Catalyst to oil mass ratio optimization on fluid catalytic cracking process in green gasoline production

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Abstract. Palm oil has potential as raw material for green gasoline as renewable energy source. One of the most important variables to support the achievement optimum operating condition in the Fluid Catalytic Cracking (FCC) process was the mass ratio of catalyst to oil (c/o). The FCC process simulation was carried out by using an Advance Cracking Evaluation (ACE) unit at mass ratio c/o (4.00, 5.00, 5.56, 6.00, 6.52) w/w ASTM D3907. The quality test of the FCC product were distribution of boiling point by using Refinery Gas Analyzer (RGA) Chromatography ASTM D2504 and using high temperature distillation simulating gas chromatography ASTM D7169, octane number by using Detailed Hydrocarbon Analysis (DHA) Chromatography ASTM D6730 and coke formation by using CO Analyzer ASTM D6316. The study shown that the most optimum c/o ratio in FCC process was at ratio 6.00 w/w with the amount of dry gas product 2.48 percent w/w, LPG 27.36 percent w/w, gasoline 41.81 percent w/w, LCO 11.54 percent w/w, HCO 0.00 percent w/w, bottom 3.71 w/w, and coke 12.99 percent w/w with octane number was 84.693. It can be concluded that FCC process of the palm oil mixture feed at this ratio has better quality than PT Pertamina's FCC feed.

1. Introduction

The need of fuel oil in Indonesia reached 1.3 million barrels per day (bpd) in 2013, so it was necessary to import 600 thousand bpd of fuel oil with a value of more than 14 thousand trillion rupiahs per day [1]. These problems prompted the government to stipulate Regulation of the President of the Republic of Indonesia Number 5 Year 2006 concerning national energy policy to develop alternative energy sources as a substitute for fuel oil. This is the country's effort in developing renewable fuels to reduce crude oil imports. One alternative material that has the potential to substitute for petroleum is vegetable oil.

Palm oil is one of the vegetable oils that has the potential to be used as an alternative fuel in Indonesia. Indonesia is one of the largest palm oil producing countries in the world. Indonesia's total crude palm oil production reached 21.0 million tons in 2010 and continued to increase to 22.2 million tons in 2011 [2]. In addition, the use of palm oil as an alternative fuel is more environmentally friendly, which is free of sulphur and nitrogen. Palm oil has a long hydrocarbon chain that has the potential to be used as biofuel [3]. This background encourages the fuel industry to use palm oil as a feed mixture in the FCC process in the production of green gasoline. Before large-scale production is held, a small-scale trial is needed first, to find out the right FCC operating conditions in an effort to obtain the most optimum green

gasoline production. One of the most important variables that support the achievement of the most optimum operating conditions in the FCC process is the catalyst, so in this experiment the optimization of the FCC process was carried out by varying the catalyst to oil (c/o) mass ratio. The mass ratio (c/o) is the ratio of the weight of the catalyst circulated to the reactor with the weight of the feed entering the reactor. Generally, this c/o ratio can vary between 3-7 (w/w) [4]. In the FCC process, this c/o ratio affects cracking reactions, coke formation, heat formation and whether the heat balance of the reactor and its regenerator is achieved. Excessive cracking reaction will cause the formation of products dominated by very mild fractions, such as dry gas, which is excessive. However, if the cracking reaction condition is not achieved, it can cause the formation of products dominated by heavy fractions, such as HCO and bottom [4]. These various effects indicate the need for optimization of the mass ratio c/o in the FCC process in the production of green gasoline.

This study aims to find out the optimum c/o mass ratio in the FCC process in the production of green gasoline, which is seen from the amount of dry gas products, liquid petroleum gas (LPG), gasoline, light cycle oil (LCO), heavy cycle oil (HCO) , bottom and coke and the value of the octane number. In addition, to find out the quality of FCC products from palm oil mixed feeds, the product yields are compared with products produced from PT Pertamina's FCC feed.

2. Methodology
This study consists of five stages, namely the characterization of palm oil (specific gravity ASTM D1298 [5], carbon residues ASTM D4530 [6], pour points ASTM D97 [7], and viscosity D445 [8]), feed preparation, catalyst preparation, the FCC process simulation stage, and the FCC product quality test stage. The Scheme of the experiment can be seen in Figure 1.
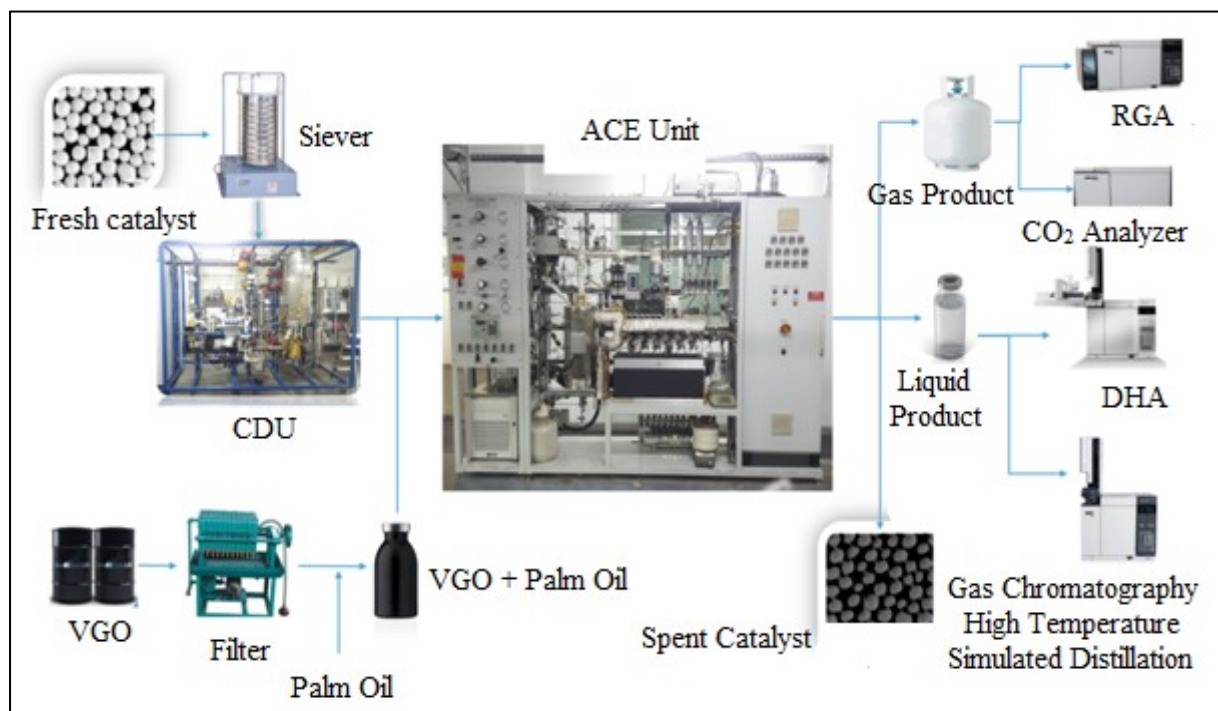

Figure 1. The scheme of the experiment.

The FCC process simulation stage is carried out at the mass ratio c/o (4.00, 5.00, 5.56, 6.00, 6.52) w/w. The simulation of the FCC process was carried out by using an Advance Cracking Evaluation (ACE) unit, which refers to ASTM D3907 [9]. The quality test of the FCC product includes the distribution of boiling points, octane numbers and coke formation. The boiling point distribution test was performed by using Refinery Gas Analyzer (RGA) chromatography to determine the amount of dry gas, LPG and light gasoline products that refer to ASTM D2504 [10] and using high temperature

distillation simulating gas chromatography to determine the amount of gasoline products, LCO, HCO and bottom which refers to ASTM D7169 [11]. Boiling point distribution can provide information about the estimated mass percent of the product based on its boiling point. The higher amount of gasoline and LPG products, followed by the lower number of dry gas products, LCO, HCO and bottom can improve the quality of FCC products. The octane number test was carried out by using Detailed Hydrocarbon Analysis (DHA) chromatography which refers to ASTM D6730 [12]. Octane numbers were numbers that indicate the ability of the fuel to resist spontaneous combustion during compression, before the spark. Easy spontaneous combustion occurs in fuel during compression, will cause knocks that potentially damage the vehicle engine. The higher-octane number, the better quality of the fuel product [13]. Testing for the formation of coke products was carried out by using CO_2 analyser that refers to ASTM D6316 [14]. This test was done to determine the amount of coke formed from the FCC process. The FCC process requires coke products, to meet the heat balance of the reactor and regenerator in the cracking process. In this optimization it was expected to know the c/o ratio with the best criteria, namely the formation of lower coke products, but not far from the value of the formation of coke from commercial feed used in PT Pertamina's FCC unit.

3. Results and discussion

3.1. Characterization of palm oil

In this study the optimization of the mass ratio c/o in the FCC process in the production of green gasoline was simulated by using the ACE unit. Before the optimization process was carried out, palm oil was characterized first. The results of testing the characteristics of palm oil can be seen in Table 1.

Table 1. The characteristics of palm oil test result.

Test Parameters	Standards	Palm Oil	VGO Commercial (JECHURA, 2014)	Unit	Expected Results	Obtained Results
Specific gravity	ATSM D1298	0.91	0.93		< Commercial VGO	As expected
Carbon residue	ASTM D4530	0.1	0.26	% (w/w)	< Commercial VGO	As expected
Viscosity	ASTM D445	40	48	cSt	< Commercial VGO	As expected
Pour Point	ASTM D97	9.0	48.0	^{0}C	< Commercial VGO	As expected

Through various parameters that have been tested, it can be seen from Table 1. that palm oil has the dominant components of paraffin or isoparaffin, compared to olefin. The paraffin and isoparafin components are needed to improve the characteristics and quality of the feed [15]. Based on Table 1. it appears that the specific gravity, Carbon residue, viscosity, and pour point value of the palm oil have expected value. The specific gravity of the palm oil sample was 0.91. Generally atmospheric residues such as VGO, have specific gravity values reaching 0.93. These results indicate that by adding palm oil to VGO, the specific gravity value is estimated to decrease, meaning that by adding palm oil to VGO can improve product quality. Low specific gravity shows high paraffinity. Conversely, if the specific gravity value is high, the olefinity oil is more dominant [16]. While Carbon residue from palm oil samples was 0.10% w/w. Generally, atmospheric residues such as VGO, have a carbon residue amount of 0.26% w/w. These results indicate that by adding palm oil to VGO, the amount of carbon residue was expected to decrease, meaning that by adding palm oil to VGO can improve product quality. Testing of carbon residues is used to give an indication of the tendency for the formation of coke from oil when processed in the FCC process [4]. The viscosity of the palm oil sample was 40 cSt. Generally, the

atmospheric residues, such as VGO, have viscosity values up to 48 cSt. These results indicate that by adding palm oil to VGO, the viscosity value was estimated to decrease, meaning that by adding palm oil to VGO can improve product quality. The pour point of palm oil sample was 9.0 □C. Atmospheric residues such as VGO, have a pour point value of up to 48.0 □C. These results indicated that by adding palm oil to VGO, the pour point value is expected to decrease, meaning that adding palm oil to VGO can improve product quality. Through some testing of these parameters, it can be seen that palm oil has the dominant components of paraffin or isoparaffin, compared to olefin. The paraffin and isoparafin components were needed to improve the characteristics and quality of the feed.

3.2. FCC process stimulation

The simulation stage of the FCC process using the ACE unit, referring to ASTM D3907 [9], is carried out at the c / o ratio used in this experiment (4.00, 5.00, 5.56, 6.00, 6.52) w/w. The flow diagram of the FCC process simulation on the ACE unit can be seen in Figure 2.
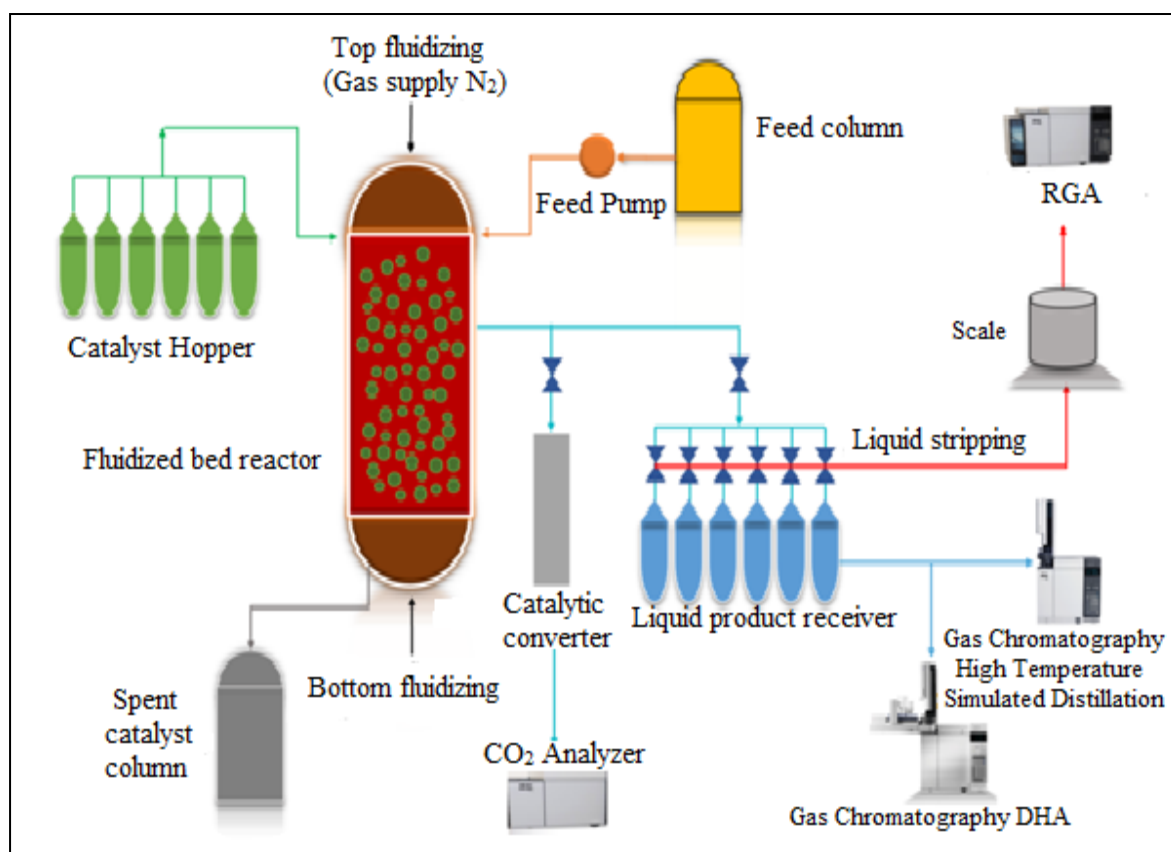

Figure 2. The scheme of the FCC process simulation at ACE unit.

In the FCC process, coke products are formed which are attached to the catalyst [17]. Coke is removed by burning the catalyst at 715 □C, the process is called the regeneration process. Catalysts with high carbon content are burned with air, as a source of oxygen, becoming active catalysts with high oxygen content. The regenerated catalyst is accommodated in a spent catalyst bottle. Gas products from the regeneration process will flow to the catalytic converter and analysed the formation of its coke products by using a CO2 analyser.

3.3. Optimization of Catalyst to oil mass ratio on FCC process for green gasoline production

The most optimum c / o mass ratio in the FCC process in green gasoline production can be seen from several parameters, namely the amount of dry gas products, liquid petroleum gas (LPG), gasoline, light cycle oil (LCO), heavy cycle oil (HCO), bottom and coke and the octane number of the product. These parameters can be identified through testing the boiling point distribution, analysis of octane numbers and analysis of coke formation. In addition, to find out the quality of FCC products from palm oil mixed feeds, the product yields are compared with products produced from commercial feeds used in PT Pertamina's FCC unit.

Boiling point distribution testing for FCC products was carried out by a distillation simulation method by gas chromatography. This test refers to ASTM D7169 [11]. The data of product conversion results based on their fractions from testing the boiling point distribution with gas chromatography simulation of high temperature distillation can be seen in Table 2.

Table 2. Optimization results of catalyst to oil ratio in FCC process in green gasoline production.

Fraction	FCC Commercial Product	Catalyst to Oil (c/o) (w/w)					Pertamina's VGO	Expected Result	Test Result
		4.02	5.00	5.56	6.00	6.52			
Dry Gas	3.72	2.28	2.40	2.40	2.48	2.40	2.48	<Pertamina's VGO	Not as expected
LPG	19.11	26.94	27.59	27.20	27.36	27.21	22.92	>Pertamina's VGO	As expected
Gasoline	40.66	41.76	41.77	41.35	41.81	41.17	40.74	>Pertamina's VGO	As expected
LCO	21.89	14.50	12.70	12.61	11.54	11.68	13.68	<Pertamina's VGO	As expected
HCO + Bottom	5.22	4.83	4.25	4.21	3.71	3.63	7.05	<Pertamina's VGO	As expected
Cokes	-	9.70	11.29	12.25	12.99	13.92	13.55	<Pertamina's VGO	Only c/o 6 w/w almost expected

3.4. FCC quality product test

Octane numbers are numbers that show how much pressure can be applied before the gasoline ignites spontaneously. In engines, a mixture of air and gasoline (in the form of gas) pressed by the piston up to a very small volume and then burned by the spark produced by the spark plug. This amount of pressure can cause the mixture of air and gasoline to ignite spontaneously, before sparks from the spark plug come out. The ability of the fuel to withstand spontaneous combustion during compression, prior to sparks, gives it a high-octane number [13]. If this gas mixture ignites due to high pressure and is not due to sparks from the spark plug, knocking will occur inside the engine. Knocking is an event when the temperature and pressure of the fuel mixture in the cylinder reaches the temperature that causes the explosion (explosion), not a perfect combustion process. This knocking can cause the engine to become faster damaged, so it is expected that the FCC process with the appropriate c/o ratio can increase the octane number [18]. The FCC product from the VGO mixed feed with palm oil which produces the highest-octane number is at the c/o ratio of 6.56, which is 85.559 can be seen in Figure 3.
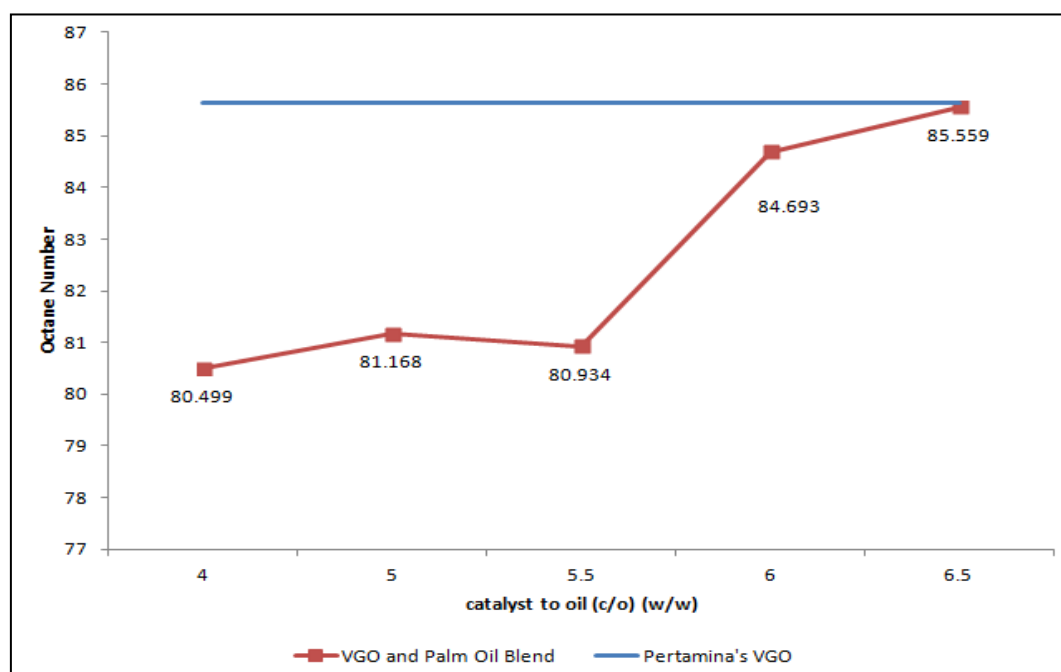
Figure 3. Relation between c/o ratio and octane number.

The octane number and PIONA test result by using DHA gas chromatography can be seen in Table 3.

Table 3. Octane numbers and PIONA elements test result of palm oil and VGO blend product.

Elements	catalyst to oil (c/o)(w/w)					Pertamina's VGO	Expected Result	Test Result
	4.02	5.00	5.56	6.00	6.52			
Paraffin	2.848	2.797	2.744	2.146	2.547	0.930	>Pertamina's VGO	As expected
Iso paraffin	17.101	17.292	16.761	17.877	17.760	16.580	>Pertamina's VGO	As expected
Olefin	9.903	10.443	10.042	10.786	8.515	15.270	<Pertamina's VGO	As expected
Naphthene	3.491	3.625	3.819	3.799	3.806	2.240	>Pertamina's VGO	As expected
Aromatic	47.156	47.011	47.567	50.085	52.931	50.610	>Pertamina's VGO	Not as expected
Octane Number	80.499	81.168	80.934	84.693	85.559	85.630	>Pertamina's VGO	Not as expected

Table 3 showed that the addition of palm oil can increase the content of paraffin and isoparaffin, and reduce the content of olefins. This change has a good effect on product quality. The addition of paraffin and isoparafin can increase the crackability of the feed. This is because compared to other types of hydrocarbons such as olefins, naphthenic and aromatic, paraffin and isoparafin are more easily cracked. Another advantage is that paraffin and isoparaffin generally produce large quantities of gasoline products and small amounts of fuel gas products [4].

Formation of coke generally comes from the residue of the feed, that is, from the heavy fractions of the feed. Formation of coke in the catalytic cracking process usually occurs constantly. The FCC produces enough coke products to be fulfilled heat balance of the reactor and its regenerator [19]. Combustion coke in the regenerator can release heat to be supplied to the reactor, this heat is needed in the cracking process. Coke is needed in the commercial FCC process only in small quantities. Formation of excessive coke will reduce the activity of the catalyst, it can cause cracking reactions and decreased product conversion [4]. In this optimization it is expected to know the ratio of c/o the most fulfilling criterion is the formation of lower coke products, but not far from the value of coke formation from commercial feeds used in PT Pertamina's FCC unit. The most fulfilling criterion is the formation of lower coke products, but not far from the value of coke formation from commercial feeds used in PT Pertamina's FCC unit. The cracking process of the VGO mixed with palm oil produces coke which increases with increasing c/o ratio as shown in Figure 4.
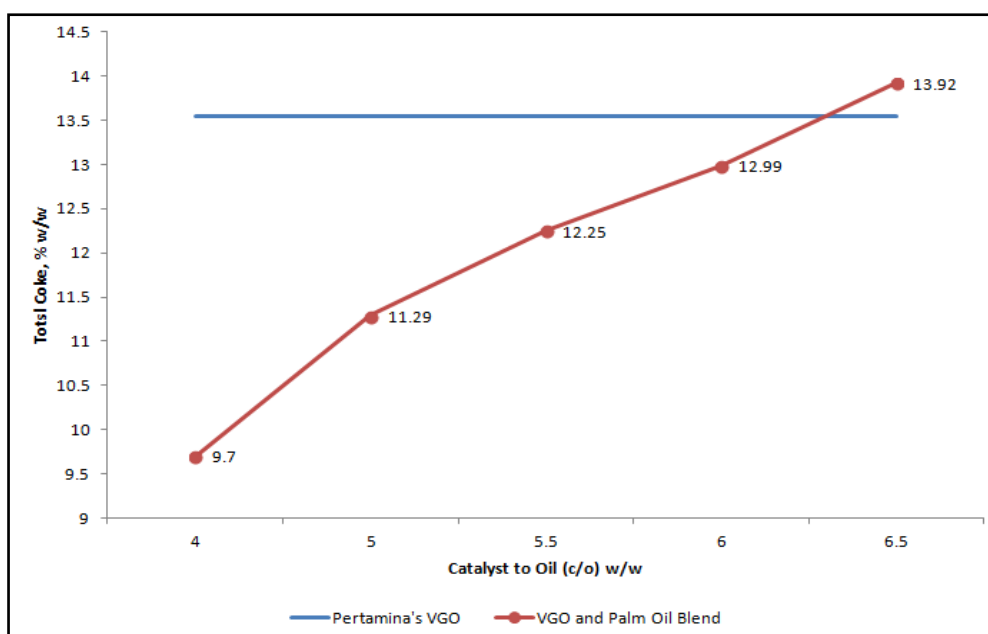

Figure 4. Relations between the ratio of c/o with total coke.

Based on various parameters that have been tested, it can be concluded that the ratio c/o 6.00 w/w is the most optimum ratio in the optimization of the FCC process from the production of green gasoline with this ACE unit. Table 2 and 3 shown that the cracking process with c/o ratio of 6.00 w/w had the most amount of gasoline products and the most significant decrease in the amount of LCO products when compared to the LCO products at other c/o ratios, products from standard VGO and FCC products commercial. In addition, the product at a ratio c/o 6.00 w/w has a high number of LPG products and a high-octane number compared to products from other c/o ratios. In this experiment it is also expected that the number of coke products formed is lower, but not too far from the VGO standard that has been used at the refinery, it can be seen in Figure 10, that the number of coke at the c/o ratio of 6.00 b / b meets these criteria. That is because the presence of coke products is needed to maintain the equilibrium of the reactor and regenerator in the cracking process at commercial FCC refineries [4].

4. Conclusions

The most optimum c/o ratio in the FCC process in the production of green gasoline that have been studied was at ratio of 6.00 w/w with the amount of dry gas product 2.48% w/w, LPG 27.36% w/w, gasoline 41.81% w/w, LCO 11.54% w/ w, HCO 0.00% w/w, bottom 3.71% w/w, and coke 12.99% w/w

and octane number 84.693. In addition, the FCC process of the palm oil mix feed at this ratio has better quality than products from PT Pertamina's FCC feed, which was indicated by the production of higher amounts of gasoline and LPG products, also lower LCO products, bottom and coke products. Based on this result study it can be concluded that the c/o ratio of 6.00 w/w can be used as mixture feed for green gasoline production as renewable energy sources that environmentally friendly.

5. References

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