

# Synthesis of Lubricant from Methyl Ester Palm Stearin

Sittiwat Watthanasringkarn, and Malee santikunaporn

**Abstract**— Lubricant was synthesized from methyl ester palm stearin (MEPS) by ketonization and deoxygenation in a fixed-bed reactor. The reactions were carried out over 5wt.% La/CaO for ketonization reaction (KT) and NiMo/Al<sub>2</sub>O<sub>3</sub> for deoxygenation (DO) reaction. The influence of reaction conditions, such as reaction temperature varied from 658 to 688 K for ketonization and 573 to 603 K for deoxygenation, pressure 100 to 300 psi for both reactions, and weight hourly space velocity (WHSV) 0.5 to 2 h<sup>-1</sup>, were studied. The conversion of MEPS during ketonization increased with temperature and WHSV. For deoxygenation, the reaction temperature did not have any significant impact on the reactant conversion. It has significant impact on the composition of ketone form the ketonization. The effect of pressure on the deoxygenation was significant for product selectivity. In addition, the final products composed of gasoline, diesel, lubricant, and other hydrocarbon.

**Index Terms**- Synthesis, Catalyst, Ketonization, Deoxygenation lubricant.

## I. INTRODUCTION

A lubricant which is a product from crude oil, is a substance introduced to reduce friction between surfaces in mutual contact, which ultimately reduces the heat generated when the surfaces move. It may also have the function of transmitting forces, transporting foreign particles, or heating or cooling the surfaces. Shortage of crude oil has threatened the stability of economies around the world. The demand of crude oil is anticipated to increase steadily. Moreover, lubricant that is currently produced from crude oil contains high content of sulfur which is toxic. The driven forces behind these researches have accelerated during the last few years as more people are aware of the effect of crude oil product on the environment. Consequently, we are looking for source of sustainable feedstock, which can be used instead of crude oil. Sustainable production of bio-oil is a solution to these problems and an important challenge [1].

Common vegetable oils consist of triglycerides that contain fatty acids molecules with 14 to 22 carbon atoms in their molecule. Triglycerides could be upgraded to methyl or ethyl ester by a process of depended on the type of alcohol use with the release of glycerol. Such esters can provide a basis for a whole range of biodegradable surface active agents [2]. In this process, palm oil was used. Esters of fatty acids obtained in this way can also provide a starting material for producing ketones.

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The ketonization of esters proceeds in the hydrogen gas under pressure in the presence of basic catalysts. It is a bimolecular reaction in which two molecules of a carboxylic acid, ester with n carbon atoms are coupled to produce the symmetric ketone. In the case of esters which contain molecule with different number of carbon atoms, a mixture of symmetrical and non-symmetrical ketones is formed, according to the general equation shown in Fig. 1.

In the case of methyl esters (when R<sup>2</sup>=H) only one ketone is obtained: R<sup>1</sup>COR<sup>1</sup> [3].

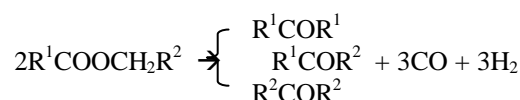


Fig. 1 Ketonization reaction

The catalysts used in ketonization reaction are metal oxide catalyst such as oxides of thorium, cerium, manganese, zirconium, and as well as rare earth metals. Additionally, alkaline earth metals were reported as active catalysts for ketonization reaction [4]. Furthermore, mixed oxide catalyst such as nickel and lanthanum can be used for deoxygenation reaction and it has high activity for ketonization reaction [5].

Ketones require the removal of oxygen to obtain hydrocarbons, according to the reactions pass way shown in Fig. 2. The oxygen atom was removed in the form of water by deoxygenation reaction. It is one of the major reaction that is performed to enhance the stability of the oil by removal oxygen atom form molecules. The deoxygenation catalysts mainly include conventional metal sulfides (e.g., sulfided CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub>) and noble metals [6]. However, bio-oil contains all other kinds of oxygenated chemical groups. Ketones, aldehydes, carboxylic acids, esters, aliphatic, aromatic alcohols, and ethers have been detected in significant quantities. However, very few studies have focused on the deoxygenation of ketone.

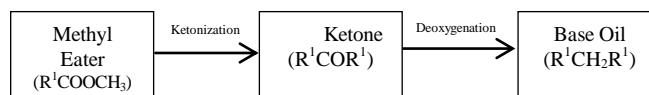


Fig. 2 reactions passway

In the present paper, we study the conversion of methyl ester palm stearin (MEPS) to synthetic lubricant with 31 to 35 carbon atoms in the molecules and fuel. Two layers of catalyst will be lanthanum (La) on Calcium Oxide (CaO) for KT and nickel (Ni) and molybdenum (Mo) on alumina (Al<sub>2</sub>O<sub>3</sub>) for DO. Particularly, the effects of temperature, hydrogen pressure and weight hourly space velocity (WHSV) on the activity and product distribution was measured by gas chromatography (GC).

## II. EXPERIMENTAL

## A. Catalyst Preparation

The 5 wt.% La/CaO catalyst was prepared by an impregnation method. The support was prepared from egg shells that were calcined in an air stream at 723 K for 1 h and crushed into the powder. The catalyst was impregnated with  $\text{LaN}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$  (Sigma–Aldrich Chemical Co. LLC., Germany) to contain 5 wt.% La onto CaO catalyst and dried at 383 K for 12 h. Then it was calcined in a furnace at 723 K for 4 h. The NiMo/ $\text{Al}_2\text{O}_3$  catalyst was supplied by PTT Public Company limited.

## B. Experimental Procedure

A 620 mm long fix-bed reactor with 14 mm inner diameter was used to investigate the activity of the catalysts for ketonization and deoxygenation reaction. Approximately, 1.3g of 5 wt.% La/Cao for ketonization catalyst was located on the upper layer of the reactor, while 3.6g of NiMo/ $\text{Al}_2\text{O}_3$  was located on the bottom layer. A high pressure Eldex pump was employed to deliver MEPS feedstock into the system. The composition of MEPS as supplied by the PTT Public Company Ltd. consisted of 65.4 wt.% methyl palmitate (C16:0), 31.3 wt.% methyl stearate (C18:0), 1.3 wt.% methyl laurate (C12:0) and methyl myristate (C14:0). The samples after passing through the ketonization and deoxygenation catalyst beds were withdrawn at the bottom of the reactor as shown in Fig. 3 before performing the reaction both catalyst beds were reduced in hydrogen gas at the flow rate of 120 ml/min at temperature 623 K and kept at 623 K for 3 hours.

After that, the reactor was cooled to the desired reaction temperature. The heating furnace was attached to a temperature control which can control the two layers of catalyst bed separately to study the ketonization and deoxygenation reaction of catalysts. Therefore, the temperature of the first catalyst bed of ketonization was varied between 658 to 688 K while the temperature of second catalyst bed of deoxygenation was varied 573 and 603 K (Packing catalyst shown in Fig. 3). A thermocouple was placed in the top layer and bottom layer of the reactor to monitor the temperature. The flow rate of hydrogen/ gas during the reaction was kept at 100 ml/min by a mass flow controller (SIERRA instrument). The liquid and gaseous products were separated at the reactor outlet in a condenser. The liquid products were analyzed by gas chromatography (GC).

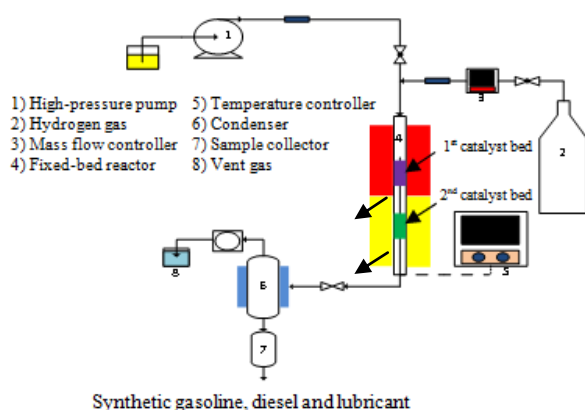


Fig. 3 Schematic of the experiment set-up

## III. RESULT AND DISCUSSION

A preliminary experiment was conducted to examine only the ketonization reaction at the temperature range between 658 to 688 K. Ketonization of methyl ester fraction produced either a liquid or a semi-liquid mixture of ketone and hydrocarbons depending on the temperature of the reaction Table 1 presents the maximum conversion (88.1%) obtains at 688 K and tends to rise with temperature in fig. 2, the total ketone was 58.1 wt.% including 31.2 wt.% 18-pentatriacontanone, 22.4 wt.% 17-hexatriacontanone, 4.4 wt.% 16-hentriacontanone and 6.7 wt.% other ketones. The collected product contained 33.4 wt.% hydrocarbons in the experiment carried out at a weight hourly space velocity (WHSV) of  $1 \text{ h}^{-1}$  with a pressure of 200 psi. However, the reaction temperature did not have any significant impact on the product selectivity as shown in fig. 4. In addition, the final product of ketonization was dark as opposed to the light yellow reactants with the use of MEPS.

TABLE I  
KETONIZATION OF MEPS OVER 5 WT.% LA/CAO AT DIFFERENT REACTION TEMPERATURES.<sup>A</sup>

| T (K) | Conversion (%) | Product Distribution (wt.%)  |                              |                              |       |                 |                 |       |
|-------|----------------|------------------------------|------------------------------|------------------------------|-------|-----------------|-----------------|-------|
|       |                | Ketones                      |                              |                              |       | Hydrocarbons    |                 |       |
|       |                | C <sub>31</sub> <sup>a</sup> | C <sub>33</sub> <sup>b</sup> | C <sub>35</sub> <sup>c</sup> | Other | C <sub>16</sub> | C <sub>18</sub> | Other |
| 658   | 75.5           | 33.8                         | 21.8                         | 3.9                          | 8.8   | 5.2             | 3.5             | 22.9  |
| 673   | 84.3           | 30.4                         | 20.9                         | 4.3                          | 8.9   | 5.5             | 3.0             | 27.0  |
| 688   | 88.1           | 31.2                         | 22.4                         | 4.4                          | 7.7   | 5.4             | 2.2             | 26.8  |

<sup>A</sup> Temperature range 658 to 688 K,  $\text{WHSV}_{\text{KT}} 1 \text{ h}^{-1}$ , Pressure 200 psi, hydrogen flow 100 ml/min, and MPES flow 0.05 ml/min

<sup>b</sup> C<sub>15</sub>H<sub>31</sub>COC<sub>15</sub>H<sub>31</sub>,

<sup>c</sup> C<sub>16</sub>H<sub>33</sub>COC<sub>16</sub>H<sub>33</sub>,

<sup>d</sup> C<sub>17</sub>H<sub>35</sub>COC<sub>17</sub>H<sub>35</sub>

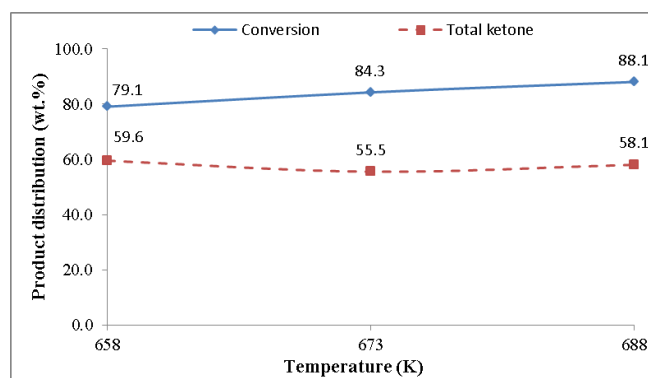


Fig. 4 Effect of reaction temperature on ketonization of the temperature range 658 to 688 K,  $\text{WHSV}_{\text{KT}} 1 \text{ h}^{-1}$ , Pressure 200 psi, Hydrogen flow 100 ml/min, MPES flow 0.05 ml/min.

For the experiment involving both the ketonization and deoxygenation reaction in multiple bed catalysts fixed-bed reactor, the influences of the three operating conditions were investigated: temperature, pressure and weight hourly space velocity. Table 2 shows conversion and composition of the liquid products at different operating pressures between 100 to 300 psi. It can be observed that the pressure at 100 psi gave conversion as high as 97.3%. An increase in pressure was found to cause a decrease in conversion. Additionally, according to Fig.5, the amount of ketone remaining after undergoing the deoxygenation reaction appeared to increase with pressure. This indicates it is easier for ketones to convert to hydrocarbon under a lower pressure environment. However, at lower pressure more

hydrocarbons with molecules containing less than 20 carbon atoms (<C<sub>20</sub>) will be form, which is due to the cracking reaction that occur simultaneously due to the high temperature and low pressure environment inside the reactor. However, the product distribution was not effected at high pressure.

TABLE II  
RESULTS FROM KETONIZATION AND DEOXYGENATION OF MEPS OVER 5 WT.% LA/CAO AND NiMO/AL<sub>2</sub>O<sub>3</sub> AT DIFFERENT PRESSURE.<sup>A</sup>

| P (psi) | Conversion (%) | Product Distribution (wt.%) |                  |                    |                 |                 |                 |
|---------|----------------|-----------------------------|------------------|--------------------|-----------------|-----------------|-----------------|
|         |                | Total ketone                | Hydrocarbons     |                    |                 |                 |                 |
|         |                |                             | <C <sub>20</sub> | C <sub>20-30</sub> | C <sub>31</sub> | C <sub>33</sub> | C <sub>35</sub> |
| 100     | 97.3           | 5.2                         | 60.5             | 9.1                | 15.0            | 8.2             | 1.8             |
| 200     | 89.7           | 12.6                        | 46.9             | 9.5                | 19.1            | 9.5             | 2.5             |
| 300     | 86.3           | 15.7                        | 48.0             | 8.2                | 17.7            | 7.7             | 2.8             |

<sup>a</sup> WHSV<sub>KT</sub> 1 h<sup>-1</sup>, WHSV<sub>DO</sub> 1 h<sup>-1</sup>, Temperature<sub>KT</sub> 673 K, Temperature<sub>DO</sub> 573 K, hydrogen flow 100 ml/min, MPES flow 0.05 ml/min, and pressure 100 - 300 psi.

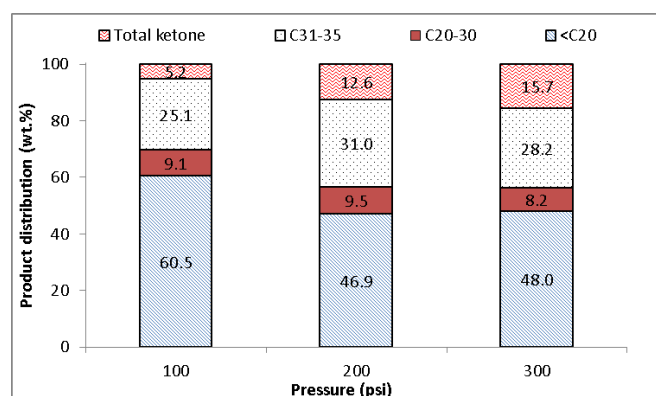


Fig. 5 The product distribution (wt.%) at different pressure range 100 to 300 psi, WHSV<sub>KT</sub> 1 h<sup>-1</sup>, WHSV<sub>DO</sub> 1 h<sup>-1</sup>, Temperature<sub>KT</sub> 673 K, Temperature<sub>DO</sub> 573 K, hydrogen flow 100 ml/min, and MPES flow 0.05 ml/min.

The effect of reaction temperature on ketonization and deoxygenation were investigated at constant temperature of ketonization and temperatures of deoxygenation at 573 and 603 K, as shown in Table 3 and Fig.6. We can find out that with the increase of temperature the deoxygenation activity increases. In general, the effect of reaction temperature on deoxygenation reaction fits the Arrhenius law [7].

TABLE III  
RESULTS FROM KETONIZATION AND DEOXYGENATION OF MEPS OVER 5 WT.% LA/CAO AND NiMO/AL<sub>2</sub>O<sub>3</sub> AT DIFFERENT TEMPERATURE.<sup>A</sup>

| T (K) | Conversion (%) | Product Distribution (wt.%) |                  |                    |                 |                 |                 |
|-------|----------------|-----------------------------|------------------|--------------------|-----------------|-----------------|-----------------|
|       |                | Total ketone                | Hydrocarbons     |                    |                 |                 |                 |
|       |                |                             | <C <sub>20</sub> | C <sub>20-30</sub> | C <sub>31</sub> | C <sub>33</sub> | C <sub>35</sub> |
| 573   | 85.3           | 13.0                        | 52.8             | 11.7               | 13.6            | 6.1             | 2.8             |
| 603   | 86.1           | 6.0                         | 56.2             | 10.7               | 14.9            | 8.3             | 3.6             |

<sup>a</sup> WHSV<sub>KT</sub> 1 h<sup>-1</sup>, WHSV<sub>DO</sub> 1 h<sup>-1</sup>, Temperature<sub>KT</sub> 673 K, hydrogen flow 100 ml/min, MPES flow 0.05 ml/min, Pressure 200 psi, and Temperature<sub>DO</sub> 573 - 603 K.

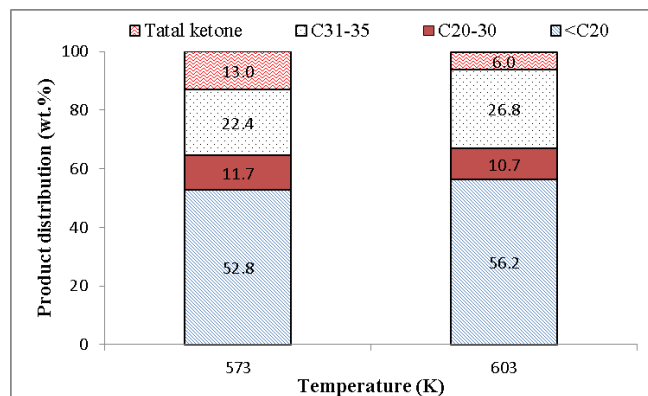


Fig. 6 The Product Distribution (Wt.%) At Different Temperature Range 573 To 603 K, WHSV<sub>KT</sub> 1 h<sup>-1</sup>, WHSV<sub>DO</sub> 1 h<sup>-1</sup>, Temperature<sub>KT</sub> 673 K, Pressure 200 Psi, Hydrogen Flow 100 MI/Min, And MPES Flow 0.05 MI/Min.

The effects of WHSV<sub>DO</sub> are shown in fig. 7. From fig. 7 we can find out that with the decrease in WHSV<sub>DO</sub>, total ketone content in the liquid decreased, but product distribution of C<sub>31-35</sub> didn't change significantly. This is approximately 20%. This is because during deoxygenation reaction. Some total ketone and long-chain component were converted into smaller component (<C<sub>20</sub>) by hydrocracking reaction. Additionally, it is shown that final product contains ketone of approximately more than 5%. This is a solid at room temperature.

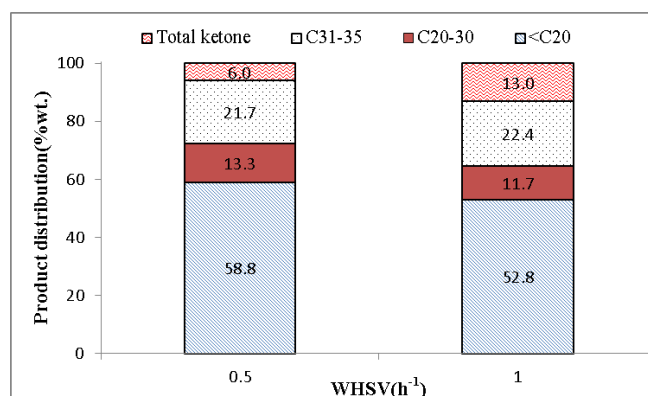


Fig. 7 The product distribution (wt.%) at different WHSV<sub>DO</sub> 0.5 and 1 h<sup>-1</sup>, WHSV<sub>KT</sub> 1 h<sup>-1</sup>, Temperature<sub>KT</sub> 673 K, Temperature<sub>DO</sub> 573 K, Pressure 200 psi, Hydrogen flow 100 ml/min, and MPES flow 0.05 ml/min.

#### IV. CONCLUSION

This study was undertaken in an attempt to investigate the ketonization and deoxygenation of MEPS over 5 wt.% La/CaO and NiMo/Al<sub>2</sub>O<sub>3</sub>, respectively. The 5 wt.% La/CaO catalyst is highly active in the ketonization at study temperature. Additionally, the product will clog the reactor at higher reaction temperature. It has high viscosity and wax.

For ketonization and deoxygenation of methyl ester palm stearin (MEPS) in a fix-bed reactor was investigated in the research the effects of reaction temperature, WHSV, and hydrogen pressure on the both reaction were investigated. The results of this study indicate that reaction is a function of both WHSV and temperature. Conversion increases with both of these variables in the studied range. However, the effect of the hydrogen pressure on conversion of MEPS to

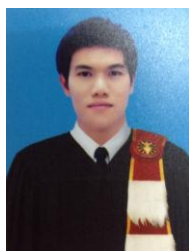
bio-oil is insignificant. For further work, the lubricant should be separated from the product and react with an acidic catalyst to improve cold-flow properties. Finding from this research will provide a fundamental knowledge for the production of fuel and base oil from MEPS.

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