC. Substituting the primary furfural production by other technologies is not a problem. It depends on the purpose of the integrated cluster.

3. Results and discussion

3.1. SEA technology for self-binding materials and plywood

Plywood and pressed boards are composites widely used in building constructions and furniture. Developed SEA technologies allow utilizing low-quality and waste-wood to make useful products.
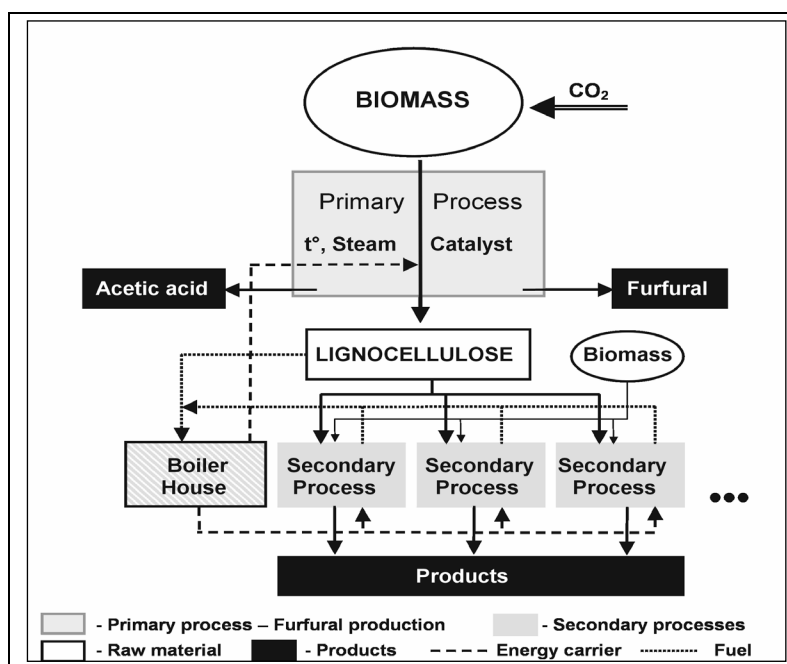
Fig. 9. General design of the flow chart of a LSIWC/LBE-EC biorefineries system (Gravitis, 2003)

Presently phenols are mainly derived from petrochemicals. The costs of these chemicals depend on the oil price. As the oil price increases, the costs of wood composites raise too – the prices of phenol adhesives correlate with the oil market prices. Another adhesive component – formaldehyde has been classified as human carcinogen in 2004.

Fibre and particle boards are bound together by a suitable synthetic thermosetting adhesive at designed pressure and temperature. Phenol and furan resins synthesized from petroleum materials are expensive, not environmentally benign.

The phenol adhesive and exploded self-binding mass after the SEA process (Fig. 10) is cheap. Phenols separated from SEA mass can be used in plywood binders.

An attempt to use lignin extracted from wood biomass after SEA in self-binding boards and plywood has been reported (Abolins et al., 2008; Gravitis et al., 2008) paying attention to economic and energy costs.
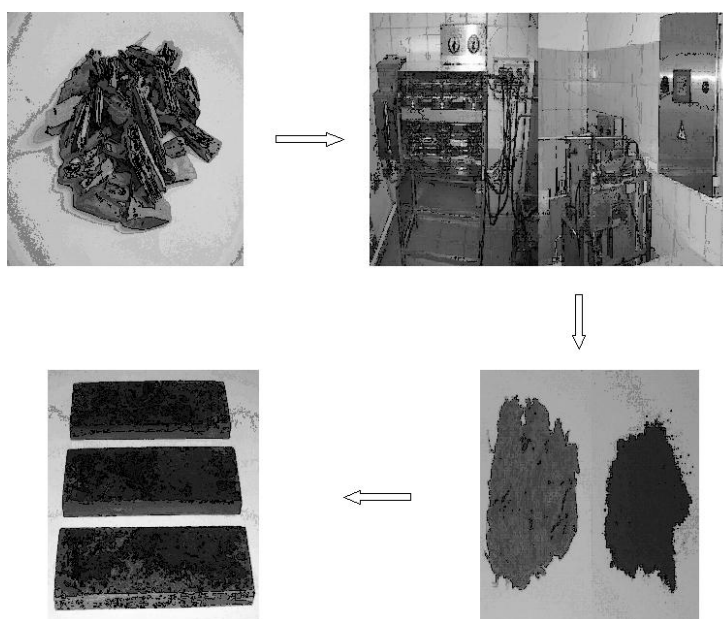
Fig. 10. From wood chips (left) to steam explosion unit, to SEA products, to self-binding boards (right) (Abolins et al., 2008).

3.3. Steam explosion energy evaluation

The critical moisture content defined by Eq. (2) is close to air-dry wood, which means that energy spent on drying biomass should be accounted.

There exists some threshold amount of moisture needed to initiate hydrolysis. Assuming that total energy consumed is 1kWh per kg dry biomass and taking transformations – the solar energy equivalents of hydroelectricity, biomass, and thermoelectricity from M. T. Brown (Brown and Ulgiati, 2004) the value of sustainability index S defined by Eq. (3) is found to be 0.15 approaching 0.1 at 3 kWh/kg and 0.3 at less than 0.5 kWh/kg.

As seen from Eq. (6), the number of processed biomass units N is a linear function of net efficiency F the slope being determined by E_0 / E_c. The number of biomass units N that can be processed by SEA per unit biomass combustion energy is shown in Fig. 11.
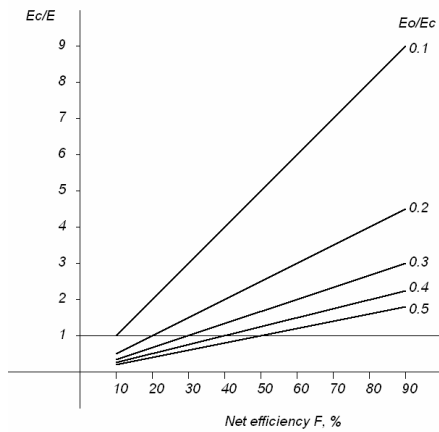
Fig. 11. The ratio of biomass combustion energy E_c to net energy E per unit biomass *vs.* net efficiency F at different pre-treatment energies in terms of E_c

The processed biomass yield, Eq. (7), in per cent of the total amount of available biomass as function of net energy per unit mass E in terms of biomass combustion energy E_c is shown in Fig. 12.

One may regard $E = E_c$ as the critical value at which 50% of the available specific biomass resource can be processed by burning the other half. At $E > E_c$ more of the available biomass needs to be burned to fuel the treatment. The critical ratio of $E_c / E = 1$ is shown by a line.

3.4. Integration of bio-based technologies in clusters

The mathematical graph on the basis of oriented graph theory used in choosing the optimal routes of raw materials, products, and wastes (Gravitis et al., 2004) is illustrated in Fig. 13.
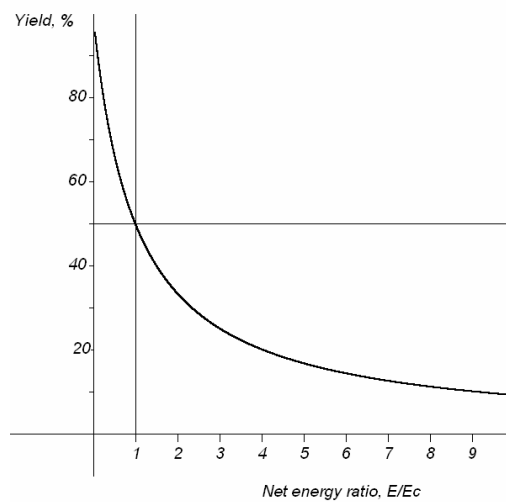
Fig. 12. Amount of biomass available for self-subsistent SEA pre-treatment as function of net energy in terms of biomass combustion energy

Producers should be located close to each other. However, many problems remain unsolved. Apart from output and waste optimization, the profit interests of companies, sometimes controversial to other factors, are significant.

An example (Gravitis et al., 2002) of integrated furfural production technologies, steam explosion, and pyrolysis is given in Fig. 14.
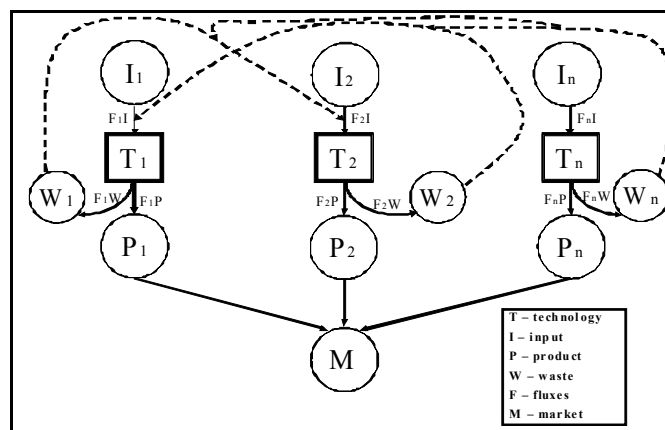
Fig. 13. Biomass refineries integrated cluster as an oriented mathematical graph (Gravitis et al., 2004)

The integrated LSIWC/LBEEC systems approach to a biomass technologies cluster is presented in Fig. 15.
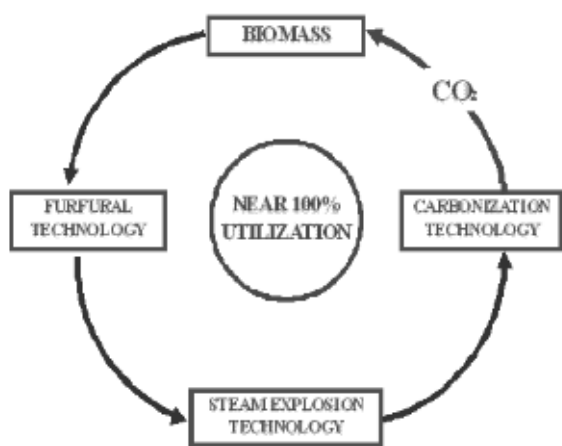
Fig. 14. Integration of three technologies: furfural, steam explosion, and carbonization (Gravitis et al., 2002)

4. Conclusions

Shift to renewable resources requires replacement the present crude oil refinery by biomass refinery. The future biorefinery technologies will be based on integration in clusters towards zero emissions.

The steam explosion autohydrolysis technology renaissance could be point for second and third biofuels resources pre-treatment.

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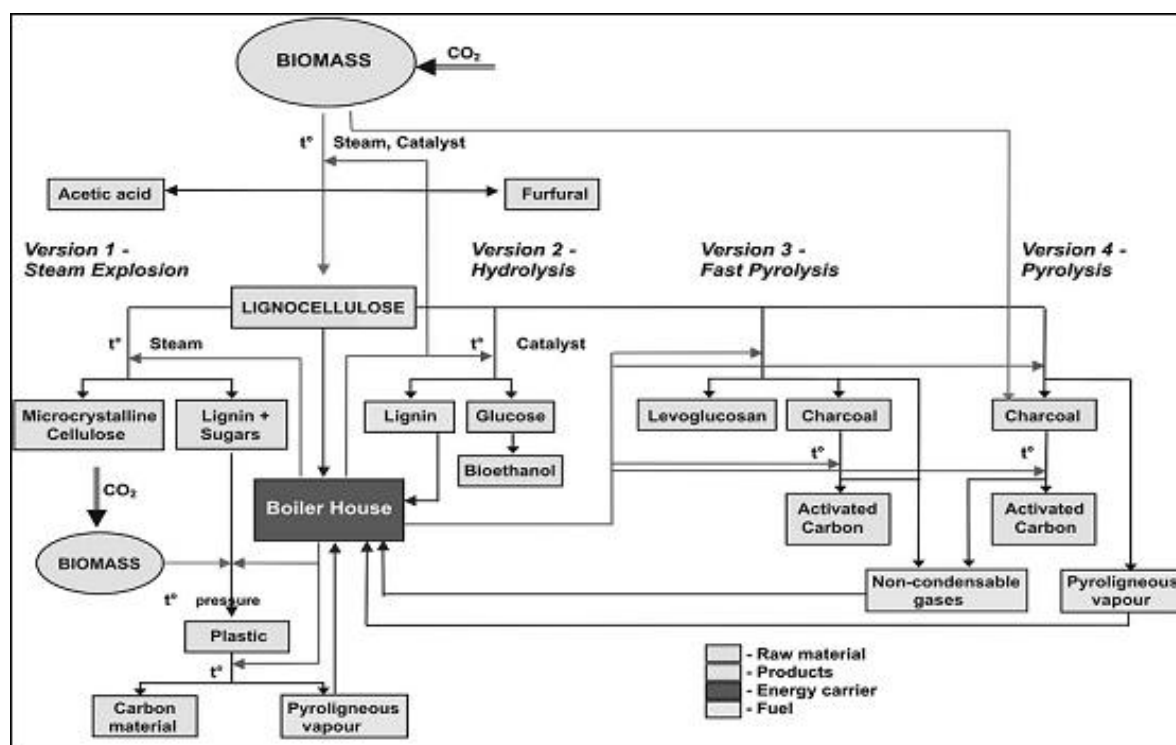
Fig. 15. Biomass based integrated technologies cluster towards Zero Emissions

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ENVIRONMENTAL ASSESSMENT LABORATORY

The Environmental Assessment Laboratory was founded in 2006, within a project financed by the INFRATECH Program, administrated by the Ministry of Education and Research.

The laboratory operates as a part of Tehnopolis Science and Technology Park Iasi – a consortium having our Technical University "Gh. Asachi " of Iasi as partner.

The laboratory is staffed by some members of the Environmental Engineering and Management Department of the Faculty of Chemical Engineering and Environmental Protection (Technical University "Gh. Asachi "of Iasi).

With a rich expertise in environmental engineering and management, the staff is especially competent in:

- Environmental monitoring
  - Specialized in complex environmental analysis such as the identification and quantification of organic pollutants (VOC, POPs, pesticides, PCBs etc.) from air, water and soil;
- Environmental impact assessment;
- Risk assessment
- Environmental consulting (Environmental permitting, Quality management certification for ISO 14.001, Emission reduction plan for VOC; Solvent management plan);

The research activity of the group members is illustrated by:

- More than 100 scientific articles, published in well-known national and international (ISI);
- More than 45 national and international patents;
- Books published in Romania (publishers accredited by CNCSIS) and abroad;
- PhD thesis approaching new and original topics in environmental engineering and management;
- Centers of excellence in research
- International collaborations (within programs such as PHARE, EcoLinks, or financed by German Ministry for Education and Research, Swiss Science Foundation, Swedish Institute Stockholm etc)

During the last decade of activity, the members of the laboratory have participated in more than 200 research contracts with the industry, on different activities:

- Environmental permitting;
- Integrated pollution prevention and control;
- Technical Inspection Certificates for VOC (according to H.G. 568/2001), being one of the six accredited laboratories in the country);
- VOC emission reduction schemes (H.G. 699/2003)
- Other projects concerning the cleaning or depollution of different industrial effluents and streams.

Facilities and Equipments

The laboratory is being organized according to the requirements of the Quality management system ISO /IEC 17025:2000 "General requirements regarding the competence of the testing and calibration laboratories".

The main equipments used in the laboratory, fully compliant with international standard methods, are:

- High resolution GC-MS with hyperbolic quadrupole mass analyzer (Agilent)
- Thermal desorber (Markes International)
- High precision analytical balances
- Ovens, automatic pipettes etc

In addition to the classical GC-MS/FID methods, our laboratory is especially interested in using the analytical thermal desorption methods for the measurement of trace level volatile and semi-volatile organic chemicals (VOCs and SVOCs). It is the technique of choice for air monitoring (indoor, outdoor, workplace, automobile interior, breath, etc.) and is an invaluable tool for the analysis of soil, polymers, packaging materials, foods, flavors, cosmetics, tobacco, building materials, pharmaceuticals, and consumer products. Indeed, virtually any sample containing volatile organic compounds can be analyzed using some variation of this technique.

In this context, we are opened for collaboration with scientific institutions in the areas covered by our laboratory.

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VALORIFICATION OF HERBS IN PHYTOTHERAPY - AN ALTERNATIVE OF CHEMICAL TREATMENTS IN AGRICULTURE

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Abstract

In agricultural culture there are numerous weeds diminishing the production which are controlled by several methods. The most common and efficient method with the modern agriculture is the chemical method of controlling weeds, using a large range of herbicides. A great part of these herbicides have long lasting remanence, even over three years. A great part of the active substances of the herbicides pollute the soil and subsequently the waters, sometimes with disastrous action for the environment. Also, some pollutants can be metabolized by culture plants which, in their turn, by consumption, can adversely affect the people's health. The use of appropriate agronomic practices is essential while growing herbicide tolerant varieties if this technology is to remain effective. To this end, it is recommended the promotion and maintenance of careful management practices for growers who use these crops to minimize the development of multiple resistances. In spontaneous flora of Romania are many herb species that are used as medicinal plants. A significant part of these plants is found in the crops as weeds. In this paper, the main weeds with therapeutic properties from crops are presented. A description of each specie, as well as the main properties and uses for some illnesses are presented in this paper. This work also presents the main species considered as weeds in culture, the organs used, therapeutic applications and some techniques of use for such plants.

Keywords: agriculture pollution, alternatives, chemical treatments, phytotherapy, prevention measure

1. The use of chemicals in agriculture

1.1. Introduction

In agricultural culture there are numerous weeds diminishing the production which are controlled by several methods. The most common and efficient method with the modern agriculture is the chemical method of controlling weeds, using a large range of herbicides. A great part of these herbicides have long lasting remanence, even over three years. A great part of the active substances of the herbicides pollute the soil and subsequently the waters, sometimes with disastrous action for the environment. Also, some pollutants can be metabolized by culture plants which, in their turn, by consumption, can adversely affect the people's health. Harvesting prior to weeding some species of weeds proving medicinal features existing in the cultures, represents an alternative of controlling weeds from the cultures friendly against the environment. Also, this technological alternative can bring significant additional income to agricultural producers (Arbuckle and Server, 1998; Bane et.al., 1993).

With weeds as with many plant species the main or first level factor determining the area of distribution is a (complex) climatic one. As they have an artificially enlarged area of distribution, they have a huge border area (in an ecological sense), where the climate is not optimal for them, and where they have a narrow ecological and sociological amplitude and are especially sensitive to some measures of modern intensified agriculture. The extensive use of chlorotriazines as selective herbicides in agriculture and their relatively high persistence imply that these compounds are now present in the environment, contaminating soil, surface and groundwater. The measures of modern agriculture bring about a gradual extinction of sensitive species from the limit of their

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range towards their centre of distribution, where they can find refuge habitats in the natural vegetation. The sensitivity of such species (also against herbicides) seems to increase towards their limits. Resistant species occur with increasing densities after the removal of their competitors. In addition, they are able to enlarge their area and to invade sites, where they had not been able to compete before, or sites where they could not previously bear the environmental conditions together with the competition of the rich weed flora.

The use of herbicide-tolerant crops encourages the heavy use of herbicides in the crop field without damage the crop. At present, breeding crops for herbicide tolerance dominates about 41% of the research on genetically engineered organisms. Herbicide tolerance does not increase crop yields, but it does increase the use of herbicides in agriculture and the pollution of agroecosystems and other ecosystems (Pimentel and Ali 1998). There are three reasons to limit the use of pesticides to situations where significant benefits will result: they may harm human health, environment and may create problems in agriculture if used in excess.

1.2. Impact on agriculture

Impact on agriculture is arising from unintended adverse effects of herbicide use on plant life. Just as bacteria can become resistant to antibiotics, mosquitoes to insecticides and rats to warfarin, so can plants become resistant to herbicides. This resistance of plants to herbicides has become a global problem. Literature showed that 216 weed types in 45 countries were found to be resistant to herbicides. The term "selection pressure" refers to the fact that the more a living organism like a germ or a cancer cell is exposed to a toxin, the greater the likelihood that a strain resistant to that toxin will emerge. In an attempt to foil the emergence of resistant strains of weeds, combinations of herbicides are now often used in agriculture.

Weeds can develop multiple herbicide resistance creating another problem for the agricultural industry. One approach to minimizing the emergence of resistant strains is to limit the exposure of the target species to the chemical agent, hence reducing selection pressure. The current approach is now advocated to limit the use of herbicides in agriculture. The development of herbicide resistant crops began in 1995 with canola and has since been widely adopted in agricultural practice, allowing for the use of the appropriate herbicide for weed control without damaging the crop plants. Nevertheless the use of herbicide- resistant crops will remain an important agricultural approach for years.

Excessive use of pesticides in the urban setting could contribute to the weed resistance problem. It should be evident that the decision to use pesticides for cosmetic purposes should not be taken in isolation from their known and evaluate the impact on human health, environment and agriculture

(LeBaron and McFarland, 1990; NAF, 1994; NASS, 1993).

1.3. Environmental impact

Environmental impact of pesticides use is a matter of considerable concern (Bane et.al., 1993; P2Pays, 1995, Robu, 2005, Robu and Macoveanu 2005a, b). A progress report of an ongoing study by the (U.S.) Environmental Protection Agency (EPA) on the presence of lawn pesticides in urban aquatic ecosystems found several at parts-per-billion levels in sediment and parts-per-trillion levels in water (Arbuckle and Server, 1998; Baldi, 1998; LeBaron, and McFarland, 1990). A study of well water showed that two or more pesticides were found in 11% of the wells including that of a non-user whose well had 5 different agents**.** It is known that pesticides can persist much longer in deep aquifers than in soil. For example the half-life of alachlor in soil is 20 days, but in deep aquifers the half-life is four years.

Most pesticides can affect the metabolism of many drugs and combinations of pesticides may be more potent than individual ones. It is little known about the possible subtle effects of environmental exposures to such combinations but, as noted above, evidence is mounting that combinations may be more toxic than single agents (Lee and Colt, 2005; Muir and Rattanamongkolgul, 2004).

1.4. Effects on human health

The effects on human health have been studied at low level exposures of humans to pesticides. The studies usually small, referred to the trace amounts of some pesticides, such as DDT, in human body fat. While definitive proof of adverse effects of low level exposures to pesticides on human health may be scanty, there is sufficient evidence to create a high index of suspicion that such exposures, over the long term, have adverse health effects. One epidemiological review of several human studies (Janzen et.al., 2003; Piementel and Ali, 1998; Sanderson and Talaska, 1997; Coombes and Grey-Wilson, 1997) found associations between pesticide exposure and cancer, especially cancers of the blood, neuro-toxicity such as Parkinson's-like symptoms, behavioral problems, and reproductive disorders such as birth defects, infertility, and birth mortality. Other studies have indicated that agricultural workers have an increased incidence of brain cancer. A recent study of farmers and farm workers in USA (Janzen et.al., 2003; Lee and Colt, 2005; Muir and Rattanamongkolgul, 2004,) found that spending 55 years or more on the farm was associated with large increases in the incidence of the brain tumor glioma and especially for certain herbicides and insecticides (paraquat, bufencarb and chlorpyrifos).

A review of epidemiological studies on the association between childhood cancer and pesticide exposure indicated that frequent occupational exposure to pesticides and frequent home use of pesticides were associated with an increased

incidence of childhood leukemia and brain cancer (leukemia occurs 6 times more often in homes were pesticides are used). It has been pointed out that exposures to pesticides rarely involve a single agent, and those studies based on a single agent alone may not adequately identify risk to human health. Evidence is emerging that toxicity may be significantly increased when more than one agent is present (Janzen et.al., 2003; Piementel and Ali, 1998).

2. Pollution prevention principle and agriculture sector

2.1. Pollution prevention in agriculture

Herbicide tolerance is the ability of a plant to survive the application of a specific herbicide. All crop plants exhibit natural levels of herbicide tolerance to specific herbicides which is why farmers are able to use herbicides to control weeds in their crops. Over the past two decades, tolerance to specific herbicides has been introduced intentionally, as a novel trait into a number of crop species to provide farmers with the additional means to control weeds without damaging their crops. Such products include canola varieties that have been developed for tolerance to the herbicide, imidazolin one. In recent years, biotechnology has been used in the development of other herbicide tolerant crops. For example, in Canada, herbicide tolerant canola varieties are commercially available with individual tolerances to herbicides containing bromoxynil, glyphosate, or glufosinate ammonium as the active ingredient.

Studies have shown that herbicide tolerant plants are no more invasive of cultivated or natural habitats than their herbicide susceptible counterparts, unless the relevant herbicide is used exclusively to eliminate competing vegetation (Downey, 1999; P2Pays, 1995).

Weeds resistant to herbicides are rapidly becoming important factors in crop production and agricultural technology. There has been a serious spread of weeds having multiple or cross resistances to various classes of herbicides and the need for research on the pollution prevention principle and management of herbicide resistance is obviously urgent. Herbicide resistant weeds may become a more serious economic problem within five to ten years than pest resistances to insecticides and fungicides due to the greater use of herbicides in agriculture. This is almost certain to be the case if we depend too much on only a few of the newer herbicides and discard the older ones. It is need all the tools that currently are, as well as those that modern technology can provide, to manage our weed pests while further reducing or eliminating soil tillage, and to conserve essential soil and water for future crop production and public use. Research on herbicide resistant weeds should complement biotechnology research aimed at developing herbicide resistant crops, but the strategy and objectives of the biotechnology research must be

altered to some extent. In particular, efforts should be aimed at developing major crops resistant to many herbicides, rather than one or two. This would provide greater flexibility in rotating or alternating herbicides to prevent resistant weeds from evolving, and controlling those resistant populations that appear.

2.2. Management practices in agriculture

The use of appropriate agronomic practices is essential while growing herbicide tolerant varieties if this technology is to remain effective. To this end, it is recommended the promotion and maintenance of careful management practices for growers who use these crops to minimize the development of multiple resistances. There are a number of beneficial management practices (BMPs) which agricultural producers can incorporate into their farming practices to decrease their impact on greenhouse gas emissions. These BMPs can be placed into four management sectors: soil and land management, livestock management, crop management, and nutrient management (Bojor and Popescu, 2003; California University, 1992; Gulden and Entz, 2005; Janzen et.al, 2003; Riekman and Cavers, 2006).

2.2.1. Soil and land management

Reducing the number of tillage passes over a field decreases CO_2 emissions by both lowering total fuel consumption and sequestering, or storing, carbon in the soil. While zero tillage systems emit less carbon (C) through fuel and machinery use, they do exhibit greater herbicide use (Table 1); however, the use of herbicides in agriculture constitutes a very small portion of total carbon emissions (less than 7 percent/year).

Table 1. Comparison of carbon emissions (C/ha/yr) in conventional and zero tillage systems (Gulden and Entz, 2005)

	Conventional tillage (CT)	*Zero tillage (ZT)*	*ZT as % of CT*
Machinery	10.55	7.08	67.1
Fuel	22.56	14.57	64.6
N fertilizer	54.9	51.53	93.9
P fertilizer	7.7	7.34	95.3
Herbicide	4.52	5.87	129.8
Total	100.23	86.39	86.2

The carbon content of restored wetland basins increases at a rate 2 times greater than if the wetland basin was left in the cropping system (Walters, 2005). As well, the crop seeded in low-lying areas of the field often drowns out, building up N concentrations in the soil; therefore, the potential for N_2O emissions in these depression areas is high. Although seeding and harvesting around wetlands may be unfavorable to producers, including these areas in the cropping system is often a waste of seed

and fertilizer (Gulden and Entz, 2005; Riekman and Cavers, 2006).

2.2.2. Livestock management

Higher quality feed needs less time in the rumen for digestion, leading to a decrease in methane emissions from cattle. The Westman Agricultural Diversification Organization (WADO) carried out a study grazing cattle on pure alfalfa using a bloat reduction product called Alfasure. Although this type of grazing system requires more management, cattle grazed on pure alfalfa exhibit greater gains. WADO reported gains of alfalfa-grazed cattle ranging from 0.48-0.81 kg/cow/day (Westman Agricultural Diversification Organization, 2003). In 2005, cattle grazed on alfalfa at the MZTRA research farm gained an extra 0.14 kg/cow/day over a 100-day grazing period compared to cattle grazed on native grass. To decrease the risk of anaerobic decomposition of manure and lower CH_4 emissions, it is important to avoid stockpiling manure. The amount of bedding should also be kept to a minimum as the high C content of straw favors CH_4 production. Avoiding excessive manure applications may also prevent the build-up of N in the soil (Gulden and Entz, 2005; Riekman and Cavers, 2006).

2.2.3. Crop management

Establishing perennial forages is an important issue in agriculture sector. Perennial forages, such as alfalfa, require fewer tillage passes, extract N from deep in the soil and have the ability to sequester C deeper in the soil (due to the deep rooting habit of the crop). Growing the legume crops is an other appropriate practice that could be applied as best management practice in agriculture because the legume crops have the ability to "fix" their own N, thus requiring less N fertilizer during the season in which they are grown.

2.2.4. Nutrient management

Nitrogen source, rate, timing and placement should all be considered to match the availability of N to the requirements of the crop (use N fertilizer efficiently). Soil testing is a key part of this strategy as it informs the producer of N availability in the soil and N requirements for the subsequent crop. It is extremely important that residual N is not carried over through the winter, considering the potential for loss as N_2O during spring thaw (Gulden and Entz, 2005; Riekman and Cavers, 2006).

2.3. Challenges in establishing Beneficial Management Practices (BMP)

The major challenge with establishing full BMPs is in the lack of quantitative data on the impact that these practices have on greenhouse gas production. In many cases, it is assumed that BMPs will decrease greenhouse gas emissions, based on current knowledge of the processes creating the gases. In the case of N_2O, research is currently being carried out on the landscape element of these emissions, but understanding the effect of landscape on emissions is complex. Nowadays, the orientation is to decrease greenhouse gas emissions, and for this it is important that precise data be collected to better understand the potential of these BMPs and their impact on mitigating greenhouse gas emissions (Gulden and Entz, 2005; Riekman and Cavers, 2006).

3. Valorification of herbs in phytotherapy - an alternative for chemical treatments

Instead of using chemicals for various treatments in agriculture, the herbs could be used in phytotherapy (Bezzi and Aiello, 1997; Fisher, 1999; Schenk, 1998). From the most frequent weeds in crops, the following herbs have phytotherapeutic properties:

3.1. Agropyron repens

Currently it is found on cultivated or uncultivated grounds, sandy or argillaceous, on hay fields, grasslands, barren slopes, roads and woods borders, bushes, orchards and gardens, from the plain area to lower mountain area (Fig.1). The important part of this plant that can be used in phytotherapy; its rhizomes (*Rhizoma graminis*), are used as infusion or decoction, and has the following therapeutically recommendations**:**

- kidney and bladder disorders, cystitis, pielitis, urethritis, renal lithiasis, nephritic colics, urinarian infections, menopause, urinarian retention, uric acid in the blood, prostate, syphilis;
- gastrointestinal disorders, virotic hepatitis, icterus, ascites, gall calculosis, gall dyskinesia, constipation, indigestions, intoxications, haemorrhoids;
- breathing disorders, influenza, chills, coughs, bronchitis, respiratory catarrh, abundant sweat, aerophagia, tuberculosis;
- rheumatic conditions, gout, arthritis;
- cardiac insufficiency with oedemas (including ankle oedemas), hyper blood pressure, eliminating blood toxins;
- obesity, cellulitis, diabetes;
- skin diseases, fractures, eczemas, dermatosis.

3.2. Anagalis arvensis

Currently it is found as seeding, vineyards, orchards, grasslands, hay fields, chopped woods, etc., and the entire plants (*Herba anagalis*) can be used in phytotherapy as infusion, decoction, fresh juice and ointment (Fig.2). The therapeutically recommendations are**:**

- neurasthenia;
- calming the cough and the cardiac asthma;

- disinfectant for the wounds;
- varix ulcer;
- eczemas;
- aphrodisiac;
- gastric ulcer;
- stimulus for the renal and hepatic secretions.

Notes: exceeding the use may give a symptom of intoxication, manifested by hyper-excitability.

Fig.1. *Agropyron repens*

Fig.2. *Anagalis arvensis*

3.3. Amaranthus retroflexus

Currently it is found as seeding, on cultivating crops, vineyards, orchards, fertilized fields (Fig.3). The important parts of this plant that can be used in phytotherapy are roots, leaves, seeds (*Herba amaranthi*), used as infusion or decoction, and has the following recommendations:

- calming the cough and the cardiac asthma;
- aphrodisiac;
- menorrhagia;
- genital candidosis.

3.4. Aristolochia clematitis

This plant (Fig. 4) could be totally used in phytotherapy, it is found in vineyards, orchards, cultivating crops, and the therapeutically recommendations are**:** recent "in vitro" and "in vivo" researches in Romania have proved that the

aristolochic acid extracted from the plant has an immunostimulating action.

This device is accomplished by the intensification of the phagocytosis, as result of the increased activity of the macrophages and granulocythes, while the effect on lymphocythes is insignificant.

Fig.3. *Amaranthus retroflexus*

It can be only used as herbal mixture made in specialized laboratories. It has to be mentioned that it is forbidden to use this plant empirically, because the aristholochic acids have also strong carcinogen and genotoxic properties.

Fig.4. *Aristolochia clematitis*

3.5. Capsella bursa-pastoris

It is found on grass fields, ditches, roads and walls borders, sunny or semi shady uncultivated grounds or gardens, common from the plain area to subalpine area, from arid to very moist soils (Fig. 5). The entire air part of the plant can be used in

phytotherapy, and the therapeutically recommendations are:

- gastric and intestinal hemorrhages, enterocolitis, calming abdominal aches, diarrhea and dysentery (due to its astrictionally properties), haemorrhoids;
- hyper and hypo blood pressure, atherosclerosis, angina pectoris, cardiac compensated insufficiency, regulating capillary's permeability;
- regulating the menstruation flux on puberty, increasing the tonus of uterin mucous membrane, irregulated menorrhea, metrorrhagia, hemorrhagical metritis, dismenorrhea, uterin hemorrhage, renal lithiasis, adjuvant in the gonorreea's treatement;
- wounds and sores continually bleeding, varix (due to its haemostatic properties).

It can be used as infusion, concentrated infusion, decoction, medicinally wine, macerate, essence, cataplasm, baths. Other uses are: in nourishment, leaves are consumed in spring for soups, salads, mash, or as filling for pies (in mixture with other vegetables).

Fig.5. *Capsella bursa-pastoris*

3.6. Convolvulus arvensis

Currently it is found in crops, seedings, cultivating crops, vineyards, orchards, very common in all areas (Fig. 6). The entire plant (*Herba convolvuli*) can be used as infusion, decoction, macerat, essence, powder or fresh leaves, and it has therapeutically recommendations, such as:

- laxative, haemostatic, memory stimulus;
- gall dyskinesia;
- constipation;
- neurasthenia;
- burns;
- hemorrhages;
- furuncles;
- cough.

3.7. Equisetum arvense

*Status***:** it is native only in the Northern Hemisphere, in Europe, North America and Asia (Iran, China). The plant (Fig. 7) grows on moistly regions, argillaceous, and moors, hay fields, orchards, moist and sandy everglades, steep slopes, river borders, gradients, railroad embankments, from the plain area until the mountain area. As weed in the crops, it can be met only on the high-moisturized grounds.

Fig.6. *Convolvulus arvensis*

The recommended organs in phytotherapy are sterile stems, leafless and rootless (*Herba equiseti*), which have the following recommendations:

- kidney and bladder disorders, renal lithiasis with elimination of sand and stones, water retention in the pericardium, evoiding uterin hemorrhages and menorrhea, evoiding enuresis (involuntary urination while sleeping), nephritis, prostatitis and prostate adenoma;
- heart diseases, cardiac insufficiency with oedema, angina pectoris, activating the blood circulation, atherosclerosis, arteritis;
- gastric and intestinal dressing in the hyper-acid gastritis, gastric ulcers, intercedes in the absorption of abnormal fermentations;
- internal hemorrhages, diarrhea with dysentery, metrorrhagia and epistaxis (due to its haemostatic and astrictionally properties)
- noninflammatory arthritis, gout, chronic articular diseases with aids recovering, tendinitis, osteoporosis;
- the suppleness of tendons and blood vessels, with favourable effects on sportsmans (tennismans, runners, cyclists);
- tuberculosis, bronchitis, relieve expectoration and calming cough (due to the saponins);
- defensive effects against slowly exhaustion on aged persons, convalescence, general and post-operator anemia, precocious aging symptoms, depression, irascibility (due to its mineralization effects);
- prevents dental caries, nails fragility, bones fractures, by increasing the cojunctive tissues resistance;

- skin disorders (old wounds, eczemas, sores, warts, paronychia, chilblains, skin eruptions with nettle rash, stomatitis, aphta, anal fissures, haemorrhoids, haemorrhoidal nodules, skin cancer, reduces foot perspiration).

It can be prepared as infusion, decoction, concentrated decoction, macerate, essence, juice made of fresh green plants, hot cataplasm and baths, and can have other uses too, such as: in animal nourishment, exceeding the dietary may give digestion disorders and intoxication. Exceptions are the goats suffering from renal disorders.

Due to her high silica content, the plant it is used for polishing objects on noble wood or metal. It is very important to mention that do not mistaking for *Equisetum palustre* or *Equisetum sylvaticum* plants, which have high contents of toxic alkaloids producing hematuria.

Fig.7. *Equisetum arvense*

3.8. Fumaria officinalis

It is found (Fig.8) in areas from the plain area until the lower hills area, prefering very sunny grounds, road borders, ditches, stubbles, gardens, vineyards, and the entire plant (*Herba fumariae*) could be prepared as infusion, decoction, ointment or fresh juice being recommended in phytotherapy:

- depurative (oust the toxins);
- hyper blood pressure;
- gall dyskinesia;
- hepatic disorders;
- calming cough and cardiac asthma;
- wounds disinfectant;
- varix ulcer;
- dysentery, leprosy, eczemas;
- gingivitis, pulpitis, periodontitis (as antiplate agent).

Fig.8. *Fumaria officinalis*

3.9. Galega officinalis

This plant (*Herba galegae*) (Fig. 9) has therapeutically effects, it is found in orchards, moistly hay fields, and has the following recommendations:

- diuretic, cholagogue;
- diabetes;
- muscular cramps;
- furuncles;
- epilepsy, cerebellum diseases;
- intestinal worms.

It can be prepared as powder, fluidextract, tonic wine, but has to be used very carefully, because exceeding may give abundant salivation, coriza and cough. It can be administrated as laxatives in case of intoxication.

Fig.9. *Galega officinalis*

3.10. Portulaca oleracea

The entire plants (*Herba portulacae*) (Fig.10) have therapeutically effects, it is found on cultivated or uncultivated grounds, gardens, and can be prepared as infusions, fresh leaves in salads. This herb has the following recommendations:

- cystitis;
- renal lithiasis;
- intestinal worms;

- digestive tract inflammations;
- hemorrhages;
- constipation, scurvy;
- respiratory tract inflammations;
- gum inflammations.

3.11. Papaver rhoeas

*Status***:** common in the entire country as weed on crops, on stubbles, road borders, uncultivated grounds, the edge of cornfields (Fig.11). The organs (petals from flowers, fresh or dried capsules) used as infusion, decoction, and different extracts have the followings therapeutically recommendations:

- migraines;
- intestinal inflammations (antiseptic);
- convulsive and irritating coughs, bronchitis (expectorant);
- insomnia (calming the nervous system);
- scarlet fever and rubeola (antiseptic);
- abscesses;
- gastritis, abdominal colics;
- pharyngitis, laringitis;
- hemorrhages;
- colorant in food industry.

Fig.10. *Portulaca oleracea*

It is necessary to mention that it can be mistaken for other *Papave* species, as *Papaver dubium*, therapeutically useless.

3.12. Verbena officinalis

This herb (Fig.12) is found in seeding, stubbles, uncultivated grounds, road borders, ditches. The entire plants (*Herba verbanae*), prepared as infusion, decoction, cataplasm, baths has the following therapeutically recommendations:

- bitter tonic, astringent, cholagogue, healing the scars;
- hepatic diseases;
- headaches;

- rheumatic aches.

3.13. Polygonum aviculare

*Status***:** common on uncultivated stamped grounds, waste lands, stadiums, road borders, ditches, paths, gardens, courtyards, different crops (especially in the plain and hills area), and the organs - the aerial part of the plant (Fig. 13), with or without roots (*Herba polygoni avicularis*) are used as infusion, decoction, concentrated decoction or fresh juice.

Fig.12. *Verbena officinalis*

The therapeutically recommendations are:
- digestive disorders: diarrhea, dysentery, gastric and duodenum ulcer, dyspepsias, enteritis, internal hemorrhages, gall lithiasis, haemorrhoids, lost of appetite;
- cardiovascular system disorders: cardiac insufficiency, cardiorenal oedema, hyper blood pressure;
- genital diseases: urinarian infections, leukorrhea, metrorrhagia, uraemia, albuminorrhea, renal lithiasis, menorrhea, urinarian retention;
- rheumatic conditions, arthritis, gout;
- inflammating disorders of the respiratory tract, chills, hemoptysis;
- disinfecting and healing the sores, varix, phlebitis, bleeding wounds.

Fig. 13. *Polygonum aviculare*

3.14. Other species

Table 2 presents other species that have therapeutically recommendations.

4. Conclusions

The resistance of plants to herbicides has become a global problem. The current approach is now advocated to limit the use of herbicides in agriculture. The development of herbicide resistant crops began in 1995 with canola and has since been widely adopted in agricultural practice, allowing for the use of the appropriate herbicide for weed control without damaging the crop plants. Nevertheless the use of herbicide- resistant crops will remain an important agricultural approach for years. There has been a serious spread of weeds having multiple or cross resistances to various classes of herbicides and the need for research on the pollution prevention principle and management of herbicide resistance is obviously urgent.

Table. 2. Species of herbs, used in pyto-therapy

Plant	*Therapeutic recommendations*	*Type of uses*
Centaurea micranthos	Chest aches, chills, ocular disorders on animals	Leaf infusion
Sisymbrium officinale	Hoarseness, stomach colics	Flower decoction
Geranium pusillum	Varix, stitches, stomachaches	Decoction, infusion
Melandrium noctiflorum	Digestive disorders	Flower infusion
Sorghum halepense	Rheumatism	Whole plant decoction
Reseda luteola	Intestinal worms	Leaf decoction
Sedum acre	Acne, rheumatism	Cataplasm of fresh juice
Cynoglossum officinale	Pulmonary catarrh, pulmonary hemorrhage, dysentery hemorrhoids, skin diseases	Decoction, infusion
Linaria vulgaris	Hemorrhages, hepatic disorders, genital disorders	*Herba* decoction, Flower infusion
Atriplex tatarica	Cough, diabetes, wounds, sores	Leaf decoction, fresh leaves
Bryonia alba	Migraines, scabies, ulcer, pulmonary disorders, rheumatism	Essence, oil extracts from roots
Lepidium ruderale	Eczema, insecticide, fevers	Whole plant decoction
Cirsium arvense	Rheumatism, typhus, amygdalate	Whole plant decoction
Erodium cicutarium	Rheumatic aches, stitches	Decoction
Thlaspi arvense	Depurative, diuretic, insecticide	Whole plant decoction
Raphanus raphanistrum	Heart diseases, chest and liver disorders	Fresh juice
Cerastium vulgatum	Hemorrhages, rheumatism	Decoction, whole plant essence
Sonchus arvensis	Skin diseases, constipation	Decoction, fresh leaves
Lamium purpureum	Rheumatism, epilepsy, tachycardia	Flower decoction
Hibiscus trionum	Furunculous, toothaches, gastric disorders	Whole plant decoction

The use of appropriate agronomic practices is essential while growing herbicide tolerant varieties if this technology is to remain effective. To this end, it is recommended the promotion and maintenance of careful management practices for growers who use these crops to minimize the development of multiple resistances.

Within the crops of Romania, the weed resource is relatively large due to the application of deficient technologies. Most of these weeds have proved therapeutic proprieties being used in numerous affections. Gathering the weeds for phyto-therapeutic uses, especially on small surfaces from households, decreases the seeds reserve from soil and meanwhile the weeding degree of the crops. In ecological agriculture the weed harvesting on medicinal purposes eliminates the herbicide treatment and soil and crop pollution, respectively. Gathering and putting to good use of some of this species may be an income alternative in the rural environment; on relatively small areas or in gardens, weeds with medicinal features can be harvested prior to weeding thus decreasing the expenses generated by the entertainment works.

Instead of using chemicals for various treatments in agriculture, the herbs could be used in phytotherapy. From the most frequent weeds in crops, some herbs, about 20 species have phytotherapeutic properties that are described herein. The use of these plants could be an alternative of chemical treatments in agriculture sector, so that the herbicides use can be avoided, and the soil and ground water pollution with chemicals is prevented.

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MICROBIAL CELLULOSE AS SUPPORT MATERIAL FOR THE IMMOBILIZATION OF DENITRIFYING BACTERIA

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Abstract

The purpose of this study was to investigate the immobilization of denitrifying bacteria on microbial cellulose (MC) for biological denitrification. A novel denitrifying bacterium, *Pseudomonas stutzeri*, was immobilized in microbial cellulose and introduced into an up flow packed bed reactor in order to remove nitrate from synthetic influent. The MC presented the high biomass concentration throughout the experiment, achieving 3.4 mg biomass/g support. The efficiency of the system for denitrification was tested under different running conditions. Complete biological denitrification of the synthetic effluent was achieved at low hydraulic residence times, less than 4 h, and high nitrate concentration (200 mg NO_3-N/L). The immobilization of the bacterium in MC increased the adsorption capacity, decreased the cell leakage from the beads, resulted in higher activity of the immobilized cells, and allowed better operational control.

Keywords: Acetobacter xylinum, biological denitrification, immobilization, microbial cellulose

1. Introduction

The application of cell immobilization techniques to the wastewater treatment process has recently gained much attention (Isaka et al., 2007). These techniques not only offer a high cell concentration in the reactor tank for increasing efficiency, but also facilitate the separation of liquids and solids in the settling tank (Chen et al., 2000). The conventional treatment processes generally require a long residence time to retain slow growing organisms such as denitrifyers in the system; moreover, a relatively large volume of reaction is necessary to obtain a high reactor capacity. The reactor capacity can be improved by increasing the biomass retention time using an immobilized cell system (Chen et al., 2000). Nitrate is a common water contaminant that can cause health problems in humans. Also, eutrophication or groundwater contaminations by nitrate, which cause serious social and economical problems, are related to an increase of nitrate concentration in the aquatic environment (Foglar et al., 2005).

Biological denitrification has proved to be one of the most feasible, advanced, selective, and cost effective processes for removing nitrate by dissimilatory reduction (Song et al., 2005), which transforms it into nitrogen gas using biodegradable carbon compounds as the energy source (Ovez et al., 2006). Denitrification can be achieved either in suspended or attached growth systems. Since the 1980s, biological denitrification has been performed using immobilized cells (Nakano et al., 2007; Zala et al., 2004). Since then, many studies of denitrification using immobilized cells have been undertaken (Li and Logan 2004). The treatment of wastewater in packed bed bioreactors using immobilized cells is attracting increasing interest and has prompted the examination of different immobilization methods and a variety of carriers (Kariminiaae-Hamedaani et al., 2003; Hsu et al., 1996). This process has been applied to nitrate removal of wastewater and contaminated groundwater, with the technology achieving a high

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removal rate per volume (Cao et al., 2004; Peres et al., 1999). The type of support media used for anoxic biomass immobilization can affect the efficiency of a bioreactor, since the number of cells adhering to the support may vary from one support to another. Several natural materials (agar, agarose, collagen, alginates and chitosan) and synthetic polymer materials (polyacrylamide, polyurethane, polyethylene glycol and polyvinyl alcohol) have been applied to the immobilization (Fang et al., 2004; Jianlong et al., 1998).

Among the various matrixes that are available, the MC has been chosen for its ease of use, low economic cost, low toxicity, and high operational stability (Rezaee et al., 2005; Son et al., 2003). The MC synthesized by *Acetobacter xylinum* is identical to that made by plants in respect to molecular structure. The secreted polysaccharide is free of lignin, pectin, and hemi celluloses, as well as biogenic products, which are associated with plant cellulose (Hong et al., 2001). This cellulose is highly crystalline, has high water absorption capacity, and has mechanical strength in the wet state, ultra fine network structure (Astley et al., 2001). Based of these features, there is an increasing interest in the development of new fields of application (Bae et al., 2004). The objective of this study was to investigate the immobilization of denitrifying bacteria on MC and performance evaluation of a pack bed reactor with MC as support media for biological denitrification.

2. Materials and methods

2.1. The microbial cellulose production

Acetobacter xylinum (ATCC 23768) was used in this study. It was grown in SH medium at 28 ºC under static culture conditions. SH medium was composed of 2% (W/V) glucose, 0.5% (W/V) yeast extract, 0.5% peptone, 0.27% (W/V) Na_2HPO_4 and 0.115% (W/V) citric acid (Kimura et al., 2001). Preinoculum for all experiments was prepared by transferring a single colony grown on SH agar medium into a 50 mL Erlenmeyer flask filled with liquid SH medium. After 5 days of cultivation at 28°C, the cellulose pellicle formed on the surface of the culture broth. Ten milliliters of the cell suspension was introduced into a 500 mL Erlenmeyer flask containing 100 mL of a fresh SH medium. The culture was carried out statically for 72 h and the cell suspension derived from the synthesized cellulose pellicle was used as the inoculum for further cultures. The stationary cultures in Erlenmeyer flasks filled with different volumes of the medium were maintained for seven days. The cellulose sheets were removed after cultivation and rinsed with distilled water and purged of from bacterial and medium residues by 2% sodium dodecyl sulfate (SDS) and 4 % NaOH solutions in a bath of water at a temperature of 90°C. They were cut into 5-10 mm pieces and used for cell immobilization and bioreactor media.

2.2. Denitrifyer and culture conditions

The *Pseudomonas stuzeri* used in the current study was isolated from an up flow anaerobic sludge blanket wastewater treatment plant, Tehran, Iran. The bacterium was isolated in basal salt medium (BSM) contained per Liter of distilled water: K_2HPO_4, 0.9 g; KH_2PO_4, 0.45 g; NH_4Cl, 0.45 g; $MgSO_4$, 0.2 g; $CaCl_2·2H_2O$, 0.02 g; $FeCl_3$, 0.005 g; and trace elements solution, 1 mL containing (mg/L): $ZnSO_4·7H_2O$, 400; $CoCl_2$, 50; $NiCl_2·6H_2O$, 200; $NaB_2Mo_4·2H_2O$, 300; $CuSO_4·5H_2O$, 10; $MnSO_4·H_2O$, 500. The culture plates were incubated at 37°C for 48 h, and the colonies were then transferred to 500 mL Erlenmeyer flasks containing 250 mL of liquid culture medium with the synthetic wastewater containing: 0.1 g $MgSO_4.7H_2O$, 1g KH_2PO_4, 2.5g K_2HPO_4, 0.17 g $CaCl_2.2H_2O$, 5g NaCl. Incubation was carried out with 120 rpm rotary shaking at 37 °C for 48 h. The cells were harvested from the culture medium by centrifugation ($2000 × g$, 10 min, 4 °C) and later used for the immobilization procedures.

2.3. Cell immobilization

The surface of the MC was modified by SDS and NaOH. After this treatment the MC were washed with distilled water before further use. The cell suspension of *Pseudomonas stutzeri* (OD 650 nm 0.5, unless stated otherwise) and MC were shaken together for 96 h on a rotary shaker (120 rpm) and subsequently washed twice with BSM to remove free cells. To determine the effectiveness of the immobilized cell mass, the method of Chen et al. (1996) was modified and a biomass estimation method based on the determination of cell protein content in the MC was established.

2.4. Pilot plant

The pilot scale plant used in this study consisted of a Plexiglass Column [90 cm . 21 cm (ID)], which was packed with immobilized MC (up to 60 cm) and closed at the top with a rubber stopper and at the bottom with glass wool. Inlet and outlet points were set at 2 cm from the bottom and top of column, respectively. The immobilized MC was suspended with the synthetic wastewater.

The column was initially filled with influent, and after complete removal of nitrate, the continuous process was started by running the influent through the reactor at different flow rates. The denitrification rate of the continuous bioreactor with immobilized cells was determined by Eq. 1.

Denitrification rate (N-NO₃L/d) = [N-NO₃]$_{in}$[M-NO₃]$_{out}$(R/V)

$$(1)$$

where R is the waste water flow rate, $[NO_3\text{-}N]_{in}$ and $[NO_3\text{-}N]_{out}$ is influent and effluent NO_3 concentration (g $N\text{-}NO_3$ L/d) respectively, and V the reactor

volume. All the experiments were conducted at a temperature of 25°C and a pH of 7.0.

2.5. Analytical methods

Samples of influent and effluent were collected and filtered through membranes of 0.45μm pore size. Filtrations were analyzed for nitrate, nitrite and COD. The analyses were performed according to standard methods (APHA, 2005). All data reported in our study refer to steady state conditions.

The specific surface area of the MC was determined using the multiple BET method (Micromeritics, Gemini) with nitrogen gas as the adsorbate. Scanning electron microscopy (SEM) and protein assays were used to identify the *Pseudomonas stutzeri* immobilized on MC surface. Biofilm morphology was studied by SEM using standard procedures (Tuscaloosa, 2003). Briefly, the immobilized bacteria were fixed on the surface of MC biofilm with 2.5% (w/v) glutaraldehyde overnight.

Fixed samples were dehydrated by successive treatment with 30, 50, and 75% (v/v) ethanol (each step for 15 min) and finally with pure ethanol for 1 h. Dehydrated MC beads were dried in a CO_2 atmosphere. The surface of particles was examined using a XL30 Philips model SEM operated at 20 kV.

2.6. Biomass determination

The MC was placed on a clear glass plate and was cut into several fine pieces with a sharp surgical knife. The crushed cellulose pieces were collected in a test tube. SDS solution was added (10 %) and sonic treatment was performed for 20 min to extract cell protein in ice water bath. After centrifugation, the cell protein of the MC was measured according to the Bradford method; thereafter, the biomass of the sample was estimated from the standard curve of biomass versus protein concentration.

2.7. Mass loss

Before the reactors were filled, the MC was oven dried at 90 ºC for a minimum of 24 h. The dried MC placed into each reactor were weighed and recorded. Upon the completion of the denitrification tests, the masses of the MC were measured again. The MC was thoroughly washed until minimal bacteria were attached to the MC. Then, the media were oven dried, following the same procedure as before, and weighed.

The loss of mass provides an objective measure of the degradation of the MC. The appearance of the MC was also observed and recorded during the course of the study as a subjective measure of degradation. This measure included changes in color, and the height of the MC in each column.

3. Results and discussion

3.1 Characterization of microbial cellulose

The thick, gelatinous membrane formed in static culture conditions. Characteristics of the MC used in the study are listed in Table 1. The cellulose produced in the form of a gelatinous membrane can be molded into any shape and size during its synthesis, depending on the cultivation technique and conditions used. *Acetobacter xylinum* is a simple gram negative bacterium which has an ability to synthesize a large quantity of high-quality cellulose organized as twisting ribbons of microfibrillar bundles.

Table 1. Main characteristics of the MC used in the experiments as support media

Characteristics	*Amount*	*Unit*
Moisture	96.28	%
Apparent density	990	g/L
Iodine number	210	-
BET	632.015	Sqm/g

During the process of actual biosynthesis, various carbon compounds of the nutrition medium are utilized by the bacteria, then polymerized into single, linear β-1-4-glucan chains and finally secreted outside the cells through a linear row of pores located on their outer membrane. This structure, which is not found in plant cellulose, results in high cellulose crystallinity (60–80%) and an enormous mechanical strength. Particularly impressive is the fact that the size of MC fibrils is about 100 times smaller than that of plant cellulose (Shirai et al., 1997). This unique nano morphology results in a large surface area that can hold a large amount of water and, at the same time, displays great elasticity, high wet strength, and conformability.

The small size of microbial fibrils seems to be a key factor that determines its remarkable performance as an effective adsorbent. Unlike celluloses of plant origin, microbial cellulose is entirely free of lignin and hemicelluloses (Lynd et al., 2002). A vigorous treatment with strong bases at high temperatures allows the removal of cells embedded in the cellulose net, and it is possible to achieve a high performance absorbent. The specific surface area of the biofilm determined by the BET method was 650 ± 0.08 m^2/g. The mass loss in the MC as a result of alkaline treatment was found to be around 15–20%, which is attributed to the loss of protein and nucleic acid contents. The loss in mass of the MC is plotted against operation time (Fig.1).

The most important loss of mass can be observed in the first 40 h. The percent loss obtained has been calculated based on the MC total mass. The losses of total mass following 72 h of shaking became as low as 0.35%. It is evident that such losses are not expected to affect the process in bioreactor.
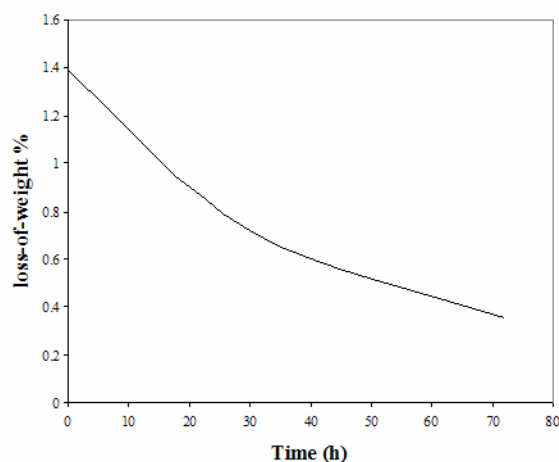
Fig.1. The loss in mass of the MC in the reactor

3.2. Immobilization of Pseudomonas stutzeri

The amount of cells immobilized on the MC was measured as a function of optical density (OD 650) of the cell suspension used for immobilization. Preliminary experiments have shown that adsorption on MC was completed after 72 h (Fig.2). The current data show that the amount of cells immobilized on the surface depended on the density of the bacterial cell suspension. The results indicate that the MC matrixes provided the best special adhesion (3.39 mg biomass/g support). However, the reactors with MC presented the highest absolute biomass retention in the reactor.
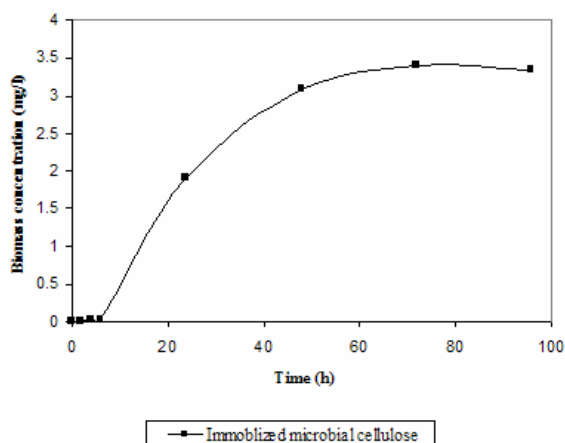
Fig.2. Amount of immobilized bacteria into the MC

This effect could be explained by increased attraction of negatively charged bacterial cells to positive groups. Micrographs of SEM illustrate the adhesion of the *Pseudomonas stutzeri* (quantified as biomass) on support material throughout the experiment (Fig .3). The immobilization of viable cells is a versatile tool that serves to increase the stability of a microbial system, allowing its application under extreme environmental conditions,

its reuse and the development of continuous bioprocesses. Advances in biotechnology using immobilization technology have shown that conditions can be modified to enhance the activity of specific microorganisms performing a desirable process. The application of immobilization for wastewater treatment has been developed and tested, and there are currently several full scale wastewater treatment plants using this technology (Tanaka et al., 1991).
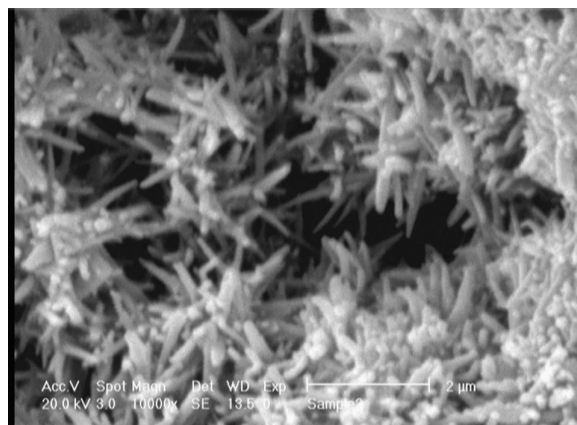
Fig.3. *Pseudomonas stutzeri* adhering to the surface of the MC (original magnification, x10,000).

Through the immobilization process, the denitrifying bacteria are provided with a very suitable environment to perform with maximum effectiveness. This is important when assessing the application of denitrification technologies for treatment plants because construction costs can be limiting factors.

3.3. Assay of biological denitrification

To measure the biological denitrification activity of immobilized MC, a lab-scale bioreactor was used for testing the reduction of nitrate in a continuous mode. In the long term operation test, the synthetic waste water was fed applied with the following conditions: 200 mg NO_3-N/L, 600 mg/L ethanol as the carbon source, and an adjusted pH of 7.2. The performance of continuous denitrification for a period of 20 days was illustrated in Fig.4. The denitrification ability of the bioreactor at the optimum carbon source (3:1 ratio) proved stable under relatively low HRT (3 h) and at a loading rate of 1.61 kg NO_3-N/m^3.d. The nitrate content of the effluent (up to 7.53 mg/L NO_3 –N) was less than the proposed WHO limit (10 mg/L NO3-N) (WHO, 2004). The average denitrification rate with MC as support media was 1.6±.02 kg NO_3-N/m^3.d.

The denitrification rate for wood chips and wheat straw as alternative biofilter media was reported to be 1.36 kg NO_3-N/m^3.d using an anoxic filter (Saliling et al., 2007). A maximum biological denitrification rate for 60 mg/L nitrate was reported as .88 kg NO_3-N/m^3.d with HRT 3 h in a continuous flow pilot bioreactor containing immobilized

Pseudomonas butanovora cells (Peter et al., 2003). Complete nitrate removal efficiency was achieved with HRTs of 9, using a bench-scale anoxic filter. The MC lost $2.3 \pm .17\%$ of its initial dry mass over a period of 20 days. There was no observed height loss in the MC reactor.
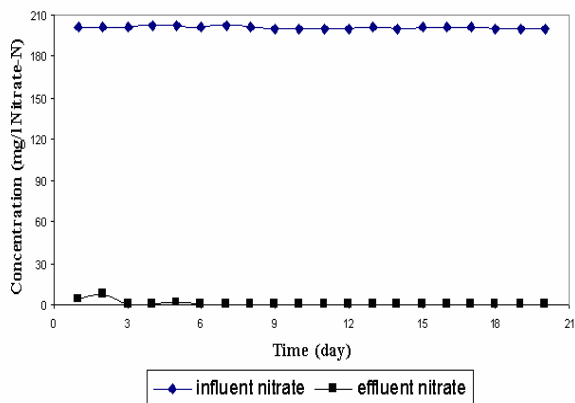
Fig.4. The time course denitrification with continuous packed bed reactor using cellulose as support for immobilization

        Wheat straw and wood chips as carriers lost $37.7 \pm 2.7\%$ (60.4 ± 4.3 g reduction) of their initial dry mass compared to only $16.2 \pm 5.2\%$ (117 ± 43 g reduction) for wood chips over a period of 140 days (Saliling et al., 2007). Soares and Abeliovich (1998) reported that when wheat straw was used as the carbon source for biological denitrification all the water soluble components and a significant portion of the cellulose and hemicellulose had been lost by the end of the experiment, while lignin and mineral components remained unchanged.

4. Conclusions

        In this study, *Pseudomonas stutzeri* was immobilized on treated MC with SDS and NaOH. The amount of bacteria attached to the MC support was to a certain extent dependent on the optical density (650 nm) of cell suspension during the immobilization process. Experimentally, it was confirmed that the immobilized bacterium on MC could achieve a nitrate removal efficiency of 99% at an initial nitrate concentration of 200 mg NO_3-N/L under continuous flow conditions. The MC offers an interesting alternative to other types of media such as plastic and ceramic. For better effectiveness, it would be useful to co-immobilize more microbial strains with complementary biodegradation activity. However, the use of MC as support media in the field scale requires more studies.

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COMBUSTION OF PITCOAL-WOOD BIOMASS BRICHETTES IN A BOILER TEST FACILITY

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Abstract

The use of composite fuels using pitcoal and sawdust represents a high perspective. The paper deals with the experimental results focusing on the combustion efficiency of composite fuel briquettes and on the polluting emissions level. A special care is given to the determination of boiler efficiency and to the establishment of exploiting economic conditions, like the supply, cleaning etc. The research of the combustion of pitcoal-wood biomass briquettes is conducted on a 55 kW boiler. A numerical modeling of the combustion processes within the boiler allowed a critical comparison between the experimental and numerical data.

Key words: composite fuel briquettes, combustion, numerical modelling, emission reduction

1. Introduction

The research of the combustion of pitcoal-wood biomass briquettes is conducted on a 55 kW boiler (Azapagic 2007). A boiler with reduced thermal power, which can supply a residential area of 500 m² or a small commercial area, was chosen.

The concept to implement the use of composite fuels in hill and mountain forestry area was the principle of the research, (Axinte et Al. 2003; Prisecaru et al. 2007; Pănoiu et al. 2008). Fig. 1 shows the boiler test facility, built by PIFATI SA, present in the Laboratory of Boilers and Combustion Installations of the Department of Classic Thermo-mechanic and Nuclear Equipment, University Politehnica of Bucharest. The boiler has a cast iron grid for combustion, with a small slope towards the supply door.

The experimental researches are focusing on the combustion efficiency of composite fuel briquettes and on the polluting emissions level (Grant 2006). A special care is given to the determination of boiler efficiency and to the establishment of exploiting economic conditions, like the supply,

cleaning etc. The boiler characteristics are presented in Table 1, (Pănoiu et al., 2008).

2. Characteristics of the 55 kW boiler

The 55 kW test facility boiler has the following dimensions of the furnace:

Depth: L_f =750 mm;
Width: l_f = 550 mm;
Height: h_f = 600 mm;
Volume: V_f = 0.25 m³.

The furnace is equipped with a grid with fixed bars, having the dimensions (Fig. 2):

Length: L_g = 520 mm;
Width: l_g = 550 mm;
Bars width: l_b = 15 mm;
Bars spacing: s = 15 mm;
Length of the free space between bars l_{sl} = 360 mm;
Grid surface S_g = 0.286 m²;
Grid active surface S_{ga} = 0.19 m².

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Table 1. Boiler characteristics

Boiler	Power[*]		Pressure	Sizes							
	Kcal/h	kW	p_{max} bar	A mm	A_1 mm	B mm	B_1 mm	E mm	E_1 mm	H mm	C mm
	50000	58	3	810	880	660	740	1590	1720	1116	1250

[*]for this boiler type a 78% efficiency is considered
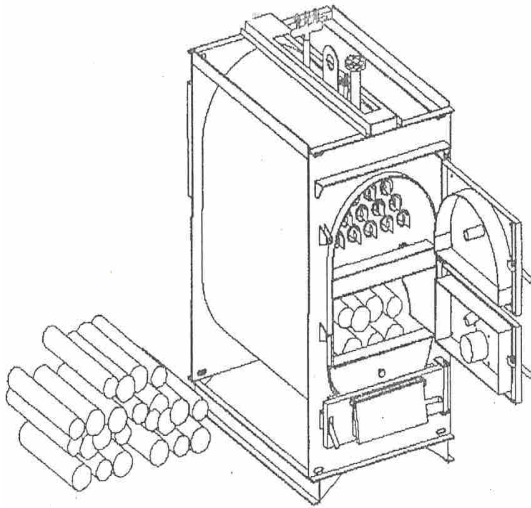
Fig. 1. 55 kW boiler
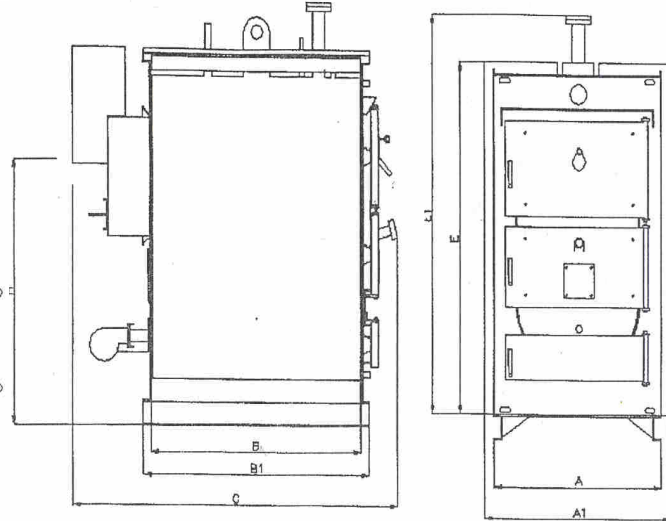
Fig. 2. The actual size of the boiler

The fuel flow necessary to achieve 55 kW thermal power (P_t) is given by Eq. (1):

$$B\left[\frac{kg}{s}\right] = \frac{P_t}{Q_i^i \cdot \eta} \qquad (1)$$

where: Q_i^i [kJ/kg] is the fuel low heat value.

For briquettes composed from pitcoal from Romanian Jiu Valley and wood wastes like sawdust, the low heat value varies between 12500 kJ/kg and 13200 kJ/kg, (Lăzăroiu et al., 2008). Elemental composition of the components and composite from the briquette is presented in Table 2.

Table 2. Elemental composition of the components and composite from the briquette

Element	*Symbol*	*U.M*	*Biomass and molasses*	*Pitcoal*	*Composite*
Carbon	C^i	%	46.48	21.20	28.23
Hydrogen	H^i	%	6.10	1.40	2.74
Oxygen	O^i	%	41.80	2.52	14.49
Azoth	N^i	%	0.63	0.14	0.28
Sulfur	S_c^i	%	0.00	0.40	0.26
Ash	A^i	%	1.17	70.52	50.18
Total	W_t^i	%	3.82	3.82	3.82

Considering a low heat value of 12,700 kJ/kg, the rate of the fuel flow is:

$$B = \frac{55}{12700 \cdot 0.7} = 0,006 \quad [kg/s] = 22.2 [kg/h] \qquad (2)$$

Using this value, the operational coefficients for the boiler are:
- total gravimetric load of the grid:

$$q_{gr} = \frac{0.006}{0.286} = 0.021 \quad [kg/m^2 \cdot s] \qquad (3)$$

- gravimetric load of the combustion area:

$$q_{gr}^* = \frac{0.006}{0.19} = 0.031 \quad [kg/m^2 \cdot s] \qquad (4)$$

- total specific thermal load of the grid:

$$q_{gr} = \frac{0.006 \cdot 12700}{0.286} = 269 \, [kg/m^2 \cdot s] \qquad (5)$$

- specific thermal load of the grid active area:

$$q_{gr} = \frac{6 \cdot 12700}{190} = 400 \, [kg/m^2 \cdot s] \qquad (6)$$

- active section of the grid: 0.346; cooling index of the grid bars: 1.33;

- thermal load of the furnace width:

$$q_l = \frac{B \cdot Q_i^i}{l_f} = \frac{0.6 \cdot 12700}{55} = 140\,[\,kW/m\,]$$

(7)

- thermal load of the grid bars width:

$$q_l^* = \frac{B \cdot Q_i^i}{l_f} = \frac{6 \cdot 12700}{275} = 280\,[\,kW/m\,]$$

(8)

- thermal load of the furnace volume:

$$q_v = \frac{B \cdot Q_i^i}{V_f} = \frac{6 \cdot 12700}{250} = 305\,\left[kW/m^3\right]$$

(9)

3. Experimental results

The experimental data are presented in Table 3 and Table 4.

The taste data values for the 50 kW load have indicated:

- a quantity of slag evacuated below the grid of 5.5-6.5%; the volume of the slag retaining room of 0.5x 0.54 x 0.6 = 0.162 m³ allows an evacuation at 6 hours;
- the disturbance of the mixture layer pitcoal-sawdust is occurring at a period of 2-3 hours;
- the temperature of the fuel layer during the combustion was of 850°C;

- the temperature of the stack flue gas was below 160°C;
- the air excess of the stack flue gas had optimal values for the combustion technology in fixed layer below 3.5;
- the measured efficiency is over 76%;
- the pollutants emissions are reduced. If a reference air excess characterized by an oxygen percentage in the exhausted gases of 11% is considered, the CO emissions are below 500 mg/m³, NO_x emissions below 185 mg/m³ and SO_2 emissions below 300 mg/m³N.

The performances of the nominal operation load were kept both for 45 kW (90%) ad 40 kW (80%) loads. For a boiler load below 60%, a reduction with 4-5% of the efficiency was observed.

The thermal power was determined by measuring the heated water flow in the boiler and the difference of the boiler outlet and inlet water temperatures.

Flame aspect after 1.5 hours from fuel feeding is shown in Fig. 3 and the smoke aspect at the stack evacuation is shown in Fig. 4.

Thermal power is expressed by Eq. (10):

$$P_t = 4.18 \cdot D_a \cdot \left(t_e - t_i\right)\,[KW]$$

(10)

where:
D_a – water flow, kg/s;
t_e – outlet temperature of the boiler water, °C;
t_i – inlet temperature of the boiler water, °C.

Table 3. Experimental data sheet no. 1

No.	Operating characteristic	U.M.	Measurement			
			1	2	3	4
1	Thermal load	kW	50	50	50	49
2	Combustible flow	kg/h	17	16.9	17	17
3	Slag	kg/h	0.88	0.9	0.9	0.89
4	Ash	kg/h	2.8	2.75	2.8	2.75
5	Stack temperature (t_{ev})	^0C	160	161	160	162
6	Water flow (D_a)	kg/h	810	812	811	812
7	Inlet water temperature (t_i)	^0C	8	8	8	8
8	Exit water temperature (t_e)	^0C	59	61	61	61
9	CO_2 emission	%	3,9	4.0	3.8	3.9
10	SO_2 emission	ppm	70	72	72	70
11	NO emission	ppm	30	30	27	26
12	NO_2 emission	ppm	0	10	0	0
13	NOx total emission ($NO+NO_2$)	ppm	30	40	27	26
14	CO emission	%	0.24	0.16	0.2	0.18
15	Furnace air excess, λ_f		3.2	3.1	3.2	3.3
16	Stack air excess, λ co		3.4	3.4	3.37	3.4
17	Oxygen in the stack exhaust gases (O_2)	%	14.8	14.6	14.6	14.7
18	Air temperature	^0C	15	17	16.5	17
19	Average ambient temperature	^0C	2	2	2	2
20	Indirect efficiency		76.7	77.1	77.2	78.1

Table 4. Experimental data sheet no. 2

No.	Operating characteristic	U.M.	Measurement			
			1	2	3	4
1	Thermal load	kW	45	44.9	45	45
2	Combustible flow	kg/h	15.2	15.2	15.2	14.9
3	Slag	kg/h	0.86	0.86	0.88	0.9
4	Ash	kg/h	2.60	2.61	2,60	2.61
5	Stack temperature (t_{ev})	^{0}C	159	157	157	157
6	Water flow (Da)	kg/h	730	726	769	728
7	Inlet water temperature (t_i)	^{0}C	8	8	8	8
8	Exit water temperature (t_e)	^{0}C	61	59	60	60.5
9	CO_2 emission	%	3.9	3.89	3.9	3.91
10	SO_2 emission	ppm	71	72	68	72
11	NO emission	ppm	30	32	31	32
12	NO_2 emission	ppm	14	15	18	17
13	NOx total emission ($NO+NO_2$)	ppm	44	47	49	49
14	CO emission	%	0.16	0.16	0.13	0.14
15	Furnace air excess, λ_f		3.3	3.55	3.3	3.3
16	Stack air excess, λ co		3.5	3.55	3.5	3.49
17	Oxygen in the stack exhaust gases	%	14.9	14.9	14.79	14.9
18	Air temperature	^{0}C	14	15	15	15
19	Average ambient temperature	^{0}C	-2	-2	-2	-2
20	Indirect efficiency		76.5	76.5	76.6	76.6

Fig. 3. Flame aspect

The air flow was controlled through the valve on the inferior side of the boiler combustion chamber, the air being conducted further to the grid and the briquettes layer. At the same time, the air admission was controlled according to the stack depression (by aid of a control valve placed at the boiler end). After the load settlement, the air and the depression are established such as the pollutant emissions to be as low as possible (CO, NO_x) and the temperature of the stack exhausted gases as low as possible; in these conditions the air excess was between 3 and 4.5. The fuel disturbance was made once every 2-4 hours, and the slag evacuation once every 4-6 hours.

Representative samples of flow slag and ash were collected and tasted in laboratory boiler.

As results were obtained: C_{zg} = 18%; C_{an} =5% (combustible material in slag and ash); a_{zg} = 0.06; a_{an} = 1 – 0.06 = 0.94 (retaining degree under the shape of slag and ash).

Fig. 4. Monitoring the smoke aspect at the stack

After computation, the values for the percentage heat losses are: loss through incomplete combustion from the mechanical point of view, q_m = 2.46; loss through incomplete combustion from the chemical point of view, q_{ch} = 3.57; loss through the enthalpy of the residuum evacuated from the furnace, q_{rf} = 0.056 %.

For a temperature of the stack exhausted gases of 160ºC and an air excess λ_{ev} = 3.4, the heat percentage loss at evacuation resulted q_{ev} = 29.3%. For computing the heat losses through incomplete chemical combustion, the CO emission had the average value of 0.18%, and the volume of the dry exhausted gases of V_{gu} = 22.56 m^3_N/kg.

On a statistical basis, the heat loss towards the ambient is determined $q_{ex} = 1.5$. Using the percentage heat losses, the installation efficiency is:

$$\eta = 100 - (2.46 + 3.57 + 15 + 0.056 + 29.3) = 63.12\%$$
(11)

The difference between the efficiency computed with the gas analyzer and Eq. (11) is given by the fact that the gas analyzer does not consider the loss q_{ev}.

The sum of the losses not considered by the gas analyzer is:

$$q_m + q_{ch} + q_{rf} + q_{ex} = 7.58\%$$
(12)

The efficiency computed only using the heat percentage losses at the stack exhausted gas will be:

$$\eta = 100 - 29.3 = 70.7$$
(13)

The efficiency measured with the gas analyzer was $\eta = 77.2$. The percentage error is

$$\Delta\eta = \frac{77.2 - 70.7}{77.2} \cdot 100 = 8.41\%$$
(14)

The combustion technology on fix grid, with manual distribution of the fuel layer, experimented on the 55 kW test boiler allow obtaining good results for the mixture pitcoal-sawdust combustion. Thus, the efficiency was within admissible limits and the pollutant emissions well below the regulated threshold of 400 mg/m³$_N$, both for NOx as well as for SO$_x$ (for CO does not exist yet a regulated threshold), (Lăzăroiu, 2007).

The experimental results were compared with the ones obtained through numerical simulation using the software FLUENT. The numerical modeling allowed the determination of the heat field within the furnace, on the grid and within the smoke pipes. These data allow also estimating the installation reliability and the efficiency value (Gavrilescu 2002).

4. Numerical modeling results

For geometric modeling of the 55 kW experimental boiler, 164483 cells were used, grouped as: 147538 cells with tetrahedron form; 16945 cells with hexagon form. For the turbulence model, the Spalart-Almaras model was used. This model is specific for the reduced turbulences (the combustion of the mixture combustible particles on the grid in a fixed layer conducts to a reduced turbulence). For the radiation model, the "6 fluxes model" was used.

For the radiation model, the physical measures imposed are: average absorption, $\varepsilon_p = 0.35$ m^{-1}; average particles spreading coefficient, 0; metallic wall emission factor $\varepsilon = 0.8$, (Mihăescu et al., 2007). For the coke particles drawn in suspension by the combustion gases the size of $4.38 \cdot 10^{-4}$ m was chosen.

For simulating the composite combustible granulation the real size of the briquettes with diameter of 40 mm and height of 40 mm was used.

The results highlighted that the combustion area of the furnace is sufficiently large to ensure a good combustion. Thus, the CO emission on the furnace end was 0.03 kg/kg. For an oxygen concentration of approximately 7% within the combustion gases, the corrected emission of CO at the flame ending was CO = 970 mg/m³$_N$.

The average temperature at the middle of the furnace was 1092ºC. This value is very high for the combustion technology on the grid with fixed layer. In practice, high values of the air excess and temperatures at the furnace end within 850-900ºC are adopted.

The numerical modeling result, through combustion performances, indicates as future perspective the possibility to reduce the air excess and to increase the layer and flame temperature. It must be mentioned that this boiler has cast iron grid and thus the operation with high temperatures within the combustion area are allowed. Fig. 5 shows the field of the thermal flux in W/m² for the area at the boiler top.
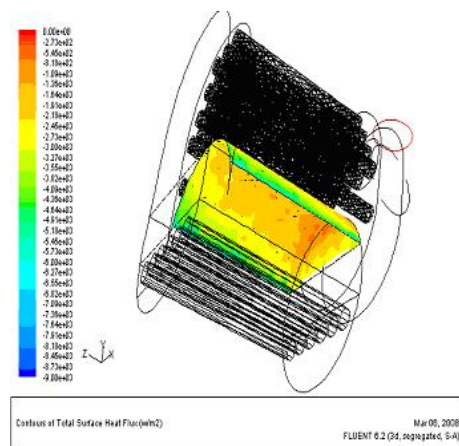
Fig. 5. Heat flux on the furnace top

The thermal flux at the flame end represents the result of the radiation process, the respective heat being taken by the first row of smoke pipes placed towards the furnace. The thermal flux received by the grid bars is shown in Fig. 6. This flux has values between 20 and 40 W/m². The air cooling of the bars allows their good operation. Fig. 7 illustrates the thermal flux distribution on the smoke pipes wall. The temperature variation from the furnace area is illustrated in Fig. 8.
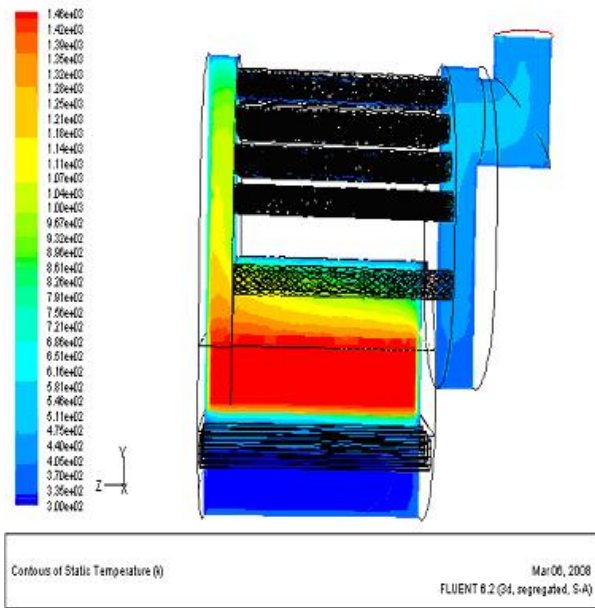
Fig. 6. Temperature field for the furnace
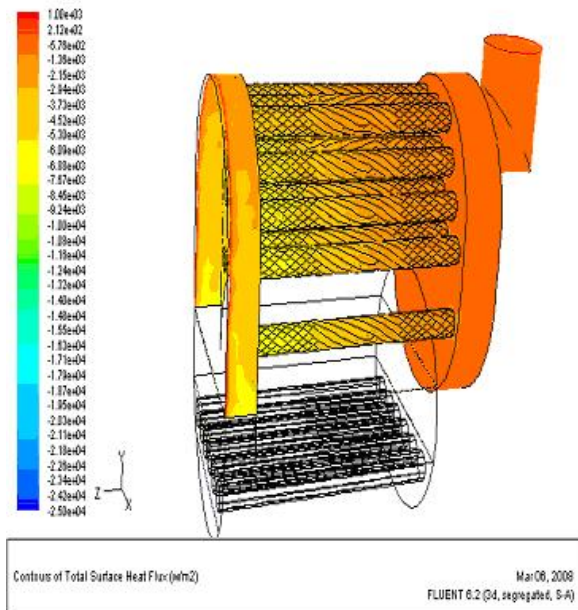
Fig. 7. Heat flux distribution on the smoke pipe walls

The resulted values during the combustion process are between the normal limits for the calorific power of the combustible mixture. It must be noted the efficient cooling of the grid bars, resulting a possibility for their long exploitation.

5. Conclusions

The numerical modeling data of the complex processes within the furnace, containing combustion reactions, heat emitting, heat exchange through radiation and partially convection, flow and pollutant emissions, can be used for the design of new installations or for

instructions for an economic exploitation of these type of installations.

The validation of the numerical computation model applied to the experimental boiler can be considered realized through the value of the exhausted gases temperature at stack outlet, around 300ºC and through the CO emission, having values approximately equal with the ones experimentally determined.
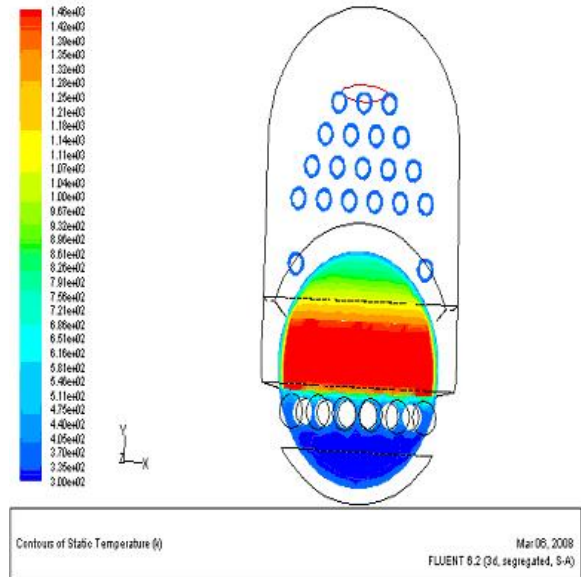
Fig. 8. Temperatures distribution for the furnace area

The numerical values obtained through the mathematical modeling of the thermal transfer process through radiation with applicability for the 55 kW experimental boiler brought new data with respect to the ones experimentally obtained. The values of the thermal flux on the furnace areas must be mentioned.

The data obtained through mathematical modeling highlighted a good cooling of the grid bars (leading to a high durability of these) and relatively low temperatures for the furnace main area.

The rate distribution highlighted a uniform distributed combustion that leads to a high efficiency. The temperatures from the furnace area within the combustion technology on the grid are very difficult measured. The most efficient method is using infrared pyrometers, but the area visible area is very reduced, such that the data obtained thorough numerical modeling represents an unique and of high value information. The same thing can be told on the rate field.

The use of composite combustibles using pitcoal and sawdust represents a certain perspective. Thus, the calorific power is high for obtaining feasible loads of the combustion space leading to corresponding efficiencies and to the enlargement of the period between two refuels. Due to the relatively sterile contain from the composite combustible, the slag quantity that must be evacuated sensible is reducing. The pollutants emissions are at the normal limits for the grid combustion technology.

The good results obtained at the combustion on fixed grids of the composite combustible recommends the enlargement of the combustion researches also on mobile grids, thing that leads to the increase of the thermal power for these boilers.

Acknowledgments

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INTERDISCIPLINARY TRAINING AND RESEARCH PLATFORM

HIGH PERFORMANCE MULTIFUNCTIONAL POLYMERIC MATERIALS FOR MEDICINE, PHARMACY, MICROELECTRONICS, ENERGY/INFORMATION STORAGE, ENVIRONMENTAL PROTECTION

The Platform aims to develop **training and interdisciplinary research in high-performance multifunctional polymeric materials**. The nucleus of the Platform is based on the **Center of Excellence POLYMERS**, officially accredited by CNCSIS (7.06.2003), center acting within the "Gh. Asachi" Technical University of Iasi.

The Platform will be *integrated in national/European networks* and will ensure the *training and improvement of human resources through high education and research*, will *enhance the research performance and the visibility* of Romania, will contribute to *Romanian high education and research integration in European Education Area and European Research Area*, to the *development of the knowledge-based society* and will increase the *socio-economic impact of research*.

To ensure the success of the Project, a set of **specific objectives** has been defined:

- *New educational programmes*, oriented towards *European priorities*, able to ensure highly qualified human resources and to integrate them into the knowledge-based modern society
- *New contents, forms and methods of training*, specific for the development of education and research in multifunctional polymeric materials and in agreement with *Lisbon Agenda* and with *Bologna Process*, as well as with *Romanian priorities*
- Elaboration and implementation *of interdisciplinary programmes of training (master, doctoral, post-doc)*
- *Consolidation of excellence in research* in the field of high performance multifunctional materials by promoting interdisciplinary programmes and by attracting the most talented graduates – from Romania and abroad – for PhD and post-doc studies
- *Extension and consolidation of the research infrastructure (hard equipment)* of the Platform, to improve the training and research process, in order to *increase Platform competitiveness in accessing national* (CNCSIS, CEEX, PNCDI 2) *and international* (FP7, NATO, NSF etc.) *programmes* and the efficiency in answering the requirements of the regional, national and European economic areas
- *Strengthening the scientific cooperation* with academic and economic partners at national and European level
- *Promoting the exchange of information and communication* between the academic and socio-economic environments, to consolidate the knowledge-based society and to accelerate the integration of Romania into the European Union.

The Project will develop **(i) education activities** through **(i-a) master studies** (two directions are proposed – **Biomaterials** – addressed to graduates of chemistry, chemical engineering, medical bioengineering, biology, medicine, pharmacy – and **Multifunctional Materials for**

Advanced Technologies, addressed to graduates of chemistry, chemical engineering, medical bioengineering, physics, electronics and electrical engineering, civil engineering, environment protection; *both master programmes will be in Romanian and/or English*), **(i-b) doctoral studies** with a pronounced interdisciplinary character and implemented within *the "co-tutelle" system*, **(i-c) post-doc studies** (financed from other programmes), and **(ii) research activities** developed within five programmes, i.e., **(ii-a) Biomaterials. Polymer-drug Systems with Controlled and Targeted Release** (polymer-drug conjugates, diffusional systems, drug inclusion in polymeric micro- or nanoparticles), **(ii-b) Smart Multifunctional Polymeric Materials** (molecular imprinting, diagnostics and bioseparation, nanocapsules and nanostructured membranes *via* core-shell particles, smart hydrogels and nanostructured gels, biomimetic polymeric networks, nanofabrication), **(ii-c) Motile Molecular Systems** (hybrid and organic polymers for biology, microelectronics, nanorobotics and energy/information storage), **(ii-d) Liquid Crystal Hetero-organic and Organic Compounds** (liquid crystals for displays, opto-electronic devices, ferro-electric liquid crystals), **(ii-e) Molecular Modeling and Artificial Intelligence** (conformational analysis and simulation of properties, neuronal networks, fuzzy systems).

All planned activities and actions are based on a **deep analysis of the tendencies in the interdisciplinary education and research**, on the **requirements of the national and European market**.

Most of Platform budget is dedicated to the serious improving of the **research infrastructure (hard equipments)**. *Additional funding and expertise* will be obtained through the facilities offered by the "Gh. Asachi" Technical University of Iasi, the infrastructure and human resources of the POLYMER Centre of Excellence, through the facilities offered by the *traditional national and European partners of the Platform*. **Platform sustainability** will be ensured by different funding attracting activities – *training of specialists from SMSs*, *consulting activities*, *national and international grants*, the **RENAR accredited laboratories**, the **Technology Transfer Center** and the **Innovation Relay Centre** established within the Platform, the *specific activities* to be performed within the **Science and Technology Park** in Iasi.

The benefits of the Platform will cover the whole high education and research environment in Iasi and in the North-Eastern Region of Romania and all Platform partners – both academic and economic.

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OPPORTUNITIES AND BARRIERS FOR DEVELOPMENT OF BIOGAS TECHNOLOGIES IN ROMANIA

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Abstract

The development of technologies for waste treatment, simultaneously with minimizing greenhouse gas emissions, has become a matter of great concern at global level. Biogas systems can help in the fight against global warming by avoiding to escape methane from organic waste, into the atmosphere. Biogas technology is of great benefit to the end-users and the environment by energy, compost and nutrient recovery. Romania is a country with a huge biomass potential. Implementing of biogas technology could be a proper solution for waste treatment and producing of electricity from renewable energy sources, as stipulated in EU and national legislation. This paper presents an overview on the progress of biogas technologies in Romania since 1980s and the main obstacles that have slow down the development of this technology in the context of the major political and economical changes registered in Romanian industry after 1990. There are mentioned the main benefits which biogas plants could bring to the environment and also some common problems with biogas plants which have been noticed in the developed countries in this field.

Keywords: organic waste, anaerobic digestion, biogas plants

1. Introduction

In the last decades pollution of the air and water from municipal, industrial and agricultural operations has grown continuously. The emission of CO_2 and other greenhouse gases (GHG) has become an important concern at global level. Governments and industries are therefore increasingly on the lookout for technologies that will allow for more efficient and cost-effective waste treatment while minimizing GHG.

Biogas is a combustible gas produced by the anaerobic digestion of organic material, e.g. animal manure, human excreta, kitchen remains, straws and leaves through the action of micro-organisms. Biogas is primarily composed of methane (CH_4) and carbon dioxide (CO_2), with smaller amounts of carbon monoxide (CO), hydrogen sulfide (H_2S), ammonia (NH_3), nitrogen (N_2) and oxygen (O_2).

Biogas plants can successfully treat the organic fraction of wastes such as food and alcohol industry waste, crop waste, farm waste, municipal waste, sewage sludge etc. When used in a fully engineered system, biogas technology not only provides pollution prevention, but also allows for energy, compost and nutrient recovery.

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Thus, biogas plants can convert a disposal problem into a profit centre.

2. Policy background

Renewable energy sources are those that produce electricity or thermal energy without depleting natural resources. Greenhouse gas emissions are blamed for the accelerated climate change throughout the world. Thus, renewable energy use and greenhouse gas emission reduction are globally recommended.

The European Commission has taken some important decisions to promote renewable energy in general and biomass in particular. The Directive 2001/77/EC on the promotion of electricity produced from renewable energy sources in the internal electricity market represents the first step of European Union in complying with the Kyoto targets of reducing the greenhouse gases. By the year 2010 the average electricity production from renewable sources should be increased from 12% to 21%. Further more, fossil fuel consumption for transport should also be increasingly substituted by biomass to reach 8% by 2020 (ANRE, 2006).

Romania was one of the first European Union candidate countries transposing the Directive 2001/77/EC stipulations into its own legislation. Romania has adopted many of the needed laws concerning fuel policy and it is working towards complete harmonization. All the directives valid on the European Community have been put into law in Romania (Ofiteru et al., 2008). The national legal framework concerning electricity from renewable energy sources focuses mainly on Electricity Law no. 13/2007 and GD no. 443/2003 regarding the promotion of electricity produced from renewable energy sources, modified by GD no. 958/2005.

According to Romanian Energy Preservation Agency (ARCE), Romania has to encourage the companies and also the citizens for making more investments in energy renewable sources based technologies. The Romanian objective target for 2010 concerning E-RES is that 30% of internal consumption (national production + imports/exports) to be covered by electricity produced from renewable energy sources. This type of non-pollutant energy source is practically endless, in long and medium terms, and is significantly cheaper than conventional sources, especially in condition of a continuous increase of oil price.

Although 40 % of Romania is agricultural area and ca 30% forest, only 10% of the biomass is used for energy production. Currently biomass is used only for heating purposes, direct burning for cooking and hot water preparation consuming the largest share. The Romanian government is planning to implement a new program for increasing the use of renewable energy that also includes biomass and biogas energy (Ionel et al., 2006).

Although in Romania, an indirect stimulating mechanism for utilization of renewable energy sources is regulated, the schemes for direct subvention of prices for which the producers of electricity from renewable sources are selling their product are lacking.

3. Stat-of-the-art in biogas technology development in Romania

Research activities for biogas generation using anaerobic digestion have been performed in Romania since 50' by some laboratory testing regarding active methanogenic bacteria which can produce biogas from different organic substrates.

The researches and experiments performed after 1980 were focused on biogas production both from dejections generated in farms and sewage sludge resulted within wastewater treatment plants. In 80s years, biogas plants operating near wastewater treatment facilities had been generated over 85.000 m^3 a day. It was also been built some biogas plants for treating organic waste in food industry companies, farms, distilleries and several farm-scale plants that facilitated small communities (Ofiteru et al., 2008).

Types of biogas plants used or still in use in Romania are the followings:
- *small facilities*, capacity up to 14 m^3, simple design, biogas production 3 m^3 per day;
- *medium capacities*, capacity 30-50 m^3, simple design;
- *larger capacities*, over 500 m^3 .

Unfortunately, started from 1990, the interest for biogas production by anaerobic digestion, using animal wastes resulted in farms and food industry residual materials, has decreased significantly, due to socio-economical and political reasons on the one hand and, on the other hand, the lack of detailed information concerning process selection and performance. Nowadays, it can be outlined the following aspects concerning biogas production:
- No major investment done in this sector after 1990;
- No maintenance work done on the existing facilities;
- Very few research projects carried out after 1990 on this field. Very few reports on the still functioning capacities;

Considering the economical development that Romania has registered in the last years and also the huge biomass potential, there are good opportunities to develop biogas technologies in Romania.

There are many sources of biodegradable waste in the country suitable for extracting biogas, such as wastes of livestock breeding and poultry farming, food wastes, industrial organic wastes and residues of crops. Municipal organic waste and sewage could also be an important source for biomass processing by anaerobic treatment (Bejan and Rusu, 2007).

Recently it can be noticed an increased tendency for livestock in the animal farms and consequently and increasingly farm slurry for disposal. In 2007, livestock consisted of about 3 mln. of cattles, 8,8 mln. of sheeps, 6,9 mln. of swines and 86 mln. of poultry. The quantity of methane that might have been produced only from animal waste in Romania in the year 2007 was estimated to be 7.05×10^6 m^3 CH$_4$/ day (MAPAM, 2007).

In spite of that statistic, the present status shows that biogas technologies are not yet widely adopted in the country.

There are few incentives of foreign companies with tradition in biogas plants to enter the Romanian market and also some laboratory research studies to improve the biochemical processes in anaerobic digesters in order to reach a high biogas yield and to make the biogas plants efficiently from economical point of view economically at current energy prices (Băran, 2008).

4. Reasons to implement a biogas technology

Biogas is a carbon neutral way of energy supply. The substrates from plants and animals only emit the carbon dioxide they have accumulated during their life cycle and which they would have emitted also without the energetic utilization. On the whole, electricity produced from biogas produces much less carbon dioxide then conventional energy supply. 1 kW of electricity produced by biogas plants prevents 7.000 kg CO$_2$ per year. Biogas burns with a hot blue flame and can be used for cooking, lighting and to run refrigerators.

Biogas can be used for all applications designed for natural gas. It can be used as a fuel in power generators, engines, boilers and burners.

While producing electricity, heat energy can also be recovered by using a co-generator which usually contains an internal combustion engine or power turbine and heat exchanger to capture the heat generated while electricity is produced. Thus, co-generators have higher efficiency in energy production when compared to other electricity generators (Butchaiah, 2006).

The sludge resulted after digestion is rich in basic nutrients such as nitrogen, phosphorus potassium and can be used as high quality fertilizer, so there is no waste in biogas technologies, as shown in Fig. 1 (Bhat et al., 2001).

Apart from getting biogas and fertilizer, decomposition and fermentation of organic material in biogas digesters improves sanitation because the gas and the slurry/sludge obtained does not usually smell, and moreover breeding site for flies and mosquitoes, which transmit disease are eliminated. Most of the pathogens are also killed during the fermentation process (www.thepigsite.com/.../2205/anaerobic-digesters).

There are many benefits resulting from the use of biogas technology, as following:

- *Waste treatment benefits*
  - Natural waste treatment process
  - Requires less land than aerobic composting
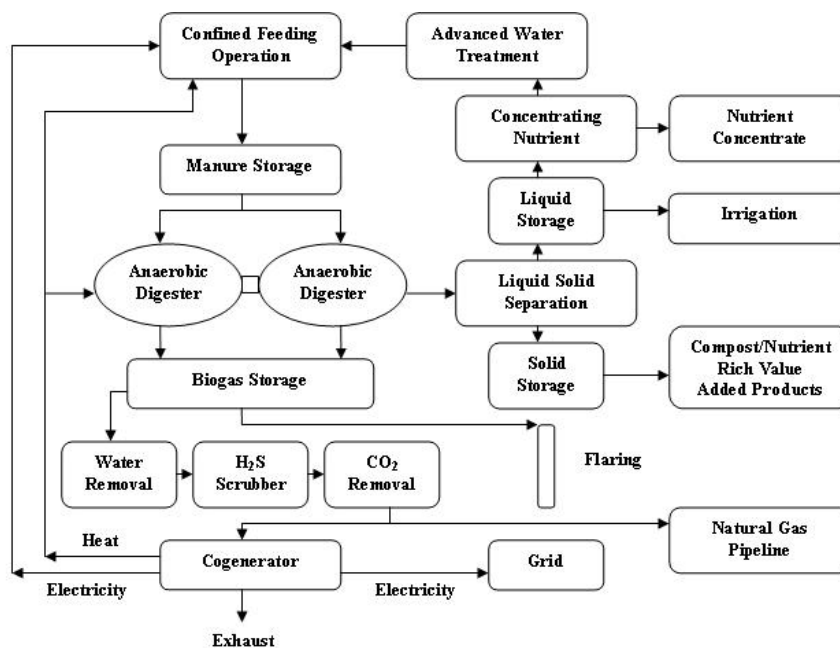 - Reduces disposed waste volume and mass

Fig. 1. Flow sheet of a biogas plant with co-generation

- *Energy benefits*
  - Net energy producing process
  - Generates high quality renewable fuel
- *Environmental benefits*
  - Significantly reduces greenhouse gas
  - Eliminates noxious odors
  - Produces a sanitized compost and nutrient-rich liquid fertilizer
- *Health-related benefits*
  - Improved sanitation (reduction of pathogens, worm eggs and flies)
- *Economic benefits*
  - Considering the whole life-cycle, it is more emissions cost-effective than other treatment options
  - Jobs are created (related to the design, operation, and manufacture of energy recovery systems).

In spite of these strong environmental and economic benefits, the production and use of biogas is not yet a common application in Romania due to the main market barriers: lack of knowledge and experience of farmers, biogas plant operators and engineering companies, lack of awareness of decision makers, and insufficient access to funding sources (www.big-east.eu).

5. Potential barriers in development of biogas plants

History shows that biogas plants have not always been introduced with success. Many years, the focus of the government policies was on biogas quantity not quality. This resulted in badly functioning digesters, many of them being not in operation today.

The situation is similar also in Romania. Many biogas plants that were treating farm waste and sludge from municipal wastewater treatment facilities are not operational now due to difficulty of financing and poor maintenance.

To develop and implement biogas technology at large scale it would be useful for Romania to benefit from the experience of the developed countries in this field and to avoid the obstacles these countries faced during their growth.

Biogas systems require a financial investment which is an important obstacle in biogas plants development in Romania and also a management responsibility. The main financial obligations associated with building an anaerobic digester include capital (equipment and construction and associated site work), project development (technical, legal, and planning consultants; financing; utilities connection; and licensing), operation and maintenance, and training costs (Koopmans, 1998).

Installing and operating costs for biogas plants vary significantly as a function of their capacities. For example, in Germany a small biogas plant (output of 100-500 kW), owned by a few farmers working together, cost about 1,5 million Euro. The government doesn't supply any funding for the construction of the plants, but because the revenue that these plants earn is guaranteed for 20 years, it is easy to get loans at a low-interest rate from commercial banks. A large capacity biogas plant which generates an electrical output of 4 MW needs an investment up to 15 million Euro. In USA, for a biogas plant with loading rate of 82 - 110 m^3/day organic waste and a biogas production of 850-1150 m^3/day, the investment costs reach 290000 - 600000 USD. A biogas plant installed at Gordondale Farms, having ca. 800 milking cows and an electrical output of 876000 kWh per year, costs ca. 520000 USD (digester system costs 290000 USD and energy generation equipment costs 230000 USD). The biogas plant installed at New Horizons Dairy Farm (owning 3750 cows), costs 1.526 million USD. Food and Agriculture Ministry of SUA brings an important funding contribution at biogas plants building, which may reach 50% of total costs.

According to the experience of biogas plant development in the past 15 years, it can be said that biogas technologies development in Romania depends on political decisions for funding renewable energies. Each country has got its own development rate and this shows that it is not possible to develop these energies without political and governmental support (Fischer and Krieg, 2005).

In making a decision to install a biogas plant, one must realize that the system will require continuous monitoring and routine maintenance and repair that should not be underestimated. The majority of digester failures over the past few decades were the result of management problems, not technological problems. All the problems of a biogas plant can be minimized or removed completely with a good design and proper operation and management.

Biogas plant projects have significant capital and operating costs and, therefore, may not be financially viable for any application. The biogas experience of some developed countries having great practice in biogas technology (Denmark, Germany, Austria etc) has demonstrated that biogas technology is not applicable for all farms and all climates. In many situations, it can be a cost-effective and environmentally friendly method for treating manure and liquid waste. Biogas production is best suited for farms that handle large amounts of manure as a liquid, slurry, or semi-solid with little or no bedding added (Widodo and dan Elita, 2005). Since anaerobic digestion is a biochemical process that occurs properly at temperatures around 35-37^{0}C, small farm-scale biogas plants are not economically feasible in the long winter climate countries like Romania (Balasubramaniyam et al., 2008). Low temperatures during the nights and the added capital investment are a significant obstacle for successful implementation of biogas plants in Romania.

In addition, operating a biogas plant involves complying with some very important specific safety

requirements. The digester should be located away from farm buildings. Methane can cause explosions even at concentrations as low as 5 percent to15 percent in air. It is desirable to install a gas detector (to monitor either the level of oxygen or methane in the room or space) and alarm devices in buildings with potential explosion hazards. Apart from being explosive, methane can displace the oxygen in a confined space and may result in injuries or even death due to asphyxiation.

The biogas plants must be designed by experienced digester designers, who are well versed with the common problems associated with these types of systems.

6. Conclusions

The energy from biogas is a renewable energy and reduces greenhouse gas emissions (carbon dioxide, methane and nitrous oxide).

Biogas technology is popular for treating biodegradable waste as valuable fuel and ecological fertilizer can be produced along with destroying disease-causing pathogens and reducing the volume of disposed waste. The production of biogas is sustainable, renewable, carbon neutral and reduces the dependency from imported fossil fuels.

In Romania, biogas has been used in the past to a larger amount. Due to socio-economical and political aspects, after 1990 the biogas production has slowed down significantly. The development of biogas plants was limited by weak domestic financial resources for investment and lack of governmental financial support. Nowadays, there are operational only few biogas plants within wastewater treatment plants.

The development and implementation of biogas technologies could bring many environmental, energetically and economical benefits, solving important problems such as waste disposal and renewable energy supply.

Romania has a significant potential in organic waste, including waste generated in forestry sector, agro-food industry, municipal biodegradable wastes and effluents from wastewater treatment facilities. This fact provides a good opportunity to develop anaerobic digestion technologies in Romania, since the funding for R&D of renewable resources and waste management has increased for the last years.

The energy policy focused on efficient and economical energy supply must be changed with a policy towards clean and environmental energy resources.

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EUROPEAN Ph.D. IN SCIENCE FOR CONSERVATION

EU Project -05-MEST-CT2005-020559, EPISCON

To promote the synergy between the cultural heritage field, natural sciences and engineering, the European Community's Marie Curie programme is funding the EPISCON - European Ph.D. in Science for Conservation. The goal of the project is to form and develop the first generation of "true" conservation scientists in Europe, a goal to be attained by providing education, training, and research opportunities in the field of science for conservation of cultural heritage to young researchers.

EPISCON started in September 2006 and makes an original contribution to national and Community policies, as well as to the already existing knowledge in the field. Recent years, the number of national and European institutions and bodies of various types supporting the development of conservation-restoration projects significantly increased, as well as the number of organisations and bodies that carry out conservation-restoration projects.

16 three-year fellowships have been offered by ten EPISCON partners' host institutions within the European Community - internationally distinguished European academic and conservation centres working in the field of cultural heritage preservation and research:

> University of Bologna, Italy (UNIBO) - coordinator
> School of Conservation (SoC), Denmark
> Eotvos Lorand University (ELTE), Hungary
> Aristotle University of Thessaloniki (AUTH), Greece
> Universidad de Oviedo (UNIOVI), Spain
> "Alexandru Ioan Cuza" University of Iasi (UAIC), Romania
> University of Perugia (UNIPG), Italy
> Instituut Collectie Nederland (ICN), The Netherlands
> Hungarian National Museum (HNM), Hungary
> Istituto Conservazione e Valorizzazione Beni Culturali (ICVBC), Italy

Four other centers are associated to the host institutions within the project:

> Istituto Centrale per il Restauro (ICR), Italy
> Institute of Atmospheric Sciences and Climate (ISAC), National Research Council (CNR), Italy
> "Petru Poni" Institute of Macromolecular Chemistry (IPPMC), Romania
> Opificio delle Pietre Dure (OPD), Italy.

The fellowships include funding of an intensive six month training at the University of Bologna - Ravenna Campus (Italy) in all aspects and levels of the conservation of cultural heritage, followed by a two and a half years research to be performed at one of the host institutions. These activities are finalized with the defence of a thesis to be recognised by the participating countries.

The 16 selected fellows are coming from all over the world, their home countries being Romania, Italy, Czech Republic, Ecuador, Japan, Canada, Denmark, Hungary, Spain, Poland, France and Greece. They graduated in different fields, i.e. chemical engineering/technology, geology, mechanical engineering, environmental management and science, physics, natural sciences, material science or civil engineering.

The training received by the young researchers will not only give them the oportunity of developing new skills in a particular form(s) of analysis, but also provide exposure to a multidisciplinary way of thinking and problem solving. These skills are essential for building a long-term research career in both conservation and scientific community.

The holistic multidisciplinary educational approach the PhD curriculum is based on, and the establishment of a common language among themselves and with the other professionals involved in conservation will allow newly trained conservation scientists to better work and share knowledge within an integrated conservation system.

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STUDIES ON TRANSFER AND BIOACCUMULATION OF HEAVY METALS FROM SOIL INTO LETTUCE

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Abstract

This paper presents the connection between the heavy metals concentration in soil and their bioaccumulation in lettuce. Lettuce is a very good bioaccumulator of heavy metals and nutrients. In general, plants manifest a certain reaction to increasing the toxic metal concentrations in soil which they are cultivated on. The differences depend on plants sensitivity, and time exposure intensity (concentration of heavy metals, cultivation length, etc.), presence or absence of nutrients and other chemical species in soil.
Lead, cadmium, zinc and cooper, in some concentrations are toxic for plants, reducing their development. Through the tests presented in this paper the transfer of heavy metals in plants cultivated on a polluted soil in the presence or absence of N, P, K nutrients, was especially followed.

Keywords: lettuce, heavy metals, bioaccumulation, fertilizer, sowing

1. Introduction

Plants as essential components of natural ecosystems and agrosystems represent the first compartment of the terrestrial food chain. Due to their capacity of toxic metals accumulating, when they grow on soils polluted with such metals, they represent a threat to the living beings which consume them. Also, their development and growth may be affected at high levels of metal concentration implying reduced cultures and economic loss.

All plants show a certain reaction to the increasing of toxic elements concentration in soil, depending upon the sensitivity of plants exposure intensity and chemical species. Some species of plants disappear from such lands, while others, on the contrary, are stimulated by these elements. On lands containing metals – some plant species (metalophytes) have developed tolerance towards metals, and others (hyperaccumulators) are characterized by the capacity to accumulate high quantities of metals in their tissues.

For example, according to some researchers cadmium shows preference, in descending order, for: spinach, carrots, rye and oak.

It has also been noticed that it accumulates mostly in lettuce, spinach, cereal, cabbage, rather than in tomatoes, corn or sweet pea (Cox, 2000).

Heavy metals such as lead, cooper, zinc, in high concentrations, are toxic for plants, preventing their proper development. Explaining the accumulation process of heavy metals in plant has led to wide research. For that purpose, species like *Agrostis* were studied, plants that grow on lands in Scotland which contain high levels of Pb, Zn, Cu and Ni. The tolerance of *Agrostis* species towards heavy metals can be explained by the fact that these plants have the capacity to rule out these metals.

From the studies performed, it was observed that a population of *Agrostis tenuis*, tolerant to copper, absorbs as much copper from nutrient mineral

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solutions as plants which are not tolerant to cooper. It has also been noticed that plants coming from a population grown on a lead rich area were tolerant for lead but not to other heavy metals (Atanasiu, 1984).

Heavy metals, through their action, disturb plant metabolism, affecting respiration, phytosynthesis, stomate opening and plant growing.

2. Phytoavailability for heavy metals in soil

Taking over the heavy metals depends on whether these appear in a shape that can be absorbed by plants. For example, lead can be heavily absorbed by particles from sediments and, thus, it is very difficult to be translocated, while cadmium ions can be directly absorbed. Also, the presence of ions that can bind metals plays a part in the metal absorption by plants.

Plants take heavy metals from soils through different reactions such as: absorption, ionic exchange, redox reactions, precipitation – dissolution, etc. As an extension to these reactions, it can be said that the solubility of trace elements depends on minerals in soil (carbonates, oxide, hydroxide etc.), soil organic matter (humic acids, fulvic acids, polysaccharides and organic acids), soil pH, redox potential, soil temperature and humidity (Tarradellas et al., 1996). From all elements in soil, only the elements which present availability are transferred in plants (Fig. 1). The amount of elements in soil solution is much lower than the amount of elements absorbed by plant. A higher rate of the bioavailable fraction is located in the solid phase. According to their mobility in soil – water system, trace elements in soil can be grouped into four compartments, as shown in Fig. 1. Metals bioavailability is presented in the first three compartments (Oros, 2001).
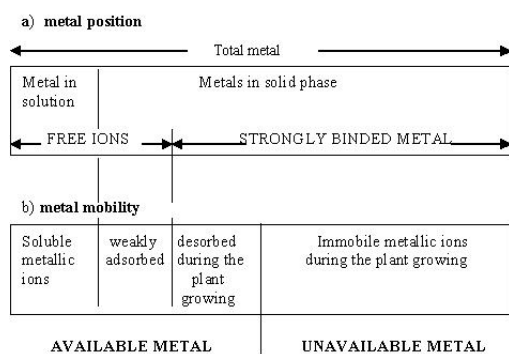
Fig. 1. Model of metal availability in soil (Tarradellas et al., 1996)

The first two compartments represent immediately available ions, ions from soil solution and weakly absorbed ions by solid phase, presenting the same mobility as soluble ions. The third compartment indicates ions bound to solid phase, but capable of passing into solution and becoming available for plants during their growing process. In the fourth compartment unavailable trace elements

throughout the whole plants growing period are presented, being strongly bound to particles.

Metal absorption and accumulation in plant depend on a few soil factors, such as: pH, Eh, clay content, organic matter content, cationic exchange capacity, nutrient balance, other trace elements concentration in soil, physical and mechanical characteristics of soil, etc.

The metals availability for plants is controlled by their requests for micronutrients and their capacity to absorb and eliminate toxic elements. This availability is different, depending on plant species and their adaptation to the environment conditions. Therefore, plants can be divided into three categories: excluderators, indicators and accumulators. Herbs absorb less metal than fast growing plants such as lettuce, spinach, carrot and tobacco. When the growing takes place on the same type of soil, the cadmium accumulation in different species decreases in the following order (Oros, 2001).

Grains < Root <Vegetables < Leaf vegetables

2.1. Metals distribution in plant

Metals distribution in plants is quite heterogenous and is controlled by genetic factors, environment and toxic factors. The metal immobilization in plant roots determines the recuperation of a high proportion of metals in roots (80 – 90 %). Some species of plants can accumulate the highest quantity of absorbed metals in their high parts (tobacco accumulates more than 80 % Cd in its leaves). Linen seeds can also accumulate high concentration of Cd (Tarradellas et al., 1996).

The edible parts of vegetables like radish, cabbage, tomatoes, carrots, green beans etc. grown on sandy soils added with mud do not indicate an important accumulation of metals (Cd, Cr, Pb), while the parts that are not edible amass metals in concentrations which would not be accepted in the edible parts. The metals distribution in plant seems to be controlled by some mechanism and this suggests the existence of some boundaries and/or change in the metal chemical state (Tarradellas et al., 1996). Different plant parts contain different heavy metals quantities, the highest ones being contained in roots and leaves, and the smallest in flower buds and fruit. The analysis of the roots may indicate the degree of heavy metal accumulation in the polluted soil and offers clues on the soil pollution degree, and the analysis of leaves may even suggest the atmosphere pollution degree. If detection of metal accumulation content in plant is desired, the plant must be washed. The time and the way it should be washed depend on certain standards.

2.2. Bioconcentration and bioaccumulation of heavy metals by living organisms

Some living species have the capacity to accumulate in their organism heavy metals in

concentrations much higher than these metal concentrations usually are in the environment.

This process can be defined by using two basic notions: bioconcentration and bioaccumulation (Bermond, 1998).

Bioconcentration is the direct growth of a pollutant concentration while it passes from the environment to an organism. In the case of terrestrial organism, this process takes place by the pollutant passage from soil into the plant through the radicular system or from air into the animal organism by direct inhaling. Bioaccumulation is specific for animal organisms and it manifests about direct pollutant absorption, to which accumulation by nutrition is added. These processes can be expressed by using the concentration factor (*Fc*). The concentration factor expresses the ratio between the pollutant concentration in an organism and its concentration in the biotope (Eq.1) (Bermond, 1998):

$$F_C = \frac{[Me]_{organism}}{[Me]_{biotop}} \qquad (1)$$

In a food network biocenosis inside, the bioaccumulation phenomenon can repeat when passing from a food level to another or from a prey organism to a predator organism. In this case the bioamplification phenomenon appears. This can be expressed by using the transfer factor (Ft) (Bermond, 1998).

If in an ecological pyramid a predator organism has the concentration (X_1) and its prey, on the food level n, has the concentration (X_0), the transfer from the food level $[n + 1]$ is given by the following relation (Eq. 2):

$$F_t = \frac{[n+1]}{[n]} = \frac{X_1}{X_0} \qquad (2)$$

If the predator organism on the level $(n + i)$ has the food level (n), which has the pollutant concentration (X_0), directly absorbs a quantity of pollutant (f_1) but also eliminates in the environment a part of the accumulated pollutant (K_1), the transfer factor from the level 0 to the level 1 will be (Eq. 3):

$$F_{t(0,1)} = \frac{a_1 f_1}{b_1 k_1} \qquad (3)$$

The equilibrium concentration for the predator organism will be expressed by (Eq. 4):

$$X_1 = \frac{a_1 f_1}{b_1 k_1} X_0 \qquad (4)$$

If this predator because in its turn is a prey for a carnivorous on a higher food level (n + 2), the transfer factor will be given by the relation (5):

$$F_{t(1,2)} = \frac{a_2 f_2}{b_2 k_2} \qquad (5)$$

The final equilibrium concentration will be (Eq.6):

$$X_2 = \frac{a_2 f_2}{b_2 k_2} \cdot \frac{a_1 f_1}{b_1 k_1} \cdot X_0 \qquad (6)$$

3. Materials

The used soil samples were taken from the land next to the three ponds of elutriation; two belonging to S.C. Remin S.A. and one to S.C. Aurul S.A. (today known as S.C. Romaltyn S.A.). The sample taking was done with an agrochemical probe for 0 – 20 cm depth.

On the 18th of March 2003, 12.00 o'clock, the following samples of alluvial soil were taken from the land between the elutriation ponds belonging to C.N. Remin S.A. and S.C. Aurul S.A. (today known as SC Romalyn S.A.):
- witness sample of alluvial soil, 0 – 20 cm depth, from land belonging to Lăpuşel village.
- agrochemical sample, from flooded soil, 0 – 20 cm depth, from the area between the three elutriation ponds.

4. Method

The taken samples were conditioned, grained in a hammer mill then screened with a screener having the mesh diameter of 2 mm. The agrochemical analyses were performed in the OSPA Maramureş Laboratory and they consisted in (Borlan et.al., 1981):
- *pH,* determined potentiometrically using a soil - water ratio of 1:2,5.
- *Mobile phosphorus* – for determination the amonium lactate acetate Egner Reihn – Domingo method was used. It is expressed in ppm.
- *SB* (base-exchange) – for determination the Kappen method was used. It is expressed in m.e. to 100 g soil.
- *Ah* (hydrolytical acidity) – determination was carried out by Kappen method. It is expressed in m.e. to 100g soil
- *Humus* – a modified Schollenberger method was used. It is expressed in (%).
- *Total nitrogen*- was determined using Kjeldalh method. It is expressed in (%).
- *Granulometry* – for determination the Kacinski method was used. It is expressed in (%).
- *Heavy metals content* was determinad by mineralization method and atomic absorption using ICP – MS (Inductively Coupled Plasma – Mass Spectroscopy).

5. Results and discussion

The agrochemical analyses were finalised on the 24th of March 2003, and on the 25th of March 2003 the seeding were done. The results are shown in Table 1.

Table 1. Agrochemical characteristics of soil

No.	Soil Type	Sampling depth (cm)	pH	Humus %	Total nitrogen %	P-Al	P$_C$-AL	K-Al
						ppm		
1	Aluvial soil (reference)	0 – 20	7.30	4.39	0.21	74	58.5	175
2	Aluvial soil (agrochemical sample)	0 - 20	6.75	2.96	0.14	6	5.5	265

Some characteristics could be revealed from Table 1, such as:
- soil is slightly alkaline, very rich in humus, well fed with potassium and phosphorus
- soil is slightly acid, rich in humus, very well with potassium, very badly fed with phosphorus

The heavy metal content, determined by mineralization and atomic absorption, is given in Table 2. For this experiment, eight pots of 400 mL soil taken from a land in Lăpușel village, polluted soil taken from the land in between the three ponds, lettuce seeds – *Latuca sativa* species, Mona type were used.

Table 2. Heavy metal content in soil

Metal	Reference sample (ppm)	Agrochemical sample (ppm)
Cu	110	310
Pb	650	4570
Zn	180	1060
Cd	-	-

The seeding was carried out twice, using four samples each time. These are symbolized as follows:
- 1 a - simple reference sample (no fertilizers)
- 1 a'- simple reference sample (no fertilizers)
- 1 b - reference sample with fertilizers
- 1 b'- reference sample with fertilizers
- 2 a - simple agrochemical sample (no fertilizers)
- 2 a'- simple agrochemical sample (no fertilizers)

- 2 b - agrochemical sample with fertilizers
- 2 b'- agrochemical sample with fertilizers

In every soil pot 12 lettuce seeds was put, three in every one of the four places, and then the soil was watered every two days (Fig. 2).

Therefore, as shown in Figs. 2, 3, and Table 3, the witness soil (1 a, 1 a', 1 b, 1 b') both with fertilizers and no fertilizers creates much better condition for lettuce development than the contaminated soil with or without fertilizers (2 a, 2 a', 2 b, 2 b').

This could be due to the higher content of heavy metals from the pots with contaminated soil. The comparison made for the lettuce development on simple or with fertilized soil showed that it was a better development where nutrients on the reference soil with fertilizers had been added, thus reaching the final height of 17 cm compared to 15 cm in the pot where nutrients had not been added (Fig. 4).

In the case of the contaminated soil, the lettuce reached 15 cm on the fertilized soil, compared to 13 cm on the soil with no fertilizer.

During the twelve weeks of lettuce growth, the following were observed:
- On the first week, the plants did not spring.
- On the second week, the lettuce had a faint appearance reaching heights of 0.75 – 1 cm. There were no true leaves.

Fig. 2. Lettuce in the second week from seeding

Table 3. Weekly medium value of lettuce growth

| Sample type	Weekly medium height (cm)											
	Week I	Week II	Week III	Week IV	Week V	Week VI	Week VII	Week VIII	Week IX	Week X	Week XI	Week XII
1a	0	1.00	1.75	3.50	5.50	5.75	6.25	7.75	9.00	9.50	10.00	12.50
1a'	0	0.75	1.75	2.00	3.75	4.50	5.50	7.00	9.00	11.00	13.00	15.00
1b	0	1.00	2.00	3.00	5.00	5.50	7.50	10.00	13.00	14.00	15.00	17.00
1b'	0	1.00	2.00	2.75	4.75	5.50	6.00	7.75	8.50	11.00	12.50	15.00
2a	0	1.00	2.00	3.00	3.75	4.75	5.25	5.75	6.00	6.50	7.00	8.50
2a'	0	0.75	1.75	2.50	2.75	3.50	3.75	4.50	5.00	7.00	8.50	11.50
2b	0	0.50	1.00	2.50	3.50	3.75	4.50	5.00	6.50	8.50	11.00	13.00
2b'	0	0.75	1.75	3.50	4.00	4.50	5.50	6.50	7.00	9.00	10.50	11.50
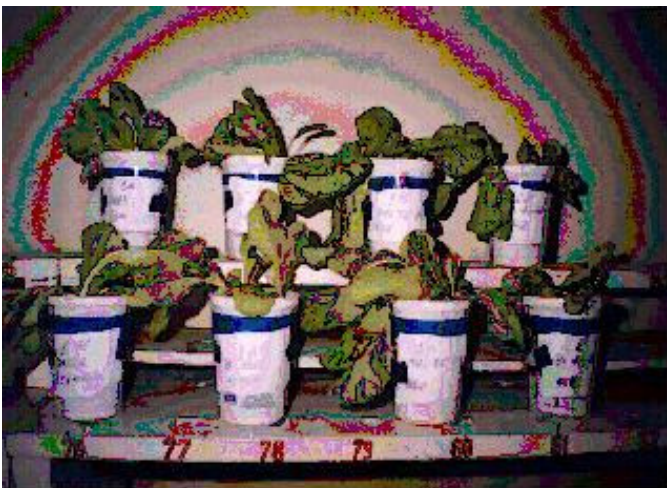
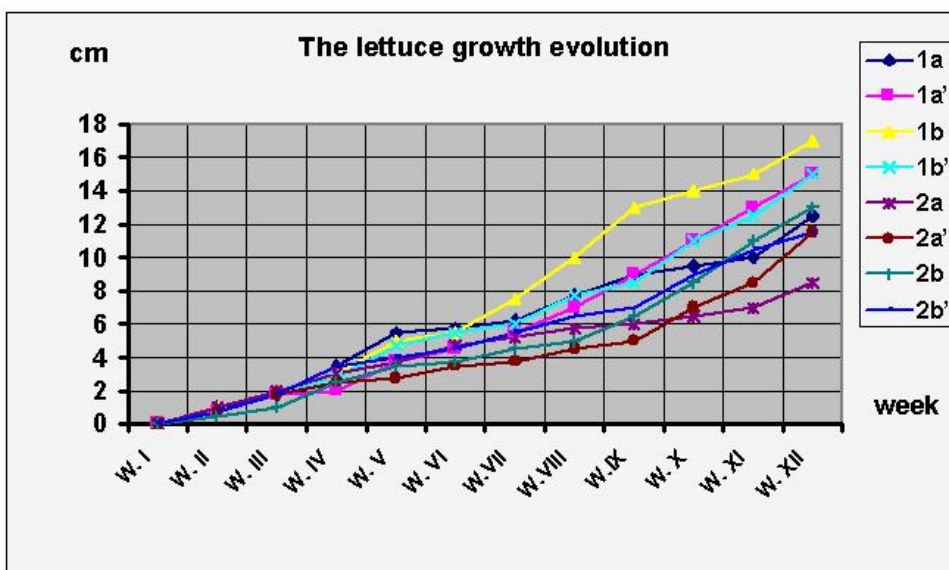**Fig. 3.** Lettuce appearance in the twelveth day from seeding

Fig. 4. Lettuce growth evolution during the twelve weeks

- On the third week, the first true leaves appeared. The soil from pots 1 b, 1 b', 2 b, 2 b' was fed with a binary N and P (27 – 13. 5 – 0) fertilizing solution, according to the Guide to fertilization planning. From this moment, these pots were watered only with nutrient solution
- The faint appearance with pale green leaves was maintained up to the end of the seventh week.
- From the eighth week, a more vigurous development of the lettuce could be noticed, the leaves colour being the specific one.
- Their continuous development was manifested progressively up to the twelveth week, when they were harvested for heavy metal content determination.

After harvest, the lettuce from every type of pot was weighted.

The obtained results are shown in Table 4.

Table 4. Sample type and lettuce mass

No.	Sample type	Lettuce mass (g)
1	Simple reference	16.20
2	Reference with fertilizers	21.69
3	Simple agrochemical sample	11.04
4	Agrochemical sample with fertilizers	14.05

For heavy metal content determination the lettuce was dried at room temperature until it became crumbly and then it was dried again in a stove at 40^0 C for eight hours. After the plant had been ground and weighed it was mineralized with HNO_3. Heavy metal content determination in lettuce was made using spectrophotometry of atomic absorption, and the results are shown in Table 5.

Table 5. Heavy metals concentration in lettuce (mg/Kg in dry plant)

No.	Metal type	Concentration in lettuce (ppm)			
		Witness 1*	Witness 2*	P1*	P2*
1	Cu	530.93	14	7.23	4338.76
2	Pb	17.92	0	50.1	107.81
3	Zn	416	19.84	422.4	8.36
4	Cd	5.77	1.26	24.26	41.68

* reference 1 – reference without fertilizers;* reference 2 – refeerence with fertilizers;* P1 – polluted soil sample without fertilizers;* P2 –polluted soil sample with fertilizers.

The transfer factor of heavy metals from soil to plant calculated using relation (5) is shown in Table 6**.** According to Hygiene Norms no. 975/1998 from Official Monitor, Part I, no. 59, bis, the maximum content admitted for heavy metals in green lettuce is 0.2 mg/kg dried substance for cadmium and 0.5 mg/kg dried substance for lead. For zinc and cooper there are no established values. The exceeding of the admitted values for heavy metals in lettuce are systematized in Table 7.

Table 6. The heavy metal transfer factor from soil into plant

No.	Metal	Witness 1	Witness 2	P1	P2
		Transfer factor			
1	Cu	4.83	0.13	0.12	13.99
2	Pb	0.03	0.00	0.01	0.02
3	Zn	2.31	0.11	0.4	0.007

Table 7. Exceeding of the maximum admitted values for heavy metals in lettuce

No.	Metal	Reference 1	Reference 2	P1	P2
1	Cu	-	-	-	-
2	Pb	35.84	0.00	100.2	215.6
3	Zn	-	-	-	-
4	Cd	28.85	6.3	121.3	208.4

6. Conclusions

According to the achieved results the following conclusions could be issued:

- Cooper from reference soil was at the limit of the alert threshold for sensitive usage, and the one from the polluted samples exceeded three times this threshold.
- Lead from reference soil exceeded 6.5 times the intervention threshold for sensitive usage and 1.3 times for less sensitive usage. Regarding the soil affected by the waters from the pond, this element exceeded 45.7 times the intervention threshold for sensitive usage and 4.57 times for less sensitive usage.
- Zinc from reference soil was under the alert threshold for sensitive usage and the one from polluted soil exceeded 1.77 times for sensitive usage.
- Cadmium from reference soil was under the value of the alert threshold for sensitive usage and its content from the polluted soil exceeded 0.8 times the intervention threshold for sensitive usage.
- During the 12 weeks of lettuce growth, the following appearances were noticed:
- On the first week, the plant did not spring.
- On the second week, the lettuce had a faint appearance, reaching heights of 0.75 – 1 cm. Real leaves could not be noticed**.**
- On the third week, the first real leaves appeared. The soil from pots 1 b, 1 b', 2 b, 2 b' was nourished with binary fertilizer with N and P (27 – 13.5 – 0), according to the Guide to fertilization planning. From that moment, the plants were watered only with nutrient solution.

The weak look of the lettuce, with pale green leaves was maintained up to the end of the seventh week. From the eighth week, a more vigorous development of the lettuce was noticed, the colour of the leaves being normal. The development continued to manifest progressively up to the twelfth week, when the plants were harvested for heavy metal content determination. Also, the mass of the lettuce from the pots containing reference soil was higher than the ones of the lettuce from the pots with polluted soil. This could be due to the higher content of heavy metals from the pots with contaminated soil which, because of the bioconcentration process that affected the normal development of the lettuce.

From the data concerning the accumulation rates of heavy metals from soil to lettuce, the following results were noticed:

In the case of lettuce from the reference pots, the lettuce from the pot with no fertilizers showed a higher capacity to accumulate metals, especially cooper, cadmium and zinc. Except for zinc, the lettuce from the pots with polluted and fertilized soil presented a higher accumulation of heavy metals than the lettuce cultivated in pots with polluted but unfertilized soil.

Zinc accumulation was higher in the lettuce from the pots with unfertilized soil than in the lettuce with fertilized soil. Compared to the very high content of lead in the polluted soil, the transfer of this metal in the lettuce is quite small. This could be due to the absorption of a high quantity of lead by the clay – humic complex.

The high accumulation content of cadmium confirms the high capacity of its translocation in plant.

Opposing the high concentration of heavy metal in the lettuce to the maximum admitted values, exceeding of over 200 times result, both in lead and cadmium, in the case of the sample from the pot with polluted soil and fertilizer.

Also, exceeding of the maximum admitted concentration of over 100 times, for the same elements, was observed in the case of the lettuce from the pot with polluted soil and no fertilizers. Also, the lettuce from reference pots presented exceeding of the maximum admitted concentrations of over 28 times for lead and cadmium, in the case of the reference sample with no fertilizers and of over 6 times for cadmium in the case of the reference sample with fertilizers.

These high exceeding of the maximum admitted values for heavy metals in lettuce impose the prohibition from eating vegetable products obtained on these lands and also suggest the increased risk of contamination implied by consuming such products.

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SOFT COMPUTING HYBRID CONFIGURATIONS APPLIED IN CHEMISTRY

IDEI PROGRAMME PNCDI II, Research Grant ID_592, Contract no. 59/2007

This project targets the use of Artificial Intelligence Techniques (neural networks, genetic algorithms, classifiers, fuzzy systems), combined in hybrid heuristic configurations, for modeling and optimization of chemical processes. The synthesis of new materials, based on ferrocene, with liquid crystal properties is considered as a case study. The problems attempted to solve are the subject of complex interdisciplinary research, requiring advanced knowledge in both chemistry and computer science.

The project objectives are organized on two parallel plans, which correspond to the domains of computer science and chemistry. Applying the methods of Artificial Intelligence (AI) to modeling and optimization of chemical systems represents the bridge between the two fields and defines the inter-disciplinary character of our proposal.

Mainly, the scientific goals of the project are:

1) Advanced research oriented toward the elaboration and improvement of techniques based on AI instruments, with a special emphasis on hybrid soft computing techniques that provide computational efficiency and large-spectrum applicability.

2) Synthesis and characterization of ferrocene based new materials with liquid crystal properties.

3) Modeling and optimization of the parameters associated to ferrocene-based materials, making use of soft computing techniques.

Meanwhile, specific goals of the research program *Idei* are as follows:

1) Obtaining scientific achievements at the international level as the result of complex research based on real novelties ("ideas"). Solving the scientific objectives will lead to acquiring advanced knowledge, contributing to generating new scientific and technical knowledge, development and strengthening of those research directions of scientific and technological top fields, in particular soft computing. The need for "excellency" as the quality level of the Romanian research, in agreement with the international standards, will create the true conditions for the participation in the European programs.

2) Development of the human resource, as a premise for constituting and consolidating of a working team suitable for interdisciplinary research, with both experienced and young researchers and engineers working effectively in AI and chemical synthesis of materials. Promoting young people, preparing them for research, stimulating them adequately to remain to work in research, and supporting them for the highest standards in the field, including Ph.D. degrees, signify important aspects involved within the project.

Starting from the continuous evolution of the life quality, which implies the need for new and higher characteristics of the materials, devices and real systems, the scientific research has to cope with current and future difficult problems. According to the estimated results of the project, the scientific impact of the project will be mainly evaluated by the number and quality of the published papers, related to the scientific level of the chosen journals (their ISI ranking), the quality of the edited monographs, and the scientific level of the Ph.D. theses accomplished within this project.

The social impact is associated to the fact that the project integrates young post-docs, Ph.D. and master students that can develop their talents in research and software product development. Organizing exploratory workshops and research documentation stages in Romania and abroad will represent useful opportunities for the young researchers and for the orientation of their future activity.

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BIOMASS POWER FOR ENERGY AND SUSTAINABLE DEVELOPMENT

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Abstract

The paper discusses some aspects concerning the utilization of biomass as a bioenergy resource worldwide and in Romania, since biomass is considered a sustainable, potentially environmentally sound and a replenishable resource.

The biomass categories for bioenergy are analyzed, considering the factors which influence its availability. Biomass energy potential and current use in different regions as well as in Europe is accounted. Also, biomass power as an important alternative for providing energy in rural sector is described and some technologies for biomass conversion are evaluated briefly. Biomass and renewable energy from biomass are considered end products, which involve new and advanced technologies to improve power production efficiency.

It is evidenced that biomass provides a clean, renewable energy source, which could improve economic, energetic and environmental sectors. Also, many factors converge in making bioenergy a key issue toward the achievement of the Millenium Development Goals.

Contributions of bioenergy to sustainable development of humanity are also discussed, based on some sustainability considerations and indicators.

The investments in biomass and bioenergy in Romania are also considered as important, since the production of renewable energy for Romania is an important topic.

The future projection on the use of renewable energy resources points toward actions for economic development where renewable energy from biomass will play more and more a growing role, without affecting the community food security.

Keywords: biofuel, bioelectricity, environmental impact, rural energy, renewable resources, sustainability indicators

1. Introduction

Organic matter, particularly cellulosic or ligno-cellulosic matter is available on a renewable or recurring basis, including dedicated energy crops and trees, wood and wood residues, plants and associated residues, agricultural food and feed crop residues, plant fiber, aquatic plants, animal wastes, specific industrial waste, the paper component of municipal solid waste, other waste materials, all of them being well-known as *biomass*. In the same context, the term *biobased product* is used to designate any commercial or industrial product (either from food or feed) that utilizes biological products or renewable domestic agricultural (plant, animal, or marine) or forestry materials (ABB, 2003; Industry Report, 2008; OCAPP, 2007). Both in the application in chemistry and in transport and the generation of energy, biomass offers great opportunities for the conservation of energy management (IPM, 2007).

At some stage in human history, biomass in all its forms has been the most important source of various basic needs: food, feed, fuel, feedstock, fibers, fertilizers (Rosillo-Calle, 2007). Nowadays, biomass continues to be a subject of growing significance worldwide, in particular due to its suitability as source of bioenergy, as a result of global increase in the demand for energy, the constant rise in the price of fossil fuels and the need to reduce greenhouse gas emissions (Perlack et al., 2005; Thornley and Cooper, 2008; Thornley et al., 2008; Yuan et al., 2008).

Throughout the past decades, bioenergy and other renewable energies have been the subject of several international declarations and commitments on sustainable development (FAO, 2005; http://www.fao.org/docrep/meeting/009/j4313e.htm#P42_5511):
- United Nations Conference on New and Renewable Sources of Energy (NRSE)**,** in 1981
- United Nations Conference on Environment and Development: in Agenda 21, emphasis was given to the role of bioenergy
- UN Millennium Declaration

- World Summit on Sustainable Development (WSSD), where energy was high on the agenda
- International Conference for Renewable Energies held in Bonn in June 2004
- Other important initiatives promoting bioenergy include the Global Environmental Facility (GEF), the G-8 Task Force on Renewable Energy; the UNDP Initiative on Energy for Sustainable Development

Since the Kyoto Conference (1997), there has been an increasing interest about renewable energy sources and possible alternatives to fossil fuels that could contribute to a significantly reduction in greenhouse gas emission and enhance the overall sustainability of modern society (http://www.avanzi.unipi.it/ricerca/quadro_gen_ric/biomass_bioenergy/Biomass&bioenergy_ENG.htm). Energy crops may contribute to the goals of the Kyoto Protocol by increasing C sequestration, thus playing a strategic role for development of sustainable energy production systems.

It's obvious that the biomass energy is nothing else than solar energy - stored thanks to photosynthesis – in the vegetable tissues. Bioenergy resources take many forms, which can be broadly classified into three categories (Rosillo-Calle et al., 2007):

(1) residues and wastes,
(2) purpose-grown energy crops
(3) natural vegetation.

Traditionally, conventional biomass is considered to come from three distinct sources: wood, waste, and alcohol fuels as summarized in the Fig. 1

(http://www.greenjobs.com/Public/info/industry_background.aspx?id=13).

From an ethical point of view, only biomass that is not competing with the food chain should be used for the production of fuels, chemicals, power or heat.

Industrialized countries have over 1,500 million hectares of crop, forest and woodland, of which some 460 million hectares are crop land. Achieving the 15 % target could require an average of 1.25 million hectares of crop land per year to be converted to energy plantations. This represents just over 2 % of the total land area in industrialized countries (Bauen et al., 2004).

In USA, the forestry category at 49% is by far the largest contributor to the state biomass, followed by municipal waste with 24%, field with 14%, and animal waste at 11% as the next most important, respectively (Fig. 2)

Under this concern, biomass is a sustainable, potentially environmentally sound and a replenishable resource, since it can be replaced fairly quickly without permanently depleting the Earth's natural resources. By comparison, fossil fuels such as natural gas and coal require millions of years of natural processes to be produced. Alternatively, biomass can easily be grown or collected, utilized and replaced. However, extracting energy from biomass is an ancient practice, dating back to when people first burnt wood to provide heat and light. Growing biomass is a rural, labor-intensive activity, and can, therefore, create jobs in rural areas and help stem rural-to-urban migration (IBEP, 2006).
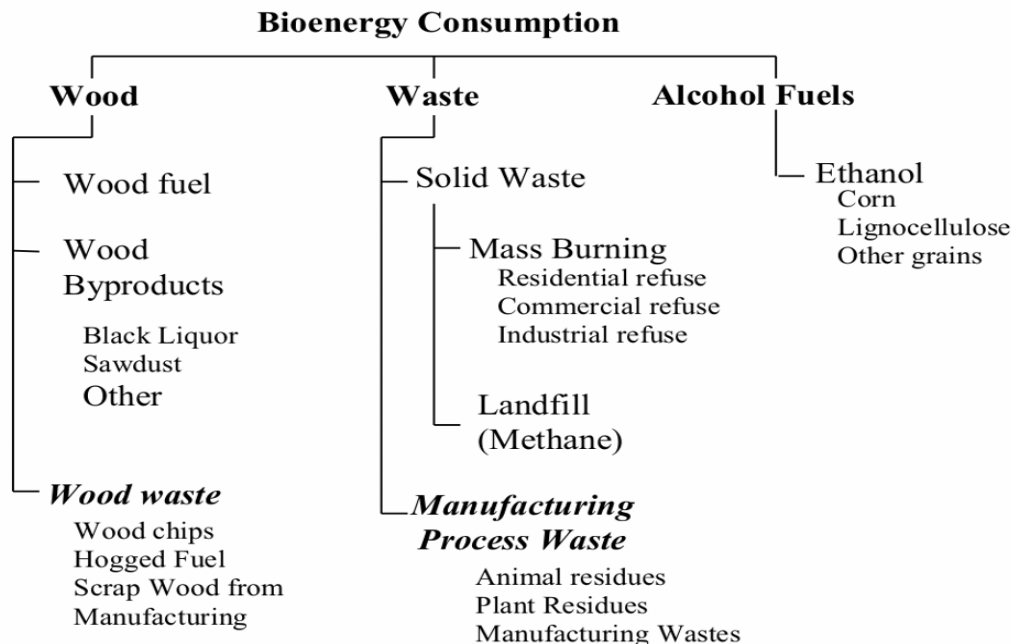
Fig. 1. Biomass sources for bioenergy (adapted upon Rosillo-Calle et al., 2007)
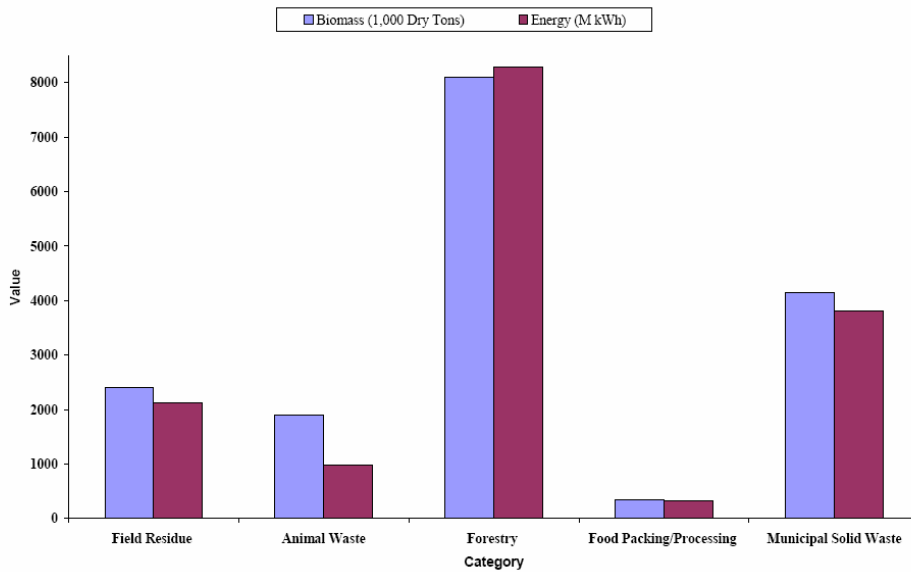
Fig. 2. Biomass categories for bioenergy

Considering the factors which influence the availability of biomass for energy purposes, it can be noted that the worldwide biomass system is complex and so availability is difficult to quantify, particularly in light of the potential competition for biomass for food, fodder, materials and energy (Fig. 3).

The availability of biomass for energy will also be influenced by population growth, diet, water availability, agricultural density, and nature (Bringezu et al., 2007; Long et al., 2006; Olesen and Bindi, 2002; Perlack et al., 2005).

2. The share of biomass as renewable energy resource

Energy is one of the more basic human needs and the trends in energy utilization are major indicators of the economic growth of a particular country/society. In the absence of conventional energy sources, the unsustainable use of biomass fuels is often the only resort. Tables 1 and 2 describe the biomass energy potential in different regions of Earth and in Europe, respectively (AFB-NET, 2000; Parikka, 2006).
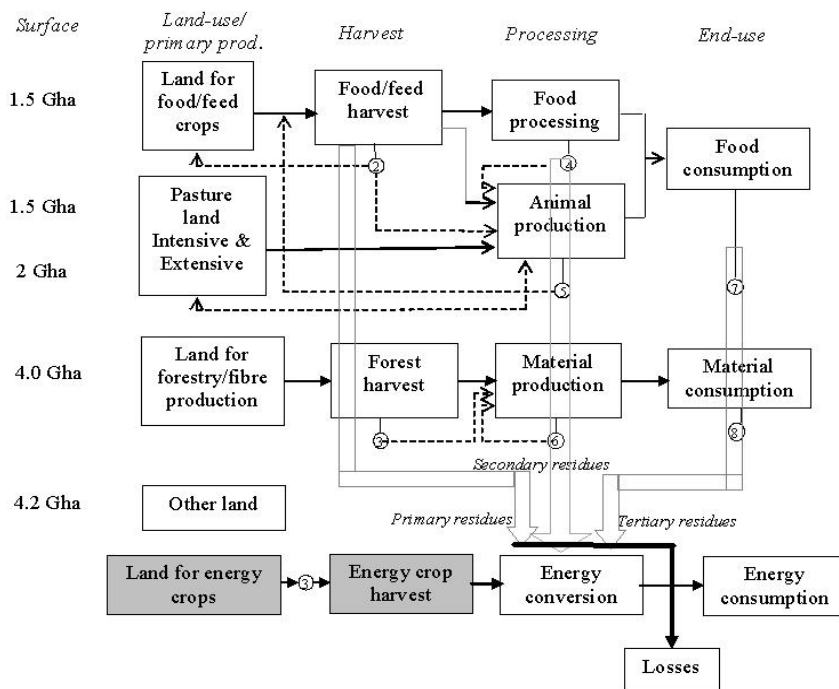
Fig. 3. Pathway of biomass from land to processing and end-uses for materials, food and energy (Bringezu et al., 2007)

Table 1. Biomass energy potential and current use in different regions, EJ/a (EJ=10^{18})

Biomass potential	North America	Latin America	Asia	Africa	Europe	Middle East	Russian Federation	World
Woody biomass	12.8	5.9	7.7	5.4	4.0	0.4	5.4	41.6
Energy crops	4.1	12.1	1.1	13.9	2.6	0.0	3.6	37.4
Straw	2.2	1.7	9.9	0.9	1.6	0.2	0.7	17.2
[a]*Other*	0.8	1.8	2.9	1.2	0.7	0.1	0.3	7.6
=Potential (EJ/year)	19.9	21.5	21.4	21.4	8.9	0.7	10.0	103.8
Use (EJ/year)	3.1	2.6	23.2	8.3	2.6[b]	0.0	0.5	39.7
Use potential (%)	16	12	108	39	29[b]	7	5	38

Table 2. Biomass energy potentials in Europe (PJ per year)

|	*Forest residues*	*Solid ind. by-products*	*Ind. black liquors*	*Firewood*	*Wood wastes*	*Densified wood fuels*	*Other biomass fuels*	*Peat*	*Total*
Austria	150.0	50.0	0.0	40.0	18.0	3.0	9.0	0.0	270.0
Belgium	7.0	13.0	8.0	0.0	3.0	0.0	0.0	0.0	31.0
Denmark	11.0	5.0	0.0	3.0	0.0	4.0	46.0	0.0	69.0
Finland	96.0	47.0	135.0	49.0	0.0	1.0	11.0	165.0	504.0
France	38.0	42.0	0.0	258.0	111.0	0.3	412.0	0.0	861.3
Germany	142.0	40.0	0.0	0.0	81.0	0.0	511.0	0.0	774.0
Greece	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ireland	3.0	7.0	0.0	3.0	1.0	0.0	0.0	40.0	54.0
Italy	0.0	36.0	0.0	83.0	24.0	0.0	0.0	0.0	143.0
Netherlands	4.0	30	0.0	0.0	45.0	1.0	24.0	0.0	77.0
Portugal	68.0	27.0	22.0	0.0	0.0	0.0	0.0	0.0	117.0
Spain	59.0	87.0	23.0	12.0	52.0	0.0	386.0	0.0	619.0
[1]Sweden	238.0	46.4	125.0	27.0	27.0	18.0	22.0	13.0	516.4
UK	16.0	12.0	0.0	27.0	175.0	0.0	70.0	0.0	300.0
Estonia	30.0	0.0	0.0	0.0	0.0	0.0	19.2	30.0	79.2
Latvia	8.0	12.0	0.0	32.0	0.0	1.0	0.0	15.0	68.0
Poland	101.0	68.0	16.0	26.0	40.0	0.0	205.0	122.0	578.0
Romania	0.0	23.0	3.0	58.0	0.4	0.0	0.1	0.0	84.5
Slovakia	6.0	0.1	5.0	3.0	3.0	0.1	13.0	0.0	30.2
Slovenia	2.0	7.0	0.0	8.0	0.1	0.0	0.0	0.0	17.1
Total	979.0	525.5	337.0	629.0	580.5	28.4	1728.3	385.0	5192.7

Leible and Kälber (2005) consider that the scientific dedication to bioenergy experienced three stages:

- the first stage of discussion started with the 1973 oil crisis and the publication of the Club of Rome's report on *The limits of growth*
- the second stage at the beginning of the 1980s was a discussion on reducing agricultural overproduction and creating income in agriculture by growing energy crops.
- the third stage started at the end of the 1980s, which continues today, triggered by increasing efforts for the mitigation of climate change and not only.

Using biomass to generate energy has positive environmental implications and creates a great potential to contribute considerably more to the renewable energy sector, particularly when converted to modern energy carriers such as electricity and liquid and gaseous fuels (IBEP, 2006; http://www.unido.org/index.php?id=4781).

Biomass is available in a variety of forms and is generally classified according to its source (animal or plant) or according to its phase (solid, liquid or gaseous) (Bauen et al., 2004; IBEP, 2006).

Biomass can be burned directly or converted to intermediate solid, liquid or gaseous fuels to generate heat and electricity. All organic materials can potentially be converted into useful forms of energy but the advantage of modern biomass-to-electricity systems is that these conversion systems can cope with a range of lignocellulose-rich materials. This is in contrast to liquid biofuel production chains that are primarily dependent on sugar, starch or oil-rich crops, typically annuals. The options for biomass conversion to energy re described below.

There are three ways of using the biomass resources, which represent the bioenergy sector (EREC, 2007; IBEP, 2006):

- biomass for heating purposes (*bio-heating*),
- biomass for electricity production (*bio-electricity*),
- biomass for transport fuels (*transportation biofuels*).

All these processes enable to take profit of the CO_2 mitigation potential of biomass. Since biomass is the result of storing sun light as chemical energy in plants through photosynthesis, when sunlight transforms CO_2 from the atmosphere and water into complex plant polymers over short periods of time, the use of this resource as a material or durable product keeps the CO_2 stored. The CO_2 released is equivalent to the amount of CO_2 absorbed by the biomass (photosynthesis) in the growing phase (Wiedinmyer and Neff, 2007).

Practically, the equivalent of 10 to 30% of the energy content of the raw biomass is used in cropping, transport, conversion and upgrading. This amount of energy can partially come from the biomass itself, which makes the overall CO_2-balance nearly neutral (Yamasaki, 2003). Therefore, biomass can substantially contribute to reach the targets of the Kyoto protocol and to reduce long-term greenhouse gas emissions (IBEP, 2006; Kashianet al., 2006; Wiedinmyer and Neff, 2007).

In European Union, renewable energies come mainly from biomass and waste, representing almost 72 million tons of primary production in 2004 (UNEP, 2007). Primary production of renewable energy: primary production of biomass, hydropower, geothermal energy, wind and solar energy are included in renewable energies (Fig. 4) (EUROSTAT, 2007). In Germany, bioenergy produced an overall turnover of €3.5 billion in 2004, without consideration of the fuel-provision businesses. For comparison, the largest German energy company E.ON AG achieved a transaction volume of €49.1 billion in the same year (EON, 2005; Plieninger et al., 2006); €1.6 billion was invested in the construction of bioenergy plants, while €1.9 billion turnover came from operation and maintenance (BMU, 2005; Plieninger et al., 2006).
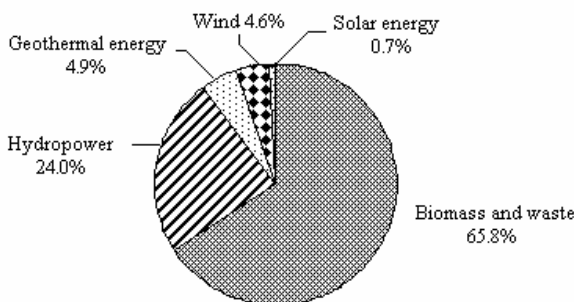

Fig. 4. Primary production of renewable energy in European Union (2004, % of total, based on 1000 tonnes of oil equivalent) (Eurostat, 2007)

Biomass is the biggest contributor (65%) to renewable energy sources, which represented 6% from energy consumption in 2002 (EIA, 2003; EUROSTAT, 2007; Parikka, 2006) (Fig. 5). Energy from biomass already contributes to about 4% of the total EU energy supply, for the most part in heat, and

to a minor extent, in combined heat and power (CHP) applications (Parikka, 2006) (Fig. 5). Biomass is expected to cover as much as 8% of the total EU energy supply in 2010 (Parikka, 2006).
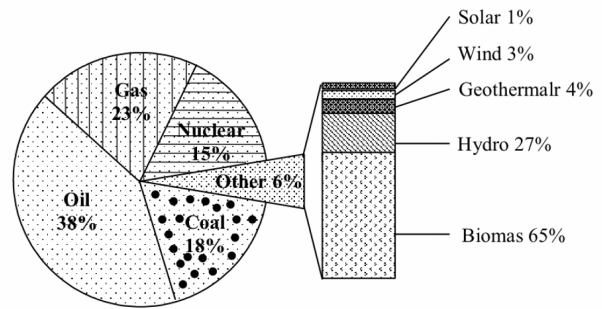
Fig. 5. Structure of energy consumption in European Union state members in 2002 (EIA, 2003; Eurostat, 2007)

Also, the share of electricity generated in EU from renewable sources relative to gross national electricity consumption was situated at almost 14% in 2004, but several of the Member States showed much higher ratios (Austria: 59 %, Sweden: 46 %) (EUROSTAT, 2007). However, the weight of biomass and waste in the primary production of production of renewable energy is not too high, comparative with that of wind, for example (Fig. 6) (EUROSTAT, 2007).

Some 40 to 50 exajoules (EJ = 10^{18} joules) per year of biomass is used for energy today out of some 400 EJ per year of total global energy use (Kartha and Larson, 2000). In order to compare various scales of using biomass as a renewable resource, some data are given in Table 3 (http://lib.kier.re.kr/common/tech/tech017/bio05.pdf).

As is suggested by the data from Table 3, biomass power became very important. It is appraised that biomass is the second-largest renewable source of electricity after hydropower, providing the baseload power to utilities. Various energy scenarios simulate high share of biomass energy in the future energy mixture.

Several scenarios of energy evolution worldwide indicate that biomass has the potential to contribute 25%-50% of the present global energy, up to 2050 (Hall et al., 2000; Hoogwijk et al., 2003). Shell International Petroleum Co. scenario calculations (1994-1996) indicate certain conditions in which new biomass sources could contribute 45%-50%.

Hoogwijk et al., (2003) studied the potential availability of primary biomass for energy and found that it is influenced by:

1) the demand for food as a function of population and diet consumed;

2) the food production system that can be adopted worldwide, taken into account the water and nutrient availability;

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Fig. 6. The weight of different renewable energy sources in the total production of renewable energy in EU countries (1994 is the basis of reference, based on tones of oil equivalent) (Eurostat, 2007)
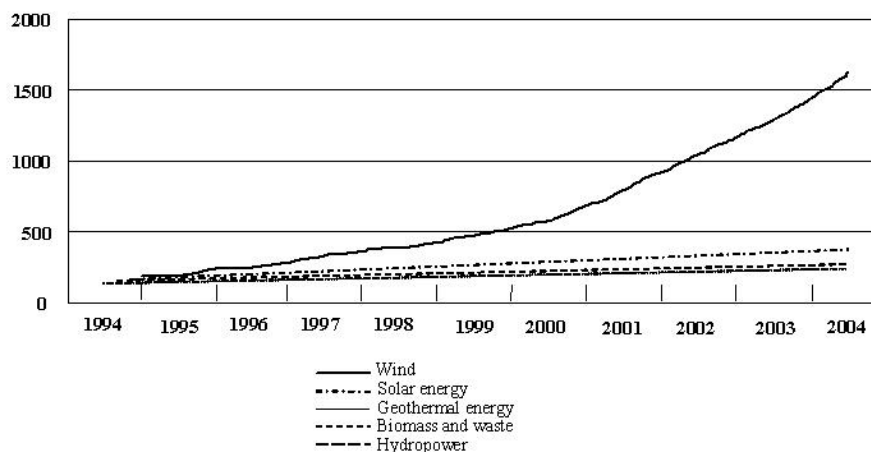
3) productivity of forest and energy crops;
4) other competing options for land-use like for nature development.

Biomass utilization in developing countries contrasts severely with biomass use in developed countries, where fuelwood and charcoal remain the dominant energy source for most households (IBEP, 2006; Kammen et al., 2003). Wood energy is also becoming an increasingly important industrial energy option in the industrialized countries of Western Europe, Asia and the Pacific and North America, as it is based on locally available, renewable and environmentally friendly raw material (IBEP, 2006).

Table 3. Energy equivalent of various energy resources worldwide

Source	Energy equivalent (exajoule, EJ) ($1EJ = 10^{18}$ joules)
All cereals worldwide	31.3
All merchantable boles	14.3
Fuel wood and charcoal used primarily in developing countries	15.3
Usable portion of the current biomass	60.9

In a report of UNEP it is shown that, on average, biomass accounts for 3 or 4 percent of total energy use in the poor areas, although in countries with policies that support biomass use (e.g., Sweden, Finland, and Austria), the biomass contribution reaches 15 to 20 percent (Kartha and Larson, 2000). Most biomass in industrialized countries is converted into electricity and process heat in cogeneration systems (combined heat and power production) at industrial sites or at municipal district heating facilities (http://socrates.berkeley.edu/~kammen/er120/ER120_L3-BiomassEnergy_for_web.pdf).

3. Conversion of biomass into energy

Biomass energy has the potential to be *modernized* worldwide, i.e., produced and converted efficiently and cost-competitively into more convenient forms such as gases, liquids, or electricity (IBEP, 2006; Larson and Katha, 2000). Modern biomass now represents only 3% of primary energy consumption in industrialized countries, and this value has remained steady over recent years. However, much of the rural population in developing countries, which represents about 50% of the world's population are reliant on traditional biomass, mainly in the form of wood for fuel.

Traditional biomass accounts for 35% of primary energy consumption in developing countries, raising the world total to 14% of primary energy consumption (http://www.rise.org.au/info/Res/biomass/index.html

Biomass power is an important alternative for providing energy in the rural sector. The inherent advantages in utilization of biomass are that employment opportunities are created even for cultivation, collection, transportation and storage of biomass.

In evaluating biomass energy chains, it is clear that simple cost-benefit analysis does not capture a range of 'external' costs and benefits that arise from the supply of energy services. Fig. 7 provides a schematic representation of biomass fuel chains (Bauen et al., 2004).

The technologies for biomass conversion mainly consist in: direct combustion processes, thermochemical processes, biochemical processes and agrochemical processes (Demirbas, 2001; IBEP, 2006).

EPA (2007) classifies technologies for biomass conversion into inert gases and organic oils, gases, and fuels that can be further used to yield desired energy products as follows:
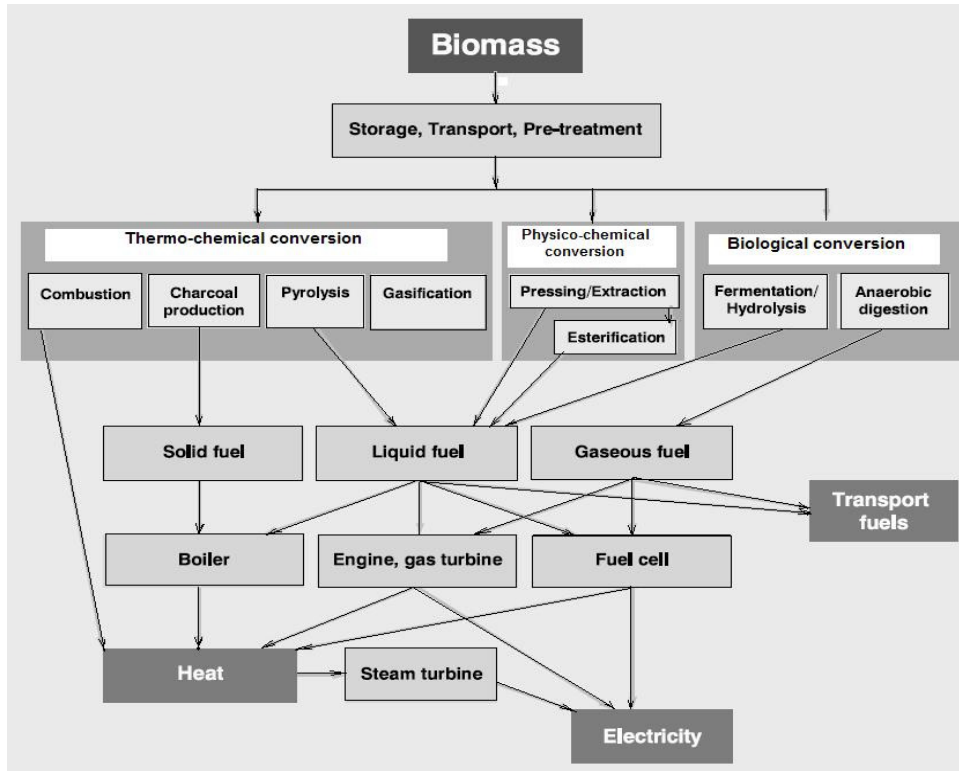
Fig. 7. The chains of biomass fuel (Bauen et al., 2004).

- **thermochemical technologies:** biomass feedstocks is converted using high temperatures to energy, typically in the form of electricity and heat. However, the technologies have the potential to produce electricity, heat, bioproducts, and fuels;
- **biochemical technologies:** biological agents convert biomass to energy (liquid and gaseous fuels).
- **chemical technologies:** chemical agents are used to convert biomass feedstocks to energy, typically in the form of liquid fuels.

These three biomass conversion technologies may also produce byproducts that can be valuable biobased products (EPA, 2007). Table 4 lists a variety of technologies, which can convert

solid biomass into clean, convenient energy carriers (Demirbas, 2001; Kaltschmitt and Weber M., 2006; http://www.esmeet.org/journal3.html).

Most of these technologies are already in commercial use, although some more than others. Each technology description - gasification, anaerobic digestion, ethanol, steam turbine, and gas turbine - includes a general discussion of key technical issues that must be addressed in any project involving these technologies. It also includes more detailed technical discussion of basic operating principles, feedstock and other material input requirements, operating and maintenance issues, capital and operating costs, environmental issues, and other factors.

Table 4. Some actual technologies for conversion of biomass in energy (Demirbas, 2001)

Technology	Scale	Energy services provided
Biogas	Small	- Electricity (local pumping, mining, lighting, communication, refrigeration, etc. and possible distribution via utility grid) - Cooking - Heating
Producer gas	Small to medium	- Electricity (local pumping, mining, lighting, communication, refrigeration, etc. and possible distribution via utility grid) - Cooking - Heating
Ethanol	Medium to large	- Vehicle transportation - Cooking
Steam turbine	Medium to large	- Electricity (for industrial processing and grid distribution) - Heating process heat
Gas turbine	Medium to large	- Electricity (for industrial processing and grid distribution) - Heating process heat

The research and development of the new technology of biomass energy, such as the research of highly efficient and low cost conversion and application of biomass energy, the making of liquefied oils at normal pressure by fast liquefaction, the research of the technology of catalytic chemical transformation and equipment for the transformation of biomass energy as well as fluidized gasification techniques are the focuses of research.

4. Biofuels from biomass

Biomass fuels in their unprocessed form comprise wood, straw, animal dung, vegetable matter, agricultural waste, while processed biomass includes methane, charcoal, sawdust and alcohol produced from fermentation processes. In developing countries they can account for 35%, on average, of primary energy needs, while in some other areas, this rises to as much as 90% with marked effect on the environment (http://www.scienceinafrica.co.za/2006/june/biomass. htm; IBEP, 2006).

Using biomass to generate heat or to drive steam engines is not new. But old-fashioned methods of burning wood, field residues, or waste were not environmentally sound because they emitted polluting smoke and volatile organic compounds into the air (Bauen et al., 2004; DOE, 2000). Today, scientists and engineers use improved processes to develop several new methods that cleanly and efficiently convert biomass to electricity. One new method uses biomass to replace a portion of the coal used to fuel a power plant through cofiring.

The cost of biomass fuel supply depends on the cost of producing or recovering the 'feedstock' – raw materials – and those incurred during its transport and pre-processing prior to use in a power plant.

4.1. Biogas

Biogas can provide a clean, easily controlled source of renewable energy from organic waste materials replacing firewood or fossil fuels.

Biogas primary energy production grew from virtually zero in 1992 to surpass renewable municipal wastes in 2002. Electricity production from biogas grew from an estimated 5,000 GWh in 1990 to 13,617 GWh in 2001 (IEA, 2007). While in the early 1990's, nearly the entire amount of biogas electricity was produced in the United States, the largest proportion of this production has moved to OECD Europe, which contributes 58.1% of biogas electricity today. Therefore, most production takes place in the member countries of the European Union. The largest producer in the European Union is the United Kingdom, which provided 2,870 GWh of biogas electricity in 2001. While the United States, with 4,860 GWh, remains the largest individual producer, its growth of 5.4% per annum since 1992 has been much slower than that of many European Union countries. Germany has an average annual growth rate of 22.7% (reaching 1986 GWh in 2001), Italy of 55.3% (684 GWh) and France of 19.8% (601 GWh) since 1992. Most of the growth in the biogas segment has taken place in the late 1990s and early 2000s, and continued strong growth is expected for the near future.

4.2. Liquid biofuels

Liquid biofuels have gained importance in the last decades in Latin America, and more recently in Europe and other countries of the Organisation for Economic Co-operation and Development (OECD), particularly in the transport sector (IBEP, 2006).

In the late 1990s and early 2000s, liquid biofuels grew in European Union from 7TJ in 1990 to almost 7,400TJ in 2002 (http://www.greenjobs.com/Public/info/industry_back ground.aspx?id=13). Today, biomass is the only available renewable energy source that can produce competitive fuels for transport in larger quantities (Parikka, 2006). The biomass resources considered as well as their classification based on fuel quality and conversion technology are presented in Table 5 (Nikolaou et al., 2003).

Liquid biofuels cover biogasoline and biodiesels:

Biogasoline: this category includes bioethanol (ethanol produced from biomass and/or the biodegradable fraction of waste), biomethanol (methanol produced from biomass and/or the biodegradable fraction of waste), bioETBE (ethyltertio-butyl-ether produced on the basis of bioethanol: the percentage by volume of bioETBE that is calculated as biofuel is 47%) and bioMTBE (methyl-tertio-butyl-ether produced on the basis of biomethanol: the percentage by volume of bioMTBE that is calculated as biofuel is 36 %).

Liquid biofuels cover biogasoline and biodiesels:

Biogasoline: this category includes bioethanol (ethanol produced from biomass and/or the biodegradable fraction of waste), biomethanol (methanol produced from biomass and/or the biodegradable fraction of waste), bioETBE (ethyltertio-butyl-ether produced on the basis of bioethanol: the percentage by volume of bioETBE that is calculated as biofuel is 47%) and bioMTBE (methyl-tertio-butyl-ether produced on the basis of biomethanol: the percentage by volume of bioMTBE that is calculated as biofuel is 36 %).

Biodiesels: this category includes biodiesel (a methyl-ester produced from vegetable or animal oil, of diesel quality), biodimethylether (dimethylether produced from biomass), Fischer Tropsch (Fischer Tropsch produced from biomass), cold pressed bio-oil (oil produced from oil seed through mechanical processing only) and all other liquid biofuels which are added to, blended with or used straight as transport diesel.

Table 5. Classification of the biomass fuel resources under study (Nikolaou et al., 2003).

Sector	Resource	Fuel category	Fuel quality (indicative)		Conversion technology
			Moisture content (% wet basis)	Ash content (% dry basis)	
Agriculture	Agricultural residues	Dry lignocellulosic (e.g. straw, pruning)	30-50	2.2-17	Combustion, gasification, liquefaction
	Livestock waste	Wet cellulosic	74-92.1	27.1-35.4	digestion
		Dry lignocellulosic (e.g. poultry litter)	75	17.5-28	Combustion, gasification, liquefaction
	Energy crops	Dry lignocellulosic	12.5-50	0.3-8.4	Combustion, gasification, liquefaction
		Oil seeds for methylesters	na	<0.02	Extraction
		Sugar/starch crops for ethanol	na	<0.02	Fermentation
Forestry	Wood fuel	Dry lignocellulosic	46.7	0.4-5	Combustion, gasification, liquefaction
	Forest residues	Dry lignocellulosic	46.7	3.2	Combustion, gasification, liquefaction
Industry	Industrial residues	Dry lignocellulosic	10-30	0.71-18.34	Combustion, gasification, liquefaction
		Wet cellulosic	80-99	3.8-5.9	digestion
		Black liquor	90	36.4	combustion
Waste	Regulated waste	Municipal waste	30	36	combustion
		Demolition wood	30-40	0.58	combustion
	Non- regulated waste	Landfill waste	30	36	Digestion
		Sewage sludge	72.8	26.4	digestion
Parks and gardens	Urban wood	Dry lignocellulosic	35	39.4	Combustion, gasification, liquefaction
	Cut grass	Wet cellulosic	75-80	8.4	digestion

Liquid biofuels grew from 7TJ in 1990 to almost 7400TJ in 2002 and represented about 1.5% in total fuel consumption for transport (Germany, in 2004) (Fig. 8, Eurostat, 2007). The price range is dependent upon plant scale and efficiency factors. Also, the price of biofuels is dependent on the source (Fig. 9). The average price for biofuels in Europe varies between 1.0 €/GJ (recovered wood) to 8.4 €/GJ (densified biofuels).

5. Renewable electricity from biomass

Electricity generation from biomass fuels currently uses the same basic technology used in power plants that burn solid fossil fuels. However, new technologies are being developed to improve power production efficiency from biomass.

The electricity directive (2001/77/EC) defines renewable electricity as the share of electricity produced from renewable energy sources in gross electricity consumption (http://themes.eea.europa.eu/Sectors_and_activities/energy/indicators/EN30,2007.04).

Worldwide, electricity production benefited during the last decade from the rise in importance of new renewable electricity production industrial sectors (wind power, biomass, geothermal energy and solar energy).

While they only represented 11% of renewable electricity in 2006, these sectors (new by their degree of industrialization) have contributed 29.3% of the increase in renewable electricity production between 1996 and 2006 (228.5 TWh out of a total of 779.6 TWh). Their share in total electricity production gained 0.9 points between 1996 and 2006 (from 1.2% to 2.1%), while that of hydraulic power lost 2.3 points (from 18.9% to 16.6%). The share of renewable energy in EU-25 electricity consumption grew only slightly over the period 1990-2004 to reach 13.7%, despite a substantial increase in the total amount of renewable electricity generation (up by 49 % since 1990) (Fig. 10).
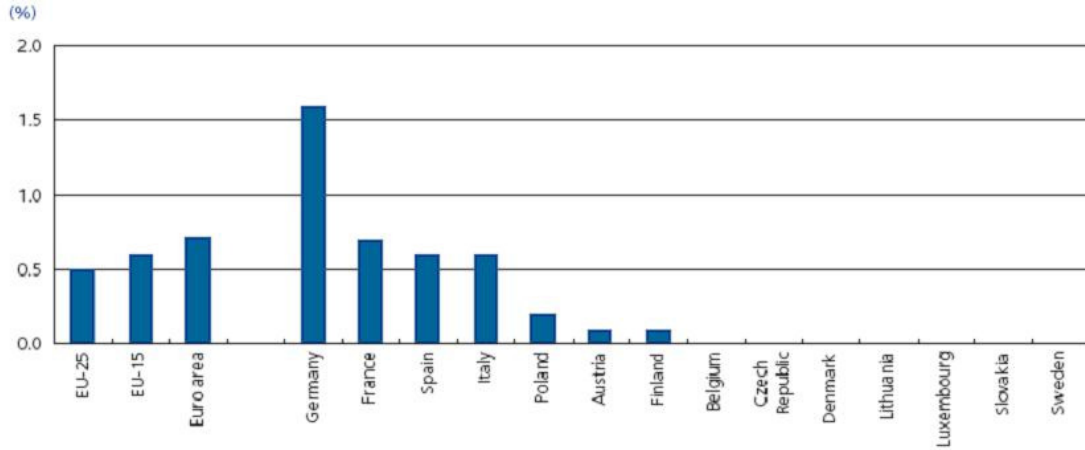
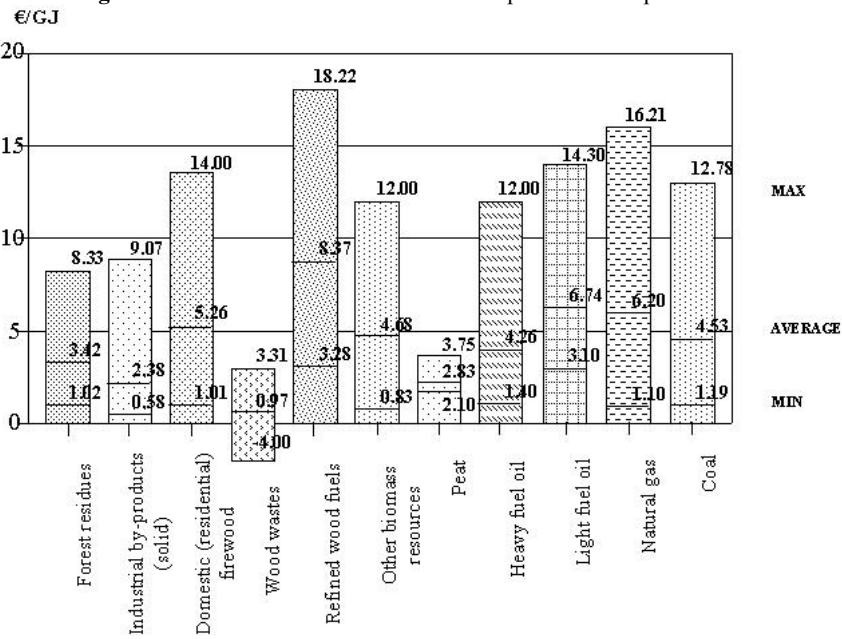**Fig. 8.** Share of biofuels in total fuel consumption for transport in 2004

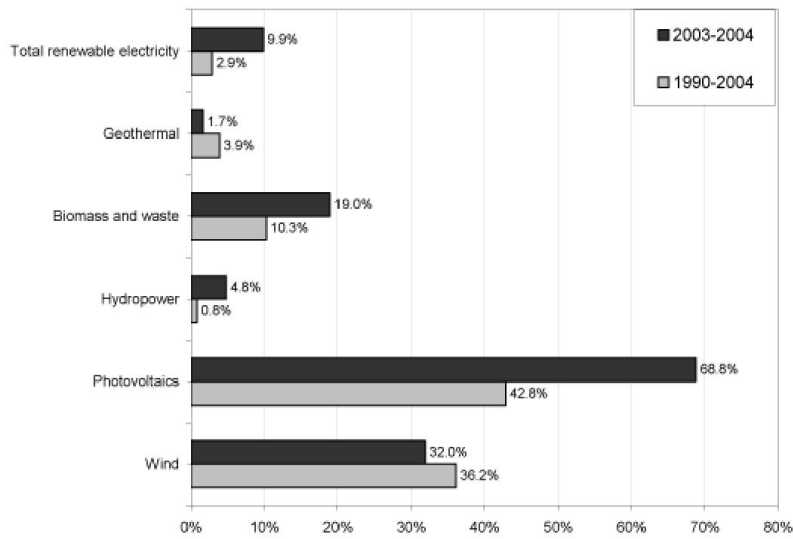**Fig. 9.** Average price for biofuels in Europe (Eurostat, 2007)

Fig. 10. Renewable electricity as a percentage of gross electricity consumption, 2004

In 2001 about 33,379 GWh of electricity were produced from renewable solid waste in the OECD. By far the largest producer of electricity from renewable municipal solid waste is the United States, generating 16,818 GWh, or 50.4% of OECD production. The second largest producer is Japan, with a production of 5,338 GWh. With 2,044 GWh, Germany represents the third largest producer. The remaining electricity production from renewable municipal solid waste is spread among smaller producers in OECD Europe. Denmark and Italy experienced the highest growth rates, increasing their production from 47 GWh to 1,068 GWh (at 32.8% per year) and from 71 GWh to 1,258 GWh (at 29.9% per year) respectively between 1990 and 2001 (IEA, 2002).

Bauen et al. (2004) estimated that bioelectricity, excluding municipal solid waste to electricity, today represents a very small fraction of world electricity production, about 30 GW representing about 1 % of installed capacity, but has a very strong potential for growth. Its growth will be driven by the need to increase the use of renewable energy sources for electricity production to ensure sustainable production of electricity.

By factoring in the pollution-related environmental and social costs generated by fossil and nuclear fuels, bioelectricity became a very competitive energy source.

6. Impacts of biomass conversion to energy

6.1. Overall environmental impacts

Biomass provides a clean, renewable energy source that could dramatically improve the environment, economy and energy security. The use of biomass for energy has effects on all the environmental media i.e. soil, water and air. In addition, these effects may have impacts on human and animal health and welfare, soil quality, water use, biodiversity and public amenity. These impacts arise from each of the individual stages of the biomass energy fuel chains (Bauen et al., 2004; http://www.fvm.dk/Environmental_impacts.aspx?ID= 19789).

Although there is a large body of research in this area, the environmental costs and benefits associated with bioenergy can be difficult to assess because of the complexity of the production systems. One technique which has been used extensively in the literature to compare the energy and greenhouse gases balances of bioenergy chains is life cycle assessment (LCA), an internationally recognised technique for evaluating the natural resource requirements and environmental impacts from the whole process and materials involved in the manufacture of a product or service (Rowe, 2008).

Several studies examined the life-cycle impact of bioenergy for power (Carpentieri et al., 2005; Heller et al., 2004; Rowe et al., 2008). That is,

the studies examined the air, land and water impacts of every step of the bioenergy process, from cultivating, collecting, and transporting biomass to converting it to energy (http://www.azocleantech.com/Details.asp?ArticleId= 87).

Fig. 11 provides a diagram which indicates some of the process steps that should be included in LCA calculation, the emissions or energy requirement associated with each process step (Rowe et al., 2008). In addition, very different impacts are likely to arise depending on which category of biomass feedstock is used and which technologies are used to convert the biomass to useful energy. Contamination with non-biomass or modified biomass streams also represents a particular problem as, even in very small quantities; these contaminants can lead to measurable toxic emissions and health hazards. The production of bioenergy on the basis of residual products such as straw, slurry, animal fat, grass and perennial crops provides a better energy balance and environmental effect when used in direct combustion, biogas or thermal gasification.

The development of biomass resources and the conservation of biodiversity and local environments can go hand in hand. The biomass production has several environmental advantages, including: substituting fossil fuel use with a CO_2-neutral alternative; reducing emissions of other atmospheric pollutants, such as sulphur; protecting soil and watersheds; increasing or maintaining biodiversity: and reducing fire risk in forestry (Bauen et al., 2004).

Biomass energy systems have a wide range of potential socioeconomic and environmental impacts—both positive and negative. Such impacts are often treated as only "secondary" effects in the planning and implementation of energy projects, even though they can greatly influence whether a project is appropriate and sustainable in the local context.

Biomass energy generates far less air emissions than fossil fuels, reduces the amount of waste sent to landfills. Energy derived from biomass results is potentially greenhouse neutral, because the carbon dioxide released by combustion was taken out of the atmosphere as the biomass grew. Carbon dioxide emissions could be cut by around 1,000 megatonnes per year, if OECD countries used biomass - fuel generated from agriculture and forest products - instead of coal to generate electricity (Bauen et al., 2004; Perlack et al., 2005).

Biodiesel, produced from vegetable oil, can substitute for fossil-diesel in transport and heating and electricity generation.

Biofuels such as biodiesel, ethanol and methanol, can be a greenhouse-neutral, renewable energy source for use in transport vehicles, stationary engines, and small electricity generators.

Biomass electricity is potentially greenhouse neutral if produced from biomass such as plantation fuel-wood.
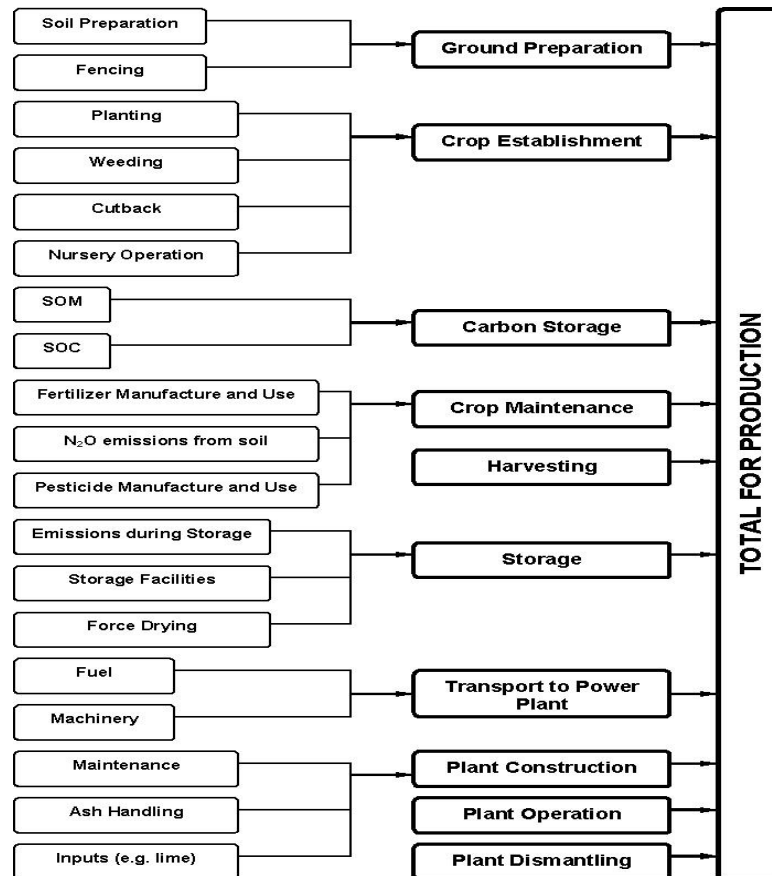
Fig. 11. Diagram of emissions breakdown for heat and power production, necessary for each bioenergy chain (Rowe et al., 2008)

Modernized bioenergy systems have environmental impacts associated both with the growing of the biomass and with its conversion to modern energy carriers. Significant impact is expected from bioenergy with respect to mitigation of climate change, development of rural areas and employment options as well as the provision of alternative energy forms.

However, the environmental impact induced by using biomass as a source of fuel varies according to the type of conversion technology.

6.2. Impact on soil

Environmental impacts of biomass production must be viewed in comparison to the likely alternative land-use activities. For example, at the local or regional level, the relative impacts of producing bioenergy feedstocks depends not only on how the biomass is produced, but also on how the land would have been used otherwise.

Biomass crops pose a particular challenge for good soil management because the plant material is often completely harvested, leaving little organic matter or plant nutrients for recycling back into the soil (Kartha, 2006). Increasing the production of biomass involves a risk of growing pressure on biodiversity and of increased leaching of nutrients

unless there is sufficiently effective environmental regulation of this, for example in the form of demands for extensive land cultivation (Bauen et al., 2004).

The use of perennial crops, where they replace annual crops, will result in reduced oil disturbance, greater soil cover and hence lower erosion, improved soil organic matter and soil carbon levels and increased biodiversity, particularly where the change results in a decreased application of inputs (fertilizers and pesticides) (Bauen et al., 2004).

Also, plants can selectively and actively absorb toxins, including heavy metals and ash recycling could cause such toxins to be concentrated in the bioenergy plantation's soils. This characteristic of certain plant species to selectively absorb toxins is sometimes used to rehabilitate polluted soils in a process known as phytoremediation.

Sometimes, the feedstock's nutrient content can be recovered from the conversion facility in the form of ash or sludge and then converted into a form that can be applied to the field rather than put in a landfill, so that the nutritive value of the ash or sludge is less than optimal (Kartha, 2006).

Soil organic matter and nutrient levels have to be maintained or even improved where bioenergy production is to be based on exploiting agricultural and forestry residues. In many cases, farmers can reduce the risk of nutrient depletion by allowing the

most nutrient-rich parts of the plant—small branches, twigs, and leaves—to decompose on the field. Also, monitoring may be required to ensure that.

6.3. Impact on water

The assessment of direct environmental impacts of energy from biomass for energy for water mainly envisages the following aspects (Bauen et al., 2004; Moret et al., 2006): absolute and relative consumption; reuse (consumption/unit produced); discharge of effluents and infiltration; monitoring of contamination by fertilizers, herbicides and insecticides; turbidity; eutrophication; suspended solid particles; environmental suitability of technology used to extract water; use of best available irrigation practices; groundwater depletion; restoration of groundwater etc.

The use of perennial crops and no-till buffer zones along water courses is already being actively considered as a cost effective method for reducing chemical and biological oxygen demand (COD and BOD) levels in agricultural water courses.

There may also be negative impacts from the introduction of energy crops on local and regional hydrology, because a significant increase in the interception and use of rainfall could result from a wide spread implementation, with potentially substantial reductions in rainfall infiltration and negative impacts of aquifers in the region (Bauen et al., 2004; Lyons et al., 2001). Certain practices, like harvesting residues, cultivating tree crops without undergrowth, and planting species that do not generate adequate amounts or types of litter, can reduce the ability of rainfall to infiltrate the soil and restock groundwater supplies, intensifying problems of water overconsumption (Kartha, 2006).

6.4. Impact on atmosphere

The contribution that biomass could make to the energy sector is still considerable, since it creates less carbon dioxide than its fossil-fuel counterpart.

The utilization of biomass is often presented as a key strategy for reducing greenhouse gases (GHG) emissions from electricity generation and transport. Using biomass potentially provides low carbon transport fuel, heat and power, as biomass crops assimilate carbon from the atmosphere during growth. Therefore, the carbon released back to the atmosphere when the biomass is combusted is that which has been recently captured and should not raise atmospheric concentrations.

Burning biomass will not solve the currently unbalanced carbon dioxide problem. Conceptually, the carbon dioxide produced by biomass when it is burned will be sequestered evenly by plants growing to replace the fuel. In other words, it is a closed cycle which results in net zero impact (http://www.azocleantech.com/Details.asp?ArticleId= 87).

Some studies found that biomass gasification with combined-cycle power plant technology would release far less SO_2, NO_x, CO_2, particulate matter, methane and carbon monoxide than coal power plants (ABA, 2005; Perlack et al., 2005; REPP, 2006;).

7. Bioenergy and sustainable development

7.1. Biomass energy systems and linkages to sustainable human development

The progress of any nation today is measured in terms of its efforts towards the achievement of the Millennium Development Goals (MDGs). Many factors converge in making bioenergy a key component and a viable opportunity in the great effort towards the achievement of the Millennium Development Goals (MDGs). Although the sustainable access to energy is not treated as a priority in itself in the MDGs, most of them have a direct energy implication, particularly Goal 1 (*Eradicate extreme poverty and hunger*) and Goal 7 (*Ensure environmental sustainability*) (FAO, 2005).According to the WSSD Johannesburg Declaration, energy must be considered a human need on a par with other basic human needs (clean water, sanitation, shelter, health care, food security and biodiversity) (ESC, 2007; IBEP, 2006)

The assessment of the sustainability of energy supply from firewood and other forms of plant biomass has changed greatly since the problems of a strong dependency on fossil energy carriers have come to the forefront (IAEA, 2005; Otto, 2007; Sheehan, 2004; Sims, 2003). Fig. 12 provides a conceptual representation of bioenergy systems, as addressed by United Nations Development Programme, in the context of sustainable human development (Kartha and Larson, 2000).

The socio-economic and environmental benefits of bioenergy projects are accepted by planners and operators of development programmes in forestry, agriculture and energy domains (http://www.spatial.baltic.net/_files/Planning_indicat ors.pdf). Also they are recognizing and are now seeing bioenergy as a way to reduce poverty and improve livelihoods in rural areas, overcoming the negative perception of bioenergy as a key symptom of under-development or an environmental hazard. Bioenergy projects contribute to the eradication of extreme poverty and to ensure environmental sustainability in several aspects highlighted in Table 6 (FAO, 2005).

7.2. Sustainable biomass use for energy

Concerns about potential negative effects of large-scale biomass production and export, like deforestation or the competition between food and biomass production, have led to the demand for sustainability criteria and certification systems that can control biomass trade (IAEA, 2005; Lewandowski and Faaij, 2006; Sheehan, 2004).
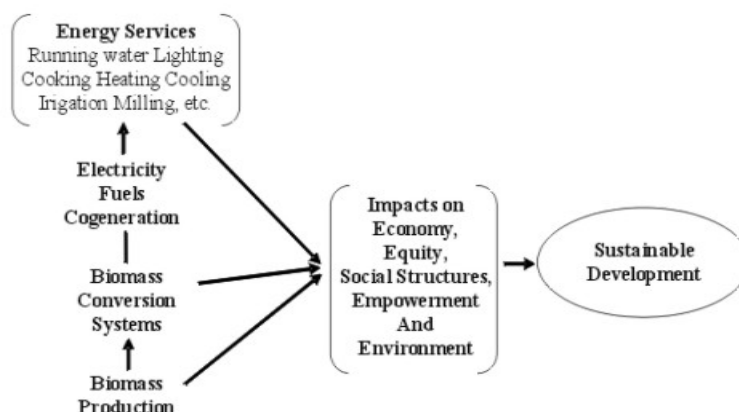
Fig. 12. Conceptual representation of biomass energy systems and linkages to sustainable human development

Table 6. Contributions of bioenergy to sustainability (FAO, 2005)

Sustainability component	*How does bioenergy contribute to MDG achievement*
Economics	- save external currencies through the substitution of imported fossil fuels - leads to improved economic development and poverty alleviation, especially in rural areas by increasing the use of biomass for energy (from sustainable resource management) - provide greater diversification and income opportunities for agriculture, agro-industries and forestry - increase the access of small rural industries to energy services - enhance the value of rural resources, encouraging private and public sector participation and investments - boost national energy security and reduce the oil import bill
Social development	- increase both access to and reliability of energy services for households in rural areas, thus improving the quality of life stimulate governance options, equity and gender equality, especially in view of women's central role in household energy management - attracts investments towards rural areas, generating new business opportunities for small-and medium-sized enterprises in biofuel production, preparation, transportation, trade and use, and generates incomes (and jobs) for the people living in and around these areas - bioelectricity production has the highest employment-creation potential among renewable energy options - bioenergy can be a lever for rural development and regeneration in areas where investment is most needed and the creation of jobs is most difficult - indicators of social accountability include participation of representatives of socio-environmental organizations; participation of the communities as decision-makers and not only being consulted; the degree of inclusion of the local population in the project design, and knowledge of the proposal and the alternatives.
Environment	reduced indoor air pollution from wood energy combustion in poor households associated to the characteristics of cooking devices with positive impacts resource conservation and ecosystem rehabilitation (through sustainable biomass production in marginal lands reduced CO_2 emissions by using cleaner fuels, such as ethanol and biodiesel

To ensure that biomass as a source of renewable sustainable energy will be produced and processed in a responsible manner, some sustainability criteria have to be incorporated into the relevant policy instruments.

Chapter 40 of Agenda 21 calls for the development of indicators for sustainable development. In particular, it requests countries at the national level, and international governmental and non-governmental organizations at the international level to develop the concept of indicators of sustainable development in order to identify such indicators. Minimum criteria for bioenergy sustainability envisage the following *aspects* (Cramer, 2006; Sheehan, 2004):
- comply with present international obligations and local jurisdiction, in addition to other specific indicators.
- comply with specific indicators and active conservation.

Some criteria and indicators of sustainability for the generation of renewable energy from biomass

discussed within the Energy Working Group of FBOMS, in an attempt to contextualize and deepen the national and international debate about future initiatives, in a participatory and engaged manner are presented in Table 7. It synthesizes both the general criteria – basic criteria applicable to any type of initiative - and specific criteria - for projects that involve the use of bioenergy (Moret et al., 2006).

Table 7. Criteria and indicators for sustainability (Moret et al., 2006).

Criteria	*Desirable and Prerequisites*	*Indicators*
Economic		
Use of bioenergy	Creating more efficient transport systems Promotion of energy efficiency	Rates of reduction of consumption Increased end-use conservation Capacity for reduction, reuse and recycling of inputs in the final activities for which the energy is destined Inclusion of demand management in the project planning horizon
Technology	Decentralized generation and production Technology appropriation by local population New technology capable of reducing pressure of energy production on ecosystems Horizontal transfer of technologies and knowledge Contribution to diversification of energy matrix	Relation between local workers and outsiders involved in project maintenance Application of clean technologies Technological innovation Capacity of reproduction of technology used Origin of equipment Existence of technology licences Need for international technical support Changes in use of sustainable energy, cogeneration
Organization of production/labor relations	Cooperatives Family agriculture	Sharing of profits from biofuels production chain by family farmers Level of satisfaction with existing contracts
Financing	Credits, access to land	Programs and lines of credit Conditions for government financing
Social		
Social accountability	Information and capacity building	Participation of local population and national socio-environmental organizations in projects design
Participation in decision making	Information and training, political forums for participation with real influence over decisions	Number, sites, nature and types of consultations, form of publicity, access to information, language and accessibility of material used
Type of management	Training for management	Organizational structures and forms of decision-making, number of participants/decision makers, involvement of organizations representing local workers, participation of women
Job creation and income generation	Training for creation of cooperatives, awareness and training of families with technical and political information	Number of jobs per unit of energy (production chain, implementation and operation), profit sharing, generation of new local opportunities and sources of income, relation between local jobs before and after the project, indexes of increase in acquisitive power of the local population

Social inclusion	Sharing of project benefits with local population	Number of families previously without access to energy who benefit from the project Measures of quality and compliance with accepted standards of the involuntary resettlements, when necessary and accepted Impact on quality life of the communities Social programmes, especially for health and education Epidemiological assessment and monitoring Contribution to access to services and infrastructure on the part of local populations to education, energy, waste and sewage services
Gender equality	Recognition of women and key actors in all stages of decision-making processes Education	Existence of programs and policies for women and youth
Environment *Environmental management*	Use of best available practices Diversity of crops Agroforestry systems Agroecology Minimizationor elimination of pesticide use Reduction of soil loss Training of producers	Monoculturea area Soil loss Atmospheric emissions and effluents into water bodies
Land use	Comply with economic/ecological zoning Regions classified as suitable by strategic environmental assessment Defined limits for occupation of biomass Diversification and decentralization of economic activities Protection of natural areas	Decentralization and diversification of production system in an area/region Sizes of continuous areas of monocultures Distance from energy source to consumer Distance traveled and time spent by workers to project area Time necessary to manage crops

Otto (2007) retains a set of internationally agreed criteria, such as:
- wide acceptance to avoid shifting the problem from one area to another
- ease of reference
- cost
- international trade
- complemented by regional/national protocols
- taking into account specificities

Lewandowski and Faaij (2006) have analyzed existing certification systems, sets of sustainability criteria or guidelines on environmental or social sound management of resources with the purpose to learn about the requirements, contents and organizational set ups of a certification system for sustainable biomass trade, by covering the following successive steps:
- first, an inventory of existing systems was made;
- second, their structures were analyzed and key finding from the analysis of internationally applied certification systems were summarized;
- third and fourth steps: different approaches to formulate standards were described and a list of more than 100 social, economic, ecological and general criteria for sustainable biomass trade was extracted from the reviewed systems;

- fifth, methods to formulate indicators, that make sustainability criteria measurable, and verifiers that are used to control the performance of indicators are described.

The Project Group established by Dutch government (IPM, 2007) has formulated sustainability criteria for the production and the processing of biomass in energy, fuels and chemistry. The project group distinguishes six relevant themes concerning bioenergy sustainability:
- *greenhouse gas emissions* (calculated over the whole chain, the use of biomass must produce fewer emissions of greenhouse gases net than on average with fossil fuel)
- *competition with food and other local applications* (the production of biomass for energy must not endanger the food supply and other local applications (such as for medicines or building materials)
- *biodiversity* (biomass production must not affect protected or vulnerable biodiversity and will, where possible, have to strengthen biodiversity)
- *environment* (biomass production must not affect protected or vulnerable biodiversity and will, where possible, have to strengthen biodiversity)

- *prosperity* (the production of biomass must contribute towards local prosperity)
- *social well-being* (the production of biomass must contribute towards the social well-being of the employees and the local population).

8. Rural areas and bioenergy

Using biomass, such as energy crops, crop processing waste, and agricultural residues, to produce energy is beneficial for the nation, especially rural areas: job creation, rural development and development of local economies through the use of bioenergy (Domac, 2002; Hillring, 2002; Plieninger et al., 2006; Sims, 2003).

Rural areas can better serve as indicator for measuring any progress made towards achieving MDGs. Increasing the use of biomass for energy (from sustainable resource management) leads to improved economic development, and poverty alleviation, especially in rural areas.

The OECD definition, taking into account population density at the local level, considers as rural those local government units with less than 150 inhabitants/km^2. Then it identifies three categories of regions (NUTS3 or NUTS2 level): mostly rural (more than 50% of the population in rural communities), intermediate (between 15 and 50% of the population in rural communities) and mostly urban (less than 15% of the population in rural communities).

The new philosophy of rural area development is based upon the concept of sustainable rural development, which presupposes the harmonious blending of the agricultural (and forestry) component and the non-agricultural rural economy component, based upon the following principles (Otiman, 2008):

- harmony between the rural economy and the environment (economy – ecology equilibrium);
- sustainable development programs should have in view a medium and long term time horizon;
- rural area naturalization, by preserving the natural environment mostly intact;
- the anthropized, man-made environment, should be as close as possible to the natural environment;
- the use of local natural resources, mainly of renewable resources, in the rural economic activity;
- diversification of the agricultural economy structure through a large variety of activities such as the development of agri-food economy, non-agricultural economy and services.

The new European rural economy model focuses on sustainable development of the agricultural sector, which implies the natural environment protection, food security, competitiveness, accelerating the economic development of the rural space (Burja and Burja, 2008). Many rural areas are growing and experiencing increasing energy demand. Smaller facilities have fewer environmental impacts and can operate with locally produced biomass fuel. Using biomass delivers a triple benefit by keeping the wealth nearby, paying farmers to grow and harvest biomass feedstocks, and providing clean energy. The national benefits include lower sulfur emissions (which contribute to acid rain), reductions in greenhouse gas emissions, and less dependence on fossil fuels. Rural benefits feature new sources of income for farmers, more jobs, and economic development—all achieved while preserving the high quality of life, local control, and clean environment.

Bioenergy feedstocks can be produced in conjunction with other local necessities—food, fodder, fuelwood, construction materials, artisan materials, other agricultural crops, etc. Feedstock production can help restore the environment on which the poor depend for their livelihoods—re-vegetating barren land, protecting watersheds and harvesting rainwater (Møller, 2006; UNEP, 2006). Bioenergy activities also serve as an efficient use for agricultural residues, avoiding the pest, waste, and pollution problems of residue disposal (Kartha and Larson, 2000). For instance, bioenergy activities can provide locally produced energy sources to:

- pump water for drinking and irrigation,
- light homes, schools, and health clinics,
- improve communication and access to information,
- provide energy for local enterprises,
- ease pressure on fuel wood resources.

Potential benefits for rural areas encompass job creation, use of surplus agricultural land in industrialized countries, provision of modem energy carriers to rural communities in developing countries, waste control and nutrient recycling (Hall, 1997; Plieninger et al., 2006).

The rural area can carry out its supply, recreation and equilibrium functions, much desired by the society, only on the condition it remains an attractive and original living space, equipped with (http://ideas.repec.org/a/iag/reviea/v5y2008i1-2p4-18.html):
– a good infrastructure;
– a viable agricultural and forestry sector;
– local conditions favorable to non-agricultural economic activities;
– an intact environment with a well-cared landscape.

9. Biomass for energy in Romania

9.1. Romanian bioenergy background

Rural development is an essential topic, especially in those countries as Romania and all East European countries, where rural space and production is still a major part of whole economic structure (Naghiu et al., 2005). This can be considered an important way to revitalize declining areas and ensure them possibilities of achieving a sustainable future.

With an area of 238 thousand km^2 and a population of more than 21 million inhabitants, Romania is an important new EU member state in terms of size, although there is a large gap between this country and the old member states as far as the level of economic and social development is concerned. Rural areas play an important part in this respect, both by their size and residential, economic and recreational dimensions.

According to the national definition, rural areas in Romania cover 87.1% of the territory, and include 45.1% of the population (on 1 July 2005 indicators of National Statistical Institute), i.e. 9.7 million inhabitants.

Romania has got various particularities of the sustainable development in the farming sector, concerning poverty in the countryside, scarcity of productive technologies, practicing subsistence agriculture, excessively cutting of the farm land estate. In the same time, there are also some advantages concerning the old traditions of Romanian rural economy, which are based on the ecological technologies and the high productive potential of the agricultural lands (Burja and Burja, 2008).

Romania was one of the first countries to sign the Kyoto Protocol and thereby show its commitment to the fight against climate change by agreeing to reduce greenhouse gas emissions by 8% by 2012. It is now one of the leading new EU Member States in achieving this objective with a reduction of more than 30 % of gas emissions since 1989 (National Strategy, 2005).

The main sources of air pollution and greenhouse gas emissions in Romania are currently the energy producing industry (thermal energy based on the burning of coal and oil still accounts for about 60% of domestic power generation), transportation, and to a lesser extent, agriculture. Low level of mechanization in Romanian agriculture, in contrast with European average, together with small areas covered by greenhouses, are generating a low contribution to climate change. However, the old park of tractors and main agricultural machines, need to be renewed in order to keep a low level of emissions. Available EUROSTAT data indicates that the agricultural emissions of greenhouse gases in 2002 were over 11.02 million tonnes of CO_2 equivalence. Total emissions from agriculture in the EU-12 for the same period were 416.4 million tonnes of CO_2 equivalence.

Romania benefits from hydro-power generation, which combined with other modest sources of renewable energy, generate about 28.8 % of the domestic energy supply (10% is generated by nuclear power plants). Agriculture and forestry also have the potential to provide significant quantities of biomass, the energy potential of which is estimated to be approximately 7 594 000 equivalent oil tons per year. This includes residue from forest enterprises and firewood (15.5%), sawdust and other wood residue (6.4%), agricultural residues (63.2%), household waste (7.2%) and bio-gas (7.7%).

Biomass resources and delivery costs are presented in Table 8 (Nikolaou et al., 2003).

Table 8. Biomass resources supply, energy crops and delivery costs in Romania (Nikolaou et al., 2003)

Sector	Resource	Fuel category	Curent use for energy 2000 (PJ/year)	Technical biomass potential 2000 (dry tons/year) [a]	Biomass not available for various reasons 2000 (dry tons/year) [b]	Available biomass (dry tons/year)= [a]-[b]	Available energy potential 2000 PJ/year
BIOMASS RESOURCES SUPPLY							
	Dry agricultural residues	Dry lignocellulosic		7826000	0	4128000	73.304
	Livestock	Wet cellulosic		5735172	4427172	1308000	11.772
Agriculture	waste	Dry cellulosic	0	757116	0	757116	10.599624
	Energy crops	Dry lignocellulosic	0	n.a	n.a	n.a	n.a
		Oil seeds for methylesters	0	n.a	n.a	n.a	n.a
		Sugar/starch crops for ethanol	0	n.a	n.a	n.a	n.a
Forestry	Woodfuel forestry byproducts	Dry lignocellulosic	109,857	6103200	0	6103200	109.8576

Sector	Resource	Fuel category					
Industry	Industrial residues	Dry lignocellulosic	9	1277800	0	1277800	23,0004
		Wet cellulosic	:	:	:	:	:
		Black liquor	2.5	300000		300000	3
Waste	Regulated waste	Municipal waste	0	379000	0	379000	4.548
		Demolition wood	:	:	:	:	:
	Non- regulated waste	Landfill gas	0	3416700	0	3416700	13
		Sewage sludge	0	134000	0	134000	0.9916
Parks and gardens	Urban wood	Dry lignocellulosic	:	:	:	:	:
	grass	Wet cellulosic	:	:	:	:	:
Biomass imports			Not existing				
Biomass exports			Very small quantities (less than 4000 dry tons annually of wood fuel+wood residues) (110)				0.072

ENERGY CROPS

Cultivated areas in 2000 (ha)		Yields	
Solid crops	0	Dry matter tons/ha/year	6
Oil containing crops	44825	Biodiesel t/ha/year	0.45
Sugar rich crops	57903	Ethanol t/ha/year	1.19
Total arable land	9906000		
Set aside land	500000		

DELIVERY COSTS

Sector	Resource	Fuel category	Delivery cost (€/GJ)				
			Production (a)	Transport (b)	Other costs (c)	Total (=a+b+c)	Oportunity cost (if any)
Agriculture	Dry agricultural residues	Dry lignocellulosic	0.58-1.9	0.7	0	1.28-2.6	:
	Livestock waste	Wet cellulosic	0	0	0	0	0
	Energy crops	Dry lignocellulosic (triticale, miscanthus)	:	:	:	:	:
		Oil seeds for methylesters (rapessed)	:	:	:	:	:
		Sugar/starch crops for ethanol	:	:	:	:	:
Forestry	woodfuel	Dry lignocellulosic	:	:	:	1.24	:
	Forestry byproducts	Dry lignocellulosic	:	:	:	0.58	:
Industry	Industrial residues	Dry lignocellulosic	:	:	:		:
		Wet cellulosic	0	0	0	0	0
Waste	Regulated waste	Municipal waste	0	0	0	0	0
		Demolition wood	0	0	0	0	0
	Non- regulated waste	Landfill gas	0	0	0	0	0
		Sludge gas	0	0	0	0	0
Parks and gardens	Urban wood	Dry lignocellulosic	0	0	0	0	0
	grass	Wet cellulosic	0	0	0	0	0
Biomass imports							
Biomass exports							

9.2. Bioenergy in rural area

As far as bio-energy is concerned, the National Strategic Plan takes into account the promotion of investment in the biogas and biomass production, as well as investment in the production of wood energy, thus using the agriculture and forest potential, mitigating pollution and combating climate changes, implicitly.

For Romania, production of renewable energy is also an important domain. Investments for producing renewable energy realized by small and medium enterprises from rural areas, involved also in the primary processing of agricultural and forestry products, are supported.

Organic farming

In compliance with the European Action Plan for Ecological Agriculture, the National Strategic Plan takes into account the development of organic farming. Organic farming is an important instrument in nature conservation and revival of rural areas. These aspects have a great importance for Romania, where it was identified the need to maintain the natural value of farmland and the need of an equilibrated rural development. Organic farming could lead to environmental, economic and social benefits for these areas.

A dynamic analysis of the main agricultural sector indicators points to the actual stage of farming in Romania (Tables 9 and 10).

Table 9. Agriculture in Romania (Burja and Burja, 2008)

Indicators	*2006*
Rural population, % (2004)	46
Agricultural labor force, % (2004)	12
Fertilizers used, Kg nutrs/ha (2003)	35
Tractors, number for 1000 ha arable surface (2003)	18
Import of agricultural products, million euro	2424.8
Export of agricultural products, million euro	854.0
Contribution of agriculture to GDP, %	10

10. Future projections

The use of renewable energy resources is an action for economic development, which will bring benefits in the coming decades. It is a consequence of striving towards sustainable economic development, stimulated by a growing concern about the impacts of global warming. Renewable energy will play a growing role in the world's primary energy mix. It is estimated that, non-hydro renewables, will grow faster than any other primary energy source, at an average rate of 3.3% per year over the period to 2030.

The 2020 world capacity projections for energy produced from biomass is shown in Fig. 13.

The data from Fig. 14 shows the large potential biomass conversion in electricity in the OECD, particularly Europe and North America.

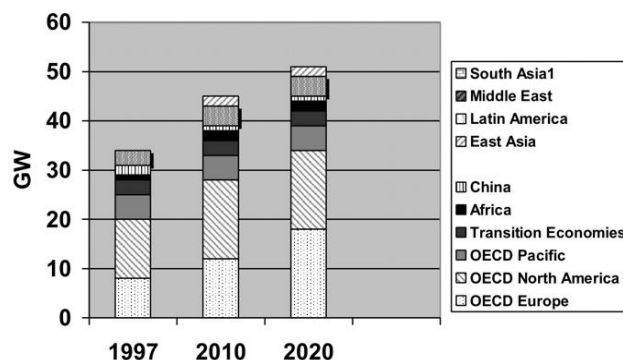There will also however be high growth in Latin America and South Asia.

Fig. 13. World biomass capacity projection, 2020 (Kharta and Larson, 2000)

A small number of countries could produce 50 % or more of their current electricity demand from biomass, most countries over 10 % and a few countries less than 10 %.

When compared to the current installed bioelectricity capacity of only 1 % of the total installed capacity, it is obvious that there is a very significant potential to increase renewable electricity supply from biomass in the OECD (Bauen et al., 2004). The 2020 capacity projections for the non-OECD countries clearly show the relative importance of Latin America and the emergence of China and Africa (Fig. 15). Aiming to increase the contribution from biomass from the current level of 5 EJ/year to 200 EJ/year in 2050 would be a realistic but still challenging goal (Fig. 16) (Hoogwijk, 2006).

Hoogwijk (2006) described an analysis which considered four scenarios with different assumptions about the rates of technology development and the levels of international trade in food along with different assumptions on population growth and diet. The projections of the volume of additional biomass that could be made available for energy purposes varied significantly with the scenarios as land use changed.

Table 10. Indicators of sustainable agriculture in Romania, 2000-2006 (Burja and Burja, 2008)

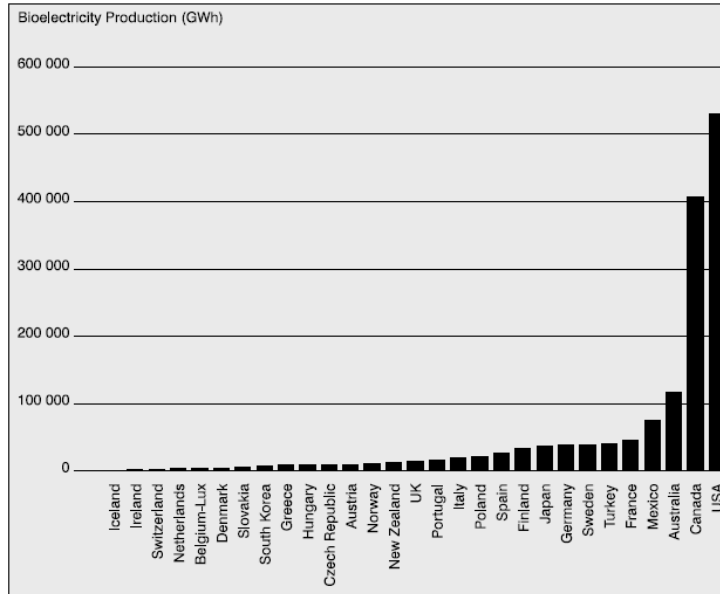| *Indicators*	*2000*	*2006*	*2006/2000*
Organic farms number	-	3676	3676
Ecologic surface, ha	17400	170000	10
Number of cows in ecologic agriculture	2100	9900	5
Number of sheep in ecologic agriculture	1700	76100	45
Number of poultry in ecologic agriculture	-	7500	7500
Ecologic crops, thousand tons	13.5	131.9	10
Milk ecologic production, thousand tons	58.4	100.0	2
Apicultural ecologic products, to	-	600	600
Contribution of exports in entire ecologic production, %	-	95	-

Fig. 14. Potential bioelectricity production in OECD countries by 2020 (Bauen et al., 2004)

One scenario included high population growth, a meat intensive diet with little improvement in agricultural intensity and high demand for biomass for competing uses or as a carbon sink. In this case the potential for additional energy use was low.

Fig. 15. Biomass capacity projection for non-OECD countries, 2010

By contrast, in the most optimistic scenario for bioenergy, where population growth is low, diet becomes less meat-intensive, agricultural intensity increases significantly (with a 100% increase in production per hectare) and there is less competition for resources, then bioenergy could increase very significantly, providing over 1000 EJ/year (Hoogwijk, 2006).

Biomass energy creates thousands of jobs and helps revitalize rural communities. The increasing use of bioenergy is also stimulated by rural development, energy security, employment and, of course, by the provisions of the Kyoto Protocol. Bioenergy projects – including those that involve the use of landfill gas, biogas, and biomass to produce heat and power – are currently significant (IEA, 2007). However, bioenergy is not a panacea for all energy problems (FAO, 2005). Long lasting solutions should be considered together with other energy options taking due consideration of local characteristics and situations.

Fig. 16. Range of biomass energy potential (Hoogwijk, 2006)

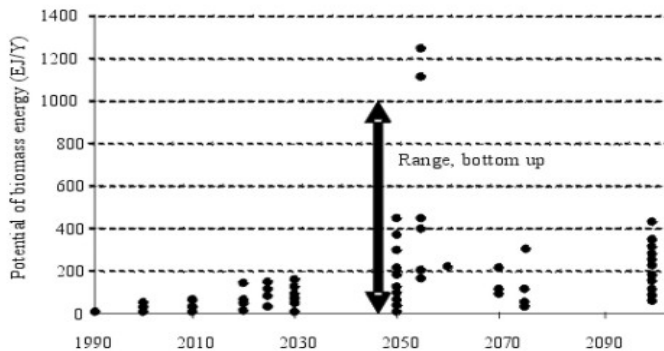However, the choice of the most appropriate energy option in relation to poverty reduction and environmental sustainability must consider a combination of local factors such as: existing productive enterprises, local energy resources, and technical characteristics of production/consumption patterns, emissions control and sustainable land-use practices.

11. Conclusions

Bioenergy projects will provide greater diversification and income opportunities for agriculture, agro-industries and forestry: they will increase the access of small rural industries to energy services; and will enhance the value of rural resources, encouraging private and public sector participation and investments. Locally produced bioenergy will boost national energy security and reduce the oil import bill. Modern bioenergy systems will increase both access to and reliability of energy services for households in rural areas, thus improving the quality of life.

The development of socially and culturally sustainable biomass production systems will inevitably stimulate governance options, equity and gender equality, especially in view of women's central role in household energy management.

Experience from different countries around the world supports the view that bioenergy can be a lever for rural development and regeneration in areas where investment is most needed and the creation of jobs is most difficult.

Long lasting solutions should be considered together with other energy options taking due consideration of local characteristics and situations. However, the choice of the most appropriate energy option in relation to poverty reduction and environmental sustainability must consider a combination of local factors such as: existing productive enterprises, local energy resources, and technical characteristics of production/consumption patterns, emissions control and sustainable land-use practices.

The long term biomass energy potential can be significant, but depends highly on: population dynamics; agricultural intensity; diet consumed; food trade influences the regional distribution; for high shares of biomass energy, trade is required; tradeoffs with sustainable forms of agriculture should exist.

Biomass power is the largest source of renewable energy as well as a vital part of the waste management infrastructure. An increasing global awareness about environmental issues is acting as the driving force behind the use of alternative and renewable sources of energy. A greater emphasis is being laid on the promotion of bioenergy in the industrialized as well as developing world to counter environmental issues.

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Book Review

HANDBOOK OF HETEROGENEOUS CATALYSIS

Second, Completely Revised and Enlarged Edition

Volume 3

Gerhard Ertl, Helmuth Knözinger, Ferdi Schüth, Jens Weitkamp (Editors)
Wiley-VCH Verlag GmbH& Co. KGaA, Weinheim, Germany,

The third volume of the **Handbook of Heterogeneous Catalysis** is organized in three sections: *Model systems*, *Elementary Steps and Mechanisms* and *Macrokinetics and Transport Processes*.

Since solid catalysts are typically complex materials, researchers have often used structurally simple models in their attempts to identify the catalytic sites and understand the reaction mechanisms.

Consequently, the first chapter (***Model Systems***) covers the structures that can be used as models for industrial catalysts. Among these, Single Crystals are usually used as models for metal catalysts because they are highly uniform, crystalline, and pure materials. Some examples given in this book are indicative for the concepts that were developed using the single crystal models: (i) the nature of the active site can be easily revealed by comparing the turnover rates on industrial, supported catalysts and single crystal catalysts for the catalytic reaction of ammonia synthesis; (ii) the classification of a reaction as structure-sensitive or structure-insensitive may be made directly by measuring the rates on the different planes of a single crystal.

The second group of model systems deals with the Supported Metal Cluster Catalysts. Metals are among the most important industrial catalysts, and in practice they are usually dispersed on supports, so that a large fraction of the metal atoms are exposed at surfaces and accessible to reactants. The aims of this chapter are to summarize methods of synthesis and characterization of supported metal clusters made from molecular precursors, and to illustrate their catalytic properties. Metallic Glasses, also referred to

as "glassy metals" have gained considerable interest in catalysis research due to their unique structural and chemical properties. In this chapter, a brief account of the state-of-the-art is provided, and some important facets of the knowledge gained are discussed. Based on the results reported so far, two principal opportunities for the use of glassy metals in catalysis have emerged, namely *as-quenched* state (based on the surface structure which, ideally, should be structurally and chemically isotropic and exhibiting no-long range ordering of the constituents, as well as on the ability to tailor the electronic properties) or as *catalyst precursors* (which opened new routes for the preparation of supported metal catalysts with unusual chemical and structural properties). Bimetallic Model Catalysts offer advantages due to "synergy": the two active metals somehow cooperate to enhance activity and/or selectivity in ways which are not seen in catalysts based only on the individual metals. In this chapter, the properties of bimetallic surfaces that contain transition and *s, p* metals are examined. Because this subject was previously reviewed in the First Edition of this Handbook, the attention is focused only on the recent studies with well-defined model catalysts, placing importance on investigations that illustrate new concepts or provide results that lead to a general and coherent picture of the behavior of bimetallic surfaces. The chapter Ultrathin Oxide Films is focused on the recent developments in the investigations of thin oxide films supported on metal single crystals. The material taken into consideration is organized as follows: first, a prototype system (MgO(100) surface) is addressed, before discussing surfaces of other oxide materials. Also, the interaction of oxide surfaces with metal and metal oxide

deposits, and how these composite systems interact with gas-phase reactants are included in this chapter. The Reactions of Model Metal Oxide Surfaces are of exceptional significance in areas such as catalysis. So far, in spite of their wide-range applications, metal oxides have been less addressed than the metals in the studies on the industrial process. The presence of two different atoms (metal and oxygen) increases the number and complexity of the surface structures, and many are less stable than their metal counterparts at elevated temperatures. The chapter Microcrystalline Oxides: Bridging the Gap between Single Crystals and Dispersed Oxides intends to show that the gap between "believed perfect" single-crystal surfaces and high-surface-area samples can be progressively reduced. The approach of this contribution (limited to MgO) should not be considered as too restricted because a lesson derived from one single example has sufficient generality to be extended to other systems. The last chapter is devoted to the Oxide Solid Solutions which covers the preparation, characterization and the catalytic applications of these materials. The catalytic applications are limited to the most relevant reactions and catalysts.

The next chapter, on ***Elementary steps and mechanisms***, gives comprehensive details about the "intimacy" between catalyst and the molecules being converted. All these things are properly presented a long of five sub-chapters. First information is given on Chemisorption where principles of chemisorption, thermodynamics and energetics, surface diffusion and structure sensitivity are very well documented. The discussion is going further with Microkinetics. This sub-chapter deals with the concept of turnover frequency (TOF) and provides examples of how this concept allows us to think about heterogeneous catalysis. How to collect the kinetic reactions data and build mechanistically-based "microkinetic" models are discussed, as well. Further, the use of the transition state theory to estimate the entropies of the adsorbed species in the models is shown. Finally, the concept of kinetically significant steps, as determined by Campbell's degree of rate control, is discussed. The third sub-chapter is devoted to the Factors Influencing Catalytic Action. Few examples and case studies are chosen in order to better understand the mechanism of the action of catalysts and, perhaps more importantly, how promoters and poisons influence this chemistry. Hydrocarbon Reaction Mechanisms provides a brief, introductory summary of mechanistic information about hydrocarbon reactions, restricted for brevity to those catalyzed by solid acids or by metals. Related information is presented in the parts of this Handbook dealing with acidity and basicity, computer simulation of sorption, diffusion and shape selectivity, petroleum refining reactions and petrochemical conversions. In addition, various chapters are concerned with catalysis by acids and metals. The fifth chapter, on Computer Simulations, proposes to show how molecular simulation is a useful tool in catalysis. In this respect, three possible applications are presented here such as

(i) modeling of structures and reactivity of solids catalysts, (ii) computer simulation of sorption and transport in zeolites and (iii) computer simulations of shape selectivity effects. It is shown that recent developments in novel simulation techniques and force field have allowed for computing the properties of catalysts to a sufficient degree of accuracy so that, they may be considered as a good alternative for real experiment data.

The chapter ending this volume of the Handbook, consisting in six sub-chapters, treats the ***Macrokinetics and Transport Processes***. The sub-chapter Rates Procurement and Kinetic Modeling describes the methods to obtain relevant data for kinetic modeling and comparison of catalysts activities for the ultimate purpose of engineering applications. Discussions on the diffusion phenomenon including (i) definitions, (ii) measurement of transport diffusion, (iii) measurement of self-diffusion, diffusion in multicomponent systems, and (iv) the correlation among different diffusivities are accurately exploited in the sub-chapter Determination of Diffusion Coefficients in Porous Media. The objective of the sub-chapter Simultaneous Heat and Mass Transfer and Chemical Reaction is to make the chemists and chemical engineers familiar with the basic concepts for a quick and effective study of the phenomena of simultaneous heat and mass transfer combined with simultaneous chemical reactions in porous media. The first part of sub-chapter Magnetic Resonance Imaging (MRI) summarizes the basic principles of this procedure and transport measurement techniques and highlights the recent developments in the field. In the second part, several examples are presented with the aim of giving the reader an overview of the state-of-the-art capabilities of MRI applied to catalysts and catalytic reactions. The sub-chapter ^{11}C, ^{13}N and ^{15}O Positron (β^+) Emitters in Catalysis Research briefly describes the radiation properties of β-emitters, the production and synthesis of β-labeled compounds and the *in situ* detection of β-labels. Several applications of ^{11}C, ^{13}N and ^{15}O in heterogeneous catalysis are also summarized. The last topic of the chapter is Computational Fluid Dynamics Simulation of Catalytic Reactions. This sub-chapter introduces the applications of CFD simulations to obtain a better understanding of the interactions between mass and heat transport and chemical reactions in catalytic reactors. Concepts for modeling and numerical simulation of catalytic reactors are presented, which describe the coupling of the physical and chemical processes in detail. The ultimate objective of these approaches is to understand and, finally, to optimize the behavior of the catalytic reactors.

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Book Review

CHEMICAL THERMODYNAMICS
Basic Concepts and Methods

Irving M. Klotz, Robert M. Rosenberg

This is the seventh edition of the book *Chemical Thermodynamics,* which was first published by professor Klotz in 1950. The fundamental objective of the book is to present to the student the logical foundations and interrelationships of thermodynamics and to teach the student the methods by which the basic concepts may be applied to practical problems. In the treatment of basic concepts, the authors adopted the classic, or phenomenological, approach to thermodynamics and have excluded the statistical viewpoint. This attitude permits the maintenance of a logical unity throughout the book. A great deal of attention is paid in this book to training the student in the application of the basic concepts to problems that are commonly encountered by the chemist, the biologist, the geologist, and the materials scientist.

The first chapter is an introduction that synthetically presents the origins of the chemical thermodynamics, objective of chemical thermodynamics and limitations of classic thermodynamics. The primary objective of chemical thermodynamics is to establish a criterion for determining the feasibility or spontaneity of a given physical or chemical transformation. Although the main objective of chemical thermodynamics is the analysis of spontaneity and equilibrium, the methods also are applicable to many other problems. For example, the study of phase equilibria, in ideal and nonideal systems, is basic to the intelligent use of techniques of extraction, distillation, and crystallization; to metallurgical operations; to the development of new materials; and to understanding of the species of minerals found in geological systems. Thermodynamic concept and methods provide a powerful approach to the understanding of such problems.

Chapter 2, *Mathematical preparation for thermodynamics* presents variables of thermodynamics (intensive and extensive variables) and analytic methods. As the state of a thermodynamic system generally is a function of more than one independent variable, it is necessary to consider the mathematical techniques for expressing these relationships. Many thermodynamic problems involve only two independent variables, and the extension to more variables is generally obvious, so authors limit our illustrations to functions of two variables.

The next three chapters present the first law of thermodynamics and this application to gases. The relationships developed for gases that are based on the first law will be useful in developing the second law will be useful in developing the second law of thermodynamics and in applying the second law to specific systems. As the behavior of many gases at low pressure can be approximated by the simple equation of state for ideal gas, and the ideal equation of state describes accurately the behavior of real gases at the limit of zero pressure, authors begin our discussion with a consideration of ideal gases.

The first law of thermodynamics, which is useful in keeping account of heat and energy balances, makes no distinction between reversible and irreversible processes and makes no statement about the natural direction of a chemical or physical transformation. The second law presented in chapter 6, like the first law, is a postulate that has not been derived from any prior principles. It is accepted because deductions from the postulate correspond to experience. Except in submicroscopic phenomena, to which classical thermodynamics does not apply, no exceptions to the second law have been found.

Chapters 7-9 present applications of the second law of thermodynamics in electrical, mechanical, biological and osmotic work. Mixtures of gases and equilibrium in gaseous mixtures are presented in chapter 10.

Chapter 11 deals with *The Third Law of Thermodynamics*. Lewis and Randal proposed the following statement of the third law of thermodynamics: "If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, every substance has finite positive entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances". The authors I. M. Klotz and R. M. Rosenberg adopt this statement as the working from of the third law of thermodynamics. This statement is the most convenient formulation for making calculations of changes in the Gibbs functions or the Planck function.

Chapter 12 present application of the Gibbs functions to chemical changes. As the Gibbs function is a thermodynamic property, values of ΔG do not depend on the intermediate chemical reactions that have been used to transform a set of reactants, under specified conditions, to a series of products. Thus, one can add known values of Gibbs function to obtain values for reactions for which direct data are not available.

In the chapter 13 authors present a deviation of the phase rule and apply the result to several examples (one-component systems, two-component systems and two phases at different pressures). Authors discussed multiphase-multicomponent systems in terms of the phase rule and its graphical representation. In the next two chapters this describes the equilibrium curves of a phase diagram in terms of analytic functions and begins by considering the ideal solutions and dilute solutions of nonelectrolytes.

Chapters 16 and 17 developed procedures for defining standard states for nonelectrolyte solutes and for determining the numeric values of the corresponding activities and activities and activity coefficients from experimental measurements.

In chapter 18, I. M. Klotz and R. M. Rosenberg shall consider the methods by which values of partial molar quantities and excess molar quantities can be obtained from experimental data. Most of the methods are applicable to any thermodynamic property *J*, but special emphasis will be placed on the partial molar volume and the partial molar enthalpy, which are needed to determine the pressure and temperature coefficients of the chemical potential, and on the excess molar volume and the excess molar enthalpy, which are needed to determine the pressure and temperature coefficients of the Gibbs function.

Chapter 19 describes the evaluation methods for activity, activity coefficients and osmotic coefficients of strong electrolytes. All methods used in the study of nonelectrolytes also can be applied in principle to the determination of activities of electrolytes solutes. However, in practice, several methods are difficult to adapt to electrolytes because it is impractical to obtain data for solutions sufficiently dilute to allow the necessary extrapolation to infinite dilution. Activity data for electrolytes usually are obtained by one or more of three independent experimental methods: measurement of the potentials of electrochemical cells, measurement of the solubility, and measurement of the properties of the solvent, such as vapor pressure, freezing point depression, boiling point elevation, and osmotic pressure. All these solvent property may be subsumed under the rubric *colligative properties*.

In chapter 20 authors been discussed of the principle of chemical thermodynamics with a consideration of some typical calculations of changes in Gibbs function in real solutions.

In most circumstance of interest to chemists, the dominant experimental variables are temperature, pressure, and composition, and our attention has been concentrated on the dependence of a transformation of these factors. On some occasions, however, a transformation takes place in a field: gravitational, electrical, or magnetic; chemists who work with macromolecules frequently use a centrifugal field in their work. Chapter 21 details the systems subject to a gravitational or a centrifugal field.

Chapter 22 *Estimation of thermodynamic quantities,* presents review some empirical and theoretical methods of estimation of thermodynamics quantities associated with chemical transformations. Precise thermodynamic data are available for relatively few compounds. However, in many situations, it is desirable to have some idea of the feasibility or impossibility of a given chemical transformation even though the necessary thermodynamic data are not available. Several groups of investigators have proposed empirical methods of correlation that allow us to estimate the thermodynamic properties required to calculate Gibbs functions and equilibrium constants. All of these methods are based on the assumption that a give thermodynamic property, such as entropy, of an organic substance can be resolved into contributions from each of the constituent groups in the molecule.

The last chapter of the book presents concluding remark. The point of view adopted toward thermodynamics in this book is the classic or phenomenological one. This approach is the most general but also the least illuminating in molecular insight. The three basic principles of phenomenological thermodynamics are extracted as postulated from general experience, and attempt is made to deduce them from equations describing the mechanical behavior of material bodies. As it is independent of the laws governing the behavior of material bodies, classic thermodynamics cannot be used to drive any of these laws. Generally, thermodynamics does not allow us to calculate a priori actual values of any of the quantities appearing in these relationships. Parallel with the phenomenological development, an alternative point

of view has developed toward thermodynamics, a statistical-mechanical approach. Its philosophy is more axiomatic and deductive than phenomenological. In principle, quantum mechanics permits the calculation of molecular energies and therefore thermodynamic properties. In practice, analytic solutions of the equations of wave mechanics are not generally accessible, especially for molecules with many atoms.

Each chapter of the book contains an up-to-date well documented list of references. The book is written in contemporary way and includes many illustrations which make the text more useful for specialists in chemical engineering. Also it is completed with Annexes containing practical analytical and graphical mathematical techniques. The book is necessary to people working into various field chemistry, biology, geology, and materials science.

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NEW APPLICATIONS OF ARTIFICIAL INTELLIGENCE TOOLS IN MODELING AND DETERMINING CERTAIN PHYSICAL-CHEMICAL CHARACTERISTICS

## Idei Programe PNCDI-II, Project ID _600 (Contract no. 64/1.10.2007)

Significant efforts have been noticed at international level these latest years, to reduce the number of experimental determinations, which has also become a more frequent requirement in the study of physical, chemical and biological processes. This trend is particularly supported by the economic advantages that may result from it, like, for instance, less time-consuming and less expensive experimental research. The use of artificial intelligence tools in modelling and determining certain physical-chemical characteristics helps the achievement of this desideratum.

To support the above considerations, the overall objective of the grant proposition is the assessment of the applicability of various artificial intelligence tools like: neuronal networks and genetic algorithms in modeling and determining certain physical-chemical characteristics, while one of the specific objectives of the project would be aimed at discovering new applications for artificial intelligence tools in the study of the characteristics of real systems by means of proper models. Also, it tries to contribute to the establishment of new mathematical models, by means of modern and topical methods, namely – neuronal networks and genetic algorithms. The new calculus concept – neuronal calculus – that led to concrete achievements also known as artificial neuronal networks (in short neuronal networks) distinguishes itself through its applicability to very different fields.

The calculus based on neuronal networks is one of the artificial intelligence areas with the fastest development due to the ability of neuronal networks to memorize different types of relations. Neuronal networks proved able to estimate any continuous non-linear function, which means that they may be applied to non-linear system modelling.

The project theme has a multi-disciplinary nature, as it combines experimental abilities with high performance computational methods, thus providing useful tools to chemical engineering and also observing the preoccupations of the researchers at international level.

The project theme is an applicative and fundamental research area based on the synergy of pluri-disciplinary approach in physics, chemistry and mathematics.
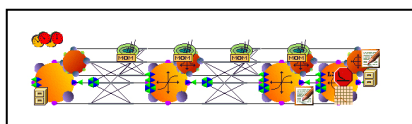
It has a multi-disciplinary nature and it is compliant with the national society computerization policy, by the transfer and implementation of the most recent information technologies in chemical engineering, aimed at obtaining high performance solutions for new technologies and products.

The scientific importance of the theme replies on the two directions of application of the artificial intelligence tools we approached: 1. – modeling and especially determination of certain physical-chemical characteristics like: excess refraction index, excess molar volume and excess superficial stress of binary fluid systems and 2. – prediction of the thermal stability of certain organic compounds based on their molecular structure.

The design of materials having certain compulsory biological, chemical and physical characteristics requires the modeling of significant interactions between the basic structural units for characteristic prediction, as well as the efficient localization of viable structures that could help achieve the wanted synthesis performance. This area of molecular design is a way to combine neuronal networks and genetic algorithms. Neuronal networks model the non-linear structure-characteristics correlations more accurately and more easily as compared to other conventional approaches and that is why they are used to solve the direct problem. The opposite problem concerning molecular design is also solved by means of neuronal networks optimized with genetic algorithms, based on the fact that, wishing to obtain certain macroscopic characteristics, molecular structures are built that could provide such characteristics. Both research directions shall contribute to the achievement of the project desideratum, namely the reduction of the number of experimental determinations required for the establishment of certain physical-chemical characteristics with implications on time and money saving.

For more information on the PN-II-ID _600 project please visit the project site at: *http://www.ch.tuiasi.ro/cercetare/PNCDI/glisa/en/index.html*

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Book Review

HANDBOOK OF HETEROGENEOUS CATALYSIS

Second, Completely Revised and Enlarged Edition

Volume 4

Gerhard Ertl, Helmuth Knözinger, Ferdi Schüth, Jens Weitkamp (Editors)
Wiley-VCH Verlag GmbH& Co. KGaA, Weinheim, Germany,
ISBN: 978-3-527-31241-2, 2008

The fourth volume of the **Handbook of Heterogeneous Catalysis** is organized in four sections: *Activity Loss*, *Special Catalytic Systems, Laboratory testing of Solid Catalysts* and *Reaction Engineering*.

The first chapter (***Activity Loss***) deals on the one hand with the Deactivation and Regeneration of catalysts and on the other hand with the Recycling of Spent Catalysts, especially those containing precious metals and base metals. Because the catalysts deactivation is a topic of real interest particularly for industrial applications, the subject has been reviewed in this chapter of the Handbook; the causes of the catalyst deactivation as well as what are the solutions of the catalyst regeneration are adequately presented. Due to their importance, the recycling of the catalysts containing precious metals as well as those containing base metals can generally be performed economically and is already successfully practiced in many applications area. Consequently, this sub-chapter briefly introduces the main groups of these catalysts and highlights (i) their important applications and (ii) recycling technologies depending on the individual characteristics of the catalysts.

Because of the diversity of chemical nature of the catalytic materials, special catalysts or catalytic systems have been developed. Accordingly, the second chapter, on ***Special Catalytic Systems***, reviews the main relevant fields of catalysis. Electrocatalysis deals with the reactions in which a charge transfer across the interface between electrode and electrolyte takes place.

In this sub-chapter the basic principles of electrolysis are reviewed: (i) the structure of the electrode/electrolyte interface and the driving force for charge transfer at electrodes, (ii) the main kinetic parameters and their relationship to mechanisms and (iii) basic concepts of electrocatalysis. Further, the electrocatalytic reactions occurring at the hydrogen electrode and the oxygen electrode are considered. The sub-chapter ends with a discussion on the importance of industrial electrolysis on the basis of the some commercially relevant examples from the fields of both organic and inorganic chemistry. The multiple environmental problem caused by the fast economical growth in the last centuries induced the necessity to develop environmentally friendly chemical processes and systems such as Photocatalysis. This sub-chapter is devoted to the most applied photocatalyst, TiO_2; ion engineering techniques for the preparation of well-defined as well as visible light-responsive TiO_2 photocatalysts are reviewed. The sub-chapter Chemical Sensors Based on Catalytic Reactions starts with useful definitions and classifications of sensors, followed by few commonly used chemical sensors examples such as amperometric gas sensors, lambda probes, Taguchi SnO_2 sensors, pellistors, biosensors to monitor of oxygen in blood and Pd-gate field effect transistors. The next sub-chapter, on Heterogeneous Catalysis in Non-Conventional Solvents focuses on non-conventional solvents as opposed to conventional liquid or gaseous reaction media for heterogeneously catalyzed conversions. The non-conventional solvents treated here include supercritical fluid, ionic liquids and gas expanded liquids. Also, examples of reactions performed in these kinds of solvents are well

documented herein such as hydrogenations and dehydrogenations, oxidations, Fischer-Tropsch synthesis etc. Other recently study options for reactions media such as polyethylene glycols, perfluorohydrocarbons and thermoregulated solvent systems have only rarely been exploited in heterogeneously catalyzed reactions and are, therefore, only briefly mentioned. Due to the fact that ultrasound became a common laboratory tool for nearly any case where a liquid and a solid must react, the last sub-chapter is devoted to Sonocatalysis. A comprehensible introduction on the origins of sonochemistry followed by the effects of ultrasound on heterogeneous catalyst can be found in the Handbook.

The third chapter, on ***Laboratory Testing of Solid Catalysts***, is divided in three sub-chapters. The first sub-chapter (Laboratory Catalytic reactions: Aspects of Catalytic Testing) is focused on (i) the reactor systems, which introduces a classification of the rectors as well as the types of the reactors used in the laboratory; (ii) mass and heat transfer; (iii) effect of transport limitations on observed behavior; (iv) diagnostic experimental tests for extraparticle and intraparticle limitations to verify the presence or absence of transport limitations; (v) proper testing of the catalysts in order to obtain the relevant information with regard to intrinsic activity, selectivity, deactivation and kinetic behavior and finally, (vi) current trends in catalyst testing, which supposes to scaling down the reactions to micro-and nano-flow with full automation. The intention of the sub-chapter Ancillary Techniques in Laboratory Units for Testing Solid Catalysts is to discuss critical building blocks of laboratory-scale catalytic units which are frequently designed in an inadequate manner.

Essentially, this sub-chapter is focused on the peripheral building blocks, that is, the devices for the preparation of the feed mixtures to be sent to the reactor and the systems downstream of the reactor for transferring product samples to an analytical instrument.

High-Throughput Experimentation in Heterogeneous Catalysis is a relatively novel technology in the development of heterogeneous catalysts. Consequently, this sub-chapter gives an analysis on the different elements of an HTE program in heterogeneous catalysis starting with the presentation of a typical program and going on with the technology elements that covers (i) aspects of the synthesis, (ii) characterization tools, (ii) reactors and analytics and finally, (iii) informatics environment, required for a fully integrated high-throughput program.

The last chapter, on ***Reaction Engineering***, is devoted to the chemical reactors and it is organized in eight sub-chapters as follows: Catalytic Fixed-Bed Reactors, Fluidized-Bed Rectors, Slurry Reactors, Unsteady-State Reactors Operation, Short-Contact Time Reactors, Catalytic Distillation, Catalytic Membrane Reactors and Microstructured Reactors. The aim of this chapter is to illustrate some of the fundamental characteristics of each type of the reactor used so far. Typical industrial applications using select examples from the literature, kinetic models and approaches to the modeling and designing of a particular catalytic reactor are adequately discussed, as well.

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Book Review

MEMBRANES IN CLEAN TECHNOLOGIES

Theory and Practice

Andrzej B. Koltuniewicz, and Enrico Drioli (Editors), vol. 1
WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany
ISBN: 978-3-527-32007-3, 2008, XIX+467 pages

In the last years, membrane processes have shown their potential in the rationalization of the production systems. However, the preparation of synthetic membranes and their utilization on a large industrial scale, is more recent development which has rapidly gained a substantial importance due to the large number of practical applications.

Membrane processes are used to produce potable water from the sea, to clean industrial effluents and recover valuable constituents, to separate gases and vapors, and to concentrate, purify, or fractionate macromolecular mixtures in the food and pharmaceutical industries.

The membranes used in the various applications differ widely in their structure and function and in the way they are operated in the various membrane processes. It is difficult to obtain a reasonably comprehensive and complete overview of the entire field of membranes and membrane processes including their applications.

The applications are extremely wide and covered in the literature by a large number of publications in different scientific journals and in several books focusing more on certain aspects of membrane science such as theoretical treatment of membrane function, engineering consideration of membrane process design, or membrane preparation and large scale production.

The book entitled *Membranes in Clean Technologies. Theory and Practice* is a practical 'how to do' guide for either reengineering existing technologies or implementing innovative processes, including over 6,000 pertinent references.

It is structured in two volumes and three parts: part I *Engineering of Membrane Processes*, part II *Membranes in Clean Industry,* and part III *Materials in Management with Membranes – Separation of Metals, Acids, and Hydrocarbons*.

The first volume focuses on the theory and engineering of membrane processes, and presents the use of membrane processes in such industries as water, textiles, tannery, paper, metal plating, electronic, and pharmaceuticals. After an introduction to the development of "clean technology" concepts, in chapter 2 are presented the separation of mixtures and mass transport in membranes. The separation of mixtures is important in many industrial branches for fractioning, purification, and concentration of final products, which make them more valuable. Semi permeable membranes are used for separation of homogenous and heterogeneous mixtures based on different rates of overall transport for different components through the membrane.

In chapter 3, *Membranes*, the main topic is the preparation and characterization of porous symmetric, asymmetric and composite membranes made from polymers or inorganic materials. The preparation of hybrid organic – inorganic membranes, supported liquid membranes and other special property membranes is also discussed.

In the next chapter of the volume, the more relevant aspects in membrane processes are described in details, and their technical and commercial advantages as well as their limitations are pointed out. New membrane processes, like membrane contactors, are more briefly treated and also, potential applications are indicated.

Part II of this book, *Membranes in Clean Industry*, deals with membranes in industries like water, textiles, paper, metal plating, electronic, and pharmaceuticals.

Chapter 5 of the first volume, *Water industry*, is dedicated to the practical application of membranes and membrane processes used in water industry. The most important aspect in water recovery, reuse, and recycling is to control the composition of the water streams. Membranes play an important role in recovery and/or destructive conversion for removal of various substances from the water, and therefore, have become more attractive to water processing and other technologies.

In the sixth chapter, after a short introduction to the water consumption and management in textile industry, some applications with membrane processes are described for water purification and reuse in textile industry. Also combined treatment schemes are suggested, which include membrane processes.

Chapter 7, *Tannery industry,* begins with general information about tannery industry. Furthermore, membrane processes potentially used to recover the majority of the chemicals used in the tannery processes are presented.

Membrane processes which can be used for removal pollutants from paper industry are presented in eighth chapter.

In chapter 9, the main topic is the use of membrane processes in reclaiming metals from the electroplating, for water recycling in electroless plating, and for water recovery from etching effluents from rinsing stainless steel.

The last chapter of the first volume presents membrane applications in pharmaceutical industry. Membrane processes play a key role in the production of a wide range of medicines. The pharmaceutical industry applies a numerous membrane types from microporous, through ultrafiltration to nanofiltration/reverse osmosis systems, which are designed for sterile filtration, cell harvesting, concentration, and purification of pharmaceuticals.

The role that membrane science and membrane engineering play in our life, justifies growing efforts in the education of young generations of researchers, processes engineers, and environmental specialists, based on their basic properties and on their possible applications. The book *Membranes in Clean Technologies. Theory and Practice* has been written with the scope of contributing to these efforts.

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Faber K., (2000), *Biotransformations in Organic Chemistry –* A Textbook, vol.VIII, 4th Edition, Springer, Berlin-Heidelberg-New York.

*** *Handbook of Chemical Engineer,* (1951), (in Romanian), vol. II, Technical Press, Bucharest.

Symposium volumes: Names and initials of authors; year; article title; full title; symposium abbreviated; volume number; place; date; page number:

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