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Cracking of Palm Oil Methyl Esters on Modified Natural Zeolite Catalysts

Perengkahan Metil Ester Minyak Sawit Pada Katalis Zeolit Alam Termodifikasi

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ABSTRAK

Perengkahan katalitik metil ester minyak sawit (POME) menjadi hidrokarbon cair telah dilakukan dengan dua katalis berbasis zeolit alam bifungsional. Metil ester diproduksi dengan transesterifikasi CPO dengan metanol/KOH dalam kondisi yang menguntungkan. Eksperimen katalitik dilakukan dalam mikoreaktor batch yang dilengkapi dengan alat pemanas dan destilasi. Campuran metil ester dan bubuk katalis dipanaskan secara bertahap hingga 673 K selama 2 jam dan diikuti dengan distilasi pada kondisi yang sama selama 2 jam. Hasil penelitian menunjukkan bahwa katalis zeolit alam termodifikasi merupakan katalis aktif dalam perengkahan POME menjadi hidrokarbon.

Kata kunci: POME, Perengkahan, Zeolit, Katalis.

ABSTRACT

Catalytic cracking of palm oil methyl ester (POME) to liquid hydrocarbons has been conducted by two bifunctional natural zeolite based catalysts. Methyl esters were produced by transesterification of CPO by methanol/KOH in a favorable condition. The catalytic experiments were conducted in a batch microreactor equipped by heating and distillation apparatus. A mixture batch of methyl ester and catalyst powder was heated gradually up to 673 K for 2 h and followed by distillation at the same condition for 2 h. The result showed that modified natural zeolite catalysts were active catalysts in the cracking of POME to hydrocarbons.

Keywords: POME, Cracking, Zeolite, Catalyst.

INTRODUCTION

In recent years many studies have been carried out to find alternative sources of fossil fuels that will run out. Vegetable oil and biomass have been selected as renewable fuel sources. The conversion of vegetable oil and biomass into biodiesel fuel has been successful through transesterification of vegetable oil with methanol into methyl esters. Currently further conversion of palm oil methyl ester (POME) to liquid hydrocarbons equivalent to gasoline or kerosene by adopting the petroleum fluid catalytic cracking process is very interesting to study.

In liquid catalytic cracking of petroleum refineries bifunctional zeolite catalysts are used (Venuto & Habib, 1979). Bifunctional catalysts have two types of active sites, namely acid sites for cracking or isomerization and metallic sites for hydrogenation or dehydrogenation (Guisnet & Perot, 1984). Various parameters affect the activity and selectivity of bifunctional zeolite catalysts, in particular the characteristics of the acid function and hydrogenation function and the balance of these two functions. The results of previous studies showed that metal impregnated natural zeolite could be used as an active catalyst in the isomerization, oligomerization, and cracking of hydrocarbon molecules (Suharto, 1997; Suharto & Widiyati, 2002; Suharto, *et al.*, 2003; Suharto, 2006; Suharto, 2010). The characteristics of the zeolite bifunctional catalyst depend on the procedure catalyst synthesis and the impregnation method of metal elements (Guisnet & Perot, 1984). The impregnation of the active metals of chromium and nickel in natural zeolites has produced a microporous bifunctional catalysts (Suharto, 2010).

Impregnation of several types of transition metals in natural zeolite has been reported to produce active catalysts to convert palm oil into liquid hydrocarbons equivalent gasoline and kerosene (Suharto, 2006; Setiadi & Fitria, 2006; Siregar, *et al.*, 2006; Nasikin, *et al.*, 2009; Hikayat, 2009; Nurjanah, 2010). Direct catalytic cracking palm oil is more difficult than that of palm oil methyl ester (POME) cracking. The catalytic cracking of palm oil with natural Ni-zeolite and natural Ti-zeolite catalysts produces only 20% of C₈ – C₁₂ liquid hydrocarbons (Suharto, 2006). Therefore, the catalytic cracking of POME is very interesting to be developed as an effort to find new processes for making renewable fuels. Here we report the results of study on the preparation, characterization, and test of the catalytic activity of Cr/ - and Ni/natural zeolite in the cracking of POME.

METHODS

The catalytic tests in the cracking of POME were performed in a batch system in a glass reactor equipped with a heater and reflux vessel. POME was obtained from the transesterification of crude palm oil (CPO) with methanol/KOH. A mixture of 25 mL of POME and 2 g of catalyst powder was heated at 300°C while stirring and refluxed for 2 h. The reaction product was separated by distillation at the same condition. Liquid hydrocarbons resulting from the cracking of POME were analysed by gas chromatography – mass spectrometry (GC-MS).

RESULTS AND DISCUSSION

The composition of POME before cracking is presented in table 1. The alkyl carbon chain is dominated by long chain of $C_{14} - C_{18}$. The chemical composition of this methyl ester is converted into liquid hydrocarbons through a cracking process with Cr/HZA and Ni/HZA catalysts at a reaction temperature of 300°C . Under these reaction conditions, the yield of liquid hydrocarbons from the cracking reaction was 53% with Cr/HZA catalyst and 61% with Ni/HZA catalyst. The physical properties of the obtained liquid hydrocarbons are presented in table 2. The cracking of POME with the Cr/HZA catalyst produces liquid hydrocarbons with a lower density than those produced with the Ni/HZA catalysts. The viscosity of liquid hydrocarbons resulting from the cracking of POME is higher than the viscosity of commercial gasoline products. The fog point of hydrocarbons produced by catalytic cracking with Cr/HZA is greater than the fog point of gasoline, whereas that produced by cracking with Ni/HZA is the same as gasoline. The pour point of liquid hydrocarbons resulting from catalytic cracking, both with Cr/HZA and with Ni/HZA, is almost the same as the pour point of gasoline.

Table 1. The composition of POME

| Esther components | Formula | / % |
|-------------------|-------------------|-------|
| Methyl myristic | $C_{15}H_{30}O_2$ | 2,64 |
| Methyl palmitic | $C_{17}H_{34}O_2$ | 38,26 |
| Palmitic acid | $C_{18}H_{34}O_2$ | 4,58 |
| Methyl oleic | $C_{19}H_{36}O_2$ | 46,60 |
| Others | - | 6, 10 |

Table 2. Physical properties of POME cracked hydrocarbons (HC)

| Properties | Unit | POME | Cracked HC | | Gasoline |
|------------|--------------------|--------|------------|--------|----------|
| | | | Cr/HZA | Ni/HZA | |
| Density | g/cm^3 | 0,8865 | 0,7875 | 0,8142 | 0,6877 |
| Viscosity | cSt | 2,4722 | 0,6564 | 0,7763 | 0,3723 |
| Fog point | $^{\circ}\text{C}$ | 13 | 1 | < 0 | < 0 |
| Cast point | $^{\circ}\text{C}$ | 9 | < 0 | < 0 | < 0 |

These key physical properties of the POME cracking product are higher than the physical properties of commercial gasoline. The liquid hydrocarbons from the catalytic cracking of POME have a heavier hydrocarbon fraction than the hydrocarbons in gasoline. This fact is shown in Figure 1 and Figure 2. The chemical composition of liquid hydrocarbons resulting from the catalytic cracking of POME are presented in table 3 and table 4.

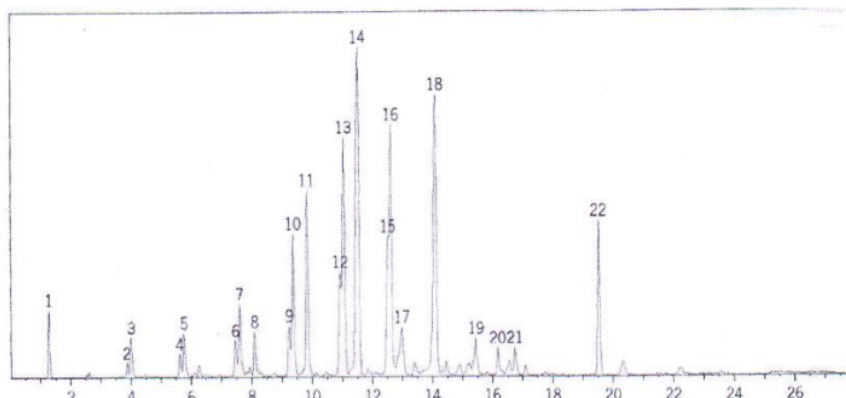


Figure 1. Gas chromatogram of liquid hydrocarbons cracking product of POME by Cr/HZA catalyst at 300°C.

Table 3. Liquid hydrocarbons cracking product of POME by Cr/HZA catalyst

| Peaks number | Component | Formula | % | Note |
|------------------------------|------------------|---------------------|-------|--|
| 7, 10, 12, 13, 15, 16, 18 | n-undecane, | $C_{11}H_{24}$, | 3,57 | (C ₁₁ – C ₁₅) liquid hydrocarbons |
| | n-dodecane, | $C_{12}H_{26}$, | 4,35 | |
| | 1-undecene, | $C_{11}H_{22}$, | 4,59 | |
| | n-tridecane, | $C_{13}H_{28}$, | 11,95 | |
| | 1-tetradecene, | $C_{14}H_{28}$, | 6,46 | |
| | n-tetradecane, | $C_{14}H_{30}$, | 15,47 | |
| | n-pentadecane | $C_{15}H_{32}$, | 17,13 | |
| 11, 14, 22 | methyl nonanoic, | $C_{10}H_{20}O_2$, | 5,69 | POME residues |
| | methyl decanoic, | $C_{11}H_{22}O_2$, | 16,43 | |
| | methyl palmitic | $C_{17}H_{34}O_2$ | 6,85 | |

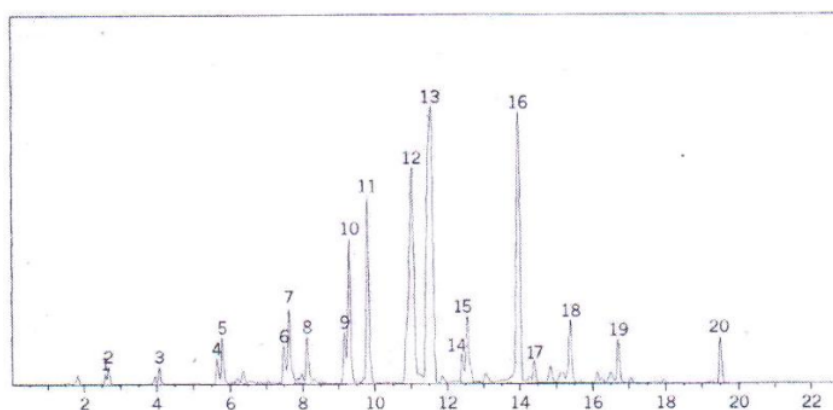


Figure 2. Gas chromatogram of liquid hydrocarbons cracking product of POME by Ni/HZA catalyst at 300°C.

Table 4. Liquid hydrocarbons cracking product of POME by Ni/HZA catalyst

| Peak number | Component | Formula | % | Note |
|-----------------|--|---|-----------------------|--|
| 5 10, 12, 16 | dodecane, tridecane, n- pentadecane | C ₁₂ H ₂₆ , C ₁₃ H ₂₈ , C ₁₅ H ₃₂ , | 5,86 8,53 11,47 | (C ₁₂ – C ₁₅) liquid hydrocarbons |
| 11 | Methyl nonanoic | C ₁₀ H ₂₀ O ₂ , | 5,79 | POME residue |

In general, it can be shown that Cr/HZA and Ni/HZA can be used as active catalysts in the cracking of POME. The catalytic cracking activity of Cr/HZA was slightly higher than that of Ni/HZA catalyst. Several types of liquid hydrocarbon compounds (C₁₁ – C₁₅) have been identified in the cracking product with Cr/HZA catalyst at 300°C (figure 1 and table 3).

The cracking of POME with Ni/HZA catalyst produced fewer types of liquid hydrocarbon compounds (figure 2 and table 4) compared to those obtained from the cracking with Cr/HZA catalysts. Ni/HZA catalyst does not produce C₁₁ hydrocarbon. Hydrocarbon component equivalent to gasoline produced from the cracking of POME by Cr/HZA catalyst is about 12% (n-undecane, 1-undecane, and n-dodecane), whereas by Ni/HZA catalyst only 5% (dodecane). With a similar zeolitic catalyst, almost the same results were obtained from the catalytic cracking of POME from the wastewater treatment of palm oil mills (Sundaryono & Budiyo, 2010). This result is lower than that of cracking POME by HZSM catalyst, which produces 29% gasoline equivalent hydrocarbons (Nurjanah, 2010). HZSM catalyst is synthetic zeolite-based catalyst which has better catalytic character than natural zeolite-based catalysts such as Cr/HZA and Ni/HZA. If compared with kerosene (C₉ – C₁₄), the hydrocarbon component equivalent to kerosene obtained from the cracking of POME by Cr/HZA catalyst reached about 52% (C₁₃ – C₁₅), while only 20% with a Ni/HZA catalyst. In addition, under the conditions of this catalytic cracking reaction, the methyl ester conversion has not yet occurred completely.

The slightly better catalytic selectivity of Cr/HZA compared to Ni/HZA in producing hydrocarbon equivalent gasoline components can be explained by the slightly higher acidity of Ni/HZA than Cr/HZA (Table 1). Zeolite-based heterogeneous catalysts with higher acidity showed higher activity in hydrocarbon cracking, but tend to produce more cracking fraction of light hydrocarbon components (C₁ – C₄) in gaseous form (Venuto & Habib, 1979). This component could not be analysed due to the GC analysis was off-line carried out and the light hydrocarbon fraction was not successfully condensed.

SIMPULAN

Cr- and Ni-supported natural zeolite catalysts showed catalytic activity in the cracking of POME to liquid C₁₁ – C₁₅ hydrocarbons. The composition of liquid hydrocarbons

resulting from the catalytic cracking of POME by Cr/HZA is 12% hydrocarbons equivalent to gasoline and 52% hydrocarbons equivalent to kerosene, whereas by Ni/HZA catalysts obtained 5% hydrocarbons equivalent gasoline and 20% hydrocarbons equivalent kerosene. Further research is needed to develop heterogeneous natural based catalysts that provide high catalytic activity and selectivity in the cracking of palm oil to hydrocarbons.

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