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The Synthesis of Cr/SiO_2 Catalyst from a Mixture of Palm Waste Ash - Charcoal and Its Application for the Catalytic Cracking of CPO into Gasoline

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Abstract :

Due to the increasing reduction in non-renewable natural resources such as petroleum and the increasing amount of ash and charcoal waste from palm oil mills that has not been utilized, the author synthesizes the silica content from a mixture of ash and charcoal from palm oil waste to be used as a Cr/SiO2 catalyst which will be used for cracking. catalytic from CPO (Crude Palm Oil) to gasoline. This research aims to determine whether a mixture of waste ash and charcoal from the PTP VI Sungai Bahar factory waste can be used as a silica source to produce Cr/SiO_2 catalysts and to determine its activity in the catalytic cracking of CPO into gasoline. The cracking process was carried out in a fixed bed reactor which consists of a horizontal reactor and a vertical reactor and equipped with an electric heater and temperature controller. Catalytic cracking was carried out with several ratios of catalyst : CPO, namely 1:20, 1:25, and 1:30. Similar cracking process without catalyst (the thermal cracking) was also carried out as a comparison. The conversion of CHP into gasoline using ratios 1:20, 1:25, 1:30 were 13.67%, 10.78%, 11.59% respectively. Meanwhile, the gasoline conversion produced by thermal cracking was only 9.46%, 9.95%, 6.86%. These results show that catalytic cracking produced more gasoline than thermal cracking.

Keywords: Catalyst, CPO, Cracking, Palm Waste Ash, Palm Waste Charcoal

1. Introduction

The world's energy needs, including Indonesia, are increasing from year to year. This is in line with economic growth, population, development and regional developments that occur every year. So far, energy supply still relies on fossil fuels originating from petroleum and natural gas. The depletion of petroleum reserves poses a threat to energy supply. This threat has transformed into a national and global issue regarding the energy crisis being experienced throughout the country at the moment. However, this increase in energy use is not accompanied by adequate energy production. Therefore, it is deemed necessary to immediately seek to develop alternative liquid fuels that can contribute to meeting Indonesia's fuel oil (BBM) needs (Soerawidjaja et al., 2005).

According to the Indonesian Central Statistics Agency (2012), Indonesian petroleum production in 2011 was 329.2 million barrels, consisting of 289.9 million barrels of crude oil and 39.4 million barrels of condensate. With a production volume of this size, it shows a decrease compared to the previous year which reached 300.9 million barrels of crude oil and 44.0 million barrels of condensate. In the last five years, crude oil and condensate production has also shown a downward trend with a decline of 1.27 percent per year for crude oil and 2.31 percent per year for condensate (Indonesian Central Statistics Agency, 2012). Meanwhile, fuel oil consumption increases every year, as seen from statistical data from the Ministry of Energy and Mineral Resources. In 2011, domestic oil consumption reached 25,783,240,553 kilo liters (premium).

This situation has triggered researchers to look for fuel sources from various non-fossil oil sources such as; processing by catalytic cracking oil or fat from plants into fuel (diesel and gasoline) has become an interesting research topic and is being discussed as the most likely alternative fuel source to be developed. (Nazarudin, 2000).

An alternative fuel to overcome this problem is made from vegetable oils such as soybean oil, palm oil and olive oil. We can use them as new fuels to replace petroleum, especially diesel engine fuel (biodiesel). Biodiesel from vegetable oils has advantages such as environmentally friendly, renewable and produces relatively cleaner exhaust emissions. The Indonesian government has developed a process for converting vegetable oils such as castor oil, rubber, CPO into biodiesel.

From data from the Central Statistics Agency of Jambi Province, Jambi province's palm oil industry products are dominated by CPO. In fact, in 2007 Jambi became the fourth largest palm oil producing province after Riau, North Sumatra and South Sumatra. The development of CPO continues to grow from year to year, which is marked by the increase in CPO production in Jambi province. In 2004, CPO production increased by 18.92 percent and 17.68 percent for the following year. While in 2006 the increase was only 8.77 percent, and in 2007 it increased by 12.87 percent (Jambi Provincial Central Statistics Agency 2009).

As CPO production from palm oil processing increases, the waste produced by palm oil mills (PKS) also increases. The main results obtained from processing palm fruit bunches are palm oil (CPO) and palm kernel. The by-products obtained are empty bunches, fiber, shells and liquid waste. Until now, waste utilization has not been carried out optimally, whether for solid, liquid or gas waste. There is still a buildup of solid waste around the factory even though efforts have been made to reduce it, namely by making ash as fertilizer and mulch from empty palm oil stalks. The accumulation of waste comes from fiber and shell waste that has not been utilized. It is estimated that 70% of the fiber and shell waste has been used to produce energy in steam boilers, while the rest has not been utilized, causing problems with waste disposal. Until now, no intensive efforts have been made to utilize palm oil solids and waste water. It is estimated that in the long term there could be pollution of river drainage bodies due to the increase in the weight of the waste produced (Dini. 2010).

Palm Oil Factory solid waste in the form of ash and charcoal from shells and husks contains a lot of silica. Silica is the main compound used as a catalyst carrier and is usually an amorphous solid (G, Erta et. La, 1999). Therefore, silica can be used as a substitute for zeolite as a carrier which is expected to increase gasoline conversion results.

Previous research, Nazarudin, 2006 has conducted research on the conversion of crude palm oil (CPO) into biofuel (vegetable fuel) by catalytic cracking using a natural Cr-Zeolite catalyst, the resulting product is based on GC-MS analysis showing that the CPO sample consists of fatty acids saturated C12 (1.65%), C14 (1.9%), C16 (39.45%), C18:1 (52.83), C18 (4.17%). GC-MS analysis of the fracture samples showed that the formation of biofuel was seen at a peak of 17.025 minutes which showed hexadecane (C14) and a peak of 26.97 minutes which showed octadecane (C18). IR analysis of the fracturing results which shows the occurrence of diesel oil has a peak of 1188.11 (Nazarudin, 2006)

Sucianti, 2008 has conducted research on the catalytic cracking of Crude Palm Oil (CPO) into gasoline with the addition of metals (K, Li, Na) on a Cr-Carbon catalyst. The catalytic cracking process is carried out by varying the concentration of each metal (K, Li, Na) in the Cr-Carbon catalyst, namely 0% -2% by weight of the catalyst. The maximum yield obtained from the catalytic cracking process was 25.5% gasoline, with the addition of 2% Na metal to the Cr-Carbon catalyst (Sucianti, 2008). Based on these facts, this research was conducted to synthesis Cr/SiO_2 catalyst from a mixture of palm oil waste ash and charcoal and to determine its performance in the catalytic cracking of CPO (crude palm oil) into gasoline.

2. Research Methods

Materials and Tools

Ash, charcoal and CPO were obtained from palm oil processing factories, PTP VI Sungai Bahar, Muaro Jambi Regency. The chemical used in this research were Hydrochloric Acid (HCl), Aquades, Sulfuric Acid (H_2SO_4) 98% (E. Merck), oxygen gas, sodium hydroxide p.a (E. Merck), $Cr(NO_3)39H_2O$ (E. Merck). The equipment used in this research were 100 mesh sieve, Mettler AT 200 electric scale, glass wool, heater, activation reactor, cracking reactor (horizontal furnace, furnace vertical), CPO injection, Welsh Duo-Seal 1400 vacuum pump, magnetic stirrer, 2000c thermometer, 10000c thermocontrol, XRD (X-ray Diffraction), SEM (Scanning Electron Microscopy), and EDS (Energy dispersive spectroscopy).

Synthesis of Sodium Silicate

Palm ash and charcoal were filtered using a 100 mesh sieve then washed with distilled water, then oven at 130˚C for 24 hours then the charcoal is heated at 600^{o}C for 6 hours. Then the ash from burning the charcoal is washed and baked in an oven at 130˚C for 24 hours. Next, the ash from the factory and the ash from burning charcoal are compared. 1:1, namely 50 grams: 50 grams, then soaked with hydrochloric acid (HCl) in a solution with a concentration of 3 molar, the ratio of a mixture of factory ash and ash from charcoal with HCl solution, namely 1: 10, soaked for 24 hours at room temperature. then the sample was filtered using a Buchner funnel to obtain the filtrate and residue, then the residue was washed with distilled water and placed in an oven at 130 ˚C, then 2.5 M NaOH solution was added with a ratio of 1:10, oven at 80 ˚C and stirred using a magnetic stirrer for 8 hours, filtered and dried in an oven (Nazarudin, et al, 2006).

Preparation of Cr/SiO_2 Catalyst

Sodium silicate from previous stage was mixed with distilled water (1:5), then 1 M sulfuric acid (H_2SO_4) was added until the pH reaches neutral (pH=7). The silica was separated from the sodium sulfate by vacuum filtering at a temperature of 50˚C in a water bath (Moreno, 2004). The separated silica was soaked in a $Cr(NO_3)39H_2O$ solution while stirring using a magnetic stirrer at a temperature of 80˚C for 8 hours, filtered and dried at 120^{o}C for 16 hours. Next, it was calcined at a temperature of 773˚C for 8 hours (Brando, 2002) then left to sit until the catalyst cools. The $Cr(NO_3)39H_2O$ solution used was at a Cr concentration of 3%.

Catalyst Characterization

The characteristic of the Cr/SiO_2 catalyst was carried out using XRD (X-ray Diffraction) to determine the crystal system, structure and constituent components of the Cr/SiO2 catalyst. SEM (Scanning Electron Microscopy) was also applied to determine the catalyst morphology. EDS (Energy dispersive spectroscopy) was applied to determine the percentage of metal content in the catalyst which carried out in the physics and biology laboratory at Padang State University (UNP).

Catalytic Cracking

The CPO sample was injected into a pipe that was heated in a horizontal furnace at a temperature of 450˚C. The furnace containing the catalyst in the vertical reactor was heated at 450˚C. The ratios of catalyst: CPO was set to 1: 20, 1:25, and 1:30. For thermal cracking, there was no catalyst being placed in the vertical reactor. The cracking reaction was carried out for 1 hour. The resulting cracking liquid (OLP=oil liquid product) was collected in a OLP container, then weighed. Coke in horizontal and vertical reactors was collected and then weighed. In catalytic cracking, the coke in a vertical reactor was mixed with the catalyst so that the coke for catalytic cracking is the weight of the mixed coke minus the amount of catalyst. Next, OLP was further separated by distillation with the gasoline boiling point range category, namely below 120^{o}C for 6 hours was gasoline.

The weight of cracking products, namely gas, liquid cracking products (OLP), and coke, gas and percentage of gasoline obtained from the cracking process was analyzed gravimetrically. Gravimetric analysis was carried out to determine the percent conversion of each cracking product. The calculation to find these percentages is:

a. % Cracked Fluid (OLP) $= \frac{weight\ of\ OLP}{weight\ of\ CPO}$ x100%

b. % gasoline in OLP $=\frac{weight\ of\ gasoline}{weight\ of\ OLP}$ x100%

c. % coke $= \frac{weight\ of\ coke}{weight\ of\ CPO}$x100%

d. % gas $= \frac{weight\ of\ CPO - weight\ of\ OLP - weight\ of\ coke}{weight\ of\ CPO}$ x 100%

e. Selectivity $= \frac{\%\ OLP + \%\ gas}{\%\ coke}$

3. Results and Discussion

Catalyst Characterization

The XRD pattern showed that the catalyst consist of Cr/SiO_2. The XRD pattern produced from Cr/SiO2 with a range of 2 theta 0-1000 was presented in Figure 1. It can be seen that the XRD pattern has a narrow peak profile, neat and even which represents a crystalline structure. An equation was carried out using the standard pattern in the HighScore Plus Software which uses the ICDD database as a reference. By using this software, the equation process can be carried out quickly with the Search and Match capability. Based on the Search and Match results, it was found that there were 3 phases identified, namely quartz (SiO_2), Sodium Chromium Silicate ($NaCr(Si_2O_6)$) and Chromium Silicate (Cr_2SiO_4).

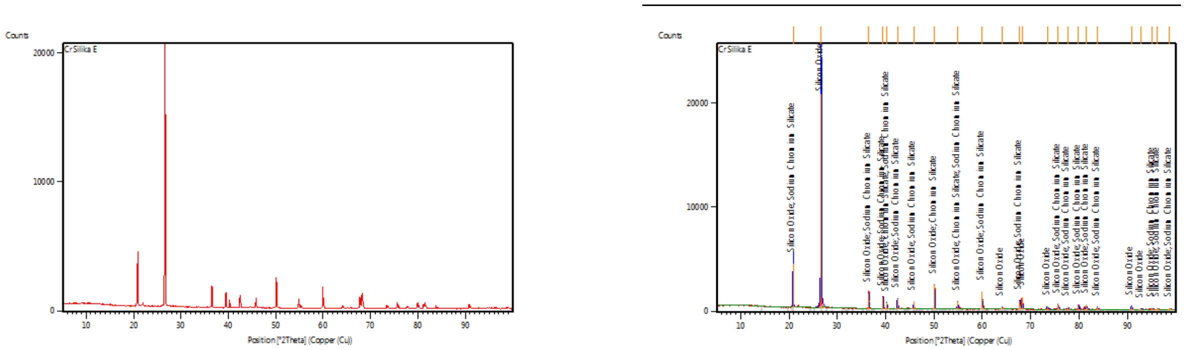

Figure 1. The XRD pattern of sample (left) and XRD Pattern Matching Results with HighScore Plus Software (right)

The characterization of the Cr/SiO_2 catalyst using SEM show that Visual analysis of the Cr/SiO2 catalyst is to visually determine the surface of the Cr/SiO_2 catalyst. The sample used was a Cr/SiO_2 catalyst in powder form. From the SEM (Scanning Electron Microscopy) results, an image of the surface of the Cr/SiO2 catalyst is obtained (Figure 2). It can be seen at Figure 2, the surface of the Cr/SiO_2 catalyst at 500x magnification shows chunks of catalyst powder, and seen in picture 12 at 5,000x magnification you can see the rectangular shape of the catalyst. At 10,000x magnification it can be seen that there are cavities and holes in the catalyst. Based on the surface image of the Cr/SiO_2 catalyst, it can be concluded that the shape of this catalyst is rectangular and hollow. In this cavity, the width of the pores was measured, namely 9.375 µm.

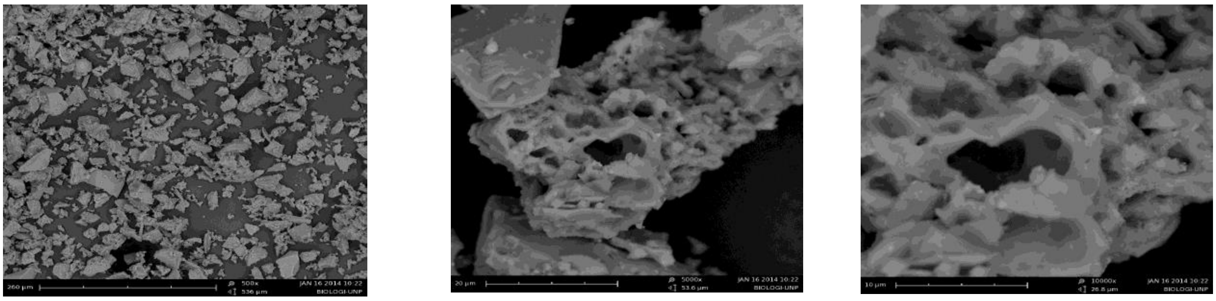

Figure 2. Cr/SiO2 catalyst surface at 500x magnification (left), 5,000x magnification (middle), 10,000x magnification (right)

Catalyst characteristics determined using EDS (Energy dispersive spectroscopy). The data was obtained from a SEM image of catalyst by zooming several points in the image to determine the content and percentage of metal present at those points. The following image is the EDS (Energy dispersive spectroscopy) result of the Cr/SiO2 catalyst sample. Judging from the SEM image, the characteristics of the Cr/SiO_2 catalyst with EDS are that the metal content and percentage in the Cr/SiO_2 catalyst is O (62.9%), Si (25.2%), N (5, 3%), Rb (4.9%), and C (1.6%). At another point in the SEM image, the characteristics of the Cr/SiO_2 catalyst with EDS are that the metal content and percentage in the Cr/SiO_2 catalyst are O

(63.7%), Si (24.8%), C (11, 5%). From the metal content and percentage, it can be concluded that the metals detected were Si, O, N, Rb, C and the most dominant metal content percentages were Si and O.

Thermal Cracking

Thermal cracking of CPO produces mainly liquid product followed by gas and cocas (Table 1). The increasing in the amount of CPO did not merely increase the conversion. The highest liquid conversion produced by using 30 gram CPO.

Table 1. CPO conversion after a thermal cracking

Experiment	CPO (gram)	Yield (%)			Gasoline in OLP (%)
		OLP	Cocas	Gas	
1	30	78.23	8.30	13.47	9.46
2	37.5	54.13	6.53	39.33	9.95
3	45	65.07	7.47	27.47	6.86

Catalytic Cracking

Similar to thermal cracking, the catalytic cracking of CPO produces mainly liquid product followed by gas and cocas (Table 2). The increase in the amount of CPO in the ratio of catalyst to CPO in the catalytic cracking CPO increased the conversion (Table 2). The highest liquid product was obtained by using ratio catalyst to sample 1:30.

Table 2. CPO conversion after a catalytic cracking at different ratio of catalyst to sample

Ratio catalyst to sample	Catalyst (gram)	CPO (gram)	Yield (%)			Gasoline in OLP
			OLP	Cocas	Gas	
1:20	1.5	30	56.07	8.07	35.87	13.67
1:25	1.5	37.5	62.56	8.59	28.85	10.78
1:30	1.5	45	73.64	8.58	17.78	11.59

Cracking Efficiency

The catalyst did not show its performance to increase the selectivity of cracking as seen in Figure 3 but the catalyst showed a good performance to increase percentage of gasoline in OLP as seen in Figure 4.

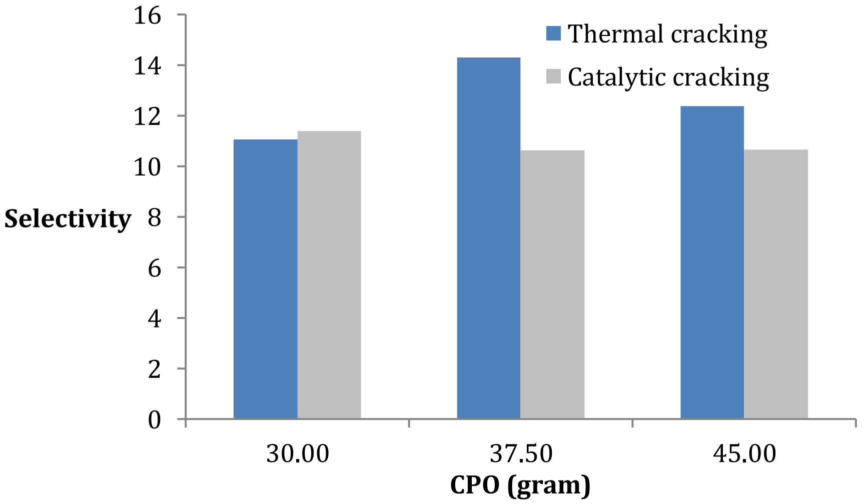

Figure 3. The selectifity of CPO cracking

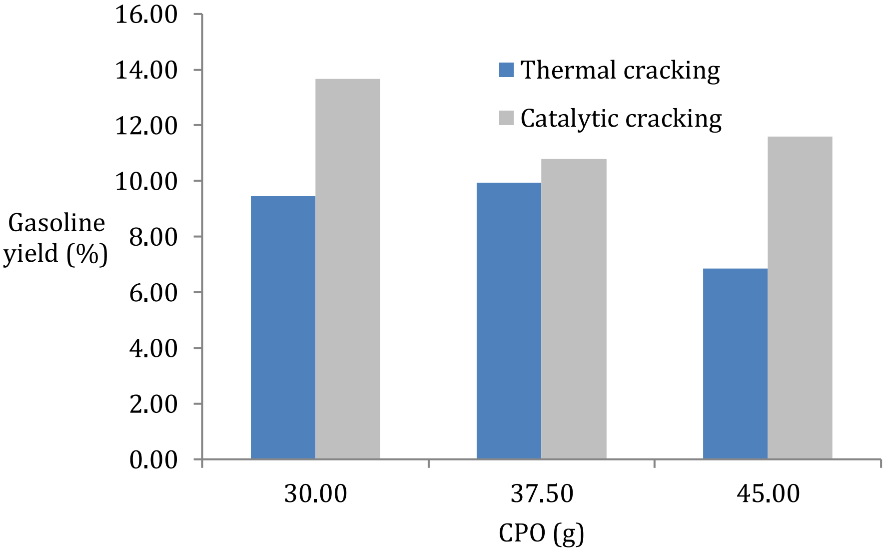

Figure 4. The percent gasoline in OLP

4. Conclusions

The mixture of ash and charcoal obtained from the PTP VI Sungai Bahar Factory waste can be used as a source of silica to produce Cr/SiO_2 catalysts. The most optimal catalytic cracking was obtained at a ratio of CPO to catalyst 1:20 producing 56.07% OLP which contain 13.67% gasoline.

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