Biogasoline from Catalytic Cracking of Refined Palm Oil using H-ZSM-5 Catalyst

Jiratchaya Chuaykleang, and Sukritthira Ratanawilai

***Abstract*—** Recently, fuels are becoming more necessary thing in daily life. Especially diesel and gasoline are primary fuel in transportation. Most of fuels made from fossil, however, this has caused global warming issue. Renewable energy is an important source for replacing fossil fuels. In this study, the catalytic cracking of refined palm oil to gasoline was studied. The effect of reaction temperature (673-823 K), weight hourly space velocity (108-1080 h^{-1}) and weight of catalyst (1-5 g.) on the catalytic cracking activity of H-ZSM-5 in fixed-bed reactor at atmospheric pressure was studied. The response surface methodology was used to design the experiments for study the operating variable effect over yield of organic liquid product. In addition, this research studies effect of operating variable on benzene and isooctane fractions. The optimum condition of maximum yield of organic liquid product, benzene and isooctane was determined.

***Keywords*—** Biogasoline, Catalytic cracking, H-ZSM-5, Refined palm oil

I. Introduction

NOWADAYS, there are two kinds of critical problems, energy crisis and global warming. Global petroleum crude oil prices are likely to become scarce and costly, it has effect to energy situations. Using fossil fuel as petroleum fuel has caused global warming problem because of air pollution emissions [1]. Biofuel can be substitute fossil fuels as renewable energy. Biofuel is defined as liquid and gaseous fuel that can be produced from utilization of biomass. In the recent years there have been several studies on the production of hydrocarbons from biomass. Biomass is any organic matter, it can be derived from plant oils or animal fats such as castor, soybean, canola, cotton and palm oil [2]. The production of biofuel is becoming as an alternative transportation fuels such as diesel and gasoline. So the transportation is the next user of biomass.

Different types of vegetable oils, edible and non-edible types are utilized in the production of biofuel. The choice of these raw materials depends on its availability, cost and climate in each country. Oil palm is widely grown in Thailand, which is considered as the third largest producer in the world. Nearly 1.2 million tons of palm oil produced in 2010 [3].

There have been several methods reported for the production of biofuel in previous studies on alternative fuel; one of these methods was, catalytic cracking. Catalytic cracking is a conversion process, converts high molecular weight oil components to lower molecular weight by catalyst. The catalyst directs the course of the cracking reactions to produce more of the desired higher octane hydrocarbon products which can be used for the production of higher octane gasoline [4].

The catalyst properties in catalytic cracking process were the catalyst can convert large hydrocarbon to small hydrocarbon, stability form high temperature and low pressure condition, small coke formation and catalyst has acidity**.** H-ZSM-5 is one type of zeolie catalyst. They are inorganic porous materials with a highly regular structure of pores and chambers that allow some molecules to pass through while others to be excluded or broken down. H-ZSM-5 have important features shape selectivity: avoids reactant oversized molecules from diffusing into its pores, allows only small molecules product to be formed during reaction to diffuse out of the zeolite pores and molecular traffic control. The reactant molecules enter the catalyst through one type of channels, and the products, due to their size and shape limitation, leave the catalyst through the other type of channel, thus minimizing counter-diffusion [5]. So the H-ZSM-5 catalyst should be the main catalyst for catalytic cracking process.

The scopes of the present study is to study the optimum condition for produce biogasoline by catalytic cracking process from refined palm oil. The effect of temperature, WHSV and catalyst weight were study. The respons surface methodology was used to design the experiments for study the operating variables effect over yield of organic liquid product. Benzene and isooctane fractions in OLP was analyzed.

II. Experiment Methods

A. Materials and Chemical

Refined palm oil (RPO) in commertail grade (density of oil = 0.889 g/ml), purchased form local market under name "Morakot". It was used as a raw material. Analytical grade of nitrogen gas (99.99% of purity) was used for carrier gas. Ammonium-ZSM-5 (code no. CBV 3024 E) with the Si/Al

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ratio of 30 and 99.98% of purity was purchased from Zeolyst International Company, USA. Benzene and isooctane analytical standard for GC (CAS no. = 71-43-2 and CAS no. = 540-84-1 respectively.) were purchased from S.M. Chemical supplies company, Thailand.

B. Catalyst preparation

Firstly, NH_4-ZSM-5 was dried at 393 K for 24 hours. Dreid NH_4-ZSM-5 was put in the furnace under N_2 flow rate of 20 ml/min. The NH_4-form was transformed to the proton form of zeolite (H^+) and ammonia (NH_3) by was heated at 823 K for 6 hours. The H-ZSM-5 catalyst was prepared for catalytic cracking process.

C. Fourier-transformed Infrared analysis

Fourier-transformed Infrared (FT-IR) is a method of obtaining infrared spectra by first collecting an interferogram of a sample signal using an interferometer. In this study, the FT-IR of H-ZSM-5 was studied. The H-ZSM-5 was prepared from NH_4-ZSM-5, heated at 823 K for 6 hours.

D. Thermo gravimetric analysis

Thermo gravimetric Analyzer (TGA) is a type of testing performed on samples that determines changes in weight in relation to change in temperature, weight loss curve can identify the point where weight loss is most apparent. TGA is commonly employed in research and testing to determine characteristics of materials to determine degradation temperatures [7]. In this study, the weight loss of refined palm oil was studied. Study between 323-1073 K, the temperature was increase with heating rate 10 K/min.

E. Catalytic cracking

The catalytic cracking was performed at atmospheric pressure with reaction temperature range of 673-823 K using a fixed-bed reactor. This study using two reators for catalytic cracking, first reactor for feed of refined palm oil and second reactor for catalytic cracking reaction. Refined palm oil fed into the first reactor and was heated. Then the oil in liquid phase was evaporated to gas phase and ready for cracking. The oil in gas phase was carried to second reactor by nitrogen gas at certain weight hourly space velocity range of 108-1080 h^{-1} and weight of H-ZSM-5 catalyst was varied between 1-5 g. After the reaction, the gas product leaving the reactor were cooled to 313K in the condenser system. The organic liquid product (OLP) were collected in glass liquid sampler at room temperature. Fig.1 shows the experimental cracking process used for this study. Finally, OLP was kept and the benzene (C_6) and isooctane (C_8) were measured by gas chromatograpy with frame ionization detector (GC-FID).

The study intents to study the activity of catalytic cracking of refined palm oil to determine the effect of reaction temperature, weight hourly space velocity and amount of catalyst. The temperature was maintained at 673-823 K, weight hourly space velocity at 108-1080 h^{-1} and weight of catalyst at 1-5 g. A response surface methodology was developed by Box-Behnken Design (BBD) and was carried out by performing 16 experiments based on a three factors. The low, center and high levels of each variable were designated as -1, 0 and +1 respectively as shown in Table I. After the reaction, the OLP was determined to for find the optimum condition of catalytic cracking. The OLP and residual products are calculated as in (1), C_6 and C_8 were analyzed.

$$Yield \quad of \quad OLP(\%wt) = \frac{Desied \quad product}{Oil \quad feed} \times 100 \tag{1}$$

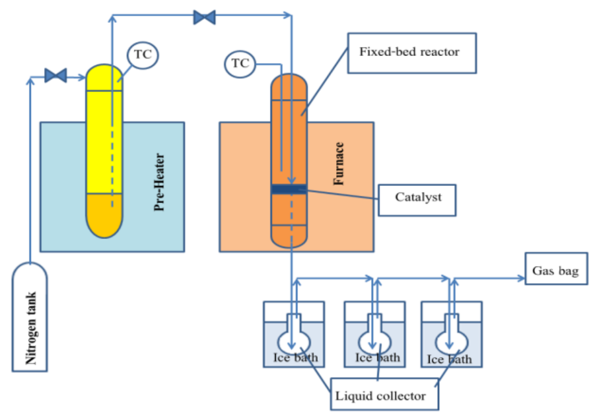

Fig.1. Diagram of catalytic cracking process.

TABLE I
INDEPENDENT VARIABLES CODED AND REAL VALUES USED IN LINEAR MODEL

Variables	Code	Real values -1	Real values 0	Real values 1
Temperature (K)	X_1	673	748	823
Flow rate of N_2 (ml/min)	X_2	10	15	20
Weight of catalyst (gram)	X_3	1	3	5

F. Design of experiment

The RSM is a collection of mathematical and statistical techniques for developing, improving and optimizing processes by finding the true relationship between the response and a set of independent variables [6].

The Box–Behnken design was used in the resent investigation to assess the effect of the reaction parameters. In this study, 3 factors, reaction temperature, nitrogen flow rate and weight of catalyst (Weight hourly space velocity (WHSV) was calculated from Nitrogen flow rate and weight of catalyst as show in (2).) were identified as important factors that influence the catalytic cracking of vegetable oil on the organic liquid product. A total number of 16 experimental runs including 3 center runs were generated. Table II

$$WHSV \quad (time^{-1}) = \frac{Mass \quad flow \quad rate \quad \left(\frac{weight}{time}\right)}{Catalyst \quad weight \quad (weight)} \tag{2}$$

The regression model was used to approximate the responses based on a second-order polynomial model show in (3)

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (3)$$

where Y is the response, β_0 is a constant coefficient, X are the independent variables and β_i, β_{ii} and β_{ij} are interaction coefficients of linear, quadratic and the second order terms respectively.

TABLE II
DESIGN OF EXPERIMENT FOR CATALYTIC CRACKING OF REFINE PALM OIL

Run No.	X_1	X_2	X_3
1	823	20	3
2	823	10	3
3	673	10	3
4	748	15	3
5	748	10	1
6	823	15	1
7	748	10	5
8	748	15	3
9	748	20	5
10	748	20	1
11	673	15	1
12	748	15	3
13	673	20	3
14	823	15	5
15	400	15	5
16	748	15	3

III. RESULT AND DISCUSSION

A. Thermogravimatic analysis studies

In this research, it is used to estimate the range of temperature that used to experiment for production of biogasoline.

Fig. 2 shows curve of derivative weight and temperature of refined palm oil. Weight of RPO was begun to change at temperature of 623 K and derivate between623 – 823 K, weight loss was not significantly changed by increasing temperature from 823-1073 K.

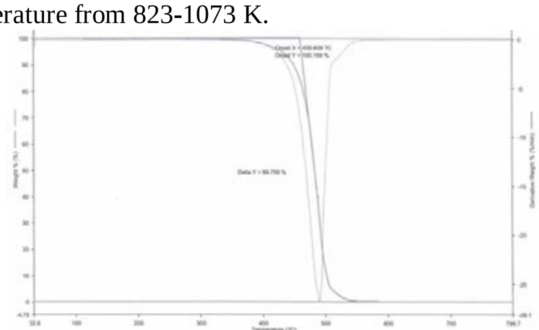

Fig. 2. Graph between derivative weight and temperature of refined palm oil .

B. FTIR analysis studies

The transmission spectroscopy of H-ZSM-5 are shown in Fig. 3. The spectrum of H-ZSM-5 has wave number in renge of 400-2000 cm^{-1} and 3400-3500 cm^{-1}. Significant transmission bands are observed at 452, 548, 801, 1107, 1226 and 3454 cm^{-1}. This transmission bands are assigned to T-O bend, double five member ring, symmetric stretching, internal asymmetric of TO_4 tetrahedral, external asymmetric of TO_4 tetrahedral and funtional group of Si-(OH)-Al respectively.

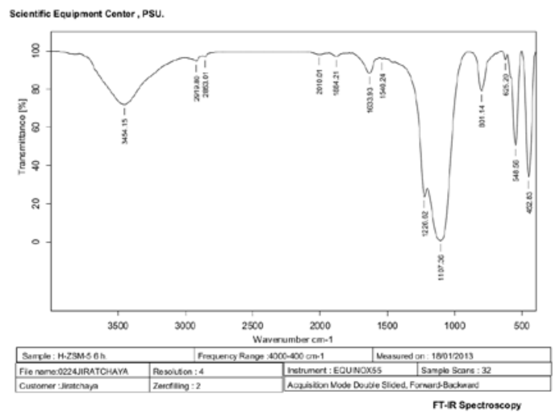

Fig. 3. Transmission spectroscopy of H-ZSM-5 from FT-IR.

C. Organic liquid product yield

The significant variables and their effects on the responses have to be identified in order to study the effects of the reaction variables on the yield of organic liquid product (Y_{OLP})

Nitrogen flow rate factor has not a significant effect on yield of OLP among the three response factors. It was nectlected from the design, so the design equation is shown in (4).

Table III shows the analysis of variance (ANOVA) at 95% confedence level for the three independent factors of yield of organic liquid product (Y_{OLP}).

$$Y_{OLP} = -260.55 + 1.245 X_1 - 11.35 X_3 - 0.00136 X_1^2 - 0.308 X_3^2 + 0.02773 X_1 X_3 \quad (4)$$

TABLE III
ANOVA FOR THE QUADRATIC EQUATION MODEL FOR (4)

Source	Sum of Square	Mean of square	F-value
Regression	362.79	72.56	42.25
Residual	17.17	1.717	
LOF Error	11.95	3.984	5.3392
Pure Error	5.223	0.746	
Total	379.96		
	$R^2 = 0.955$		

Table IV shows the analysis of variance (ANOVA) at 95% confedence level for the three independent factors of yield of organic liquid product (Y_{OLP}). Yield of OLP of catalytic cracking process is between 15 to 27 percentage by weight (%wt). Yield of OLP increased with temperature more than 673 K and decreased with temperature up to 823 K. The predicted optimum condition of temperature, weight of catalyst and nitrogen flow rate were 770 K, 3.96 g respectivly , with no effect of nitrogen flow rate. On the optimum condition from RSM was shown WHSVs of 136, 204 and 272 h^{-1}. WHSVs were calculated by (2) with optimum catalyst weight of 3.96 g. and various nitrogen flow rate of 10, 15 and 20 ml/min respectively. In this predicted optimum condition show 26.66 %wt yield of OLP. Fig. 4. presents temperature and weight of catalyst effects on yield of OLP.

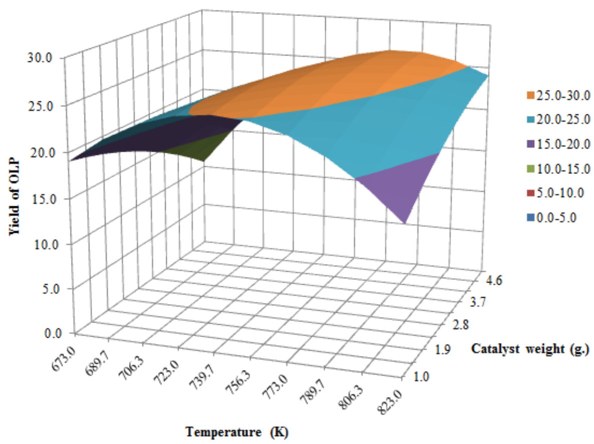

Fig. 4. Percentage yiled of OLP as a function of temperature and weight of catalyst.

TABLE IV
MATRIX FOR THE SIXTEEN EXPERIMENTAL AND PREDICTED YIELD OF OLP

X_1	X_2	X_3	Yield of OLP (%wt)	
			Experimental	Predicted
823	20	3	21.95	21.19
823	10	3	22.05	21.19
673	10	3	15.22	16.06
748	15	3	27.24	26.29
748	10	1	23.47	25.11
823	15	1	16.01	15.85
748	10	5	25.19	25
748	15	3	26.43	26.29
748	20	5	26.9	25
748	20	1	24.97	25.11
673	15	1	20.68	19.05
748	15	3	25	26.29
673	20	3	15.58	16.06
823	15	5	22.28	24.06
673	15	5	10.31	10.62
748	15	3	26.2	26.29

D.Benzene and Isooctane analysis

On this above discussion, nitrogen flow rate hasnot a direct effect on the yield of OLP, hence, the study on percentage of gasoline and isooctane was carried out depenting on two factors (Temperature and weight of catalyst). This study selected some of experimental to study the effect of temperature and weight of catalyst in benzene and isooctane concentration. The experiments were devided in to two parts. Study of the effect of temperature (T) in 673, 748 and 823 K with the constant weight of catalyst (3 gram) and study the effect weight of catalyst (WC) with constant temperature (748 K). The experiments are shown in table V. Benzene and Isooctane were analyzed by GC-FID. The result of Benzene and Isooctane Concentration with effect of temperature and catalyst weight are shown in table VI and VII.

TABLE V
EXPERIMENTAL OF BENZENE AND ISOOCTANE STUDIED.

Effect of Temperature		Effect of Catalyst weight	
T (K)	WC (g.)	WC (g.)	T (K)
673	3	1	748
673	3	1	748
748	3	5	748
748	3	3	748
823	3	5	748
823	3	5	748

TABLE VI
EFFECT OF TEMPERATURE FOR BENZENE AND ISOOCTANE CONCENTRATION.

Temperature	Concentration (%by weight)	
	Benzene	Isooctane
673	0.3539	0.0414
673	0.3271	0.0385
748	4.9685	0.0311
748	4.1160	0.0525
823	4.5544	0.0179
823	5.6209	0.0007

TABLE VII
EFFECT OF CATALYST WEIGHT FOR BENZENE AND ISOOCTANE CONCENTRATION

Catalyst weight	Concentration (%by weight)	
	Benzene	Isooctane
1	1.3847	0.0825
1	2.9114	0.1149
3	4.9686	0.0319
3	4.1161	0.0526
5	0.0042	0.00013
5	0.0044	0.00016

It has been observed that the concentration of benzene increased with the increase of temperature, particularly above 673 K, however for isoocatne, temperature has no significant effect because the concentration did not change with temperature

Effect of catalyst weight, while the benzene concentration increases with catalyst weight increase, reach to the maximum at 1-3 gram and then level off at higher catalyst weight regions. Isooctane concentration is decresed with catalyst weight incrase.

In adddition, the catalyst is important effect for catalytic cracking process. Amount of catalyst is directly affecting catalytic cracking reaction, as the reaction used higher catalyst weight, the longchain hydrocarbon was broken to small hydrocarbon. When the reaction was put more catalyst weight, some hydrocarbon was cracked in smaller hydrocarbon than gasoline range(less than benzene and isooctane range) and it did not show in this study.

IV. Conclusion

The response surface methodology was used to design the experiments to study the operating variable effect of catalytic cracking reaction over yield of organic liquid product. The optimum condition from RSM prediction was temperature of 770 K, weight of catalyst of 3.96 g. and no effect of nitrogen flow rate (WHSVs are 136, 204 and 272 h^{-1}). The yield of OLP obtained was 26.66 %wt.

The Effect of temperature on benzene and isooctane concentration was studied, and it was observed that, benzene concentration increased with the increase of temperature, which had not a significant effect on isoocatne concentration.

Furthermore, the effect of catalyst weight on benzene and isoocatne concentration was studied, too. The concentration of benzene increased with the increase of catalyst weight and decreased at higher weight of catalyst. Isooctane concentration decreased with the increase of catalyst weight.

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