

Co-processing of Algae Hydrothermal Liquefaction of Oil with VGO via Fluid Catalytic Cracking: Process Simulation and Optimization

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Abstract

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Biofuels are expected to play a vital role in decreasing greenhouse gas emissions and facilitating the progressive transition from fossil fuels, resulting in low-carbon, high-sustainability fuels. The inclusion of biofuel sources into conventional petroleum refineries is gaining interest due to the increased crude oil prices, environmental concerns, and the necessity to maintain an energy supply. Processing alternative feedstocks would not necessitate substantial capital investments because refineries already have a well-established infrastructure for creating fuels and basic chemicals. There are several technological obstacles when converting bio-oil to transportation fuel on a large scale. The sensitivity analysis was used to confirm the improved simulation result, then compared to an experimental result from the literature. The effect of reactor temperature on feed conversion and product yield, mainly naphtha, light cycle oil (LCO), and fuel gas, was investigated. Furthermore, the effectiveness of various algae-hydrothermal liquefaction (AHTLO) mix ratios with VGO, ranging from 5, 10, and 15 wt%, was investigated. Moreover, a study was conducted on optimizing riser output temperatures and feed mass ratios to maximize the total naphtha and LCO or naphtha and LPG output and increase the production capacity. It was found that as the ratio of AHTLO increased, the conversion of all products and fuel gas yield decreased while the LCO increased. However, there was no discernible variation in the ratio of Naphtha.

Introduction

The quality of crude oil resources worldwide is deteriorating [1,2]. After 2020, heavy crude oil reserves are expected to account for almost half of all recoverable reserves [3]. In refineries, the FCC unit has a significant impact on the conversion of heavy oil into light fraction products such as dry gas, liquefied petroleum gas (LPG), high octane number gasoline, and light cycle oil (LCO) [4]. Crude oil is a nonrenewable resource; however, oil and its derivatives continue to draw global attention because they account for 32% of global energy supply capacity [5]. Most of the fuels used in transportation equipment like cars, aircraft, and ships are petroleum products. The petroleum refining sector mainly generates the primary organic petrochemicals (ethylene and propylene) [6]. Furthermore, increases in industrialization are expected to increase demand for different petroleum and petrochemical products shortly [7].

Renewable energy and renewable fuels are critical for our society's long-term viability [8]. Bioenergy is a

carbon-free, renewable energy source. Gaseous products, biofuels, and other compounds may be made [9]. As a result, biomass-based biofuels may be a viable alternative to fossil fuels [10]. Biofuels of the first generation are mostly made from food, restricting their widespread usage due to competition for food supply and agricultural land. Because of their poor conversion rates, second-generation biofuels generated from non-food crops and non-edible components of food crops, agricultural and forestry wastes, and municipal solid wastes are commercially unviable for the market [11,12]. As a result, attention has shifted to microalgae to produce third-generation biofuels.

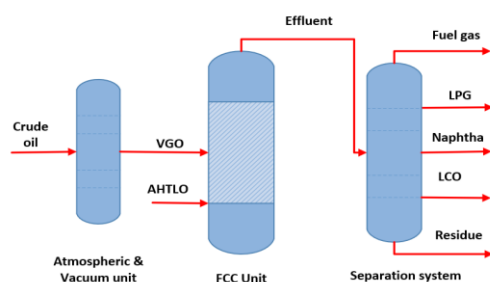


Figure 1 The basic flowsheet of the coprocessing system via FCC unit.

Microalgae is a renewable biomass source. They may be produced on non-arable terrain, in freshwater, or even in brackish/saline water on a large scale [11]. These single-celled photosynthetic bacteria overgrow and may be grown all year [13]. Microalgae may reduce global warming by absorbing CO₂ at a rate of 1.83 kg CO₂ per kg of dried algae [14]. Additionally, microalgae produce bio-oil more than other biomass feedstocks [15]. According to life cycle assessments, HTL-derived algae fuels have lower energy loads and GHG emissions than petroleum fuels, conventional biofuels, and algal biofuels produced using methods other than HTL [16, 17]. Developments in downstream processing, afforded by the ability to process HTL bio-oils in current petroleum refineries with regular FCC inputs, might help algal HTL fuels achieve even better energy and GHG profiles [16]. The biocrudes generated are expected to be suitable for upgrading conventional crude oil refining plants, lowering capital expenditures [18]. Hydrothermal liquefaction also decreases post-processing issues since only a small amount of nitrogen in algal feedstock increases in the oil phase [15].

The hydrothermal liquefaction process can use wet algal efficiently without preprocessing, avoiding energy-intensive drying and fractionation stages [19, 20]. In addition, pyrolysis bio-oil includes more heteroatoms (sulphur, nitrogen, and oxygen), are more acidic, and have a lower heating value than HTL bio-oils. [21-23]. Because bio-oils must be improved before being used as transportation fuel, Co-processing bio-oils with petroleum feedstocks in existing petroleum refineries might lower the capital expenditures while also avoiding several difficulties arising from processing bio-oils alone [21, 23].

Co-processing guarantees the long-term full utilization of existing facilities. Co-processing bio-oil in present refineries can decrease the cost of upgrading [24]. Catalytic hydrocracking and fluid catalytic cracking (FCC) are the primary methods for co-processing bio-oil with petroleum fractions [25]. Co-processing bio-oil with petroleum fraction under FCC conditions is less technologically complex [25, 26]. The FCC is a noteworthy unit for co-processing because of its catalytic activity, which accelerates the deoxygenation reaction since bio-oil includes a specific number of oxygenates [26]. The majority of investigations in the literature have used zeolite

catalysts that have been proven effective for deoxygenation.

In general, as shown in Figure 1, this study has taken the lead in the simulation and optimization of the co-processing of AHTLO with VGO via FCC to include AHTLO in current refiners. The goal is to study the change in conversion and the yield of primary products at various operating conditions using varied ratios of AHTLO to VGO. The process was then optimized to increase the yield of naphtha and LPG or naphtha and LCO. Through this development, the existing refinery would be further improved, integration would be made possible, and the cost of the current competition would be decreased. As a result, progressively increasing attempts to switch from fossil fuels to biofuels will be supported, lowering greenhouse gas emissions.

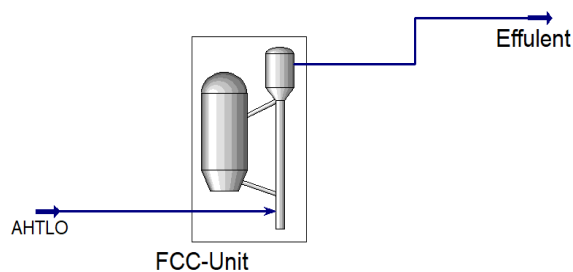


Figure 2 The diagram for the simulation process in HYSYS.

Materials and Methods

Process Simulation

The simulation process, as shown in Figure 2, was done using the commercial code Aspen HYSYS V12 and applying the "Peng–Robinson" equations of state fluid package. Based on the literature [27], a base case simulation for the FCC unit was completed and validated. The operating conditions for the FCC unit are given in Table 1. The simulation model was modified by co-processing bio-oil with the VGO in the FCC unit by a co-processing blend having a VGO content of 0, 5, 10, and 15 wt% of AHTLO.

Table 1 FCC operating conditions.

Operating condition	Value [27]
Volume Flow (ton/h)	115
Temperature (°C)	175
Pressure (kPa)	601.3
Total Feed Temperature (°C)	175
Steam Mass (kg/h)	5200
Steam Temperature (°C)	200
Steam Pressure (kPa)	1301
Riser Outlet Temperature (°C)	518
Stripping Steam Rate (kg/h)	5000
Regenerator Pressure (kPa)	296.5

Feed Composition and Properties

The properties of reference feed VGO were taken from Chang et al. [27] and are shown in Table 2. The AHTLO composition from the literature [28] is shown in Table 3.

Table 2 Reference feed VGO properties.

Feed	VGO
Specific Gravity	0.9233
Distillation Type	D1160
Initial point (°C)	269.0
5%	358.6
10%	376.4
30%	419.0
50%	452.3
70%	488.0
90%	541.8
95%	567.9
End Point	665.8
Nitrogen (ppm wt)	2409.0
Sulfur (wt.%)	0.56

Process Optimization

After doing a simulation for co-processing of AHTLO with VGO and comparing the results, 5% showed the best results in the product yields compared to 10% and 15%. So, we decided to optimize the process with 5% AHTLO to maximize the yield of a good product slate. That will decrease the economic cost of co-processing with a green base oil by maximizing the profits of both products, and that will encourage the refineries to use the AHTLO with VGO in the feed. Refiners may need to maximize

the production of gasoline and diesel or maximize the production of gasoline and LPG, depending on external constraints [27]. We can use the Aspen HYSYS model to study naphtha and LCO or naphtha and LPG production yields at different ROT and feed mass ratios. The LPG yield is calculated as the sum of propane, propylene, i-butane, n-butane, and butenes.

Table 3 Compounds used to model AHTLO feed.

HTL OIL	Wt%
1-ethyl-2-pyrrolidinone *	6.79%
N-methylthiopyrrolidone	1.03%
Ethylbenzene	2.55%
4-methyl phenol	5.09%
4-Ethylphenol	5.09%
Indole	5.09%
7-Methylindole *	3.4%
Myristamide (C14 amide) *	3.4%
Palmitamide (C16 mide) *	15.28%
Stearamide (C18 amide) *	6.79%
Palmitoleic acid (C16:1FA) *	13.58%
Palmitic acid (Hexadecanoic acid)	10.19%
Oleic acid	1.7%
Naphthalene	5.09%
Fused rings (cholesterol)	1.7%
Aromatic amines	8.14%
1,2-Benzenedicarboxylic acid *	5.09%
	100%

Note: * the component is not present in the Aspen HYSYS database, so it was created as a hypothetical component from the Aspen Plus database.

Results and Discussion

Simulation Results

The total of fuel gas, LPG, gasoline, coke, carbon dioxide, carbon monoxide, water, light cycle oil (LCO), and residual bottoms was defined as reaction conversion [27]. Figure 3 shows feed conversion at different riser output temperatures (ROT) ranging from 480°C to 540°C for pure VGO and AHTLO ratios of 5%, 10%, and 15%. The increased temperature is unfavorable due to the increased generation of undesirable light gases. The pure VGO was used as the standard for a comparison study of co-processing AHTLO. As shown in Figure 3, the pattern between pure VGO and co-processing shows that the conversion increases as the ROT increase. Compared to the baseline VGO feed, co-processing the AHTLO blends with 5%, 10%, and 15% resulted in corresponding decreased conversion levels in the FCC reactor. That was

related to higher catalyst inhibition in the biocrude blends because of the nitrogen and oxygen compounds [29].

Figure 4 shows naphtha yield at different ROT, ranging from 480°C to 540°C for pure VGO and 5%, 10%, and 15% by wt. of AHTLO ratios. The Figure shows that when ROT increases, the production yield of naphtha also increases. Naphtha production achieves its maximum profit at a ROT of 535°C, and the naphtha yield decreases after this point. These patterns indicate to the stream being "over cracked" [27]. The increased generation of lightweight components (C1–C4) via the catalytic and thermal cracking pathways is an undesired result of the high temperature, which is an unintended outcome given that we want to maximize naphtha yield compared to dry gases [27]. Furthermore, as shown in Figure 4, the yield production of naphtha is not affected much by the coprocessing with 5%, 10%, and 15% by wt. AHTLO ratios, in compared with the pure VGO feed.

Figure 5 shows the result of LCO yield with a different AHTLO ratio of 5%, 10%, and 15% by wt. at ROT from 500°C to 540°C. According to the Figure, the LCO yield decreases as the ROT increases because a higher temperature would crack light cycle oil into lighter products [27]. The coprocessing with AHTLO produces a higher LCO yield when compared with pure VGO. The production yield of LCO increases as the amount of AHTLO in the feed increases. Zhang et al. explained that increasing the LCO yield at the coprocessing is the higher amount of diaromatic compounds in HTL biocrude, which are the LCO precursors in FCC [29].

Figure 6 shows the result of the fuel gas production yield for coprocessing with 5%, 10%, and 15% by wt. AHTLO ratios at ROT from 480°C to 540°C. As shown in the Figure, the yield of fuel gas increases as the ROT increases. Thermal cracking produces many light compounds, which explains the rise in fuel gas yield [27]. Coprocessing with AHTLO has a lower product of fuel gas when compared with pure VGO. Increasing the conversion yield of the coprocessing VGO with HTL biocrude leads to more undesirable fuel gas [29], which correlates to our results. The conversion yield decreases by increasing the output of AHTLO compared with pure VGO (see Figure 3).

Optimization Results

As shown in Figure 7, while naphtha reached the maximum production yields at 535°C ROT, the LCO yield dropped. This means that the feed is being "over-cracked." Furthermore, fuel gas and LPG yields are rapidly increasing. Fuel gas is not of significant value compared to the other liquid products. Through catalytic and thermal cracking pathways, the high temperature accelerates the generation of light components. On the other hand, increasing ROT will increase LPG production yields. LPG is a valuable product used in the petrochemical industry as a feedstock. In addition, the Figure shows the coke yield as a function of ROT on the catalyst. ROT strongly affects the amount of coke present on the catalyst leaving the riser. When using a regenerating catalyst with higher coke deposits, the energy required to

regenerate the coke is increased. The allowable range of values for the ROT is limited because of these adverse effects.

Maximize the production of naphtha and LCO

The production of naphtha and LCO is a typical complicated function with ROT. Figure 8 shows the effect of both ROT and feed mass rate on the sum of naphtha and LCO production yields. The Figure depicts the link between the total output and the unit feed mass ratio. The yield of products reduced as the quantity of feed increased. Higher feed rates result in a shorter contact time with the catalyst, which reduces component cracking and thus decreases liquid product yield. Furthermore, as the ROT approaches 535°C, the naphtha production rapidly decreases. It happens when we've reached the "over cracking" peak for this feed. Therefore, the ROT must be set below 520°C to increase naphtha and LCO yield and feed rate simultaneously. Finally, we recommend the refineries select the suitable feed rate from the Figure that suits the other results of unpreferred products (coke-fuel gas) and the utility capacity of the FCC unit.

Maximize the production of naphtha and LPG

Figure 9 shows the impact of ROT and feed mass rate on the total yield of naphtha and LPG. As many chemicals in the cut are particularly fascinating as petrochemical raw materials, it is always interesting to know how LPG yields behave. Propylene, for example, is in a growing market and on the growth, while isobutane is a key ingredient in alkylation. Furthermore, in some countries with limited natural resources, LPG is a vital gas fuel [30]. Therefore, some refineries prefer to increase the yield of LPG and naphtha to meet the feedstock needs of the petrochemical industry. Thus, as shown in Figure 6, as the ROT increases, the product of LPG directly increases. However, as shown in Figure 8, as the mass feed ratio increases, the production yield of naphtha and LPG decreases. Therefore, to increase naphtha and LPG yield and feed rate simultaneously, ROT needs to be set at 540°C.

We recommend that refineries operate at ROT in the range of 530°C to 540°C to ensure a higher production yield of naphtha and LPG combined and choose the suitable feed rate from the Figure that matches the other unpreferred product yields (coke-fuel gas) and the FCC unit's utility capacity.

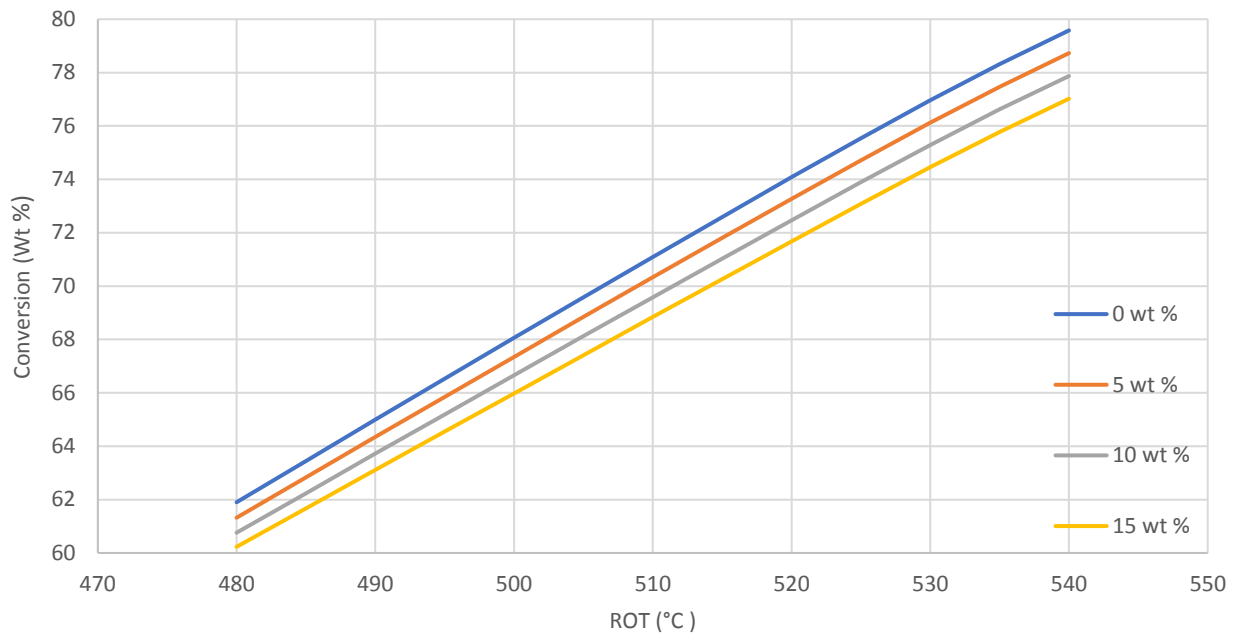


Figure 3 Effect of ROT on Conversion wt% of co-processing

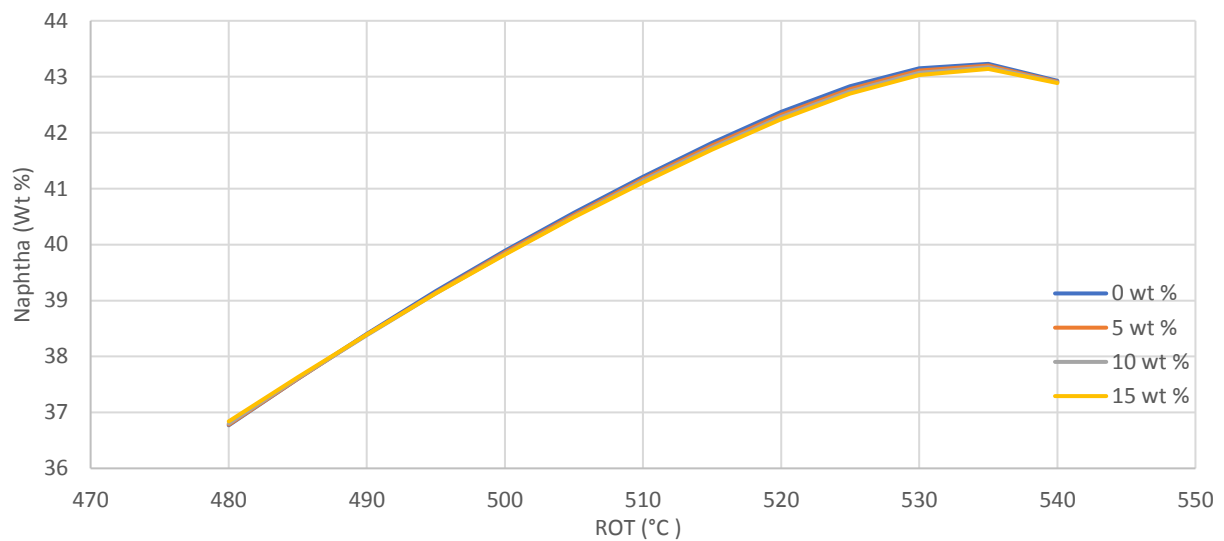


Figure 4 Effect of ROT on Naphtha yield of co-processing.

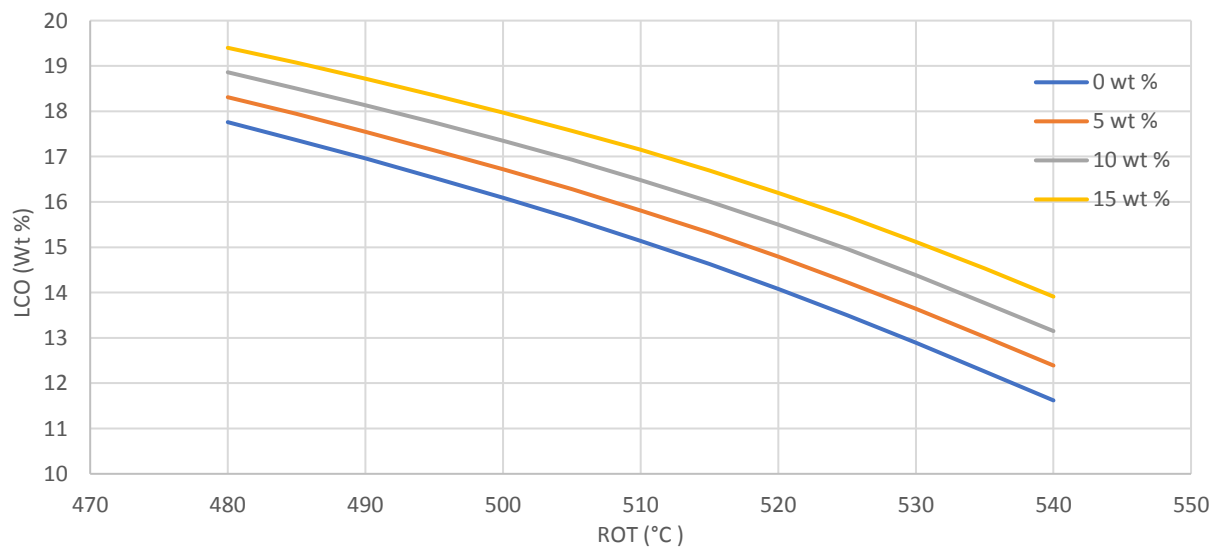


Figure 5 Effect of ROT on LCO yield of co-processing.

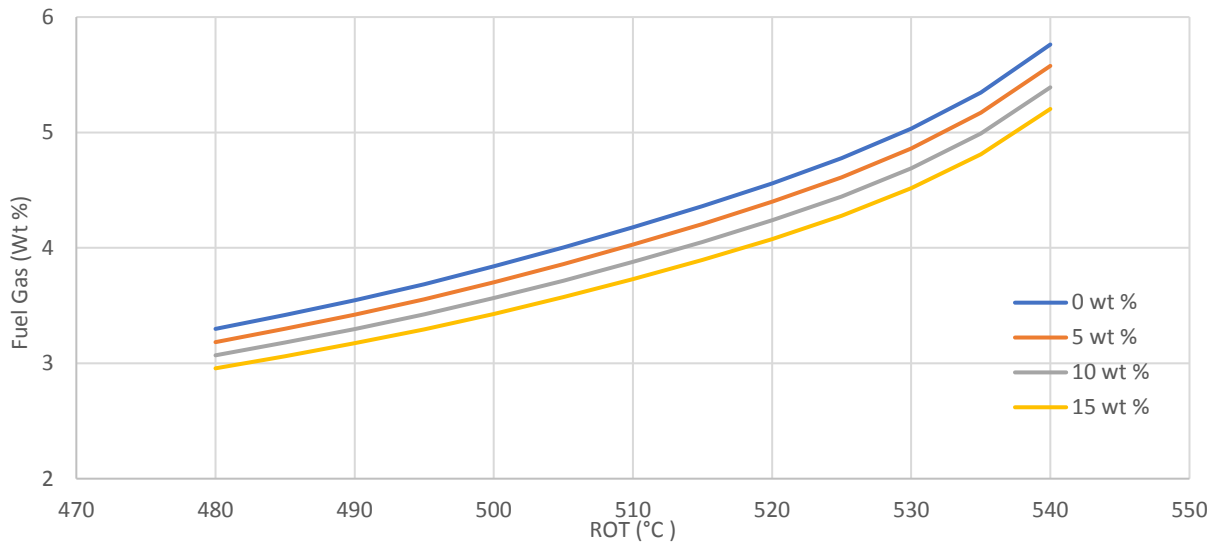


Figure 6 Effect of ROT on Fuel gas yield of co-processing.

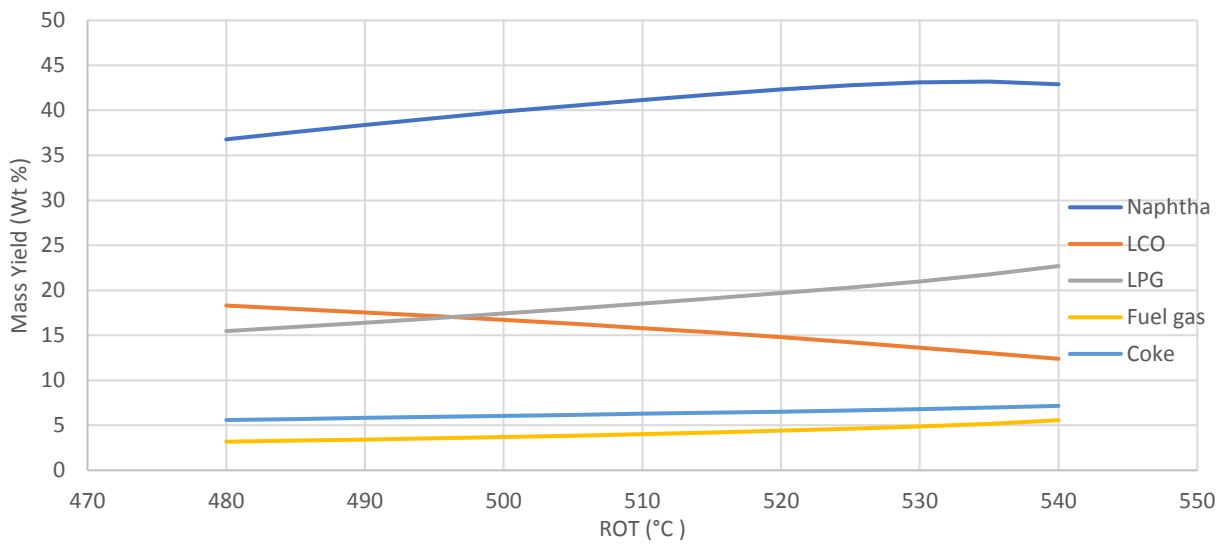


Figure 7 Effect of ROT on products yield of co-processing.

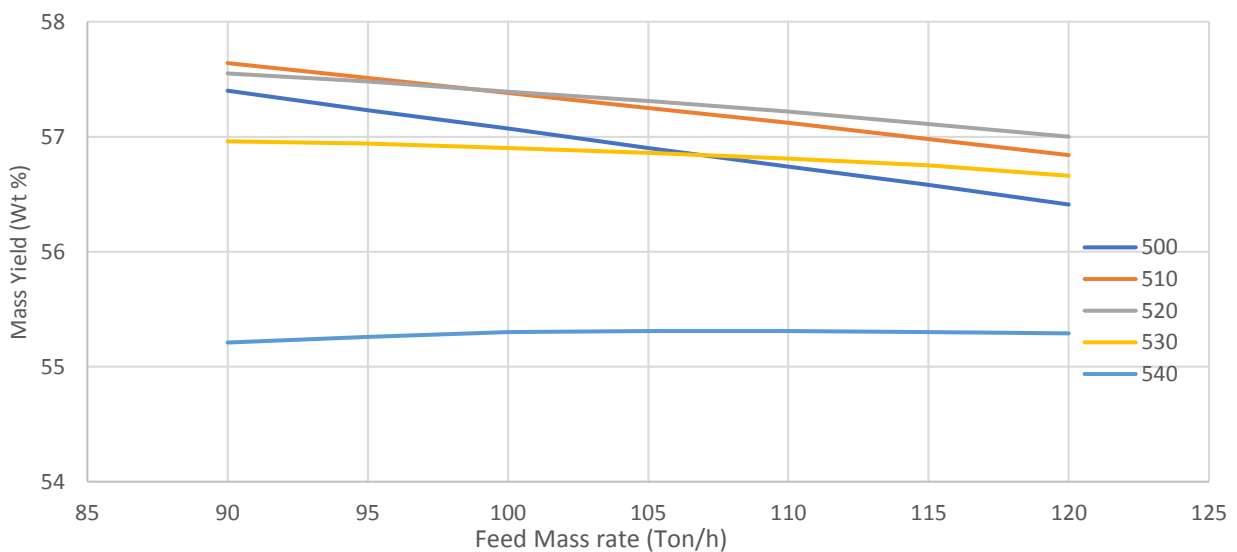


Figure 8 Effect of ROT and mass feed on Naphtha and LCO yield of co-processing.

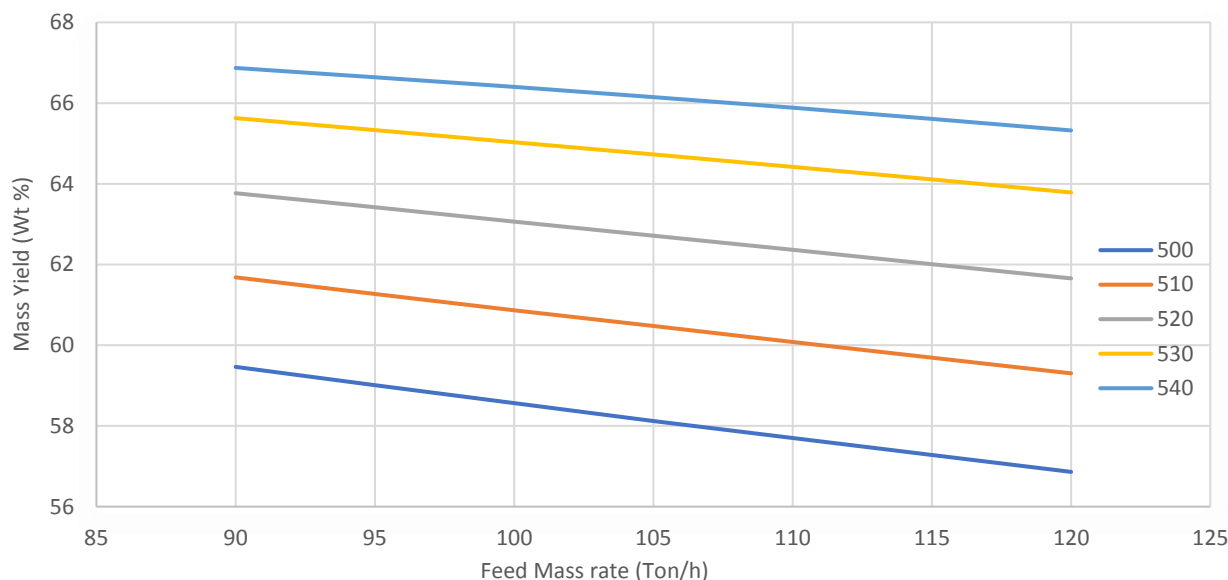


Figure 9 Effect of ROT and mass feed on Naphtha and LPG yield of co-processing.

Conclusions

In this work, Aspen HYSYS was used to simulate and optimize the co-processing of AHTLO and VGO via the FCC unit. At the same time, the effects of ROT and the AHTLO feed ratio on conversion and product yields were studied. According to the results, it can be concluded that:

- The co-processing decreased the conversion yield, and the 15% AHTLO obtained the lowest conversion yield. As the ROT increases, the conversion rate also increases.
- The naphtha production yield is not affected much more by the coprocessing with all AHTLO blends. As the ROT increases, the naphtha yield rises until it reaches 535°C ("over cracking"), and the output starts to fall after that.
- The LCO yield increases with the increase in the AHTLO ratio. The 15% AHTLO obtains the highest LCO yield. As the ROT increases, the LCO yield decreases.
- The fuel gas yield decreases with an increase in the AHTLO ratio. As the ROT increases, more fuel gas cracks, increasing the output.
- The optimization results for 5% AHTLO show that to increase the total yield of naphtha and LCO, and ROT should be between 510 and 520°C; for naphtha and LPG, ROT should be between 530 and 540°C.

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