



Treatment of pyrolysis oil in the context of plastics recycling

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Abstract— Mixed plastic waste pyrolysis oil (PPO) is a suitable feedstock for steam-cracking to recover monomers such as ethylene or propylene to name a few. As part of a year-round project at the University of Liège, students have investigated the design and environmental implications of an upgrading process required for PPO prior to steam-cracking. This process aims to mitigate risks of fouling in the cracker mainly due to the presence of unsaturated compounds in the oil. On TotalEnergies' suggestion, an adapted version of their patented upgrading treatment is discussed on the basis of an Aspen Plus model. In this paper, the reader can find a comprehensive overview of the thermodynamic model, reaction kinetics, and separation units employed in the process implementation. Besides, a discussion about the way that heat integration was used to optimise the process by reducing energy requirements is presented. Additionally, a cost evaluation is carried out to assess economic feasibility, followed by a life cycle analysis that evaluates potential environmental improvements. Overall, this paper provides a detailed examination of the key factors influencing the efficiency, cost, and sustainability of the process. This report concludes on the necessary further research of the project in a European industrial hub.

Keywords— Plastics recycling, pyrolysis oil treatment, process design, Aspen Plus modelling

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2.5.3	Aspen validation	6		Although more than 29 million tonnes of plastic waste were collected across Europe in 2019 [1], only a third of it was treated in recycling facilities while the majority was either landfilled or incinerated for energy recovery, contributing to pollution along with littering [2]. It is believed that the promotion of a proper circular logic would massively contribute to our economy. In a trend report of the European plastics industry [3], a representative at SABIC declared that “there is currently greater demand for recycled plastics than the supply available” and that scaling up will be crucial to instigate real change. However, most of the waste is still downcycled into materials with low-value or niche applications which have been struggling to motivate manufacturers and investors [4].	
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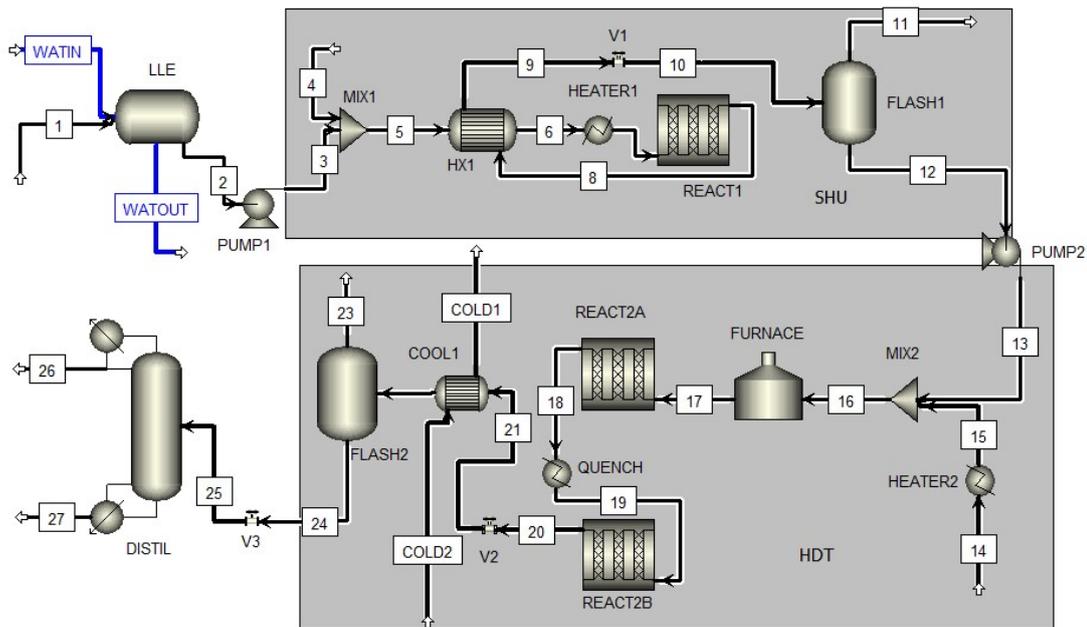


Fig. 1: Process flowsheet

cycling, tertiary (chemical) recycling, and quaternary recycling or energy recovery. Hopewell, Kosior and Dvorak (2009) [5], state that: "recycling has been shown to save more energy than that produced by energy recovery even when including the energy used to collect, transport and re-process the plastic".

Despite the clear advantage of mechanical recycling energy-wise over chemical recycling [6], it is not suited to the large-scale recycling of any polymers. In this matter, chemical recycling, and pyrolysis, propose a viable solution for mixed plastic waste.

Pyrolysis consists in heating up plastic in the absence of oxygen to break down its constituents into smaller molecules, resulting in a plastic pyrolysis oil (PPO) and char. This oil can either be diluted with fuel, or steam-cracked into plastic monomers. Another product yielded by pyrolysis is a hydrocarbon-rich gas that can be used in energy recovery units [7]. The process is nonetheless hindered by the high content in unsaturated compounds that are prone to cause coking in the steam-cracker. Along with these, other metal and nitrogenated impurities can poison the catalysts used in the cracker whilst oxygenated and chlorinated compounds are corrosive, and generally unwanted in the final, recycled product.

To tackle these issues, the proposition of TotalEnergies' R&D team is to adapt an existing process that has proved successful for the catalytic hydrogenation of gasoline [8]. The following article will shed more light onto the composition of this oil and the specific issues of this process regarding the pyrolysis oil of plastic waste particularly.

Incidentally, pyrolysis as in plastics-to-fuels recycling is considered a mature technology as several operating start-up-sized commercial plants were identified and have been running for years [9, 10]. As far as plastics-to-plastics recycling is concerned, "the only plant that has been in operation at a commercial scale for over a decade is that operated by

Plastic Energy in Spain" [11] which is targeted at PE and PP recycling exclusively [12]. The scope of the process at hand is actually enlarged to poorly sorted municipal plastic waste.

In this article, chemical engineering students at the University of Liège study this proposal through simulation on Aspen Plus with the help of an engineer at TotalEnergies' R&D. Focus is cast upon the hydrotreatment step of the PPO in order to provide a detailed analysis of its mechanism, operation, and significance in the chemical recycling pathway. The challenges that remain to be addressed are also discussed to fully realise the potential of pyrolysis as a sustainable solution for plastic waste management.

2 PROCESS

2.1 General description

As stated in the introduction, the pre-treatment of the PPO is the core of the present study. Fig. 1 describes all the units and required equipment in the form of a process flow diagram (PFD) representing their connections with each other. This process is designed to treat 10 t/h of PPO. The starting point of the studied process is the patented pre-treatment unit from TotalEnergies [8]. It consists in both cases in the selective hydrogenation of conjugated dienes, followed by the complete hydrogenation of all unsaturated compounds, up to about 90% conversion, and hydrotreatment of impurities to almost complete elimination in the form of light gaseous products like ammonia, HCl, H₂S and water that are stripped away in flash tanks. All reactions are carried out continuously and used catalyst. Both reactors operate at high temperature and pressure conditions. Finally, a distillation column clears the PPO from its heaviest fraction that would again become a liability in the steam-cracker because these heavy products are not vaporised, prone to coking compounds.

Starting at the inlet of the process (see Fig. 1), the extractible impurities of the oil are water-washed in a decanter

unit. When it reaches the inlet of the first reactor (REACT1) in the selective hydrogenation unit (SHU), it has been mixed in with an excess of pure hydrogen that reacts once dissolved in the oil. A first difference with the conventional hydrogenation process is the absence of a recycling stream back into the reactor because its goal was primarily to slow down the reaction to restrain the exothermicity, but PPO does not release as much heat as pygas does [13]. Secondly, there is no further separation than the removal of gases before entering the hydrotreatment unit (HDT). Originally, several strippers isolate lighter fractions of the oil up to *n*-hexane which is also the smallest molecule reported in the PPO. However, gases separation is maintained because the HDT operates at higher pressure conditions and, generally, no gas phase is allowed in a pump because it is very energy-inefficient to try and compress a gas.

A fresh input of pressurised hydrogen follows immediately. Then, two different catalyst beds (REACT2A, REACT2B), with different catalysts, are separated by an interbed quench. It was chosen in this study to simply consider this as a cooler unit, although the name “QUENCH” remained. The first catalyst helps saturate the remaining unsaturated hydrocarbons whilst the second scraps the impurities. This distinction between the two beds results in the presence of a third reactor in the PFD. All reactions occur in the gas phase and the hot output flow of the reactor is cooled down once more. The liquid outlet of the subsequent flash tank is fed to the distillation column where so-called “heavies” are sorted out. The saturated oil (final product) then gets to be steam-cracked but this is out of the scope of this article. The gas outlet can be recycled because it contains an important excess of hydrogen but, again, it was chosen to ignore this feature.

More complete descriptions of separation units, reactors and heat exchangers can be found in the corresponding sections. Information about their modelling and simulation are provided and later analysed in the report as data for cost analysis and life cycle assessment.

2.2 Composition

One of the biggest challenges for the realisation of this project turned out to be the modelling of the PPO based on TotalEnergies information. In Aspen Plus, the chemical properties of all molecules are user-defined for the most part. In that respect, all reaction mechanisms and kinetics must be implemented directly (see section 2.4). On the other hand, physical properties including the density, the viscosity, the heat capacity, the boiling point, or the solubility were predicted numerically through thermodynamic models (see section 2.3). The struggle to fit these properties even remotely to the experimental data provided by TotalEnergies was strongly interfering with the simple objective of representing the composition accurately. Because design was mostly dependent on conversion, the composition-based model was preferred and only the most important physical properties to the design, such as the solubility of hydrogen in the liquid oil and heat capacity, are discussed in this report.

The PPO was characterised through GC-MS and GCxGC by TotalEnergies so that a variety of hydrocarbons could be identified and quantified in the mixture. In decreasing or-

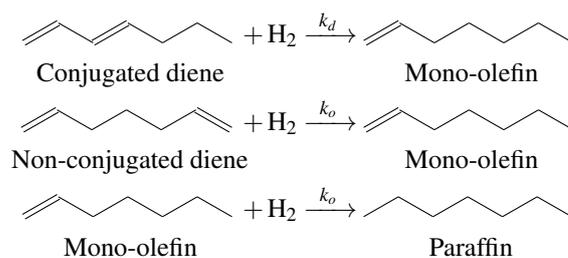


Fig. 2: Hydrocarbons hydrogenation

der of abundance, the model incorporates linear and ramified paraffins (44.3%), singly unsaturated olefins and dienes (29.5%), naphthenes (15.8%), aromatics (10.3%) and impurities. The main criterion for the selection of model molecules was that all these *fractions* get the right proportions of the total mass of PPO. Furthermore, all fractions were further discriminated with respect to the chain length of molecules. To this end, mass fractions of entire classes of molecule sizes are lumped into one representative molecule of average chain length. Significant quantities of molecules were identified to have as many as 30 carbon atoms with a minimum of 6 (*n*-hexane or benzene) so lumping was necessary to reduce the size of the model to a reasonable number of molecules. It must be noted that not all molecules are involved in chemical reactions. Out of all the molecules listed above, the only reactions considered in this model are the hydrogenation of diolefins into mono-olefins, and mono-olefins into paraffins eventually. The number of insaturations as well as the content in conjugated dienes was identified too, in such a way that it was necessary to consider two kinds of diolefins: conjugated and non-conjugated, the former being more reactive than the others (see Fig. 2). This effect is documented by several sources [8, 14].

Finally, the mixture is also contaminated with impurities containing Cl, N, O and S. Out of all the molecules identified by TotalEnergies, only the most frequent and/or detrimental to the process (e.g. carboxylic acids) ended up in the model. They are all collected in Fig. 3. The latter figure presents all considered hydrogenation reactions for these impurities. Main products of hydrogenation are hydrogen chloride, ammonia, water and hydrogen sulphide. It was assumed that, since these impurities only make up for a minor fraction of the bulk, their other products—that will be referred to as by-products from now on—do not matter and the most simple solution is always considered. Lastly, chloride also exists in the oil in equilibrium with its dissolved ions but as the reader will find out later, it only enters the reactor in negligible amounts (see section 2.6.1).

2.3 Thermodynamic model

In order to simulate a pyrolysis oil hydrotreatment process, it is necessary to select an appropriate thermodynamic model that accurately represents the mixture of hydrocarbons and hydrogen under the pressures range of the process[15], i.e. from 1 to 50 bar. To select a model, experimental data of liquid-vapour equilibrium curves for binary mixtures found in Aspen data base are compared with thermodynamic model

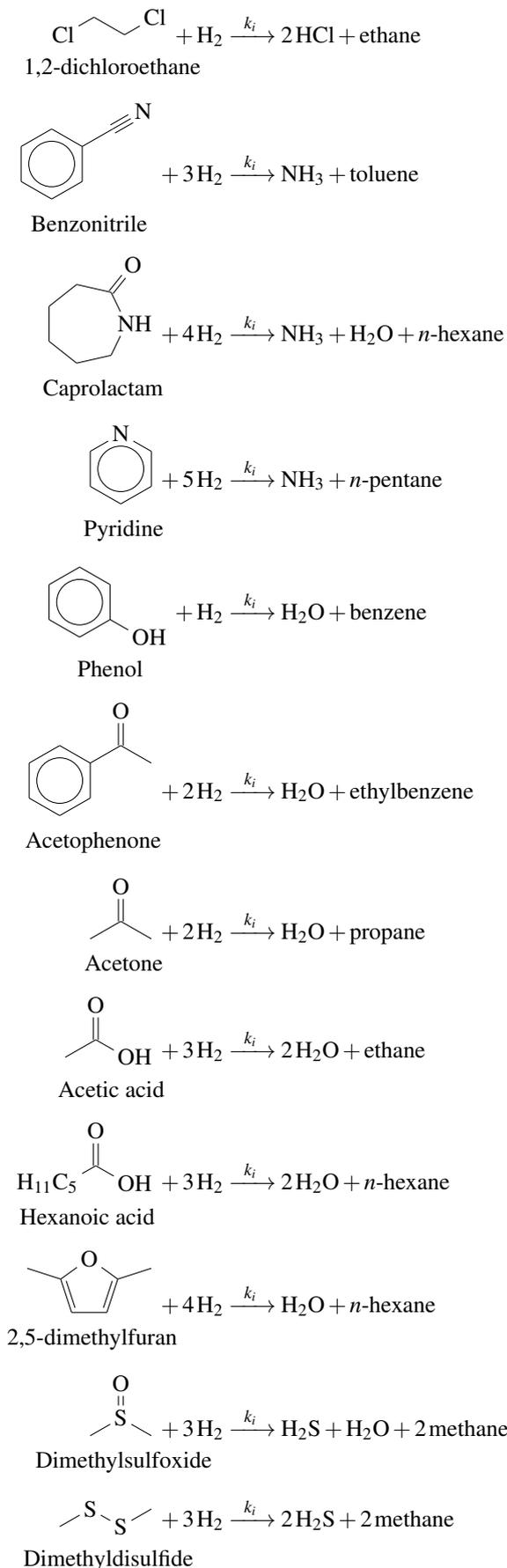


Fig. 3: Simple reactions of the impurities

simulations as shown in Fig. 4. In this figure, the mixture is benzene-hexene and the models used are Benedict-Webb-Rubin (BWR), Peng-Robinson (PR), Predictive Peng-Robinson (PPR) and Soave-Redlich-Kwong (SRK). After comparing several binary mixtures, it was determined that the Peng-Robinson model produced the best results.

The Peng-Robinson model is a cubic equation of state that is commonly used in the petroleum industry to model the behaviour of complex hydrocarbon mixtures. It is known to provide accurate results for a wide range of temperatures and pressures, making it a suitable choice for the simulation of the hydrotreatment process [16].

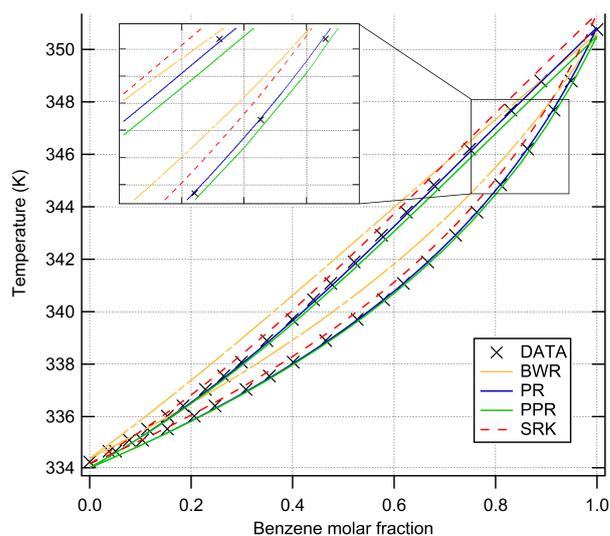


Fig. 4: T_{xy} diagram of benzene/*n*-hexene at 1 bar

However, this model does not accurately represent the solubility of hydrogen in the liquid phase of the mixture, which is an important property in hydrotreating processes.

To address this issue, the predictive version of the Peng-Robinson (PPR) model was considered. Firstly, the model reproduces the experimental data accurately, as shown in Fig. 4. Secondly, this model allows for the estimation of missing binary interaction coefficients between hydrogen and hydrocarbons using a group contribution method.

It is critical to validate that the predictive Peng-Robinson model accurately models the hydrogen solubility in the plastic pyrolysis oil, as the reactivity in the SHU reactor is governed by the concentration of hydrogen in the liquid phase and thus its solubility. To compare the predictive Peng-Robinson model with the classical one and determine the more suitable model for modelling hydrogen solubility, Aspen simulation results were compared to experimental data for pure compounds and complex mixtures under conditions close to the process.

For the hydrogen solubility in pure compounds, experimental data for cyclohexane [17] and benzene [18] were used. The measured hydrogen liquid molar fraction was compared with the Aspen simulation results using both thermodynamic models. The comparison shows that both models are relevant in the modelling of the hydrogen solubility, but the predictive model is more reliable than the classical one.

For the complex mixtures, experimental data for gasoil

[17] and pyrolysis gas [18] were used. For the gasoil study, it was assumed that the composition of the mixture was sufficiently similar to the composition of the gasoil to make a relevant comparison. In the pyrolysis gas study, the exact composition of the pygas was given, allowing for Aspen simulations with the exact same composition. The results indicate that the predictive Peng-Robinson model is suitable for modelling hydrogen solubility in pyrolysis oil, particularly in the pressure conditions of the system as shown in Figure 5. Additionally, the error made by the classical Peng-Robinson model was found to be greater than the error made by the predictive model.

In conclusion, it has been shown that the predictive Peng-Robinson model accurately describes the interactions between the hydrocarbon molecules as well as the hydrogen solubility in the pyrolysis oil. The model is a powerful tool, especially when experimental data are lacking, which is particularly common for heavy hydrocarbon fractions where interaction coefficients are rare. Therefore, the predictive Peng-Robinson model will be used for the hydrotreatment process.

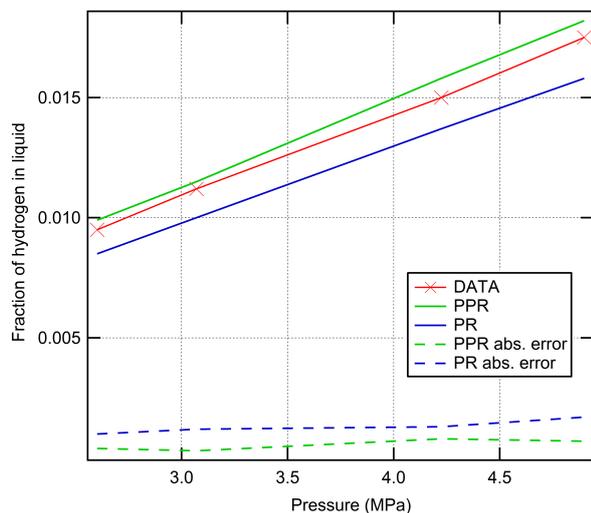


Fig. 5: Hydrogen solubility in pygas at 298K

2.4 Kinetics

The study of kinetics is essential to describe and design the reactors. Due to missing information concerning the kinetic constants and activation energies for the hydrogenation of dienes and olefins as well as for the hydrotreatment of impurities, these values were tuned in order to reach the desired conversion in a determined reactor volume. Both these information were known from experimentation on the pilot unit.

In the SHU reactor, about 90% of dienes and 9% of mono-olefins react. In the first bed of the HDT reactor the rest of dienes as well as 95% of mono-olefins have to react, while in the second bed of the HDT reactor, all impurities are hydrotreated. The catalyst volume discharged in each reactor is approximately 15 m^3 with a bed voidage of 0.6 [13]. Moreover, one has to recall that conjugated dienes are more reactive than mono-olefins. Thus the activation energy for dienes is lower than the one considered for the mono-olefins. The rate laws for the hydrogenation of conjugated dienes (index

d) and mono-olefins (index o) are respectively

$$r_d = k_d \cdot C_{H_2} \cdot C_d, \quad (1)$$

$$r_o = k_o \cdot C_{H_2} \cdot C_o, \quad (2)$$

with the reaction rate r expressed in $\text{kmol}/(\text{m}^3 \text{ s})$, concentrations C expressed in kmol/m^3 and kinetic constants k expressed in $\text{m}^3/(\text{kmol s})$.

Due to the lack of information, it was assumed that all impurities (index i) react according to the same rate law.

$$r_i = k_i \cdot C_i \quad (3)$$

with the reaction rate r expressed in $\text{kmol}/(\text{m}^3 \text{ s})$, concentrations C expressed in kmol/m^3 and k expressed in s^{-1} .

Finally, since the reactors are in adiabatic mode, the temperature dependence of kinetic constants has to be considered. Thus, the kinetic constants are expressed according to Arrhenius law:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

with A a pre-exponential factor, E_a the activation energy [J/mol], R the ideal gas constant ($= 8.314 \text{ J}/(\text{mol K})$) and T the temperature [K].

The final values for the different kinetic constants used for the reactor design are listed in Table 1.

TABLE 1: KINETIC CONSTANTS AND ACTIVATION ENERGIES

Parameter	Value	Units
A_d	1.01	$\text{m}^3/(\text{kmol.s})$
A_o	55	$\text{m}^3/(\text{kmol.s})$
A_i	70	1/s
E_{ad}	25	kJ/mol
E_{ao}	50	kJ/mol
E_{ai}	50	kJ/mol

Another crucial aspect of the study was the investigation of potential issues related to mass and heat transfers in the extrudates used in the process. The analysis did not reveal any notable issues concerning concentration or heat gradients in the extrudates employed in the hydrogenation process. This normally indicates that the extrudates are well-designed and functioning as intended. However, this analysis is linked to the reaction kinetics used. As these have been tuned to the empirical data already, they represent the apparent reaction rates in the reactors so these results are to be taken with hindsight. Typically, this analysis aims to assess the correction that must be made on documented reaction rates because the temperature and concentration inside the pellet are not always those one could expect from the operating conditions. The same methodology would serve to re-evaluate potential gradients if reliable values for the kinetic constants were provided.

2.5 Reactor engineering

The reactors design was a focal point of the process modelling since they were the pieces of equipment that mainly modified the composition throughout the process.



2.5.1 General considerations

Three different reactors are considered: the selective hydrogenation unit (SHU), and a hydrotreatment reactor split into two beds (HDT). In the SHU reactor, about 90% of dienes and 9% of mono-olefins react. In the first bed of the HDT reactor, the rest of dienes as well as about 95% of mono-olefins have to react. In the second bed of the HDT reactor, all molecules containing heteroatoms, namely nitrogen, oxygen, chlorine and sulphur, are hydrotreated.

The SHU reactor was assumed to operate in a biphasic medium while the reaction occurs in the liquid phase which is consistent with an inlet temperature of 250°C. Both beds of the HDT reactor were assumed to operate in gaseous phase. The inlet temperature of these beds was thus fixed at 435°C to fulfil this assumption. However, in reality that temperature is way too high, leading to an increased coke deposition. Moreover, all reactors are considered as plug flow reactors (PFR). Since adiabatic reactors are considered for the future plant, only adiabatic reactors have been studied in this article. The operating pressures in all reactors have been fixed to 46 bar and 31 bar respectively in the SHU and HDT reactors. No pressure drop has been considered.

The reactor design was done in several steps going from a Matlab implementation to an Aspen validation and simulation.

2.5.2 Matlab implementation

The first step implied a Matlab implementation of the problem assuming an ideal behaviour. This modelling of the reactors was done following the Chemical Reaction Engineering Algorithm [19] composed of four steps. First, the mole balances have to be written as differential equations since concentration profiles exist throughout the reactor. Then, the rate law determined in section 2.4 have to be considered. Next, stoichiometry step is considered to allow computation of concentrations and volumetric flowrates. Finally, heat effects are taken into account for the adiabatic reactors.

2.5.3 Aspen validation

Since the entire process is modelled on Aspen Plus, a reactor validation step was crucial. This validation step aims to compare the results obtained by Matlab and those obtained by Aspen Plus for the ideal model. The validation is presented only for the SHU reactor. It should be noted that when the reactor validation was carried out, the final kinetics were still unknown. Thus, the following volumes and conversion do not reflect the reality.

The biggest difference between both software is the way of computing the reactor volume. Since the SHU reactor was assumed to operate in the liquid phase with a constant concentration of hydrogen, Matlab computes only the volume of the reacting phase, that is the liquid phase. However, in Aspen Plus, the required reactor volume considers both phases, namely the reacting liquid phase and the gaseous hydrogen. To take into account this difference, the ideal gas law is considered to convert the entering volumetric flowrate of gaseous hydrogen entering the reactor into an additional reactor volume based on the residence time in the reactor. On top of the additional reactor volume related to

the gaseous hydrogen, temperature effects on the reaction enthalpies ΔH_r , heat capacities c_p and volumetric flowrates \dot{v} have to be considered. The temperature dependencies observed in Aspen were encoded in the Matlab code to mimic the behaviour observed during the Aspen simulations. In Table 2 are depicted the obtained volumes, conversions and temperatures.

TABLE 2: COMPARISON OF MATLAB AND ASPEN IN THE ADIABATIC CASE

	Matlab	Aspen	Relative difference (%)
Volume (m ³)	7.43	8.23	10.70
Mono-olefins Conversion (%)	62.88	63.26	0.61
Dienes Conversion (%)	89.92	90.00	0.08
Inlet temperature (°C)	240	240	0
Outlet temperature (°C)	289.2	285.8	-1.17

The difference in the computed volumes could be explained by the volumetric flowrate of gaseous hydrogen that is not constant along the reactor, not only because of the dissolution towards the liquid phase but also because of the variation of temperature. Moreover, since in the Matlab code all dienes flowrates and all olefins flowrates were lumped into two different variables, an average enthalpy of reaction for the hydrogenation of dienes and of olefins was computed and does not potentially perfectly describe what's happening during the Aspen simulations.

Since the relative differences listed in Table 2 are acceptable, both Aspen and Matlab software can be used interchangeably for an ideal model.

2.5.4 Final design

The three reactors have been modelled as cylindrical plug-flow reactors of fixed diameter, equal to 1.5m for all of them, a typical value for hydrotreatment reactors. The reactor length has been varied in order to reach the desired conversion in each reactor.

The adiabatic SHU reactor operates in liquid phase, at a constant pressure of 46 bar and an inlet temperature 250°C. With a reactor volume of 33.6 m³, the reached conversions for dienes and mono-olefins are respectively 93.74 and 9.70%. The exiting temperature is 314°C.

The adiabatic HDT reactor operates in gaseous phase, at a constant pressure of 31 bar and an inlet temperature 435°C for both beds. In the first bed, with a reactor volume of 44.5 m³, the reached conversions for dienes and mono-olefins are respectively 99.96 and 91.57%. In the second bed, all impurities, i.e. molecules containing heteroatoms, are hydrotreated.

Considering a bed voidage of 60% for all three reactors, namely the SHU reactor and both beds of the HDT reactor, respectively 13.4 m³, 17.8 m³ and 16.3 m³ of catalyst are necessary which is close enough to the 15 m³ predicted by TotalEnergies.

The obtained reactor characteristics and catalyst volumes are depicted in table 3.



TABLE 3: FINAL REACTOR DESIGN

	SHU	HDT (bed 1)	HDT (bed 2)
Dienes Conversion (%)	93.74	99.96	0
mono-olefins Conversion (%)	9.70	91.57	0
Impurities Conversion (%)	0	0	99.58
Reactor Volume (m³)	33.58	44.53	40.64
Catalyst Volume (m³)	13.43	17.81	16.26
Pressure (bar)	46	31	31
Inlet temperature (°C)	240	435	435
Outlet temperature (°C)	314.6	466.7	443.4

2.6 Separation units

The following sections will describe the separation units of the process, i.e. the decanter, the flashes, and the distillation column.

2.6.1 Decanter

A handful of impurities identified in the PPO are water miscible. For instance, the amount of chlorine in the oil was determined from the fraction of chlorine left in the mix after water washing. Other significant amounts of sulphur and oxygen, and nitrogen to a lesser extent can be withdrawn from the oil by performing a water-based liquid-liquid extraction (LLE). A decanter unit allows the oil and water to settle into two distinct phases, one of which is heated up and pressurised to the inlet conditions of the first reactor whilst the other is treated as a waste. This waste water contains the extracted salts, soluble acids, and other water-miscible compounds of the oil.

In Aspen Plus, the decanter block is set up using partition coefficients that describe the ratio of concentrations of each and every impurity in both liquid phases (table 4). This method was preferred over thermodynamic models because the values returned by both NRTL and UNIQUAC models did not match the documented partition coefficients—nor did they validate one another. These models were used because, out of all thermodynamic models available in Aspen Plus, only these two feature the option to account for the presence of electrolytes in the solution (H^+ , Na^+ and Cl^-). On the other hand, the thermodynamic models were considered trustworthy when it came to the sensitivity of the LLE to the temperature and the composition of the oil. By this means, almost null dependence on temperature was concluded over a realistic freshwater temperature range (0 to 50 °C) whereas the partition coefficient showed to fluctuate by a maximum of 10% (relatively to the biggest value in the range) for mass fractions of 2 to 10% in impurities at 20 °C. That is to say, according to both thermodynamic models used with a reference ternary mixture of *n*-octanol/water plus all impurities considered individually. As a matter of fact, the mass fraction of the impurities in the model PPO adds up to about 2.5%.

TABLE 4: *n*-OCTANOL/WATER PARTITION COEFFICIENTS AT 20 °C. SOURCES: *Hazardous Substances Data Bank* (1), *International Chemical Safety Cards* (2) AND *Human Metabolome Database* (3)

Molecule	$\log K_{ow}$	Source
1,2-dichlorethane	1.48	1
Benzonitrile	1.56	1
Caprolactam	-0.19	2
Pyridine	0.65	1
Phenol	1.46	1
Acetophenone	1.58	1
Acetone	-0.24	1
Hexanoic acid	1.92	1
Acetic acid	-0.17	1
2,5-dimethylfuran	2.24	3
Dimethyl disulfide	1.77	1
Dimethyl sulfoxide	-1.35	1

TotalEnergies' pilot unit also provided additional data for chloride and water whose concentrations in the organic phase were set to zero because negligible amounts were reported in the oil past the LLE. It is also known that 1% of the mass of PPO is lost overall to the waste water. Given the number of molecules to take into account, the 1% loss is considered a design of the model to tune the partition coefficients of all other hydrocarbon compounds, which was assumed to be the same whatever the molecule.

The Aspen simulation showed that feeding 3.3 m³/h of clean water to the decanter washes out oxygen, nitrogen, chlorine, and sulphur in fractions validated by the experiment on the pilot unit. For these four elements, the biggest relative error on the experimental abatement rates was a little over 9%. Given the throughput at the inlet of the decanter, its dimensions are computed based on the residence time which in turn is dependent on the fluids' characteristics [20]: the vessel is cylindrical with 1.25 m in diameter, 6.25 m in length which corresponds to a volume of 7.66 m³. Note that, eventually, the mass of PPO lost to wastewater was indeed 1% as opposed to the 0.8% simulated from the *n*-octanol/water partition coefficient of *n*-undecane, the most abundant molecule in the mixture (*Hazardous substances Data Bank*, $\log K_{ow} = 5.74$). Favours were nonetheless given to the pilot results since the design of the following units was always referring to 99% of the 10 t/h feed.

2.6.2 Flash tanks

Two flash tanks are considered in the process. The first one, i.e. the FLASH1 unit, is placed right after the SHU reactor and the second one, i.e. the FLASH2 unit, is placed after the second bed of the HDT reactor, see Fig. 1. They are considered as isothermal and isobaric.

The effluent exiting the first reactor, i.e. the SHU reactor, consists of hydrogen and a mixture of hydrocarbons. The FLASH1 unit aims to eliminate in the vapour phase at least 90% of the hydrogen entering the flash and less than 5% of

the hydrocarbons entering the unit [13]. In a first approach, to reduce the capital costs, it was decided to work at the exiting temperature of the hot stream of the HTX1 unit. To avoid cavitation in the pump that follows the FLASH1 unit, the pressure must remain as high as possible. Thus, the operating conditions for the FLASH1 unit were determined by carrying out a sensitivity analysis in which the flash temperature is kept constant during the analysis, and equal to 201°C, and the pressure of the flash is varied between 1 and 40 bar. The ratio between the mass flowrate of all hydrocarbons leaving in the vapour phase and the mass flowrate of all hydrocarbons entering the flash is studied. The same ratio is observed for hydrogen. From this sensitivity analysis, it comes out that the FLASH1 unit must work at 201°C and 14 bar, with an approximate volume of 4 m³ in order to respect the elimination criterion.

In the HDT reactor, an excess of hydrogen is injected. At least 90% of this excess will be eliminated in the FLASH2 unit. Moreover, the hydrotreatment of impurities in the HDT reactor leads to the production of ammonia NH_3 , hydrogen sulphide H_2S and hydrochloric acid HCl . At least 90% of these components have to be removed in the vapour phase. Moreover, the operating conditions of this second flash tank must be determined such as to meet the elimination criterion previously mentioned as well as inducing a maximal loss of hydrocarbons of 7% of the hydrocarbons entering the unit. The operating conditions were determined once by carrying out the same type of sensitivity analysis as for the FLASH1 unit except that temperature has been varied to meet all criteria. From that sensitivity analysis, it comes out that the FLASH2 unit must work at 110°C and 21 bar. The flash volume is about 21 m³.

2.6.3 Distillation column

The final separation step of the process involves a distillation column to remove compounds with a boiling point above 380°C that could potentially clog the downstream steam cracker. Specifically, the distillation column task is to remove 99% of such compounds from the feed mixture prior to sending it to the steam cracker [13].

To simulate the operation of the distillation column in Aspen, the DSTWU model, based on the Winn-Underwood-Gilliland shortcut method, was employed. This model provides important information, including the minimum reflux ratio, the minimum number of theoretical stages required, the work required by both the condenser and reboiler as well as the composition of the output streams.

To ensure the reliability of results, the Aspen simulations were cross-checked by constructing McCabe-Thiele diagrams. To best represent the complete mixture, it was chosen to consider a binary mixture of C22 aromatics (boiling temperature = 378°C) and C24 paraffins (boiling temperature = 391°C). The column's purity specifications were defined as recovering 99% of the lightest key compound (C22 aromatics) and only 1% of the heaviest key compound (C24 paraffins) in the distillate. Both the Aspen model and McCabe-Thiele diagrams produced similar results, allowing to proceed with the Aspen model to design the column as shown in Table 5. During the implementation process, a partial condenser was used, as a total condenser would require signifi-

cant cooling due to the presence of gases such as ethane and hydrogen in the feed stream of the column, making it impossible to reach the boiling point of the mixture at atmospheric pressure.

To specify the optimal fraction of steam in the distillate related to the partial condenser on Aspen, a sensitivity analysis was performed. As a result, the optimal vapour fraction in the distillate, minimising operating costs, was 0.9.

Ultimately, the simulations on Aspen yielded an optimal number of theoretical stages of 75 and a reflux ratio of 0.54, with the inlet temperature of the mixture into the column set to 109.1°C, and operating at atmospheric pressure to avoid considering pressure losses. Further information on the minimum reflux ratio, the minimum number of theoretical stages, the composition of the output streams, as well as the duties of the condenser and reboiler in kW can be found in Table 5.

TABLE 5: MAIN CHARACTERISTICS OF THE OPTIMAL DESIGN OF THE DISTILLATION COLUMN ON ASPEN

Minimum reflux ratio	0.38
Actual reflux ratio	0.54
Minimum number of stages	38
Number of actual stages	75
Feed stage	38
Number of actual stages above feed	37
Reboiler heating required (kW)	1 548.73
Condenser cooling required (kW)	1 448.58
Distillate temperature	257.25
Bottom temperature	388.40
Distillate to feed fraction	0.97

2.7 Heat exchanger design

The design of a counter-current shell & tube heat exchanger is also considered. As can be seen in Fig. 1, the HTX1 exchanger was placed upstream of the reactor as its purpose is to recover heat from the reactor outflow. The hot stream is introduced into the exchanger on the tube-side while the cold stream is inserted on the shell-side due to the viscosity of each stream.

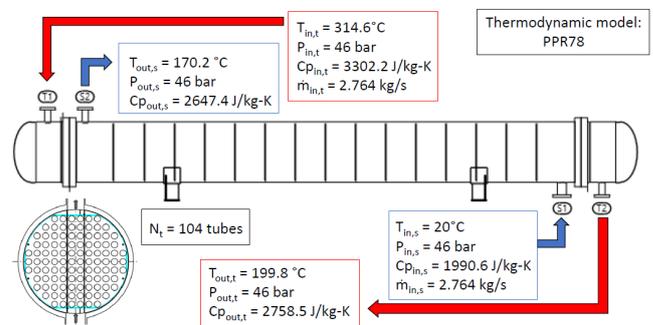


Fig. 6: Heat exchanger characteristics

The methodology that has been used in order to achieve the design of the exchanger is described in the following. First of all, a so-called preliminary design was carried out in accordance with the TEMA Tables [21]. These tables include all existing and feasible combinations of variables like the number of tubes in function of the shell diameter and so

on. This design will then serve as a first approximation for the following steps.

Then, a rating was carried out in Aspen software and through EES (Engineering Equation Solver) to ensure that the preliminary design matches or not the desired output values. As both software packages take into account pressure drops and calculate the real overall heat transfer coefficient, it is expected that the results obtained are different from the output of the preliminary design. As a result, various variables such as shell diameter, number of passes, external and internal diameter of the tubes had to be modified and then underwent the rating again.

Finally, once the values derived from the rating were compatible with the desired output values such as the heat duty or the pressure drop, the design was validated to carry out further evaluations such as cost assessment for example.

The final design is summarised in Fig. 6, Table 6, Table 7 where \dot{Q} corresponds to the heat duty, U to the heat transfer coefficient, A to the heat exchanger area, ΔP_s to the pressure drop in the shell-side and ΔP_t in the tube-side. $D_{o,t}$, $D_{i,t}$ and D_s are respectively the outer diameter of the tubes, the inner diameter of the tubes and the inner diameter of the shell. L_s is the shell length, n_p is the number of pass, p_t is the tube pitch and $Pitch$ is the tube layout. Moreover, the cross-section with the number of tubes can be found in Fig. 6.

TABLE 6: RESULTS OF THE FINAL DESIGN

\dot{Q} (kW)	U (W/m ² K)	A (m ²)	ΔP_s (bar)	ΔP_t (bar)
966	158.45	38.01	0.015	0.043

TABLE 7: RESULTS OF THE FINAL DESIGN - CONTINUED

$D_{o,t}$ (mm)	$D_{i,t}$ (mm)	D_s (mm)	L_s (mm)	n_p (-)	p_t (mm)	Pitch
31.75	27.53	488.95	5000	1	39.68	Square

2.8 Heat integration

In order to optimise the energy consumption, the heat integration of the process was performed. This method allows a recovery of the heat available in the streams of the process and a minimum need of additional heating or cooling duty. The pinch analysis followed by the heat exchanger network design were performed like presented in the course given by Pr. G. Léonard [22]. The QUENCH unit seen in Fig. 1 is not considered in this integration as it is actually a recirculation of a cold stream of the process.

2.8.1 Pinch analysis

To determine the pinch point, an inventory of the cold and hot streams has to be done. In this process, two hot and three cold streams are identified. In practice, the outlet streams of the reactors (streams 8 and 21 in Fig. 1) have to be cooled before entering the separation units while the inlet streams of the reactor (streams 6 and 16) and the hydrogen introduced before the second reactor have to be heated. In addition to the previously mentioned streams, the reboiler and the con-

denser of the distillation column are also considered in the heat integration by assuming an additional cold stream passing through the column reboiler and an additional hot stream passing through the column condenser. The minimum temperature difference ΔT_{min} , used to shift temperatures, was set to 20°C.

To determine graphically the pinch temperature, the Grand Composite Curve (GCC), depicted in Fig. 7, is drawn using the enthalpy of the streams and the temperature differences. It provides the position of the pinch temperature as well as the maximum additional heating and cooling duties to bring into the process. The pinch point is found at 304.63°C. Above the pinch, only heating utilities are allowed with a total duty of 1755.67 kW while below the pinch, only cold utilities are allowed with a duty of 96.87 kW.

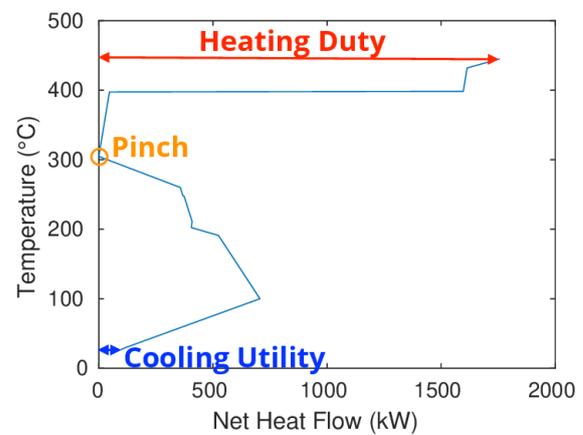


Fig. 7: Grand Composite Curve

2.8.2 Heat exchanger network design

With the information found with the pinch analysis, the heat exchanger network can be designed. The final design is portrayed in Fig. 8. To optimise the energy recovery between streams, some streams had to be split and reconnected after getting to the right temperature. In this design, 7 heat exchangers are used between hot and cold streams. Two heaters and four coolers, which are actually heat exchangers used with cold water, are added to the process in replacement of the heating and cooling equipment used in the original PFD shown in 1. The major heat transfers of the network happens between the inlet of the first reactor and the outlet of the second reactor, as well as between the outlet of the first reactor and the inlet of the second reactor. A simplified process flow diagram resulting of the heat integration is shown in Fig. 9. The application to the optimised network induces some improvement energy-wise. The duty required to bring to the process goes from 4842 kW to 1755.67 kW. As prices of energy can fluctuate, it is important to optimise the process with a heat integration to limit the cost related to energy consumption.

3 COST EVALUATION

Once all the technical aspects have been discussed, it is important to consider the costs associated with the studied process. For this purpose, Turton's book [23] as well as several

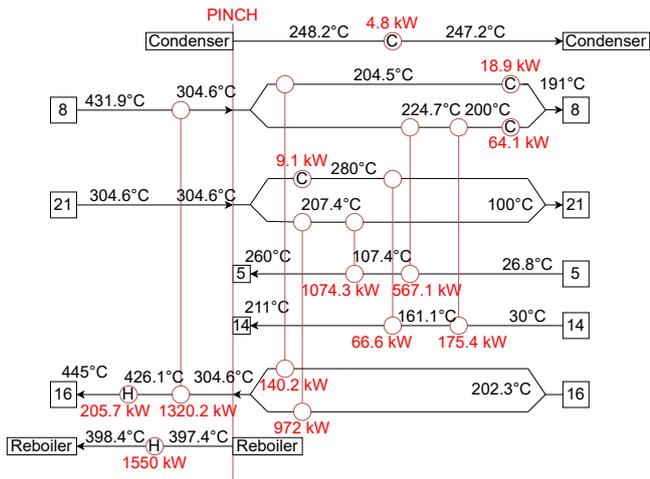


Fig. 8: Heat exchanger network

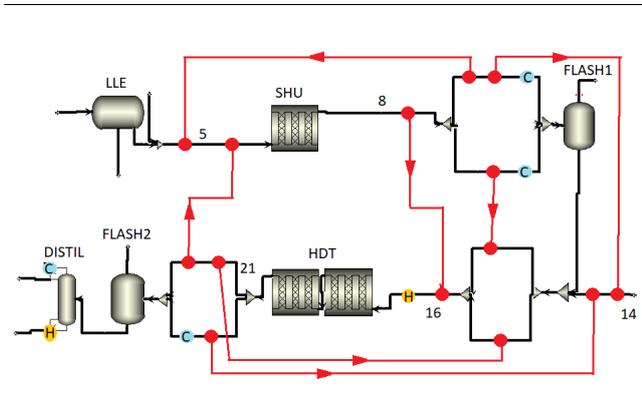


Fig. 9: Simplified flow diagram after heat integration

course slides given by Pr. G. Léonard [24] have been used. This cost analysis is divided into two main steps. First, the capital expenditure (CAPEX) and the operating expenditure (OPEX) are evaluated. Then, a cash flow diagram (CFD) and a break-even cost analysis are carried out to discuss.

3.1 CAPEX

The CAPEX calculation procedure can be summarised in 4 steps. First, the bare modulus cost C_{BM} is calculated for each piece of equipment following Turton's book [23]. This cost takes into account exclusively the type and the size parameter of each considered equipment. Secondly, the operating pressure of the equipment as well as the material of the equipment is taken into account. The pressures can be found in the sections related to each equipment and the material chosen is stainless steel. In fact, the treated mixture contains HCl, NH_4Cl and carboxylic acid which are too corrosive for carbon steel. Thirdly, since the reference book is based on the Chemical Engineering Plant Cost Index (CEPCI) of 2001 equal to 397, it is necessary to update the costs with the latest known index, i.e. January 2023 index of 802.6 [25] as shown in Pr. G. Léonard course [24]. Finally, once the sum of all the costs has been determined, additional costs such as the construction of buildings, warehouses, laboratories and the transport of equipment are taken into account, following the method in [24]. The total cost is converted into euros with the exchange rate of 1.113\$ for 1€ [26]. All this gives an

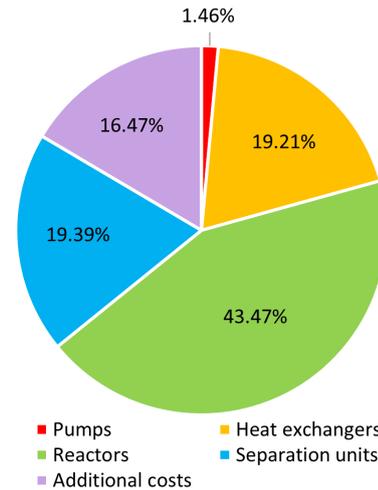


Fig. 10: CAPEX distribution

estimated CAPEX of 11.288 M€. Fig. 10 depicts the breakdown of CAPEX.

3.2 OPEX

To obtain the OPEX, an assumption of 8000h/year operation of the plant was made. Indeed, although the plant operates as much as possible, it must be regularly maintained. For example, the reactor catalysts must be changed every 3 months and the plant takes 1 week to return to steady-state [13]. OPEX is mainly a function of 5 variables: the cost of raw materials C_{RM} , the cost of waste treatment C_{WT} , the cost of utilities C_{UT} , the cost of operating labour C_{OL} and additional costs. The raw material cost corresponds to the cost of oil and hydrogen purchase. The price of the oil has been set to 800€/t. This value is based on the current price of pyrolysis oil supplied by TotalEnergies [13], but also on the fact that in the future, this price is susceptible to decrease by 10% up to 20% due to the increased recycling of plastics. For hydrogen, based on TotalEnergies price [13], its cost was established at 1500€/t. The quantities of raw materials consumed are respectively 10 t/h for oil and 0.381 t/h for hydrogen. The cost of waste treatment is only due to the cost of water treatment in the LLE (see LLE section 2.6.1). This unit consumes 3.3 m³/h of water and the cost associated with this water treatment is of 106.84 €/m³ [24] because a so-called tertiary treatment must be applied to remove impurities and hydrocarbons. This previous cost is updated with the CEPCI index as it dates back from 2001 in the reference. Concerning the cost of treating the waste generated by the process, i.e. the unwanted outflows from the flashes and the column, i.e. they do not generate costs nor profits. Indeed, their purification for reuse and/or resale means that no costs are associated with their treatment. The cost of utilities is related to the cost of electricity and the cost of water. Due to the heat integration and the power of the pumps, the annual electricity requirement is obtained and is worth 14.35 GWh. Taking a price of 0.15 €/kWh [27], the electricity cost is found. The total water flowrate is obtained summing the flowrate consumption of the LLE, 3300 kg/h, as well as the flowrate of cooling water in the coolers 5555 kg/h. The latest value is obtained with a cooling duty Q of 96.87 kWh,

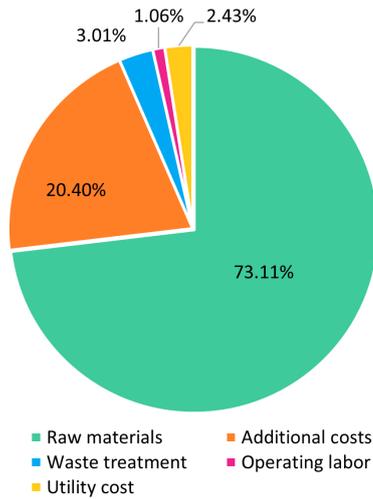


Fig. 11: OPEX distribution

see section 2.8.1, and a $\Delta T = 15^\circ\text{C}$. Multiplying this flowrate by a water price of 0.0018 €/kg [28], allows one to find the cost of water. The cost of operating labour is equal to 991 824 €/year, assuming 14 operators and an average wage of 70 824 €/year [29]. Finally, the additional costs correspond to the maintenance, the operating cost of the research laboratory or the losses for example. These costs are calculated using a weighting of C_{RM} , C_{WT} , C_{UT} , C_{OL} and the annualised CAPEX as specified in [24]. The CAPEX is annualised taking into account a 10 year life for the project and an interest rate of 8%. With all that, the OPEX is estimated at 93.796 M€ each year. The results and the distribution of costs are available in Fig. 11. As one can see, the major part of the OPEX, nearly 75%, consists of the raw materials cost.

3.3 Cash flow diagram

In order to determine the profitability of the project, a cash flow diagram (CFD), based on a discounted profitability analysis, is drawn. To do this, the method described in detail by Pr. G. Léonard was followed [24]. Here are the main hypotheses to keep in mind. The construction period of the plant was set at 2 years and the operating period at 10 years. The price of the land was evaluated on the basis of a surface of 250 m² located in Antwerp at 5000 €/m². The choice of location is discussed in the section 4. In the first year of construction, only 60% of the total CAPEX, also called FCI_{land} , is considered and then 40% in the second year. The working capital WC , added in year 2, is calculated by adding the cost of raw materials C_{RM} and the price of catalysts. The latter is obtained from the volume of catalysts required in the reactors, i.e. 47.5 m³, multiplied by the density, between 500 kg/m³ and 900 kg/m³ depending on the reactor, and by the estimated price per kilogram of catalyst, i.e. 6 €/kg [13]. The depreciation was calculated following the MACRS convention. The revenue is calculated on the basis of a sales price of 1400€/t. Although the current selling price is around 800€/t [30], it is reasonable to think that a premium of around 500-600 €/t will be added to this amount in light of what already exists in the Netherlands with bio-fuels [31]. This gives an annual income of 97.286 M€, as the plant produces 8.6863 t/h of recoverable product. The company's tax

rate is 25% [32] as the plant is located in Antwerp. The salvage value S is zero. The inflation adjusted interest rate i' is given by the subtraction between the interest rate and the inflation, fixed at 2% [24]. For different interest rate scenarios, the CFD curves have been plotted. This can be seen in Fig.12. The NPV acronym means Net Present Value.

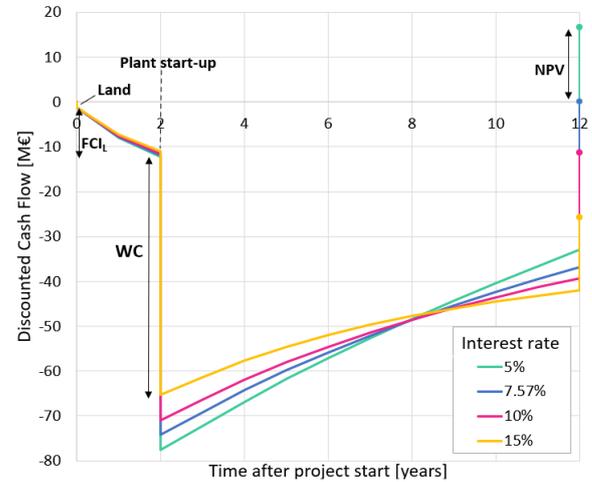


Fig. 12: Cash Flow Diagram

This sensitivity study makes it possible to determine the maximum interest rate, called discounted cash flow rate of return (DCFRROR), with which an investor can be repaid through the project, i.e. when the net present value NPV is equal to zero. Looking at Fig. 12, one can see that this rate is 7.57%. Given the risk of investing in such a project, if a bank's interest rate is lower than 5%, the process studied in this article, with the conditions and hypothesis described, is more profitable.

3.4 Break-even curve and discussion

It is now interesting to discuss the situation in which the purchase prices of raw materials and the sale prices of products vary. Indeed, OPEX is by far the most important part of the total annual cost, as can be seen in Fig.13, and raw materials are the most important part of OPEX, see Fig.11.

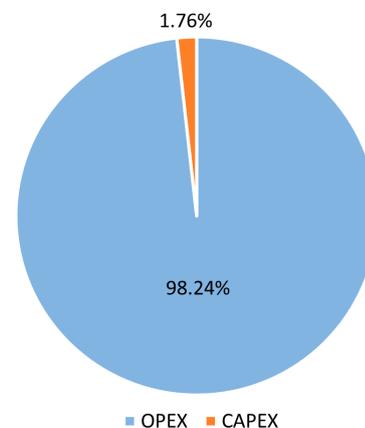


Fig. 13: Annual costs distribution

It is therefore interesting to form what is called the break-even curve. This is a curve whose points are formed by find-



ing the combination between the different values of the purchase and sale prices that make the process arrive at an NPV of zero at the end of the project. Above this curve, a profit is generated, below it, the process is in deficit. These curves have been plotted for different values of interest rates. The interest rate is used in the calculation of the annualised cost of the CAPEX and in the calculation of the Discounted Profitability. This gives Fig.14.

For the same purchase price, the selling price must therefore increase if the interest rate promised to investors increases. In the situation used to analyse the previous point, i.e. a sale price of 1400 €/t, a purchase price of 800 €/t and an interest rate of 8%, the process is profitable. This means that without the premium or the price reduction due to increasing availability of the raw material, the process is not profitable in the current state of affairs. However, there is a strong possibility that legislation will be introduced requiring a percentage of plastics produced from recycled plastics. Therefore, it would still be worth building the plant, even if it is loss-making.

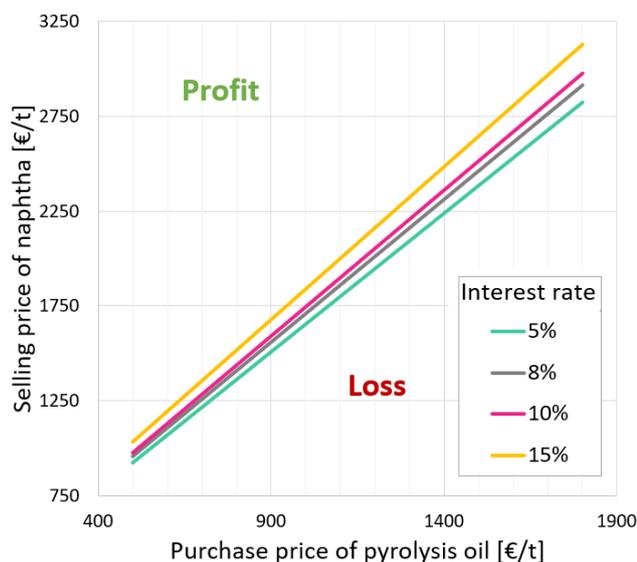


Fig. 14: Break-even curves

4 LIFE CYCLE ASSESSMENT

Plastic waste pollution is a global environmental issue that has been gaining increasing attention in recent years. Plastic is a synthetic material which, in most cases, is non-biodegradable and can persist in the environment for hundreds of years.

Plastic waste in the environment can cause harm to aquatic life and wildlife, affect development of vegetation and impact human health. Moreover, the disposal of plastic waste can contribute to air pollution, with the burning of plastic releasing toxic chemicals and greenhouse gases into the atmosphere.

Recycling techniques are being developed to tackle this problem. However, in order for plastic recycling to be effective and worthwhile, it must also be ensured that it is not associated with another form of disguised pollution and significant consumption of energy resources. It is therefore necessary to evaluate the energy consumption and emissions associated with the process. This can be done by performing a

Life Cycle Assessment (LCA), a methodology used to evaluate the environmental impact of a process throughout its entire life cycle, from the extraction of raw materials, through production, use, and disposal or recycling. Of course, the LCA is realised by considering the process with the heat integration.

4.1 Goal and scope

The aim of the process is the pre-treatment of 80 000 tonnes of plastic pyrolysis oil per year. Then, the functional unit, used to establish a clear and consistent basis for comparing the environmental impacts of different products or processes, was defined as one tonne of processed pyrolysis plastic oil.

The process is destined to be installed in the industrial zone of TotalEnergies in Antwerp. This location seems optimal given that the steam-crackers are located on this same site. Besides, as the pre-treated PPO leaves the distillation column in vapour phase, the proximity of the steam-cracker is particularly beneficial to avoid the additional costs linked to the compression of this vapour stream which would have been necessary for transport over a greater distance.

The raw material, the non-treated pyrolysis oil, is transported by tank trucks from the TotalEnergies refinery located in Grandpuits-Bailly-Carrois, in the agglomeration of Paris (FR), to the industrial centre of Antwerp, which corresponds to a total distance of about 400 km.

4.2 Life Cycle Inventory

In this step, the inputs and outputs of the system have been evaluated, including duties of heaters and coolers with water flowrates needed for cooling, as well as waste streams and emissions generated throughout the life cycle. All these data have been implemented in the SIMAPRO software and are gathered in Tables 8, 9 and 10.

TABLE 8: INPUT DATA INVENTORY

Input	Aspen values (kg/h)	Functional unit (t/t-PPO)
Pyrolysis oil with impurities	10 390.54	1.0395
Hydrogen	59.07	0.0059
Water	8 889.105	0.889

TABLE 9: OUTPUT DATA INVENTORY

Output		FLASH1 & FLASH2	Distillate	Residue
Oil	Aspen values (kg/h)	1 050.9	8671.9	543.17
	Functional unit (t/t-PPO)	0.1509	0.87	0.054
Impurities	Aspen values (kg/h)	12.67	0.64	1.43.E-12
	Functional unit (t/t-PPO)	0.0013	6.44.E-5	1.43.E-16
By-products	Aspen values (kg/h)	11.78	3.23	1.22.E-12
	Functional unit (t/t-PPO)	0.0012	0.0003	1.23.E-16



TABLE 10: POWER DATA INVENTORY

Required Duty	Required Power (kJ/s)	Required Power relative to one functional unit (kJ/t-PPO)
PUMP 1	38.29	13 924.51
PUMP 2	16.00	5 818.33
Heater 1	205.68	74 791.84
Cooler 1	9.11	3 313.32
Cooler 2	64.08	23 303.44
Cooler 3	18.88	6 867.00
Reboiler of the distillation column	1 548.73	563 174.55
Condenser of the distillation column	1 448.58	526 756.36

As can be seen in Table 8, the PPO with its impurities, as well as the hydrogen needed for hydrogenation reactions and the water required for the LLE unit, for the coolers and for the condenser of the column constitute the main input streams of the process.

As far as the process outputs are concerned (see Table 9), it is necessary to consider separately the vapour streams from the flash units, the distillate of the distillation column, and the latter's residue. Indeed, these three different streams are not treated in the same way.

Actually, it has been stated that flash units make it possible to separate the hydrogen from the mixture supplied to them. In Section 2.6.2, it was elucidated that certain hydrocarbons along with by-products like ammonia NH₃, hydrogen chloride HCl, and hydrogen sulfide H₂S are also separated from the mixture.

Within the framework of the LCA, it was decided to consider that 100% of the hydrogen separated in the flash tanks is recycled in the process. In fact, it would have been meaningless to consider that the hydrogen, which is an important reagent of the process, is just rejected and not reused.

Nevertheless, it was assumed that the hydrogen separated by the flash was directly returned to the process but actually no additional separation unit was taken into account whereas the gas output of the flash tank is not pure hydrogen. Thus, in a further analysis, it would be necessary to find information on the units that would allow the separation of hydrogen from impurities and other hydrocarbons and by-products of the process and to quantify the exact recycled fraction that could be obtained.

Then, still considering the flashes, it is important to point out that hydrocarbons, impurities, as well as by-products were considered as just discharged with no information on the downstream units that could potentially receive these compounds. This hypothesis is strong insofar as ways of valuing these components could be envisaged, at least for hydrocarbons. However, by gathering the quantity of hydrocarbons lost at the exit of the two flashes, it appears that approximately 700 kg/h of hydrocarbons are thus rejected in total after the passage of the mixture through the two flashes. This represents only about 7% of the input stream of the process, which does not seem to be a significant loss but it would be potentially interesting to consider recycling and assess whether it is economically interesting or not.

Regarding the distillation column output streams, in Table 9, it is important to remember that the distillate is the feed stream for the steam-cracker. Concerning the residue, since it contains 99.8% by mass of tetracosane (C₂₄ paraffin), it was considered that it could be burned in order to cover the heat requirements of the process through heat exchangers (see Table 10), plus a valuable excess. This assumption was made because it was necessary to find a heat source for the process and given the temperatures required by the process, steam would not be suitable. In further analysis, this assumption should be studied in more details to quantify the benefit of the use of this energy.

4.3 Impact Assessment and interpretation

The impact assessment method used on SIMAPRO to represent the environmental impact related to the treatment of one ton of pyrolysis oil is the the CML-IA (Cumulative Energy Demand). This method contains different environmental impact categories for the life cycle analysis [33]. Then, Fig.15 and Fig.16 could be generated using this method.

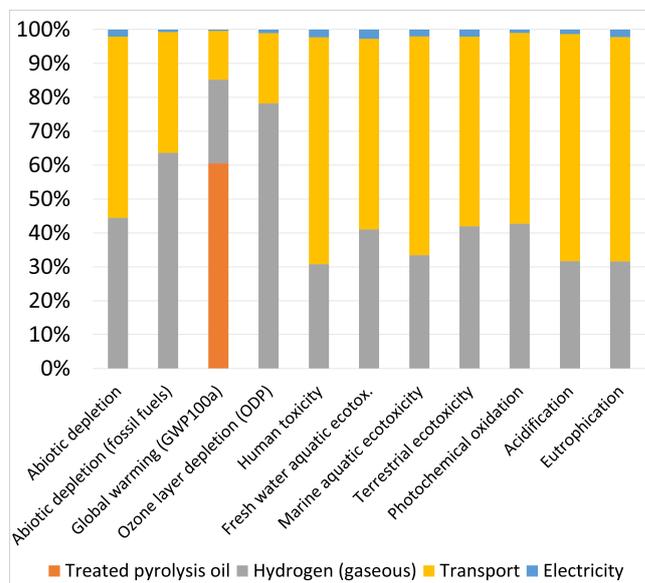


Fig. 15: LCA results

In Fig.15 one can see that hydrogen and transport are predominant factors whatever the impact category considered. On the one hand, hydrogen is overwhelmingly present as it is the only needed reactant in the process, and non-interchangeable. On the other hand, the transport is done over a long distance (more or less 400 km) and that is why it is so impactful on all categories. As mentioned previously, raw materials are transported by trucks and calculation was based on EURO5 trucks. Actually, the use of new EURO6 trucks could reduce the impact of the transport as they are more environmentally friendly in accordance with the stricter legislation. Another way to reduce the amount of emissions would be to consider transport on a barge, as Antwerp has the possibility to accommodate them but there exists—at the time this article is being written—no fluvial route from Paris to Antwerp.

Another important observation concerns electricity that has a very small influence on the different categories. The

electricity comes from the Belgian grid and was considered low-voltage because it simply costs less overall and requires less complex implementation.

Finally, 60% of the impact on global warming of the unit is due to the combustion of the residues from the column. This is because all the CO₂ generated during the combustion of the distillation column residue is released in the environment. This could be improved by considering CO₂ capture and storage techniques for example or by finding other ways to valorize the residue. Besides, TotalEnergies has already invested in this latter technologies.

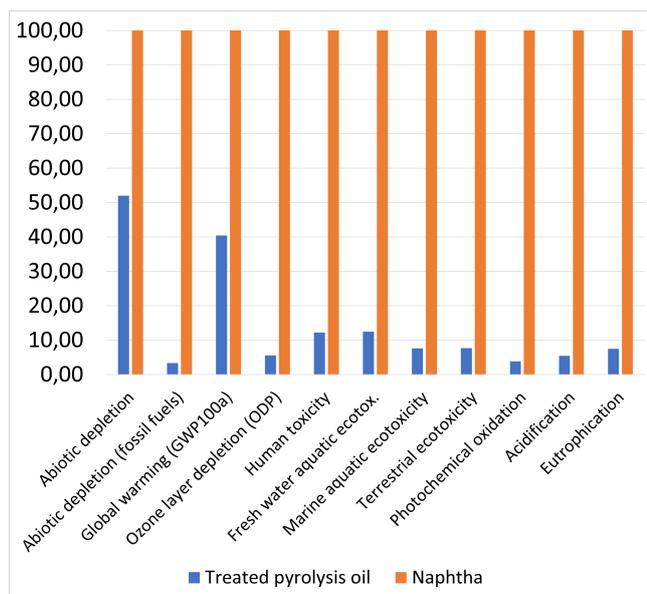


Fig. 16: Comparison between pyrolysis oil and naphtha oil

The comparison between the PPO and a naphtha cut already implemented in SIMAPRO is shown in Fig. 16 in order to check if it is interesting to implement the recycling process.

The two most important impact categories for the recycling process are abiotic depletion and global warming potential. One accounts for almost 50% and the other for 40%. Even if the overall impact categories are much lower for the recycling process, this seems very unsettling and it must be reminded that multiple optimistic assumptions have been made.

Indeed, as explained in previous section the hydrogen contained in the flash output streams was assumed to be 100% recycled. Furthermore, the water at the end of the process is sent to a treatment unit but there is no information about this treatment unit and how the water is treated. More accurate model could constitute an opportunity for improvement.

4.4 Remarks

It is important to note that these LCA results should be interpreted with caution due to hypotheses made during the analysis and that input consumption may have been neglected. In this study, an assumption was made that crude oil is free. Indeed, the environmental impact of the LCA is not considered but it is important to highlight that it is not the case in reality. The environmental impact should be considered when pre-treating PPO but no information is provided on the process

that produced this oil. The electricity used in the calculations comes from the low voltage network. In further analysis, it would be interesting to identify the impact of the source of electricity in the LCA.

5 CONCLUSION

Using the predictive Peng-Robinson model, the hydrotreatment of PPO has successfully been simulated on Aspen Plus software, from the composition modelling to the reactor design and separation units. Once preliminary designs were obtained, further improvements have been investigated based on sensitivity analysis on different units. Moreover, a heat integration has been considered to reduce the costs associated with heating and cooling as well as the environmental impact of the process by reducing the input of additional energy in the process. After the determination of the optimised flowsheet has been determined, the cost evaluation could be carried out, quantifying the capital expenditure as well as the operating expenditures. This cost analysis allowed to determine which are the key cost. Lastly, since the environmental aspect is also a key point, a Life Cycle Assessment was carried out to quantify the environmental impacts of the studied process and thus prevent green-washing. Different aspects have been taken into account, from the hydrocarbons waste to the energy consumption, including the environmental cost of transporting raw materials.

Some perspectives can also be stated on different technical aspects. The biggest problem of the process modelling concerns the lack of kinetic data. Further investigations are needed to refine the reactors' design and thus obtain a more accurate modelling of the process. Moreover, the HDT reactor modelling needs to be corrected to better describe reality. In fact, due to the oversimplifying assumption about the mixture phase, considering that both beds of the HDT reactor operate in vapour phase, the inlet temperature considered for the reactor design is way too high, potentially leading to coking. Furthermore, catalyst ageing have not be taken into account. Concerning the mixture composition, some solid impurities have not been taken into account, such as silica and iron.

Unfortunately, for now, the hydrotreatment of plastic waste pyrolysis oil is considered as in deficit. However, if the selling price of the plastic waste decreases as expected or if the premium granted for such a process increases, a benefit could be expected. Moreover, legislations about plastics recycling are expected. Thus, even if the process is not profitable, investing in this kind of technology could be a good solution to meet legislation expectations. In addition, the "pressure" induced by competitors on this type of research constitutes a driving force for this process development.

Moreover, the environmental impact of the studied process, quantified through a life cycle assessment, could be improved by modifying several assumptions. The hydrocarbon waste, i.e. the residue at the bottom of the column, could be burnt to recover energy that could be used to heat the considered heaters or valorize in other units. Moreover, the different impurities removed in the flash tanks could be recovered and sold instead of treating them as waste. Finally, a minimisation the environmental impact related to the PPO transport could be imagined by installing a pyrolysis unit in Antwerp



instead of transporting PPO from Grandpuits.

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7 REFERENCES

- [1] Plastics Europe, "Market Data [Online]," 2022. Retrieved 3 October 2022.
- [2] European Parliament, "Plastic waste and recycling in the EU: facts and figures [Online]," 2021. Retrieved 3 October 2022.
- [3] K Trade Fair, "K 2022 - Trend Report Europe [Online]," 2022. Retrieved 3 October 2022.
- [4] D. Calleja, "Why the "new plastics economy" must be a circular economy," *Field Actions Science Reports*, vol. Special issue 19, pp. 22–27, 2019.
- [5] J. Hopewell, R. Dvorak, and E. Kosior, "Plastics recycling: challenges and opportunities," *Philosophical transactions of the Royal Society of London, Series B, Biological sciences*, vol. 364, no. 1526, pp. 2115–2126, 2009.
- [6] F. Perugini, M. Mastellone, and U. Arena, "A life cycle assessment of mechanical and feedstock recycling options for management of plastic packaging wastes," *Environmental progress*, vol. 24, no. 2, pp. 137–154, 2005.
- [7] M. Saad Qureshi, A. Oasmaa, H. Pihkola, I. Deviatkin, A. Tenhunen, J. Mannila, H. Minkkinen, M. Pohjakallio, and J. Laine-Ylijok, "Pyrolysis of plastic waste: Opportunities and challenges," *Journal of Analytical and Applied Pyrolysis*, vol. 152, p. 104804, 2020.
- [8] C. Adam, D. Minoux, W. Vermeiren, S. Leplat, E. Van Looek, and C. Breton, "Purification of waste plastic based oil via a two steps hydrotreatment," International Patent No 204817A1, 2021.
- [9] D. Meier, B. van de Beld, A. Bridgwater, D. Elliott, A. Oasmaa, and F. Preto, "State-of-the-art of fast pyrolysis in iea bioenergy member countries," *Renewable and Sustainable Energy Reviews*, vol. 20, pp. 619–641, 2013.
- [10] M. Solis and S. Silveira, "Technologies for chemical recycling of household plastics – a technical review and trl assesment," *Waste Management*, vol. 105, pp. 128–138, 2020.
- [11] H. Jeswani, C. Krüger, M. Russ, M. Horlacher, F. Antony, S. Hann, and A. Azapagic, "Life cycle environmental impacts of chemical recycling via pyrolysis of mixed plastic waste in comparison with mechanical recycling and energy recovery," *Science of The Total Environment*, vol. 769, p. 144483, 2020.
- [12] INEOS, "The solution to end pollution," *INCH Magazine*, vol. 19, pp. 22–23, 2020.
- [13] C. Adam, 2023. Personal communication.
- [14] A. Alzaid, *Impact of conjugated olefins on Ni–Mo–S/ γ -Al₂O₃ catalyst deactivation and fouling of naphtha hydrotreaters*. PhD thesis, University of British Columbia, Vancouver, CA, July 2016.
- [15] J. De Hemptinne and E. Béhar, "Thermodynamic modelling of petroleum fluids," *Oil & Gas Science and Technology-Revue de l'IFP*, vol. 61, no. 3, pp. 303–317, 2006.
- [16] J. Vidal, *Thermodynamic application in chemical engineering and the petroleum industry*. Technip.
- [17] D. Ronze, P. Fongarland, I. Pitault, and M. Forissier, "Hydrogen solubility in straight run gasoil," *Chemical Engineering Science*, vol. 57, no. 4, pp. 547–553, 2002.
- [18] Z. Zhou, Z. Cheng, D. Yang, X. Zhou, and W. Yuan, "Solubility of hydrogen in pyrolysis gasoline," *Journal of Chemical & Engineering Data*, vol. 51, no. 3, pp. 972–976, 2006.
- [19] H. S. Fogler, *Elements of chemical reaction engineering, 5th edition*. Pearson, 2016.
- [20] W. McCabe, J. Smith, and P. Harriot, *Unit Operations of Chemical Engineering, Fifth Edition*, ch. 2, pp. 35–37. Singapore, ID: McGraw-Hill, 1993.
- [21] S. Kakaç, H. Liu, and A. Pramuanjaroenkij, *Heat Exchangers: Selection, Rating, and Thermal Design, Third Edition*. Taylor & Francis, 2012.
- [22] G. Leonard, "Introduction to the modelling of chemical processes," 2022. Uliège.
- [23] R. Turton *et al.*, *Analysis, Synthesis, and Design of Chemical Processes, 4th edition*. Pearson, 2013.
- [24] G. Leonard, "Techno-economic assessment of chemical processes," 2023. Integrated project, Uliège.
- [25] C. Maxwell, "[Online] Cost index (consulted on 08/05/23)," 2023.
- [26] "[Online] COURS EUR/USD SPOT (consulted on 07/05/23)," May 2023.
- [27] "[Online] DareToCompare.be Belgian electricity prices (May 2023) (Consulted on 04/05/23)."
- [28] SAWater, "[Online] Non-residential water prices (consulted on 8/05/23)."
- [29] STATBEL, "[Online] Salaires mensuels bruts moyens (consulted on 08/05/23)."
- [30] Trading Economics, "[Online] Commodities - Live Quote Price Trading data (Consulted on 08/05/23)."
- [31] Dutch Emissions Authority, "[Online] Market mechanism and HBes (Consulted on 08/05/23),," 2023.
- [32] SPF Finances, "[Online] Belgian corporation rate (Consulted on 08/05/23)."
- [33] Leiden University, "[Online] CML-IA Characterisation Factors (consulted on 10/05/23)," September 2016.

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