Evaluation of parameters for biofuel production in CSTR

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Abstract

Catalytic deoxygenation of refined palm oil have been investigated in a 300mL Parr's semibatch reactor with a PID controller, dodecane as solvent and nickel molybdenum as catalyst. The reactant examined was refined palm oil. The main operating parameters studied were temperature, pressure, turbine speed and gas atmosphere. Liquid samples were collected every three hours and analyzed by a gas chromatography (GC) to quantify desired products (C13-C18) in diesel range. In conclusion, it was found that the amount of desired products is plateau with temperature. On the other hand, lowering operating pressure increases the conversion by almost 20%. In addition, the faster the turbine speeds the higher is the conversion. Ultimately, between hydrogen gas and argon gas, hydrogen was more preferable due to its ability to deoxygenate triglyceride.

Keywords: Deoxygenation, palm oil, nickel-molybdenum

1. Introduction

Due to rapid depletion of fossil fuel and an increased in awareness of global warming, many kinds of alternative sources of renewable energy have been developed. For instance, the production of first generation biofuel or fatty acid methyl ester (FAME) through tranesterification of vegetable oil, such as palm oil, canola oil, soy bean oil and jatropha oil have been regarded as a promising source of vehicle fuel. However, when FAME is blended with petroleum-based diesel some undesirable properties, such as high oxygen and unsaturated content have been clearly observed. It has recently been proposed that one of the possible ways to produce a better biofuel is to apply a new reaction path called the deoxygenation reactions. Since biofuel derived via deoxygenation reactions is proven to be more environmental friendly and more suitable for blending with diesel, it is being regarded as green diesel or the second generation biofuel. The deoxygenation reactions consist of three other reactions which are decarboxylation, decarbonylation and hydrogenation. In generally, these reactions involved removing oxygen from the structure by eliminating the carboxylic functional group and hydrogenating

unsaturated bond in order to produce linear hydrocarbons with chain length ranged from n-pentadecane to n-octadecane.

The main aim of this experiment was to elucidate the parameter variabless for production of the second generation biodiesel through deoxygenation of fatty acids present in refined palm oil. Temperature was varied between 300 – 400 $^{\circ}$C, pressure varied between 300 – 500 psi, while the agitator speed varied between 500 – 600 rpm.

2. Experimental

Feedstock for the experiment was commercial refined palm oil. Dodecane (99%) purchased from Acros was used as solvent. Nickel mollidinum with paricle size 7 mm was employed as the catalyst for the deoxygenation reaction.

The deoxygenation reaction took place in a 300 mL semi-batch Parr's reactor coupled with a heating jacket and cooling water commanded by the 4848 PID controller as shown in Fig.1.
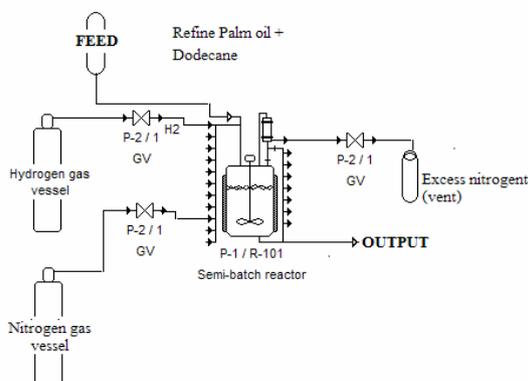

Fig. 1 Experimental setup for deoxygenation reaction with 300 mL semibatch reactor.

In typical experiment 15g of NiMo catalyst was reduced in situ by hydrogen at constant temperature of 365 $^{\circ}$C and stirrer speeds between 50-90 rpm. The flow of H_2 from gas vessel was monitored and control by a mass flow meter from Sierra Instrument Inc. Nitrogen gas was employed to purge air and maintain the pressure inside the reactor. The catalyst would be reduced for 2-4 hours prior to the input of feedstock into the reactor. The pressure was varied according to the experimental condition. The size of NiMo used was approximately 7mm. After catalyst's reduction, the temperature was lowered from 365 $^{\circ}$C to 50 $^{\circ}$C. Then feedstock, which was composed of 5% wt refined palm oil and 95%wt dodecane, was fed into a Parr's sample cylinder rating and forced into the reactor using pressure greater than the pressure inside the reactor. Samples from the reactor were collected every 3 hours. Approximately 0.4g of samples was used for analyzing using GC.

Liquid products were analyzed by using the gas chromatography instrument (HP 6890 series Auto-injection). The GC system operated with ramp temperature of 15°C per minute and the oven temperature of 240 $^{\circ}$C. Flame ionization detector (FID) employed the used of He as carrier gas. Acid value (ASTM D664-04) was used to calculate the amount of free fatty acid in the produced bio-diesel.

3. Results and discussion

3.1 Effect of Temperature on the deoxygenation reaction

During the deoxygenation reaction free fatty acids are broken from triglyceride and then converted into smaller hydrocarbon alkane. Since palm oil usually consists of 45.2%wt Oleic acid (free fatty acids that contain 18 carbon atoms and one double bond) and 40.8%wt of Palmitic acid (free fatty acids that contain 16 carbon atoms and no double bond), the expected ranged of products is from n-heptadecane (C15) to n-octadecane (C18).
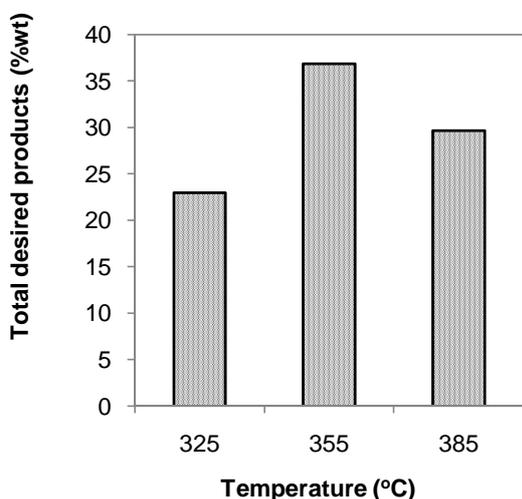
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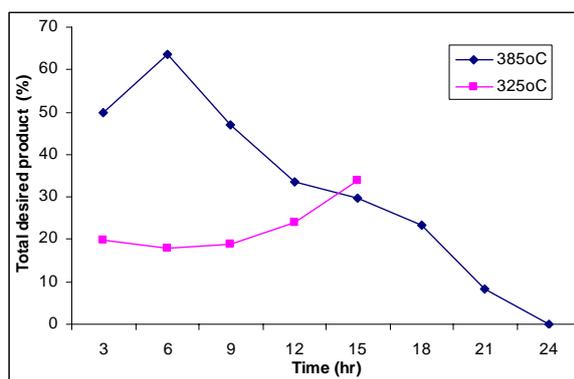
(b)

Fig. 2 a) Total desired products as a function of temperature. b) Total desired products as a function of reaction time.

For this experiment the temperature was varied between 325°C and 385°C. Other condition such as concentration of refined palm oil in dodecane, pressure and turbine speed were kept constant at 5%wt, 400psi and 500 rpm. It can be generalized, from Fig. 2a, that the product yielded was the highest at temperature of 355°C. The total desired products at 355°C were approximately 35%wt whereas at 325°C the product yield was only 22.56%wt. However, at 385°C total desired product declined from 35%wt to only 30%wt, indicating possibly lower consumption rate of the fatty acid due to catalyst deactivation at elevated temperature. Catalyst deactivation occurred because coke produced from the reactant covers the catalyst's surface inhibiting possible activity. Another reason why total desire product decreased at higher temperature is because of thermal cracking. Although according to Fig. 2b it can be seen that initially the percentage of total desire product generated from reaction at 385°C inclined much more rapidly than that at 325°C, but after 6 hours it is possible that some product generated might be turned to smaller hydrocarbon.
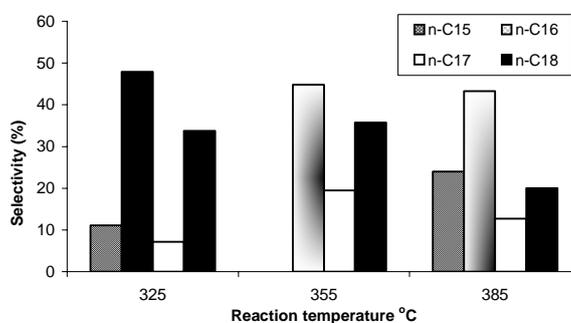

Fig. 3 Selectivities of desired products as a function of temperature.

Selectivity as a function of reaction temperatures over the catalyst NiMo at reaction time of 15 hrs, 400 psi and 500 rpm was calculated. According to Fig.3, the ratio between n-octadecane and n-heptadecane decreased from 4.72 at 325°C to 1.58 at 385°C. This indicated that as reaction's temperature increased, more deoxygenation of palm oil via hydrodecarbonylation took place.

3.2 Effect of catalyst on the deoxygenation reaction

The effect of catalyst was investigated at reaction temperature of 355°C, pressure of 400 psi and agitator's turbine speed of 600 rpm.
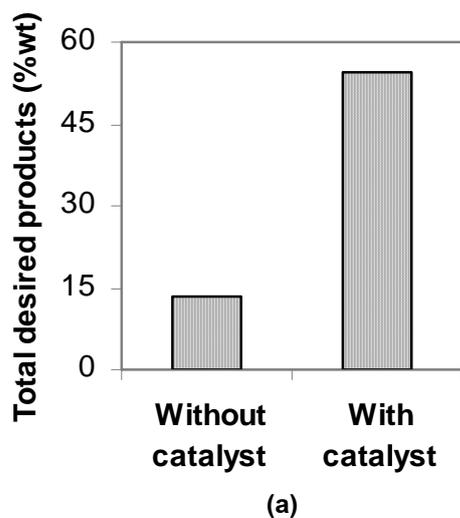
The results showed that total desired products increase significantly from 15%wt without using any catalyst to almost 60%wt when catalyst is employed. Selectivity patterns, as shown in Fig.4b, suggested that the presence of NiMo accelerated the rate of hydrogenation. According to the selectivity C18/C17 ratio, which was approximately 3.8, more n-octadecane was produced. Since palm oil contained mostly oleic acid with 18 carbon atom, the massive amount of n-octadecane generated indicate that the reaction rate of hydrogenation was accelerated. This is by products that results from the hydrogenation reaction contain the same number of carbon atoms. In this case oleic acid with 18 carbon atoms was converted to n-octadecane.
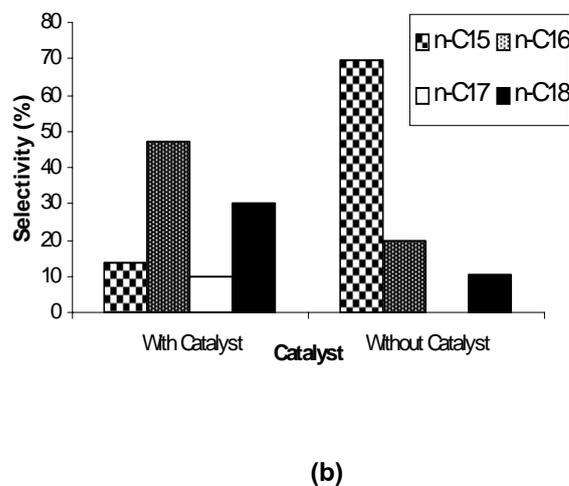

(a)

(b)

Fig. 4 a) Desired products obtained from reaction with and without catalyst. b) Selectivities of desired products obtained from the reaction with and without catalyst.

3.3 Effect of agitator turbine speed on deoxygenation reaction

Samples at reaction time of 24 hours and 45 hours were collected and analyzed in gas chromatography. According to Fig. 5a, total desire products were higher when the reaction was performed at a turbine speed of 600 rpm. It

can therefore be speculated that at higher turbine more desired product was likely to be generated perhaps due to the elimination of mass-transfer limitation.

The selectivity ratio between C18 and C17 suggested that more hydrogenation took place at higher turbine speed for reaction time of

24 hrs. However, at reaction time of 45 hrs more hydrodecarbonylation occurred at higher turbine speed, as shown in Fig. 5b. When the turbine speed was increased to 600 rpm the C18/C17 ratio increased from 2.4 to 2.99. This indicated clearly that at reaction time of 24 hrs more hydrogenation will occurred when the turbine speed was increased to 600 rpm.
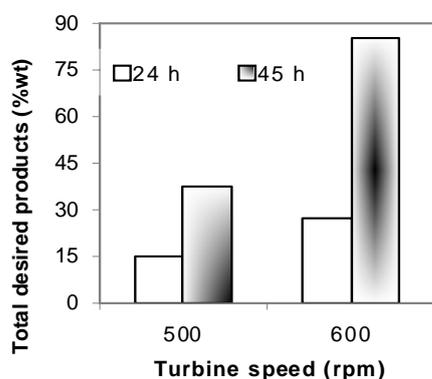
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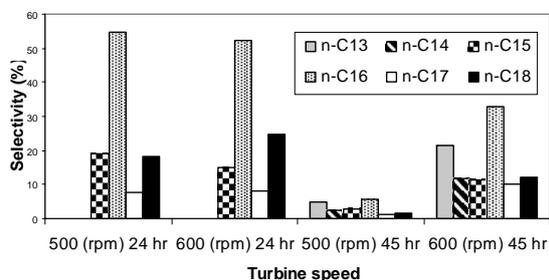
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Fig. 5 a) Two different turbine speed (500 rpm and 600 rpm) at 24 hours and 45 hours of reaction time. b) Selectivity as a function of turbine speed at two different reaction times.

3.4 Effect of reaction atmosphere in deoxygenation reaction

The effect of hydrogen atmosphere in the deoxygenation reaction of free fatty acid was observed using pure hydrogen and pure argon.

The results illustrated that hydrogen has a paramount effect on the formation of hydrocarbon via deoxygenation reaction. Under argon gas atmosphere, gas-phase analysis showed that approximately 0.00254%wt of CO was detected in the gas solution. CO is harmful to the reaction because it causes the catalyst to deactivate lowering the amount of free fatty acid converted to hydrocarbon, which is again manifested in titration to find acid value of solutions from hydrogen and argon gas atmosphere. The acid value or percentage of free fatty acid of solution from argon is much higher indicating large amount of free fatty acid still haven't been converted. Hydrogen gas can lower the partial pressure of CO is capable of combining with CO to form methane, which does not hinder the deoxygenation reaction.
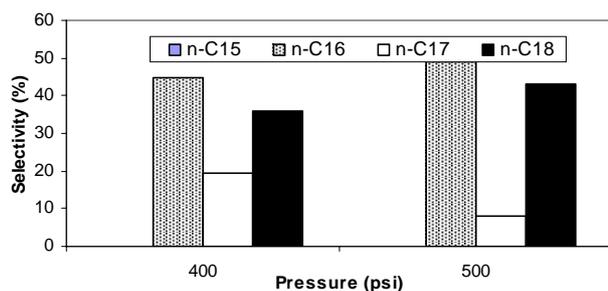
3.5 Effect of pressure on deoxygenation reaction

For this experiment, 5%wt refined palm oil was mixed with 95% dodecane under NiMo at 355°C and 500 rpm. Results obtained demonstrate and proved that the reaction at lower pressure is better than that at higher pressure such as 500 psi. Reaction under 400 psi produced roughly 35.5 % wt of desired products. However, according to Fig.6a, when the pressure was increased to 500 psi, the total desired product dropped dramatically to nearly 17 %wt.

According to Fig. 6b the selectivity ratio increased dramatically from 1.837 at reaction pressure of 400 psi to 5.47 when reaction pressure was increased to 500 psi. This

obviously suggested that at higher reaction pressure the hydrogenation reaction path was favored.
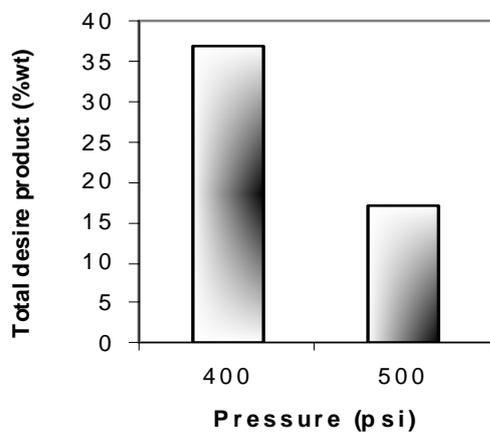
(a)

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Fig. 6 a) Total desired products as a function of pressure. b) Selectivity as a function of pressure.

4. Conclusions

In this experiment, the effect of temperature, turbine speed, catalyst, types of gas used and pressure on deoxygenating reactions of refined palm oil have sucessfully been observed. It can be concluded that the temperature that yielded the most desired product was a moderate temperature. Reaction that occurred under low pressure produced more desired products than reaction at high pressure. Turbine speed should be as fast as possible in order to eliminate mass-transfer limitation. Moreover, using catalyst in the reaction was much more effective than not using any catalyst and hydrogen gas was preferred over argon gas.

5. Acknowledgements

6. References

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