

Comparison of Cr/C and Cr₂O₃/Z Catalysts on Hydrocracking of Bio-Oil from Pyrolysis of Palm Empty Fruit Bunches

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ABSTRACT. The bio-oil that is derived from palm empty fruit bunch (PEFB) is not suitable for fuel purpose due to its high acidity and low heating ability. Therefore, Cr₂O₃/Z and Cr/C catalysts were developed to upgrade it through hydrocracking reaction. The catalysts were prepared via impregnation method, followed by oxidation-reduction, then ammonia and pyridine adsorption was utilized to evaluate their acidity and their crystallinity were assessed using XRD. The hydrocracking reaction was carried out using the following variables, 0.5-3.0 L/min of hydrogen gas flow rates, 1,497.07-1,652.58 m²/g Cr/C catalyst's surface area, 450 to 700°C temperature and 0.5 to 2.5 g of catalyst's weight. The results of the acidity tests showed that Cr₂O₃/Z was more acidic compared to pristine zeolite. Also, the XRD pattern showed that Cr₂O₃/Z had higher crystallinity, as indicated by the sharp and pointed diffraction peaks. Further tests discovered that the optimum conditions for these variables to aid the hydrocracking process were at 2.5 L/min for H₂ gas flow rate, and 500°C and 600°C for the temperatures of Cr₂O₃/Z and Cr/C respectively. Meanwhile, the best weight of the Cr₂O₃/Z catalyst which aided the hydrocracking reaction was 1.5 g, while the surface area of the Cr/C catalyst was 1,554.48 m²/g, the outcome of these was a low density hydrocarbon. Furthermore, the GCMS data showed increase in the number of straight chain compounds after the hydrocracking process.

Keywords: Catalyst, Carbon, Chromium, Oil Palm Empty Bunches, Zeolite

INTRODUCTION

Currently, the availability of petroleum resources in the world has decreased with time, due to extensive mining and lack of new oil well drill. Crude oil drilling in some countries is not sufficient anymore to fulfill their petroleum need, making importation unavoidable. Therefore, the development of alternative and renewable resources, in an attempt to replace oil dependence and keep sustainable development of society is needed. One renewable fuel resource that has attracted attention recently is the bio-oil, which is generated from waste biomass. It is a liquid fuel, with a dark color, and a smoke like taste, it is produced from wood, bark, paper, and other biomass through pyrolysis (Wang, Hu, Chen, Lv, & Jia, 2013).

Basically, any substance containing cellulose has the potential to be converted into bio-oil. Materials, such as wood, bark, bagasse, and others, produce various yields of bio-oil, through pyrolysis depending on its composition. Raw materials with high lignin content, such as wood, tends to produce low yield of

bio-oil (60-65%), while those with high cellulose content, such as paper, have higher yield with approximately 75-93% (Ling Pua et al., 2013).

Palm empty fruit bunch (PEFB) is a major solid waste, produced from palm plantation (PP), every 1 ton of fresh fruit bunch (FFB) gives 22-23% PEFB. Therefore, in a PP with 100 ton/h production capacity, the solid waste recorded are about 22-23 ton of PEFB. And the amount of PEFB waste all over Indonesia in 2004 was approximately 18.2 million ton (Chan, Yusup, Quitain, Uemura, & Sasaki, 2014).

PEFB is a solid waste that contain lignocellulose, a substance that is yet to be utilized optimally. Palm empty fruit bunch are majorly used as boiler feed in PPs, and sometimes it is made into a compost and used for road hardening across the plantation. Wibowo, Efiyanti, & Pari., (2020) reported effort of upgrading crude bio-oil (CBO) obtained from pyrolysis of PEFB using Ni/NZA catalyst as a batch reactor. The results showed that the CBO was successfully thermal cracked, and yielded 26.42% fuel

with 0.995 specific gravity and calorific value of 30.85 MJ/kg.

The performance of the Bio-oil produced from pyrolysis needs to be improved, and this is performed through via hydrocracking. Which is a process of removing feed contaminants from heavy gas oil with the aid of bi-functional catalysts i.e. metal, which is impregnated in a particular solid and acid solid catalyst. The metal catalyst in this composition functions to bring about hydrogenation, while the acid solid activates cracking. Metal catalysts commonly used are transition metals. Santi, Triyono, Trisunaryanti, & Falah (2020) reported approximately 52.72% yield of fuel from hydrocracking bio-oil, and when this process was conducted in the presence of M_xO_y/mesoporous carbon catalyst for the same bio-oil, there was an increase in the yield, which was at 75.33%. In this study, chromium was utilized as the metal catalyst, it was chosen because it has the highest unpaired electron among the transition metals' group. The metal catalyst was supported with zeolite and carbon (Triantafyllidis, Lappas, & Stöcker, 2013).

The Ni/Co catalyst which is impregnated in natural zeolite (Ni/Co/Z) had been reported, to have the ability to crack coal tar, and produce fractions of gasoline, kerosene and solar. Similarly, when it is applied on the hydrocracking of bio-oil, it increases the quality and it is even able to produce biogasoline and biokerosene (Dewi & Fanani, 2017).

Bio-oil upgrading is usually conducted via the hydrocracking process, which is a combination of hydrogenation and cracking procedures. Cracking was performed using catalyst that were infused with zeolite and carbon, while hydrogenation was conducted using those that are composed with transition metal. The transition metals commonly used for hydrogenation process are, Pt, Pd, Ni, Co and Cr. Metals of Pt and Pd are known as good catalysts of hydrogenation, however, they are very expensive. Metals of Cr has empty d-orbital which are quite large compared to others, therefore, it provides multiple oxidation state, and this has proven that it is an efficient catalyst in several chemical processes. Currently, research on hydrocracking using Cr impregnated in zeolite and carbon as catalyst for the production of bio-oil with better quality from PEFB has not been reported. Therefore, this study aims to report the production of biofuel fractions from hydrocracking of bio-oil over zeolite and carbon-based catalyst, and to also determine the best condition for PEFB hydrocracking.

EXPERIMENTAL SECTION

Materials

The Palm empty fruit bunch (PEFB) used in this study was obtained from local plantations, while the Cr(NO₃)₃.9H₂O and sulfuric acid were purchased from Sigma-Aldrich, oxygen and hydrogen gas were bought from local supplier, and the ammonia

and pyridine were obtained from Merck-Millipore. The main instrumentations were GCMS, XRD which has a scan speed of 5000 deg/min, 30kV voltage and a current strength of 10 mA. A set of hydrocracking instrumentations are as shown in **Figure 1**.

Preparation of Active Carbon and Zeolite

The carbon and zeolite were pulverized to 200 mesh, and was refluxed in H₂SO₄ 1 N solution for 6 hrs. The precipitate was filtered and washed until the filtrate had a pH of about 6.5-7. The resulting solid was regrinded into 200 mesh size and dried at 110°C for 3 hrs. The carbon/zeolite compost obtained was labeled as active carbon/zeolite (Sevilla, Sanchís, Valdés-Soh, Morallón, & Fuertes, 2007).

Preparation of Cr/C and Cr₂O₃/Z Catalysts

Impregnation of Cr catalyst

The active carbon/zeolite was soaked in a solution of Cr(NO₃)₃.9H₂O for 24 hrs while being continuously stirred. However, within the first 4 hrs of the stirring process, ammonia was added to it drop wisely. Then, the active carbon/zeolite containing Cr was dried at 130°C for 3 hrs, which resulted in a paste and then it was calcined at 550°C for 5 hrs. The impregnation process of Cr catalyst was carried out using weight ratio of Cr and active carbon at 1:3 (25% by weight).

Catalyst oxidation

Oxidation of active carbon/zeolite that had been impregnated with Cr was conducted by releasing O₂ gas at 20 mL/sec flow rate. Amount 20 gram of the impregnated product was introduced into the reactor, which was prepared with glass wool in its bottom. O₂ gas was released into the reactor, and then, it was introduced into the vertical furnace. The voltage regulator which was connected with the furnace was set at 160 V. After the temperature reached 350°C, oxidation was started and monitored. The furnace temperature was adjusted to 345°C – 355°C for 2 hrs by controlling the voltage regulator (Linares-Solano, Lozano-Castelló, Lillo-Ródenas, & Cazorla-Amorós, 2008).

Catalyst reduction

Active Cr/Carbon catalyst material that was produced from calcination was then reduced with H₂ gas at 400°C for 2 hrs.

Hydrocracking of PEFB

For the hydrocracking process, 15g of dry PEFB at 100 mesh was introduced to the reactor in batch system (e). Hydrocracking was conducted using varied temperature of 450-700°C (c), different weight of catalyst 0.5-2.5 g (d) and hydrogen gas flow rate at 0.5-3.0 L/min (b). The liquid product obtained was collected in the container (i), and Hydrocracking was considered complete, when no more liquid product dropped out of the reactor (**Figure 1**). The product was weighed and its density was measured, then it was analyzed using Gas Chromatography Mass Spectrometry (GCMS).

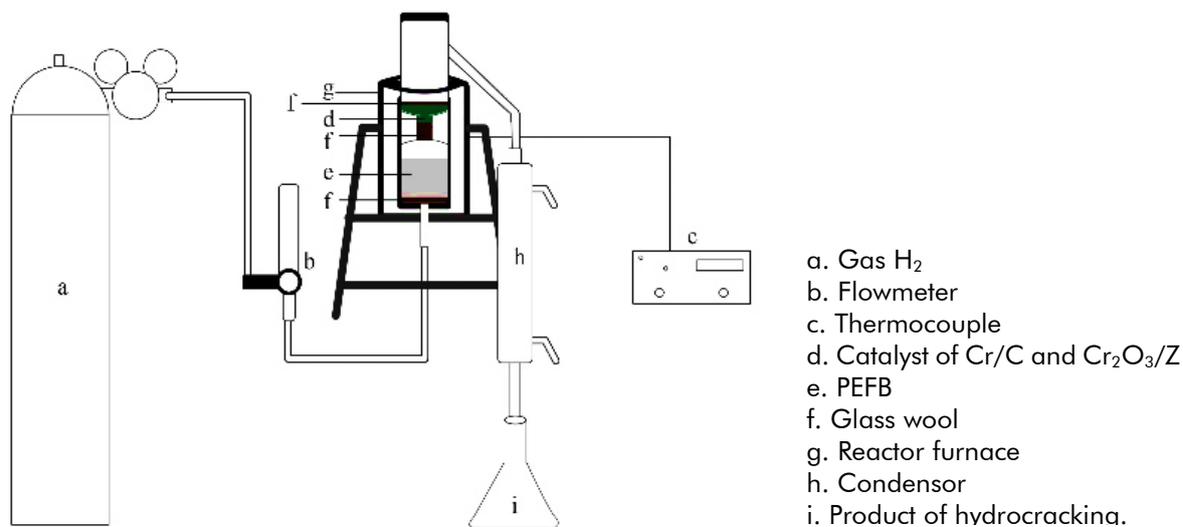


Figure 1. Scheme of the apparatus for hydrocracking of bio-oil

RESULTS AND DISCUSSION

Acidity Test of Cr₂O₃/Z Catalyst Using Pyridine and Ammonia as Probes

The acidity of the catalyst was assessed using ammonia and pyridine as probe molecules. High acidity value corresponds with the catalyst's ability to effectively assist in the cracking reaction (Nor, Lau, Lee, & Mohamed, 2013). The results of the acidity test with pyridine and ammonia adsorption is observed in **Figure 2**. The molecular size of ammonia is smaller than pyridine, therefore, it was adsorbed faster into the catalyst. The impregnation of Cr metal onto zeolite increased the acidity of the catalyst, as confirmed both by the ammonia and pyridine adsorption. For ammonia adsorption, the catalyst increased from 0.4087 to 9.9238 mmol/g, while for pyridine adsorption, the increase was from 0.8659 to 0.9803 mmol/g. As observed above, the increase of ammonia

adsorption is higher compared to that of pyridine. This finding confirmed the possibility that the more available the acid site are, the higher the basic molecule it readily adsorb, in this case, ammonia. And also, that metal Cr impregnation increases catalyst acidity. Where higher acidity correspond with increase in catalyst activity (Ceyhan, Şahin, Baytar, & Saka, 2013).

Characterization of Specific Surface Area of Catalyst

After the natural zeolite had been activated using H₂SO₄ 1 N (ZAA-H), and it was impregnated by Cr(NO₃)₃.9H₂O. The resulting solid was then calcined (Cr₂O₃/Z-HK), followed by oxidation using O₂ at flow rate of 20 mL/sec (Cr₂O₃/Z). The surface area of each variation was then calculated, prior to their usage as catalyst, this was performed using *Gas Sorption Analyzer*.

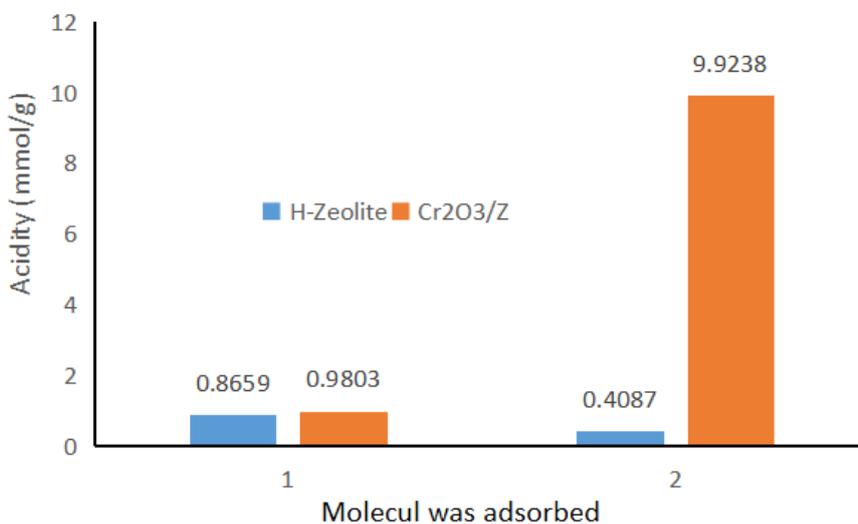


Figure 2. Acidity test of the catalysts (1) pyridine and (2) ammonia

Table 1. Specific surface area of catalysts prepared

Catalyst type	Surface area m ² /g (BET)
ZAA-H	153.654
Cr ₂ O ₃ /Z-HK	40.469
Cr ₂ O ₃ /Z	51.001

Table 1 shows that the surface area of Cr₂O₃/Z-HK is obviously smaller than that of ZAA-H. This is because the calcination treatment caused an increase in the specific surface area. However, the impregnation of Cr(NO₃)₃·9H₂O on ZAA-H in form chromium oxide, coated the zeolite surface, which affected it otherwise. The surface covering of the zeolite by chromium oxide resulted in a decrease in its specific surface area. Moreover, the Cr₂O₃/Z-HK was oxidized with O₂ and reduced with H₂ at temperature of 400°C for 2 hrs with a gas flow rate of 20 mL/sec. The oxidation process converted the metal ions into oxides, which also assisted in the removal of H₂O ligands in metal complex ions that were firmly attached to the catalyst pores. The reduction process was carried out at 400 °C using H₂ gas at flow rate of 20 mL/sec for 2 hrs, this process converted metal ions into atoms (neutral/zero charge).

The surface area of Cr₂O₃/Z increased because the chromium oxide present on the zeolite surface had turned into metal after undergoing the oxidation and reduction processes. Furthermore, the presence of Cr in the pores of ZAA-H caused the catalyst to possess dual functions, namely, cracking and hydrogenation.

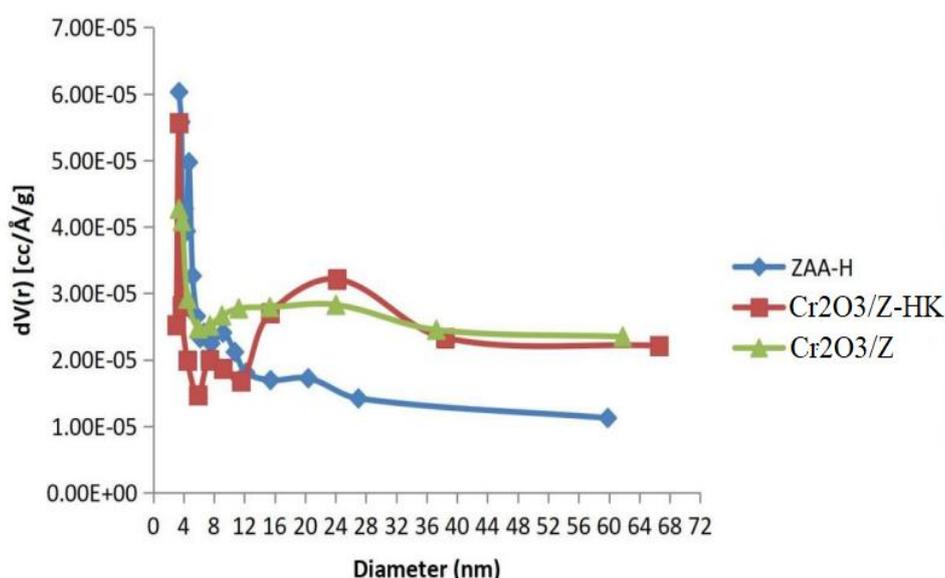
The BJH (Barret, Joiner, Halenda) Pore Type Catalyst

Prior to being used in the hydrocracking process, the pore size of catalyst was determined by evaluating the change in differential pore volume (dV(r)) against

its diameter, for each catalyst prepared. Differential pore volume (dV(r)) is the change of adsorbate at each pore diameter per gram of sample. The catalysts characterized were, active natural zeolite (ZAA-H), Cr₂O₃/Z-HK (Cr/zeolite which had undergone calcination process) and Cr₂O₃/Z (calcined Cr/zeolite that had been reduced and oxidized).

The characteristics of meso-porous solids are determined by the pore size of the catalyst, this is measured using the BJH (Barret, Joiner, Halenda) method, as shown in **Figure 3**. All the catalyst samples showed meso-sized pores with an increase in the dV(r), which continued to increase in its diameter till about 2-50 nm. The results showed that the increase in dV(r) of ZAA-H was 6.03 × 10⁻⁵ cc/nm/g, at a diameter of 3.38908 nm. Furthermore, the highest level recorded for Cr₂O₃/Z-H dV(r) was 2.52 × 10⁻⁵ cc/nm/g at a diameter of 3.0383 nm, and for Cr₂O₃/Z-KOR dV(r), it was 4.2 × 10⁻⁵ cc/nm/g at diameter of 3.39894 nm. This indicates that the type of pore size on all catalyst ZAA-H, Cr₂O₃/Z-HK or Cr₂O₃/Z, are in the mesoporous range.

Based on the results of the BJH analysis in **Figure 3**, it was concluded that the best catalyst for the hydrocracking process was Cr₂O₃/Z with a pore diameter of 3.39894 nm. The catalyst belonged to the mesopore type because the value of its diameter is within the range, i.e., 2-50 nm (Wang et al., 2009).

**Figure 3.** The sample pore size in ZAA-H, Cr₂O₃/Z-HK and Cr₂O₃/Z

Characterization of Crystallinity of Cr₂O₃/Z Catalyst

The Cr₂O₃/Z catalyst was prepared through oxidation, by releasing oxygen gas into it at 350°C. **Figure 4** shows a high crystallinity diffraction pattern with sharp and pointed peaks on the Cr₂O₃/Z catalyst at particular angle (2θ). The pattern matched the Joint Committee of Powder Diffraction Standard (JCPDS No. 038-1479), which confirmed the formation of Cr₂O₃ oxide on the pore surface of zeolite.

The Effect of Flow Rate on Density of Hydrocracking Product

Hydrocracking was carried out with various level of hydrogen gas flow rate at 1.0-3.0 L/min, with a constant temperature of 500°C and catalyst weight of 1g, the results is presented in **Figure 5**.

The flow rate of the hydrogen gas has the ability to increase or decrease the density of the hydrocracking product. Reports has stated that higher hydrogen gas flow rate increases product's density, because it reduce the effectiveness of collision between the reactant and hydrogen gas, which makes the breaking process become less effective (Dewi & Fanani, 2017).

Therefore, the hydrocracking product still possess high molecular weight, which in turn lead to increase in density. Increasing hydrogen gas flow rate also has the ability to decrease density because it triggers more breaking process of carbon chain. The molecules with short chains becomes dominant, leading to decrease in the density of hydrocracking product (Dewi & Fanani, 2017). The results of density measurement with variation of hydrogen gas flow rate indicated that hydrogen gas flow rate of 2.5 L/min was the optimum rate, because it produced the lowest density at 0.9584 g/ml.

Effect of Catalyst Surface Area on Density of Hydrocracking Product

Hydrocracking of PEFB was carried out with catalyst variation at 500 °C, and H₂ flow rate was utilized as reactant carrier gas and simultaneously as reduction agent at 2.5 L/min. The surface area of catalyst of Cr/C obtained were 1,497.07 m²/g, 1,536.19 m²/g, 1,544.05 m²/g, 1,554.48 m²/g and 1,652.58 m²/g (**Figure 6**).

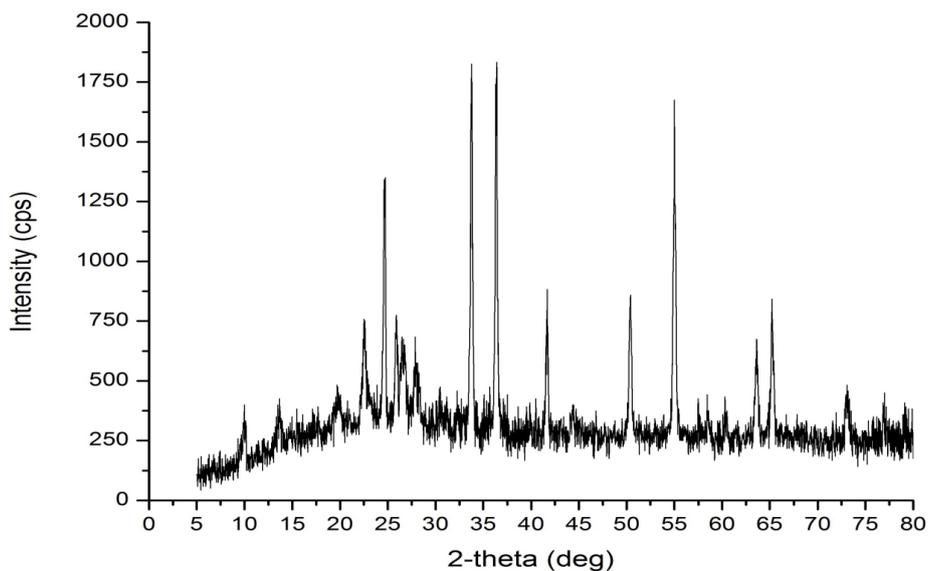


Figure 4. XRD diffractogram of Cr₂O₃/Z catalyst characterization

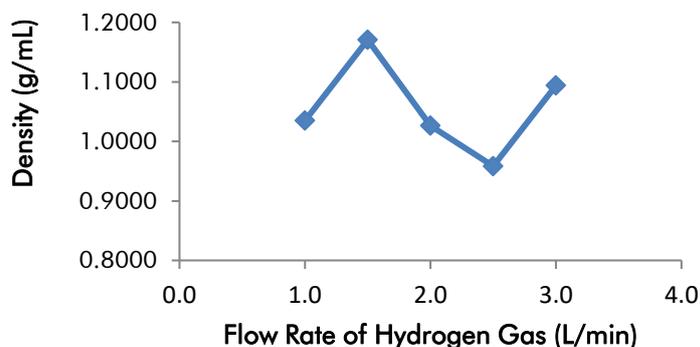


Figure 5. Effect of hydrogen gas flow rate on the density of hydrocracking product

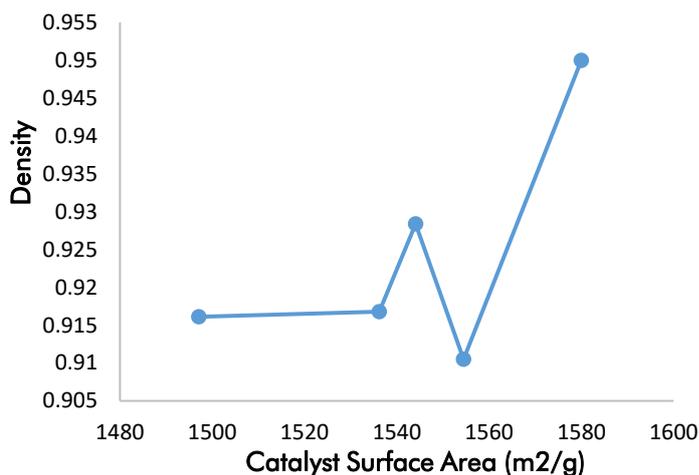


Figure 6. Effect of catalyst surface area on the density of hydrocracking product

Figure 6 shows that the surface area of the Cr/C catalyst affected the density of the hydrocracking product. This is because catalyst activity and selectivity depends on specific surface area, which determine the active site available. Larger surface area tends to increase reactivity and produce smaller molecule of hydrocracking products. Theoretically, the amount of hydrocracking product tends to increase with the surface area of the catalyst. Figure 6 displays this overall tendency except for one data. The complex reaction mechanism that occur during hydrocracking also contribute to this slight difference, due to unexpected factors, such as, unequal heat or stream of hydrogen gas. Furthermore, the breakdown of bio-oil macromolecule does not support with continuous stream of hydrogen, which causes coupling reaction between chains resulted from cracking, to produce substances with higher molecular weight (Danish, Hashim, Ibrahim, & Sulaiman, 2014). According to Anand, Sibi, Verma, & Sinha (2014) minimizing the C-C coupling reaction is achieved by higher pressure and hydrogen to feed ratio. And also, condensation as well as ketonization between reaction intermediates,

produced a longer oxygenated products, where O₂ are accumulated on the catalyst's surface.

Effect of Temperature on the Density of Hydrocracking Product

Furthermore, hydrocracking process of PEFB was carried out at temperature variation from 450°C to 700°C. The results showed that, optimum temperature was achieved at 600°C as observed in Figure 7. Hydrocracking process at 600°C increased the kinetic energy of the reactant, which resulted in more collision frequency between it and the catalyst. High temperature tends to breaks more bonds in the bio-oil to produce shorter chains. Which led to the the discovery of liquid product with a density that was close to that of diesel fuel, i.e., 0.836 – 0.850 g/cm³ (Nurdini et al., 2020). Hydrogenation played an important role after breaking the C-C bond, where sufficient H₂ streams compelled the hydrocracking process to form shorter chain compounds. In the case of higher temperature with insufficient hydrogen, the heat created vastly chemical bond break-up, and since there was limited H₂, it led to oligomerization, which caused an increase in the density of the liquid product.

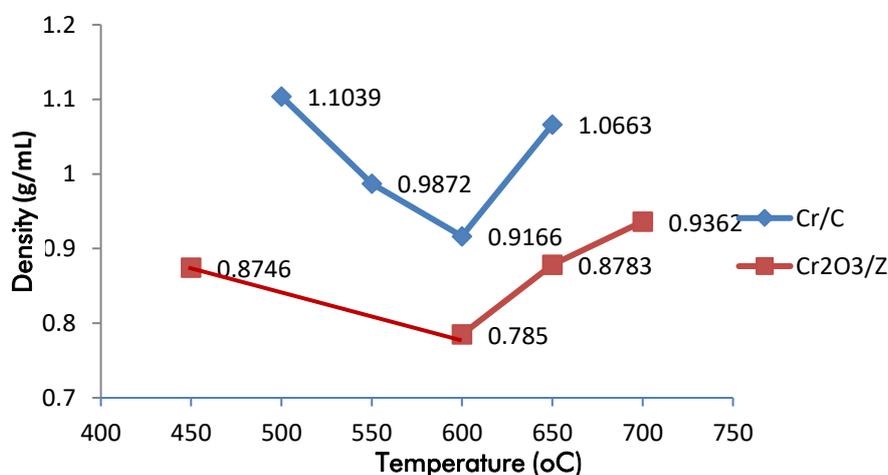


Figure 7. Effect of temperature on the density of hydrocracking product

Figure 7 also shows that catalyst $\text{Cr}_2\text{O}_3/\text{Z}$ had better activity compared to Cr/C . This is obvious from the fact that at the same condition, $\text{Cr}_2\text{O}_3/\text{Z}$ produced hydrocracking product with lower density (García, Bertero, Falco, & Sedran, 2015). Some studies reported that lower bio-oil was upgraded using zeolite and carbon-based catalyst, and the results showed that the C- based produced a better upgraded bio-oil as compared to the metal catalyst (Omar, Yang, & Wang, 2021). However, the results of this study, showed that zeolite-based catalyst produced a better bio-oil upgraded product as indicated by the lower density. Zeolite-based catalysts are well known for their acidity and higher thermal and hydro-thermal stability. The micropores contained within the zeolite allowed the diffusion of small molecule, which provide its unique activity and selectivity (Saab, Polychronopoulou, Zheng, Kumar, & Schiffer, 2020).

Analysis of Hydrocracking Product Using Gas Chromatography Mass Spectrometry (GCMS)

Analysis of hydrocracking product using GC-MS showed decrease in the amount of cyclic compounds and increase in straight chain hydrocarbon compared to the initial bio-oil. This is probably due to the cracking of the cyclic chemicals to become substances with straight chain. Breaking up by zeolite is closely related with the fluid catalytic cracking of petroleum, where

dehydration and dealkylation occurs simultaneously (Si, Zhang, Wang, Ma, & Dong, 2017). This was shown by the existence of substance with straight chain which prior to the cracking did not exist. These GC-MS analysis results are shown in **Table 2** and **Table 3**.

The amount of cyclic compounds according to **Table 2** was decreased after hydrocracking using both catalysts, which was indicated from percentage area of chromatogram. The decrease of cyclic compound shows the effects of the breaking process, followed by dehydration and dealkylation to forms straight chain hydrocarbon. This finding is confirmed by the formation of new substances in the form of straight chain materials (**Table 3**). **Table 3** shows that before hydrocracking some straight chain hydrocarbon were not detected, however, after this process their presence were evident.

Data from the GCMS analysis results indicate that the phenolic and benzoic compounds of the aromatic hydrocarbon diminished due to breaking process (cracking) to form substances with lower molecular weight of alkane compounds. Straight chain hydrocarbons detected by Mass Spectrometry, includes Undecane, 5-Tridecene and $\text{C}_{40}\text{H}_{60}$. The results strongly suggest a successful bio-oil upgrading through hydrocracking process using Cr/C and $\text{Cr}_2\text{O}_3/\text{Z}$ catalysts.

Table 2. Analysis of cyclic substances of product after and before hydrocracking.

Catalyst	Retention Time (min)	Before (% Area)	After (%Area)	Name of Compound
$\text{Cr}_2\text{O}_3/\text{Z}$	8.15	7.30	0.16	Phenol 2,6-dimethoxy-phenol 1,2,3-trimethoxy-5-methyl-benzene
	14.66	8.09	0.49	
	16.96	5.38	0.21	
Cr/C	11.33	2.01	1.48	2,5 dimethyl phenol 2-(1-hydroxyethyl) norbornadiene 2H-1-Benzopyran-2-on,3-methyl
	13.33	0.49	0.15	
	16.82	0.33	0.16	

Table 3. Analysis of some straight chain substances in the hydrocracking product

Catalyst	Retention Time (min)	Before (% Area)	After (%Area)	Name of Compound
$\text{Cr}_2\text{O}_3/\text{Z}$	23.74	0.00	5.92	Henisikanoate acid Heksatrioktane Octasilosane
	26.89	0.00	4.40	
	27.04	0.00	5.34	
Cr/C	7.31	0.00	0.02	5-Octadekanal 6-Tridekane 7-Tetradekane 8-Heptadekane 9-Octadekane
	13.76	0.00	0.62	
	15.19	0.00	0.61	
	18.92	0.00	0.20	
	20.01	0.00	0.14	

CONCLUSIONS

The hydrocracking of bio-oil from pyrolyzed PEFB using zeolite and carbon based chromium catalyst yielded liquid products with lower density. Also, the Cr₂O₃/Z catalyst produced a better result compared to Cr/C at 600°C hydrocracking process. Moreover, the results of the mass spectrometry showed that straight chain hydrocarbon were formed from the aromatic compounds, which were initially present within the bio-oil. The resulting upgraded bio-oil density were 0.7850 and 0.9166 g/ml for Cr₂O₃/Z and Cr/C catalysts, respectively, which implies that the Cr₂O₃/Z catalyst is more effective than Cr/C.

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