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ROLE OF BRØNSTED ACID SITES IN COMPOSITE CATALYST FOR  
TRIGLYCERIDE CRACKING  
(PERANAN TAPAK ASID BRØNSTED DI DALAM MANGKIN KOMPOSIT  
UNTUK PERETAHAN TRIGLISERIDA)

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PUSAT PENGURUSAN PENYELIDIKAN  
UNIVERSITI TEKNOLOGI MALAYSIA

2005

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**BORANG PENGESAHAN  
LAPORAN AKHIR PENYELIDIKAN**

TAJUK PROJEK : ROLE OF BRONSTED ACID SITES IN COMPOSITE CATALYST FOR  
TRIGLYCERIDE CRACKING

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## ABSTRACT

The diminishing source of non-renewable energy has spurred the interests of researchers to explore the possibility to use alternative sources. Catalytic cracking of vegetable oil to liquid fuels was studied by a number of individuals and the results were encouraging to continue with this study. Palm oil was chosen because of its abundance in Malaysia. Composite catalyst, Al-MCM-41/ZSM-5 was used to catalytically convert palm oil to gasoline. The effects of temperature, hydrogen addition before (activation) and during (hydrocracking) reaction towards acidity and catalytic cracking were investigated. Catalysts used were characterized using X-ray Diffraction (XRD), Nitrogen Adsorption (NA) and Pyridine Infrared Spectrophotometry (Py-IR) methods. The liquid and gaseous products were analyzed using Gas Chromatography. The results showed that increase in temperature had profound effects towards conversion. The highest Organic Liquid Products (OLP) yield and gasoline selectivity was found at 550°C. Increasing the flow rate of hydrogen activation increased conversion, OLP yield and gasoline selectivity. However, the longer time used for activation had adverse effects on cracking activity. Conversely, increased H<sub>2</sub>: palm oil molar ratio decreased palm oil conversion and gasoline selectivity.

## ABSTRAK

Sumber tenaga yang tidak boleh diperbaharui semakin berkurangan dan ini menyebabkan para penyelidik berusaha untuk mendapatkan sumber tenaga alternatif. Peretakan bermangkin minyak sayuran kepada gasolin telah menjadi sumber kajian beberapa penyelidik dan keputusan yang diperolehi adalah cukup memuaskan. Minyak kelapa sawit dipilih untuk kajian ini kerana ia adalah sumber yang mudah didapati di Malaysia. Mangkin komposit MCM-41/ZSM-5 digunakan untuk menukarkan minyak kelapa sawit kepada gasolin. Kesan suhu, penambahan hidrogen sebelum dan semasa eksperimen terhadap keasidan dan aktiviti mangkin diperhatikan dalam kajian ini. Mangkin dicirikan menggunakan kaedah pembelauan sinar-X, penjerapan nitrogen dan spektrofotometri infra merah piridina. Hasil cecair dan gas dianalisa menggunakan Kromatografi Gas. Keputusan yang diperolehi menunjukkan bahawa peningkatan suhu yang digunakan semasa eksperimen meninggikan penukaran minyak kelapa sawit. Hasil organik cecair dan kepemilihan kepada gasolin yang tertinggi diperolehi pada suhu 550°C. Kenaikan kadar laju alir hidrogen sebelum eksperimen meningkatkan penukaran, hasil organik cecair dan kepemilihan gasolin. Walaupun begitu, pengaktifan menggunakan hidrogen yang lebih lama mengurangkan aktiviti mangkin. Peningkatan nisbah H<sub>2</sub> kepada minyak kelapa sawit mengurangkan penukaran minyak kelapa sawit dan kepemilihan gasolin.

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Research Background

Csicsery (1995) had outlined several challenges that the chemical industry will face during the next decades. One of them is diminishing raw material supplies and therefore, the increasing need to use other available sources such as natural gas, syngas and biomass.

In 1899, Rudolf Diesel tested vegetable oil as fuel for his diesel engine (Shay, 1993). In the 1930's and 1940's vegetable oils were used as diesel fuels but only in emergency situations (Ma and Hanna, 1999). Since the oil embargo in the 70's, newfound interests in alternative energy have seen more research being done on this subject. Due to climate constraints, most of the research was limited to vegetable oil that are home grown, such as sunflower oil in Turkey (Yorgun, Sensoz and Kockar, 2001), tiger nut oil in Nigeria (Barminas *et al.*, 2001) and canola oil in Canada (Prasad and Bakhshi, 1985; Bakhshi *et al.*, 1986a,b; Adjaye and Bakhshi, 1995a,b,c; Katikaneni, Adjaye and Bakhshi, 1995; Idem, Katikaneni and Bakhshi, 1997).

Malaysia is the largest producer of palm oil (A. Ibrahim and M.J. Ahmad, 1993), thus it is imperative for us to exploit this abundant resource. The production of Crude Palm Oil (CPO) in the 2004 is 28.7 million tones and this figure is expected to rise steadily (Foreign Agricultural Service, 2004). Table 1.1 and 1.2 shown below showed that Malaysia has consistently been the largest producer and exporter of CPO in the world.

**Table 1.1:** World major producers of palm oil (Tonnes)

	2000/2001	2001/2002	2002/2003	2003/2004	2004/2005 (f)
Malaysia	11,937	11,858	13,180	13,416	14,000
Indonesia	8,300	9,200	9,800	10,600	11,500
Nigeria	730	760	770	780	800
Thailand	580	780	640	840	780
Colombia	560	518	540	575	605
Papua New Guinea	330	370	380	380	380
Ecuador	245	300	320	340	340
Cote d'Ivoire	248	260	234	310	310
Others	1,353	1,373	1,398	1,445	1,447
<b>TOTAL</b>	<b>21, 821</b>	<b>25,419</b>	<b>27,262</b>	<b>28,686</b>	<b>30,162</b>

Note:

( f)forecast

Source : Foreign Agricultural Service, 2004

**Table 1.2:** World major exporters of palm oil (Tonnes)

	2000/2001	2001/2002	2002/2003	2003/2004	2004/2005(f)
Malaysia	10,475	10,500	11,650	11,765	12,200
Indonesia	4,776	5,979	6,600	7,000	7,650
Papua New Guinea	320	328	326	367	315
Singapore	177	177	212	208	210
Colombia	69	91	108	150	160
EU-25	199	136	149	149	150
Others	686	616	767	886	850
<b>TOTAL</b>	<b>16,702</b>	<b>17,827</b>	<b>19,812</b>	<b>20,525</b>	<b>21,535</b>

Note:

( f)forecast

Source : Foreign Agricultural Service, 2004



Most of the researches done on palm oil conversion are using refined, bleached, deodorized (RBD) palm oil. This is due to the high viscosity of CPO, which cause problems such as incomplete combustion, poor fuel atomization and coking of fuel injectors if used directly without treatment (De Filippis *et al.*, 1995).

Catalytic conversion of palm oil to fuels been performed using various catalysts, most notably ZSM-5 (F.N. Ani and B. Salam, 1995; Tan, A.R. Mohamed and S. Bhatia, 1997,1999; F.A. Twaiq, N.A.M. Zabidi and S. Bhatia, 1999). The use of ZSM-5 catalyst is due to the fact that it favors the conversion of n-alkanes to aromatics and this zeolite selectively cracks low octane components into higher-octane components (Nalbandian *et al.*, 1994; Adjaye and Bakhshi, 1995b).

Acidity and shape selectivity of catalysts are governed by several factors such as acidity, pore size and its distribution and also shape of the pores (F.A. Twaiq, N.A.M. Zabidi and S. Bhatia, 1999; Adjaye and Bakhshi, 1995a). Beta and Y are both large pore zeolites and acidic in nature. Corma *et al.* (1988) studied the activity and selectivity for zeolite beta and compared it with zeolite Y. They found that H-beta is more active in n-heptane cracking than H-Y, while for gas oil cracking the opposite occurs. Hybrid catalysts were used to increase the shape selectivity of catalyst (F.A. Twaiq, N.A.M. Zabidi and S. Bhatia, 1999).

The use of zeolite in catalytic cracking has been under study and several have been commercialized. The re-discovery of the MCM-41 materials in 1992 (Kresge *et al.*, 1992) has spurred a lot of interest from researchers in catalysis because there is a need for zeolite-like materials with bigger pore sizes to process heavier hydrocarbons efficiently. This material has been synthesized using different methods such as hydrothermal, sol-gel, grafting and template cation exchange method (Kugita *et al.*, 2003). The difference in synthesis methods resulted in different acidity and thus, different catalyst activity.

## 1.2 Problem Statement

Vegetable oil as liquid fuels has long been the subject of interest among researchers. The oil crisis in the mid-80's only served to enhance the work to explore various possibilities to convert vegetable oil to liquid fuels. Vegetable oil has a high viscosity and this would lead to a number of problems in engines.

The introduction of shape selective catalyst (Weisz, Haag and Rodewald, 1979) in vegetable oil cracking was an important one because this opened up a new horizon in catalysis by zeolites. Since then, vegetable oil cracking was performed by molecular sieves and the results were encouraging (Prasad and Bakhshi, 1985; Prasad *et al.*, 1986a,b; Adjaye and Bakhshi, 1995a,b,c; F.N. Ani and B. Salam, 1995; F.A. Twaiq, N.A.M. Zabidi and S. Bhatia, 1999). ZSM-5 was often used, either as single catalyst or hybrid with other zeolites. However, the use of microporous zeolite limits their uses to small molecules. Thus, the discovery of mesoporous materials known as MCM-41 (Beck *et al.*, 1992) was crucial in catalysis. This material provided the mesoporosity needed for cracking larger molecules, though its weak acidity was a major challenge for its use in acid catalysis (Hunger *et al.*, 1999).

Catalytic cracking of palm oil to gasoline has been performed for over a decade. It was shown that palm oil could be converted to gasoline using shape selective catalysts, as reported by several researchers (F.N. Ani and B. Salam, 1995; B. Salam, F.N. Ani and M.N. Islam, 1997; Tan, A.R. Mohamed and S. Bhatia, 1997, 1999; F.A. Twaiq, N.A.M. Zabidi and S. Bhatia, 1999; N.A. Saidina Amin and H.N.M. Ekramul, 1999; F.H. Kasim, 2001). Although this process was sufficient to crack vegetable oil to gasoline, hydrocracking could do improvements in catalytic performance.

### 1.3 Objectives of Study

1. To investigate the catalytic activity of MCM-41/ZSM-5 composite materials.
2. To analyze the effect of hydrocracking and hydrogen pretreatment towards catalytic performance of the composite materials of MCM-41/ZSM-5.

## CHAPTER 2

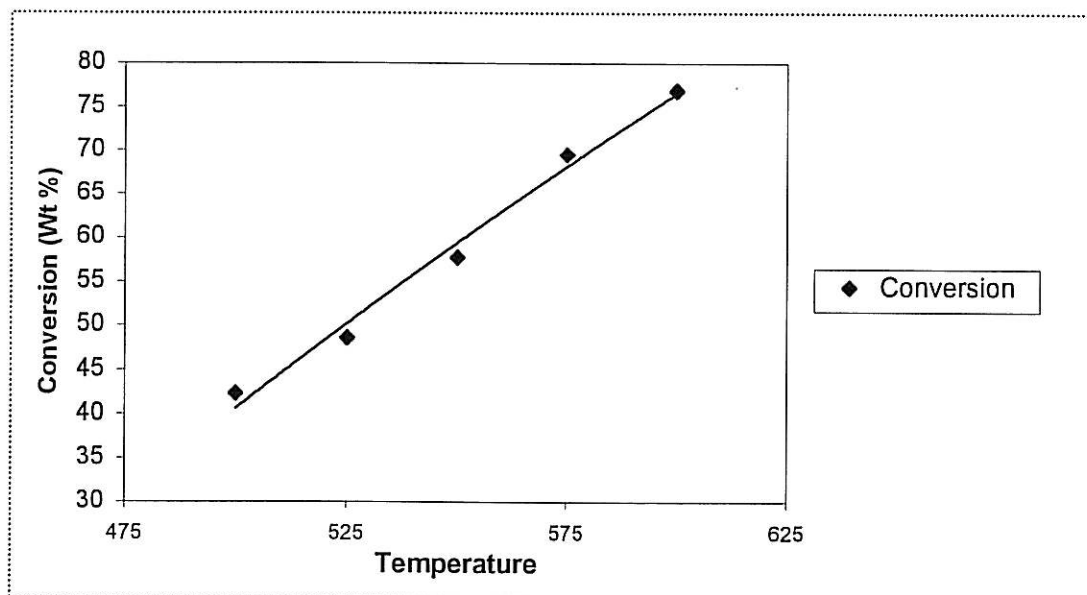
### EFFECT OF TEMPERATURE TOWARDS PALM OIL CRACKING OVER COMPOSITE CATALYSTS

#### 2.1 Introduction

Process conditions has always played vital role in catalytic cracking. Temperature had a profound effect on vegetable oil cracking, often affecting conversion and product yield (Prasad *et al.*, 1986a; Katikaneni *et al.*, 1995; Idem *et al.*, 1997; Tan *et al.*, 1999). Conversion was found to increase with increase in temperature. OLP yield inclined with temperature until a maximum, 370°C (Adjaye and Bakhshi, 1995b) before declining. Similar trends were also reported with different maximum, depending on WHSV and types of feed used (Prasad *et al.*, 1986a; Katikaneni *et al.*, 1995; Idem *et al.*, 1997; Tan *et al.*, 1999). Thus, it is the objective of this chapter to examine the effects of temperature towards catalytic cracking of palm oil over composite catalyst, MCM-41/ZSM-5.

## 2.2 Conversion

It is clearly demonstrated in Figure 2.1 that conversion increased linearly with temperature. Temperature strongly influenced conversion at WHSV higher than  $2 \text{ h}^{-1}$  (Prasad *et al.*, 1986a; Katikaneni *et al.*, 1995; Idem *et al.*, 1997; Tan *et al.*, 1999). However, conversion in this work was lower than those reported by Farouq *et al.* (2004), which could be attributed to the very low acidity obtained from the catalyst synthesized. Py-IR peaks (Appendix A) and calculated Brønsted acidity (Appendix B) show that a very low amount of Brønsted acid sites were found in this catalyst. Since these sites were responsible for cracking, this explains the low activity of this catalyst. Nevertheless, the residual oil from cracking was not analyzed and it could be possible that some of the heavier hydrocarbons were included in this fraction, leading to decrease in conversion.



**Figure 2.1** Effect of temperature on conversion

### 2.3 Product Yield

Figure 2.2 shows that OLP yield inclined with temperature until 550°C, and then declined with further increase in temperature. On the other hand, gas yield increased while the amount of coke decreased with temperature increase. High reaction temperature and low WHSV was found to favour gas yield (Prasad *et al.*, 1986a; Sharma and Bakhshi, 1991; Ooi *et al.*, 2004) and reduce coke yield (Adjaye and Bakhshi, 1995b). Decline in OLP yield at temperature higher than 550°C could be due to increase in secondary cracking reaction, thus contribute to the high amount of gas produced. Partial gasification of coke could also be a factor to the huge gas fraction and low coke fraction.

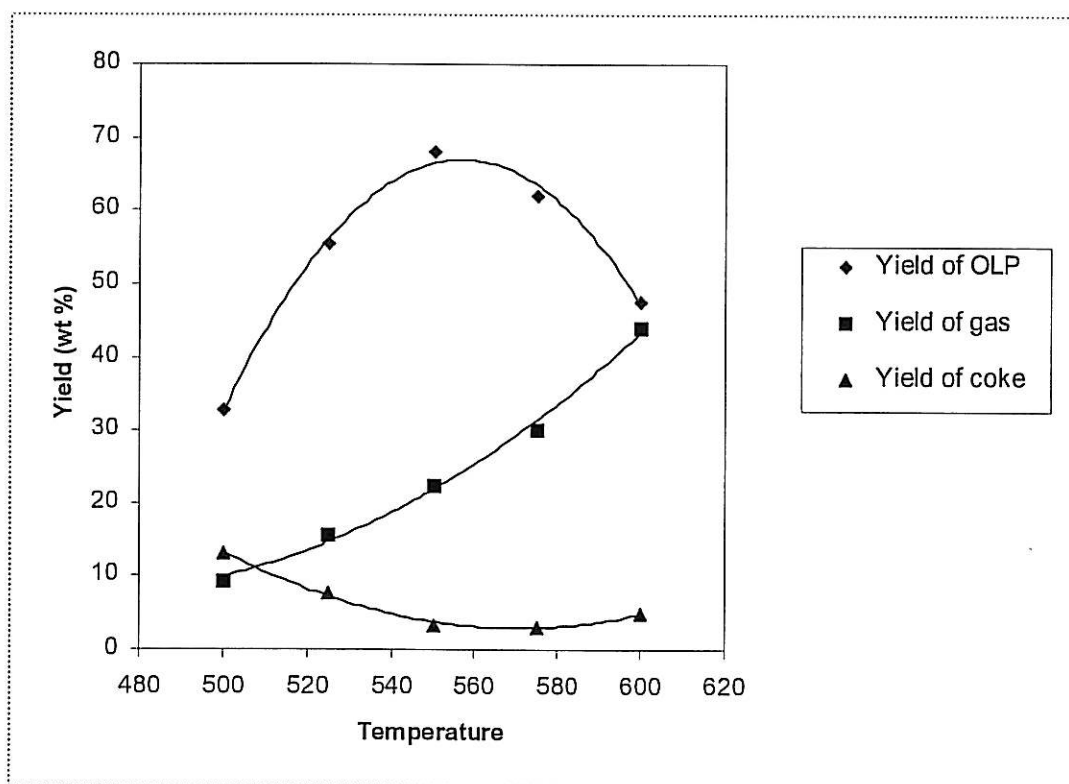
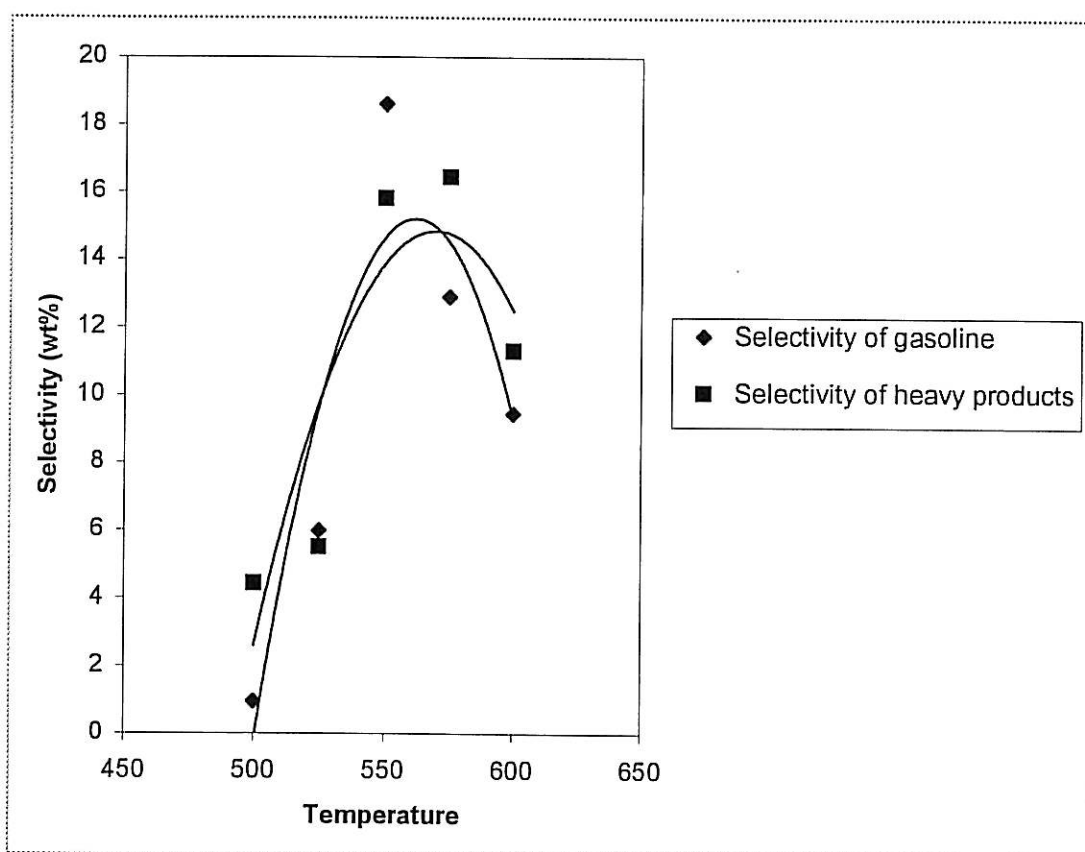


Figure 2.2 Effect of temperature on product yield

## 2.4 Gasoline and Heavy Products Selectivity

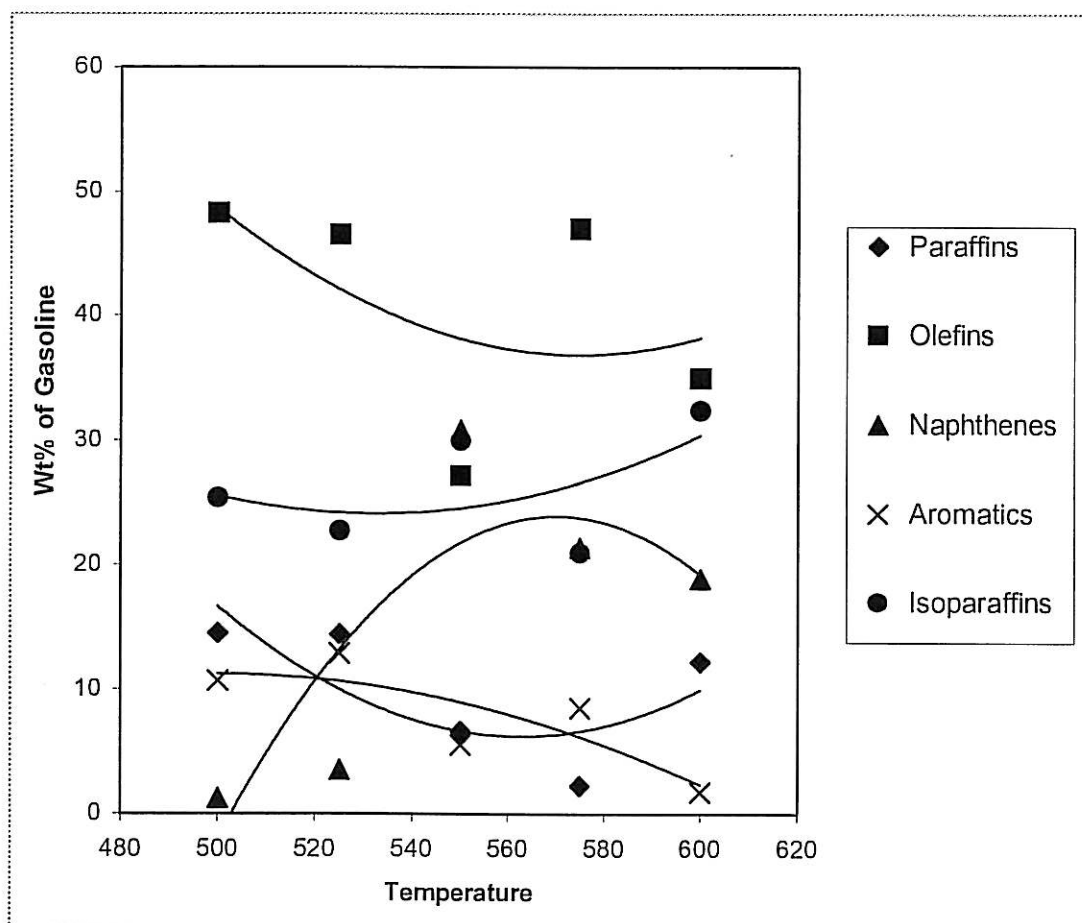
It can be seen in Figure 2.3 that selectivity of gasoline and heavy products follow the same trend. Both increased with temperature before decreasing. Maximum selectivity for gasoline was at 550°C while slightly higher temperature, 575°C was needed for maximum heavy products selectivity. Similar results for gasoline trend were obtained from catalytic cracking of canola oil (Prasad *et al.*, 1986a) and palm oil (Tan *et al.*, 1999). On the other hand, result from heavy products was contrary to report by Tan *et al.* (1999), who exhibited that heavy products were at minimum when gasoline fraction was at maximum.



**Figure 2.3** Effect of temperature on gasoline and heavy products selectivity

## 2.5 Product Distribution of Gasoline Fraction

Figure 2.4 illustrates that isoparaffins and olefins were the major components in gasoline. Isoparaffins and naphthenes were found to increase with temperature. Higher selectivity towards isoparaffins and naphthenes might be due to higher cyclization and isomerization steps at high reaction temperature. Aromatics, paraffins and olefins decreased with temperature. Prasad *et al.* (1986a) observed a declining trend for aromatics at temperature higher than 370°C. However, this result differed from Tan and co-workers (1999), who observed increased production of aromatics at higher temperatures. In this work, it would seem that formation of aromatics was suppressed at high temperatures, which was in agreement with the earlier work by Prasad *et al.* (1986a).



**Figure 2.4** Effect of temperature on product distribution of gasoline



## 2.6 Gas Composition

From Table 2.1, it can be seen that there was no general trend for gaseous products distribution relative to temperature. Nonetheless, it can be noted that only C<sub>3</sub> and C<sub>4</sub> components were found in the gas composition. No components from C<sub>1</sub> and C<sub>2</sub> fractions were observed, suggesting that the reaction proceeded via carbenium ion mediated mechanism (Satterfield, 1991).

**Table 2.1:** Gaseous products composition

Temperature (°C)	500	525	550	575	600
Gas Composition (mol %)					
C <sub>3</sub>	65.3	0	87.8	86.2	85.7
<i>i</i> C <sub>4</sub>	28.1	61.3	7.5	8.2	9.2
<i>n</i> C <sub>4</sub>	6.6	38.7	0	0	0
1C <sub>4</sub> =	0	0	4.8	5.6	5.0

## 2.7 Conclusions

This chapter presents the effect of temperature towards palm oil cracking over composite MCM-41/ZSM-5. It is shown throughout this chapter that temperature plays an important role in palm oil cracking. Conversion was found to increase with increasing temperature. OLP yield and gasoline selectivity was highest at 550°C. Major components in OLP were olefins and isoparaffins. Olefins decreased whereas isoparaffins increased with temperature, indicating that isomerization was favoured at higher temperature. The components in gaseous products were C<sub>3</sub> and C<sub>4</sub> compounds, suggesting carbenium ion mediated mechanism.

## CHAPTER 3

### EFFECT OF HYDROGEN TOWARDS PALM OIL CRACKING OVER COMPOSITE CATALYSTS

#### 3.1 Introduction

Hydrocracking was used to upgrade heavy oil and/or large molecules to useful middle distillates. Hydrotreated light cycle oil was hydrocracked in a fixed bed reactor at 5 MPa over several MCM-41-based catalysts (Corma *et al.*, 1997). Pt/Al-MCM-41 showed good activity and resistance to sulfur compared to Pd/Al-MCM-41 and Rh/Al-MCM-41. Comparison of MCM-41 with other zeolite catalysts such as USY showed that MCM-41 was more selective towards middle distillates (Corma *et al.*, 1996). Upgrading of bulky molecules such as 1,3,5-triisopropylbenzene (TiPB) was also performed using MCM-41-type catalysts with different structure. Structures with tubular morphology were found to be superior, attributed to diffusion limitations by other structure such as particulates (Chen *et al.*, 2003).

Hydrogen activation study is rather sparse in literature. Bernas *et al.* (2002) reported a dramatically enhanced isomerization of linoleic acid when reaction took place in nitrogen atmosphere and activated by hydrogen. They proposed a new pathway involving double-bond migration to explain the increase in isomerization activity. One of the key factors influencing this reaction was the amount of chemisorbed hydrogen either on the metal or support surface. Hence, it was the objective of this chapter to investigate the effect of hydrogen towards palm oil cracking.

### 3.2 Hydrocracking: Effect of Temperature

Based on Table 3.1, conversion of palm oil increased dramatically from 525°C to 550°C. At higher temperature, the increment was negligible. The effect of temperature on product yield for palm oil hydrocracking followed identical tendency with palm oil cracking. Nevertheless, the conversion with hydrocracking at low hydrogen feed ratio was higher than cracking at temperatures higher than 525°C. This might be due to elimination of coke precursor sites via hydrogenation (Shishido and Hattori, 1996), which slowed down catalyst deactivation.

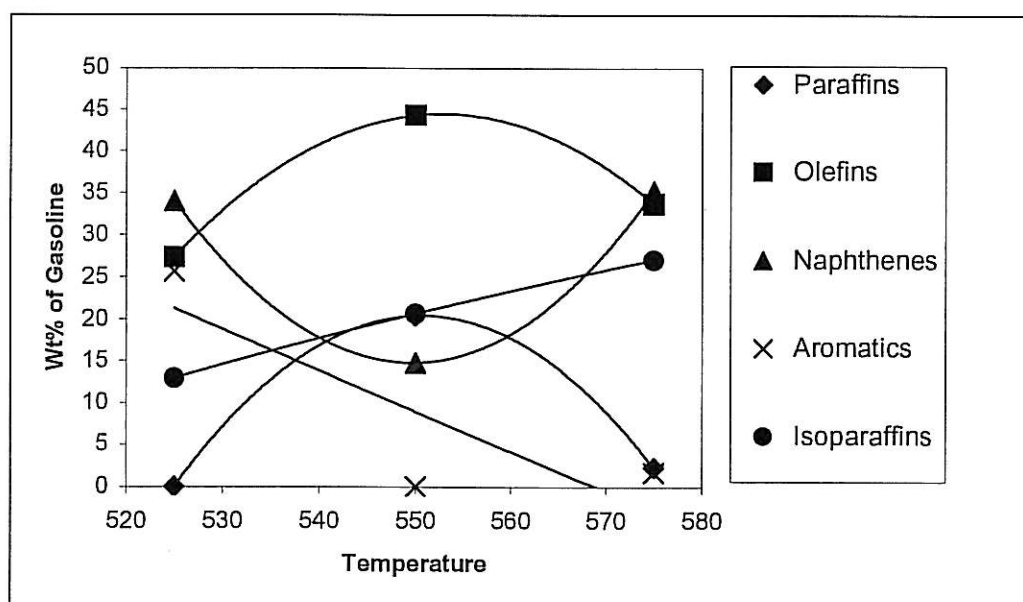
OLP yield had a maximum value at 550°C, which was 59.2 wt%. Gas yield increased with temperature, whereas coke yield decreased. Tan *et al.* (1999) observed similar trend in product yield. However, the maximum temperature was lower than 550°C, probably due to low ambient temperature for this study. Experiments conducted in this study were done at ambient temperature of 20°C. Decrease of OLP at higher temperatures was influenced by higher secondary cracking, which promoted the production of gas. Coke decline at higher temperature could also be caused by partial gasification of coke at high temperature, which increased gas production further.

The highest selectivity for gasoline was obtained at 550°C, and declined with further increase in temperature. This observation also held true for heavy products selectivity, with highest point of about 17 wt%. Gas product composition consisted of C<sub>3</sub> and C<sub>4</sub> compounds, with higher ratio of C<sub>3</sub> production.

**Table 3.1:** Effect of temperature on hydrocracking of palm oil to gasoline over MCM-41/ZSM-5 at palm oil:hydrogen = 1:2

Temperature (°C)	525	550	575
Conversion (wt%)	42.1	76.3	78.8
Product yield (wt%)			
Organic liquid products	48.6	59.2	50.5
Gas	19.5	32.5	42.3
Coke	6.6	4.1	2.0
Product selectivity (wt%)			
Gasoline	9.5	20.2	13.8
Heavy Products	5.6	17.0	15.9
Gas Composition (mol %)			
C <sub>3</sub>	71.3	75.2	80
<i>i</i> C <sub>4</sub>	28.7	24.8	20

Product distribution analysis on the gasoline fraction in Figure 3.1 showed that olefins were the major component. Olefins production followed similar trend with gasoline and OLP. The highest amount of olefins was found at 550°C, which was about 45 wt% of gasoline fraction. Isoparaffins increased while aromatics decreased with increasing temperature. At temperature higher than 550°C, aromatics were almost absent from gasoline fraction. Prasad *et al.* (1986a) observed a declining trend for aromatics at temperature higher than 370°C. However, this result differed from Tan and co-workers (1999), who observed increased production of aromatics at higher temperatures. In this work, it would seem that formation of aromatics was suppressed at high temperatures, which was in agreement with the earlier work by Prasad *et al.* (1986a). At this reaction temperature, cracking was favoured as evidenced by the high formation of olefins and increase in paraffins.



**Figure 3.1** Effect of temperature on gasoline composition for hydrocracking of palm oil over MCM-41/ZSM-5 at palm oil:hydrogen = 1:2

### 3.3 Hydrocracking: Effect of Palm Oil to Hydrogen Ratio

Table 3.2 exhibits that the increase in palm oil to hydrogen molar ratio had negative influence on palm oil hydrocracking conversion. The lowest ratio gave a conversion of 76.3 wt%, while the highest ratio gave only 41 wt% conversion. Loss in conversion indicated incomplete cracking reaction. The addition of hydrogen slowed down the rate of conversion in 2-methylpentane cracking over ultra stable HY (Zhao and Wojciechowski, 1993). The authors proposed that the addition of hydrogen “passivate” the strength of active sites. However, comparison with reaction without H<sub>2</sub> showed that addition of H<sub>2</sub> during cracking increased conversion only for 1:2 ratio. This could probably be due to the low amount of hydrogen added in the reaction, which was insufficient to “passivate” the active sites.

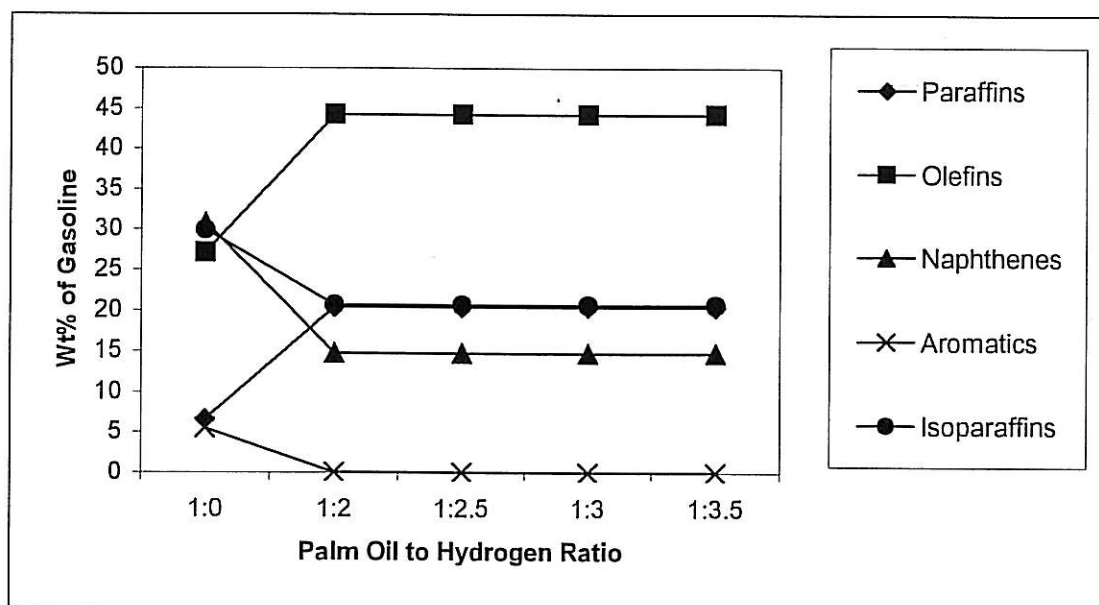
The yield of products had little influence from palm oil to hydrogen molar ratio. Nevertheless, yield of OLP decreased while gas yield increased when compared to cracking without H<sub>2</sub>. OLP yield increased slightly while gas yield decreased less than 10 % with further increase in H<sub>2</sub>. The yield of coke stayed constant with change in palm oil to hydrogen molar ratio.

Both gasoline and heavy products decreased in selectivity with increasing H<sub>2</sub>. The highest gasoline and heavy products selectivity were obtained at 1:2 ratio, 20.2 wt% and 17.0 wt% respectively. Inhibition of secondary cracking appeared to accompany the increase in hydrogen. Nevertheless, gas composition remains unchanged with palm oil to hydrogen molar ratio. C<sub>3</sub> formed a major proportion in gas production, followed by C<sub>4</sub>.

**Table 3.2:** Effect of palm oil to hydrogen ratio on hydrocracking of palm oil over MCM-41/ZSM-5 at temperature = 550°C .

Palm oil/H <sub>2</sub> molar ratio	1:0	1:2	1:2.5	1:3	1:3.5
Conversion (wt%)	57.7	76.3	54.8	52.4	41.1
Product yield (wt%)					
Organic liquid products	68.1	59.2	59.5	60.4	62.8
Gas	22.3	32.1	30.9	27.4	22.3
Coke	3.4	4.1	2.9	3.4	3.5
Product selectivity (wt%)					
Gasoline	18.6	20.2	10.9	10.2	6.4
Heavy Products	15.6	17.0	14.1	8.0	7.1
Gas Composition (mol %)					
C <sub>3</sub>	87.8	75.2	76.6	81.0	78.3
<i>i</i> C <sub>4</sub>	7.5	24.8	23.4	19.0	21.7
1C <sub>4</sub> =	4.8	0	0	0	0

A very interesting observation was seen for gasoline product distribution shown in Figure 3.2. No aromatics were found in the gasoline composition. The major component was olefins, followed by other compounds in this order: isoparaffins ~paraffins>naphthenes. The gasoline distribution remained constant with the increase in hydrogen feed. However, experiments conducted without hydrogen showed a different order in gasoline composition, where isoparaffins, naphthenes and olefins were distributed at nearly the same percentage, followed by nearly equal amounts of paraffins and aromatics, which were about 30 wt% and 6 wt% respectively. Increase in paraffins and olefins with simultaneous decrease in isoparaffins, naphthenes and aromatics suggest that cracking was favoured while aromatization and cyclization was suppressed when hydrogen was introduced in the feed at 550°C.



**Figure 3.2** Effect of palm oil to hydrogen ratio on gasoline composition for hydrocracking of palm oil over MCM-41/ZSM-5 at temperature = 550°C

### 3.4 Hydrogen Activation: Effect of Flow Rate

From Table 3.3, it can be seen that the increase in H<sub>2</sub> flow rate for catalyst activation increased palm oil conversion. The highest conversion for catalyst activation in H<sub>2</sub> was found when using H<sub>2</sub> flow rate of 1.5 L/h.

OLP yield decreased with increasing flow rate, but increased at activation flow rate of 1.5 L/h. Gas yield passed through a maximum at 1 L/h. However, it is interesting to note that increasing H<sub>2</sub> activation flow rate also yielded more coke. This could be due to increase in isomerization, which was known to occur when catalyst was activated in hydrogen, with nitrogen as carrier gas (Bernas *et al.*, 2002).

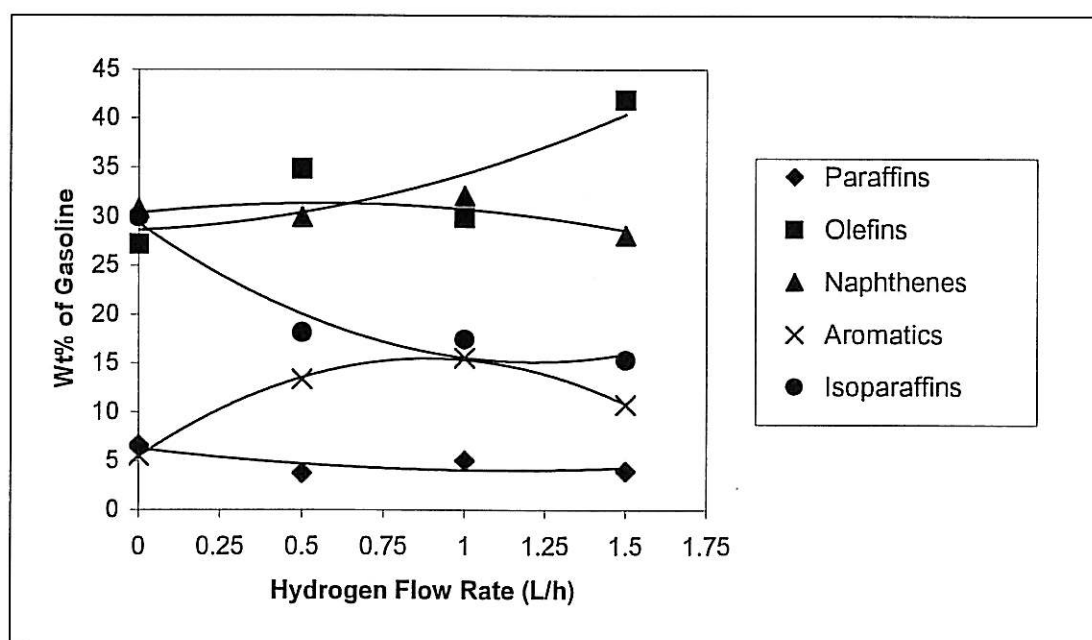


On the other hand, increase of hydrogen flow rate had a positive effect on gasoline selectivity. The highest gasoline selectivity was obtained at 1.5 L/h. Only C<sub>3</sub> and C<sub>4</sub> compounds were formed in gas product, except for hydrogen flow rate of 1.5 L/h. At this flow rate, C<sub>5</sub> dominated gas product, followed by C<sub>3</sub> and C<sub>4</sub>.

**Table 3.3:** Effect of hydrogen activation flow rate on cracking of palm oil over MCM-41/ZSM-5 at duration = 1h

Flow rate (L/h)	0	0.5	1.0	1.5
Conversion (wt%)	57.7	65.1	65.9	76.3
Product yield (wt%)				
Organic liquid products	68.1	58.8	56.6	66.9
Gas	22.3	34.1	36.8	18.9
Coke	3.4	2.5	2.8	7.7
Product selectivity (wt%)				
Gasoline	18.6	11.9	15.7	25.7
Heavy Products	15.6	18.0	8.2	9.4
Gas Composition (mol %)				
C <sub>3</sub>	87.8	82.4	91.9	35.7
<i>i</i> C <sub>4</sub>	7.5	17.6	8.1	4.3
<i>n</i> C <sub>4</sub>	4.8	0	0	1.7
<i>i</i> C <sub>5</sub>	0	0	0	58.2

The gasoline product composition using hydrogen activation is shown in Figure 3.3. With hydrogen activation, olefins and naphthenes were the major components in gasoline fraction. At higher flow rate, olefins dominated the gasoline fraction, while naphthenes remained constant. Other components were generally present in this order: isoparaffins>aromatics>paraffins. Isoparaffins decreased with increase in hydrogen activation flow rate, while aromatics increased. The amount of paraffins remained constant with increasing flow rate for activation.



**Figure 3.3** Effect of hydrogen activation flow rate for cracking of palm oil over MCM-41/ZSM-5 at duration = 1 h

### 3.5 Hydrogen Activation: Effect of Duration

Table 3.4 demonstrates that conversion increased at 1 h of activation and further declined with increase in duration of hydrogen activation. Nonetheless, the yield of OLP was enhanced slightly with longer catalyst activation in H<sub>2</sub>. Moreover, coke yield decreased when duration of activation increased. On the other hand, longer activation duration had negligible effect on gas yield.

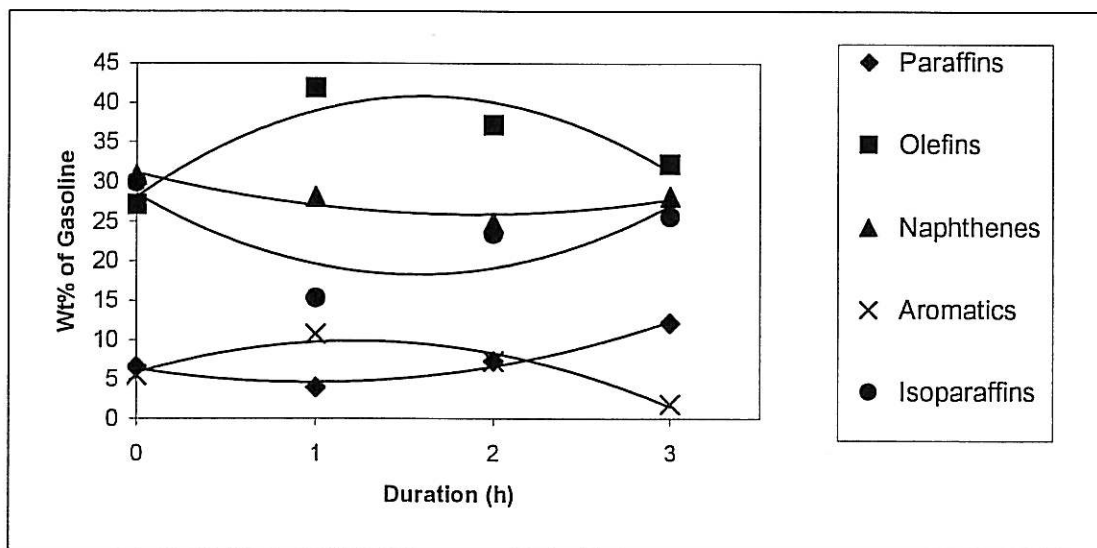
This table (Table 3.4) displays that increment of H<sub>2</sub> activation duration has an adverse effect on gasoline selectivity. Activation for 3 h caused the gasoline selectivity to decrease to 10.6 wt% from 25.7 wt% for 1 h activation. The selectivity for heavy products increased slightly with longer duration. It appears that longer activation in hydrogen had negative effect on conversion and gasoline selectivity. Hydrogen might inhibit secondary cracking reaction through partial blocking of active sites. Zhao and Wojciechowski (1993) suggest the passivation of active sites by hydrogen attributed to the inhibition. Gas product consisted of C<sub>3</sub>-C<sub>5</sub> compounds, with C<sub>5</sub> formed in higher amount at shorter time of activation. C<sub>3</sub> increased with time of activation and formed major proportion of gas product with longer duration of activation.

**Table 3.4:** Effect of hydrogen activation duration on cracking of palm oil over MCM-41/ZSM-5 at H<sub>2</sub> flow rate = 1.5 L/h.

Duration (h)	0	1	2	3
Conversion (wt%)	57.7	76.3	58.7	60.2
Product yield (wt%)				
Organic liquid products	68.1	66.9	68.9	73.6
Gas	22.3	18.9	21.8	17.4
Coke	3.4	7.7	1.9	2.4
Product selectivity (wt%)				
Gasoline	18.6	25.7	18.5	10.6
Heavy Products	15.6	9.4	12.2	16.5
Gas Composition (mol %)				
C <sub>3</sub>	87.8	35.7	45.6	59.7
<i>i</i> C <sub>4</sub>	7.5	4.3	10.3	15.6
<i>n</i> C <sub>4</sub>	4.8	1.7	0	0.3
<i>i</i> C <sub>5</sub>	0	58.2	44.1	24.4

Figure 3.4 shows the effect of activation duration on gasoline product distribution. Olefins were the major component in gasoline fraction, which was at maximum at 1 h of hydrogen activation. Aromatics increased with 1 h of activation but decreased with longer duration. At 3 h of activation, nearly no aromatics were obtained. The absence of aromatics was also found with hydrogen addition during cracking. This suggests that the presence of hydrogen during cracking either as diluent or from longer activation time suppressed the formation of aromatics. The amount of naphthenes remained constant, while isoparaffins and paraffins increased with longer duration. Hydrogen transfer and isomerization seems to be favoured with longer duration of hydrogen activation. According to the possible reaction proposed by Bernas and co-workers (2002), hydrogenation and isomerization proceeds via two different routes, depending on the amount of chemisorbed hydrogen. Since both reactions were reversible, chemisorbed hydrogen on the

catalyst surface would promote hydrogenation initially, before promoting isomerization when hydrogen coverage on the catalyst surface was low.



**Figure 3.4** Effect of hydrogen activation duration for cracking of palm oil over MCM-41/ZSM-5 at  $H_2$  flow rate = 1.5 L/h

### 3.6 Conclusions

This chapter presents the effect of hydrogen, either as diluent or for activation towards palm oil cracking over composite MCM-41/ZSM-5. Increase in hydrogen feed concentration had negative effects on conversion and gasoline selectivity. Similar effects were also found when longer duration of hydrogen activation was employed. On the other hand, increase in hydrogen activation flow rate gave simultaneous increase in conversion and gasoline selectivity. Olefins were the main components in gasoline for cracking with hydrogen at 550°C. Aromatics were absent when hydrogen was used as diluent or when longer duration of activation was employed. Gas composition was mainly  $C_3$ , followed by  $C_4$  compounds.

## CONCLUSIONS

### 4.1 General Conclusions

Chapter 2 presents the effect of temperature towards palm oil cracking over composite MCM-41/ZSM-5. It is shown throughout this chapter that temperature plays an important role in palm oil cracking. Conversion was found to increase with increasing temperature. OLP yield and gasoline selectivity was highest at 550°C. Major components in OLP were olefins and isoparaffins. Olefins decreased whereas isoparaffins increased with temperature, indicating that isomerization was favoured at higher temperature. The components in gaseous products were C<sub>3</sub> and C<sub>4</sub> compounds, suggesting carbenium ion mediated mechanism.

Chapter 3 presents the effect of hydrogen, either as diluent or for activation towards palm oil cracking over composite MCM-41/ZSM-5. Increase in hydrogen feed concentration had negative effects on conversion and gasoline selectivity. Similar effects were also found when longer duration of hydrogen activation was employed. On the other hand, increase in hydrogen activation flow rate gave simultaneous increase in conversion and gasoline selectivity. Olefins were the main components in gasoline for cracking with hydrogen at 550°C. Aromatics were absent when hydrogen was used as diluent or when longer duration of activation was employed. Gas composition was mainly C<sub>3</sub>, followed by C<sub>4</sub> compounds.

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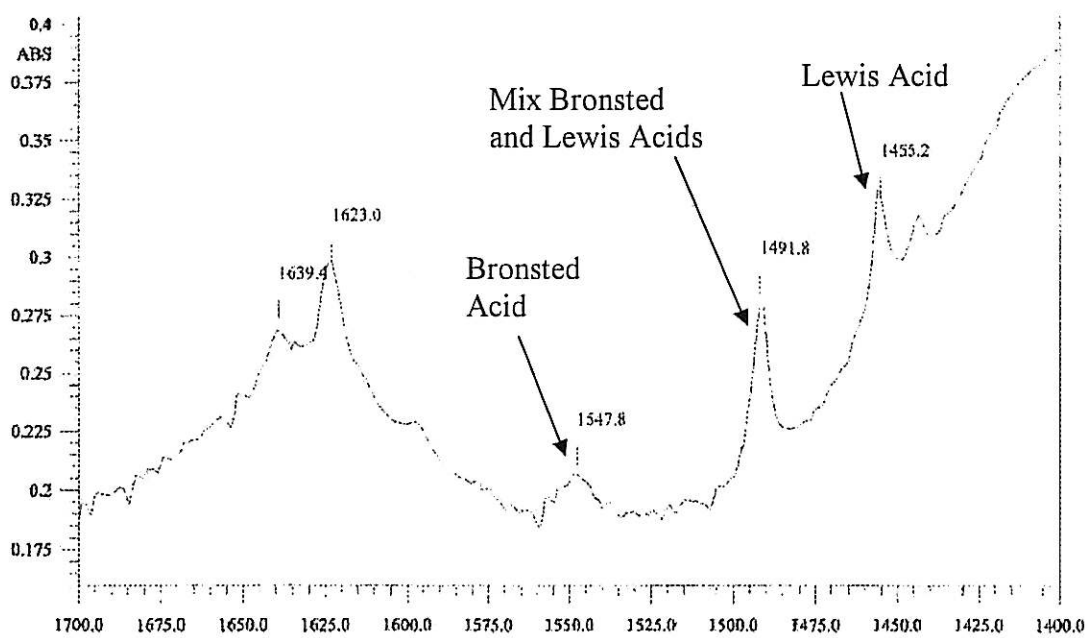
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## APPENDIX A

## PYRIDINE ADSORPTION PEAKS FOR COMPOSITE MCM-41/ZSM-5

**Figure A1** Pyridine Adsorption peaks for MCM-41/ZSM-5

## APPENDIX B

## CATALYTIC PROPERTIES OF COMPOSITE MCM-41/ZSM-5

Table B1: Catalytic properties of composite MCM-41/ZSM-5

BET Surface Area (m <sup>2</sup> /g)	280.65
BET Micropore Volume (cm <sup>3</sup> /g)	0.01
BJH Average Pore Size (Å)	33.28
Brønsted Acidity (μmol/g)	12
Lewis Acidity (μmol/g)	14