

# Modeling of Waste Tire Pyrolysis and Hydrotreatment for Jet Fuel Applications

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This thesis investigated the pyrolysis modeling of waste tires and the hydrotreatment modeling of pyrolysis oil and analyzed the potential of the oil resulting from both processes for jet fuel applications using *Aspen Plus*® V11. The tire pyrolysis modeling was done using *Ismail et al. 2017* kinetic model. Whereas the hydrotreatment modeling was done using *Olmo 2015* HDA kinetic. An improvement to the pyrolysis model was made by parameter estimation, performed using *gPROMS ModelBuilder* V7.07®. Through this work, pyrolysis oil did not reach jet fuel specifications. However, hydrotreated oil nearly did, showing the potential of pyrolysis for jet fuel application.

## 1 Introduction

The world's population growth directly impacts the global development of the automobile industry. As a result, the global tire market, which is the foundation of the automotive industry, is expanding. Approximately 1.6 billion new tires are produced globally, but the recycling sector processes only 100 million, and approximately 1 billion of waste tires are generated. (*Jansen, van der Walt, and Crouse 2022*)

On the global estimation of waste tire management, 3–15% of tires are recycled, 5–23% reused, 20–30% landfilled/stockpiled, and 25–60% incinerated annually. (*Abbas-Abadi et al. 2022*) Despite significant progress in waste tire management, more study is required to improve current practices and create better alternatives. Pyrolysis is a method of waste tire treatment that is becoming increasingly popular, and it has been the focus of numerous articles.

Pyrolysis is a thermochemical process that causes the cracking of polymeric chains in the absence of oxygen, resulting in a liquid

fraction, a gas phase, and a solid fraction. Oil accounts for 40–60 %wt percent of the pyrolysis products, according to numerous studies. Due to its high calorific value (38–45 MJ/kg), it has been considered an alternative to fossil fuels. (*Martín et al. 2022; Han, Stankovikj, and Garcia-Perez 2017; Zhang et al. 2021*)

Modern industrial society rely heavily on fossil fuels, which causes significant environmental issues including global warming. The global aviation community has set a goal of lowering net aviation carbon emissions by 50% by 2025 compared to 2005 levels. To reduce emissions, alternative low-emission fuel has been recommended. This is where pyrolysis oil as a potential alternative fuel comes into play. The composition of pyrolysis oil has been described as having 3%wt paraffin&isoparaffin content, more than 55%wt aromatic compounds, and more than 20%wt naphthenes. (Hita, n.d.) Currently available jet fuel derived from fossil petroleum contains approximately 20% paraffin, 40% isoparaffin, 20% naphthene, and 20% aromatic compounds. (*Han, Stankovikj, and Garcia-Perez 2017*) As a result,

pyrolysis oil contains all of the components needed to produce jet fuel. However, it must be improved because it cannot be used directly due to high sulfur content. By hydrotreating and hydrocracking, the pyrolysis oil composition can be upgraded to meet the required standard. (Somsri 2018; Speight 1999)

## 1. Literature Review

### 1.1 Tire

The primary function of a tire is to provide secure contact between the vehicle and the road surface. Tire compositions vary significantly due to the wide variety of tire applications. More than 200 distinct raw materials are used to manufacture a tire. Tires contain carbon black, steel, natural rubber (NR), and synthetic rubber (SR) as their primary components. Synthetic rubber examples include butadiene rubber (BR) and styrene-butadiene rubber (SBR). The combination of these materials enables the production of tires with a wide range of properties suitable for any application.

Waste tires are characterized using proximate and ultimate analyses. Proximate analysis is used to determine the weight percentages (wt.%) of moisture, volatile matter, fixed carbon, and ash. In contrast, ultimate analysis determines the weight percentages of chemical elements (carbon, hydrogen, nitrogen, oxygen, and sulfur). In the ultimate analysis, the oxygen content of given tires is usually determined by difference.

### 1.2 Jet Fuel

There are numerous varieties of jet fuel, but they can be divided into two categories: military fuel (JP-5, JP-8) and civilian fuel. Jet A-1, Jet A, and Jet B are the three types of jet fuel used for commercial aviation. The main difference between them is their freezing points,

with the first at -47° C, the second at -40° C, and the third at -60° C. Jet A/A-1 alternative fuels are already commercially available, and AJF's have been used on over 300,000 flights since 2011.

The main specifications for jet fuel are flash point, smoke point, freezing point, aromatics content, olefin content, and sulfur content. Jet fuel contains maximum levels of aromatics (25 vol %), sulfur (3000 ppm), and olefins (5 vol %) to control the freezing point, sulfur oxide emissions, and the formation of gums and sediments during storage. (Cheng and Brewer 2017).

### 1.3 Pyrolysis

The pyrolysis process consists of the thermochemical decomposition of organic matter in the absence of oxygen and at high temperatures ranging from 400 to 800°C. The absence of oxygen prevents the combustion of the products of the decomposition reaction. (Lombardi, Carnevale, and Corti 2015) Pyrolysis, in general, results in total mass recovery as solid (non-volatile material), liquid (condensable fraction), and gaseous (non-condensable fraction) products.

The pyrolysis process products distribution depends on precise parameter settings, including the type of reactor, temperature, retention time, and pressure.

### 1.4 Simulation of waste tire pyrolysis

In the published literature, numerous articles on the simulation of waste tire pyrolysis process were discovered. As an example, (Altayeb 2015; Bi et al. 2022; Ismail et al. 2017; Mulaudzi 2017; Wu et al. 2022) implemented the pyrolysis process in Aspen Plus®. Altayeb 2015 simulated the pyrolysis reaction using the Gibbs free energy minimization approach.

### 1.5 Hydrotreatment

Hydrotreatment (HDT) refers to several catalytic hydrogenation processes that saturate unsaturated hydrocarbons and remove S, N, O, and metals from different petroleum streams in a refinery, thereby increasing cetane number, density, and smoke point. Hydrogenolysis reactions eliminate heteroatoms, and polycyclic aromatic hydrocarbons undergo partial hydrogenation, while unsaturated hydrocarbons such as olefins and diolefins are also hydrogenated. HDS, HDN, and HDA are waste tire oil's most important hydrogenolysis reactions. The extent of the reaction for various component classes varies based on the nature of the catalyst and the operating conditions. (Hita, n.d.; Lødeng et al. 2013, 11)

This process generally occurs in a trickle bed-reactor where hydrogen reacts with oil in the presence of a catalyst. The reactor is divided into multiple beds to redistribute the liquid so that the wetting of the catalyst in each bed is more homogeneous, using the voids between the beds as quenching boxes.

Typically, atmospheric gas oils have been hydrotreated at temperatures ranging from 315 to 400 °C and pressures ranging from 30 to 100 bar. The hydrogen flow is often designed to be 3-4 times more than what is used in the process. The hydrogen to liquid feed ratio is commonly in the 70-1000 Nm<sup>3</sup> hydrogen per m<sup>3</sup> liquid feed range. (Boesen 2011; Ortega 2021)

### 1.6 Modelling OF Hydrotreatment in Aspen Plus

Plazas-González et al., 2018 developed a model for the hydrotreatment of palm oil components in order to create green diesel. An equilibrium reactor (REquil) was used in the Aspen Plus® program to predict how

these reactions would behave. Bandyopadhyay and Upadhyayula 2018 studied in Aspen Plus® the HDS, HDN, and HDA reactions with representative compounds to gain insight into the equilibrium conversion of these reactions, utilizing an RGibbs reactor with the temperature, pressure, stoichiometric ratios typically used in an industrial hydrotreating reactor.

## 2 Pyrolysis modeling

The modeling of the pyrolysis process was made in Aspen Plus® V11. Here, the thermophysical properties were acquired using built-in parameters in the software database. Peng Robinson with Boston-Mathias alpha function equation of state (PR-BM) has been cited in multiple articles (Altayeb 2015; Mulaudzi 2017; Adeniyi and Ighalo 2020) as the preferred property method to be used for the pyrolysis process. The HCOALGEN and DCOALIGT property models were used to estimate the density and enthalpy of non-conventional components. (Kabir, Chowdhury, and Rasul 2015; Mulaudzi 2017) Missing thermophysical properties were estimated using the UNIFAC group contribution model (Fredenslund, Jones, and Prausnitz 1975) and the process simulator's Property Constant Estimation System.

The Ismail et al., 2017 kinetics was used to simulate the pyrolysis of waste tires. The decision to use these reaction rates to model the pyrolysis process was made because they were the only ones available in the literature with such a high degree of product explanation for the pyrolysis of waste tires.

## 2.1 Experimental Results Reproduction

*Ismail et al. 2017* kinetics was implemented to reproduce his simulation results. The simulations were performed for *Ismail et al. 2017* 116 reactions, and later with 38 reactions based on an existing *Aspen Plus*<sup>®</sup> file entitled “Pyrolysis of waste tires” (waste\_tires\_pyrolysis-V11.apw), with different kinetic parameters. The results were compared with the experimental results from *Laresgoiti et al., 2004* and *Olazar et al., 2008*.

The average relative error of both works was used as a metric used for deciding which kinetic model was the best at reproducing the experimental results.

## 2.2 Results

Table 1 shows the new average relative errors obtained from the figures of *Ismail et al., 2017* article, the *Aspen Plus*<sup>®</sup> simulation results with 116 reactions and *Ismail et al., 2017* kinetic parameters, and the *Aspen Plus*<sup>®</sup> simulation results with 38 reactions and the waste\_tires\_pyrolysis-V11.apw original kinetic parameters. It is possible to see that the average error for the 38 reaction implementation is significantly high in comparison with the other two situations. This might be due to the fact that there were not enough reactions used to adequately represent the experimental findings or that the new parameters estimated by *Aspen Plus*<sup>®</sup> significantly affected the reaction rate. The latter could be the main cause, as the reaction rate constant of limonene, one of the main products of pyrolysis, in *Ismail et al. 2017* work (0.619) is nearly double that of Aspen File (0.35). The difference between the 116 reactions implemented results and *Ismail et al., 2017* results could be due to some parameters being

incorrectly inserted, leading to parameter introduction confusion.

Table 1 – Average relative error comparison between *Ismail et al. 2017* simulation results and the implementation of 116 and 38 reactions results with the experimental results of *Laresgoiti et al. 2004* and *Olazar et al. 2008*.

	Average Relative Error (%)
<i>Ismail et al 2017</i> work	37
116 Reactions	42
38 Reactions	59

To reduce the disparity between the current implementation and the results of *Ismail et al. 2017*, parameter estimation was performed, to find new pre-exponential constants for each reaction rates

## 3 Parameters Estimation

The *gPROMS ModelBuilder V7.07*<sup>®</sup> software was used to perform the Parameter Estimation since this program can process data from experiments to estimate the values of unknown model parameters.

Prior to estimating the parameters, a mathematical model was required. The mathematical model of the RPlug for the kinetic model presented in the work of *Ismail et al., 2017* was implemented in *gPROMS*<sup>®</sup> and is described by Equations (1)-(3).

$$\frac{\partial F_i}{\partial z} = \frac{A}{m} \times \sum_{j=1}^{No\ Reac} v_{ij} R_j \quad (1)$$

$$\frac{\partial m_i}{\partial z} = \frac{\partial F_i}{\partial z} \times M W_i \quad (2)$$

$$m = \sum_{i=2}^{No\ Comp} F_i M W_i \quad (3)$$

Where, *i* is the number of components aside from the carbon element, *i*=2..*Nocomp* (dimensionless), *z* the reactor tube axial position,  $\in ]0, L[$ , (*m*), *L*, reactor length (*m*), *Nocomp*, number of compounds (dimensionless), *R<sub>i</sub>* reaction rate of species *i* at the position *z*, (mol/m<sup>3</sup>s), *F<sub>i</sub>* the molar flow rate of species *i* at the position *z*, (mol/s), *m<sub>i</sub>* the mass flow rate of species *i* at the position *z*, (kg/s), *m* the

total flow rate at position  $z$  (kg/s),  $M_{wi}$  the molecular mass of species  $i$ , kg/kmol,  $\nu_{ij}$  is the stoichiometric coefficient of species  $i$  in reaction  $j$ , (dimensionless),  $j$  is the number of reactions, 1, ..., NoReact, (dimensionless) and NoReact the number of reactions (dimensionless).

Equations (1)-(3) are responsible for the mass balance within the reactor, while Equation (4) for the reaction rate.

$$R_j = A_j e^{\frac{-E_a}{RT}} T^{n_j} \prod_{i=1}^{No\ comp} F_i^{O_{ij}} \prod_{i=1}^{No\ Comp} M_{W_i}^{O_{ij}} \quad (4)$$

$E_a$  the activation energy (J/mol),  $A_j$  the rate pre-exponential constant of reaction  $j$ , ( $s^{-1}$ ),  $R$  the universal gas law constant (J/kmol),  $T$  the temperature in reactor (K),  $n_j$  the temperature exponent of reaction  $j$ , (dimensionless),  $O_{ij}$  the reaction order of component  $i$  in reaction  $j$ , (dimensionless) and  $R_j$  the Reaction rate of reaction  $j$ , ( $mol/m^3s$ ).

The parameters were estimated using the described model and experimental data from *Laresgoiti et al., 2004* and *Olazar et al., 2008*.

### 3.1 Results

Through parameter estimation it was possible to obtain a 3% improvement in relation to the *Ismail et al. 2017* simulation results.

The reason for the lack of a higher improvement might have been due to the fact that only the pre-exponential constants were varied, whereas the activation energy and the temperature coefficient were maintained constant. Since this variables were optimized for the *Olazar et al. 2008* work, which was made using a conical spouted bed reactor, the fact that data from a different reactor was used to estimate the parameters (*Laresgoiti et al. 2004* work was conducted using a autoclave batch reactor), not varying this variables might be the reason as to why there was practically no improvement.

### 3.2 Sensitivity Analysis

The operating conditions for the sensibility can be seen in Table 2.

Table 2 – Operating conditions used for the sensibility analysis.

	Min	Max	Units
Residence Time	50	500	kg/hr
Pyrolysis Reactor Temperature	200	700	°C

To assess the pyrolysis oil's potential for jet fuel application, the Jet A requirements that could be obtained via *Aspen Plus®*, were applied: Volumetric amount of aromatic (4°C); Net Heating Value (NHV); Flash Point API (*Riazi 1986*); Naphthalene Volumetric amount (15°C); Viscosity at -20°C; Density at 15°C; Sulfur total, by mass.

#### Temperature

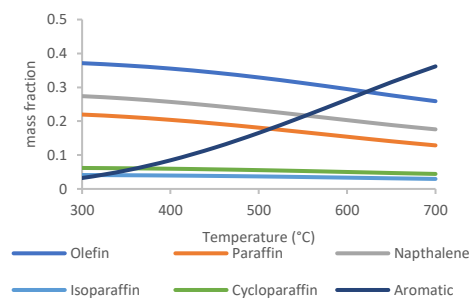


Figure 1 - Impact of temperature variation on the mass fraction at the reactor effluent for the multiple compounds class.

#### Residence Time

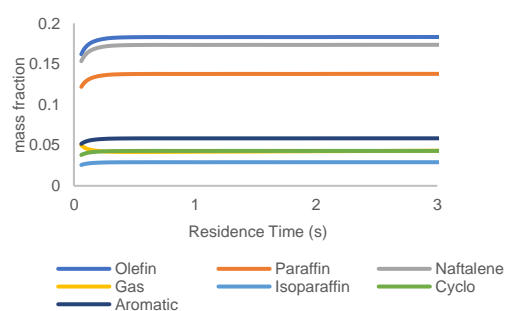


Figure 2 - Residence time variation and impact in the multiple compounds class present in the tire in terms of the mass fraction at the reactor end.

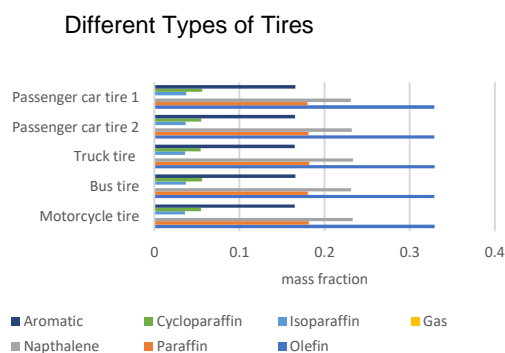


Figure 3 Representation of how each classification lumps mass fraction changes for the different types of tires, for the oil obtained in the condenser for the case scenario.

After analyzing Figure 1-Figure 3 it was concluded that this kinetic model does not allow to control the product distribution using residence time, that temperature is an important factor as it affect immensely the composition of the pyrolysis oil obtained. This kinetic model also does not allow to differentiate between different tires due to its kinetic limitation of only taking into account the elemental composition of the tires and not the molecules that are constitutes the tire. As a result, if different types of tires have the same hydrogen elemental composition, their product outcome will be equal even though the literature has shown that is not the case.

#### 4 Pyrolysis Oil Hydrotreatment

The *Olmo 2015* kinetic model, whose kinetic parameters were obtained for a NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst was used to simulate the hydrotreatment of pyrolysis oil. This model was selected because it is the only kinetic model available for the hydrotreatment of used tires. The hydrotreatment process was modeled in *Aspen Plus*<sup>®</sup> V11, and the same property method (PR-BM), and missing thermophysical properties (UNIFAC), as in the pyrolysis process, were used.

This kinetic model requires the lumping of the pyrolysis oil into various lumps. When separating the compounds into different lumps,

it was possible to discern that compounds present in a certain lump of the HDA pathway, for example, compounds in the A1 lump, some might in the Gasoil lump of the HC process, whereas others might be in the Diesel lump.

It was decided to only simulate the HDA pathway over the others since the HDA kinetic model, aside from taking into account the cracking of the compounds, where naphthene cracks into paraffin, it also allows for a more precise characterization of the stream composition. The HDS kinetic model was not implemented because the sulfur component in the pyrolysis oil simulated does not have associated kinetic parameters.

The trickle bed reactor model could not be implemented in *Aspen Plus*<sup>®</sup> since the model is not available, and as a result, the ideal plug flow reactor model was used. This choice was based on the literature findings, where a trickle bed reactor has been mentioned to be simulated using an ideal plug flow reactor. (Yadav and Roy, 2022)

As in *Olmo 2015* kinetic model, the inverse reaction constants are derived from the equilibrium constant, whose value varies with temperature, a custom equation was developed to account for the calculation of this term in *Aspen Plus*<sup>®</sup>.

In order to understand if the implementation of the HDA kinetic model was well done, a reproduction of the experimental data was made.

##### 4.1 Reproducing Experimental Data

In order to make the experimental reproduction, the scrap tire composition used by *Olmo 2015* had to be obtained. It was found that composition was indeed available in the literature (Hita et al. 2015), however, when considering that for two ring aromatics, which

account for 17.7% of the STPO, the only available compound was biphenyl, which accounts for 0.12% of the STPO it made more sense to find a more in depth characterization of the scrap tire. In the same article, a composition of a simulated scrap tire oil (SSTPO) was described in greater detail, and this composition served as the basis for the experimental reproduction.

During the initialization of the experimental reproduction, it was found that when mixing the simulated pyrolysis oil with the hydrogen ratio mentioned in *Olmo 2015*,  $1000 \text{ Nm}^3/\text{m}^3$ , the resulting mixture was in the vapor phase at the operating conditions of the literature. Since, in reality, the pyrolysis oil is introduced in the trickle bed reactor in the liquid phase, the total vaporization of the feed stream when using the ratio of the article is a problematic situation.

In order to deal with this issue, multiple situation strategies were tested. The total average relative error was used as the model performance criteria.

#### 4.1.1 Liquid phase

As previously stated, mixing the feed with hydrogen in the proportion used by *Olmo 2015* results in total vaporization of the stream. So, the  $\text{H}_2/\text{feed}$  ratio was adjusted in order for the mixture to enter the reactor with only partial vaporization. The lowest  $\text{H}_2/\text{feed}$  ratio found in the literature for hydrotreatment processes was  $70 \text{ Nm}^3/\text{m}^3$ . At this value the pyrolysis oil was 38% vaporized at  $300^\circ\text{C}$ , 63% at  $340^\circ\text{C}$  and totally vaporized at  $375^\circ\text{C}$ .

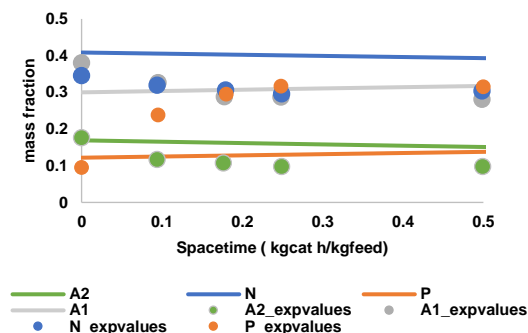


Figure 4 - Reproduction of *Olmo 2015* experimental results and comparison of simulation and experimental data for  $300^\circ\text{C}$  and 65 bar for a liquid phase kinetic rate.

Figure 4 shows that this approach leads to a linear trend of the simulation results, in contrast with the experimental results, which have a curved trend. This might be due to a low conversion rate brought on by having a small amount of feed in the liquid phase. The associated total average relative error for this approach is 36 %.

#### 4.1.2 Vapor phase ( $1000 \text{ Nm}^3/\text{m}^3$ ratio)

In this approach, the ratio of  $\text{H}_2/\text{feed}$  used by *Olmo 2015* was employed ( $1000 \text{ Nm}^3/\text{m}^3$ ). However, to bypass the total vaporization of the feed problem, the reaction phase, instead of being liquid, was assumed to be in the vapor phase to see if at least it was possible to reproduce the extension of the reaction.

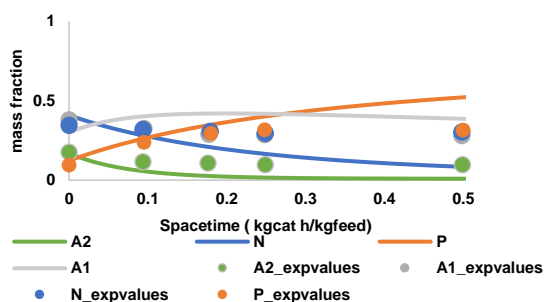


Figure 5 - Reproduction of (*Olmo 2015*) experimental results and comparison of simulation and experimental data for  $300^\circ\text{C}$  and 65 bar for a vapor phase kinetic rate.

Figure 5 shows that this approach led to more reasonable results compared to the previous situation since the curvature present in

the experimental data was mildly captured. On the other hand, the extension of the simulation results was much higher than the experimental results. This can be justified by the excess of hydrogen present in the reactive mixture. are dependent on the concentration of hydrogen in the liquid phase. In a trickle-bed reaction, that concentration would depend on the mass transfer limitations between the gaseous and liquid phases present in the system. As it is considered that the entire reactive mixture is in one single phase, this means that the hydrogen concentration in the vapor phase is much higher than what its solubility in the liquid phase would be. This might be the reason as to why even though the curvature trend of the experimental data is mildly captured, the total average relative error increased from the previous approach to 37%.

#### 4.1.3 Reduction of the hydrogen ratio

Taking into account what has already been stated, the hydrogen-to-feed ratio was reduced, while keeping the reaction mixture in the vapor phase, in order to reduce the quantity of hydrogen in the vapor phase and thus emulate the solubility of excess hydrogen in a trickle bed reactor with pyrolysis oil.

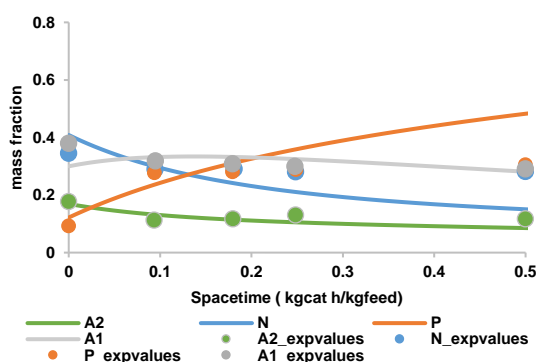


Figure 6 - Reproduction of Olmo 2015 experimental results and comparison of simulation and experimental data for 375 °C and 65 bar for the 420 Nm<sup>3</sup>/m<sup>3</sup> ratio.

Figure 6 shows that the A2 lump is being well modelled, the A1 lump model results are close to the experimental results, even though the

curvature trends is not similar, the same overshoot present in the paraffin modelling continues and the N lump curvature trend is being modelled but the results obtained differ from the experimental results. Through reducing the H<sub>2</sub>/feed ratio while maintaining the mixture in the vapor phase it was possible to reduce the average relative error from 37% to 19%. This backs the previous assumption (reducing hydrogen quantity allows to emulate the solubility of hydrogen in the liquid phase in an industrial setting), and as a result, it can be said that reducing the amount of hydrogen allows for better modeling results.

#### 4.1.4 Custom Term

Considering the idea of diminishing the mass fraction of hydrogen until a certain point to try and emulate the "solubility" of hydrogen in the oil, as previously mentioned, another route was considered. Since hydrogen is in excess, the idea that as soon as hydrogen is consumed, its mass fraction is kept constant due to the excess hydrogen was simulated. To implement this approach, it was necessary to add a custom term that would be constant and would not vary depending on the amount of hydrogen added.

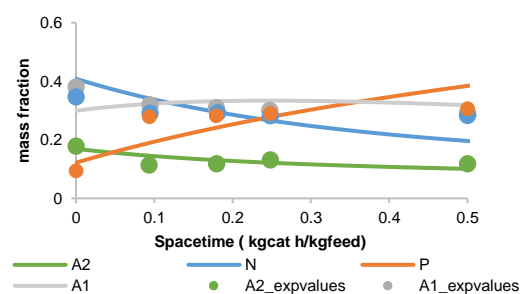


Figure 7 - Reproduction of Olmo 2015 experimental results and comparison of simulation and experimental data for 375°C and 65 bar, for the 0.023 custom term value.

Figure 7 shows the simulation results and the experimental data for 375 °C using a custom term of 0.023 for a H<sub>2</sub>/feed ratio of 1000 Nm<sup>3</sup>/m<sup>3</sup>. The curvature trends and results obtained in the previous approach are similar to



those obtained in this approach. The major difference between them is the reduction of the overshoot of the paraffin lump.

Through this approach it was possible to reduce even further the average relative error, from 19% to 16%, with a custom term value of 0.023.

This approach was chosen to generalize the current results to the pyrolysis oil obtained from the simulation was to implement the current best custom term and consider it constant. This meant that hydrogen solubility was assumed to be constant, independent of the type of oil and temperature and that the correcting effect of naphthalene, aromatic, naphthene, and paraffin was also constant.

#### 4.2 Lumping

For the sensitivity analysis, which uses a stream made of multiple compounds, to implement *Olmo 2015* altered HDA model, the compounds must be grouped according to their chemical class in order to simulate the reaction.

In the scientific literature, lumping has been performed using the average molecular weight. By first agglomerating the compound and determining its average molecular weight, the compound with the molecular weight closest to the average molecular weight was selected as the representative of that lump. (*Choe et al., 2021*) Creating a pseudo component that mimics the compound that best represents the compounds grouped within a classification is an alternative method. In *Aspen Plus*<sup>®</sup>, this is accomplished by creating a pseudo component and providing three basic parameters, although only two are required to generate the compound: the Average Normal Boiling Point (NBP), the average molecular weight, and the specific gravity. There are multiple metrics to calculate the average normal boiling point, in

*Aspen Plus*<sup>®</sup> this value is represented by the mean average normal boiling point.

##### 4.2.1 Lumping by Average Molecular Weight

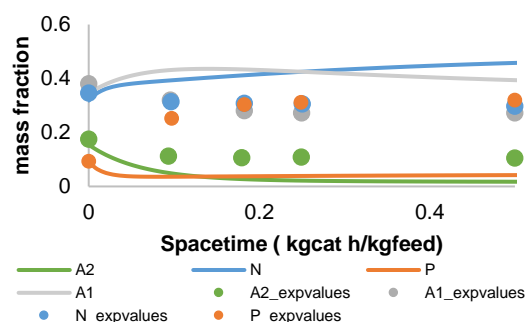


Figure 8 - Comparison of the experimental data with the lumping molecules representative, with the reactions in the vapor phase, at the ratio of  $1000 \text{ Nm}^3/\text{m}^3$  without a custom term, for  $340 \text{ }^\circ\text{C}$ ,  $65 \text{ bar}$

Figure 8 shows that at  $340 \text{ }^\circ\text{C}$  there is a reverse trend between paraffin and naphthene lumps, indicating that instead of increasing, paraffin content decreases and vice versa. The same happens at higher temperatures, namely  $375 \text{ }^\circ\text{C}$ . This is problematic because hydrotreatment process trends cannot be captured. This may suggest that this lumping method may not be the most appropriate for lumping the compounds in the oil.

##### 4.2.2 Lumping by Pseudo components

In contrast to the average weight molecular weight lump, at the same temperatures, the same trends present in the experimental data can be reproduced for all temperatures.

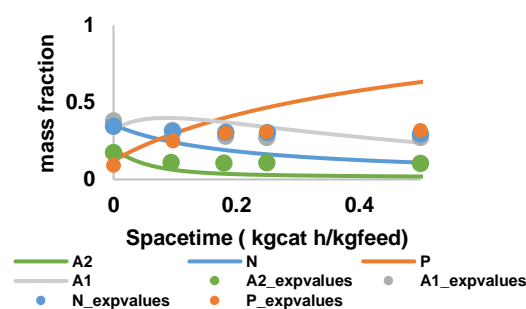


Figure 9 - Comparison of the experimental data with the pseudocomponents, with the reactions in the vapor phase, at the ratio of  $1000 \text{ Nm}^3/\text{m}^3$  without a custom term, for  $340 \text{ }^\circ\text{C}$ ,  $65 \text{ bar}$ .

In conclusion, using pseudo components to represent each stream lump yields better, more meaningful results than the average molecular weight lumping methodology.

#### 4.3 Sensitivity Analysis

Afterwards the hydrotreatment flowsheet and sensitivity analysis was made.

The base conditions for the sensibility study were the following: Reactor temperature = 375 °C, Pressure = 65 bar, H<sub>2</sub>/Feed= 1000 Nm<sup>3</sup>/m<sup>3</sup>, diameter=1 meter, length = 1 meter, and catalyst amount = 604 kg. Also, the base stream used for the sensitivity analysis matches the pyrolysis oil obtained from the pyrolysis reaction done at 500 °C, 1 bar and condenser at 30°C.

##### Temperature

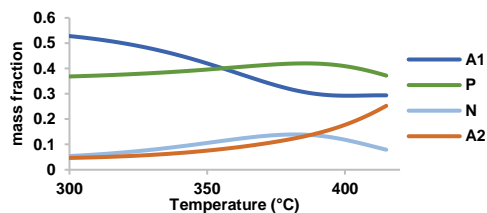


Figure 10 - Lumps mass fraction variation in the stripped hydrotreated oil within a temperature range of 300-415 °C, using the custom term model.

##### Catalyst Amount

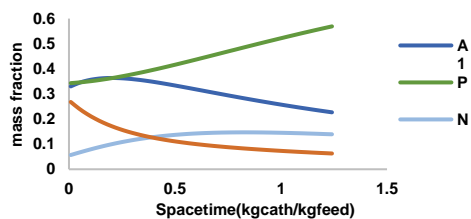


Figure 11 - Lumps mass fraction variation in the stripped hydrotreated oil within a catalyst range of 10-1500kg, using the custom term model.

Through Figure 10 and Figure 11, it is possible to understand the importance of temperature and catalyst amount. The increase in temperature leads to the formation of naphthalene content (A2) which is undesired. However, the increase in catalyst diminishes

this increase, which means that a combination of both variables would allow to reach the desired jet fuel specifications.

##### Sensitivity best conditions

In order to find the best combination of temperature and catalyst amount to meet jet fuel criteria, a sensitivity analysis was conducted in which these two variables were varied. The temperature was varied between 300-415 °C, and the catalyst amount was varied within the LSHV range, 0.5-3 hr<sup>-1</sup>, assuming a catalyst density of 1500 kg/m<sup>3</sup>.

Table 3 – Example of a temperature and catalyst resulting oil property that almost matches all the jet fuel specification requirements.

Catalyst (kg)	Temperature (°C)	Density 15, kg/m <sup>3</sup>	Viscosity -20 °C cP	NHV (Mj/kg)	Flash point (°C)	Naphtalene v/v%	Aromatic v/v%
1879	350.4	738.2	1.84	43.1	38.1	2.74	24.1

Through this sensitivity analysis, it was possible to find values for temperature and catalyst weight that would indeed lead to an oil whose specification nearly matched jet fuel requirements for all the imposed specification except density and viscosity. An example of such combination can be seen in Table 3. However, this hydrotreated oil still need to be tested for other jet fuel requirements which were not covered, such as freezing point. Regarding the viscosity and density values below the jet fuel requirements, a possible solution to increase their value is to add additives. However, if this addition does not lead to obtain a matching jet fuel oil, then distilling the oil and hydrocracking it might be an alternative as it would lead to decrease the aromatic and naphthalene content, which would lead to an increase density and density.

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