

CRACKING OPTIMIZATION OF PALMITIC ACID USING Fe³⁺ MODIFIED NATURAL MORDENITE FOR PRODUCING AVIATION FUEL COMPOUNDS

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Abstract. Natural mordenite from Turen village Malang district Indonesia has been modified to Fe³⁺-mordenite for heterogenous catalyst in cracking process of palmitic acid to produce Aviation fuel components. Cation exchange method has been used in mordenite modification using FeCl₃. The Fe³⁺-mordenite was characterized by structure analysis, Fe content, Si/Al ratio, number of acid sites, pore size, pore volume, and surface area. The catalytic performances, conversion, and selectivity were measured at 583 K by GC-MS for 1, 2, and 3 hours. The high content of Fe in mordenite has larger Brønsted-Lewis's acid site, pore volume and surface area than the natural mordenite. The crystal structure of Fe³⁺-mordenite is still the same with natural mordenite. The Fe³⁺-mordenite also has a smaller pore size than the natural mordenite. In cracking process of palmitic acid, Fe³⁺-mordenite performed 61.94 % of conversion and 92.90 %, which produced aviation fuel compounds, namely alkanes, alkene, cycloalkane and aromatic.

Keywords: aviation fuel, mordenite, cation exchanged, acid site, palmitic acid.

1. Introduction

Population growth in Indonesia has caused the need for facilities and infrastructure, including the mobility with air transportations. On accompanying those condition, many researches were developed on producing biodiesel as renewable source and its modification on increasing the product efficiency.¹ In aviation aspect, air-transport mobility also increases the demand of aviation fuel especially aviation turbine fuel (avtur).² Avtur needs in 2016 are 4.8 million KL increased in 2017 and 2018 respectively to 5.4 million KL and 5.72 million KL. The Indonesian government must import avtur because domes-

tic production is insufficient to meet those needs. The number of imported avtur by the government in 2018 was 1.87 million KL.³ In general, aviation fuel imports by the Indonesian government can cause an imbalanced balance of government finances and inflation. It also has a negative impact on aircraft traffic, passenger traffic, cargo traffic, postal traffic, medical services, and tourism. This is because imported aviation fuel causes avtur prices and airplane ticket prices to be expensive, so that air transportation service users are reduced. To overcome this problem, the Indonesian government through PT. Pertamina increased the aviation fuel production and since 2018 the aviation fuel import was reduced, even in middle 2019 the aviation fuel import was stopped.⁴ Therefore, the research of avtur production from natural resources are urgently needed.

Avtur is a multicomponent fuel with a C₈-C₁₆ carbon chain length developed from kerosene. Avtur contains 70-85 % mixture of hydrocarbon (HC), alkane and alkene compounds with straight, branch or cyclic chains and 20-25 % aromatic compounds ring-6.⁵ Some researchers report that compounds of avtur component or bioavtur can be synthesized from free fatty acids (FFA) by catalytic cracking reactions using zeolite-based catalysts. According to Sousa *et al.* in 2018, bioavtur can be obtained from deoxygenation, cracking and isomerization of FFA from the hydrolysis of palm kernel oil using β-zeolite catalyst for 5 hours at 623 K with conversion of 72 %.⁶ Oleic acid has been used as a reactant for bioavtur synthesis by the hydrodeoxygenation and catalytic cracking reaction using a NiMo/zeolite catalyst for 1.5 hours at 648 K with conversion of 36.32 %.⁷ In our previous work, avtur components, namely alkanes and alkenes with carbon chains C₁₀-C₁₅, was synthesized from palmitic acid by catalytic cracking reactions using catalyst α-Fe₂O₃/zeolite Y at 653-673 K for 3 hours with conversion of 85,89 %.⁸

FFA and zeolite for bioavtur synthesis are found easily in Indonesia. One of the many FFAs in Indonesia is palmitic acid which is abundant in palm oil (± 43.5 %) production up to 36.59 million tons.⁹ On the other hand,

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natural zeolites are distributed in Indonesia and in East Java, especially in Pacitan, Ponorogo and Malang which have deposits of 2.6, 1.3, and 19.36 million tons, respectively.¹⁰ Based on the geological resource center in 2008, more than 50 natural zeolite forming minerals are known and the most found are mordenite. To improve the activity of mordenite as a catalyst, mordenite is usually modified with transition metals, one of which is iron. The potential for iron in East Java is large, especially in Tulungagung with 14.69 thousand tons.¹⁰ In this research preparation of Fe³⁺-mordenite from natural mordenite of Turen as a catalyst for compounds synthesis of avtur component by decarboxylation and catalytic cracking reactions palmitic acid is done.

2. Experimental

2.1. Materials

The materials in this study are: natural mordenite from Turen Malang, HF 40 % (Sigma Aldrich), HCl 37 % (Sigma Aldrich), NH₄Cl 99 % (Sigma Aldrich), AgNO₃ 99,8 % (Sigma Aldrich), *n*-hexane, ethanol, N₂ gas, distilled water, FeCl₃ 98 % (Sigma Aldrich), pyridine and palmitic acid 98 % (Merck).

2.2. Characterizations

The instruments were the Spectrometer X-Ray Fluorescence (XRF), spectrometer X-Ray Diffraction (XRD), surface area analyzer (SAA), spectrophotometer Fourier transform infrared (FTIR), dan gas chromatography-mass spectrometry (GC-MS), thermocouple, oven, furnace, desiccator, reflux, magnetic stirrer, hotplate, and some glassware that is commonly used in laboratories.

2.3. Preparation and Characterization of Fe³⁺-Mordenite Catalyst

Turen Malang mordenite sample was crushed to 100 mesh. Furthermore, a qualitative test with XRD is carried out to ensure that the sample used contains mordenite. The catalyst preparation is carried out by several processes, namely the process of purification of natural mordenite and cation exchanged. In the purification stage, 50 g of mordenite was added to 100 mL of 1 % HF solution while stirring for 30 minutes. The solids are formed, then separated from the HF solution and washed with distilled water until it is free of fluoride ions (washed water has a pH≈7). Solid then was added to 100 mL of 6 M while stirring for 30 minutes at a temperature of 323 K. The formed solid is then washed by distilled water until it is free of Cl⁻ ions (it is not white precipitate if washed water added AgNO₃ solution). The next step was

cation exchanged. A total of 5 g of purified mordenite was put into 100 mL of NH₄Cl 1N while stirring 3 hours per day for a week at 363 K and closed so that not to evaporate. The formed solid was washed until free of Cl⁻ ions. The solid was then dried at 378 K overnight and is called H⁺-mordenite.¹¹ For the preparation of Fe³⁺-mordenite, 5 g of H-mordenite was added into 100 mL FeCl₃ 1 M while refluxed at 363 K for 24 hours. The formed solid was filtered and washed by distilled water until free of Cl⁻ ions. Fe³⁺-mordenite was then calcined at 773 K under N₂ gas.

Fe³⁺-mordenite was characterized, including crystallite phase by XRD, functional groups by FTIR, elemental composition by XRF, type and number of acid sites by pyridine-FTIR method, surface area and size of the pores by SAA.

2.4. The Activity Test of Fe³⁺-Mordenite Catalyst

The catalyst activity test was carried out by the fractionated cracking method.¹² A total of 5 g of palmitic acid and 0.25 g of Fe³⁺-mordenite catalyst were put into the reaction flask which was equipped with a 60 cm long fractionation column, condenser, and thermocouple. Cracking reaction was carried out by fractional distillation at 583 K. Observing the reaction products every hour up to 3 hours, the mixture was sampled as much as 0.1 mL and dissolved in 10 mL mixture of *n*-hexane-ethanol (1:1). The reactants and reaction products are separated easily from the catalyst by centrifugation. Furthermore, the liquid was analyzed by GC-MS.⁸ The procedure was repeated for natural mordenite catalysts and H⁺-mordenite to determine the performance of Fe³⁺-mordenite in the decarboxylation and catalytic cracking reaction of palmitic acid.

3. Results and discussion

3.1. Fe³⁺-Mordenite Catalyst

Fe³⁺-mordenite catalyst has a crystalline structure. The diffraction pattern of Fe³⁺-mordenite catalyst was similar to the natural mordenite of Turen Malang which has similarities with mordenite synthetic in ICSD No: 00-049-0924 (Fig. 1). This shows that purification of mordenite (using HF and HCl solutions) and cation exchanged reactions (using NH₄Cl and FeCl₃ solutions) does not change the crystal structure of mordenite. However, the process caused slight shifting of peak position, this was observed from the change in peak position at an angle of 2θ from 6.50 to 6.41° and *d*_{spacing} from 13.61 to 13.76 Å (Table 1).

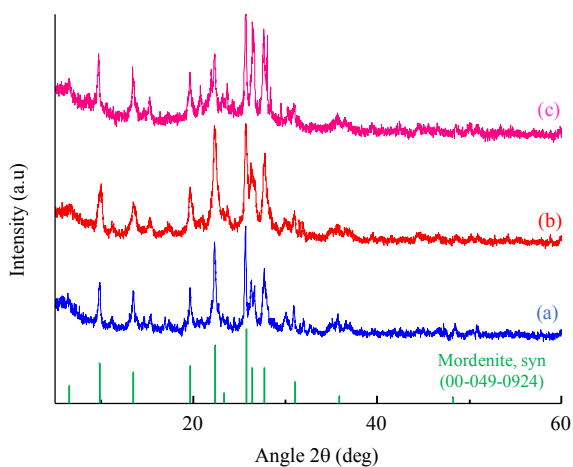


Fig. 1. Matching of the diffraction patterns mordenite, syn (00-049-0924) with (a) natural mordenite Turen Malang, (b) H⁺-mordenite, and (c) Fe³⁺-mordenite

Purification of natural mordenite is carried out to remove quartz and adsorbed metal atoms as well as to increase Si/Al ratio. The percentage of some metal elements decreased, and the Si/Al ratio increased as shown on Table 2. The metal elements Ca and Fe change significantly. This shows that most of the charge balancing cations in the Turen Malang natural mordenite are Ca²⁺ and Fe³⁺ ions. The percentage of all metal elements is reduced during the catalyst preparation process, except Fe has fluctuations. The amount of Fe decreased from 14.20 % to 9.62 % after the cation exchanged reaction using NH₄Cl solution and increased to 31.50 % after the cation exchanged reaction using FeCl₃ solution. This result indicates that Fe ions in the framework of natural mordenite replace Al position by an isomorphic substitution reaction. The amount of Fe ions in the mordenite framework increase significantly from 9.62 % to 31.5 % after cation exchange.

Table 1. Position of angle 2θ and *d*_{spacing} of the sample by XRD analysis

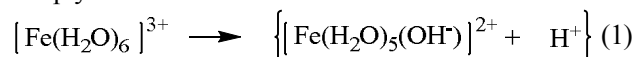
Natural mordenite		H ⁺ -mordenite		Fe ³⁺ -mordenite	
2θ (deg)	<i>d</i> _{spacing} [Å]	2θ (deg)	<i>d</i> _{spacing} [Å]	2θ (deg)	<i>d</i> _{spacing} [Å]
6.50	13.61	6.66	13.28	6.42	13.76
9.86	8.97	10.06	8.79	9.71	9.11
13.50	6.56	13.50	6.56	13.49	6.56
19.67	4.51	19.67	4.51	19.63	4.52
22.32	3.98	22.34	3.98	22.31	3.99
25.67	3.47	25.70	3.47	25.70	3.47
26.64	3.35	26.71	3.34	26.47	3.37

Table 2. The percentage of elements of the sample by XRF analysis

Element	Composition (%)		
	Natural mordenite	H ⁺ -mordenite	Fe ³⁺ -mordenite
Si	55.00	74.70	57.40
Al	6.80	6.80	5.90
Ca	16.60	4.28	2.46
K	4.40	3.03	1.72
Cr	1.05	0.00	0.00
Mn	0.14	0.08	0.07
V	0.08	0.03	0.00
Ti	1.60	1.33	0.83
Fe	14.20	9.62	31.50
Cu	0.13	0.13	0.13

Cation exchanged reactions also cause the rising number of acid sites to increase as shown in Fig. 2. The cation exchanged by the Fe³⁺ ion caused the number of Brønsted acid sites to increase from 8.39 mmol/g to 79.40 mmol/g and the Lewis acid site increased from 11.21 mmol/g to 26.77 mmol/g (Table 3). The number of Brønsted acid sites increases because the H⁺ ion from the dissociation of water molecules which bound to cations or hydrate cations is increasing like in reaction (1). Fe³⁺ cations have the greater polarization power than in natural

mordenite since the greater ratio of charge to the cation radius (*z/r*) and the *z/r* value of Fe³⁺ cation.¹³ As for the number of Lewis acid sites increases because the number of empty orbitals increases.¹⁴



The presence of water in mordenite is observed by the absorption band at the wave number ~1630 cm⁻¹ which is the bending vibration of H-OH trapped in the mordenite framework. Especially for H⁺-mordenite, water

molecules also interact with H^+ ions (absorption band 1440 cm^{-1}). Bending vibration of the $-OH$ group is also shown by the absorption band at the wave number $\sim 3600\text{ cm}^{-1}$ (Fig. 3).^{15,16} In addition to vibrations caused by water molecules, the FTIR spectrum also shows the presence of Si-O or Al-O vibrations in the $\sim 450\text{ cm}^{-1}$ and Si-O-Al vibrations at ~ 1060 to 1097 cm^{-1} . Vibration of Si-O – Al bonds is shown at the 798 cm^{-1} .¹⁷ Changes in cation and Si/Al ratio ultimately cause the surface area and pore size to change. Surface area increased from

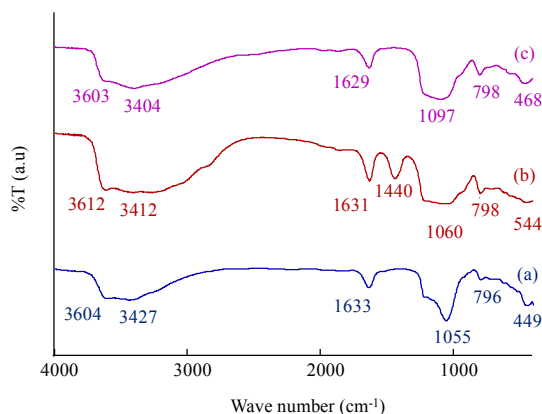


Fig. 3. The spectrum of FTIR analysis results of samples (a) natural mordenite Turen Malang, (b) H^+ -mordenite, and (c) Fe^{3+} -mordenite

$149.66\text{ m}^2/\text{g}$ to $197.71\text{ m}^2/\text{g}$ and pore size reduced from 9.47 nm to 7.36 nm (Table 4). Based on the size of the porosity of the Malang natural mordenite and Fe^{3+} -mordenite catalyst including mesoporous material.

Table 3. Number of acid sites of sample

Sample	Acid Species (mmol/g)	
	Brønsted	Lewis
Natural mordenite	8.39	11.21
H^+ -mordenite	48.97	27.05
Fe^{3+} -mordenite	81.66	26.77

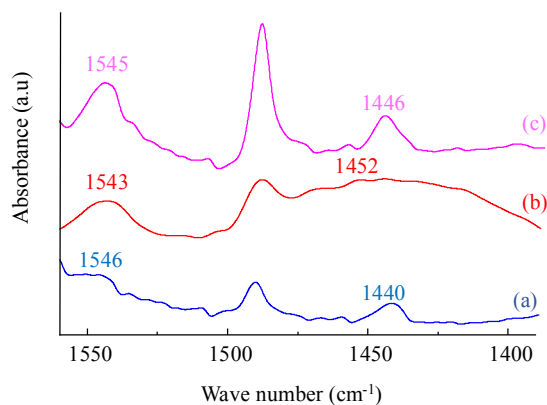


Fig. 2. IR spectrum results from acid site analysis using pyridine-FTIR method on (a) natural mordenite, (b) H^+ -mordenite, and (c) Fe^{3+} -mordenite

Table 4. Si/Al ratio, surface area, pore size, and pore volume

Sample	Si/Al	Surface area (m^2/g)	Pore size (nm)	Pore volume (mm^3/g)
Natural mordenite	7.80	149.66	9.47	67
H^+ -mordenite	10.59	180.63	8.73	65
Fe^{3+} -mordenite	9.38	197.71	7.36	99

3.2. The Activity of Fe^{3+} -Mordenite Catalyst in the Compound's Synthesis of Avtur Component

The activity of Fe^{3+} -mordenite catalyst is determined based on the amount of conversion of palmitic acid to the product and the selectivity of the reaction product, namely the aviation fuel component hydrocarbons. Based on the chromatogram analysis of samples during the 1 h reaction, there were 5 peaks (Fig. 4) and according to NIST database search 14.L MS spectrum, the 5 peaks were 1-pentadecene compound, pentadecane, ethyl hexadecanoate, hexadecanoic acid, and 5-dodecyldihydro-2(3H)-furanone which has a similarity index (SI) value of ≥ 90 (Table 5). Ethyl hexadecanoate and hexadecanoic acid are the IUPAC names of ethyl palmitate and palmitic acid. Ethyl palmitate is the result of esterification of

palmitic acid with ethanol. This reaction occurs when a sample containing a mixture of palmitic acid, the reaction product and catalyst is put into a solvent containing a mixture of *n*-hexane-ethanol before the catalyst separation process. From Table 5, ethyl hexadecanoate and hexadecanoic acid have a total area of 72.97 %. This amount indicates the amount of palmitic acid that has not reacted. In contrast, the total area of 1-pentadecene, pentadecane and 5-dodecyldihydro-2(3H)-furanone is the amount of conversion of palmitic acid to the product, which is 27.03 %. Of the three compounds which are avtur component compounds are 1-pentadecene and pentadecane with a total area of 22.77 %.

Pentadecane is obtained from the decarboxylation reaction of palmitic acid, according to the reaction mechanism shown in Fig. 5.⁸ Initially, there is a bond between the carbonyl group in palmitic acid and the Lewis acid site contained in the Fe^{3+} -mordenite catalyst. Then

the ion arrangement and release of hydrogen atoms occur. Furthermore, the C α atom will bind to the hydrogen that has been released to produce pentadecane. Some pentadecane then experiences a dehydrogenation reaction to

produce 1-pentadecene. The 5-dodecyldihydro-2(3H)-furanone compound is the result of the oxidative reaction of lactonization of palmitic acid, as reported by Duhamel and Muñiz¹⁸ (Fig. 6).

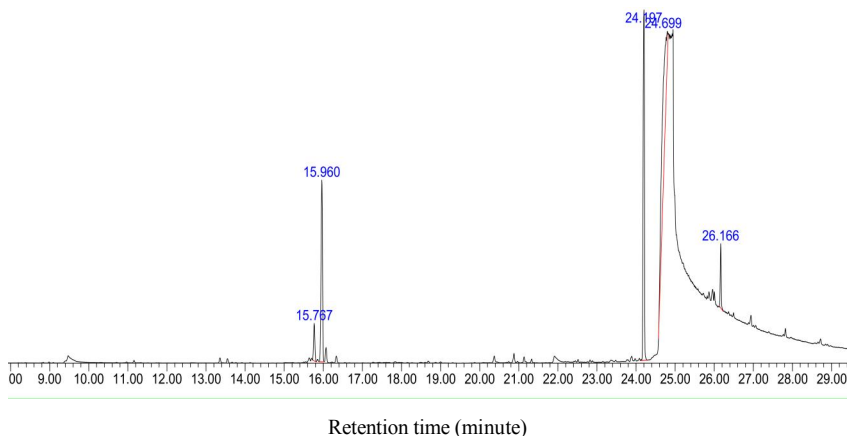


Fig. 4. Chromatogram of the sample of the reaction of cracking of palmitic acid by Fe³⁺-mordenite catalyst at 1 hour

Table 5. The compound in the sample for the catalytic cracking reaction of palmitic acid with Fe³⁺-mordenite at 1 hour

RT (minute)	Compound	SI	Area (%)
15,76	1-Pentadecene	94	3.44
15,96	Pentadecane	92	19.33
24,19	Ethyl hexadecanoate	99	34.09
24,69	Hexadecanoic acid	99	38.88
26,16	5-Dodecyldihydro-2(3H)-furanone	99	4.26

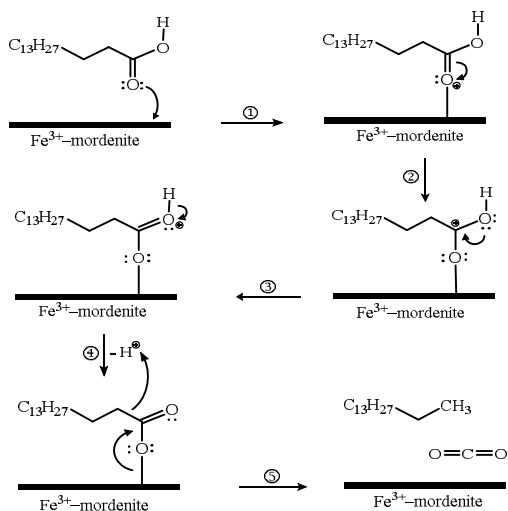


Fig. 5. Decarboxylation of palmitic acid to pentadecane

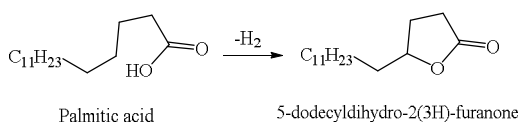


Fig. 6. Oxidative lactonization of palmitic acid to 5-dodecyldihydro-2(3H)-furanone

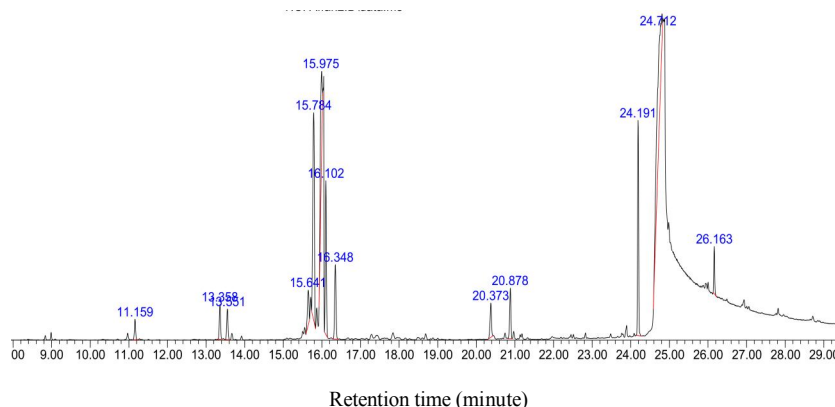


Fig. 7. Chromatogram of palmitic acid cracking reaction sample during two hours reaction

The amount of avtur component compound produced by the cracking reaction of palmitic acid with Fe^{3+} -mordenite catalyst is increasing after the reaction lasts 2 hours. Based on sample chromatograms from GC-MS analysis (Fig. 7) and NIST 14.L database search for MS spectrum (Table 6), there are 7 avtur component compounds with SI values ≥ 90 which have a total area of 47.75 %, namely pentadecane, 1-pentadecane, tetradec-

ane, 1-tetradecene, tridecane, cyclopentadecane, and decyl benzene. In addition, there are 4 compounds with SI values ≥ 90 which have a total area of 14.26 %, namely, 1-tetradecanol, 1-hexadecanol, heptadecane, and 5-dodecyldihydro-2(3H)-furanone. This shows that the amount of conversion of palmitic acid and avtur component compounds obtained from this reaction increased to 62.01 % and 47.75 %, respectively.

Table 6. NIST database search results 14.L spectrum of MS samples when cracking reaction of palmitic acid 2 hours

RT (minute)	Compound	SI	Area (%)
11.16	Tridecane	94	1.36
13.36	1-Tetradecene	97	2.37
13.55	Tetradecane	98	2.18
15.65	1-Tetradecanol	90	2.19
15.79	1-Pentadecene	95	18.07
15.99	Pentadecane	90	11.44
16.10	Cyclopentadecane	90	9.68
16.34	1-Hexadecanol	95	5.59
20.37	Decyl-benzene	95	2.65
20.88	Heptadecane	98	3.41
24.19	Ethyl hexadecanoate	99	12.32
24.71	Hexadecanoic acid	99	25.67
26.16	5-Dodecyldihydro-2(3h)-furanone	98	2.35

There were 13 compounds found in the sample when the reaction lasted 2 hours, there were 8 compounds that had not been obtained during one hour reaction, namely heptadecane, decyl-benzene, hexadecanol, cyclopentadecane, tetradecane, 1-tetradecene, 1-tetradecanol, and tridecane. 1-Tetradecene is the result of the pentadecane cracking reaction, according to the reaction mechanism shown in Fig. 8. At the beginning of the reaction, pentadecane interacts with the Lewis acid site (L^{\oplus}) contained in the Fe^{3+} -mordenite catalyst to produce 3-pentadecyllium. Furthermore, the 3-pentadecyllium ion undergoes a termination reaction β to produce 1-tetradec-

ne. In the next step, 1-tetradecene interacts with the Brønsted acid site to produce 2-tetradecallium ions and undergo H transfer to form tetradecane. With the same mechanism, some tetradecane undergoes cracking reactions resulting in tridecane. 1-tetradecene also undergoes a hydration reaction with water derived from cation hydrates to form 1-tetradecanol. In addition, in conjunction with the catalytic cracking reaction an isomerization reaction can occur producing cyclic compounds and aromatic compounds.¹⁹ Cyclopentadecane is obtained from the 1-pentadecene isomerization reaction (Fig. 9) and decyl-benzene is obtained from the 1-hexadecene isomerization reaction (Fig. 10). 1-Hexadecene also undergoes a hydra-

tion reaction producing 1-hexadecanol. The formation of decyl benzene, 1-hexadecanol, and heptadecane (compounds having more than 15 carbon chains) indicates the alkene dimerization reaction. Abbot and Wojciechowski²⁰ reported that alkenes can undergo a dimerization reaction together with a cracking reaction. 1-Pentadecene (C₁₅) can undergo dimerization reaction to form 1-triacontene (C₃₀) and experience cracking reaction to produce 1-tridecene (C₁₃) and 1-heptadecene (C₁₇) can undergo transfer of H to form tridecane and heptadecane or produce 1-tetradecane (C₁₄) and 1-heptadecene (C₁₇) can undergo transfer of H to form tridecane and heptadecane or produce 1-tetradecane (C₁₄), and 1-hexadecene (C₁₆).

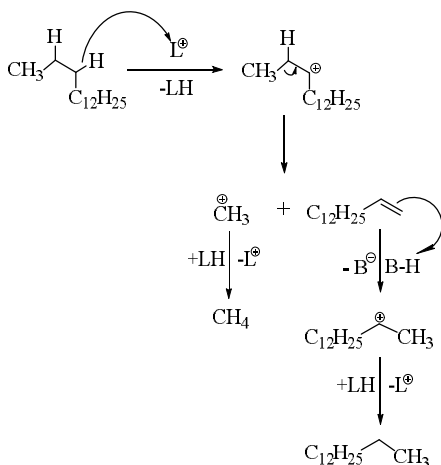


Fig. 8. Formation 1-tetradecene and tetradecane from pentadecane

The amount of avtur component compound and palmitic acid conversion increases when the reaction lasts 3 hours. Based on the chromatogram GC-MS analysis results (Fig. 11) and NIST 14.L database search on the MS spectrum (Table 7), the total conversion of palmitic acid and avtur component compounds were 98.47 % and 61.94 %, respectively. Avtur component compounds produced with SI values ≥ 90 are dodecane, tridecane, 1-tetradecene, tetradecane, 1-pentadecene, cyclopentadecane, and decyl-benzene. The avtur non-component compo-

unds produced are 1-dodecanol, 1-tetradecanol, 1-hexadecanol, heptadecane, 2-heptanodecanone which have SI values ≥ 90 and hexacosane which have SI values of 86. Of the 13 compounds, there are 4 compounds that have not been produced when the reaction lasts 2 hours, namely dodecane, 1-dodecanol, hexacosane, and 2-heptadecanone. Dodecane compounds are the result of the tridecane cracking reaction or the result of the pentadecane cracking reaction through the mechanism of 2-pentadecylium formation (Fig. 12). 1-Dodecanol is the result of a 1-dodecene hydration reaction. Hexacosane is obtained from the dimerization reaction between 1-tetradecane and 1-dodecene. The 2-heptadecanone is the result of a Claisen's condensation reaction between palmitic acid and acetic acid which is the result of cracking palmitic acid (Fig. 13) followed by a decarboxylation reaction, as reported by Thomas *et al.*²¹

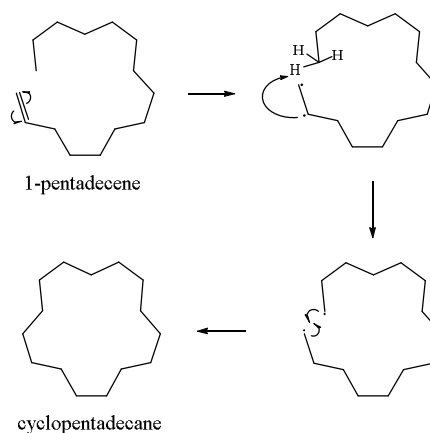


Fig. 9. Isomerization 1-pentadecene to cyclopentadecane

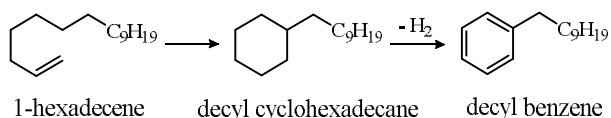


Fig. 10. Isomerization 1-hexadecene and dehydrogenation decyl cyclohexadecane to decyl benzene

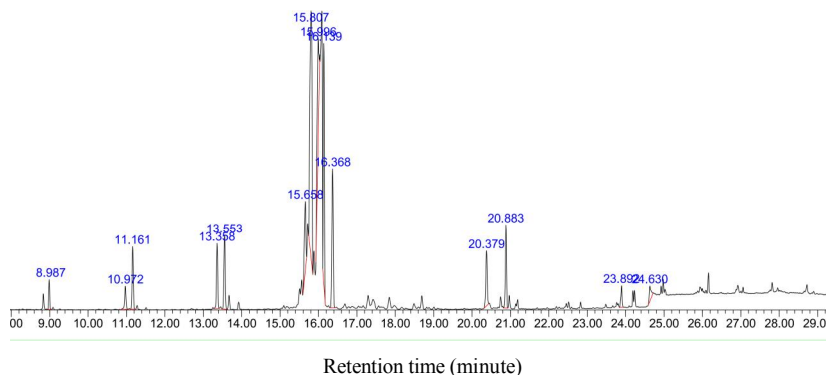
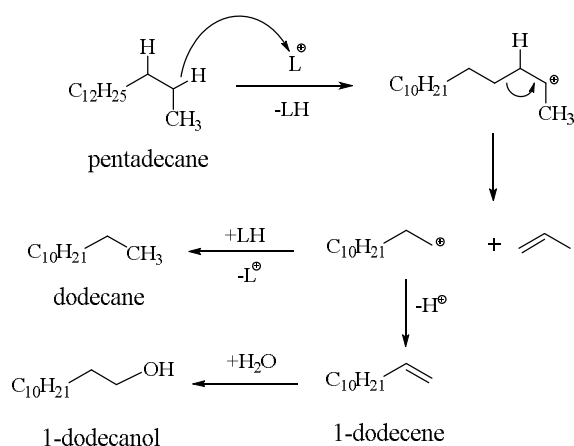
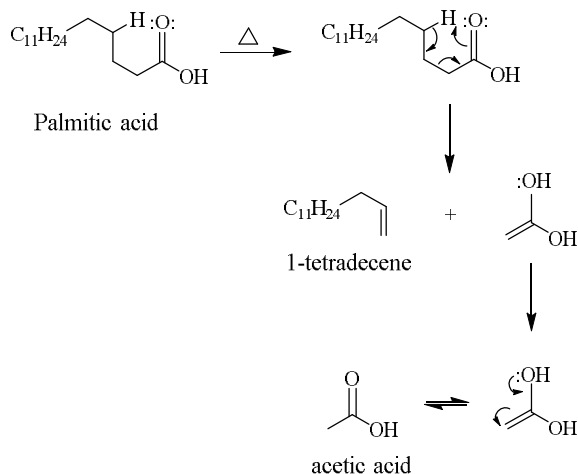


Fig. 11. Chromatogram of samples during the cracking reaction of palmitic acid 3 hours

Table 7. Resulted searching NIST 14.L database of spectrum of MS samples at the cracking reaction of palmitic acid 3 hours

RT (minute)	Compound	SI	Area (%)
8.98	Dodecane	95	1.53
10.97	1-Dodecanol	91	1.77
11.16	Tridecane	94	4.1
13.36	1-Tetradecene	97	4.39
13.55	Tetradecane	98	5.25
15.65	1-Tetradecanol	90	6.05
15.81	1-Pentadecene	94	28.36
15.99	Hexacosane	86	11.55
16.14	Cylopentadecane	91	14.05
16.36	1-Hexadecanol	95	10.44
20.38	Decyl-benzene	95	4.26
20.88	Heptadecane	95	5.27
23.89	2-Heptadecanone	95	1.45
24.63	Hexadecanoic acid	99	1.53

**Fig. 12.** Formation dodecane, 1-dodecene, and 1-dodecanol from pentadecane**Fig. 13.** Formation 1-tetradecene and acetic acid from palmitic acid**Table 8.** The activity of Fe^{3+} -mordenite catalyst in the cracking reaction of palmitic acid

Parameter	Time reaction (h)		
	1	2	3
Conversion (%)	27.03	62.01	98.47
Avtur ($\text{C}_8\text{-C}_{16}$) (%)	22.77	47.75	61.94
Selectivity (%)	84.24	77.00	62.90
Pentadecane (%)	19.33	11.44	0.00

Table 9. The catalyst activity of Fe^{3+} -mordenite compared to natural mordenite and H^+ -mordenite during a 3 h reaction

Parameter	Natural mordenite	H^+ -mordenite	Fe^{3+} -mordenite
Conversion (%)	100.00	100.00	98.47
Avtur ($\text{C}_8\text{-C}_{16}$) (%)	68.77	15.46	61.94
Selectivity (%)	68.77	15.46	62.90
Pentadecane (%)	32.77	15.46	0.00
HC $\text{C}<15$ (%)	19.53	0	61.94

Based on observations of the reaction for 1, 2, and 3 hours, it was shown that the amount of palmitic acid decreases with increasing reaction time. Added to palmitic acid, pentadecane as a result of the decarboxylation reaction of palmitic acid also decreases with increasing reaction time. This shows that pentadecane is an intermediate product. Pentadecane can undergo catalytic cracking reactions which subsequently produce alkanes and alkene with shorter chains. Pentadecane undergoes a dehydrogenation reaction to produce 1-pentadecene. With increasing reac-

tion time, the resulting alkene compounds undergo an isomerization, dimerization, and hydration reaction. This causes the selectivity of Fe³⁺-mordenite catalyst decrease along increasing reaction time (Table 8). However, the

activity of Fe³⁺-mordenite catalyst for catalytic cracking reaction of palmitic acid produces hydrocarbons that have carbon chains shorter than 15 better than H⁺-mordenite or natural mordenite in Turen Malang (Table 9).

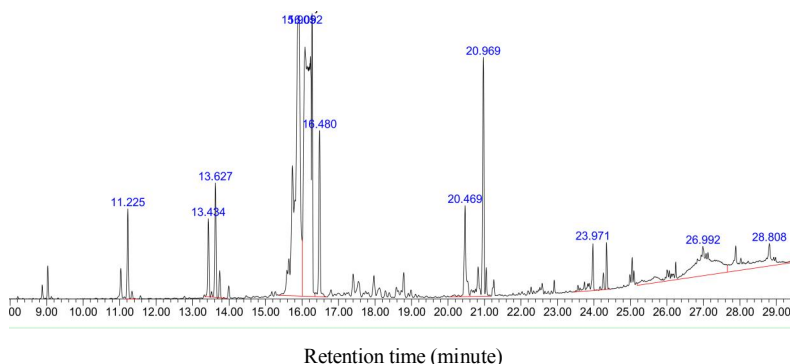


Fig. 14. Chromatogram of samples during the cracking reaction of palmitic acid 3 hours by natural mordenite

Table 10. Resulted searching NIST 14.L database of spectrum of MS samples at the cracking reaction of palmitic acid 3 hours by natural mordenite

RT (minute)	Compound	SI	Area (%)
11.23	Tridecane	94	1.98
13.43	1-Tetradecene	97	1.74
13.63	Tetradecane	96	2.98
15.91	1-Pentadecene	94	26.33
16.09	Pentadecane	95	32.77
16.48	1-Hexadecanol	94	4.09
20.47	Decyl-benzene	93	2.97
20.97	Heptadecane	98	7.53
23.97	2-Heptadecanone	93	2.78
26.99	Linoleic acid	92	10.96
28.81	Others	42	5.86

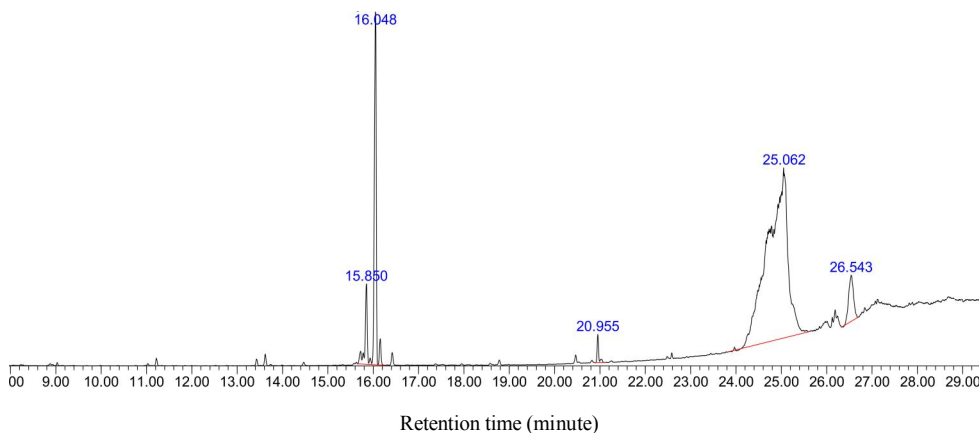


Fig. 15. Chromatogram of samples during the cracking reaction of palmitic acid 3 hours by H⁺-mordenite

The activity of Fe³⁺-mordenite catalysts in palmitic acid cracking is slightly decreased compared to natural mordenite and H⁺-mordenite catalysts. However, the type of avtur compound produced is greater than natural mor-

denite catalyst and H⁺-mordenite. Based on the chromatogram GC-MS analysis results (Fig. 14) and NIST 14.L database search of the MS spectrum (Table 10) of the sample when natural mordenite catalyst activity test lasted

3 hours, obtained 6 avtur component compounds (decylbenzene, pentadecane, 1-pentadecene, tetradecane, 1-tetradecane, and tridecane) which have a SI value of ≥ 90 and 4 avtur non-component compounds (1-hexadecanol, heptadecane, 2-heptadecanone, and linoleic acid) which have a SI value of 90. The H^+ -mordenite catalyst only produces one avtur component compound (pentadecane)

which has SI value ≥ 90 and one non avtur component compound (heptadecane) which has SI value ≥ 90 (Fig. 15 and Table 11). From the activity of Fe^{3+} -mordenite, H^+ -mordenite and natural mordenite catalysts, it can be stated that catalytic cracking reactions are more appropriate using metals or metal ions supported by supporting catalyst materials.

Table 11. Resulted searching NIST 14.L database of spectrum of MS samples at the cracking reaction of palmitic acid 3 hours by H^+ -mordenite

RT (minute)	Compound	SI	Area (%)
15.85	1-Tetradecanol	4.07	91
16.05	Pentadecane	15.46	93
20.96	Heptadecane	0.98	98
25.06	Others	74.62	45
26.54	Others	4.87	53

4. Conclusions

The Fe^{3+} -mordenite catalyst has a mordenite structure, including mesoporous material with a pore size of 7.36 nm, pore volume of 99 mm³/g, surface area 198.71 m²/g, Si/Al ratio 9.38, Lewis's acid site 26.77 mmol/g, and Brønsted acid site 81.66 mmol/g. Fe^{3+} -mordenite catalyst can be used to convert palmitic acid into avtur component compound with 61.99 % conversion and 62.90 % selectivity.

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ОПТИМІЗАЦІЯ КРЕКІНГУ ПАЛЬМІТИНОВОЇ КИСЛОТИ З ВИКОРИСТАННЯМ ПРИРОДНОГО МОРДЕНІТУ, МОДИФІКОВАНОГО Fe³⁺, ДЛЯ ВИРОБНИЦТВА СПОЛУК АВІАЦІЙНОГО ПАЛИВА

Анотація. Природний морденіт із села Турен, округ Маланг, Індонезія, був модифікований до Fe³⁺-морденіту з метою одержання гетерогенного каталізатора процесу крекінгу пальмітинової кислоти для виробництва компонентів авіаційного палива. Для модифікації морденіту за допомогою FeCl₃ було застосовано катіонообмінний метод. Fe³⁺-морденіт було охарактеризовано структурним аналізом, вмістом Fe, співвідношенням Si/Al, кількістю кислотних центрів, розміром пор, об'ємом пор і площею поверхні. Ефективність каталізатора, конверсію та селективність визначали за температури 583 К за допомогою газової хромато-мас-спектрометрії протягом 1, 2 і 3 годин. Морденіт із високим вмістом Fe має більше кислотних центрів Бренстеда-Льюїса, більші об'єм пор і площу поверхні порівняно з природним морденітом. Разом з тим, кристалічна структура Fe³⁺-морденіту така ж, як у природного морденіту. Fe³⁺-морденіт також має менший розмір пор, ніж природний морденіт. У процесі крекінгу пальмітинової кислоти Fe³⁺-морденіт забезпечив конверсію 61,94 % та вихід сполук авіаційного палива 92,90 %, а саме алканів, алкенів, циклоалканів і ароматичних речовин.

Ключові слова: авіаційне паливо, морденіт, катіонний обмін, кислотний центр, пальмітинова кислота.