

Catalytic cracking of crude palm oil using Cr/palm shell charcoal impregnation catalyst

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ARTICLE INFO	ABSTRACT
<p><i>Article history:</i> Received: 20 March 2023 Received in revised form: 28 September 2023 Accepted: 13 October 2023</p>	<p>The study of synthesizing Cr/activated palm shell charcoal catalyst by impregnation method has been done. Cr/Activated Charcoal was made using variation of chromium concentration (1%, 2% and 3%). Change in diffraction pattern in XRD analysis for charcoal before modification and after modification showed chromium has been successfully impregnated to the catalyst. The higher the chromium compound concentration used, the greater %-weight of chromium in the catalyst. It was found that the use of Cr-2%/Charcoal catalyst was able to increase the percentage of cracking liquid yield at the temperature of 550°C as much as 62.44% compared to the percentage of liquid yield from thermal cracking was 60.1% at the same temperature. It was also observed, using the Cr/Charcoal catalyst from impregnation method is more effective than catalyst from ion exchange method. However, the density of the cracking liquid yield is not yet close to the standard density range for fuel. Utilization of Cr/charcoal catalyst that was made by impregnation method in this research could be potential in CPO cracking to be fuel but a purification process is required to fulfill the fuel standard qualification.</p>
<p><i>Keywords:</i> Chromium, Charcoal, crude palm oil, catalytic cracking, biofuel</p>	

1. Introduction

Crude palm oil (CPO) is an oil that originated from the flesh of oil palm fruit that has passed a stirring process to separate the fruit flesh from its seed as well as the crushing and pressing process. CPO is commonly composed of triglycerides-triglycerides acid-acid grease with the biggest amount dominated by palmitate acid and oleate acid which could differ for every country. Indonesia's CPO has 42.45-48.93% palmitate acid content and 34.85-40.78% oleate acid content [1]. The triglycerides in CPO make CPO could be used as fuel. Since 1900, Knothe (2001) and Shay (1993) reported that oil that originated from a plant (vegetable oil) has been used as diesel machine fuel by Rudolf Diesel who invented the machine [2, 3]. In fact, in 1930 and 1940 when World War II happened, vegetable oil was used as fuel continuously because of emergency situations such as a petroleum embargo. However, the direct utilization of vegetable oil as fuel causes several problems with engine combustion such as complete combustion, carbon deposition, and the formation of fouling caused by oil characteristics that have high viscosity, low volatility and big mass molecule [4].

Therefore, an appropriate method is necessary if CPO should be used as a fuel. One of them is the cracking method [5-7]. This method is conducted by heating CPO at a certain temperature so that fatty acid triglycerides-triglycerides that have a dual bond and a long bond could decompose to be a short bond compound in the gas or liquid phase thus a compound in

the range of a liquid fuel such as gasoline (C₅-C₁₁) and diesel (C₁₁-C₂₀) could be produced, this method could be done with or without a catalyst. The proper use of a catalyst would produce a high yield of liquid product with an enormous product's selectivity.

The CPO cracking process in this research is conducted by utilizing chromium (Cr) as a catalyst with Charcoal as support site that is made with the impregnation method by varying Cr concentration. Selecting Cr catalyst as the catalyst's active site is because Cr catalyst is known to be capable to cyclizing hydrocarbon paraffin compound C₃ to C₅, disproportionated olefin and dehydrogenated cyclo-hexane [8]. In addition to being reported the chromium has a high-level acid with small pores and a big surface area [9]. Whilst charcoal utilization as a support in catalyst has an advantage that is known widely from its porosity and surface area aspect. Thus Cr/charcoal catalyst is expected to be compatible to be used in cracking reactions and able to produce expected liquid fuel. Then, after catalyst production is conducted, characterization is conducted and then it is used in a cracking process that is varies in temperature. A study was conducted regarding the influence of the use of Cr variation concentration that is impregnated in Cr/charcoal catalyst production and temperature variation influence to cracking result (% liquid product) as well as density measurement to find out the type of compound produced.

2. Materials and Methods

The research utilizes a set of laboratory glassware, hot plate, magnetic stirrer, analytic scale, porcelain, spatula,

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vacuum pump, flat porcelain funnel, 100 mesh filter, digital scale, oven, modified cracking reactor (see Figure 1) from the research of Nazarudin (2012) [10], X-ray diffraction (XRD) and SEM-EDX. Whereas the substance used in this research is the CPO obtained from PTPN VI, active charcoal from palm shell, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, NaOH , CH_3COOH , distilled water, steam, litmus paper, and filter paper.

2.1. Charcoal activation

The first research procedure is charcoal activation which is made from palm shells. Charcoal is activated with NaOH and distilled water with 1:1:1 ratio, then the stirring process is conducted for 2 hours. Next, washing with CH_3COOH and distilled water with pH up to 7 is conducted and filtering is also conducted. Charcoal is dried at 105°C temperature using an oven for 4 hours then is advanced by steaming for 6 hours at 550°C . Next, active charcoal is characterized using SEM-EDX and XRD.

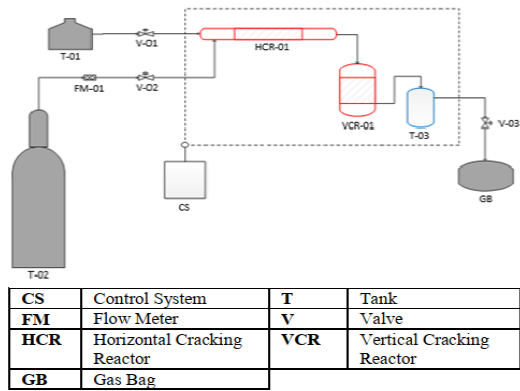


Fig. 1. Cracking Flow Diagram

2.2. Cr/charcoal catalyst synthesis

The second procedure is making the Cr/charcoal. $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution is made with 1%, 2%, 3% concentration variation. This chromium solution is the residual from the catalyst production process with an ion-exchange method. $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution is impregnated with charcoal with 10:1 ratio for 24 hours at 45°C temperature. That solution

is filtered without washing. After being filtered, the catalyst is dried by using an oven for 12 hours with 105°C temperature. Then the calcination process is conducted at 450°C temperature for 5 hours. The formed catalyst is then characterized using XRD and SEM-EDX.

2.3. Cracking of CPO

The third procedure is the CPO cracking procedure. There are two types of cracking procedures in this research. The first is thermal cracking at temperatures of 450°C , 500°C , and 550°C for 100 minutes with 20 gram CPO. The second is catalytic cracking. Cracking is conducted with a semi-batch process and the ratio CPO and catalyst ratio is 30:1. Reactor has been filled with the catalyst by the variation concentration then CPO is entered. Cracking at the temperature of 450°C , 500°C , and 550°C is conducted for 100 minutes. The liquid product is taken every 25 minutes. Then the % yield is calculated as well as the density test of the liquid product.

3. Results and Discussion

According to the studies, vegetable oil catalytic cracking reaction mechanism in producing liquid fuel occurs at the deoxygenation reaction phase and oligomerization [11, 12]. To reach this phase various kinds of other reaction phases should be passed which are decomposition, second phase cracking, deoxygenation, decarboxylation, and decarbonylation. In addition to the primary reaction in producing liquid fuel, a side reaction to the expected product such as aromatization, isomerization, and alkylation thus produces a hydrocarbon aromatic compound that next could go through an advanced reaction which is polymerization that forms coke. The reaction mechanism is shown in Figure 2.

Some researchers have been reported chromium is a catalyst that has a high activity and selectivity for oligomerization reaction [13–16]. Hence this has become a theoretical basis for chromium utilization as a catalyst that is used in CPO catalytic cracking reaction for producing fuel. Chromium as the catalyst active site matched with charcoal from palm shell as support catalyst because of its known surface with porosity and high surface area as well as having high stability at acid and hot environment [12].

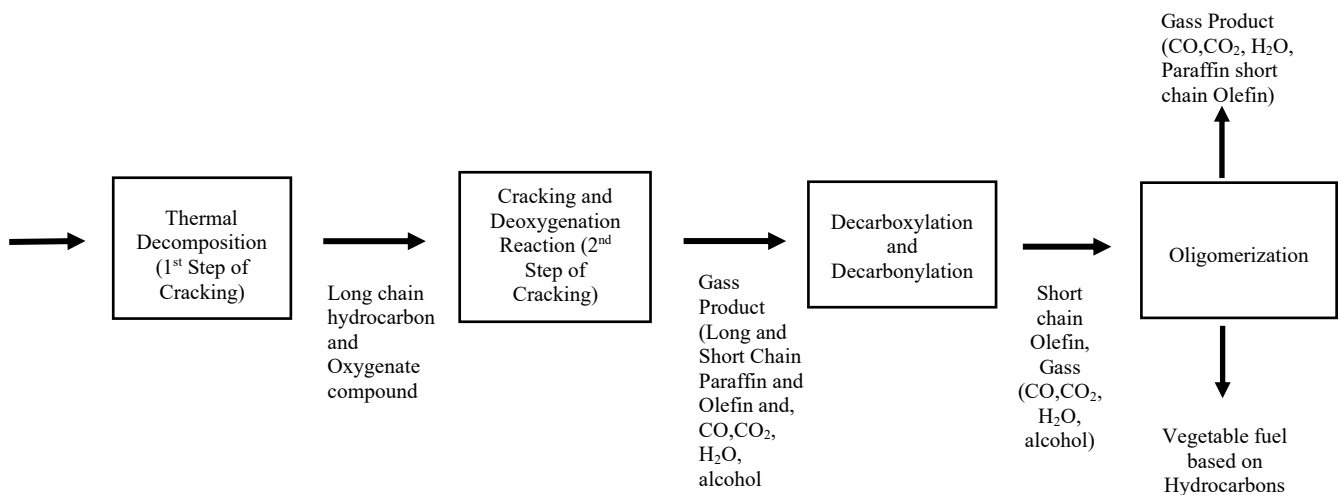


Fig. 2. Vegetable oil to fuel cracking mechanism

Table 1. Component quantity in active charcoal before modification and Cr/charcoal catalyst variation according to EDX analysis

Component	Content in %-weigh			
	Active charcoal	Cr-1%/charcoal	Cr-2%/charcoal	Cr-3%/charcoal
Cr	0	0.51	1.07	14.38
C	41.23	97.85	79.93	70.57
Si	35.35	0.33	1.69	8.22
P	2.14	1.06	0	3.01
Mg	0	0.24	0	0
Ca	0	0.12	0	3.83
Co	0	0	0	0
Al	0	0	0	0
O	0	0	17.30	0

Table 2. The results of CPO in thermal and catalytic cracking

Cracking Type	CPO (g)	Temperature (°C)	Liquid product (%)	Residue (%)	Gass (%)
Thermal Cracking	20	450	55.06	-	-
		500	57.97	-	-
		550	60.10	-	-
Catalytic Cracking Cr-1%/Charcoal	60.75	450	50.78	0.35	48.05
		500	56.22	0.76	43.05
		550	51.81	2.79	43.83
Catalytic Cracking Cr-2%/Charcoal	63.10	450	61.84	2.57	35.47
		500	51.95	4.13	43.92
		550	62.44	0.89	41.29
Catalytic Cracking Cr-3%/Charcoal	60.83	450	53.12	3.04	43.84
		500	54.82	0.81	44.38
		550	56.66	1.41	41.93

Table 3. Fuel density standard

Fuel type	Density (g/ml)
Biodiesel	0.850-0.890 ¹
Gasoline (premium)	0.715-0.770 ²

¹accessed at <http://sispk.bsn.go.id/> at

6th of February 2021, 8.00 am.

² accessed at pertamina.com at

6th of February 2021, 8.00 am.

3.1. Characterization of activated charcoal and Cr/Charcoal catalyst using SEM-EDX and XRD analysis

Active charcoal morphology structure from palm shell before the modification as support catalyst that is shown in Figure 3 shows a rough surface and uneven as well as a cavity and basin that indicate the forming of pores on the charcoal. The diffraction pattern for active charcoal (see Figure 4) shows the existence of peak intensity that indicates the forming of the crystalline phase. This matter differs from the result of active charcoal research from coconut shells obtained by Aziz et al [9], a diffraction pattern is produced that is rough and without a peak. Whilst for catalysts with the variation of Cr-1%/charcoal, Cr-2%/charcoal, and Cr-3%/charcoal that is made with the impregnation method show diffraction pattern changes between active charcoal from palm shell to Cr/charcoal catalyst proved that Cr metal as an active phase has been successfully charged on the charcoal as support phase. Besides the peak diffraction intensity increase along with the Cr metal concentration increase that is used show that Cr metal addition assists crystal growth on the catalyst. This is also supported by EDX analysis in Table 1, types and component content found in active charcoal prior to modification and after modification to be Cr/charcoal catalyst shows changes in Cr metal amount, where the higher the utilized compound concentration the higher the chromium metal content found in the catalyst. However, the highest diffraction pattern produced in this experiment is at 2θ 21.9° for catalyst Cr-1%/charcoal; 21.0° for catalyst Cr-2%/charcoal; 20.83° for catalyst Cr-3%/charcoal.

This diffraction angle is different from than typical diffraction angle for Cr metal according to Kilicarslan et al., [17], the peaks that represent the presence of Cr metal is shown at 2θ 24.5°; 33.74°; 36.1°; 50.84°; 54.6°; 64.04°; 65.8° [17].

Table 4. Liquid product density from catalytic cracking using various concentration catalyst

Catalyst type	Temperature (°C)	Density (g/ml)
Cr/Charcoal 1%	450	0.92018
	500	0.91394
	550	0.91718
Cr/ Charcoal 2%	450	0.91272
	500	0.92016
	550	0.91124
Cr/ Charcoal 3%	450	0.91592
	500	0.91632
	550	0.91580

3.2. Thermal and catalytic of CPO cracking

According to the result of the thermal cracking experiment that is shown in Table 2, it is discovered that the liquid product with the highest 60.1% percentage was obtained at 550°C temperature. This verifies that the higher the cracking temperature, then there would be more decomposed the amount of raw material. Then catalytic cracking with a 30:1 ratio of CPO and catalyst at the same temperature and time by the thermal cracking method is conducted. It is obtained that at the same 550°C cracking temperature, the highest liquid product is 62.44% by utilizing Cr-2%/charcoal catalyst. This shows that the use of catalysts would be able to increase the yield of liquid products. It has been explain previously, chromium catalysts play a role in carrying out the oligomerization reaction stage in the cracking process (see Figure 2), in this stage the liquid and gas product are obtained. So, using chromium as a catalyst affects the amount of liquid product. However, in contrast to previous study, in used cooking oil cracking by utilizing Cr/charcoal catalyst made with the ion-exchange method, catalyst utilization does not show significant results from thermal cracking [18]. It is suspected that making the catalyst using salt metal with the impregnation method is far more

effective in dispersing the active site of the support site compared to ion-exchange method. Anggoro et al. [19], reported that in the experiment of making Co-Mo/Zeolite Y catalyst, making the catalyst with impregnation method produce a catalyst with higher similarity compared to ion exchange method, this acidity is related to producing higher liquid product yield.

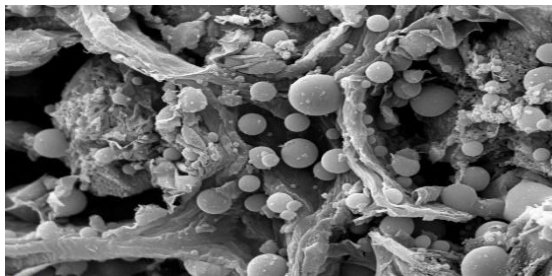


Fig. 3. SEM image of activated palm shell charcoal

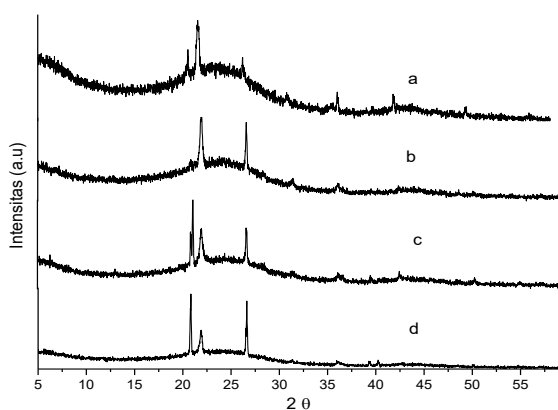


Fig. 4. Diffractogram of a) active charcoal b)Cr 1%/charcoal catalyst c) Cr-2%/charcoal catalyst d) Cr-3%/charcoal catalyst

The density produced from catalytic cracking that is listed in Table 4 shows that liquid product density does not come near to fuel standard density issued by National Standardization Agency of Indonesia (BSN) and Pertamina in Table 3. Hence the purification process is needed after the cracking process to separate liquid products with complex composition to be more simple thus fuel under standard specifications could be produced.

4. Conclusion

Dispersion of Cr metal to activated charcoal of palm shell by applying the impregnation method has been successfully conducted. This is shown by the diffraction pattern changes between active charcoal before and after metal addition. Crystalline phase formation on Cr/charcoal at peak diffraction intensity is found at Cr-3%/charcoal catalyst. The bigger Cr concentration solution used in the making of catalyst would produce bigger metal content. Catalyst utilization is proven to be capable of increasing CPO cracking liquid yield, at the same temperature condition which is

550°C, thermal cracking yield with the amount of 60.1% increase to 62.44% using Cr-2%/charcoal catalyst. This result is far better compared to using the Cr/charcoal catalyst that is made with ion-exchange method. However, the density produced from liquid products has not come near to the fuel range standard according to BSN and Pertamina, thus a purification process is needed to obtain the liquid product under those criteria.

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