

Conversion of used vegetable oils to liquid fuels and chemicals over HZSM-5, sulfated zirconia and hybrid catalysts

Witchakorn Charusiri^{*,**,*}, Withaya Yongchareon^{*} and Tharapong Vitidsant^{**}

^{*}Energy Research Institute, ^{**}Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
(Received 25 May 2005 • accepted 22 November 2005)

Abstract—Thailand's food manufacturing uses about 47 Million liters per year of vegetable oil. Used vegetable oil is classified as waste, but has potential for conversion into liquid fuel. This research studied the catalytic conversion of used vegetable oil to liquid fuel, where investigation was performed in a batch microreactor over a temperature range of 380-430 °C, initial pressure of hydrogen gas over 10-20 bars, and reaction time of 45-90 minutes. Catalysts such as HZSM-5, Sulfated Zirconia and hybrid of HZSM-5 with Sulfated Zirconia were used to determine the conversion and yield of gasoline fraction. The major products obtained were liquid products, hydrocarbon gases and small amounts of solids. Liquid products were analyzed by simulated distillation gas chromatograph and the product distribution was obtained. Hybrid catalyst HZSM-5 with Sulfated Zirconia showed the highest yield of gasoline with a 26.57 wt% at a temperature of 430 °C, initial hydrogen pressure at 10 bars, and reaction time of 90 minutes in the ratio of hybrid HZSM-5 with Sulfated Zirconia at 0.3 : 0.7.

Key words: Used Vegetable Oil, Catalytic Cracking, HZSM-5, Sulfated Zirconia

INTRODUCTION

Currently, conventional energy sources are being depleted while there is an increasing demand for transport fuels. Therefore, many researchers are concentrating on developing alternative and renewable sources of liquid fuels, which are new energy resources to replace commercial petroleum products and are also environmentally friendly. Thailand's manufacturing sectors use about 47 million liters per year of vegetable oil for cooking and food processing [Charusiri et al., 2003, 2005] such as fried instant noodles, fried snacks, etc. This amount does not include vegetable oil used in large restaurants, fast food shops and households. Used vegetable oil is not collected or disposed of suitably and there are no official reports concerning actual amounts of how much is used. Unscrupulous cooking suppliers will normally regenerate vegetable oil by bleaching the used vegetable oil and blend it as new. They usually supply the reused vegetable oil to small and medium enterprises or general consumers. Street food vendors are customers of these suppliers and buy the reused vegetable oil because it is cheaper than fresh vegetable oil. The used vegetable oil is classified as waste, while its potential as a liquid fuel through physical and chemical conversion remains highly interesting. Used vegetable oil is increasingly attracting much interest because of its great potential to be used as diesel substitutes known as bio-diesel. Direct synthesis via transesterification reaction of vegetable oils will yield bio-diesel. Another fascinating alternative route is the direct upgrade of vegetable oils to clean premium transportation fuels using catalytic cracking. These vegetable oils are long chain hydrocarbon molecules, which can be converted to light hydrocarbon using many types of catalysts. HZSM-5 was found to be most efficient in the oil cracking process of or-

ganic liquid fuel production [Prasad et al., 1986; Satterfield, 1991] giving mainly aromatic hydrocarbon from the properties of pore size and shape selective. Adjaye et al. [1995] also observed high conversion (greater than 75%) of canola oil over HZSM-5 at the condition of temperature of 370-410 °C. The high conversions were probably due to the effectiveness of HZSM-5 catalyst to convert triglycerides such as oleic, linoleic, palmitic and linoleic fatty acid belonging to the carboxylic groups) which are the gasoline fraction. In an earlier work by Kantikaneni et al. [1995] it was observed that compounds with the carboxylic functional group were highly reactive over HZSM-5 with conversions above 72.5% at a temperature of 400 °C and weight hourly space velocity 1.8 hr⁻¹. In addition, Sulfated Zirconia has been termed as super acid catalyst which is a strong solid acid catalyst, effective for hydro-isomerization of n-butane at room temperature [Hino et al., 1979] and more relative cracking of long-chain paraffins and has found various uses as a commercial catalyst in many industrial processes. Furthermore, Kantikaneni et al. [1996] also observed the effectiveness of HZSM-5 produced more aromatic than silica-alumina and is highly selective of aromatic due to its selective shape property and pore structure while silica-alumina has acidity but no pore structure property. Adding amounts of HZSM-5 to silica-alumina increased acidity and selective shape property of hybrid catalyst due to the presence of HZSM-5 which implied increased deoxygenation by dehydration [Adjaye et al., 1996; Charusiri et al., 2003]. It seems that the addition of HZSM-5 to silica-alumina was a route to modify performance of catalytic cracking to aromatic fuels and could be increased more than if only using silica-alumina. The objective of this research was to study and investigate the effect of temperature, pressure, time and types of super acid catalysts such as HZSM-5, Sulfated Zirconia and their hybrid catalysts on the liquid yield conversion as transportation fuels and their associated products distribution such as gasoline, kerosene, gas oil, and unwanted long chain hydrocarbon.

^{*}To whom correspondence should be addressed.
E-mail: Witchakorn.C@Chula.ac.th

Table 1. Analysis of used vegetable oil compared with the composition of fresh vegetable oil

Composition of fatty acid		Fresh oil	Used oil
C12:0	Lauric acid	1.58	0.32
C14:0	Myristic acid	1.35	0.93
C16:0	Palmitic acid	43.39	38.38
C18:0	Stearic acid	1.34	4.00
C20:0	Arachidic acid		0.34
Total saturated fatty acid		48.26	43.97
C16:1	Palmitoleic acid		0.25
C18:1	Oleic acid	41.00	45.59
C18:2	Linoleic acid	10.10	10.03
C18:3	Linolenic acid	0.41	0.16
Total unsaturated fatty acid		51.24	56.03

EXPERIMENTAL

1. Raw Material

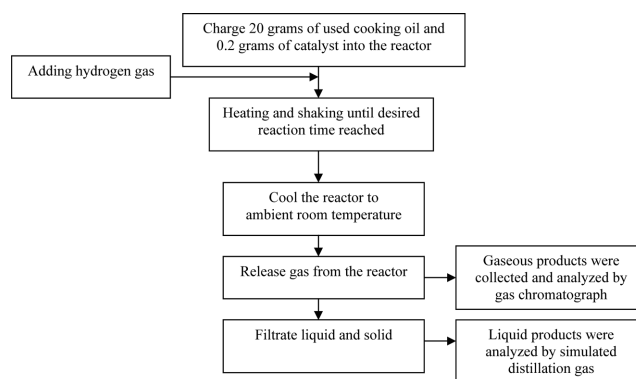
Used vegetable oil was obtained from fried chicken fast food shop in Bangkok, Thailand. It consisted mainly of total saturated fatty acid 43.97% and total unsaturated fatty acid 56.03%; AOCS 1993Ce2-66Ce1-62 method is American Oil Chemist Society's standard used to determine the composition of fatty acid, which is shown in Table 1. Moreover, the analysis of used vegetable oil before cracking using the simulated distillation gas chromatograph showed a composition only of gas oil fraction of 16 wt% and long residues of 84 wt% whereas no composition of gasoline and kerosene.

2. Catalysts

HZSM-5 powder micro porous catalyst with a ratio of Si/Al 40 and surface areas were obtained by application of the Brunauer-Emmett-Teller (BET) procedure of 393 m²/gram, while Sulfated Zirconia as a commercial powder catalyst in range of 60-70 wt% metal support with surface area of 133 m²/gram. Moreover, hybrid catalysts were prepared by thoroughly physically mixing in various ratios of HZSM-5 and Sulfated Zirconia. In the ratio 0.1 : 0.9, 0.3 : 0.7, 0.5 : 0.5, and 0.8 : 0.2 the surface areas were determined by BET procedure at range of 191 m²/gram to 385 m²/gram. At the ratio of 0.3 HZSM : 0.7 Sulfated Zirconia has the highest BET surface area about 385 m²/gram.

3. Experiment Procedures

20 grams of used vegetable oils was put in 316-stainless steel cylindrical micro-reactor, volume of 70 cm³. 0.2 grams of catalyst was added and hydrogen gas was supplied from a hydrogen tank to fill the inside of the reactor. The reactor was constructed to a reaction unit, with injection heater and insulator. The reactor was heated from the ambient room temperature to desired temperature and maintained at the desired temperature for all reaction times. The reaction temperature was controlled by a programmable temperature controller with K-type thermocouple used as a temperature detector. After the reaction was finished, the reactor was cooled to 30 °C or ambient room temperature to prevent the effect of temperature gradient and solidification of residual oil. The liquid product was collected by vacuum filtration to separate the liquid oil products from solids. The liquid oil products were analyzed by using a simulated distillation gas chromatograph (Variance Model CP-3800) by ASTM

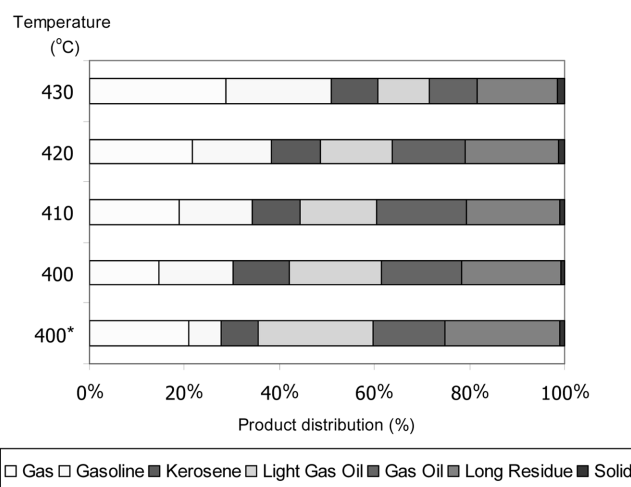
**Fig. 1. Schematic diagram for the catalytic cracking of used vegetable oil.**

2887-D86 method on a capillary glass column with FID detector. The oven temperature was programmed at a heating rate of 10 °C/minutes in range of 30-320 °C. The liquid oil compositions were defined according to the boiling point range of the petroleum products; the liquid products with distillate fraction from C5 to materials boiling at about 200 °C are called gasoline; kerosene boils from 200 to 250 °C; diesel fuel or so called gas oil boiling range is from 250 to 350 °C, and long residue more over 375 °C was classified to long residue.

RESULTS AND DISCUSSION

1. Performance of HZSM-5 Catalyst

The previous work [Charusiri et al., 2003] was to study the conversion of used vegetable oil to liquid fuels over HZSM-5 as a catalyst using the 2^k design of experiment considering the factors which were mainly effecting the conversion of used vegetable oil to gasoline and other chemical fractions. We found that temperature and the time of reaction were mainly significant to the yield of gasoline fraction in the amount of 30%, while initial pressure of hydrogen gas only promoted hydrogenation and insignificantly to the yield and

**Fig. 2. The product distribution on the effect of temperature where initial pressure 10 bars, time of reaction 60 minutes over HZSM-5 (*: without catalyst).**

selectivity of gasoline fraction. Fig. 2 shows the effect of temperature, in the blank run showing the result of cracking without catalyst. The fraction of gases was more than the other run with the catalyst 20.88 wt% of gases shown in Fig. 2, whereas gasoline fraction was only 6.74 wt%. It seems that in the first step thermal cracking process affected the long chain hydrocarbon cracking, removing CO_2 from triglyceride. Temperature is the factor which mainly influenced the initiation of the gaseous products. The liquid yield was decreased with an increase of temperature, whereas the yield of gasoline fraction increased with increase of temperature because the higher temperature (400°C) accelerated the thermal cracking [Kantikaneni et al., 1995; Adjaye et al., 1996] and hence changing the long chain of a hydrocarbon molecule from thermal cracking into a middle hydrocarbon molecule such as kerosene and gas oil. Thereafter kerosene and gas oil were catalytically cracked at the surface of HZSM-5, converting them into gasoline and gaseous fuel (normally C_1 - C_4). It can be identified as deoxygenation cracking and aromatization with H-Transfer from catalytic cracking processes; deoxygenation can occur from decarboxylation and dehydration regarding the primary cracking of triglyceride, which is assumed to occur predominantly within the internal pore structure [Kantikaneni et al., 1995; Idem et al., 1997; Twaiq et al., 2000]. The possibility is that the initial fragmentation can occur on the external surface of zeolite and followed by diffusion into the pore. The subsequent reaction, such as cyclization, isomerization, or hydrogen transfer leads to the formation of aromatic hydrocarbon [Idem et al., 1997]. On the contrary the total solids increased with the reaction time, which meant that coking also occurred during the same reaction time. When the temperature reached 430°C , a large amount of gaseous products were observed to increase substantially. It seemed that when higher temperature was used, light hydrocarbon could be cracked more, because thermal cracking was faster than catalytic cracking. The result of this effect showed that temperature of 430°C gave the appropriate fraction of gasoline and a large fraction of light gaseous hydrocarbon.

Fig. 3 shows the initial effect of hydrogen gas on the products distribution. The catalytic cracking takes place very well given the

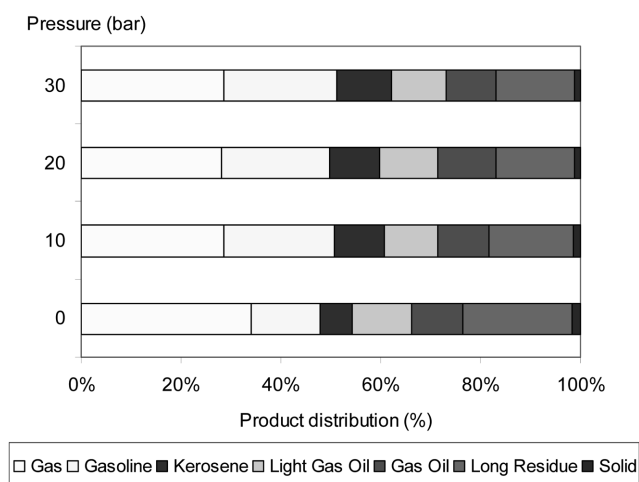


Fig. 3. The product distribution on the effect of initial of hydrogen pressure at temperature 430°C time of reaction 60 minutes over HZSM-5.

pressure of hydrogen. Normally, HZSM-5 gave protons from the structural surface of zeolite to the long chain hydrocarbon for cracking and this hydrogen was compensated at the surface by hydrogen feed, but the effect of initial hydrogen pressure was insignificant with increasing pressure. The initial hydrogen pressure was responsible for the catalytic cracking step. It was noticed that when the pressure was increased, the yields of gasoline, kerosene, light gas oil and small solids also increased. In both cases the initial pressure was high enough so that similar results were reached. It seemed a pressure of 10 bars was enough to give gasoline fraction amounting to 22.15%. The time of reaction contributed mainly to the liquid yield and product distribution; Fig. 4 shows that the yield of gasoline increased with increasing reaction time from 45-60 minutes and decreased with decreasing reaction time from 75-90 minutes. It seemed the temperature was mainly affecting the thermal cracking of long chain hydrocarbon molecules into light molecules, and continued cracking led to a light hydrocarbon gaseous product with

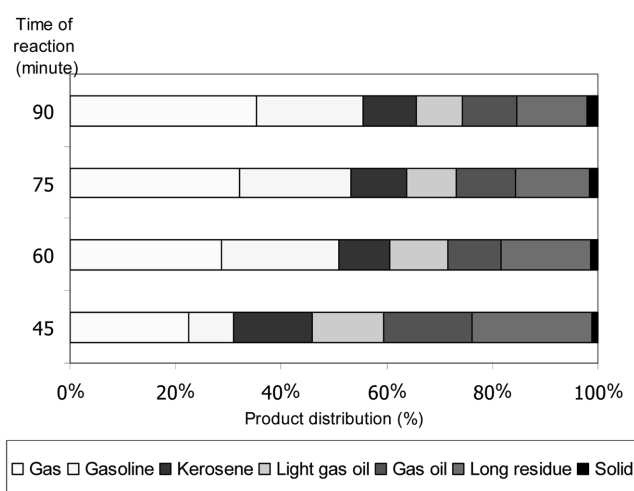


Fig. 4. The product distribution on the effect of time of reaction at temperature 430°C initial pressure of hydrogen gas 10 bars over HZSM-5.

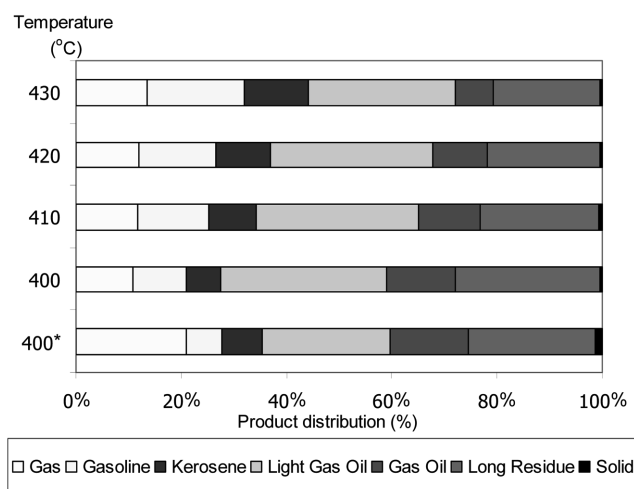


Fig. 5. The product distribution on the effect of temperature where initial pressure 10 bars, time of reaction 60 minutes over Sulfated Zirconia (*: without catalyst).

increasing the reaction time. The result of increased reaction time shows that the gaseous products increased, whereas the product distribution such as gasoline, kerosene, light gas oil and gas oil decreased. The time of reaction was found to favor aromatic hydrocarbon formation and lead to formation of light gaseous products predominantly. The effect of reaction time shows the results in greater amounts of aromatic and gasoline boiling range fraction which also increased with increase in reaction temperature reaching a maximum of 430 °C and later decreased. Furthermore, the gasoline fraction represents the boiling range 0-200 °C fraction, which increased with increase in the reaction of time. At the conditions of temperature 430 °C, initial hydrogen pressure of 10 bars and reaction time of 60 minutes, the liquid yield of 69.94% was obtained with the composition of gasoline 22.15%, kerosene 9.85%, light gas oil 10.84%, gas oil 10.12% and long chain hydrocarbon molecule 16.98% whereas the light gaseous by product of 28.66% and solids of 1.40% were obtained.

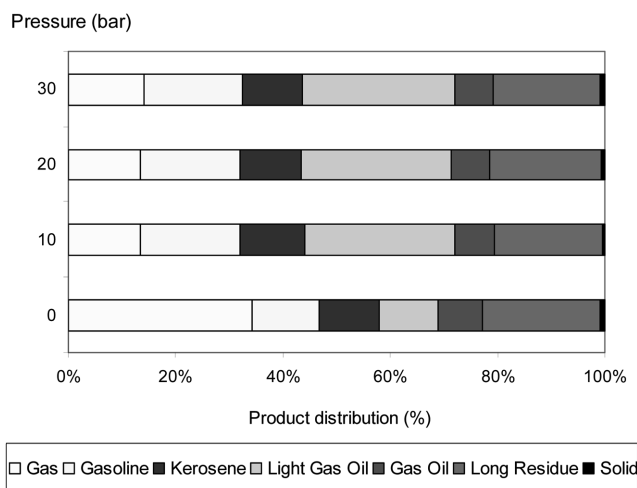


Fig. 6. The product distribution on the effect of initial of hydrogen pressure at temperature 430 °C time of reaction 60 minutes over Sulfated Zirconia.

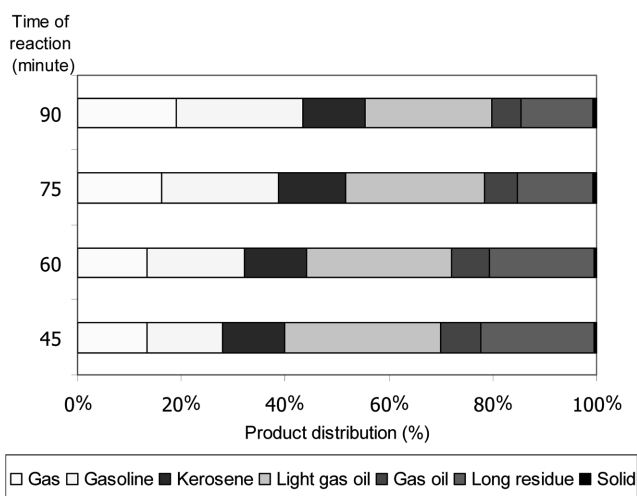


Fig. 7. The product distribution on the effect of time of reaction at temperature 430 °C initial pressure of hydrogen gas 10 bars over Sulfated Zirconia.

2. Performance of Sulfated Zirconia

Sulfated metal oxides have been widely studied as potential solid acid catalysts, such as super acid for isomerization, esterification and cracking [Hino et al., 1979; Katada et al., 2000; Zhou et al., 2003]. However, when compared with conventional catalysts such as zeolite or HZSM-5, Sulfated Zirconia has relatively low hydrothermal stability [Hino et al., 1979], weaker acidity, lower surface area, and no pore selective properties [Katada et al., 2000]. This study investigated the effect of temperature on the catalytic cracking of used vegetable oil over Sulfated Zirconia which was performed by operating at various reaction temperatures: 400, 410, 420 and 430 °C using 0.20 grams of Sulfated Zirconia as catalyst under fixing hydrogen pressure of 10 bars and reaction time of 60 minutes. Fig. 5 shows the effect of temperature which mainly affected the liquid yields. Increasing the fraction of gasoline with temperature ranges 400-430 °C thus causing thermal cracking and hydrocracking, which changed long chain of triglyceride into kerosene and gas

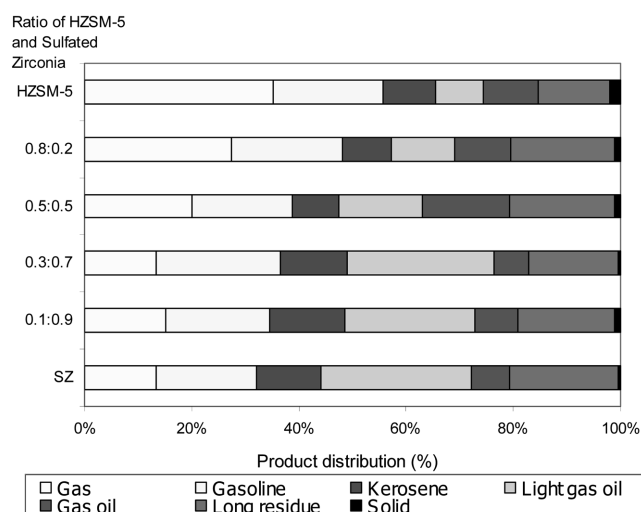


Fig. 8. The product distribution on the effect of ratio of hybrid catalyst at temperature 400 °C initial pressure of hydrogen gas 10 bars and time of reaction at 60 minutes.

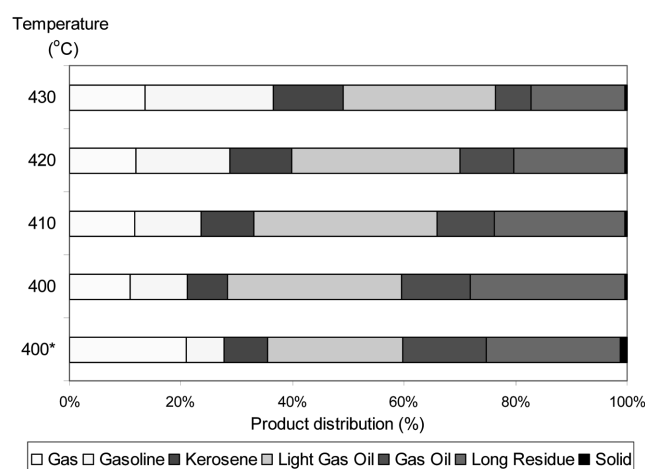


Fig. 9. The product distribution on the effect of temperature where initial pressure 10 bars, time of reaction 60 minutes over 0.3 : 0.7 HZSM-5 : Sulfated Zirconia (*: without catalyst).

oil. It was then catalytically cracked over Sulfated Zirconia, which converted it into gasoline and light gaseous products. At temperature of 430 °C, the used vegetable oil was converted to a gasoline fraction of about 18.61% with light gaseous products of about 13.46%. The effect of initial hydrogen pressure was insignificant with increasing pressure; Fig. 6 shows the effect of variation of hydrogen pressure ranging from 10-30 bars with production distribution remaining almost unchanged in the product distribution. Meanwhile the product distribution shows the fraction of gasoline was mainly affected by the reaction time (Fig. 7). Long chain hydrocarbon molecule was cracked to gasoline and kerosene fraction from thermal and catalytic cracking and continued to be converted to light gaseous products by thermal cracking processes. If reaction time was maintained, the conversion continued into light gaseous products by thermal cracking. We found that the fraction of gases continued to increase when the reaction time reached 75 minutes to 90 minutes.

3. Performance of Hybrid Catalysts

The catalytic properties of HZSM-5 are strong acid sites, prop-

erties of pore size affected selective shape [Kantikaneni et al., 1995; Satterfield, 1991; Idem et al., 1997] which was beneficial for cracking and aromatization, whereas Sulfated Zirconia had relatively low hydrothermal stability and weaker acidity compared with HZSM-5 [Katada et al., 2000]. The hybrid catalysts were prepared by thoroughly physically mixing various ratios of HZSM-5 and Sulfated Zirconia in the ratio 0.1 : 0.9 to 0.8 : 0.2 with temperature fixed at 400 °C initial hydrogen pressure of 10 bars and reaction time of 60 minutes. Fig. 8 shows the effect of ratio of HZSM-5 and Sulfated Zirconia used as catalysts for the cracking of used vegetable oil. It seemed that the ratio of hybrid catalyst had significantly affected the product distribution. Due to the physical mixing of catalysts the implication was that by adding HZSM-5 to Sulfated Zirconia, it is possible to substantially increase the aromatic hydrocarbon yield. At the ratio 0.3 : 0.7 of HZSM-5 and Sulfated Zirconia, 23.07 wt% of gasoline and 12.48 wt% of kerosene were obtained. The high gasoline fraction with HZSM-5 was due to its selective shape and pore structure [Idem et al., 1997; Twaiq et al., 1999] which are known

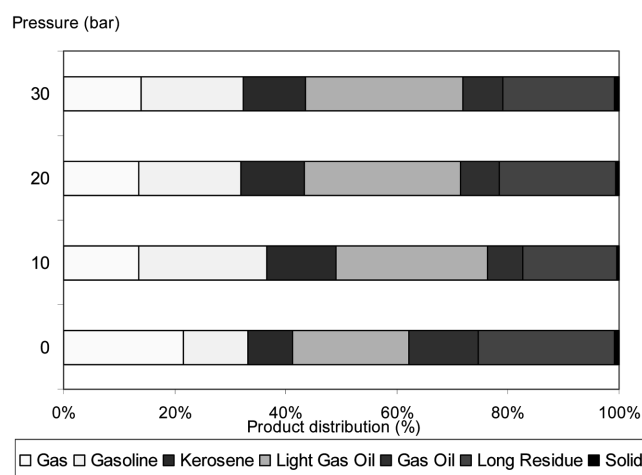


Fig. 10. The product distribution on the effect of initial of hydrogen pressure at temperature 430 °C time of reaction 60 minutes over 0.3 : 0.7 HZSM-5 : Sulfated Zirconia.

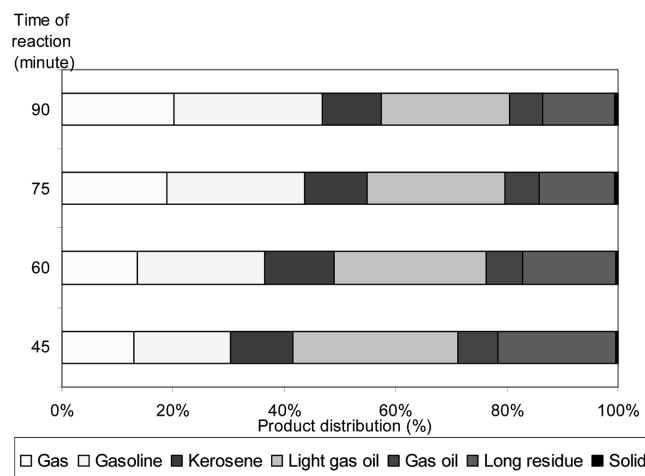


Fig. 11. The product distribution on the effect of time of reaction at temperature 430 °C initial pressure of hydrogen gas 10 bars over 0.3 : 0.7 HZSM-5 : Sulfated Zirconia.

Table 2. The product distribution of catalytic cracking of used vegetable oil over HZSM-5 (* not use catalyst: blank run)

Temp (°C)	Pressure (bar)	Time (min)	Composition (%wt)						
			Gas	Gasoline	Kerosene	Light gas oil	Gas oil	Long residue	Solid
400*	10	60	20.88	6.74	7.93	24.18	15.02	24.12	1.13
400	10	60	14.63	15.57	11.83	19.32	16.98	20.83	0.84
410	10	60	18.81	15.52	9.99	16.03	18.95	19.77	0.93
420	10	60	21.63	16.76	10.15	15.15	15.4	19.64	1.27
430	10	60	28.66	22.15	9.85	10.84	10.12	16.98	1.4
430	0	60	34.14	13.71	6.43	11.84	10.29	21.95	1.64
430	10	60	28.66	22.15	9.85	10.84	10.12	16.98	1.4
430	20	60	28.2	21.55	10.12	11.6	11.57	15.82	1.14
430	30	60	28.48	22.82	10.75	10.99	10.03	15.68	1.25
430	10	45	22.48	8.54	14.75	13.65	16.7	22.73	1.15
430	10	60	28.66	22.15	9.85	10.84	10.12	16.98	1.4
430	10	75	32.05	21.23	10.58	9.24	11.35	13.91	1.64
430	10	90	35.23	20.34	10	8.84	10.12	13.46	2.01

to enhance cyclization and aromatization while Sulfated Zirconia has strong acidity but no pore structure property [Hino et al., 1979; Katikaneni et al., 1995; Twaiq et al., 1999]. Hence, the cracking over HZSM-5 was added to Sulfated Zirconia in order to enhance its cracking activity. There was increased acidity of the hybrid catalyst due to the presence of HZSM-5 which implied increased deoxygenation by dehydration [Katikaneni et al., 1995; Adjaye et al., 1996; Idem et al., 1997]. Furthermore, hybrid catalyst was obtained with physical mixing of HZSM-5 and Sulfated Zirconia, which showed mostly aromatic and small aliphatic hydrocarbon. It seems that the addition of HZSM-5 to Sulfated Zirconia was a route to modify performance of catalytic cracking to aromatic fuels and could be

increased more than if only Sulfated Zirconia was used. In the temperature range of 400-430 °C the product distribution from the thermal cracking in the first step and catalytic cracking was mainly converted into liquid products. Fig. 9 shows that the temperature mainly affected the catalytic conversion of liquid production into gasoline fraction. At 430 °C, the highest gasoline fraction was about 23.07 wt%, whereas the yield of gaseous product was much lower over the hybrid catalyst as compared to that of HZSM-5 or Sulfated Zirconia. In addition, the initial amount of hydrogen gas was negligible. Fig. 10 shows the initial hydrogen pressure where the product distribution was obtained in vicinity in range of initial pressure of 10-30 bars. Increasing the reaction time of 45-60 minutes, the frac-

Table 3. The product distribution of catalytic cracking of used vegetable oil over Sulfated Zirconia (* not use catalyst: blank run)

Temp. (°C)	Pressure (bar)	Time (min)	Composition (%wt)						
			Gas	Gasoline	Kerosene	Light gas oil	Gas oil	Long residue	Solid
400*	10	60	20.88	6.74	7.78	24.18	15.02	24.12	1.28
400	10	60	10.87	10.04	6.51	31.57	13.04	27.58	0.40
410	10	60	11.66	13.60	8.89	30.84	11.89	22.49	0.63
420	10	60	11.93	14.68	10.32	30.82	10.36	21.43	0.46
430	10	60	13.46	18.61	12.01	27.99	7.25	20.14	0.54
430	0	60	34.14	12.71	11.13	10.84	8.29	21.95	0.94
430	10	60	13.46	18.61	12.01	27.99	7.25	20.15	0.54
430	20	60	13.50	18.41	11.48	28.07	7.01	20.82	0.71
430	30	60	13.99	18.46	11.07	28.46	7.14	20.05	0.83
430	10	45	13.38	14.48	12.15	29.94	7.69	21.86	0.50
430	10	60	13.46	18.61	12.01	27.99	7.25	20.14	0.54
430	10	75	16.18	22.54	12.95	26.69	6.48	14.54	0.62
430	10	90	19.07	24.38	11.98	24.35	5.70	13.86	0.65

Table 4. The product distribution of catalytic cracking of used vegetable oil over Hybrid catalyst (Various ratio of HZSM-5 : Sulfated Zirconia; * not use catalyst: blank run)

Temp. (°C)	Pressure (bar)	Time (min)	Ratio HZSM-5: SZ	Composition (%wt)						
				Gas	Gasoline	Kerosene	Light gas oil	Gas oil	Long residue	Solid
400*	10	60	-	20.88	6.74	7.93	24.18	15.02	24.12	1.13
400	10	60	0.3:0.7	10.87	10.27	7.29	31.20	12.21	27.85	0.32
410	10	60	0.3:0.7	11.66	12.05	9.45	32.83	10.21	23.43	0.37
420	10	60	0.3:0.7	11.93	16.79	11.10	30.13	9.65	20.04	0.36
430	10	60	0.3:0.7	13.46	23.07	12.48	27.31	6.42	16.83	0.43
430	0	60	0.3:0.7	21.66	11.45	8.08	21.05	12.44	24.38	0.94
430	10	60	0.3:0.7	13.46	23.07	12.48	27.31	6.42	16.83	0.43
430	20	60	0.3:0.7	13.50	18.41	11.48	28.07	7.01	20.82	0.71
430	30	60	0.3:0.7	13.99	18.46	11.07	28.46	7.14	20.05	0.83
430	10	45	0.3:0.7	12.82	17.55	11.06	29.81	7.22	21.04	0.50
430	10	60	0.3:0.7	13.46	23.07	12.48	27.31	6.42	16.83	0.43
430	10	75	0.3:0.7	18.75	24.99	11.06	24.84	6.25	13.54	0.57
430	10	90	0.3:0.7	20.20	26.57	10.65	23.02	6.05	12.88	0.63
430	10	60	SZ	13.46	18.61	12.01	27.99	7.25	20.14	0.54
430*	0.3	60	-	15.15	19.43	14.01	24.23	8.04	18.01	1.13
430	0.05	60	0.3:0.7	13.46	23.07	12.48	27.31	6.42	16.83	0.43
430	0.1	60	0.5:0.5	19.99	18.84	8.63	15.49	16.32	19.58	1.15
430	0.2	60	0.8:0.2	27.45	20.62	9.13	11.84	10.46	19.43	1.07
430	0.1	60	HZSM-5	35.23	20.34	10.00	8.84	10.12	13.46	2.01

tion of gasoline was observed to be much higher than the dose obtained by hybrid catalysts and it dropped after the reaction time had reached 75 minutes because the light hydrocarbon molecule from catalytic cracking continued its cracking process into light gaseous products. The result of increasing reaction time more than 75 minutes showed that gasoline and gaseous increased (Fig. 11) whereas the product distribution such as kerosene, light gas oil, gas oil and long chain residue decreased. Actually, the gaseous products were lower when compared to that of HZSM-5 or Sulfated Zirconia. The product distribution of catalytic cracking of used vegetable oil when hybrid catalyst was used with various factors found that the catalytic cracking of used vegetable oil with a hybrid catalyst ratio of 0.3 : 0.7 HZSM-5 : Sulfated Zirconia gives the highest fraction of gasoline at temperature of 430 °C, initial hydrogen pressure of 10 bars and reaction time of 90 minutes. The product distribution obtained the liquid yield amount of 79.17 wt% with the composition of gasoline 26.57 wt%, kerosene 10.65 wt%, light gas oil 23.02 wt%, gas oil 6.05 wt% and long chain residues about 12.88 wt%.

CONCLUSIONS

1. The cracking over HZSM-5 was added to Sulfated Zirconia in order to enhance its activity, increasing acidity and the property of pore structure, which was a route to upgrading hybrid catalyst and it was more effective in aromatization of the conversion of used vegetable oil to light hydrocarbon fuels.

2. Catalytic activity of used vegetable oil with hybrid catalyst containing a ratio of 0.3 HZSM-5 and 0.7 Sulfated Zirconia was prepared by thoroughly physical mixing giving the highest selectivity of gasoline of 26.57 wt% at the temperature of 430 °C, hydrogen pressure at 10 bars, and reaction time of 90 minutes. The trend of light gaseous hydrocarbon was observed to be much lower with the hybrid catalyst as compared to that of HZSM-5 or Sulfated Zirconia.

ACKNOWLEDGMENTS

The financial support by Energy Research Institute of Chulalongkorn University and Thailand Energy Conservation Promotion Fund of the Energy Policy and Planning Office were gratefully acknowledged. The assistance provided by Department of Chemical Technology Faculty of Science, Chulalongkorn University for obtaining laboratory and analysis of the liquid product composition is also acknowledged.

REFERENCES

- Adjaye, J. C., Adjaye, S. P. R. and Bakhshi, N. N., "Catalytic conversion of a biofuel to hydrocarbons: effect of mixture of HZSM-5 and silica-alumina catalysts on product distribution," *Fuel Processing Technology*, **48**, 115 (1996).
- Billaud, F., Guitard, Y., Tran Minh, A. K., Zahraa, O., Lozano, P. and Piock, D., "Kinetic studies of catalytic cracking of octanoic acid," *Journal of Molecular Catalysis A: Chemical*, **192**, 281 (2003).
- Charusiri, W., "Catalytic conversion of used vegetable oil to liquid fuels over HZSM-5 and sulfated zirconia," Doctoral Dissertation, Chulalongkorn University (2005).
- Charusiri, W. and Vitidsant, T., "Catalytic cracking of used cooking oil to liquid fuels over HZSM-5," *J. Energy*, **5**, 58 (2003).
- Hino, M., Kaboyashi, S. and Arata, K., "Solid catalyst treated with anion 2 reactions of butane and isobutene catalyzed by zirconium oxide treated with sulfate ion solid super acid catalyst," *J. Am. Chem. Soc.*, **101**(21), 6439 (1979).
- Idem, R. O., Katineni, S. P. R. and Bakhshi, N. N., "Catalytic conversion of canola oil to fuels and chemicals: roles of catalysts acidity, basicity and shape selectivity on product distribution," *Fuel Processing Technology*, **51**, 101 (1997).
- Katada, N., Endo, J., Notsu, K., Yasunobu, N., Naito, N. and Niwa, M., "Superacidity and catalytic activity of sulfated zirconia," *Journal of Physical Chemistry*, **104**, 10321 (2000).
- Paul, B. V., *Fluid catalytic cracking with zeolite catalysts*, USA, Marcel Dekker (1979).
- Satterfield, C. N., *Heterogeneous catalysis in industrial practice* (2nd ed.), USA, McGraw-Hill (1991).
- Twaiq, F. A., Zabidi, N. A. M. and Bhatia, S., "Catalytic conversion of palm oil to hydrocarbons : Performance of various zeolite catalysts," *Ind. Eng. Chem. Res.*, **38**, 3230 (1999).
- Twaiq, F. A., Zabidi, N. A. M., Mohamed, A. R. and Bhatia, S., "Catalytic conversion of palm oil over mesoporous aluminosilicate MCM-41 for the product of liquid hydrocarbon fuels," *Fuel Processing Technology*, **84**, 105 (2003).
- Yadav, G. D. and Nair, J. J., "Sulfated zirconia and its modified versions as promising catalysts for industrial processes," *Microporous and Mesoporous Materials*, **33**(1), 1 (1999).
- Zhou, Z., Zhang, Y., Tieney, J. W. and Wender, I., "Hybrid zirconia catalysts for conversion of Fischer-Tropsch waxy products to transportation fuels," *Fuel Processing Technology*, **83**, 67 (2003).