การแตกตัวด้วยความร้อนเชิงตัวเร่งปฏิกิริยาของน้ำมันสบู่ดำไปเป็นเชื้อเพลิงเหลวบน HZSM-5

THERMAL CATALYTIC CRACKING OF JATROPHA OIL TO LIQUID FUELS OVER HZSM-5

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บทคัดย่อ

งานวิจัยนี้มีจุดมุ่งหมายที่จะศึกษาปฏิกิริยาการแตกตัวเชิงตัวเร่งของน้ำมันสบู่ดำไปเป็นเชื้อเพลิงเหลวด้วย HZSM-5 บนเครื่องปฏิกรณ์แบบแบตช์ขนาดเล็ก เพื่อศึกษาอิทธิพลของตัวแปรต่างๆ ที่ส่งผลต่อการเปลี่ยนไปเป็นแนฟทา โดยออกแบบการทดลองเชิงวิศวกรรมแบบสองระดับเพื่อหาภาวะที่เหมาะสมต่อการเปลี่ยนไปเป็นผลิตภัณฑ์น้ำมัน ใช้สภาวะการทดลองที่อุณหภูมิระหว่าง 390 ถึง 440 องศาเซลเซียส เวลาในการทำปฏิกิริยา 30 ถึง 60 นาที ใช้ตัวเร่งปฏิกิริยา HZSM-5 ร้อยละ 2.5 ถึง 10 โดยน้ำหนัก ความดันแก๊สไฮโดรเจนเริ่มต้น 100 ปอนด์ต่อตารางนิ้ว ผลิตภัณฑ์น้ำมันที่ได้นำมาวิเคราะห์ด้วยเครื่องแก๊สโครมาโตกราฟจำลองการกลั่น ผลการทดลองโดยการใช้โปรแกรม design expert ที่ใช้คำนวณหาภาวะที่เหมาะสมพบว่า ที่อุณหภูมิ 426 องศาเซลเซียส เวลาในการทำการทดลอง 56 นาที โดยใช้ตัวเร่งปฏิกิริยา HZSM-5 ร้อยละ 6.25 โดยน้ำหนัก เป็นภาวะที่เหมาะสมต่อการเปลี่ยนน้ำมันสบู่ดำไปเป็นแนฟทา โดยให้ผลิตภัณฑ์เป็นน้ำมันถึง 58.62% โดยน้ำหนัก และมีองค์ประกอบเป็นแนฟทา 40.60% โดยน้ำหนัก แสดงให้เห็นว่าปัจจัยที่ส่งผลต่อการเปลี่ยนน้ำมันสบู่ดำไปเป็นน้ำมันเชื้อเพลิง ประกอบด้วย อุณหภูมิ เวลา และปริมาณของตัวเร่งปฏิกิริยา HZSM-5 และเมื่อทำการทดลองโดยใช้ภาวะที่ได้จากการคำนวณโดยซอฟต์แวร์ก็ให้ผลการทดลองที่ไม่แตกต่างกันอย่างมีนัยสำคัญ

คำสำคัญ: การแตกตัวด้วยตัวเร่งปฏิกิริยา HZSM-5 น้ำมันสบู่ดำ

Abstract

This research aimed to study the catalytic cracking of Jatropha oil to liquid fuels with HZSM-5. A microreactor was used for the study of the effect of variables of liquid fuel products especially naphtha by using a two level factorial design of experiment to determine the optimum condition. The operating condition was the temperature between 390°C and 440°C, the reaction time from 30 minutes to 60 minutes and the percentage by weight of HZSM-5 between 2.5 and 10 at initial hydrogen pressure of 100 lb/in^2. The liquid products were analyzed by simulated distillation gas chromatograph. Based on the analysis from a design-expert program to determine the appropriate condition of experiment, it was found that the reaction temperature of 426°C, the reaction time of 56 minutes by using 6.35 percent by weight of HZSM-5 was the best condition that gave the highest yield of naphtha. The oil yield was 58.62 percent by weight, and the naphtha yield was 40.60 percent by weight. The result also showed that 3 factors, namely temperature, reaction time and percentage by weight of HZSM-5 significantly affected the oil yield. Both the result derived from the conversion and the fraction of liquid fuels from the experiment and the result calculated from the program concluded similar outcome insignificantly.

Keywords: Catalytic cracking, HZSM-5, Jatropha oil

Introduction

The renewable energy resources are expected to take an increasing role in the future energy consumption to reduce the environmental impacts with regard to air and water quality, acid rain, global warming, and so forth. Biomass is now being considered as an important energy resource all over the world because they are readily available at low cost and environmentally friendly.

Jatropha is one of the biomass to use for the production of liquid fuels. It is non-edible oil being singled out for large-scale plantation on wastelands [1]. Jatropha plant can thrive under adverse conditions. It is a drought-resistant, perennial plant, living up to fifty years and has capability to grow on marginal soils. The oil content from Jatropha seeds ranges from 30% to 40% by weight. [1-2] Fresh Jatropha oil is slow-drying, odorless and colorless, but it turns yellow after aging. The only limitation of this crop is that seeds are toxic and the press cake cannot be used as animal fodder.

Jatropha oil is converted into liquid fuel through transesterification and cracking process. In recent years, there have been several literatures on the production of hydrocarbon from Jatropha oil mainly bio-diesel carried out using cracking catalysts in a micro-reactor. Zeolite has shown excellent performance as a solid acid cracking catalyst due to their higher selectivity. In this research, HZSM-5 is used as a catalyst. It is a MFI 10 ring structure which has channel dimension of 5.15.5. [3-5] It gives lighter products from petroleum.

From an economic point of view, the optimization of operating condition in catalytic cracking of Jatropha oil will be beneficial. [6-9] There are classical as well as statistical methodologies available for process optimization. Statistical methodologies involve the use of mathematical methods for designing and analyzing results. The response surface methodology (RSM) is a statistical modeling technique employed for multiple regression analysis using quantitative data obtained from properly designed experiments to solve multivariable equations simultaneously. [10] The benefits of using statistical approach with the minimum number of experiments to obtain the optimum operating conditions have drawn interest of the researcher for complex reactions. Previous studies by demonstrated the use of design of experiments (DOE) in the study of Jatropha oil cracking process to optimize the significant reaction parameters.

Objectives

The objective of the present research is to optimize the process operating conditions for the production of gasoline fraction in liquid hydrocarbon fuel from Jatropha oil using DOE and respond surface methodology. The gasoline fraction is produced from Jatropha oil using MFI as a cracking catalyst in a micro-reactor.

Methods

Experimental

1. Jatropha oil Jatropha oil is predominantly composed of Palmetic acid, oleic acid and linoleic acid. It has the highest percentage of long residue shown in table 1 and 2 respectively. Crude Jatropha oil is available from Thai Jatropha oil companies in Patumthani.

Table 1 Composition of fatty acid in Jatropha oil

Composition of fatty acid	g/100 ml
Palmetic acid (C16:0)	15.29
Palmitoleic acid (C16:1)	0.98
Heptadecanoic acid (C17:0)	0.13
Stearic acid (C18:0)	5.84
Cis-9-Octadecanoic acid (C18:1 n-9)	37.32
Cis-9,12-Octadecanoic acid (C18:2 n-6)	39.78
Cis-9,12,15-Octadecanoic acid (C18:3 n-3)	0.19
Arachidic acid (C20:0)	0.18
Behenic acid (C22:0)	0.04
Lignoceric acid (C24:0)	0.04

Table 2 Composition of carbon chain in jatropha oil

Boiling point (°C)	composition	%
IBP-200	Naphtha (C_5-C_{12})	4.52
200-250	Kerosene (C_{12}-C_{15})	0.50
250-350	Light Gas oil (C_{15}-C_{25})	10.30
350-370	Gas oil (C_{25}-C_{33})	3.02
370-FBP	Long Residue (>C_{33})	81.66

2. Catalyst Zeolite MFI was used for this research. It is a commercial grade product imported from Japan. Surface area Al/Si ratio equal to 18 from XRF technique [5, 11] in figure 1 and has a structure similar to ZSM-5 from figure 2.

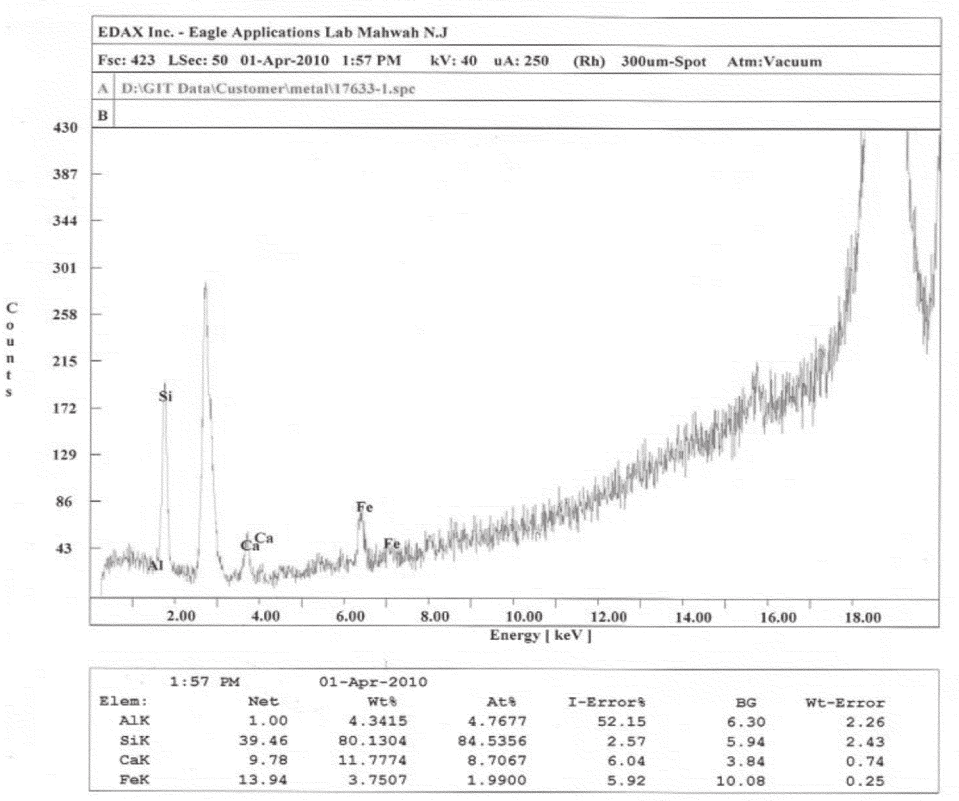

Figure 1. composition of Jatropha oil by XRF technique.

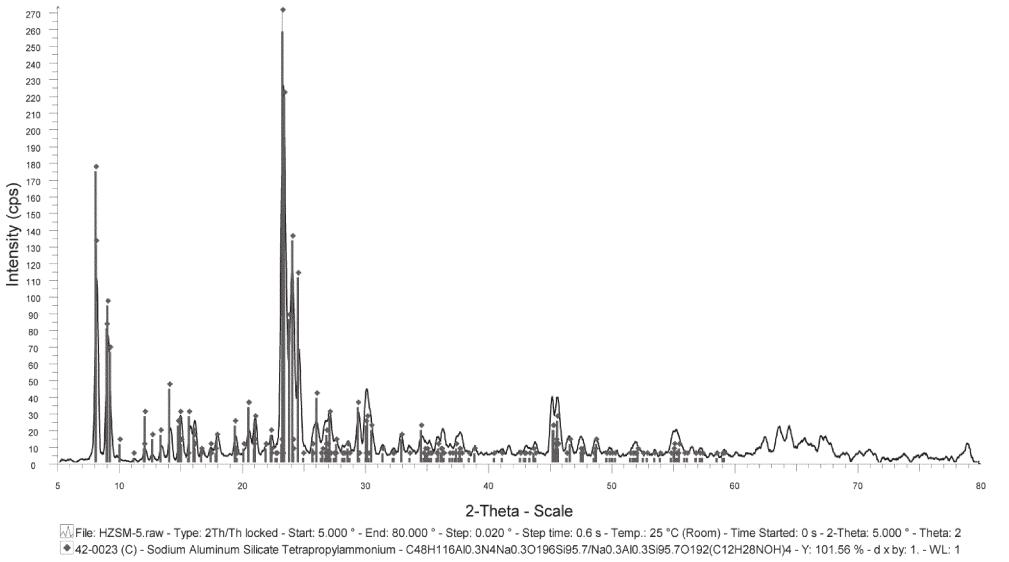

Figure 2. structure of catalyst prepare to ZSM-5.

3. Experimental setup In the present study, the catalytic cracking was carried out in a micro-reactor that can be operated under batch mode. The reactor is shown in figure 3.

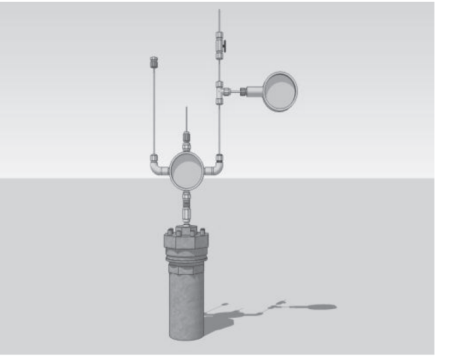

Figure 3. The reactor in the experiment.

4. Experimental design and mathematical model

The cracking reaction was conducted at the temperature of 390-440°C; the resident time of 30-60 minutes and the weight of catalyst 2.5-10%wt. The statistic method of factorial design of experiments (DOE) eliminates the systematic errors with an estimate of the experiment error and minimizes the number of experiments. [10, 12-13] The experiments were conducted with three response variables in central composite design (CCD) with rotatable

value of 0.5. Temperature, resident time and weight of catalyst were chosen as independent variables in the experiment (CCD), each was considered at two levels, namely low (-1) and high (+1) and was used as shown in table 3. Alfa (a) was used in the experiment to build a two-order model, which was shown in a geometric 2^3 design (figure 4).

Accordingly, 33 experiments were conducted with the first 17 experiments organized in a factorial design and the remaining 4 involving the replication of the central point of each stage. In order to carry out a comprehensive analysis of the catalytic cracking process, 3 main dependent response were considered which were: % yield liquid fuels, % conversion and % yield naphtha. [10, 14-15] They are defined as:

$$\%\ \text{yield liquid fuels} = \frac{\text{weight of liquid fuel}}{\text{weight of initial Jatropha oil}} \times 100 \quad (1)$$

$$\%\ \text{conversion} = \frac{\text{weight of initial long residue} - \text{weight of final long residue}}{\text{weight of intial long residue}} \quad (2)$$

$$\%\ \text{yield of naphtha} = \frac{\%\ \text{yield of naphtha from DGC analysis} \times \%\ \text{yield of liquid fuels}}{100} \quad (3)$$

Model terms were selected or rejected based on the P values with 95% confidence level. The results were completely analyzed using analysis of variance (ANOVA) by Design Expert software. Three-dimensional plots were obtained based on the effect of the three factors and their levels. From these three-dimensional plots, the simultaneous interaction of the three factors on the responses was studied.

Table 3 Factors and levels used in the 2^3 factorial design study.

Variables	low (-)	High (+)
temperature (°C),A	390	440
time (minutes),B	30	60
catalyst (%wt),C	2.5	10

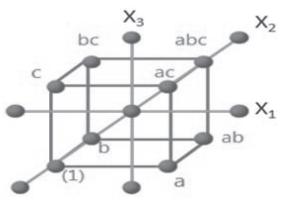

Figure 4. Geometric notations for calculating effects in the 2^3 design.

Results

1. Design of experiments (DOE)

The cracking of Jatropha oil gave liquid product, gas and coke. In this study from table 4 summarizes the activity and main product distribution of catalytic cracking which are % yield liquid fuels, % conversion and % yield naphtha at different temperatures, resident times and percentages of weight catalyst. Several variables were studied. Thus, the conditions that significantly affected the product distribution were to be identified statistically. Therefore, the analysis of variance (ANOVA) was performed at 95% level of confidence for the designed experiments using the Design-Expert program software. The significance of the individual and iteration of the factors were determined by the F-value. The result of ANOVA in table 4 indicates that the conversion of Jatropha oil was high and ranged from 76.78-98.54%. The conversion of Jatropha oil increased steadily with an increase in temperature and a rise in resident time. The highest Jatropha oil conversion was 98.54% at 440°C, 60 minutes and 2%wt catalyst. The conversion of jatropha oil increased with temperature, resident time and % weight of catalyst as shown in figure 5.

In figure 6, the yield of liquid fuels decreased with an increase of temperature and a rise in % weight of catalyst. However, the yield steadily increased with resident time between 30 and 60 minutes. % yield liquid decreased significantly with an increase in temperature indicating that the fraction of % yield liquid was converted to gas. % yield liquid decreased with resident time, noticed that long resident time gave % yield of liquid fuels tend to convert from gas and condensed to liquid product. [8-9, 13-14] For % yield of naphtha, it has the same trend with % conversion. Thus, it can be concluded that the higher the percent conversion, the higher the percent yield of naphtha.

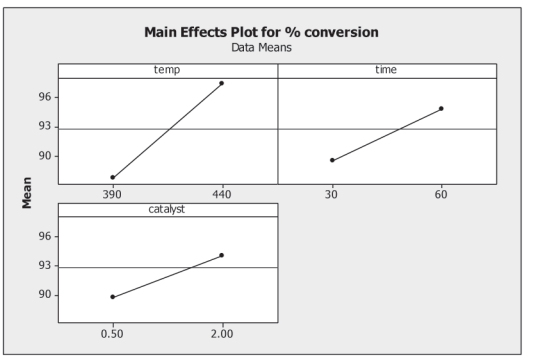

Figure 5. main effect for % conversion of Jatropha oil

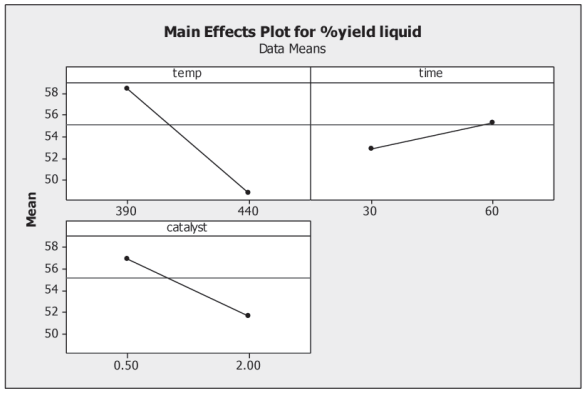

Figure 6. main effect for % yield liquid fuels of Jatropha oil

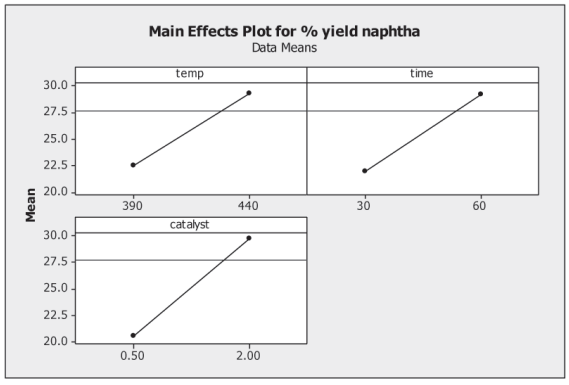

Figure 7. The main effect for % yield naphtha of Jatropha oil

Table 4 Number of the experiment

number	Condition temperature (°C)	Time of reaction (minutes)	catalyst (g)	% yield liquid	% conversion	% yield naphtha
1	390	30	0.5001	62.69	76.95	12.72
2	390	30	0.5000	69.42	76.78	13.06
3	440	30	0.5002	35.88	98.21	16.94
4	440	30	0.5001	32.23	97.92	14.06
5	390	60	0.4992	47.36	90.04	13.53
6	390	60	0.5006	61.47	84.18	15.74
7	440	60	0.4992	57.05	97.54	32.01
8	440	60	0.5005	63.24	96.91	33.69
9	390	30	2.0003	48.29	81.36	17.64
10	390	30	1.9966	61.08	87.07	27.55
11	440	30	2.0048	40.05	97.64	25.76
12	440	30	2.0094	50.34	97.21	32.50
13	390	60	2.0023	51.55	96.81	31.49
14	390	60	1.9990	48.76	96.74	29.12
15	440	60	2.0103	56.73	97.44	38.52
16	440	60	2.0086	45.70	98.54	31.86
17	440	60	2.0078	55.44	96.76	36.24
18	415	45	1.2572	61.12	96.46	38.37
19	415	45	1.2571	53.82	95.96	33.39
20	415	45	1.2504	60.60	95.64	37.31
21	415	45	1.2524	65.49	95.68	40.60
22	415	45	1.2494	58.27	95.05	34.87
23	390	60	0.5083	68.22	92.19	29.56
24	390	30	2.0203	58.84	87.87	25.97
26	390	60	2.0010	51.85	95.53	29.35
27	390	30	0.5001	71.55	87.22	24.24
28	457	45	1.2493	47.40	97.09	31.21
29	373	45	1.2552	69.52	83.74	30.97
30	415	45	2.5136	52.14	97.17	25.91
31	415	45	0	50.45	90.02	22.92
32	415	70.2	1.2517	49.64	97.24	25.97
33	415	19.8	1.2515	54.36	95.45	26.35

2. Process Optimization

The results were calculated by Design Expert version 6.1 and Minitab version 15.0. It shows the main effect of variables, and three-dimensional plots (respond surface) for % yield naphtha are indicated in figure 8. The optimum condition for catalytic cracking of Jatropha oil were the temperature of 426°C, the reaction time of 56 minutes and 6.35% weight of HZSM-5.

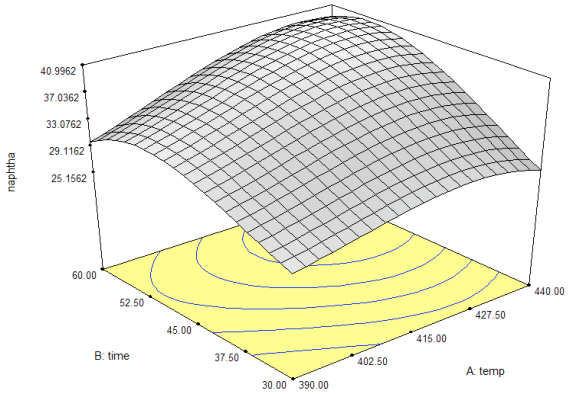

Figure 8. Respond surface for % yield naphtha, temperature and resident time with weight catalyst of 6.25%

Conclusions and Discussion

Three factors, namely temperature, time of reaction and % weight of HZSM-5 have effects on product yield liquid, % conversion and yield naphtha and the optimum condition for cracking Jatropha oil were the temperature of 426°C, the reaction time of 56 minutes by using 6.35% weight of HZSM-5.

Acknowledgements

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