

Catalytic Pyrolysis of Used Cooking Oil by Magnesium Oxide Supported on Activated Carbon in Continuous Reactor

Chettha Jungjaroenpanit¹, and Tharapong Vitidsant²

Abstract— This research studies the pyrolysis of used cooking oil to liquid fuels on magnesium oxide catalyst with activated carbon support in a continuous reactor. The objective is to investigate the influence of factors that affect the continuous pyrolysis process and determine the optimum condition that produces the maximum liquid yield while containing a high diesel fraction. This is achieved with the assistance of the 2^k factorial experimental design. Increasing reaction temperature from 380 °C to 430 °C causes the liquid yield to increase from 58.75%wt to 70.83%wt while improving diesel fraction from 38.75%wt to 52.50%wt. Varying the catalyst amount from 30%wt to 60%wt increases the liquid yield from 58.75%wt to 73.33%wt with an increase in diesel fraction from 38.75%wt to 50%wt. An increase in used cooking oil flow rate from 60 to 180 mL/hr improved the liquid yield from 58.75%wt to 74.17% but decreases the diesel fraction from 38.75%wt to 45%wt. Increasing the carrier gas flow rate from 100 to 300 mL/min improved the liquid yield from 58.75%wt to 68.13%wt but decreased the diesel fraction from 38.75%wt to 36.75%wt. The optimum condition is the reaction temperature of 430 °C, used cooking oil flow rate at 154.20 mL/hr, the carrier gas flow rate at 102.73 mL/min and catalyst loading of 60%wt. The liquid yield at optimum condition is 81.42%wt and contains a diesel fraction of 57.07%wt.

Keywords— Pyrolysis; Used cooking oil; Liquid product yield; Diesel fraction

I. INTRODUCTION

THE increasing consumption of petroleum oil throughout the world is causing urgent economic, security, and environmental problems. One of the best ways to reduce our dependence on petroleum is to develop alternative fuels that are produced from renewable sources. The main advantages of biofuels include renewability and low emission of pollutants

Biodiesel is attracting attention due to its ability to supplement or even potentially replace conventional diesel. It is comprised of fatty acid methyl esters (FAMES), which are conventionally produced batchwise by the trans-esterification process. Unfortunately due to technical problems, the application of biodiesel as a fuel for conventional automobile

diesel engines is limited. The biodiesel physical characteristics, such as solvent properties and cold flow properties adversely affect engine performance or reduce an engine's durability. The development of biofuels that are sustainable and able surpass the limitations of conventional biodiesel is being pursued by various organizations.

A potential source for the production of biofuels is used cooking oil (UCO). They are recovered from food industry and are generally composed of long-chain saturated compounds along with free fatty acids derived from animal fats. The former has a high freezing point and the latter forms a soap with the alkali catalyst typically used in conventional biodiesel production, these two issues reduce the biodiesel yield in conventional biodiesel production process.

To solve this issue, we have applied the catalytic pyrolysis method utilizing a magnesium oxide catalyst supported on activated carbon to produce a high quality biodiesel (HiBD) [1][2]. From this method, a bio-oil composed of paraffin and olefins is produced. Separation of the obtained bio-oil will yield lighter high value hydrocarbon molecules, such as naphtha, kerosene, and diesel. The obtained HiBD possesses better low temperature properties and calorific values when compared to FAMES of equivalent carbon numbers.

This research aims to determine the optimum condition for maximum liquid product yield while maintaining a high diesel fraction and to study the joint effect of factors that affect the continuous catalytic pyrolysis process of used cooking oil. This is achieved with the assistance of the 2^k factorial experimental design [3].

II. MATERIALS AND METHODS

For analysis, the operating conditions were set to a reference value. The reference operating condition was reaction temperature of 380°C, carrier gas flow rate 100 mL/min, 30 (%v/v) catalyst of reactor and used cooking oil flow rate at 60 mL/hr. Each variable was then independently varied. Its effect on the liquid product yield and product diesel fraction were then recorded and evaluated. These observations were then statistically evaluated using the statistical method of Analysis of Variance (ANOVA).

The experiment was setup as shown in fig 1. The catalyst was prepared by physically mixing activated carbon with magnesium oxide in a 9 to 1 ratio. Catalytic reactions were conducted in continuous plug flow reactor at temperatures between 380- 430 °C while under atmospheric pressure. The reactor is equipped on the outside with an electrical heater to

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provide the necessary heating. Used cooking oil that was filtered was fed continuously at a rate of 60 - 180 mL/hr for 5 hr. The amount of catalyst was studied between 30% - 60% (v/v) catalyst of the reactor. At the same time a carrier gas was fed alongside the used cooking oil feed. The carrier gas, N₂, flow rate was fed 100 - 300 mL/min. Product exiting the reactor was cooled with a condenser kept at 30°C. The liquid product after two hours reaction time was then analyzed with simulated distillation gas chromatography (DGC) equipped with capillary flame ionization detector (FID) and gas chromatography-mass spectrometry (GC-MS). Variables were varied following a 2^k experimental design and results recorded.

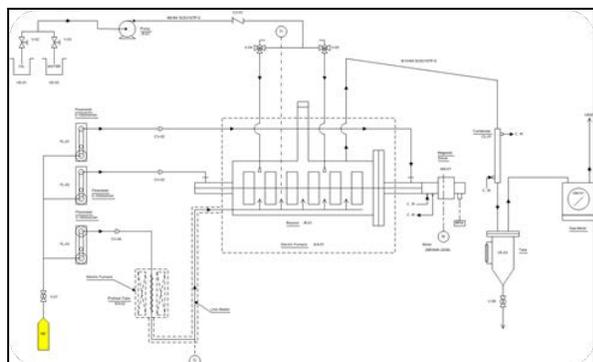


Fig. 1 Diagram of continuous reactor units

III. RESULT AND DISCUSSION

A. Effect of used cooking oil flow rate

The initial composition of used cooking oil was analyzed using a simulated distillation gas chromatograph device. Results from the analysis are presented in table 1. The used cooking oil contained a high amount of long residue, up to 68.75 %wt, which can be cracked to obtain high value lighter hydrocarbons. Detailed analysis by Gas Chromatograph, shown in table 2, reveals that the majority of fatty acid is composed of palmitic acid (C16:0) and cis-9-octadecenoic acid (C18:1 n-9). The thermal decomposition temperature, 345.79°C, was determined by thermal gravimetric analysis. Based on works by other authors on catalytic pyrolysis, an operating temperature 380 - 430°C for pyrolysis was chosen for this experiment [4].

Composition	yield (%wt)
Naphtha	9.00
Kerosene	2.25
Diesel	30.00
Long Residue	68.75

TABLE II
THE FATTY ACID COMPOSITION OF USED COOKING OIL.

Fatty acid	Abbreviation	Used oil (g/100g)
Caprylic acid	C8:0	0.06
Capric acid	C10:0	0.03
Lauric acid	C12:0	0.28
Myristic acid	C14:0	0.96
Pentadecanoic acid	C15:0	0.06
Palmitic acid	C16:0	36.89
Palmitelaidic methyl ester	C16:1t9	0.1
Palmitoleic acid	C16:1 n-7	0.84
Hepradecanoic acid	C17:0	0.12
Cis-10-Heptadecenoic acid	C17:1	0.05
Stearic acid	C18:0	5.05
Cis-9-Octadecenoic acid	C18:1 n-9	41.81
Cis-Vaccenic acid	C18:1 n-7	0.8
Cis-9,12-Octadecadienoic acid	C18:2 n-6	10.87

TABLE III
THE OVERVIEW ON THE LIQUID PRODUCT YIELD.

Manipulated Variable	Reference operating condition Liquid Product Yield	Liquid product Yield
+ Temperature		70.83 % wt
+Catalyst Quantity	58.75 %wt	73.33 % wt
+UCO Flow Rate		74.17 % wt
+Carrier Gas		57.00 % wt

B. Effect of reaction temperature

Increasing the temperature from 380°C to 430°C resulted in an increase in liquid product yield as shown in table 3.

Fig 2 provides a comparison between initial used cooking oil composition, the reference liquid product composition and temperature modified liquid product composition. It can be observed that an increase in temperature from 380°C to 430°C also increases the diesel proportion from 38.75%wt to 52.50%wt while decreasing long residue proportion from 48.75 %wt to 22.50 %wt. This is due to the strong influence of temperature on the cleaving of large hydrocarbons where continuous high temperature promotes the decarboxylation of catalyst.

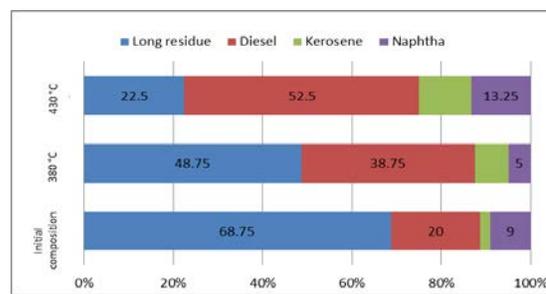


Fig. 2 Composition comparison with temperature as the manipulated variable

C. Effect of catalyst quantity

The amount of catalyst is directly proportional to the liquid product yield and diesel fraction within the liquid product. Varying the amount of catalyst in reactor from 30 % (v/v) to 60 % (v/v) resulted in an increase in liquid product yield as shown in table 3.

The composition of the liquid product is presented in fig 3. It shows that the presence of catalyst, at 60% (v/v), noticeably increases the diesel proportion from 38.75% wt to 50% wt while significantly reducing long residue fraction from 48.75% wt to 2.50 %wt. Increasing the amount of catalyst provides an increased number of total surface area or active sites for the transfer of hydrogen atoms which in turn further promotes the conversion of large hydrocarbons into small hydrocarbons. This resulted in an increase in the diesel fraction in the liquid product.

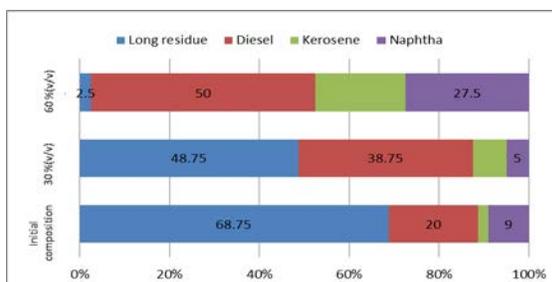


Fig. 3 Composition comparison with amount of catalyst as the manipulated variable

D. Effect of used cooking oil flow rate

An increase of used cooking oil flow rate from 60 to 180 mL/hr results in an increase in liquid yield from as shown in table 3.

The liquid product was analyzed and the results are presented in fig 4. The diesel fraction decreases from 38.75% wt to 34% wt due to the fact that increasing the used cooking oil flow rate reduced the retention time of the reaction so longer hydrocarbons increase in the product as shown in fig 4.

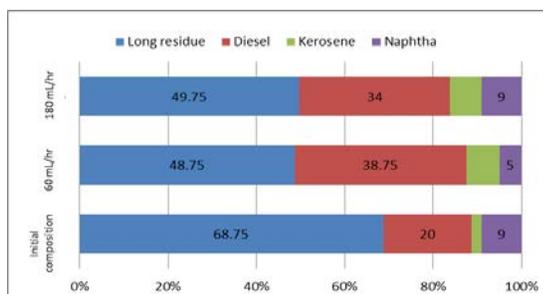


Fig. 4 Composition comparison with used cooking oil flow rate as manipulated variable

E. Effect of carrier gas flow rate

The liquid product yields at carrier gas flow rate 100 mL/minutes and 300 mL/min are shown in table 3.

As can be seen in fig 5, increasing the carrier gas flow rate causes the diesel fraction in the liquid product to decrease from 38.75% wt to 36.75% wt. This increase in carrier gas flow rate reduces the retention time of the reactants so a larger quantity of longer hydrocarbons chain still remain within the liquid product, resulting in a lower diesel and lighter hydrocarbon fraction.

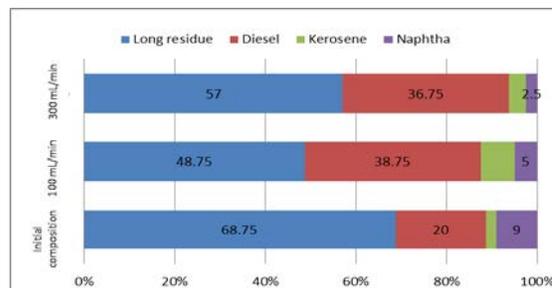


Fig. 5 The diesel yields when increase the carrier gas flow rate

F. Optimum condition

The liquid and gas yield from each experiment run is recorded and evaluated to determine the optimum condition. The obtained data on liquid yield was then tested for normality. This is to verify if the data obtained from the experiments is suitable for further statistical evaluation. The calculated R-squared value (R^2) of the data is 0.95. This is over the standard value of 0.90 and signifies that the data on liquid yield fits the normal distribution and contains no outliers.

The variance of factors was analyzed by analysis of variance table (ANOVA) as shown in table 4. It presents the individual and joint influence of the factors on the liquid yield of the product. The factors evaluated are used cooking oil flow rate (A), the reaction temperature (B), the carrier gas flow rate (C), and the amount of catalyst (D). Results from the ANOVA test showing factors that have significant individual or joint influence are shown in table 4. Factors that have significant effects on the liquid product yield are those with F-value lower than probability value of 0.05.

The optimum condition from the 2k experimental design [3] is the reaction temperature of 430 °C, used cooking oil flow rate at 154.20 mL/hr, the carrier gas flow rate at 102.73 mL/min and catalyst loading of 60% wt. The liquid yield at optimum condition is 81.42% wt and contains a diesel fraction of 57.07% wt.

It can be observed that the long chain residue, previously seen in the used cooking oil, was reduced to shorter chain hydrocarbons. Peaks at C_{16} and C_{18} that shown in fig 6 indicate the presence of some left over fatty acids mentioned in Table 2. The increase in reaction temperature and the presence of catalyst facilitate the decomposition of long chain residue into shorter chain hydrocarbons. Initially the used cooking oil contains large amounts of long chain residue, 68.75% wt. After undergoing catalytic pyrolysis, the long chain residues are reduced to lighter hydrocarbons.

TABLE IV
THE ANALYSIS OF VARIANCE ON LIQUID YIELD.

Source	Sum of Squares	Degree of Freedom	Mean Square	F Value	Prob>F Value
Model	623.6	6	103.93	21.31	<0.0001
A	170.96	1	170.96	35.05	0.0002
B	207.36	1	207.36	42.51	0.0001
D	70.39	1	70.39	14.43	0.0042
AB	46.24	1	46.24	9.48	0.0132
ABC	27.14	1	27.14	5.56	0.0427
ABCD	101.51	1	101.51	20.81	0.0014
Residual	43.90	9	2.42		
Total	667.50	15			

*note; A is used cooking oil flow rate
B is the reaction temperature
C is the carrier gas flow rate
D is the amount of catalyst

This degree of reduction is dependent on various experimental factors, such as feed flow rate, pyrolysis temperature, and catalyst quantity. Currently the experiment that results in the largest amount of long chain residue reduction produces 42.5%wt Naphtha, 41.25%wt Kerosene, and 34.5%wt Diesel with only 2.50%wt long chain residue remaining in the liquid product as shown in fig 6.

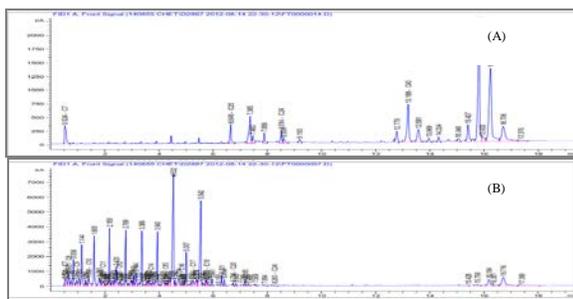


Fig. 6 The chromatograph of DGC (capillary FID) (A) used cooking oils, (B) liquid product (430°C, 60 mL/hr used cooking oil, 60% (v/v) catalysts, 100 mL/min N₂ flow rate)

IV. CONCLUSION

In this study, the catalytic pyrolysis of used cooking oil to liquid fuel by magnesium oxide supported on activated carbon in a continuous reactor was studied. The variables; reaction temperature, used cooking oil flow rate, and amount of catalyst were determined to have equally significant individual effect on the yield and composition of liquid fuel. Joint effect on liquid fuel yield can also be observed from the analysis and it was determined that following combination of factors AB, ABC, ABCD have a significant effect on the liquid fuel yield. Increasing the temperature from 380°C to 430°C significantly increases the diesel fraction from 38.75%wt to 52.5%wt while decreasing long residue. Raising the quantity of catalyst

increases the diesel fraction from 38.75%wt to 50%wt. An increase in carrier gas flow rate and used cooking oil flow rate resulted in a decrease in diesel fraction of the liquid product. The obtained liquid fuel product is composed of several high value light hydrocarbons. The optimum condition is the reaction temperature of 430 °C, used cooking oil flow rate at 154.20 mL/hr, the carrier gas flow rate at 102.73 mL/min and catalyst loading of 60%wt. The liquid yield at optimum condition is 81.42%wt and contains a diesel fraction of 57.07%wt.

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REFERENCES

- [1] HiBD, [online] Available on <http://www.hibd.net/en/index.html>
- [2] Haruki Tani, Makoto Shimouchi, Hiroyuki Haga, and Kaoru Fujimoto, “Development of Direct Production Process of Diesel Fuel from Vegetable Oils” *Journal of the Japan Institute of Energy* 90 (2011) 466-470.
- [3] Douglas C. Montgomery, “Design and Analysis of Experiments, Student Solutions Manual”, 6 edition (July 29, 2005)
- [4] Takuya Ito, Yusuke Sakurai, Yusuke Kakuta, Motoyuki Sugano, Katsumi Hirano, “Biodiesel production from waste animal fats using pyrolysis method” *Fuel Processing Technology* 94 (2012) 47–52.
- [5] Xu Junming, Jiang Jianchun, Sun Yunjuan, Chen Jie, “Biofuel production from catalytic cracking of woody oils” *Bioresource Technology* 101 (2010) 5586–5591.
- [6] Xu Junming, Jiang Jianchun, Sun Yunjuan, Chen Jie, “Production of hydrocarbon fuels from pyrolysis of soybean oils using a basic catalyst” *Bioresource Technology* 101 (2010) 9803–9806.
- [7] H. Tani, T. Hasegawa, M. Shimouchi, K. Asami, K. Fujimoto, “Selective catalytic decarboxy-cracking of triglyceride to middle-distillate hydrocarbon” *Catalysis Today* 164 (2011) 410–414.