



“Gheorghe Asachi” Technical University of Iasi, Romania



CONVERTING END-OF-LIFE PLASTIC WASTE INTO METHANOL: THE GASIFORMING™ PROCESS AS NEW, EFFICIENT AND CIRCULAR PATHWAY

Kristiano Prifti¹, Andrea Galeazzi¹, Irene Margarita², Andrea Papale², Sergio Miele³,
Enrica Bargiacchi³, Massimo Barbieri⁴, Michelangelo Petea², Flavio Manenti^{1*}

¹Politecnico di Milano, CMIC Dept. “Giulio Natta”, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

²ACEA SpA, P.le Ostiense 2, 00154 Roma, Italy

³INSTM, Interuniversity National Consortium for Material Sciences and Technologies, Via G. Giusti 9, 50121 Firenze, Italy

⁴Politecnico di Milano, Technology Transfer Office, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

Abstract

The mixed plastic waste problem is becoming an important issue in scientific and technological communities in light of the environmental pollution caused by its poorly management. In this paper a new and efficient thermo-catalytic pathway to convert plastic waste into methanol is presented in its key features and global yields. The process has been mainly developed in silico using Aspen HYSYS V10 with support from experimental data where simulation could not provide reliable information such as the gasification step. Consolidated kinetic models are used both for the reforming and methanol synthesis steps, while the pre-reforming reactor is simulated at the thermodynamic equilibrium. The temperature, pressure, and mass flow balances of the system are reported alongside some of the most important key performance indicators for reforming (methane slip) and methanol synthesis (SN ratio).

Key words: circular economy, methanol, plasmix, plastic wastes, process simulation

Received: April, 2020; *Revised final:* August, 2021; *Accepted:* September, 2021; *Published in final edited form:* October, 2021

1. Introduction

Worldwide plastic production in 2017 was estimated at 348 million tonnes (PMERG, 2018) with a strong rising trend that has seen the rate of production rise from 202 million tonnes in 2002 up to 368 million tonnes in 2019 with no signs of slow down.

The total European demand in 2019 amounted to 50.7 million tonnes, with packaging applications consuming 39.6% of this figure, the construction (20.4%) and the automotive (9.6%) sectors following as the main plastic consumers in Europe. However, while the expected turnover of plastics in the construction and automotive sector could be qualitatively guessed to be in the order of years, the

life span of a packaging application is typically very short and exhausts its purpose after a single use. These large volumes of waste generated within a short time have led to significant dispersion of plastic waste in the environment (Ilyas et al., 2018) leading to a new set of pollution issues concerning, in particular but not limited to, marine pollution (Jambeck et al., 2015). The packaging sector, being the most important one in terms of yearly plastic waste generation, is characterized by a specific subset of polymers.

These polymers are: Low Density PolyEthylene (LDPE), Linear Low-Density Polyethylene (LLDPE), Medium Density PolyEthylene (MDPE), High Density PolyEthylene (HDPE) which will be referred to simply as PE from now on, PolyPropylene (PP), PolyEthylene

* Author to whom all correspondence should be addressed: e-mail: flavio.manenti@polimi.it

Terephthalate (PET), while combined PolyStyrene (PS) and its Expanded variant (EPS) make more than 85% w/w of the total packaging plastic demand.

The same distribution can be seen in post-consumer plastic waste in Table 1. The end of life of this waste mixture has drastically changed in recent years spurred both by European endeavours for a more sustainable economy, synthesized in the European Green Deal and in the EAP for 2030, and by China’s 2017 National Sword policy which imposed stricter restrictions on recyclable plastics imports and drastically reduced the country’s imports. This led to a reduction of recyclable plastic exports outside the EU by 39% from 2016 to 2018 making available for recycling further 29.1 million tonnes of collected plastic waste. Of this figure, only 32.5% was recycled and brought back to the market as a consumer product. Energy recovery is still the primary treatment method for plastic waste, being used on 42.6% of the waste.

The residual plastic, about 7.2 million tonnes, has no current application and is destined to landfill. This numbers vary greatly depending on the considered country, with landfill restrictions playing a major role in the split between landfill and energy recovery as shown in Fig. 1. The current primary recycling method used at industrial level is melt blending, popular due to its cheap, large-scale, solvent free nature and relatively extensive range of plastics to which it can be applied (Schyns and Shaver, 2021). This technique is applied through an extruder to induce thermal softening and plasticization of the polymeric waste and extrude the material into new pellets. The thermal treatment of the plastic over time will lead to degradation of the polymeric chains and loss of mechanical performance, which will be exacerbated by the presence of contaminants in the

polymeric matrix.

Table 1. Mass composition of post-consumer plastic waste in Italy as reported by COREPLA in 2018 (COREPLA, 2019)

Polymer	Weight fraction %
PE	40
PP	25
PS	15
PET	7.5
PVC	2.5
Others	10

When different large enough polymers are mixed their Gibbs free energy will disfavour their blending, causing phase separation that will lead to very poor mechanical performance of the resulting mix (Flory, 1953). Due to inefficiencies in the sorting of the waste and accumulation of contaminants only a limited number of mechanical recycling cycles is possible (La Mantia et al., 2017).

The growing pressures towards the management of plastic waste have pushed towards new pathways that could make use of the portion of plastic waste currently destined to incineration and landfill to make new consumer products. The elemental composition of plastics, strongly resembling that of a crude oil vacuum distillation residue from the point of view of physical properties, while being relatively rich in hydrogen with a known aromatic content, makes the feedstock interesting as a crude oil alternative, also considering that the largest European plastic users (Germany, Italy) also lack this natural resource. For these reasons chemical recycling pathways have started to attract a lot of attention in recent years.

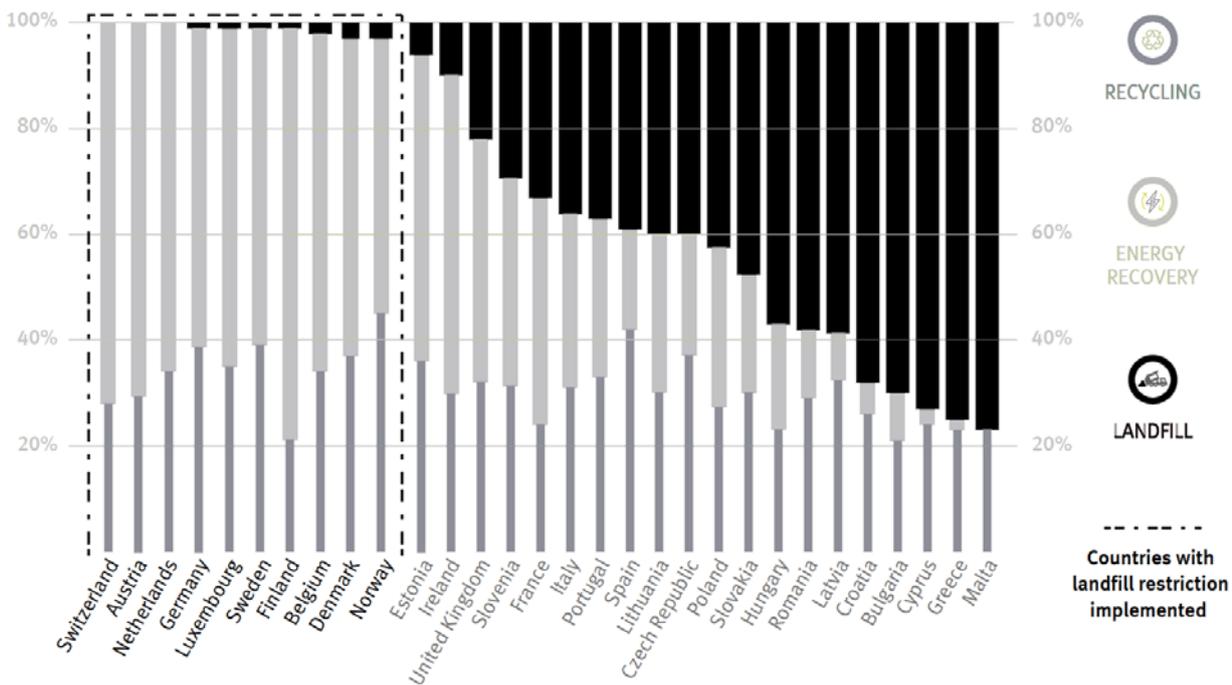


Fig. 1. End of life of plastic waste in EU countries (PMERG, 2018)

The current focus is on Pyrolysis to produce fuel gas and synthetic fuels (Encinar and González, 2008; Onwudili et al., 2009; Wu and Williams, 2010; Ranzi et al., 2016) with positive effects on global emissions with respect to incineration (Quantis, 2020). The process itself, being endothermic, necessitates for important energetic inputs which constitute an important part of the footprint of these plants. Another chemical thermal treatment is based on gasification techniques, typically implemented in fluidized bed reactors with similar designs to those currently used for biomass (Wu and Williams, 2010; Lopez et al., 2018).

Plastic gasification plants of industrial scale are not yet operative, however experimental campaigns have been carried out to evaluate feasibility and yields of the process. Arena et al. (2010) investigated yields at different temperatures and with various fluidizing supporting agent of different synthetic plastic feedstocks as well as sorted plastic refuse waste. An extended review on plastic waste pyrolysis, steam gasification and co-gasification of plastic waste with biomass and coal was carried out by Lopez et al. (Lopez et al., 2018) showing that plastic waste gasification plants at the moment are still not diffused, and how they differ from biomass and coal mature technologies. The most important difference shown by Ahmed and Gupta (2011) and Lopez et al. (2016) concerns the fact that char gasification is not the limiting kinetic step in plastic gasification as it is the case with biomass and coal and consequently limited solid residue is present.

Moreover, as seen in Pinto et al. (2003) by combining gasification with a fixed bed of Dolomite and Ni-Alumina it is possible to reduce residual tar to negligible contents. Similar results are obtained using commercial reforming Ni catalyst operating at a temperature up to 600°C downstream of a spouted bed by Lopez et al. (2015), which also showed improved hydrogen yield. A similar approach was used in this simulated work to deal with possible residue tar. The patented design is applied to achieve gasification of the plastic waste with low CO₂ yield in mild

conditions approaching optimal conditions for Methanol production.

2. Material and methods

Inspired by the design of the Texaco process for asphalts gasification the Gas-forming process applies a similar concept to plastic waste. The layout shown in Fig. 2 involves the pre-treatment stages of the plastic waste up to their gasification and preliminary reforming. The waste is first milled in mechanical unit (Unit 1) operating in ambient conditions, reducing the characteristic dimensions of the plastic waste to a diameter of a couple centimetres. These pellets are then immersed in two successive tanks with a different solvent in each. The first solvent is water in which PP, PE and most of the PS will float, while PET and PVC will sink. In a second tank brine with a density of 1350 kg/m³ is used, PET and rigid PVC will still sink while flexible PVC will float, this fraction of PVC, being the majority of polymer in the mix, is removed while the PET PVC mixture is sent is collected at the bottom (Unit 2). The collected PET and PVC are washed to remove deposited salts (Unit 3) and then sent, alongside the other polymers collected as floating material in the first sedimentation tank, to the pre-melter (Unit 4). In Unit 4 the plastic mix is heated at a temperature of 300°C. At this temperature, the mixture will behave as a liquid and partially react decomposing in light components. The residual PVC in particular will release chlorine as HCl (Ranzi et al., 2016) which can be removed from the system alongside a minor quantity of light components which will be sent to gas treatment. The liquid plastic mix is sent to a second melting tank (Unit 5) where the temperature is further raised to 350°C to improve viscosity. Light hydrocarbons released in this tank are collected and sent to the gasification chamber while the liquid is sent to a pump (Unit 6) to be pressurized at 15bar for atomization. Finally, the plastic melt is mixed in a twin fluid atomizer with mid pressure steam and pure oxygen and ejected through a nozzle in Unit 7 losing up to 5 bars in the atomization step.

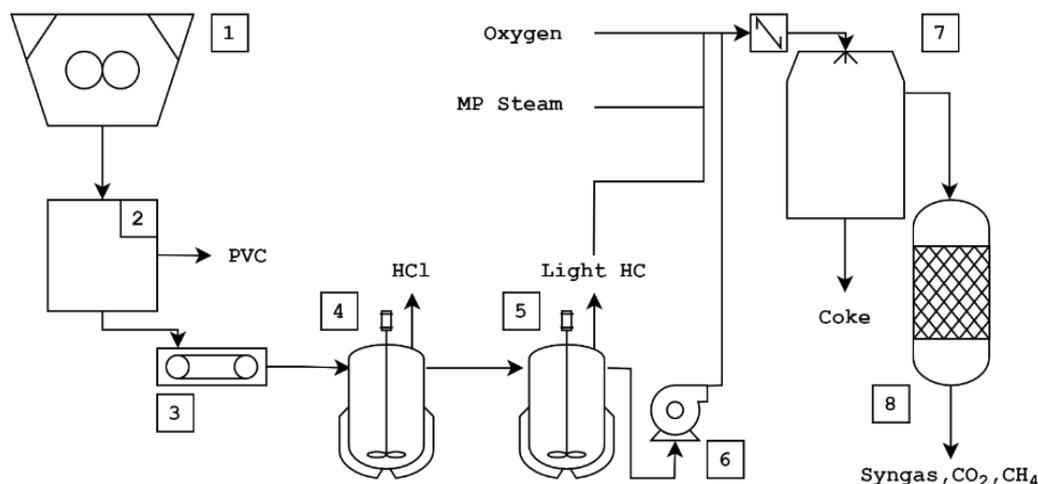


Fig. 2. Gasiforming process layout

In the gasification chamber a series of reactions degrade the polymer mix to hydrogen, carbon monoxide, carbon dioxide, methane, ethane, propane, ethylene, toluene, benzene, and carbon coke. Carbon coke is collected at the bottom of Unit 7 while the gaseous stream, still rich in heavy and aromatic hydrocarbons is sent to a pre-reforming unit (Unit 8) where ethane, propane, benzene, and toluene are degraded to methane and syngas. The richness of the syngas in CO₂ coming from the gasification makes the feedstock suitable for methanol synthesis.

The syngas is first mixed with more medium pressure steam and fed to a steam reforming unit (Unit 9) where methane is converted to syngas. Steam is added with a H₂O/CH₄ ratio higher than 3 due to the difficult conversion and high methane slip in the reformer caused by the presence of CO and H₂ in the feed that further complicate the thermodynamically limited reactor (Farshchi Tabrizi et al., 2015); the same reason stands for the unconventionally low operating pressure of the unit. The residual heat in the output is captured by a series of exchangers and then fed to a flash (Unit 10) where the condensed water is removed before compression to 80bar (Unit 11). Typical pressures for methanol synthesis go from minimum values of 60bar up to 120 bar (Mäyrä and Leiviskä, 2018), the value of 80 bar was considered a reasonable middle operating point for adiabatic bed reactors operated with commercial CZA (Cu-Zn-Al) catalyst. A crucial optimization parameter for methanol synthesis is the Stoichiometric Number defined as Eq. (1):

$$SN = (H_2 - CO_2)/(CO + CO_2) \quad (1)$$

In the analysed system there was an excess of CO₂ which had to be removed. A patented system using physical adsorption with water (Unit 12) was applied to remove food grade quality CO₂ from the syngas, which was then sent to a two stage, intercooled, adiabatic methanol reactor (Unit 13) and finally to a distillation column as shown in Fig. 3.

In the current work a simplified simulation of the plant starting from Unit 8 is presented. The exclusion of the mechanical pre-treatment and melting phases is due to their relatively low complexity (Units

1, 3 and 6) and the lack of appropriate kinetics (Units 4 and 5) to make the simulation of that section possible in Aspen HYSYS V10. Unit 7 yields were found with two experimental campaigns in a fluidized bed reactor described in detail in Parrillo et al. (Parrillo et al., 2021). Moreover, PET and PS were not available for the validating experimental campaign in the desired quantities, so a synthetic mix of polymers was used to simulate the waste: 49% w/w HDPE, 49% w/w PP, and 2% EPS.

Finally, the steam generating capacity of the experimental plant was not able to provide more steam than the input used in this work, which represented an operating limitation of the experimental campaigns. During the experimental campaign, the gasification unit was operated at atmospheric pressure at a steady state average bed temperature of 785°C with air (instead of pure oxygen, which was not available). The feed consisted in 35 kg/h of plastic mix, 23 kg/h of oxygen, and 12 kg/h of steam. Several simplifying assumptions were made at this stage:

- Negligible effect of pressure on the system yield and product distribution, which is not correct (Li et al., 2010), but was considered negligible for a 8bar difference and a preliminary feasibility stage.
- The yield of a fluidized bed reactor is not significantly different from the yield of the atomized reactor as both systems will reasonably reach thermodynamic equilibrium at the outlet (Silva et al., 2019)
- Nitrogen is inert in the system and does not significantly influence the chemistry of the reaction. The presence of nitrogen will lower the partial pressure of the system and, for what said before, influence in a small extent the yields, this effect is considered negligible also in this case due to the low pressures of the system.

While these approximations introduce significant errors in the system due to unreliable predictions on the performance of the atomization chamber, they still represent a relatively accurate prediction of what can be obtained from a plastic waste mixture through gasification and are in line with other previous literature (Brems et al., 2013; Lopez et al., 2018; Ragaert et al., 2017).

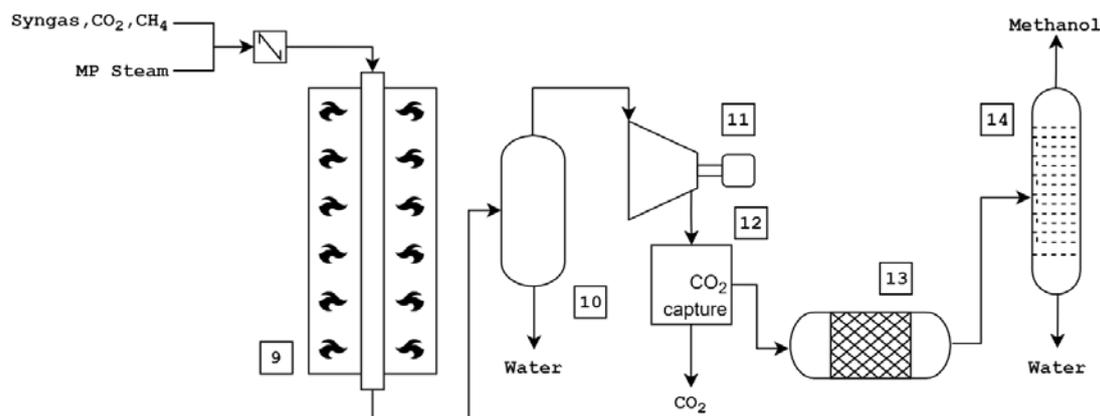


Fig. 3. Methanol synthesis from Gasiforming process

Moreover, this source of error is further dampened in its effects by the presence of a Gibbs reactor operating at 500°C after the gasification chamber. The purpose of this reactor is to degrade residual tar and favour the water gas shift reaction. Since the outlet of the Gibbs reactor will be at thermodynamic equilibrium the effect of pressure variation in the gasification chamber will be compensated for in this step.

The feedstock to the plant was normalized after removing nitrogen which cannot be tolerated in the system since it would require complex separation techniques. This stream was set at 10 bar and introduced in Aspen HYSYS V10 at 785°C. Flowrate was scaled to treat 1000 kg/h of plastic mix since this value is the target dimension for the experimental plant to be build and every flowrate was scaled proportionally leading to 1000 kg/h of plastic waste, 658 kg/h of pure oxygen, 344 kg/h of steam. From the experimental campaign negligible formation of solid was observed, while tars, represented in the simulation by naphthalene (Lopez et al., 2018), were present in significant amounts. Aromatics, especially benzene were also measured in significant quantities. The detailed composition of the gasification output is reported in Table 2.

Table 2. Normalized composition obtained from experimental campaign at 1 bar, 785°C

<i>Component</i>	<i>mol/mol</i>
Hydrogen	11.7
H ₂ O	24.4
Naphthalene	0.3
CO	8.0
CO ₂	19.7
Methane	17.5
Ethane	12.5
Propane	0.4
Acetylene	0.5
Ethylene	2.0
Toluene	0.2
Benzene	2.8

This stream was used as an input in Aspen HYSYS V10 simulation. After being cooled at optimal temperature of 500°C in a process-process exchanger to generate steam, the hydrocarbon mixture is fed to a pre-reforming unit operated adiabatically (Christensen, 1996). The unit in HYSYS is simulated as a Gibbs reactor accounting only for thermodynamics, but this situation is considered in line with conventional pre-reforming operation (Christensen, 1996). The reactor results in an exothermic behaviour rising the temperature of the syngas at 597.5°C. While several endothermic reactions take place in pre-reforming units, the exothermic water gas shift reaction is also significant, and due to the higher concentration of water and carbon monoxide with respect to higher hydrocarbons an overall exothermic reaction is observed. Steam is added to the stream until the H₂O/CH₄ ratio is 4 and

fed into a reforming unit at a inlet temperature of 422.5°C. The lower inlet temperature (typical value is 500°C) is tolerated here because of the low concentration of methane that gives the system more thermal inertia and makes it less endothermic. The steam reforming reactor is modelled as a PFR with Xu-Froment reaction kinetics with commercial Ni based catalyst (Xu and Froment, 1989) operated at a pressure of 899 kPa and at an outlet temperature of 900°C, achieving methane conversion of 92.2%, with an outlet H₂/CO ratio of 2.977. The high H₂/CO ratio is determined by the pre-reformer which consumes water to break down the heavy hydrocarbons while introducing further hydrogen in the stream components. The stoichiometric number is low (1.47) due to excess presence of CO₂. Before compression water removal is necessary. The stream is cooled down to 50°C while generating the medium pressure steam necessary for the reformer. Condense water is removed and the syngas is sent to a two-stage intercooled compression system to be pressurized at 80bar. After compression, the SN ratio is regulated using a patented CO₂ removal technique capable of removing 568.3 kg/h of CO₂ with a minimal loss of 0.71 kg/h of H₂ and 4.37 kg/h of CO and requiring 190.7 electrical kWh. The sweetened syngas, now having a SN of 2 is then fed to the methanol synthesis loop. Two PFR adiabatic reactors are used in series with an intermediate cooler. The first reactor is fed with syngas at 220°C (temperature at which the copper-based methanol catalyst is active) and the stream exits at 328.4°C in thermodynamic equilibrium. The second stage is still fed at 220°C but the output is at 301.9°C degrees due to lower conversion in the second stage. In both reactors Graaf kinetics for CZA catalysts are used (Graaf et al., 1988). The crude methanol mixture is cooled to 65°C by pre-heating the syngas feed to the first reactor and in an exchanger later. A flash at 77.4bar is used to separate the unconverted syngas, which compressed back at 80bar to recover the pressure drops, from the crude methanol that is collected and sent to a methanol distillation system.

The separation section is subject to another issue. Due to the kinetic scheme used crude methanol contains only methanol and water, which is not the case in actual methanol plants (Ross, 1986), where also higher alcohols and ethers are formed during synthesis. The yields of each depend on the specific catalyst and operating conditions of system. Assuming the simple case simulated is true, it makes the downstream trivial and 99.5% mol/mol Methanol can be distilled with a single 12 stage column with 99% component recovery. In a more complex case (Zhang et al., 2010) multiple columns are necessary to achieve high purity of methanol. The detailed Aspen HYSYS V10 flowsheet is reported in Fig. 4. The reported plasmix se feed consists in n-C30, which acts as a stand in for the polymer plastic mix to allow a gross estimate of the necessary duties for heating and pumping the material. In the Gasification Chamber

sub-flowsheet, the experimental data is used to reconstruct the output of gasification.

3. Results and discussion

The simulation carried out for a preliminary investigation of the feasibility of methanol production from plastic waste showed interesting potentiality in its ability to generate 1.35 ton/h of 99.5% pure methanol starting from 1 ton/h of generic plastic waste. In Table 3 the material streams as simulated are reported in key positions in the plant. Several optimizations are being considered at this stage of development but were not implemented as new experimental campaigns are necessary to validate the behaviour of the pre-reformer and its ability to tackle the degradation of tars, which are thermodynamically unfavoured as the simulation shows, but the kinetics and the limits of HYSYS in predicting actual coke formation could lead to significant issues during plant operations and thus lower overall methanol yields.

The formation of solid residues in the gasification chamber is a significant concern despite not being observed in the two experimental campaigns currently performed in fluidized beds. This could lead to the formation of coke, in a best-case scenario, or an undefined ash with high carbon content. Both scenarios are not necessarily bad, since the design of the chamber can easily cope with solid particles and the formation of coke would lead to higher hydrogen content in the formed syngas, but they require changes in the plant design to account for possible solid entrainment. Moreover, the presence of unknown compounds and the naturally evolving nature of waste could involve the presence of unforeseen compounds in the stream. This issue is considered unlikely to be problematic in actual operations since waste collected

over a large basin exhibits only marginal seasonal changes and is overall stable in composition. Vulcanized rubbers might introduce sulphur-based compounds in the system which are harmful to the catalyst of the reformer and pre-reformer, but rubbers are typically removed and collected in previous treatment stages of the waste since the presence of sulfurated compounds is harmful even in case of incineration.

A similar role might be taken by additives used in plastic manufacturing and contaminants of metallic nature which must be removed either prior to reaching the plant or in the in the melting units. The case of metallic residues being particularly easy as they can be separated by simple decantation once the plastic is liquefied. Finally, the melting phase effects on the properties of the plastic mix is subject to significant predictive errors due to the fact that the correlations used for the computation of viscosities and properties of the polymers in the mix (Cornish, 2012) are regressed on data that seldom comes near to the pyrolysis temperatures ($T > 250^{\circ}\text{C}$).

While there is significant margin for error there is also a really appealing yield of the plant made even more interesting by the role methanol can have in a hydrogen-based economy as a transition element.

4. Conclusions

The design of a plastic wastes to methanol process was shown and described in its most important features. While several issues require to be addressed in a manner not suitable for simulation and significant room for optimization and improvement is still present the yield showcased yield already makes a case for an interesting alternative to direct incineration of the plastic waste and pyrolysis.

Table 3. Temperatures, Pressures, and Flowrates measured in kg/h of each component in specific points in the plant reported in Fig. 4

	1	2	3	4	5	6	7	8	9	10
T [°C]	350	500.0	597.5	422.5	50.0	21.4	301.9	34.0	65.0	52.6
P [kPA]	1500	999.0	999.0	899.0	899.0	8000.0	7740.0	200.0	200.0	150.0
H ₂	0.0	18.4	15.5	15.5	271.5	270.7	778.8	0.5	0.0	0.0
H ₂ O	344.1	343.0	69.8	3096.5	55.6	2.0	138.3	137.2	136.3	0.4
naphthalene	0.0	29.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO	0.0	174.3	383.1	383.1	1266.9	1262.6	2356.7	2.3	0.0	0.0
CO ₂	0.0	674.9	844.6	844.6	1198.4	641.9	2397.2	79.1	8.3	8.3
CH ₄	0.0	219.2	689.4	689.4	53.5	53.5	530.8	1.9	0.0	0.0
C ₂ H ₆	0.0	292.7	0.5	0.5	0.5	0.5	4.4	0.0	0.0	0.0
C ₃ H ₈	0.0	15.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₂	0.0	10.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₄	0.0	43.9	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Toluene	0.0	13.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Benzene	0.0	167.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
O ₂	658.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₃ OH	0.0	0.0	0.0	0.0	0.0	0.0	1485.1	1402.9	1357.6	1344.0
PE	490.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
PP	490.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
PS	20.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TOT	2002.7	2002.8	2002.8	5029.4	2846.3	2231.2	7691.4	1623.9	1502.2	1352.6

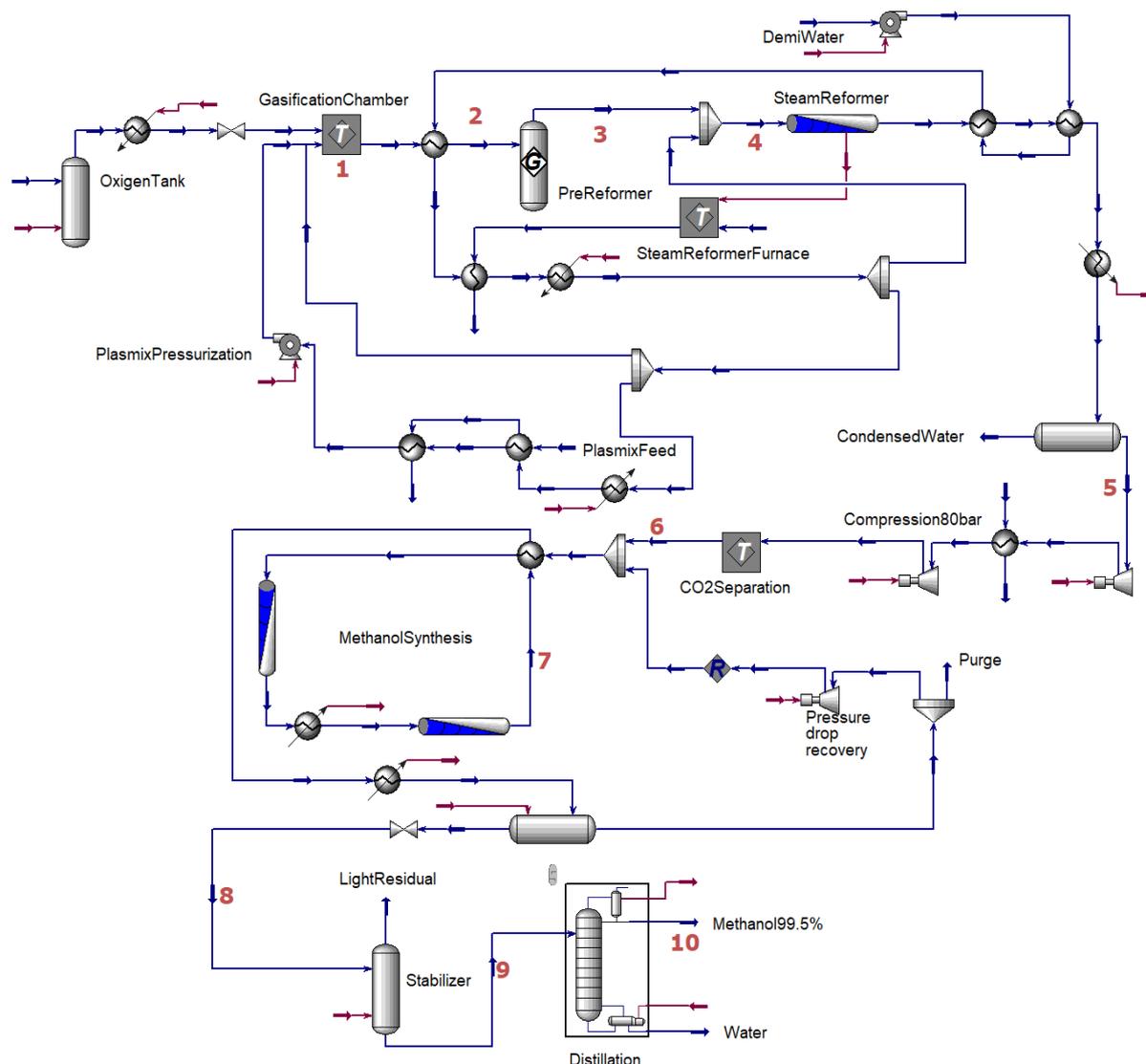


Fig. 4. Plant layout in Aspen HYSYS V10

The choice of methanol as a product is related to the significant presence of CO₂ in the system, but the availability of low-cost syngas from plastic waste could lead to several new pathways to commodity chemicals such as ammonia (enriched air gasification would be feasible in this case), dimethyl ether (further CO₂ utilization) and direct hydrogen production (simplest plant design with WGS reactor after the reformer).

This solution is even more interesting in realities like those typical of Europe where plastic collection is well developed, the densely populated urban areas produce a reliable and continuous amount of waste, hydrocarbon natural sources are not present, but methanol is in high demand for its role as gasoline additive.

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