Bio-Gasoline Production from Bio-Diesel via Catalytic Cracking Reaction on Platinum Zeolite Catalyst

Nantawat Usomboon, Malee Santikunaporn, and Suchada Butnar

Abstract— *The catalytic cracking of bio-diesel has been investigated in a continuous fixed bed reactor over Pt/zeolites. Three different zeolites (Y, BETA and MOR) were used as supports impregnated with 1 wt% of platinum metal. The reacations were carried out in hydrogen flow under the following conditions, the temperature range of 573 K - 653 K, and WHSV of 22.9-43.7 h*$^{-1}$*. The results showed that these composite catalysts have the potential to be used in bio-gasoline production. At 613 K, the Pt/MOR showed complete conversion of bio-diesel to cracking products. The Pt/Y showed not only high conversion, but also high selectivity to bio-gasoline when compared to Pt/BETA. In addition, the conversions were strongly dependent on both temperature and WHSV.*

Keywords— **Composite catalyst; bio-diesel; catalytic cracking.**

1. INTRODUCTION

The rapid increase of energy consumption and the environmental concerns have made biofuels gain more attention over last decade. Biofuel or blend of biofuels can be substituted for regular fuel in all vehicle types. In addition, it has been literally reported that the performance and combustion of bio-fuels are as good as regular fuels [1].

Bio-gasoline, one of alternative fuels used in gasoline engines, is hydrocarbon biofuel produced from biomass. While much attention has been given to the use of biomass to produce ethanol, methods are currently being developed for producing hydrocarbon fuel from biomass. This is because the hydrocarbon biofuels are energy equivalent to and chemically the same as petroleum-based fuels. Many novel pathways to produce bio-gasonline have been studied. However, it is literally reported that catalytic cracking process would be the potential route to provide clean fuel [2-4]. The catalytic cracking process shows several clear advantages in comparison with pyrolysis, fermentation and transesterification processes. The reaction temperature for the catalytic cracking process is lower than pyrolysis. The production of ethanol via fermentation requires a necessary pretreatment of feedstock with processes such as saccharification and hydrolysis. In addition, fermentation requires a much longer reaction time than the catalytic cracking process. Transesterification is only applied to the production of biodiesel whereas catalytic cracking can be applied for the production of kerosene, gasoline and diesel [4-5].

The key factor for the catalytic cracking reaction is the choice of catalysts. It is well-known that zeolites show excellent efficiency on catalytic cracking reactions. The important property of zeolites is the shape selectivity that controls product distribution in the process. Activity and selectivity of zeolites are managed by several factors such as acidity, pore size, pore distribution and pore shape. It is reported that cracking activity decreases with decreasing acidity [3,6]. For the catalytic cracking of palm oil on the composite zeolites, the maximum yield of gasoline and conversion obtained on REY composited with HZSM-5 showed 95.9 wt% conversion and 40.9 wt% gasoline yield due to high acidity [6]. For the meso-porous material MCM-41 and SBA-15, the similar results were obtained [7-8]. The effect of acidity on activity has been confirmed by Junming et al. [9]. The main products from the catalytic cracking over basic catalysts were liquid hydrocarbons in diesel range. As for the effect of pore size on selectivity, the smaller pore size provided the shorter chain of products [10].

The aim of the present work is to study the effect of bifunctional catalysts (Pt/HY, Pt/beta and Pt/MOR) on the conversion and selectivity to hydrocarbon products in gasoline range.

2. EXPERIMENTAL SECTION

2.1. FEED

Feed was the mixture of straight chain hydrocarbons containing carbon atoms in range of C15-C18 produced from the hydrodeoxygenation of palm oil. It can be referred to Bio-diesel. The distribution of compounds is reported in Table 1.

2.2. Catalysts

Bifunctional catalysts used in the catalytic cracking of bio-diesel were platinum supported on different zeolites (Y, beta and MOR). All zeolites were supplied from Zeolyst International Corp., USA. The properties of each zeolite are presented in Table 2.

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Table.1 Feed conposition

Component	Chemical structure	wt%	Total (%wt.)
Gasoline (C7-C10)	Straight chain	-	-
	Branched chain	-	
Kerosene (C11-C14)	Straight chain	1.1	1.1
	Branched chain	-	
Diesel (C15-C18)	Straight chain	98.7	98.8
	Branched chain	0.1	

Table 2 Zeolite properties

Properties	Y	BETA	MOR
Pore size (nm)	0.8	0.56 x 0.74	0.4
Surface area (m^2/g)	730	710	500
Si/Al ratio	5.1	38	4-12

2.3 Catalyst Preparation

Catalysts were prepared by an impregnation technique with 0.1 wt% of platinum metal. The precursor was tetraammineplatinum(II) nitrate ($Pt(NH_3)_4(NO_3)_2$, 99.995% metals basis) obtained from Aldrich Corp. After the impregnation, catalysts were dried at 393 K for 12 h and then calcined in air at 773 K for 6 h.

2.4 Activity Test

The cracking reaction of bio-diesel was performed over Pt/zeolites at 2.76 kPa, 22.9 h^{-1} and 573-653K. Fig. 1 shows the experimental setup for the catalytic cracking reaction. The catalyst was in a powder form in order to avoid mass transfer effect. In each run, the desired amount of catalyst was packed in the middle of reactor between quartz wool. The ceramic balls were placed above and below the catalyst bed. Before testing, catalyst was reduced under hydrogen flow at 723 K for 4 h. Subsequently, feed was injected by a syringe pump at the desired rate into the reactor. The temperature was monitored by a thermocouple positioned at the center of the catalyst bed. Hydrogen was used as a carier gas when the reaction takes place. The products then were cooled in a cooler. The condensed liquid was collected and analyzed by a gas chromatography equipped with a FID detector.

2.5 Product Analysis

Organic liquid products (OLP) were analyzed and categorized into 3 types based on molecular sizes and boiling temperatures: gasoline fraction (C7-C10), kerosene fraction (C11-C14) and diesel fraction (C15-C18). The standard properties are shown in Table 3.

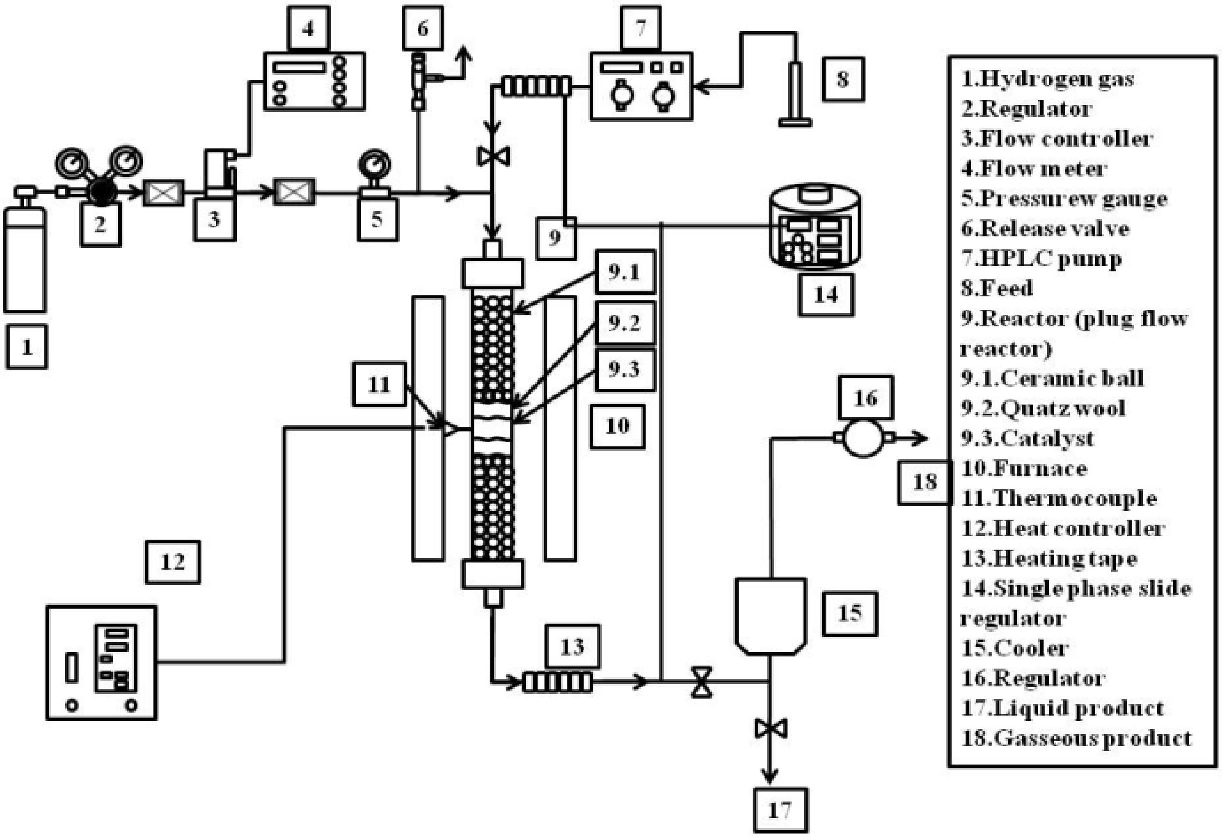


Fig. 1 Schematic reaction.

Table 3 Fuel standard

Property	**Gasoline**[(a)]	**Kerosene**[(b)]	**Diesel**[(a)]
Chemical formula	C4 - C12	C8 - C16	C8 - C25
Boiling point (K)	299.66 - 528	392 - 573	453 - 613
Freezing point (K)	-40	Below 233	233 - 243
Auto ignition temp. (K)	530.22	No report	~588.66
Flash point (K)	230.22	311	333 - 353
Density (kg/m^3 at 288 K)	718.96 – 778.87	775 - 840	848.25
Viscosity at 253 K (mm^2/s)	0.8 – 1.0	8	9.0 – 24.0
Octane no. (RON/MON)	88 – 98/80 - 88	-	-
Cetane no.	-	-	40 - 55
Lower heating value (kJ/m^3)	32.3x10^6	n/a	35.8x10^6
Higher heating value (kJ/m^3)	34.6x10^6	n/a	38.3x10^6

a.United state department of energy, www.Energy.gov.

b.Fuel properties – effect on aircraft and infrastructure, Aviation rulemaking advisory committee.

Table 4. Composition of liquid products obtained from the catalytic cracking reaction over various Pt/zeolites. Reaction condition: Temperature 613 K, Pressure 2.76 kPa and WHSV 22.9 h^{-1}.

		Feed	**Catalyst**		
			Pt/Y	**Pt/BETA**	**Pt/MOR**
Conversion (%)		-	78.6	33.4	100
Gasoline (C7-C10)	Straight chain	-	16.9	11.8	57.3
	Branched chain	-	28.5	17.6	42.7
	total	-	45.4	29.4	100
Kerosene (C11-C14)	Straight chain	1.1	3.9	2.1	-
	Branched chain	-	11.9	1.4	-
	total	1.1	15.8	3.5	-
Diesel (C15-C18)	Straight chain	98.7	21.2	65.8	-
	Branched chain	0.1	17.7	1.3	-
	total	98.8	38.9	67.1	-

The catalytic performance was measured in terms of conversion, yield and selectivity to products. The conversion and selectivity are defined as follows:

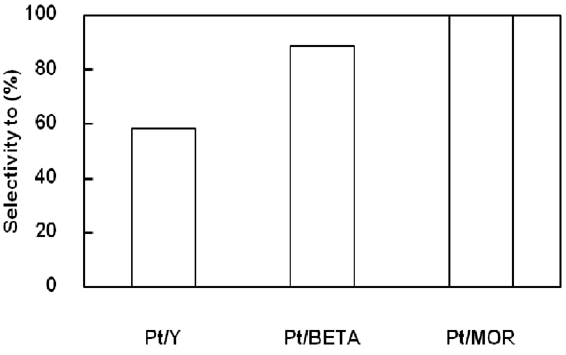
$$conversion\ (\%) = \frac{feed - OLP}{feed} \times 100 \qquad (1)$$

$$selectivity\ to\ A(\%) = \frac{product\ A}{conversion} \times 100 \qquad (2)$$

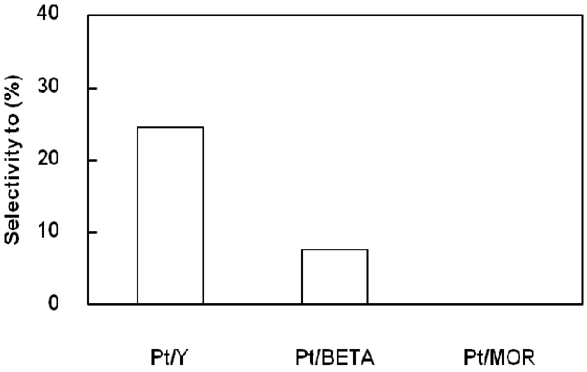
3. RESULTS AND DISCUSSION

The catalytic performance of three different catalysts was studied in terms of conversion and selectivity to products in gasoline fractions. It is known that the quality of gasoline is evaluated based on its octange rating which denotes the percentage by volume of branched-chain in the combustible mixture. In this present work, to investigate on the quality of bio-gasoline, the chemical composition of products in gasoline range was analyzed and classified, according to their molecular structures, into straight-chain and branched-chain hydrocarbons.

Table 4 shows the chemical compositions of feedstock and liquid products obtained from catalytic cracking reactions over Pt/Y, Pt/beta and Pt/MOR under the same reaction condition (2.76 kPa, 613 K and WHSV 22.9 h^{-1}). It was noticed that the Pt/MOR gave the complete conversion and the feedstock was completely converted into gasoline fractions. The Pt/Y gave a higher conversion than the Pt/beta about 2 times. This may be due to their characteristics such as pore size and acidity. As illustraed in Table 2, it is suggested that the pore size of Pt/MOR is the smallest, followed by Pt/BETA and Pt/Y whereas Pt/Y contains a higher acidity than Pt/beta.



(a) Selectivity to gasoline fractions.



(b) Selectivity to kerosene fractions.

Fig. 2 Selectivity to gasoline and kerosene fractions over various catalysts. Reaction conditions: T = 613 K, P = 2.76 kPa, and WHSV = 22.9 h^{-1}.

Fig. 2 represents the selectivities to gasoline and kerosene fractions. It is evident that the highest selectivity to gasoline fraction was obtained when the cracking reaction were tested over Pt/MOR. In contrast, the highest selectivity to kerosene fraction was obtained when the Pt/Y catalyst was used. As mentioned above, the branched-chain structure are preferred to the straight-chain structure due to its knock resistance charactersitic. The ratio of branched-chain hydrocarbons to straight-chain hydrocarbons (B/S ratio) therefore was analyzed and illustrated in Fig. 3. The B/S ratios of the reactions on Pt/MOR, Pt/BETA and Pt/Y catalysts were 0.74, 1.49 and 1.69 respectively. It is implied that the Pt/Y gave the highest yield of branched-chain hydrocarbons.

It is evident that the Pt/BETA and Pt/Y gave the high yield of branched-chain hydrocarbons according to their B/S ratio. Therefore, the catalytic cracking reactions over both catalysts were further studied. To investigate the effect of reaction temperature on the product distribution, the reactions were conducted in a temperature range of 573 K to 653 K. Fig. 4 shows the comparison between the conversions obtained from catalytic cracking on Pt/Y and Pt/BETA. In the presence of both catalysts, the conversion of bio-diesel increases with increasing reaction temperature. It is however obvious that the conversion on the Pt/Y catalyst was higher than that on the Pt/BETA.

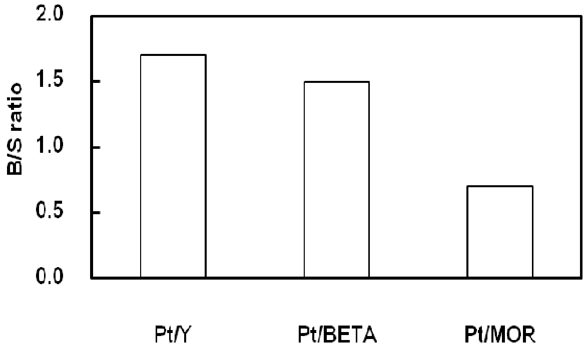


Fig. 3 The ratio of branched chain hydrocarbons to straight chain hydrocarbons in the gasoline fraction at 613 K.

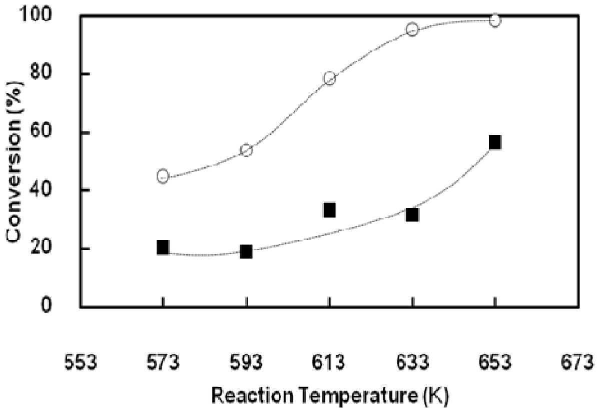
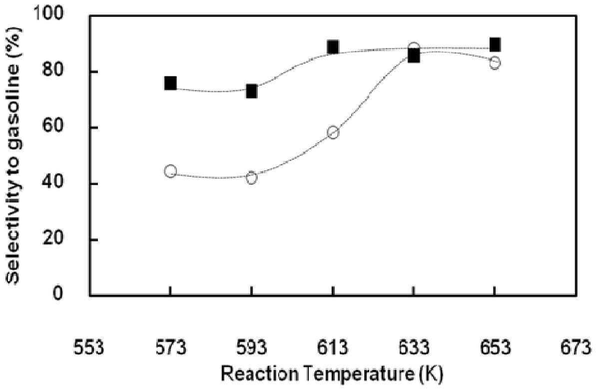
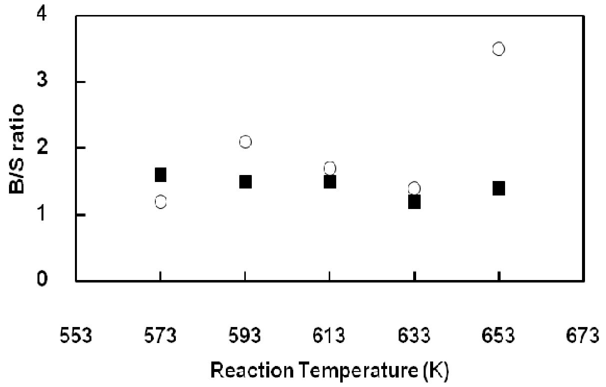


Fig. 4 Conversion obtained from catalytic cracking over Pt/Y and Pt/BETA as a function of temperature. Symbols: (○) for Pt/Y and (■) for Pt/BETA.

Fig 5 shows the effect of reaction temperature on the selectivity and B/S ratio of the cracking reactions. Interestingly, the reactions on both catalysts showed high selectivities to gasoline whereas the B/S ratios were not signifantly dependent on temperature reaction. It therefore may be concluded that the products obtained from the reactions on both catalyst would have the similar octane rating.



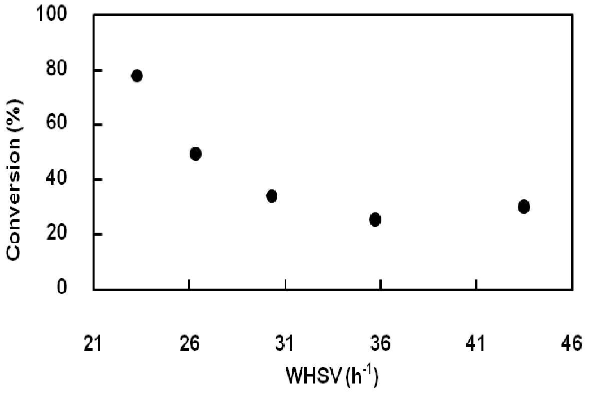
(a) Selectivity to gasoline fraction.



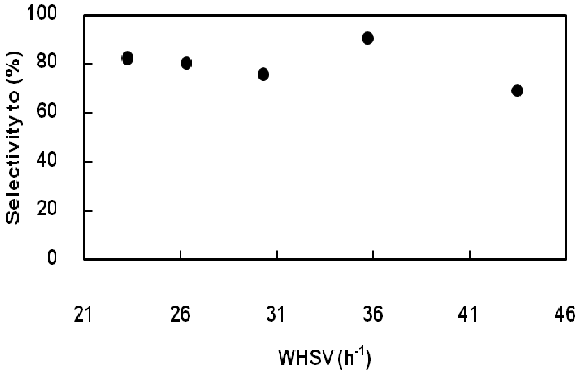
(b) The ratio of branched chain to straight chain hydrocarbon.

Fig. 5 Comparison of selectivity and ratio of branched chain to straight chain hydrocarbon over Pt/Y and Pt/BETA. Reaction conditions: T = 573-653 K, P = 2.76 kPa, and WHSV = 22.9 h^{-1}. Symbols: (○) for Pt/Y and (■) for Pt/BETA.

Finally, focusing on the catalytic activity of Pt/Y, the effect of space velocity were studied The catalyst reactions were conducted in a space velocity range of 23.3 – 43.5 h^{-1}. The conversion and selectivity to gasoline fraction were illustrated in Fig.6. It is evident that the conversion of bio-diesel decreases with increasing WHSV. However, the selectivity to gasoline fraction was independent of the WHSV.



(a) Conversion



(b) Selectivity to gasoline fraction

Fig. 6 Conversion and selectivity to gasoline fraction over Pt/Y catalyst. Reaction condition: T = 613 K, P = 2.76 kPa, and WHSV = 23.3 – 43.7 h^{-1}.

4. CONCLUSION

Bio-gasoline produced from catalytic cracking of bio-diesel was studied over three different zeolites in the continuous packed bed reactor in a temperature range of 573-653 K. Among the three catalysts Pt/MOR showed the highest conversion and yield of gasoline fraction but the lowest B/S ratio. Both Pt/Y and Pt/BETA showed more suitable for this aspect. However, under the studied reaction conditions, the Pt/Y was the most efficient catalyst due to its high conversion and high selectivity to gasoline fraction compared to Pt/BETA.

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REFERENCES

[1] Adrian Zhou, Elspeth Thomson 2009. The development of biofuels in Asia. *Applied Energy* , s11-s20.

[2] Dr.SamaiJai-In. (n.d.). *BiofuelPrograms in Thailand : A Solution for Energy Sufficiency and Poverty Eradication?* URL www.mtec.or.th Access on 14/11/2010

[3] Yee Kang Ong, Subhash Bhatia (2010). The current status and perspectives of biofuel production via catalytic cracking of edible and non-edible oils. *Energy* , 111–119.

[4] Chew T.L and Bhatia S. 2008. Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery. *Bioresource Technology*, 99(17):7911–22.

[5] Klass DL. (1998). Biomass for renewable energy, fuels, and chemicals. San Diego, *CA: Academic Press*.

[6] Bhatia, S. 1999. Catalytic Conversion of Palm Oil to Hydrocarbons: Performance of Various Zeolite Catalysts. *Ind. Eng. Chem. Res.*, 3230-3237.

[7] Farouq A.A. Twaiq, A. M. (2004). Performance of composite catalysts in palm oil cracking for the production of liquid fuels and chemicals. *Fuel Processing Technology* , 1283– 1300.

[8] Bhatia, S. (2003). Catalytic conversion of palm oil over mesoporous aluminosilicate MCM-41 for the production of liquid hydrocarbon fuels. *Fuel Processing Technology* , 105-120.

[9] Xu Junming, J. J. (2010). Biofuel production from catalytic cracking of woody oils. *Bioresource Technology* , 5586–5591.

[10] Yean-Sang Ooi, S. B. (2007). Aluminum-containing SBA-15 as cracking catalyst for the production of biofuel from waste used palm oil. *Microporous and Mesoporous Materials* , 310–317.