

CATALYTIC CRACKING OF PALM OIL TO GASOLINE USING ZEOLITE
CATALYSTS

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IN THE SWEET MEMORY OF MY LOVELY ELTERN

AND

DEDICATED TO MY BELOVED GRANDCHILDREN

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ABSTRACT

The refined, bleached and deodorized palm oil (RBDPO) was converted to gasoline by passing its vapor through catalyst in a fixed bed reactor at atmospheric pressure. The resulting gas and liquid products were analyzed with a gas chromatograph. The catalysts were characterized with X-ray diffraction (XRD), Pyridine absorption-infrared spectrophotometry (Py-IR) and nitrogen adsorption (NA) methods. The selection of a promising zeolite for palm oil cracking using H-ZSM-5 and H-Beta catalyst was performed with reaction temperature ranging from 450°C to 525°C and a weight hourly space velocity (WHSV) of 2.5h⁻¹. The H-ZSM-5 produced the best results with 96.12 wt% palm oil conversion and 29.92 wt% of gasoline selectivity at 525°C. The gasoline contained mostly naphthenes, followed by isoparaffins, aromatics, and olefines. Pretreatment of H-ZSM-5 at hydrogen (H₂) flow rate of 1 L/h for 1 hour gave higher gasoline selectivity and conversion of 34.96 wt% and 95.7 wt% at 500°C. Increasing the H₂ flow rate for pretreatment catalyst decreased the conversion and gasoline selectivity. The gasoline composition was enriched with naphthenes, aromatics and isoparaffins. Loading copper (Cu) on H-ZSM-5 from 2 wt% to 8 wt% decreased the conversion and gasoline selectivity. Consequently, highest conversion of 86.30 wt% and gasoline selectivity and 19.53 wt% was obtained with 2 wt% of Cu-ZSM-5 catalyst. Copper loading effected in the decreasing of crystallinity, surface area and Brönsted acidity of HZSM-5. Gas as side products consisted mainly of C₃ and C₄ compounds. The coke was obtained about 1 wt%.

ABSTRAK

Minyak kelapa sawit yang telah diproses (RBDPO) dapat ditukarkan kepada gasolin dengan mengalirkan wapnya melalui mangkin zeolit dalam reaktor lapisan terpadat pada tekanan atmosfera. Gas dan cecair yang terhasil dianalisis menggunakan kromatografi gas dengan pengesan *TCD* dan *FID*. Pencirian mangkin dijalankan menggunakan kaedah pembelauan sinar-X (*XRD*), spektroskopi infra merah-penjerapan piridina (*Py-IR*) dan penjerapan nitrogen (*NA*). Pemilihan zeolit yang efektif bagi pemecahan minyak sawit menggunakan mangkin H-ZSM-5 dan H-Beta pada suhu tindak dilakukan pada balas 450°C hingga 525°C dan kelajuan berat per jam (*WHSV*) sebanyak 2.5 jam⁻¹. H-ZSM-5 menunjukkan hasil yang baik dengan 96.12 % penukaran dan 29.92 % kepemilihan terhadap gasolin pada suhu 525°C. Komponen gasolin tertinggi adalah naftena, diikuti oleh isoparafin, aromatik dan olefin. Rawatan mangkin H-ZMS-5 menggunakan hydrogen (H_2) pada kadar alir 1 L per jam selama 1 jam memberikan penukaran dan kepemilihan terhadap gasolin yang lebih tinggi iaitu sebanyak 95.7 % dan 34.96 %. Peningkatan kadar alir hidrogen (H_2) bagi rawatan mangkin menurunkan penukaran dan kepemilihan terhadap gasolin. Gasolin yang diperolehi kaya dengan naftena, aromatik dan isoparafin. Peningkatan dalam peratus berat kuprum(Cu) dalam Cu-ZSM-5 dari 2% kepada 8% menurunkan penukaran dan kepemilihan terhadap gasolin. Akibatnya, penukaran dan kepemilihan terhadap gasolin tertinggi adalah pada 2% berat Cu yaitu 86.30% dan 19.53%. Adanya kuprum dalam H-ZSM-5 menurunkan kekristallan, luas permukaan dan keasidan Brönsted daripada HZSM-5. Hasil sampingan adalah gas yang kaya dengan komponen C_3 dan C_4 . Sedangkan perolehan arang sekitar 1% berat.

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LIST OF SYMBOLS AND ABBREVIATIONS

A_{cs}	-	Molecular cross-sectional area
BET	-	Brunauer Emmett Teller
β	-	Beta
C	-	BET constant
d	-	Pore diameter, interplanar spacing
boe	-	billion barrels of oil equivalent
F	-	Feed
FID	-	Flame Ionization Detector
GC	-	Gas Chromatography
M	-	Molecular Weight
n	-	Number
N	-	Avogadro's Number

NA	-	Nitrogen Absorption
OLP	-	Organic Liquid Product
P	-	Pressure, Product
Py-IR	-	Pyridine Infra Red
R	-	Residue
RBDPO	-	Refined Bleached Deodorized Palm Oil.
S	-	Surface Area
TCD	-	Thermal Conductivity Detector
XRD	-	X – Ray Diffraction
ZSM-5	-	Zeolite Socony Mobile-5
W	-	Weight
WHSV	-	Weight Hourly Space Velocity
θ	-	Diffraction angle
λ	-	Beam wavelength

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CHAPTER 1

INTRODUCTION

1.1 Background

The fossil fuel as a petroleum fuel is a limited energy resource. The dependencies on petroleum as a main energy source cannot be denied. Presently, the energy for transportation alone consumes about 38% of petroleum, followed by the industrial sector, which consumes about 14% of petroleum. The other sectors that consume a lot of energy are aviation, power generation, and marine (Absi *et al.*, 1997). Figure 1.1 indicates the distribution of crude petroleum oil consumed by various sectors.

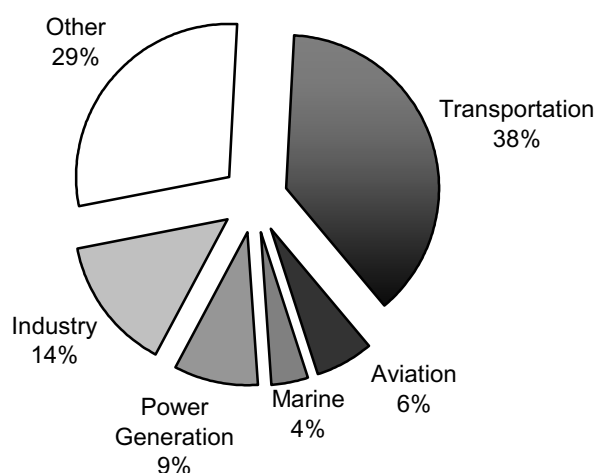


Figure 1.1 Distribution of crude petroleum oil consumption by various sectors (Absi *et al.*, 1997)

The increasing demand for gasoline, kerosene and diesel will eventually raise big problems because petroleum is not a renewable source. As petroleum reserves deplete faster year by year, more rapidly than it is formed, thus a continuous supply of petroleum is required in searching for new alternative sources. Natural gas looks like the best alternative, but the problem of transportation and safe handling makes it difficult to distribute the gas to rural areas. On the other hand, coal can be converted to gasoline; however, that involves a high production cost and unfortunately this product has poor quality. Moreover, the extraction of coal by underground mining is relatively dangerous and an unhealthy occupation, while the establishment of deep mines demands considerable capital expenditure (Haag *et al.*, 1980).

Malaysia is the 24th and 13th largest crude oil and natural gas reserves respectively in the world. Combined, Malaysia has total domestic reserves of 19.345 billion barrels of oil equivalent (boe): 75% gas and 25% oil. As at 1 January 2004, Malaysia's crude oil reserve stood at 4.841 billion barrels and natural gas reserve stood at 87 ton cubic feeds (14,504 million boe). Gas reserves remain three times the size of oil reserves (Oil & Gas Malaysia Profile, 2004).

Bio-fuel appears as a promising alternative for energy source. This resource is renewable and also environmental friendly due to none of sulfur and nitrogen content. Furthermore it is easy to be handled and transported, as it appears in liquid form. Vegetable oils contain triglycerides of long chain fatty acids and glycerols, which are the best choice to obtain hydrocarbons fuel (Chen *et al.*, 1986). Thus, vegetable oils of different origins such as palm oil, canola oil, coconut oil, soybean oil, rapeseed oil, jojoba oil and others offer the source of hydrocarbons, which can be transformed into desired liquid fuel. Because of their high viscosity (at room temperature they have 10-time diesel's viscosity), direct utilization of these triglycerides into the combustion engines would cause severe problems. Therefore, the viscosity should be reduced either by converting the glycerides into different compound which pose low viscosity, or by breaking it into smaller hydrocarbon chain.

Palm oil is one of the vegetable oils that is abundantly grown in Malaysia. It has the potential to be the raw material for bio-fuel production. Statistics by Foreign Agricultural Service, Official USDA Estimates for December, 2004 (Figure 1.2) has shown that for five consecutive years, Malaysia produced the largest volume of palm oil. In year 2004, Malaysia produced about 14 million tons of palm oil, followed by Indonesia, which was about 11.5 million tons of palm oil.

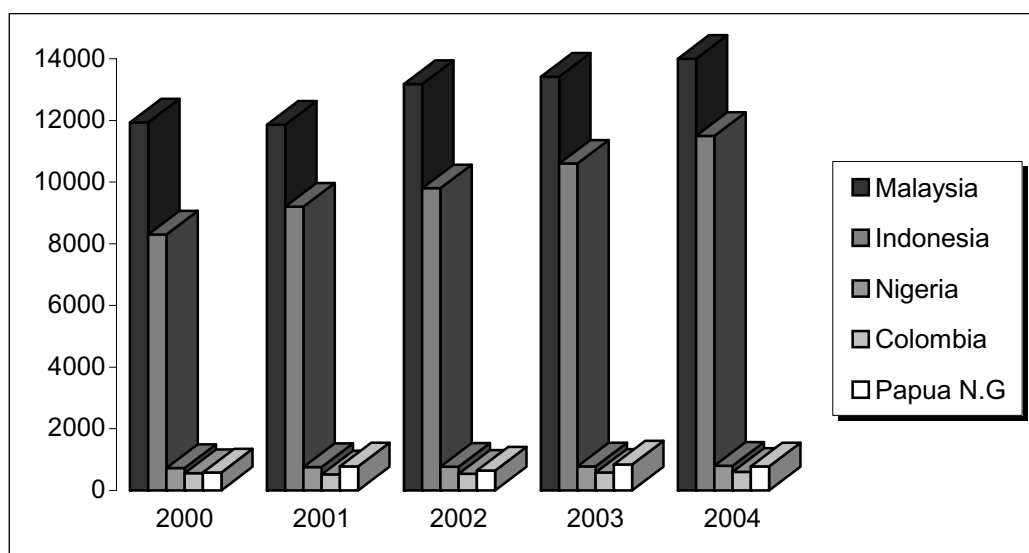


Figure 1.2 World production of palm oil, 2000–2004 (Foreign Agricultural Service, Official USDA Estimates for December 2004)

Most of the researches done on palm oil conversion to gasoline used refined, bleached, deodorized (RBD) palm oil. This is due to the high viscosity of CPO, which causes problems such as incomplete combustion, poor fuel atomization and cooking of fuel injectors if used directly without treatment (Salam *et al.*, 1996; Bari *et al.*, 2002).

The suitable method to crack the triglycerides from vegetable oil is essential and the yield of the gasoline obtained should be also observed. The fluctuation of palm oil price gives an advantage to this process; because it will be cheaper for the future. However, more studies have to be done to make sure this process is economically viable.

The ultimate challenge still lies in the development of catalyst and cracking process. A stable, shape selective and high acidic catalyst is needed in order to achieve high conversion and gasoline selectivity in this process. The difference between cracking with and without hydrotreating for conversion of palm oil was studied. The researches in this field agree that the process of converting palm oil to

gasoline depends on the acidity of catalyst, especially Brønsted acid sites (Corma *et al.*, 1991). On the other hand, products obtained by using hydrogen pretreatment on catalyst of several organic processes were higher than without hydrogen pretreatment (Shishido and Hattori, 1996; Ravasio *et al.*, 2002; Wojcieszak *et al.*, 2004). Therefore, this research tries to find a suitable catalyst and determine the effect of metal loading on catalyst for palm oil cracking to gasoline by comparing between H-ZSM-5 and H-Beta, furthermore subsequently using impregnated copper on better zeolite chosen.

1.2 Problem Statement

The oil crisis in the 70's caused researchers to explore various possibility to convert vegetable oil to liquid fuel (Haag *et al.*, 1980; Prasad and Bakhshi, 1985; Craig and Coxworth, 1987; Sharma and Bakhshi, 1991; Adjaye and Bakhshi, 1995a; Bhatia *et al.*, 1998; Twaiq *et al.*, 1999; Kasim and Amin, 2001; Ooi *et al.*, 2002; Twaiq *et al.*, 2003; Twaiq *et al.*, 2004). However the experimental process of vegetable oil conversion can still be improved.

The research on vegetable oil catalytic cracking, especially palm oil, has a bright prospect in the future in Malaysia. The decrease of palm oil price gives an advantage to this process

The effect of hydrogen pretreatment on the catalytic activity of zirconium oxide modified with sulfate ion and platinum ($\text{Pt}/\text{SO}_4^{2-}\text{-ZrO}_2$) for cumene cracking was studied by Shishido and Hattori (1996). They found that pretreatment of the catalyst with hydrogen gave high activity for cumene cracking.

Cu/SiO₂ activated with hydrogen for hydrogenation of rapeseed oil showed good activity and excellent selectivity towards formation of high oleic derivatives (Ravasio *et al.*, 2002). Wojcieszak and co-workers (2004) carried out the hydrogenation of benzene to cyclohexane using hydrogen pretreated Ni/MCM-41 and Ni/AlMCM-41. They found that Ni/MCM-41 showed high catalytic activity compared to Ni/AlMCM-41.

Besides that, the important factors to develop are the improvement in preparation of catalysts for palm oil cracking. Stability, shape selective, pore structure and high acidity are needed in order to achieve high gasoline selectivity in the product. Consequently, this research is carried out by flowing of hydrogen through the catalyst and loading copper on zeolite as catalyst.

1.3 Objectives of Study

The objectives of this research are as follows:

1. To select better catalyst, either H-ZSM-5 or H-Beta zeolite for palm oil cracking to gasoline, in terms of conversion and gasoline selectivity.
2. To study the effects of hydrogen pretreatment on zeolite for palm oil cracking to gasoline.
3. To study the effect of copper loading in hydrogen pretreatment copper-zeolite catalyst for palm oil cracking to gasoline.

1.4 Hypothesis

As mentioned earlier, hydrogen pretreatment on catalyst for cracking and hydrogenation showed better result than its process alone, however recently study about hydrogen pretreatment on catalyst for palm oil cracking has not founded yet. Thus it has been hypothesized that hydrogen pretreatment on catalyst for palm oil cracking is anticipated to gain higher selectivity of gasoline compared to catalytic cracking alone.

The hydrogen pretreated catalysts that have been studied for cracking and hydrogenation were transition metal such as platinum, copper and nickel impregnated on a support. Addition of metal on the support improved the support's catalytic activity (Shishido and Hattori, 1996; Ravasio *et al.*, 2002; Wojcieszak *et al.*, 2004). Although, the reducibility of platinum and nickel is higher than copper, however in this study, copper is chosen as impregnated metal on zeolite. The reasons are because its cost is cheaper than platinum and nickel; in addition it is expected to improve cracking activity of palm oil.

1.5 Scopes of Study

The experiment was designed to study the hydrogen pretreatment effect on catalysts for palm oil cracking to gasoline. This research focuses on several aspects such as follows: the setting up of an experimental rig, the applied catalysts, the products obtained and the effects of operation conditions.

Firstly, the experimental rig and micro distillation unit were set up before the sub sequential study carried out. Secondly, the catalyst selection tests are conducted

in order to determine better catalyst, between H-ZSM-5 and H-Beta zeolite, for palm oil cracking. Thirdly, the reaction parameters effects (reaction temperature and hydrogen flow rate) for hydrogen pretreatment catalyst were investigated. Lastly, the effect of copper loading on zeolite in hydrogen pretreated copper zeolite for palm oil cracking was also investigated. X-ray diffraction (XRD), Pyridine adsorption for infra red spectroscopy (PY-IR) and nitrogen adsorption (NA) analysis were carried out to characterize the catalysts.

1.6 Layout of the Thesis

This thesis reports the research of the experimental rig design for hydrogen pretreatment on catalyst (*in situ*) and catalytic palm oil cracking to gasoline. This work was also to study the relation between catalyst properties and obtained products from the experiments. Chapter 1 describes the introduction, the problem statement, objectives, hypothesis and scopes of this research.

Chapter 2 reviews literatures those related to the vegetable oil cracking and hydro pretreatment of catalyst on several organic reactions. The palm oil and gasoline properties as well as the characteristics of ZSM-5, Beta and copper are also reviewed.

Chapter 3 explains the methodologies of the experimental and characterization of the catalysts. The experimental rig set up for hydrogen pretreatment of catalyst and palm oil cracking are described. Furthermore, the catalyst preparation and catalytic testing procedure, as well as the methods to analyze liquid and gaseous products are included. Finally, the catalyst characterization techniques are explained.

Chapter 4 discusses the comparison of results by using H-ZSM-5 and H-Beta for palm oil cracking to produce gasoline. Chapter 5 discusses the effect of reaction temperature, hydrogen flow rate on hydrogen pretreatment of zeolite for palm oil cracking to produce gasoline using better catalyst. The effect of different weight percentage of copper in hydrogen pretreated copper loaded zeolite for palm oil cracking process were described detail. Finally the general conclusions and recommendations for future studies were stated in chapter 6.

6.2 Recommendations

Treated crude palm oil can be used as a feed instead of RBD palm oil. Economically, the price of crude oil is cheaper than RBD palm oil. The residual oil after frying can also be used as a raw material. This will give advantage to this process in terms of economy besides preserving the environment. Effect of co-feeding steam in the feed stream is also recommended for future. Steam is cheaper than nitrogen gas as a carrier gas and it also can activate the catalyst. Gas, as the side product from palm oil cracking has a high distribution of C₃-C₄ compounds. This product still has economical value by converting them to gasoline or other chemical products. Accuracy of the result can also be improved by using standard equipment. Optimization of temperature for the second preheated palm oil and flow rate carrier gas of nitrogen for palm oil cracking to gasoline over H-ZSM-5 and pretreated H-ZSM-5 is also suggested to be carried out. Lastly using lower reducibility metal and oxidative metal as metal loading on H-ZSM-5 such as cobalt, chromium, manganese and iron for palm oil cracking are also recommended.

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