Chemical and Process Engineering: New Frontiers, 2025, 46(1), e84
DOI: 10.24425/cpe.2025.153669

Simulations of multi-stage fractionation of waste plastic pyrolytic oil in a rectification plant based on crude oil processing system

Roman KRZYWDA*, Bogumiła WRZESIŃSKA

Warsaw University of Technology, Faculty of Chemical and Process Engineering, ul. Waryńskiego 1, 00-645 Warsaw, Poland

*** Corresponding author, e-mail:**
Roman.Krzywda@pw.edu.pl

Article info:
Received: 05 November 2024
Revised: 20 January 2025
Accepted: 04 February 2025

Abstract

The aim of the work was to investigate the possibility of advanced fractionation of plastic waste pyrolytic oil into products corresponding to classic fuels. Typically, fractionation is limited to two-stage condensation. The paper proposes a new approach by using an innovative configuration of the fractionation unit. Due to the similarity of pyrolytic and crude oil chemical composition, advanced fractionation based on crude oil processing methods has been investigated. The ChemCad package was used to model and analyse different pyrolytic oil fractionation strategies. First, the use of a classic two-column oil rectification installation for fractionation of pyrolytic oil was simulated. It was found that a classic installation is not advisable due to the different boiling temperature ranges of both feeds. However, a small addition of pyrolytic oil to crude oil feed, as 10%, does not cause a significant change in the products and is worth further research. Two simplified cases of a modified rectification installation were also proposed. The obtained products were compared to typical crude oil fractions, and regarding boiling temperature ranges and some properties, a great similarity to naphtha, kerosene, and diesel was found. Fractionation in the proposed rectification unit is a promising way for pyrolytic oil processing.

Keywords

plastic waste pyrolysis, pyrolytic oil, fractionation, rectification, process simulation

1. INTRODUCTION

The plastic market is constantly growing, and the cumulative global plastic production is expected to increase to 34 billion metric tons by 2050 (Statista Research Department, 2024). The problem of the increase in plastic waste is solved in two ways: either the waste is deposited in landfills or subjected to mechanical, biological, or thermochemical recycling such as pyrolysis, liquefaction, gasification, hydrocracking, catalytic cracking, and incineration (Panda et al., 2010).

During pyrolysis, i.e., thermal decomposition in anaerobic conditions, chemical bonds in polymer chains break. As a result, hydrocarbons with relatively short chains, which can be widely used in the chemical or energy industries, are formed. In the process, liquid, gaseous, and solid products are produced. The quantities and properties of the products depend on the pyrolysis conditions: temperature, pressure, residence time, heating rate, reactor type, catalyst, plastic composition (single-component or mixture of plastics, other additives), its purity (post-production waste, municipal waste), degree of fragmentation, pre-treatment techniques, i.e. (Fulgencio-Medrano et al., 2022; Murthy et al., 2023; Vijayakumar and Sebastian, 2018).

The economic profitability of pyrolysis plants depends largely on the quality of the products. Oil is the most important pyrolytic product, due to its produced volume and potential application, but raw oil is not suitable for direct use and requires valorization. When obtained at appropriate pyrolysis conditions and with the application of additional post-treatment, its properties may be similar to petroleum products. The high calorific value of pyrolytic oil implies that it can be used as a component of engine fuel or heating oil. The literature and industrial practice indicate these two essential and most important application areas.

Various aspects of the suitability of pyrolytic oil as a motor engine fuel regarding the performance and emission characteristics of a diesel engine are summarised in (Faisal et al., 2023; Jahirul et al., 2022a). In detailed experimental studies (Kalargaris et al., 2017; Kumar et al., 2013), the behaviour of a compression ignition engine powered by oil obtained by plastic pyrolysis and its blends with diesel fuel in various proportions was examined. The results suggested that plastic pyrolytic oil is a promising source of alternative fuel. However, lower engine efficiency and higher NO_x, CO and unburnt hydrocarbon emissions indicate the need for improvement of pyrolytic oil properties by different post-treatment procedures such as distillation and hydro-treatment.

The recovery of individual hydrocarbons from oil is also sometimes mentioned, but this is feasible mainly for the pyrolysis of homogeneous and clean plastics (Siddiqui and Redhwi, 2009; Zhao et al., 2020).

The need for refining pyrolytic oil by fractional distillation is considered the main step towards fuel applications. The fractional composition is essential in terms of the desired use of the product. Too many heavy components can cause problems with incomplete fuel combustion, while the concentration of light hydrocarbons negatively affects the flash point. When analysing the applications of the oil as a fuel, it is also necessary to meet corresponding quality parameters defined by the standards, e.g., viscosity, density, flash point, sulphur content, water content, cetane number, lubricity, oxidation stability, etc.

To obtain products with a high utility value, the oil is divided into fractions boiling at the desired temperature ranges, and then additional refining processes (e.g. hydro-desulfurization, dearomatization, and saturation of olefins) are carried out. In another work (Jahirul et al., 2022b), batch vacuum distillation was used to separate raw pyrolytic oil into two fuel fractions: gasoline and diesel. The fractions were characterized, finding an improvement in their fuel properties compared to raw pyrolytic oil derived from various types of plastics. The hydroprocessing of the mid-distillate fraction of the pyrolytic oil was investigated by (Bezergianni et al., 2017). It was found that the product, in most cases, meets the requirements of the EN 590 standard (EN 590:2022-08) for automotive diesel, but upgrading cost is unattractive.

In typical pyrolysis plants, liquid fractions are obtained by one or a few stages of pyrolytic gas condensation, as described in (Zeller et al., 2021). Oil components are separated out during condensation, but no general rules define this process's temperature ranges. They are set individually for a specific raw material, process conditions, and the desired product. Pyrolytic plant operators often declare that the received products can be used as substitutes for liquid fuels, such as diesel or heating oil. However, the fundamental problem of using liquid pyrolytic products as fuels is meeting all quality standards. Legal regulations specify the physicochemical properties and the content of contaminants in fuels. Detailed analyses indicate that raw pyrolytic oil does not meet all the standards requirements. The main problems usually refer to too low ignition temperature, incorrect distillation range, and low cetane index (Jahirul et al., 2022b).

Many previous studies were focused on simple batch distillations of raw pyrolytic oil (Kunwar et al., 2017; Pradipta et al., 2019; Zeb et al., 2023). Since simple distillation cannot guarantee sharp splits, some degree of overlapping components in the distillates is unavoidable.

A more advanced approach to liquid product fractionation directly in a pyrolysis plant is to replace the multi-stage condensation unit with a simple rectification column. The column is fed by pyrolytic gas, improving the economics of the process. The application of a rectification column directly after a pyrolytic reactor makes it possible to use the energy of hot post-pyrolytic gas. Distillation in a lab-scale bubble cap plate column consisting of 4 trays was investigated by other researchers (Thahir et al., 2019; Thahir et al., 2021). The impact of condensation and fractionation equipment on the quality and quantity of oil products was analysed by (Krzywda and Wrzesińska, 2021). The results of this work show that the rectification column allows precise control of oil fraction composition by changing the process parameters, such as reflux ratio and the number of theoretical stages. It was concluded that the column with 10 theoretical stages is sufficient to divide the oil into two well-separated fractions. However, obtaining a larger number of narrow fractions requires a more sophisticated rectification system.

In the literature, there are no reports focused on complex rectification processes to obtain from pyrolytic oil a range of products with a narrow boiling point range corresponding to classic petroleum fuels. To fill this gap, the possibility of sharp fractionation of the liquid pyrolytic product in a multi-stage rectification system was examined. For this purpose, ChemCad process simulation software was used. Due to the similarity of pyrolytic oil to fossil oil, the authors decided to adapt the solutions used in crude oil rectification and implement them for the fractionation of pyrolytic oil. A classic crude oil processing installation was chosen as the starting point. To compare the quality of pyrolytic oil fractions to typical petroleum products, simulations were carried out for crude oil, pyrolytic oil, and a mixture of both materials (case 1). Based on the results of these simulations, modified installations fed with pyrolytic oil (cases 2 and 3) were also proposed.

Finally, the discussed solutions were compared with methods commonly used in plastic pyrolysis installations, pointing out their advantages and disadvantages as well as potential areas of application.

2. MATERIALS AND METHODS

Based on pyrolytic and crude oil parameters, the ChemCad 8.1 software (Chemstations Inc.) was used to process simulations.

"Tower Plus" was used as the operation unit for simulating continuous rectification. Layout details of this type of rectification columns are shown in Figs. 1 and 4. "Tower Plus" is a module that simulates rectification columns with side strippers and pumparounds. Strippers are used to separate the lightest fractions from the liquid side products by additional steam distillation. Pumparounds ensure internal reflux to regulate the vapor and liquid loadings. Both the column and strippers are bottom-fed with steam. Steam inputs are part of the "Tower Plus" specification and are not counted as input streams. Decanted water from the condenser is not considered as output stream. Therefore, neither steam nor decanted water are shown in the flowsheet. Side strippers and pumparounds are treated as part of the "Tower Plus" module and are solved simultaneously with the main column without going through the recycle calculation. A "Batch Distillation Column" unit was used to simulate batch distillation.

The composition of pyrolytic oil from waste plastic processing, as a set of 25 chemical compounds, was assumed according to (Krzywda and Wrzesińska, 2021). In this work, the model oil composition was determined based on the GC-FID chromatographic analysis and laboratory batch distillation of the pyrolytic oil from an industrial plant according to EN ISO 3405 (EN ISO 3405:2019). As ChemCad thermodynamic settings for pyrolytic oil, UNIFAC was chosen as a global K-value model (vapour liquid equilibrium), and Latent Heat as a global enthalpy model. The UNIFAC model was selected based on the recommendation of the "Suggest Thermodynamics" module in ChemCad. However, simulations were performed for two thermodynamic models (Grayson-Streed and UNIFAC) and the same results were obtained.

The crude oil composition was defined by pseudo-components with a specific TBP (True Boiling Point). ChemCad allows to enter the whole curve data as a petroleum assay, which is then broken into pseudocomponents that cover the entire distillation range. Once the material has been divided into pseudocomponents, these fractions are treated as pure components. This option is available from the Thermophysical menu. A light crude oil data was taken from the ChemCad example "Atmospheric Distillation of Crude Oil". The crude oil with an API gravity of 35 was characterized by 29 pseudocomponents and a light end containing propane, i-butane, and n-butane. Grayson-Streed was selected as the global K-value model, and Lee-Kesler as the global enthalpy model. Grayson-Streed method is traditionally used by the petroleum industry for describing the VLE of hydrocarbon systems.

3. RESULTS AND DISCUSSION

3.1. Rectification in a classic crude oil processing installation – case 1

In the first part of the research, rectification in a classic fossil crude oil processing installation (case 1) was simulated. The diagram of a model plant for crude oil rectification, imported from the ChemCad package, is shown in Fig. 1. The installation allows the separation of the feed stream into 6 fractions.

The system consists of two "Tower Plus" columns with strippers and pumparounds. The first column, T-1001, operates at elevated pressure, and the second, T-1002, at nearly atmospheric pressure. Both columns and strippers are fed from the bottom by steam. The condensers are equipped with water decanters. The parameters listed in Table 1 were used in the ChemCad program to define the "Tower Plus" calculation modules in case 1. The data relates to the topology (feed stage number. draw stage number, return stage number) and structure (type of condenser, number of strippers, pumparounds and stages) of the columns as well as the required operational parameters (temperature, pressure).

Three simulations were performed using as a feed stream: crude oil, pyrolytic oil and a mixture of 90% mol of crude oil and 10% mol of pyrolytic oil. The 10% mixture was chosen as an example of a small addition of pyrolytic oil to the feed of a crude oil processing installation to test whether it would significantly affect the properties of the final products.

As a result of simulating the separation of crude oil in the installation described above, six product fractions were obtained: Gasoline, Naphtha, Heavy naphtha, Kerosene, Diesel, and Topped crude. In the case of the separation of pyrolytic oil and the mixture, the same fraction names were used. The faction names were assigned to the point where they were withdrawn (as shown in Fig. 1). Despite the same names, the properties of pyrolytic oil fractions do not correspond to those from crude oil processing. This is discussed below.

Table 2 shows the mass ratio of fractions obtained for the three tested feeds. As can be seen, the yield of the first fraction, called Gasoline, is much higher for pyrolytic oil than for crude oil. The opposite trend is observed for the last fraction called Topped crude. A small addition of pyrolytic oil to crude oil does not significantly change the proportion of its fraction.

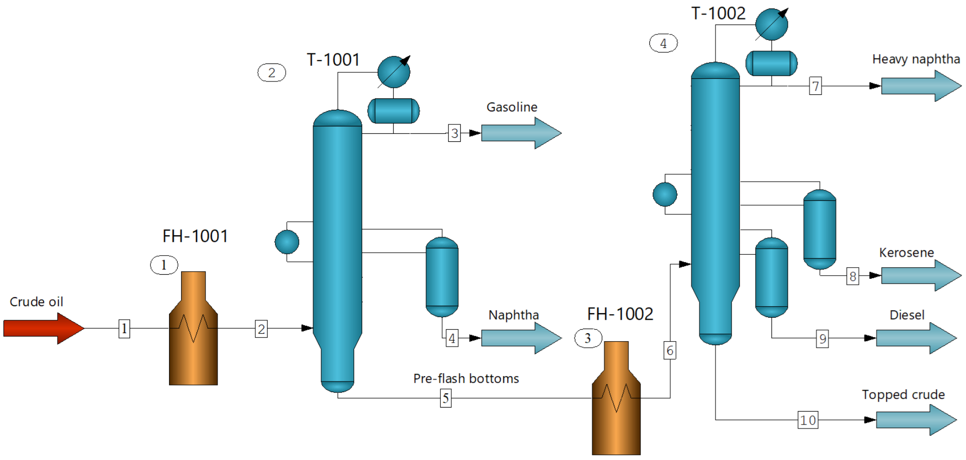

Figure 1. Model plant for crude oil rectification, case 1.

Table 1. Parameters of rectification columns used in the ChemCad simulation in case 1.

Column T-1001	Column T-1002
Tower configuration: • Number of strippers – 1 • Number of pumparounds – 1 Main column: • Number of stages – 13 • Feed stage number – 11 • Feed stream temperature – 204 °C Condenser: • Total with water decant • Subcooled temperature – 37.8 °C • Pressure – 3.3 bar Side Stripper: • Number of stages – 2 • Draw from stage – 8 • Return to stage – 7 Pumparound: • Draw from stage – 8 • Return to stage – 6	Tower configuration: • Number of strippers – 2 • Number of pumparounds – 1 Main column: • Number of stages – 16 • Feed stage number – 14 • Feed stream temperature – 315 °C Condenser: • Total with water decant • Subcooled temperature – 37.8 °C • Pressure – 1.4 bar Side Stripper no 1: • Number of stages – 2 • Draw from stage – 8 • Return to stage – 7 Side Stripper no 2: • Number of stages – 2 • Draw from stage – 12 • Return to stage – 13 Pumparound: • Draw from stage – 12 • Return to stage – 10

The next Tables 3–6, present the lists of selected properties of raw materials and their fractions: density, average mol weight, flash point, and cetane index. These data come from ChemCad simulations and were calculated as averaged stream properties. Therefore, they should be treated as approximate values. Especially the flash point and cetane index calculations are more uncertain because these are not additive values.

Generally, the density of pyrolytic oil and its fractions is lower than that of crude oil, as shown in Table 3. However, a 10% addition of pyrolytic oil to crude oil causes less than 2% change in the density of the products compared to pure crude oil.

The calculated by ChemCad mol weight of both raw materials results from their different origin and, consequently, chemical composition. The largest difference is observed for the last fraction, as seen in Table 4.

Comparing the data from Table 5, it can be concluded that all pyrolytic oil fractions are characterized by higher flash point values compared to crude oil. Therefore, the addition of pyrolytic oil to crude oil slightly increases the product's flash point. The flash point is an indication of the safety hazards with respect to fire and explosion.

Table 6 shows that a small addition of pyrolytic oil increases the cetane index of the crude oil products.

To better understand and explain the trends observed in Tables 2–6, boiling point ranges of all feedstocks and fractions were determined by simulation. To compare the distillation curves, batch distillation simulations at atmospheric pressure were carried out using a "Batch Distillation Column" module (Fig. 2). The calculations were made assuming 2 theoretical stages (including total condenser and reboiler) and zero reflux ratio, which imitates simple distillation conditions of the standard EN ISO 3405:2019 (ASTM D86-23).

As a result of the batch distillation calculations, an effect of the vapor temperature on the degree of distillation (fraction distilled) was generated. The comparison of simulation results for the three feeds is shown in Figure 3. Three sets of distillation curves illustrate the boiling point ranges for the following feedstocks: crude oil, pyrolytic oil, crude oil + pyrolytic oil, and fractions obtained from them in case 1.

The used column configuration and operational parameters resulted in 6 products with relatively narrow boiling temperature ranges and sharp cut-offs.

Table 2. Mass ratio of fractions, case 1 [% mass].

Feed	Gasoline	Naphtha	Heavy Naphtha	Kerosene	Diesel	Topped Crude
Crude Oil	8.7	19.9	7.1	15.3	15.9	33.2
Pyrolytic oil	27.7	17.3	6.0	12.2	12.4	24.4
Crude Oil+Pyrolytic oil	10.7	20.0	7.0	14.9	15.3	32.2

Table 3. Density of fractions at 15 °C, case 1 [kg/m^3]/[API].

Feed	Feed	Gasoline	Naphtha	Heavy Naphtha	Kerosene	Diesel	Topped Crude
Crude Oil	850/35	654/85	782/50	790/48	860/33	897/26	963/15
Pyrolytic oil	776/51	758/55	771/52	760/55	779/51	792/46	795/45
Crude Oil+Pyrolytic oil	841/37	673/79	793/47	796/46	850/35	873/31	946/18

Table 4. Average mol weight of fractions, case 1 [kg/kmol].

Feed	Feed	Gasoline	Naphtha	Heavy Naphtha	Kerosene	Diesel	Topped Crude
Crude Oil	173	78	113	118	172	242	414
Pyrolytic oil	196	127	210	174	239	289	304
Crude Oil+Pyrolytic oil	176	82	121	125	184	252	401

Table 5. Flash point of fractions, case 1 [°C].

Feed	Feed	Gasoline	Naphtha	Heavy Naphtha	Kerosene	Diesel	Topped Crude
Crude Oil	–12	–64	–1	7	80	112	134
Pyrolytic oil	46	36	87	61	112	128	134
Crude Oil+Pyrolytic oil	–5	–66	7	14	78	114	138

Table 6. Cetane index of fractions, case 1.

Feed	Feed	Gasoline	Naphtha	Heavy Naphtha	Kerosene	Diesel	Topped Crude
Crude Oil	32	6	35	36	37	40	43
Pyrolytic oil	76	51	80	71	86	92	94
Crude Oil+Pyrolytic oil	35	11	36	38	43	50	50

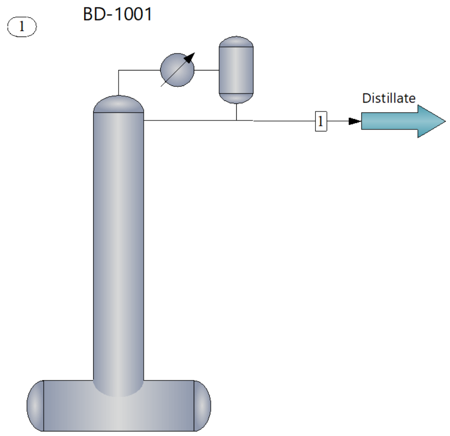

Figure 2. "Batch Distillation Column" module used for simple distillation.

As can be seen in Fig. 3, the boiling range of pyrolytic oil is much narrower compared to crude oil. Crude oil and pyrolytic oil distill in the temperature range of approx. 0–630 °C and 70–380 °C, respectively. Due to the different boiling point ranges, none of the pyrolytic oil fractions is similar to Gasoline and Topped crude from crude oil.

The properties of pyrolytic oil fractions produced in the plant in Fig. 1 do not correspond to typical fractions from crude oil withdrawn at the same points in the installation. For example, as shown in Fig. 3, the crude oil fraction received from the upper stripper of the atmospheric column, called Kerosene, distills from 170 °C (for a distillation degree of 5%) to 260 °C (95%). The range for the analogous fraction of pyrolytic oil is 270–325 °C. Due to the different boiling temperatures, the physicochemical properties of the crude oil and corresponding pyrolytic oil fractions are also different, as shown in Tables 3–6.

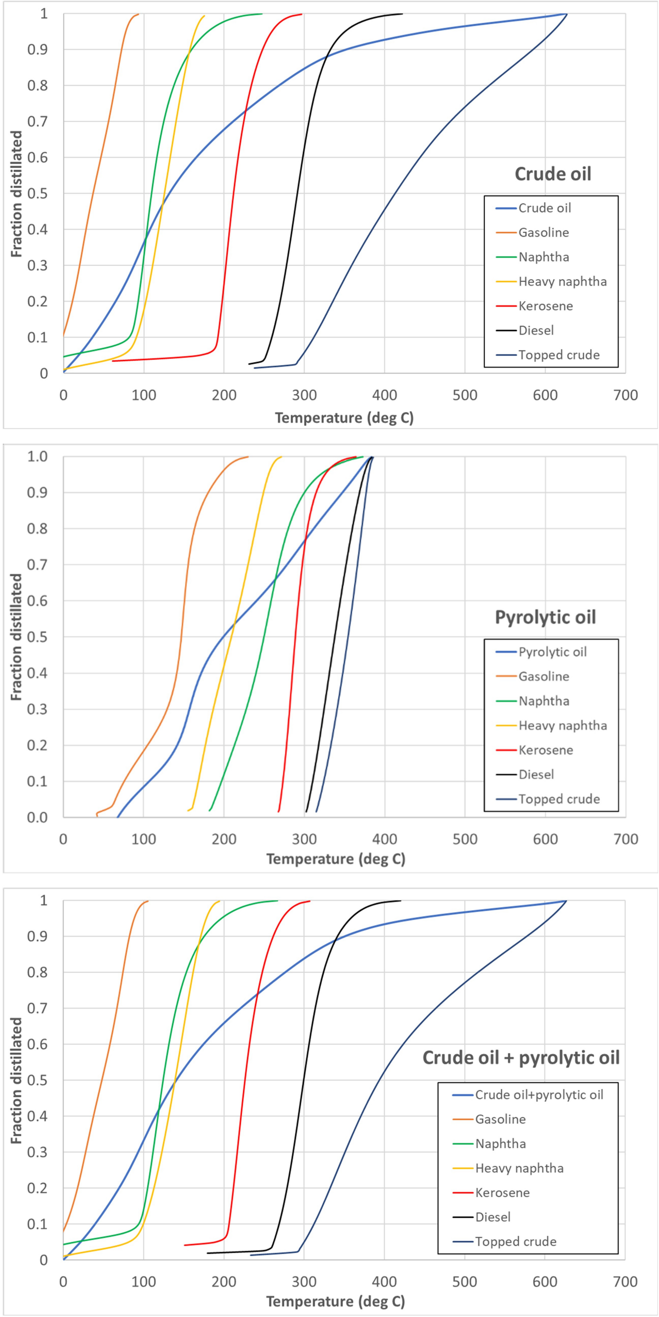

Figure 3. Comparison of the batch distillation curves for: crude oil, pyrolytic oil, crude oil + pyrolytic oil, and fractions obtained from them in case 1.

To sum up, the rectification of pyrolytic oil in a typical plant results in products with different properties compared to crude oil processing. However, it can be noticed that some pyrolytic oil products have properties similar to those of crude oil fractions; for example, the fraction called Kerosene from pyrolytic oil corresponds well to Diesel from crude oil. Both fractions have a similar boiling point range, Kerosene from pyrolytic oil 270–325 °C, Diesel from crude oil 250–350 °C. Although the average mol weight of both streams is approx. 240 kg/kmol (Table 4), and the flash point is 112°C (Table 5), they have different densities (Table 3) and cetane index (Table 6).

Due to the similarity of the properties of pyrolytic oil to crude oil middle products, fractionation of the mixture of both raw materials was also performed. It was found that a small addition of pyrolytic oil to crude oil (10 mol% was assumed in the simulation) did not significantly change the properties of the obtained products. This can be seen by comparing the distillation curves in Figure 3 and the product properties in Tables 3–6. Considering the above, the strategy of processing pyrolytic oil as a small additive to crude oil is worth attention and further detailed analysis. By simulations, it is easy to determine the maximum percentage of pyrolytic oil addition to crude oil that is acceptable from the point of view of the properties of the final products. However, selecting a key parameter as an optimization objective function is crucial. The number of simulation output parameters is very large, these can be fraction mass flows, as well as their composition and the resulting fuel properties. The goal may be, for example, to obtain the maximum yield of a chosen fraction even at the expense of its quality or to maintain the key fraction property (e.g. flash point, viscosity, freezing point) within an acceptable range. Calculations should always be based on the properties of crude oil processed in the rectification plant and the available pyrolytic oil.

3.2. Rectification in modified installations – cases 2 and 3

Since the boiling temperature range of pyrolytic oil is narrower than that of crude oil, it is proposed to split the oil into a smaller number of fractions. The separation concept is similar to a typical crude oil installation, except for reducing the number of strippers.

Two versions of a modified installation for rectifying pyrolytic oil are proposed. In the first option of the simplified installation (case 2), shown in Fig. 4, one stripper in the second column was eliminated. Due to the similarity of the fractions from stripper 1 and the distillate from the second column, it is also proposed to join them as Mix stream.

In case 3, shown in Fig. 5, the stripper in the first column was additionally removed. The topology, the structure of the columns and the required operational parameters of both modified plants are presented in Table 7.

In Tables 8 and 9, the fractions' mass ratio and selected properties are presented, respectively for cases 2 and 3.

Figures 6 and 7 present sets of distillation curves of fractions from the modified installations, respectively for cases 2 and 3.

As shown in Fig. 6, the boiling curve of Distillate 2 is very narrow and is fully within the distillation range of Stripper 1. Also, the properties of these fractions are very similar, as presented in Table 8. Therefore, in the installation diagram, these two streams are combined into one product called Mix. As a result, in case 2, the number of products is reduced to

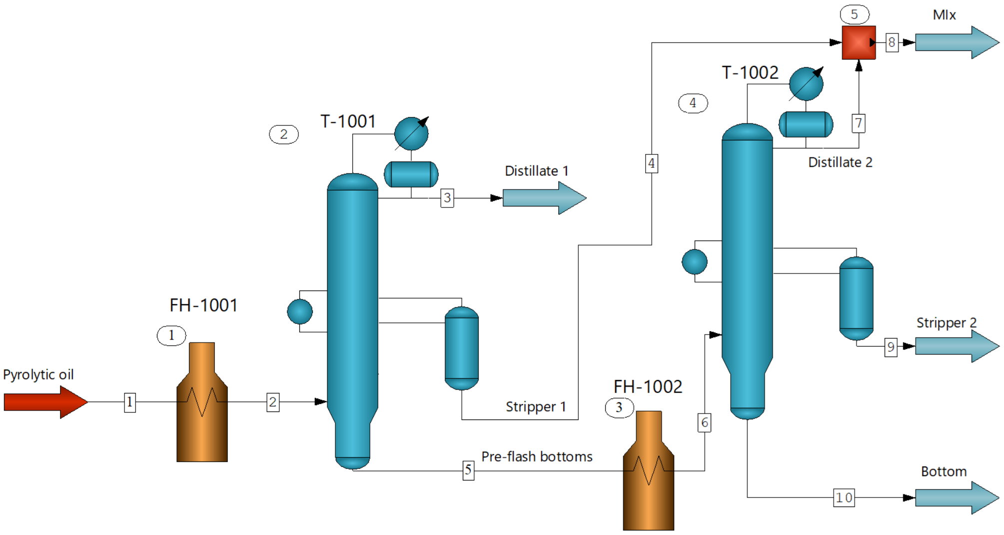

Figure 4. Modified plant for pyrolytic oil rectification, case 2.

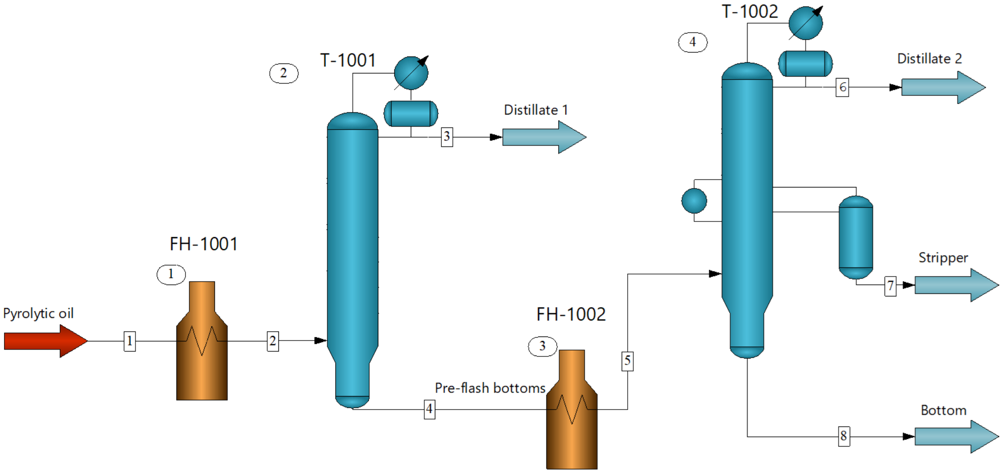

Figure 5. Modified plant for pyrolytic oil rectification, case 3.

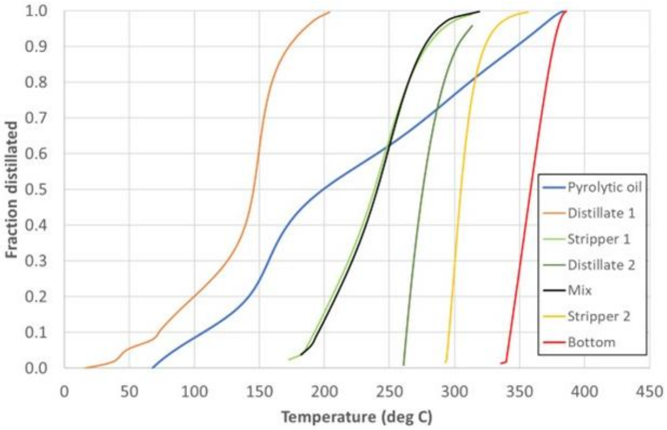

Figure 6. Batch distillation curves for pyrolytic oil fractions obtained in case 2.

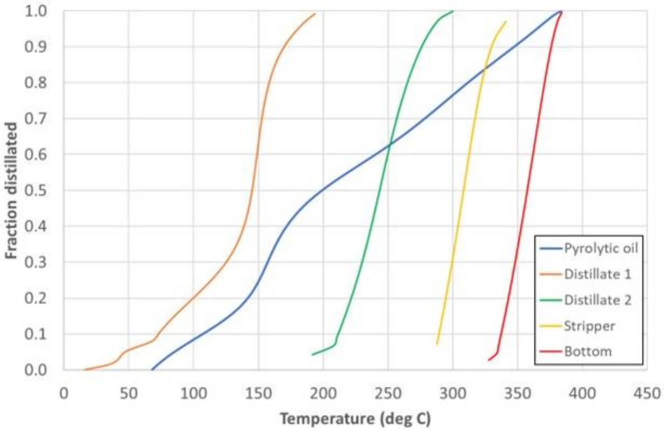

Figure 7. Batch distillation curves for pyrolytic oil fractions obtained in case 3.

four. Since Distillate 2 flow rate is more than four times lower than Stripper 1, the Mix distillation curve almost overlaps Stripper 1 curve. This is analogous to the graphs of Naphtha and Heavy Naphtha from crude oil rectification plant (Fig. 3).

For that reason, it was decided to eliminate the stripper and pumparound in the first column, simplifying its construction – case 3 (Fig. 7). Finally, there are also four products, as in case 2. The simplification of the plant structure in case 3

Table 7. Parameters of rectification columns used in the ChemCad simulation in cases 2 and 3.

Column T-1001	Column T-1002
Tower configuration: • Number of strippers – 1 • Number of pumparounds – 1	Tower configuration: • Number of strippers – 1 • Number of pumparounds – 1
Main column: • Number of stages – 13 • Feed stage number – 11 • Feed stream temperature – 300 °C	Main column: • Number of stages – 13 • Feed stage number – 11 • Feed stream temperature – 315 °C
Condenser: • Total with water decant • Pressure – 3 bar	Condenser: • Total with water decant • Pressure – 1.5 bar
Side Stripper (only case 2): • Number of stages – 2 • Draw from stage – 8 • Return to stage – 7	Side Stripper no 1: • Number of stages – 2 • Draw from stage – 8 • Return to stage – 7
Pumparound (only case 2): • Draw from stage – 8 • Return to stage – 6	Pumparound: • Draw from stage – 8 • Return to stage – 6

Table 8. Properties of pyrolytic oil distilled fractions – case 2.

	Pyrolytic oil	Distillate 1	Stripper 1	Distillate 2	Mix	Stripper 2	Bottom
Mass ratio [$\%_{\text{mas.}}$]		26.8	22.0	5.2	27.2	12.0	34.0
Density at 15 °C, [kg/m^3]/[API]	776/51	759/55	767/54	768/54	767/54	782/50	796/45
Average mol weight [kg/kmol]	196	123	198	200	198	252	307
Flash point [°C]	46	35	81	91	83	121	138
Cetane index	74	50	78	79	78	88	94

Table 9. Properties of pyrolytic oil distilled fractions – case 3.

	Pyrolytic oil	Distillate 1	Distillate 2	Stripper	Bottom
Mass ratio [$\%_{\text{mas.}}$]		26.8	27.2	12.0	34.0
Density at 15 °C, [kg/m^3]/[API]	776/51	759/55	767/54	783/49	795/45
Average mol weight [kg/kmol]	196	123	199	256	306
Flash point [°C]	46	35	87	121	137
Cetane index	74	50	79	89	94

does not result in significant changes in the quality of the products, as can be seen from the chart of distillation curves (Figs. 6 and 7) and the list of properties (Tables 8 and 9).

While comparing the pyrolytic oil fractions from both simplified plants (cases 2 and 3) to the crude oil fractions from the original installation (case 1), it was found that there are no fractions similar to Gasoline and Topped crude, which is obviously due to the different compositions of the feed streams.

The boiling temperature range of Distillate 1 is close to Naphtha from crude oil. Distillate 1 distills from approx. 50 °C (for a distillation degree of 5%) to 180 °C (95%). For crude oil Naphtha this range is 0–180 °C. Also, the average molar weight (123 and 113 kg/kmol) and density (759 and 782 kg/m^3) of both products do not differ much. Typical Naphtha used as the main raw material for the petrochemical industries boils at 30–200 °C (Silva et al., 2023).

In terms of boiling range Mix stream from case 2 and the corresponding Distillate 2 from case 3 are similar to Kerosene from crude oil. The temperature ranges are 180–280 / 200–285 °C for Mix/Distillate 2 and 170–260 °C for Kerosene. However, there are significant differences in the estimated densities of these products. Kerosene is a light petroleum distillate used in space heaters, stoves, lamps, as fuel or jet fuel ingredient, and as a solvent. The obtained Kerosene-like fractions have boiling point ranges similar to the ASTM D3699-19 standard (ASTM D3699-19).

The Stripper 2 fraction from case 2 and the corresponding Stripper from case 3 have distillation curves similar to Diesel from crude oil. The boiling temperature range of Stripper 2/Stripper (295–330)/(280–340) °C is slightly narrower than that of Diesel 250–350 °C. The boiling point ranges correspond to the requirements of the standard EN 590 (EN 590:2022-08). However, the density of pyrolytic oil fractions is lower than Diesel.

The boiling temperature range of the Bottom fraction derived from both modified installations, 335–380 °C, is close to crude oil Diesel's upper part of the distillation curve.

By adjusting the operating parameters, it is possible to control the product's mass ratio, e.g., reducing the Bottom and increasing the Stripper 2/Stripper fraction.

3.3. Discussion of strategies for waste plastic pyrolytic oil fractionation

Considering the above detailed conclusions, it may be assumed that the products from the separation of pyrolytic oil in the proposed simplified installation (case 3) can be combined with appropriate fractions from crude oil rectification and further processed together. However, it is necessary to emphasize that the analyses are based only on the results of distillation simulations and are focused on comparisons of distillation curves. Taking into account the different chemical compositions of pyrolytic and crude oil, it cannot be definitively stated whether the pyrolytic oil fractions have all the properties resembling the products of crude oil separation and can be upgraded together.

Despite the simplifications, the modified installations are still quite complex regarding equipment, requiring steam supply, maintaining appropriate pressure and precise parameters control. These kinds of installations may be too complicated and costly for small plastic pyrolysis plants. Therefore, it seems advisable to use this solution in large-scale plastic pyrolysis plants, where the stream feeding the column comes directly from the pyrolysis reactor.

Alternatively, the rectification installation can also be built as an independent, stand-alone unit for processing unrefined pyrolytic oil collected from several regional pyrolysis plants operating without oil fractionation (Faussone, 2018). A similar approach to the problem of pyrolytic oil management is applied in the ChemCycling project (ChemCycling, 2024). Local partners transfer plastic waste and end-of-life tires into pyrolytic oil. Oil is then collected and converted back into feedstock for the chemical industry in an integrated chemical production network.

It should be pointed out that all simulation results are determined for a selected set of operating parameters. Selecting the number of column stages and process parameters (temperature regime, pressure, flow ratio, reflux ratio, etc.), one can provide any required accuracy of oil blend fractionation. Thus, it may result in a better adjustment of the properties of plastic pyrolysis products to petroleum products.

The presented results were calculated for defined crude and pyrolytic oil compositions. A feature of both raw materials is the variability of their chemical composition depending on their origin (Maqsood et al., 2021, Shishkova et al., 2022). Each fossil oil, as well as pyrolytic oil, has unique properties, which is a challenge for refinery operators. Knowing the distillation curves of raw materials makes it possible to perform quick calculations and adjust the settings of the installation's operating parameters to obtain the desired product.

This work demonstrates the usefulness of simulation programs, such as ChemCad, for analysing complex industrial problems. Simulation software enables quick and low-cost calculations and adjustment of the installation parameters to the desired product quality.

Considering both the literature information and the simulation results discussed above, various concepts of pyrolytic oil fractionation plants can be considered to obtain products with high utility value. Table 10 summarizes the different strategies. The first two simple methods are typically used in existing commercial installations. The next two more advanced systems based on experience with crude oil processing are proposed as a result of this work.

A full quantitative comparison of all fractionation strategies, based on the mass & energy balances and investment & manufacturing costs, would require calculations of all variants for assumed production efficiency. It would also be necessary to define the goal function (e.g. cost minimization, return on investment time or product quality).

Table 10. Comparison of discussed pyrolytic oil fractionation strategies.

Fractionation strategy	Advantages	Disadvantages
Simple condensation unit (Krzywda and Wrzesińska, 2021)	• Simple equipment • Direct condensation in the pyrolysis plant • Oil separation into several factions possible	• Unsharp fraction cut-off • Inability to precisely control product quality
Simple rectification column (Krzywda and Wrzesińska, 2021)	• Sharp fraction cut-off • Direct fractionation in the pyrolysis plant • Adjusting product composition and yield by changing process parameters • Use the energy of hot post-pyrolytic gas to rectification process • Process experimentally tested	• Oil separation into two fractions only • More complex equipment
Classic crude oil processing plant, fed with crude oil with a small addition of pyrolytic oil (case 1)	• Commonly used, well-known rectification plant • Potential to obtain typical products with utility values	• Process not experimentally tested • Different pyrolytic and crude oil chemical compositions can reduce the quality of petrochemical products • Oil transport from the pyrolysis plant to the refinery is necessary
Independent, complex rectification plant (case 3)	• Sharp fraction cut-off • Fractions with a narrow boiling range corresponding to Naphtha, Kerosene, and Diesel • Products can potentially be refined together with petrochemical fractions • Precise control of composition and fraction ratio	• Sophisticated two-column installation with stripper • High technical operation requirements – variable pressure, steam supply • Dedicated to large-scale oil processing • Process not experimentally tested

4. CONCLUSIONS

The commonly used strategies of pyrolytic oil fractionation are based on stage condensation or simple rectification with a limited possibility of controlling product parameters. To increase the utility value of products, in order to meet the requirements for market fuels, a new approach to this problem was proposed. Based on crude oil processing experience, the fractionation unit's innovative configurations were analysed using ChemCad simulation software. The use of a classic crude oil rectification installation (case 1) and designed on its basis simplified units (cases 2 and 3) were considered for fractionation of pyrolytic oil derived from waste plastic.

It was concluded that, due to the different compositions and properties of crude oil and pyrolytic oil, mainly different boiling temperature ranges of both raw materials, the direct use of a classic crude oil rectification installation does not seem advisable. However, a small addition of pyrolytic oil to the crude oil stream does not cause significant changes in the properties of the six obtained products. The strategy of mixing pyrolytic oil with crude oil and processing them together is worth experimental research.

The installations proposed in cases 2 and 3 reduce the number of obtained streams from six to four. The products resemble Naphtha, Kerosene, and Diesel from crude oil separation, so further upgrading of the combined pyrolytic and crude oil fractions may be considered. This strategy is dedicated to large-scale pyrolysis plants or independent, stand-alone units for processing raw oil collected from local pyrolysis reactors.

The use of advanced rectification unit is a promising direction in increasing the value of pyrolysis as a method of plastic waste recycling.

ACKNOWLEDGEMENTS

This work was supported by the Scientific Council of the Discipline of Chemical Engineering (I. Chem-3, project no. 3-3.3), Warsaw University of Technology.

REFERENCES

ASTM D3699-19. *Standard Specification for Kerosine*. DOI: 10.1520/D3699-19.

ASTM D86-23. *Standard test method for distillation of petroleum products and liquid fuels at atmospheric pressure*. DOI: 10.1520/D0086-23AE01.

Bezergianni S., Dimitriadis A., Faussone G.-C., Karonis D., 2017. Alternative diesel from waste plastics. *Energies*, 10, 1750. DOI: 10.3390/en10111750.

ChemCycling, 2024. *Creating a circular plastics economy with chemical recycling*. Available at: https://www.basf.com/global/en/who-we-are/sustainability/we-drive-sustainable-solutions/circular-economy/mass-balance-approach/chemcycling.html.

EN 590:2022-08. *Automotive fuels – Diesel – Requirements and test methods.*

EN ISO 3405:2019. *Petroleum and related products from natural or synthetic sources. Determination of distillation characteristics at atmospheric pressure.*

Faisal F., Rasul M.G., Jahirul M.I., Chowdhury A.A., 2023. Waste plastics pyrolytic oil is a source of diesel fuel: a recent review on diesel engine performance, emissions, and combustion characteristic. *Sci. Total Environ.*, 886, 163756. DOI: 10.1016/j.scitotenv.2023.163756.

Faussone G.C., 2018. Transportation fuel from plastic: two cases of study. *Waste Manage.*, 73, 416–423. DOI: 10.1016/j.wasman.2017.11.027.

Fulgencio-Medrano L., García-Fernández S., Asueta A., Lopez-Urionabarrenechea A., Perez-Martinez B.B., Arandes J.M., 2022. Oil production by pyrolysis of real plastic waste. *Polymers,* 14,553. DOI: 10.3390/polym14030553.

Jahirul M.I., Faisal F., Rasul M.G., Schaller D., Khan M.M.K., Dexter R.B., 2022a. Automobile fuels (diesel and petrol) from plastic pyrolysis oil – production and characterisation. *Energy Rep.*, 8, 730–735. DOI: 10.1016/j.egyr.2022.10.218.

Jahirul M.I., Rasul M.G., Schaller D., Khan M.M.K., Hasan M.M., Hazrat M.A., 2022b. Transport fuel from waste plastics pyrolysis – a review on technologies, challenges and opportunities. *Energy Convers. Manage.*, 258, 115451. DOI: 10.1016/j.enconman.2022.115451.

Kalargaris I., Tian G., Gu S., 2017. Combustion, performance and emission analysis of a DI diesel engine using plastic pyrolysis oil. *Fuel Process. Technol.*, 157, 108–115. DOI: 10.1016/j.fuproc.2016.11.016.

Krzywda R., Wrzesińska B., 2021. Simulation of the condensation and fractionation unit in waste plastics pyrolysis plant. *Waste Biomass Valorization*, 12, 91–104. DOI: 10.1007/s12649-020-00994-7.

Kumar S., Prakash R., Murugan S., Singh R.K., 2013. Performance and emission analysis of blends of waste plastic oil obtained by catalytic pyrolysis of waste HDPE with diesel in a CI engine. *Energy Convers. Manage.*, 74, 323–331. DOI: 10.1016/j.enconman.2013.05.028.

Kunwar B., Chandrasekaran S.R., Moser B.R., Deluhery J., Kim P., Rajagopalan N., Sharma B.K., 2017. Catalytic thermal cracking of postconsumer waste plastics to fuels. 2. Pilot-scale thermochemical conversion. *Energy Fuels,* 31, 2705−2715. DOI: 10.1021/acs.energyfuels.6b02996.

Maqsood T., Dai J., Zhang Y., Guang M., Li B., 2021. Pyrolysis of plastic species: a review of resources and products. *J. Anal. Appl. Pyrolysis*, 159, 105295. DOI: 10.1016/j.jaap.2021.105295.

Murthy K., Shetty R.J., Shiva K., 2023. Plastic waste conversion to fuel: a review on pyrolysis process and influence of operating parameters. *Energy Sources, Part A*, 45, 11904–11924. DOI: 10.1080/15567036.2020.1818892.

Panda A.K., Singh R.K., Mishra D.K., 2010. Thermolysis of waste plastics to liquid fuel: a suitable method for plastic waste management and manufacture of value added products – a world prospective. *Renewable Sustainable Energy Rev.,* 14, 233–248. DOI: 10.1016/j.rser.2009.07.005.

Pradipta I.Z., Rochmadi, Purnomo C.W., 2019. High grade liquid fuel from plastic waste pyrolysis oil by column distillation. *IEEE Conference on Energy Conversion (CENCON),* Yogyakarta, Indonesia, 2019, 240–244. DOI: 10.1109/CENCON47160.2019.8974811.

Shishkova I., Stratiev D., Kolev I.V., Nenov S., Nedanovski D., Atanassov K., Ivanov V., Ribagin S., 2022. Challenges in petroleum characterization – a review. *Energies,* 15, 7765. DOI: 10.3390/en15207765.

Siddiqui M.N., Redhwi H.H., 2009. Pyrolysis of mixed plastics for the recovery of useful products. *Fuel Process. Technol.*, 90, 545–552. DOI: 10.1016/j.fuproc.2009.01.003.

Silva A.P., Bahú J.O., Soccol R., Rodríguez-Urrego L., Fajardo-Moreno W.S., Moya H., León-Pulido J., Cárdenas Concha V.O., 2023. Naphtha characterization (PIONA, density, distillation curve and sulfur content): An origin comparison. *Energies*, 16, 3568. DOI: 10.3390/en16083568.

Statista Research Department, 2024. *Global cumulative production of plastic 1950–2050*. Available at: https://www.statista.com/statistics/1019758/plastics-production-volume-worldwide.

Thahir R., Altway A., Juliastuti S.R., Susianto, 2019. Production of liquid fuel from plastic waste using integrated pyrolysis method with refinery distillation bubble cap plate column. *Energy Rep.*, 5, 70–77. DOI: 10.1016/j.egyr.2018.11.004.

Thahir R., Irwan M., Alwathan A., Ramli R., 2021. Effect of temperature on the pyrolysis of plastic waste using zeolite ZSM-5 using a refinery distillation bubble cap plate column. *Results Eng.*, 11, 100231. DOI: 10.1016/j.rineng.2021.100231.

Vijayakumar A., Sebastian J., 2018. Pyrolysis process to produce fuel from different types of plastic – a review. *IOP Conf. Ser.: Mater. Sci. Eng.*, 396, 012062. DOI: 10.1088/1757-899X/396/1/012062.

Zeb W., Roosen M., Knockaert P., Janssens S., Withoeck D., Kusenberg M., Hogie J., Billen P., Tavernier S., Van Geem K M., De Meester S., 2023. Purification and characterisation of post-consumer plastic pyrolysis oil fractionated by vacuum distillation. *J. Cleaner Prod.*, 416, 137881. DOI: 10.1016/j.jclepro.2023.137881.

Zeller M., Netsch N., Richter F., Leibold H., Stapf D., 2021. Chemical recycling of mixed plastic wastes by pyrolysis – pilot scale investigations. *Chem. Ing. Tech.*, 93, 1763–1770. DOI: 10.1002/cite.202100102.

Zhao D., Wang X., Miller J.B., Huber G.W., 2020. The chemistry and kinetics of polyethylene Pyrolysis: a process to produce fuels and chemicals. *ChemSusChem.*, 13, 1764–1774. DOI: 10.1002/cssc.201903434.