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Bio-gasoline production from SSHCs via catalytic cracking reaction

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Abstract

This research was focused on the role zeolites in the catalytic cracking process for the production of bio-gasoline by using synthetic straight-chain hydrocarbons (SSHCs) as feed stock in the continuous plug flow reactor. Three different zeolites (Y, BEA and MOR) were used as support impregnated with platinum metal. Catalytic activity of each catalyst was determined at various reaction conditions, temperature and space velocity. The results showed that these catalysts had potential in the production of bio-gasoline. A Pt/MOR showed the most activity followed by Pt/Y and Pt/BEA. However, selectivity to gasoline range of Pt/BEA was higher than Pt/Y.

1. Introduction

Biofuels production for transportation has gain more and more interest in the recent year due to the depletion of fossil fuel and pollution from fossil fuel that cause climate change to the world. Thailand's also looking into biofuels. The government of Thailand has a two-phase gasohol program (phase 1 started in 2004) in order to raise the production of biofuels by using plantation development of palm and jatropha as a key element [1]. As Thailand is the world 3rd biggest exporter for palm oil this makes Thailand one of the most potential for biofuels producer in Asia [1-2]. To ensure sufficient feedstock Thailand must not only rely on the production of palm oil and jatropha for example in 2011 palm oil price rise rapidly because of the flood in southern region this problem cause a shortage of palm oil for produce biofuels. It's must looking for the alternate way to produce biofuels too. Biofuels can be produce by several methods but catalytic cracking process has been identified to be the potential route to providing clean fuel. The choices of catalysts play an importance role in catalytic cracking. There is various type of zeolite catalysts such as HZSM-5, zeolite Beta and zeolite Y are reported in catalytic cracking for the production of biofuels [3]. Mesoporous materials such as MCM-41 [4] and SBA-15 [5] are also used as catalysts for cracking reaction. These finding show that zeolites posses a great potential as cracking catalyst due to its structure, acidity and high selectivity for the production of biofuels from vegetable oil.

The properties and shape selectivity of catalysts is the main feature to control product distribution of the process. Activity and selectivity of catalysts are managed by several factors acidity, pore size, pore distribution and pore shape. Bhatia reported the activity of catalyst decrease when decrease its acidity and the pore size of the zeolite has effect on product distribution [3,6].The effect of catalysts acidity on activity has been confirmed by Junming and co worker [7]. They used basic catalysts for catalytic cracking reaction. The main products from their reaction are liquid hydrocarbon that has carbon number in diesel range. Bhatia et al. studied the catalytic cracking of palm oil by use composite zeolites to study the effect of acidity on catalytic cracking reaction. The maximum yield of gasoline and conversion were obtained by use the acid catalyst REY composite with HZSM-5 (Si/Al = 40) conversion 95.9 wt% and gasoline yield 40.9 wt% while use catalyst REY/HZSM-5 (Si/Al=140) they got conversion 89.9 wt% and gasoline yield 37 wt% [8].

As for effect of pore size on selectivity of the catalysts Bhatia et al. [3-6] reported that the smaller pore size tend to have the shorter chain of product. They conducted the experiment by used several type of zeolite such as HZSM-5, zeolite y and zeolite beta and found that the smallest pore size HZSM-5 has the highest yield of gasoline and gaseous product at the same condition with the other two. For zeolite beta has a pore size 0.56 x 0.48 nm with an interconnecting 12 ring system and chiral pore sections while zeolite y has a pore opening 0.8 nm and a 12 ring pore system. Compare to a result product at the same condition with the other the conversion of zeolite beta higher than zeolite y also yield of the gasoline too [3]. Bhatia et al. [6] also reported how to increase yield of gasoline and reduce coking phenomenon by use short contact time between catalyst and oil vapor at moderate temperature. These have been confirmed by many researchers.

Many researchers are widely applied composite catalysts in order to modification properties of the catalysts. There've been reported the use of mix zeolites and hybrid catalyst [8]. The result depends on type of zeolites and ratio of composition. For example there have been study of hybrid catalyst between HZSM-5 and USY they found the selectivity toward gasoline improve with increasing HZSM-5 content however hybrid catalyst between HZSM-5 and zeolite beta the result not in the same trend as HZSM-5 and USY. The results show drop in yield of gasoline and percent conversion because of size of coke formation decrease the chance of second cracking. This make zeolite beta alone gave higher conversion and yield of gasoline than hybrid catalyst [6].

Mordenite is a zeolite with two dimensional pores. The pore system of mordenite consists of main channel of 6.5 x 7 Å, which are connect by tortuous pores of 2.6 x 5.7 Å also called side pocket. Mordenite are widely use in catalysis, separation and purification because of it uniform, has a small pore size and high internal surface area [9].

Beta zeolite is an old zeolite discovered by Mobil. Zeolite beta consists of an intergrowth of two distinct structures termed Polymorphs A and B. The polymorphs grow as two-dimensional sheets and the sheets randomly alternate between the two. Both polymorphs have a three dimensional network of 12-ring pores. The intergrowth of the polymorphs does not significantly affect the pores in two of the dimensions, but in the direction of the faulting, the pore becomes tortuous, but not blocked. [10]

Zeolite Y and zeolite beta are one of the popular catalysts for catalytic cracking of biofuels study. Zeolite y can be built by linking sodalite cage through double six rings. These create a large cavity in structure called supercage accessible by a three-dimensional 12-ring pore system. Zeolite y has pore size opening 8 nm. [13]

Zeolite beta is a high silica zeolite that was found by Mobil in 1967. Zeolite beta has been demonstrated to be useful in hydrocarbon conversion process especial cracking, dewaxing and dealkylation. Zeolite beta has a large pore size due to its structure has 12 ring framework.As for zeolite beta has a high yield of silica the acidity of this zeolite normally lower than zeolite y. [14]

The objectives of this research are to study the effect of 3 types of bi functional catalysts Pt/zeolite Y, Pt/zeolite beta and Pt/mordenite on the conversion and selectivity of bio-dehydrogenate diesel for maximum yield of gasoline. The structure of gasoline preferred is branched chain because it has high octane number. Octane number is a measure of the ignite quality of gasoline. Higher this number, the less susceptible is the gas to knocking when burnt in engine. Octane number denotes the percentage by volume of isomer-chain in the combustible mixture. Octane number does not relate to the energy content of the fuel. It is only a measure of the fuel's tendency to burn in a controlled manner, rather than exploding in an uncontrolled manner [11,12].

2. Experimental

2.1 Synthetic straight chain hydrocarbons (SSHCs)

Synthetic straight chain hydrocarbons (SSHCs) obtained from the hydrodeoxygenation reaction of palm oil were used as the feed stock in catalytic cracking reaction. The SSHCs is composed of 98.8 wt% diesel fraction (45.6 %wt of *n*-octadecane, 12.6 wt% of *n*-heptadecane, 32.7 wt% of *n*-hexadecane and 7.9 wt% of *n*-pentadecane).

2.2. Catalysts

All catalysts used in the catalytic cracking of SSHCs were platinum supported on three different zeolites, Y, Beta and MOR. All zeolites were supplied from Zeolyst International Corp., USA. The properties of each zeolite are presented in Table. 1

Table 1 Zeolite properties

Properties	Y	BEA	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

2.2. Catalyst preparation

Platinum supported zeolite catalysts having 0.1 wt% of Pt metal were prepared by an impregnation technique. The precursor was

$Pt(NH_3)_4(NO_3)_2$ obtained from Aldrich Corp. After the impregnation sample was dried at 393 K for 12 h. and calcined at 773 K in the flow of air for 6 h.

2.4 Reaction procedure

The cracking reaction of SSHCs was performed over Pt/zeolites at a constant pressure of 2.8 MPa, weight hourly space velocity of 22.9 h^{-1} and the reaction temperature ranging from 573 K to 653 K. Figure 1 shows the experimental setup for the catalytic cracking reaction. The catalyst was in powder form in order to avoid mass transfer effect. In each run, the desired amount of catalyst was packed in the middle of reactor. The ceramic balls were put above and below catalyst bed. Before testing, catalyst was reduced under a flow of hydrogen at 623 K for 4 h. After that, feed was injected by a high pressure syringe pump at the desired rate. The products were cooled in the cooler. The condensed liquid products were collected and analyzed by a gas chromatography equipped with a FID detector. Some products were determined for a heating value.

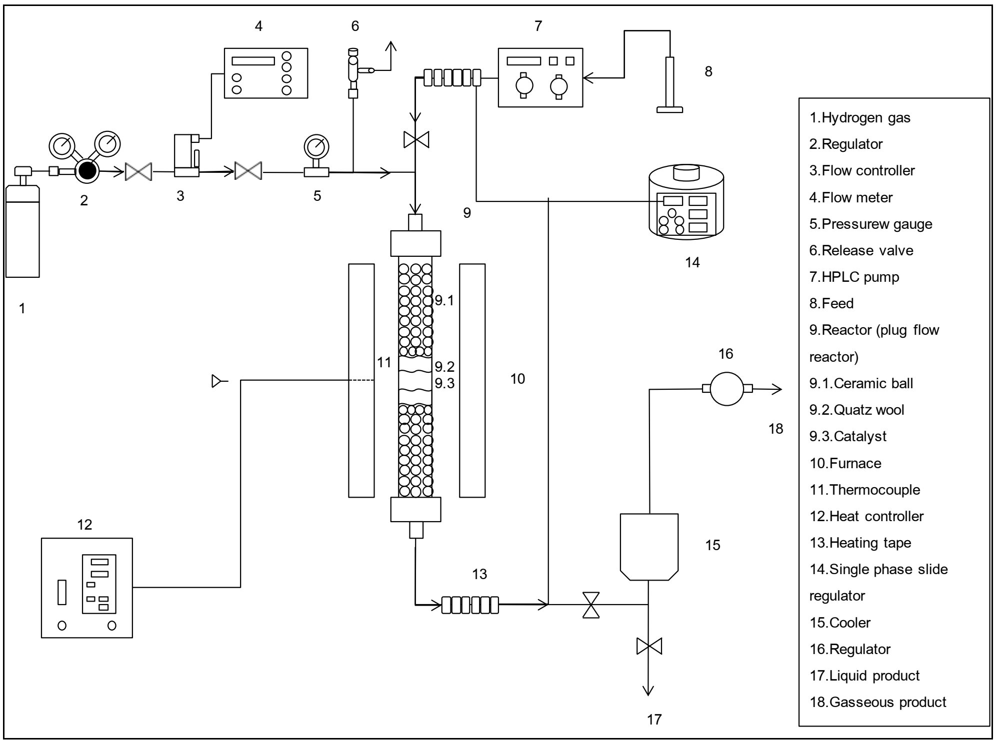


Fig. 1 The experimental set up.

2.5 Product analysis

The organic liquid products were analyzed and categorized into 3 according to its molecular size and the boiling range of petroleum products as shown in Table 2.

The performance of the catalysts was measured in term of conversion, yield and selectivity to the product. The conversion, yields and selectivity of the product are defined as,

$$Conversion(\%wt.) = \frac{Products}{Feed} \times 100 \qquad \text{---Eq. (1)}$$

$$Yield\ \ A(\%wt.) = \frac{Product\ \ A}{Feed} \times 100 \qquad \text{---Eq. (2)}$$

$$Selectivity\ A(\%wt.) = \frac{Product\ \ A}{Conversion} \times 100 \qquad \text{---Eq. (3)}$$

Table 2 Comparison between product fractions obtained from the catalytic cracking of SSHCs and the commercial products.

Property	Gasoline	Kerosene	Diesel
Product obtained from the experiment			
Chemical formula	C7 to C10	C11 to C14	C15 to C18
Commercial products			
Chemical formula	C4 to C12[a]	C8 to C16[b]	C8 to C25[a]
Octane no. (RON/MON)	88 – 98/80 - 88	-	-
Cetane no.	-	-	40 - 55
Lower heating value (kJ/m^3)	$32.3x10^6$	-	$35.8x10^6$
Higher heating value (kJ/m^3	$34.6x10^6$	-	$38.3x10^6$

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

[b.]Fuel properties-effect on aircraft and infrastructure, Aviation rulemaking advisory committee.

3. Results and discussion

The performances of three catalysts were studied in the terms of conversion and selectivity toward a gasoline fraction. Table 3 shows composition of SSHCs used as feed compared with liquid products obtained from the catalytic cracking reactions over Pt/Y, Pt/BEA

Table 3 Composition of feed and liquid products obtained from the catalytic cracking reaction over various Pt/zeolites.

Catalyst	Conversion (wt%)	Gasoline fraction (wt%)			Kerosene fraction (wt%)			Diesel fraction (wt%)		
		Straight chain	Branched chain	Total	Straight chain	Branched chain	Total	Straight chain	Branched chain	Total
Feed										
		-	-	-	1.1	-	1.1	98.7	0.1	98.8
Product										
Pt/Y	60.6	16.9	28.5	45.4	3.9	11.9	15.8	21.2	17.7	38.9
Pt/BEA	32.1	11.8	17.6	29.4	2.1	1.4	3.5	65.8	1.3	67.1
Pt/MOR	100.0	57.3	42.7	100.0	-	-	-	-	-	-

and Pt/MOR at the same reaction condition (2.8 MPa, 613 K and WHSV 22.9 h^{-1}). A Pt/MOR gave a highest conversion and completely converted into gasoline fraction. In case of others, a Pt/Y gave a higher conversion than a Pt/BEA about 2 times. This may be due to their characteristic such as the pore size and acidity. From Table 2, it is suggested that the pore size of Pt/MOR is the smallest, followed by Pt/BEA and Pt/Y whereas Pt/Y contains a higher acidity than Pt/BEA.

Fig. 2 presents the selectivities to gasoline and kerosene fractions. It had been confirmed that selectivity to gasoline fraction is the highest when the reaction was tested over Pt/MOR. Moreover, when focusing on the expected octane number of the gasoline product, it prefers the branched structure of hydrocarbons. Then, the ratio of branched chained hydrocarbons to straight chain hydrocarbons (B/S ratio) was calculated and illustrated in Fig. 3. The ratio was decreased from Pt/Y, Pt/BEA and Pt/MOR.

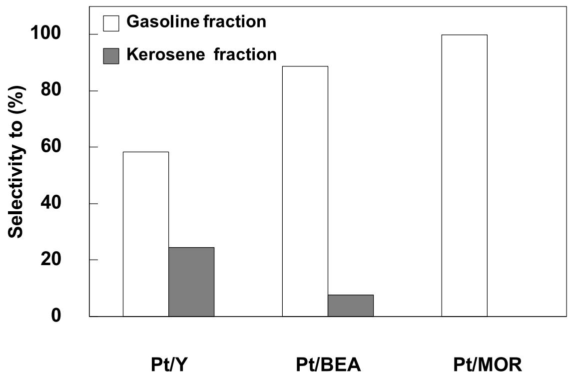


Fig. 2 Selectivity to gasoline and kerosene fractions obtained from the catalytic cracking of SSHCs over different catalysts

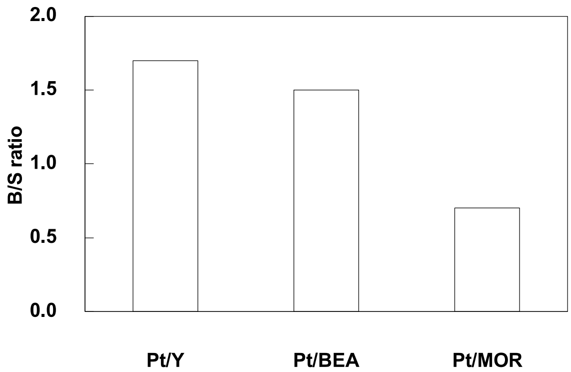


Fig. 3 The ratio of branched chain hydrocarbons to straight chain hydrocarbons in the gasoline fraction.

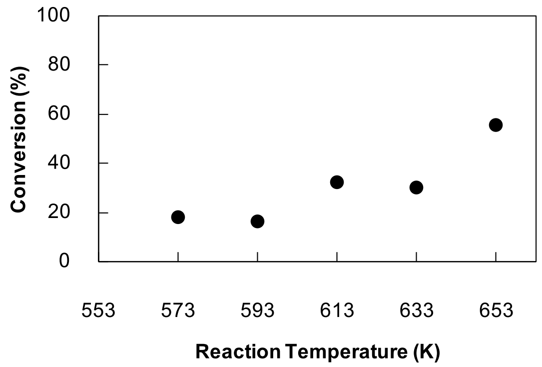
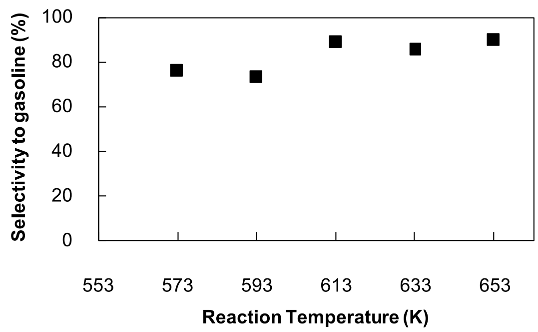
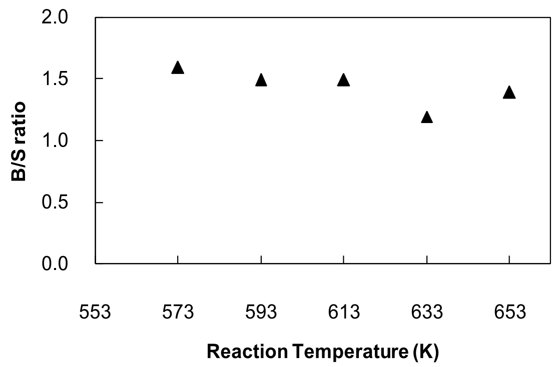


Fig. 4 Conversion of SSHCs obtained from the catalytic cracking over Pt/BEA as a function the reaction temperature



(a) Selectivity to gasoline



(b) The B/S ratio

Fig. 5 Products obtained from the catalytic cracking over Pt/BEA as a function of the reaction temperature.

As previously discussed, the octane number is significantly important parameter that measure the ignite quality of gasoline. Therefore, only Pt/BEA was further studied due to the high selectivity of gasoline and B/S ratio. The effect of reaction temperature on the product distribution was evaluated in a range of 573 K to 653 K. The results show in Fig. 4 and Fig. 5(a) and 5(b).

From Fig. 4 the conversion increased as increasing the reaction temperature. However, from Fig. 5 the selectivities to gasoline were nearly changed with the reaction temperature. They were slightly increased with temperature. Unlike the selectivity, the B/S ratio was decreased when the reaction temperature increased.

5. Conclusion

The Pt/Y, Pt/BEA and Pt/MOR showed a high potential to produce product in a gasoline fraction. Among these three catalysts, Pt/BEA was suitable for this purpose due to not only high selectivity, but also high B/S ratio. However, its catalytic reaction depended on the reaction temperature.

6. Acknowledgement

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