Production of Hydrocarbons from Palm Oil over NiMo Catalyst

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A R T I C L E I N F O

A B S T R A C T

Catalytic hydrodeoxygenation of palm oil in dodecane over NiMo/Al$_2$O$_3$ has been investigated in a 300mL Parr's reactor. Triglycerides have been converted to hydrocarbons with various molecular sizes due to the compositions of fatty acids in palm oil. In this experiment, parameters of interest are temperature, pressure and turbine speed. Liquid samples were collected and analyzed by a gas chromatography (GC) to quantify desired hydrocarbon products (C15-C18) in the diesel range. It was found that the amount of desired products depends on the studied parameters. The conversion increases as the reaction temperature and a turbine speed increase, but the operating pressure decreases. In addition, the ratios of C$_n$/C$_{n-1}$ (C18/C17 and C16/C15) have been presented.

1. Introduction

Due to rapid depletion of fossil fuels and an increased awareness of global warming, many kinds of alternative sources of renewable energy have been developed (Bressler *et al*., 2007). For instance, production of solid fuel from glycerol and agricultural wastes has been studied (Asavatesanupap and Santikunaporn, 2010). Moreover, the production of first generation biofuel

from natural oils, such as palm oil, canola oil, soybean oil and jatropha oil have been regarded as a promising source of vehicle fuels (Vanichseni *et al*., 2002). Palm oil consists of triglycerides, which contain a combination of fatty acids such as hexadecanoic (palmitic acid, a saturated fatty acid with 16 carbon atoms), cis-9-octadecenoic acid and cis-9,12-octadecadienoic acid (oleic acid and linoleic acid, unsaturated fatty acids with 18 carbon atoms) (Gawrilow, 2003). The typical structure of fatty acids is straight chain aliphatic with a carboxylic acid functional group (Scrimgeour, 2005). Fatty acids can be transformed into fatty acid methyl ester (FAME) or biodiesel (Vargas *et al*., 1998). The process is referred to as transesterification. However, the disadvantage of this reaction with a homogeneous alkaline catalyst is the production of soap, which results in the reduction of FAME's yield. Apart from the saponification issue, this process consumes a large amount of water in the neutralization step, which is a waste of resources (Lee *et al*., 2009). Unfortunately, these are not the only drawbacks in ultilizing the transesterifcation reaction to produce biodiesel. Some undesirable properties of FAME are low oxygen stability and high viscosity (Erhan *et al*., 2006).

A new reaction path called the deoxygenation reactions has recently been proposed as a possible way to produce a better biofuel. Since biofuel derived via deoxygenation reactions is proven to be more environmental friendly and more suitable for blending with the conventional diesel, it is being regarded as green diesel or the second generation biofuel. The liquid-phase deoxygenation reactions consist of three reactions which are decarboxylation, decarbonylation and hydrogenation. In general, these reactions involved removing oxygen from the structure in order to produce linear hydrocarbons with chain length ranged from *n*-pentadecane to *n*-octadecane for palm oil. It was suggested that the oxidation stability and viscosity of this product will be improved.

Previous research showed that the yield of C_{n-1} alkanes produced from the deoxygenation of stearic and palmitic acids (saturated FFAs with 18 and 16 carbon atoms) in a semi-batch reactor under He, 573K and 1.5 MPa was more than 98%wt conversion. However, for the deoxygenation of unsaturated fatty acid, such as oleic and linoleic acids, they have to be hydrogenated first (Lamb *et al*., 2009). Recently, Morgan *et al*. observed the catalytic deoxygenation of triglycerides, such as tristearin, triolein and soybean oil, over Ni, Pd and Pt metals. The result suggested that Ni showed higher activity for both deoxygenation of triglyceride and cracking of fatty acids than Pd or Pt.

Malee Santikunaporn and Sanankeam Ejaroj

Santikunaporn *et al*. studied the hydrodeoxygenation of palmitic acid, oleic acid, and linoleic acid, which are major fatty acids found in palm oil over NiMo catalyst in a continuous packed bed reactor showed high conversion with more than 80% selectivity to desired products.

In this study, the hydrodeoxygenation reaction of palm oil in dodecane over NiMo catalyst under various reaction conditions in a CSTR was demonstrated. Liquid samples were collected and analyzed using a Gas Chormatography equipped with a FID. The main aim of this experiment was to elucidate the parameter variables which were turbine speed, temperature and pressure for the production of the straight-chained hydrocarbons in a diesel range.

2. Experimental

2.1 Materials

Reactant for the experiment was a commercial palm oil. The palm oil was diluted with *n*-Dodecane (99%wt. purchased from Acros) to obtain a 10%wt. A NiMo/Al$_2$O$_3$ with particle size of approximately 2 mm was employed as the catalyst for the hydrodeoxygenation reaction. The fatty acid compositions of palm oil were listed in Table 1.

Table 1: Composition of fatty acids in the palm oil.

Name of fatty acid	Symbol*	Amount (%wt.)
Myristic acid	C14:0	1.0
Palmitic acid	C16:0	40.1
Stearic acid	C18:0	4.4
Cis-9-oleic acid	C18:1	40.7
Cis-9,12-Linoleic acid	C18:2	12.1
Others		1.7

*CX:Y where x refers to no. of carbon atom in a molecule;

y refers to no. of unsaturated C-C bond in a molecule.

2.2 Experimental procedure

The hydrodeoxygenation reaction was carried out in a 300 mL stirred reactor coupled with a heating jacket and cooling water commanded by the 4848 PID controller. The schematic configuration was illustrated in Figure 1.

In a typical experiment, 15 g of NiMo catalyst was reduced in situ under the flow of hydrogen at a constant temperature of 638 K and stirred at speed of 50-90 rpm for 4 h prior to the flow of feedstock. After the reduction, the temperature was decreased from 638K to the reaction temperature. Then, feedstock was pumped into the reactor by an Eldex pump 1SMP. Liquid samples were collected and analyzed by a gas chromatography (HP 6890) equipped with a DB-petro column and a flame ionization detector.
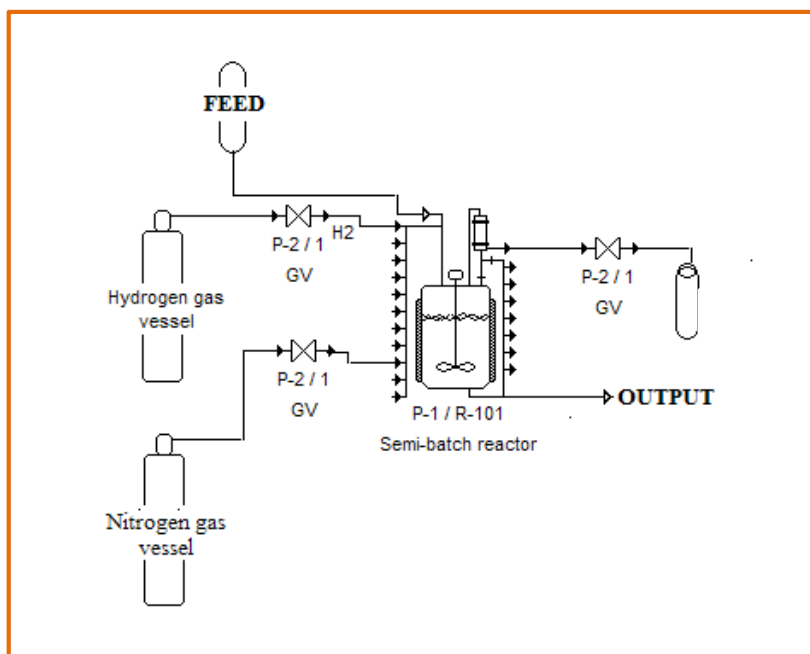

Figure 1: Schematic experimental set-up.

3. Result and Discussion

From Table 1, the major fatty acid compositions of a palm oil are 46.3%wt. of saturated fatty acid (40.1% palmitric acid, 4.4% stearic acid and 0.9% others) and 53.7%wt. of unsaturated fatty acid (40.7% oleic acid, 12.1% linoleic acid and 0.9% others). Since palm oil consists of triglyceride combining 1 mole of glycerol and 3 moles of fatty acids, the proposed hydrodeoxygenation steps are presented in Figure2.

Triglycerides are firstly broken to form both saturated and unsaturated fatty acids. Before the deoxygenation, some unsaturated fatty acids were hydrogenated to saturated compounds. After that the saturated compounds were converted into hydrocarbons with different molecular sizes, the expected hydrocarbon products are from n-pentadecane (C15) to n-octadecane (C18) as shown in Table 2.
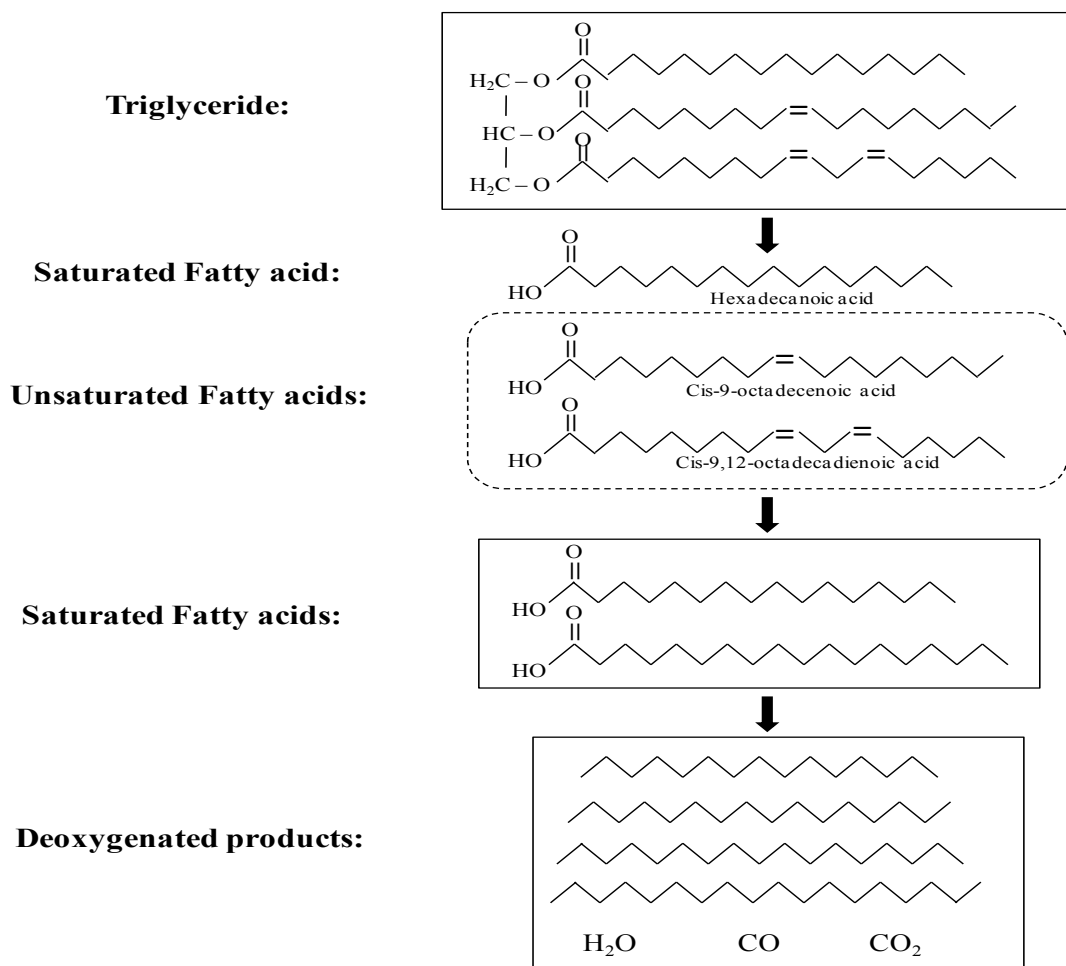
Malee Santikunaporn and Sanankeam Ejaroj

Figure 2: Proposed steps for the hydrodeoxygenation of palm oil over NiMo catalyst under a flow of hydrogen.

Table 2: The expected products from the hydrodeoxygenation reactions of refined palm oil.

Fatty acid	Major Products	
	One carbon atom less than feed	Same carbon atoms as feed
Palmitic acid ($C_{16}H_{32}O_2$)	n-Pentadecane ($C_{15}H_{32}$)	n-Hexadecane ($C_{16}H_{34}$)
Cis-9-oleic acid ($C_{18}H_{34}O_2$)	n-Heptadecane ($C_{17}H_{36}$)	n-Octadecane ($C_{18}H_{38}$)
Cis-9,12-linoleic acid ($C_{18}H_{32}O_2$)	n-Heptadecane ($C_{17}H_{36}$)	n-Octadecane ($C_{18}H_{38}$)

3.1 Effect of catalyst

The effect of catalyst was studied under the two experiments-with and without NiMo catalyst under the same reaction conditions. The hydrodeoxygenation reactions were investigated at the reaction temperature of 628 K, a pressure of 2.7 MPa and a turbine speed of 600 rpm. The results were compared and presented in Figure 3.
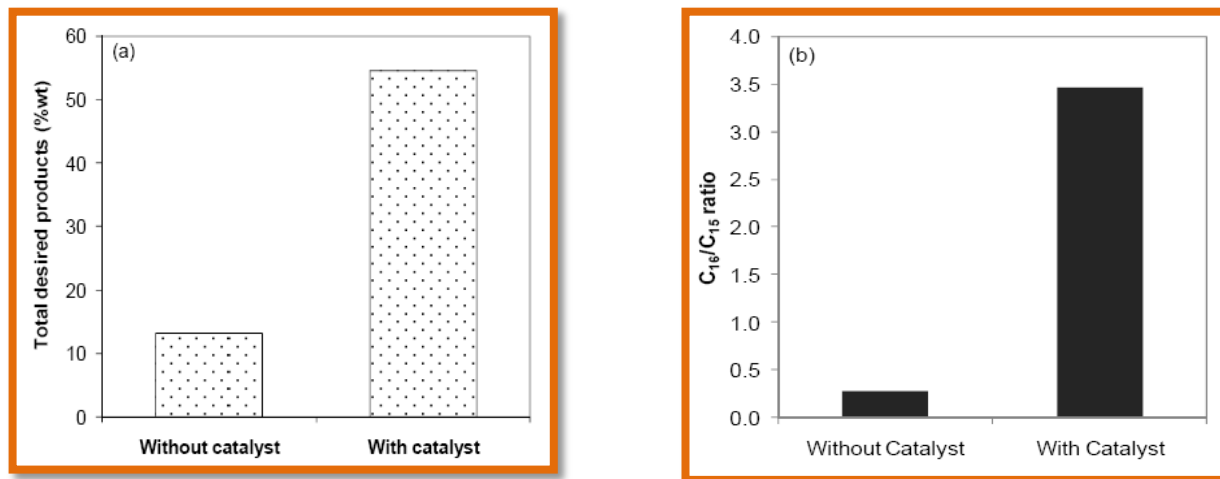

Figure 3: The comparison of (a) total desired hydrocarbon products and (b) the C16/C15 ratio obtained from the hydrooxygenation of palm oil in the presence and in the absence of catalyst.
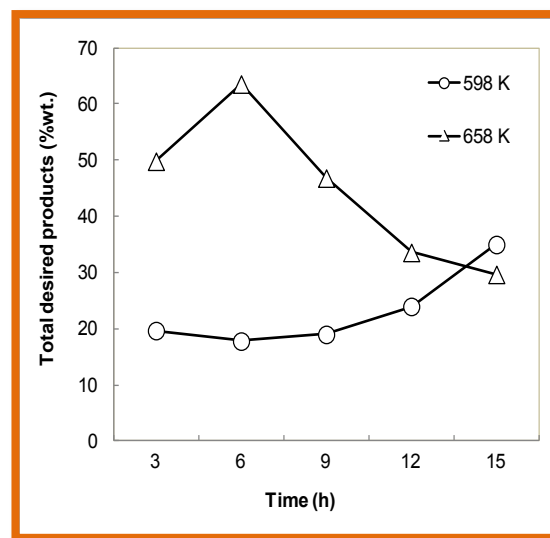
Total desired products increased significantly from 15%wt. to 60%wt. when catalyst was employed. Focusing on hydrocarbons obtained from palmitic acid, in the presence of catalyst, the ratio of C16/C15 was 3.5 whereas the C16/C15 ratio was dropped to 0.3 when the reaction was performed in absence of the catalyst. Since palm oil mostly contains of palmitic acid (C16:0), the massive amount of *n*-hexadecane (C16) generated indicated that the reaction rate of hydrogenation was accelerated in the presence of a catalyst.

3.2 Effect of temperature

The effect of reaction temperature was studied by varying three different temperatures starting from 598 K to 658 K and other parameters such as pressure and turbine speed were kept constant at 2.7 MPa and 500 rpm, respectively.

Malee Santikunaporn and Sanankeam Ejaroj
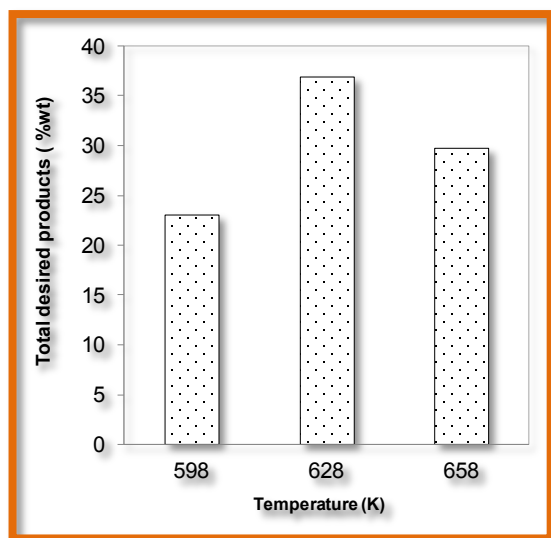
| (a) Total desired products examined at 15 h time on screen. | (b) Total desired products as a function of the reaction time. |

Figure 4: Effect of the reaction temperature on total desired products.

Focusing only on the total desired hydrocarbon products (C15-C18) as shown in Figure 4(a), the yield of products at 628 K was the highest. The total desired products were approximately 35.0%wt. whereas at 598 K the product yield was only 22.5%wt. However, at 658 K total desired products declined from 35.0%wt. to 30.0%wt. This may indicate the possibly consecutive reactions (cracking reaction) at elevated temperature. A cracking reaction was generally preferable at high temperature.

According to Figure 4(b), at 658 K the amount of total desired products initially increased, but after time on stream of 6 h it decreased. Unlike the results obtained at 658 K, at 598 K the amount of total desired product slowly increased. This might be due to the cracking reaction occurred at high temperature. Another plausible reason was due to the formation of coke on catalyst surfaces. However, the amount of coke formation had not been reported.

Figure 5 shows selectivities to desired hydrocarbon products as a function of reaction temperatures over NiMo catalyst at a time on stream of 15 h, a pressure of 2.7 MPa and a turbine speed of 500 rpm. At all reaction temperatures, the selectivity to *n*-hexadecane (C16) was higher than that of *n*-pentadecane (C15). Also, the selectivity to *n*-octadecane (C18) was higher than that

of *n*-heptadecane (C17).   As previously reported, the C16 and C15 products were obtained from the conversion of the palmitic acid (C16:0), but under different pathways.   Generally, the C16 product was produced via the hydrogenation of palmitic acid, but the C15 product was produced via decarbonylation and decarboxylation.   Thus, it can be concluded that under these reaction conditions the products containing the same number of carbon atoms as feed were preferred. The explanation was also valid for the case of oleic (C18:1) and linoleic acids (C18:2).   Moreover, from Figure 6 when focused on the ratios of C16 to C15 and C18 to C17, these two ratios decreased as the reaction temperature increased.   This indicated that the decarbonylation/decarboxylation prefers at high temperature.   This might be due to the thermodynamics favor.   In addition, the cracking reaction of longer hydrocarbons was more pronounced at higher temperature.
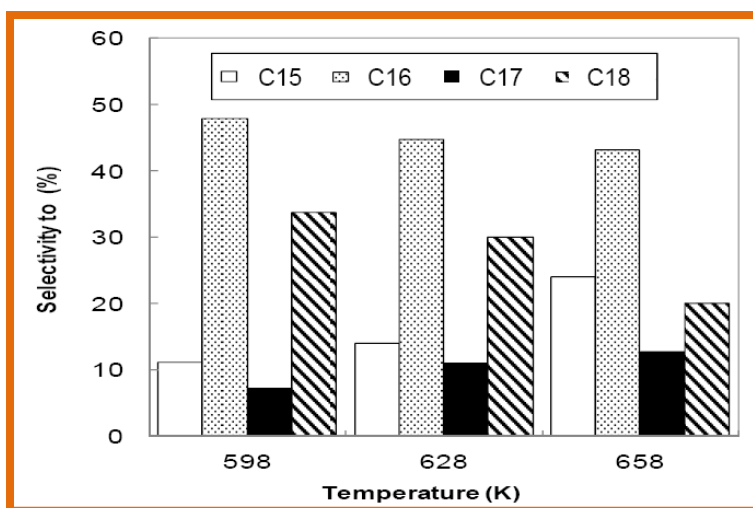

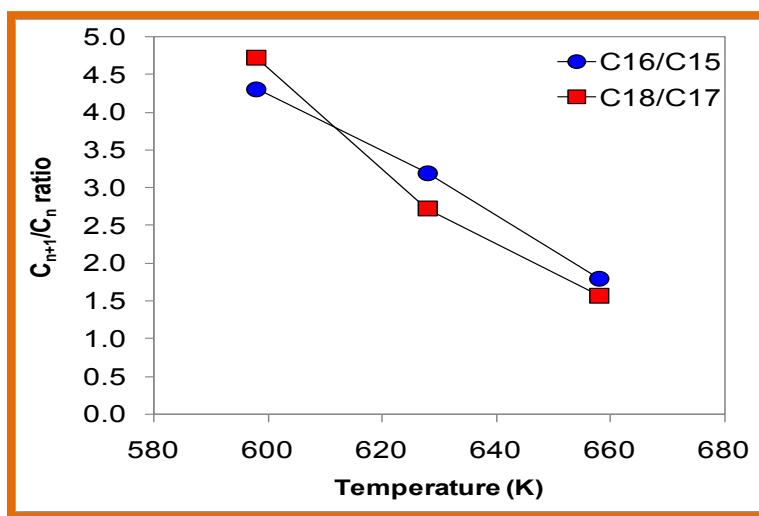**Figure 5:** Selectivity to desired products as a function of temperature.

Figure 6: The C_{n+1}/C_n ratio as a function of reaction temperature.

Malee Santikunaporn and Sanankeam Ejaroj

3.3 Effect of Turbine Speed

The reaction of palm oil over NiMo/Al$_2$O$_3$ at two different turbine speeds was compared. Samples were collected at time on stream of 24 and 45 h. The results are presented in Figure 7(a), 7(b) and 7(c). It was obviously seen that total desired products increased when the reaction was performed at a turbine speed of 600 rpm. It can therefore be speculated that at higher turbine speed more desired products was likely to be generated perhaps due to the elimination of mass-transfer limitation. However, more products especially <C14 products was observed when collected sample at longer time (45 h). This situation should be occurred if the consecutive reactions existed. Concentrated on product selectivity, it can be concluded that the turbine speed does not change the selectivity of products.
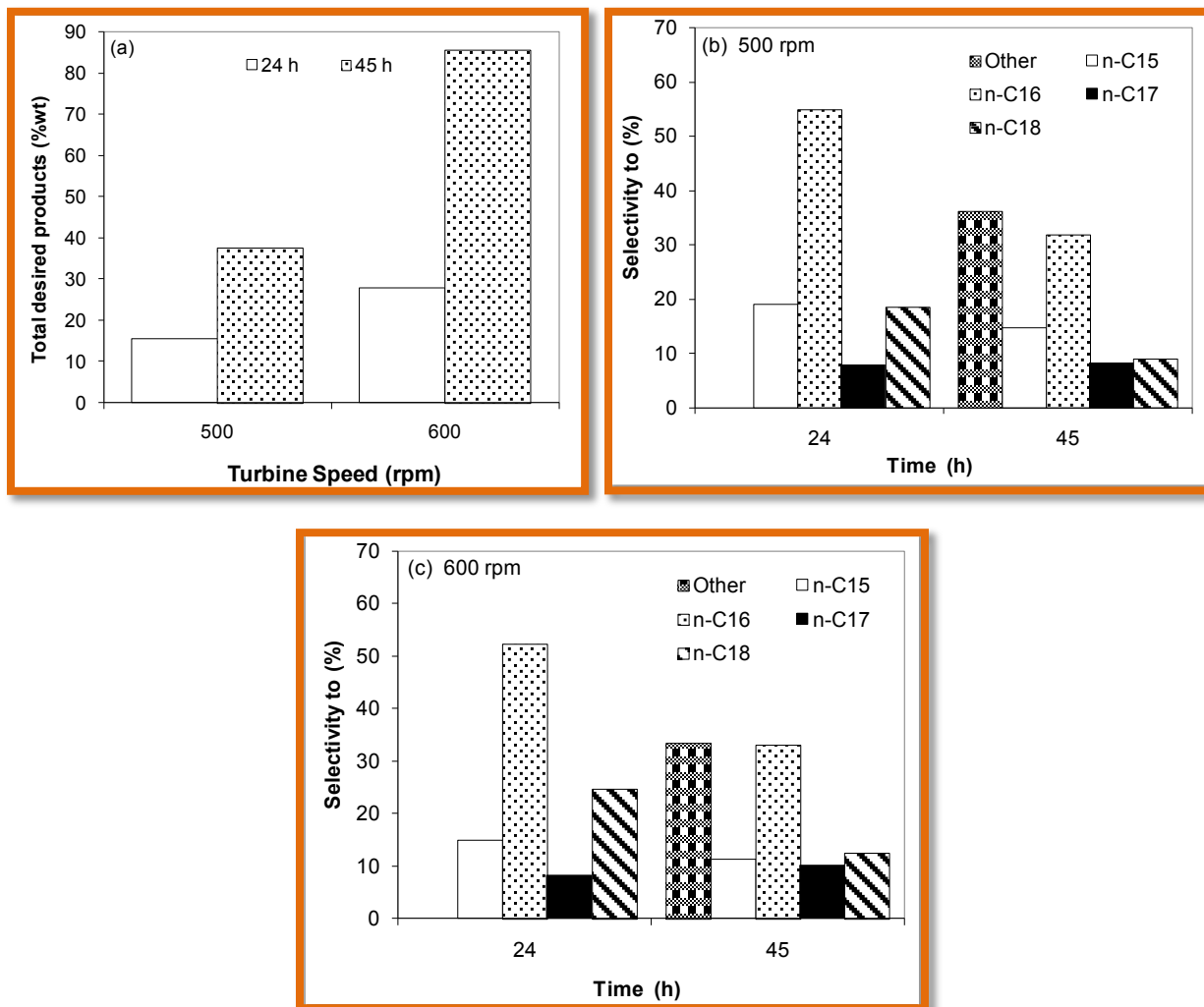

Figure 7: Effect of turbine speed.

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Figure 8 shows the comparison of the C18/C17 and the C16/C15 ratio obtained from the hydrodeoxygenation reaction at different turbine speeds. The turbine speed increased from 500 rpm to 600 rpm resulting in an increasing the C_{n+1}/C_n ratio. The C18/C17 ratio increased from 2.3 at 500 rpm to 3.0 at 600 rpm. This clearly indicated that at high turbine speed products occur via hydrogenation pathway.
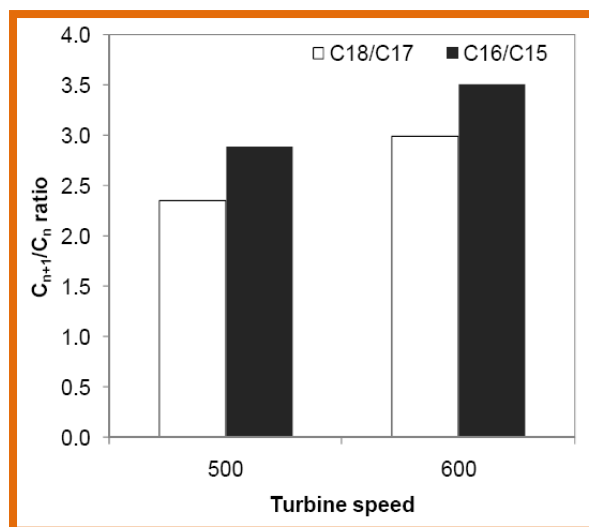

Figure 8: The C_{n+1}/C_n ratio as a function of turbine speed.

3.4 Effect of pressure

The hydrodeoxygenation was determined at 628 K under 2 different pressures, 2.7 and 3.4 MPa as illustrated in Figure 9.
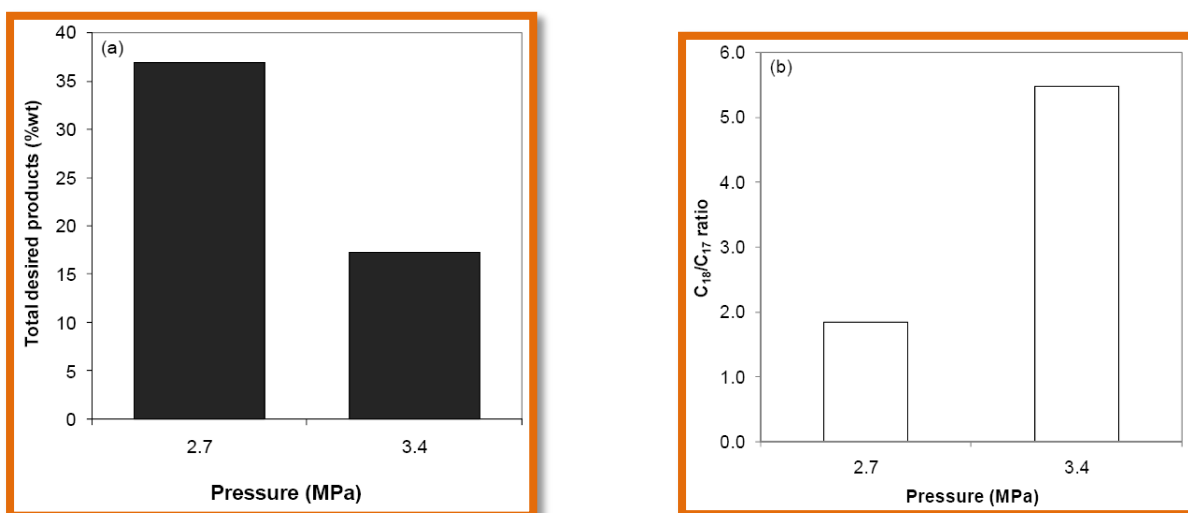

Figure 9: Effect of pressure.

Malee Santikunaporn and Sanankeam Ejaroj

The results demonstrated that the amount of total desired products at 2.7 MPa is roughly 35.5 %wt., whereas the total desired products at 3.4 MPa drop dramatically to nearly 17 %wt. The selectivity ratio increased dramatically from 1.83 at reaction pressure of 2.7 MPa to 5.47 when reaction pressure was increased to 3.4 MPa. This obviously suggested that at higher reaction pressure the hydrogenation reaction path was favored.

4. Conclusion

Catalytic hydrodeoxygenation of palmitic acid was performed over NiMo catalyst in a batch reactor. The major liquid products were pentadecane, hexadecane, heptadecane, and octadecane, which can be categorized in a diesel range. NiMo showed a high activity for the hydrodeoxygenation of palm oil. The yield of desired products significantly depended on the reaction conditions. It was the highest at a moderate temperature. Further increase of pressure, however, lower the amount of desired products. Unlike pressure, the amount of desired products increased with the turbine speed. Finally, under the studied conditions, the C_n/C_{n+1} ratios were more than 1. This may suggested that hydrocarbon products are produced via the hydrogenation pathway.

5. Acknowledgements

6. References

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