

CHAPTER II

LITERATURE REVIEW

Jet fuel is a specialized fuel blended from the light distillates fractionated from crude petroleum. All jet fuels must meet the very rigorous requirements of aircraft turbine engines and fuel systems, which must be pristine and free from oxidation deposits in high temperature zones. Combustors require fuels that atomize and ignite at low temperatures, burn with controlled radiation and adequate heat release, do not produce smoke, and do not attack hot turbine parts. The operation of jet aircraft in long-duration flights at high altitudes necessitates a special requirement of good low-temperature flow behavior.

The most common jet fuel is a kerosene and paraffin oil-based fuel classified as JET A-1, which is produced to comply with an internationally standardized set of specifications. (Kerosene is thin oil distilled from petroleum or shale oil, and is used as a fuel for heating and cooking, in lamps, and as a denaturant for alcohol.)

The only other jet fuel that is commonly used in civilian aviation is called JET B. JET B is a fuel in the naphtha-kerosene "family" that is prized for its superior cold-weather performance. However, JET B's lighter composition makes it more dangerous to handle, and it is thus restricted only to areas where its cold-weather characteristics are absolutely necessary.

2.1 Biojet Fuel

Sustainable aviation biofuels ("biojet fuels") are one of the most promising solutions to meet the industry's ambitious carbon emissions reduction goal.

Bio-jet fuel is a renewable fuel that can be used instead of jet fuel derived from petroleum. Similar to biodiesel, vegetable oils and other biomass derived oils can be used as feedstock for biojet fuel production. Among the vegetable oils, sources are soybean, canola, palm, jatropha, and rape. Biojet fuel usually blends with petroleum-based Jet A/Jet A-1 fuel and 50 percent sustainable biofuels.

2.2 Raw Materials in Hydrotreated Renewable Jet Production

The fraction of raw materials for world commercial biodiesel production is rapeseed oil 84 %, sunflower oil 13 %, palm oil 1 %, soybean oil and others 2 %. Using edible oils to produce biodiesel in developing countries such as China with limited arable land per capita is not feasible and is banned. Therefore, only non-edible plants are considered as favorable resources for biodiesel production, such as Chinese tallow and *Jatropha curcas* L. trees which are producing non-edible oil in appreciable quantity.

The fatty acid composition of *Jatropha* oil is similar to other edible oils, but the presence of some toxic materials in kernel (e.g., curcin) renders the oil unsuitable for cooking purposes. The oil content in *Jatropha* seed ranges from 25 % to 40 % by weight and in the kernel itself ranges from 45 % to 60 %. Nowadays, *Jatropha* trees, as a potential alternative biodiesel crop, are widely cultivated in Southwest of China such as Yunnan, Sichuan, and Guangxi provinces. In the near future, it will supply part of crude oil for commercial biodiesel production in China. (Deng *et al.*, 2010)

Jatropha (*Jatropha curcas*) is one of such non-edible oils, contains about 14 % free fatty acid (FFA), which is far beyond the limit of 1 % FFA level that can be converted into biodiesel by transesterification using an alkaline catalyst. Hence, integrated optimized procedure for converting *jatropha* oil, which contains high FFA % into biodiesel, is very much required. Few researchers have worked with feed stocks having higher FFA % levels using alternative processes, which include a pretreatment step to reduce the FFAs of these feed stocks to less than 1 % followed by transesterification reaction with an alkaline catalyst. This procedure yielded more than 95 % biodiesel. (Tiwari *et al.*, 2007)

Table 2.1 Fatty acid composition of jatropha oil (Tiwari *et al.*, 2007)

Fatty acid	Systemic name	Formula	Structure ^a	wt%
Palmitic	Hexadecanoic	C ₁₆ H ₃₂ O ₂	16:0	11.3
Stearic	Octadecanoic	C ₁₈ H ₃₆ O ₂	18:0	17.0
Arachidic	Eicosanoic	C ₂₀ H ₄₀ O ₂	20:0	4.7
Oleic	<i>cis</i> -9-Octadecenoic	C ₁₈ H ₃₄ O ₂	18:1	12.8
Linoleic	<i>cis</i> -9, <i>cis</i> -12-Octadecadienoic	C ₁₈ H ₃₂ O ₂	18:2	47.3

Some physical properties of the most common fatty acids in vegetable oils and animal fats are shown in Table 2.2. Besides these fatty acids, numerous other fatty acids occur in vegetable oils and animal fats, but their abundance usually is considerably lower. Table 2.3 summarizes the fatty acid composition of some vegetable oils. Some sources of biofuel and yield of the parent crop oil are shown in Table 2.2.

Table 2.2 Selected properties of some common fatty acids (Knothe *et al.*, 1997)

Trivial (Systematic) Name ; Acronym ^b	MW	m.p. (°C)	b.p. (°C)	Formula	Heat of Combustion
Caprylic Acid (Octanoic Acid); 8:0	144.22	16.5	239.3	C ₈ H ₁₆ O ₂	-
Capric Acid (Decanoic Acid); 10:0	172.27	31.5	270	C ₁₀ H ₂₀ O ₂	1453.07 (25°)
Lauric Acid (Dodecanoic Acid); 12:0	200.32	44	131 ¹	C ₁₂ H ₂₄ O ₂	1763.25 (25°)
Myristic Acid (Tetradecanoic Acid); 14:0	228.38	58	250.5 ¹⁰⁰	C ₁₄ H ₂₈ O ₂	2073.91 (25°)
Palmitic Acid (Hexadecanoic Acid); 16:0	256.43	63	350	C ₁₆ H ₃₂ O ₂	2384.76 (25°)

Table 2.2 Selected properties of some common fatty acids (Knothe *et al.*, 1997)
(con't.)

Trivial (Systematic) Name ^a ; Acronym ^b	MW	m.p. (°C)	b.p. (°C) ^c	Formula	Heat of Combustion
Stearic Acid (Octadecanoic Acid); 18:0	284.48	71	360 ^d	C ₁₈ H ₃₆ O ₂	2696.12 (25°)
Oleic Acid (9Z-Octadecenoic Acid); 18:1	282.47	16	286 ¹⁰⁰	C ₁₈ H ₃₄ O ₂	2657.4 (25°)
Linoleic Acid (9Z,12Z- Octadecadienoic Acid); 18:2	280.45	-5	229-30 ¹⁶	C ₁₈ H ₃₂ O ₂	-
Linolenic Acid (9Z,12Z,15Z- Octadecatrienoic Acid); 18:3	278.44	-11	230-2 ¹⁷	C ₁₈ H ₃₀ O ₂	-
Erucic Acid (13Z-Docosenoic Acid); 22:1	338.58	33-4	265 ¹⁵	C ₂₂ H ₄₂ O ₂	-

a) Z denotes is configuration.

b) The numbers denote the number of carbons and double bonds. For example, in oleic acid, 18:1 stands for eighteen carbons and one double bond.

c) Superscripts in boiling point column denote pressure (mm Hg) at which the boiling point was determined.

Table 2.3 Fatty acid composition in vegetable oils (Fangrui and Milford, 1999)

Vegetable Oil	Fatty Acid Composition (wt. %)								
	14:0	16:0	18:0	20:0	22:0	24:0	18:1	18:2	18:3
Corn	-	11.67	1.85	0.24	-	-	25.16	60.60	0.48
Cottonseed	0.70	28.33	0.89	-	-	-	13.27	57.51	-
Peanut	-	11.38	2.39	1.32	2.52	1.23	48.28	31.95	0.93
Rapeseed	-	3.49	0.85	-	-	-	64.40	22.30	8.23
Soybean	0.10	11.75	3.15	-	-	-	23.26	55.53	6.31
Sunflower	-	6.08	3.26	-	-	-	16.93	73.73	-
Palm	1.00	42.8	4.50	-	-	-	40.50	10.10	0.20
Jatropha	0.06	13.81	6.89	0.22	0.04	0.05	45.84	31.77	0.21

Table 2.4 Comparison of some sources of biodiesel (Chisti, 2007)

Crop	Oil Yield (L ha ⁻¹)
Corn	172
Soybean	446
Canola	1,190
Jatropha	1,892
Coconut	2,689
Palm	5,950
Microalgae ^(a)	136,900
Microalgae ^(b)	58,7000

^(a) 70 % oil (by wt) in biomass

^(b) 30 % oil (by wt) in biomass

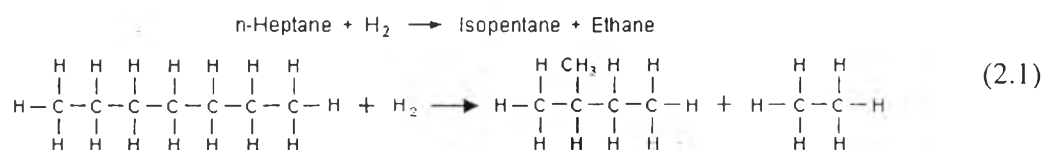
2.3 Biojet Fuel Production

2.3.1 Reaction for Biojet Fuel Production

Hydrocracking and hydroisomerization of *n*-paraffins are important refinery processes used to produce highly valuable chemicals, such as high-octane reformulated gasoline, diesel and lubricating oil. Hydroconversion reactions are efficiently carried out over bifunctional catalysts, consisting of a metal, which is responsible for hydrogenation–dehydrogenation reactions, and an acidic functionality, which is responsible for C–C and C–H bond activation. Therefore, in order to promote the hydroisomerization reaction, different oxides, such as alumina, zirconia, and sulfides were applied to the reaction. Also, the zeolites (e.g., MOR, BEA, ZSM-5, MAZ, OFF, USY, ZSM-22, MCM-22), and zeolite-like solid acids (e.g., SAPO-11, AIPO-5, SAPO-41) have been used as acidic components together with a metal (i.e., Pt, Ni, Pd, Co, Mo, Ir, Ru, Rh, Re). Over zeolites, both process proceed through consecutive branching reactions (i.e., isomerization of *n*-paraffins), while cracking reactions occur in parallel with isomerization. (Santos *et al.*, 2011)

2.3.1.1 Hydrocracking

Hydrocracking is a catalytic chemical process used in petroleum refineries for converting the high-boiling constituent hydrocarbons in petroleum crude oils to more valuable lower-boiling products such as gasoline, kerosene, jet fuel and diesel oil. The process takes place in a hydrogen-rich atmosphere at elevated temperatures (260 – 425 °C) and pressures (35 – 200 bar).

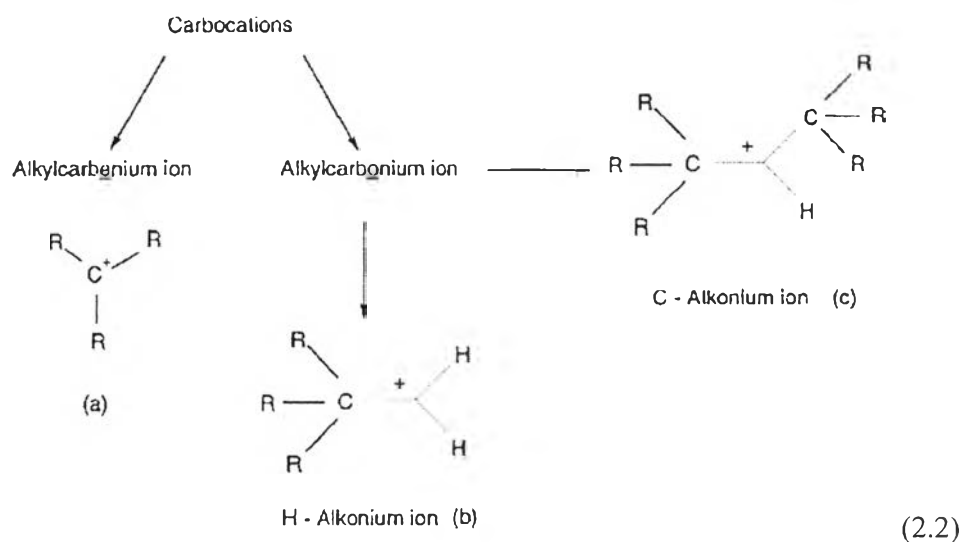


Modifications of an HY zeolite for *n*-octane hydroconversion were studied by Santos. This work HY zeolite were modified by either dealuminization (D) followed by chemical vapor deposition of silicon (CVD).

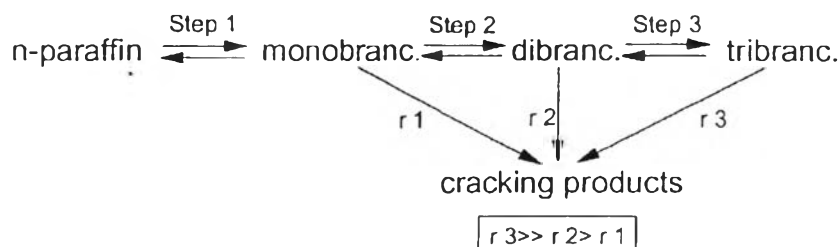
Additionally, impregnation of Pt or Ni was performed over selected D and CVD solids.

The catalytic cracking of aliphatic hydrocarbons using zeolites (i.e., C–C bond scission) can be classified in accordance with the following mechanisms: (a) a classical cracking mechanism consisting of a hydride transfer step to a carbenium ion followed by β -scission, (b) a non-classical Haag–Dessau (protolytic) cracking mechanism proceeding via a carbonium ion transition state, or (c) oligomerization cracking.

The mechanism consists of a carbenium ion that abstract an alkane forming another carbenium ion, and the latter cracks by β -scission (e.g., cleavage of the C–C bond located in the β position to the trivalent positively charged carbon) forming an alkene (Equation 2.2) (Santos *et al.*, 2011).



Reaction pathway of the *n*-alkane is first isomerized into its monobranched isomers and subsequently into di- and tri-branched isomers. According to the Equation 2.3 (Calemma *et al.*, 2000), the cracking products are formed mainly through β -scission of di- and tri-branched isomers since they can crack through a more energetically favorable β -scission mode not allowed for the monobranched and linear molecules (Calemma *et al.*, 2000).



(2.3)

2.3.1.2 Hydroisomerization

Isomerization is one of several reactions that is used during naphtha reforming, to upgrade low octane naphtha to a higher octane effluent. Under the process conditions of reforming, other reactions could occur like aromatization (or dehydrocyclization) and dehydrogenation, which are accompanied by some cracking products. (Hanafi *et al.*, 2014).

Hydroisomerization of *n*-dodecane over Pt/Y zeolites with different acid characteristics was study by Hyung Won Lee. The Y zeolites used were NaY, HY (SiO₂/Al₂O₃ = 5.1), HY (SiO₂/Al₂O₃ = 80), and HY (SiO₂/Al₂O₃ = 200). NaY was ion-exchanged with NH₄Cl to impart acidity. HY (SiO₂/Al₂O₃ = 5.1) and HY (SiO₂/Al₂O₃ = 80) were silylated to modify their acidity. The Pt loading was 0.5 wt% by using the incipient wetness impregnation method. Additionally, 0.1, 0.2, and 1 wt% Pt was loaded on HY (80) for investigate the effect of Pt content on hydroisomerization activity.

From the result, NaY, HY (SiO₂/Al₂O₃ = 5.1), HY (SiO₂/Al₂O₃ = 80) and HY (SiO₂/Al₂O₃ = 200), the conversion of *n*-dodecane decreased with increasing SiO₂/Al₂O₃, whereas selectivity of isomerization increased with increasing SiO₂/Al₂O₃. HY (SiO₂/Al₂O₃ = 80) showed the best hydroisomerization activity. The catalytic activities of NaY and HY (SiO₂/Al₂O₃ = 5.1) were enhanced significantly by ion-exchange and silylation treatment due to the effect of acidity control. The experiments range of temperatures and pressures to find the optimal reaction condition showed that the *iso*-dodecane yield increased with decreasing pressure. And the amount of impregnated metal was changed within the

range of 0.1–1.0 %, the yield of *iso*-dodecane increased slightly with increasing metal concentration, but the effect was not large. This suggests that the effect of the acid sites is greater than that of the impregnated metal.

2.3.1.3 Hydrogenation and Dehydrogenation

Hydrogenation is the chemical reaction that can obtain from the addition of hydrogen until becoming saturated substances, and dehydrogenation is pulled hydrogen out and reverted to unsaturated substances. Hydrogenation of the carbon-to-carbon double bonds in triglycerides, especially of vegetable oils, is a major industry in many parts of the world. Principal products, obtained by catalytic hydrogenation, include oleomargarines, shortening, soap stock and industrial greases and oils. However, hydrogenation mechanism is not completely clarified, until now. The chemistry of triglycerides partial hydrogenation process is complicated. Both mono- and poly-unsaturated acid groups in the oil hydrogenate at various rates, depending on the operating conditions. Furthermore, the geometrical and positional isomerization of the double bonds in mono- and poly-unsaturated acid groups occurs in significant numbers during the hydrogenation (Jovanović *et al.*, 2000).

In the petroleum industry, numerous processes involved in the manufacture of gasoline and petrochemical products are based on the destructive hydrogenation of hydrocarbons. In the late 20th century the production of liquid fuels by hydrogenation of coal has become an attractive alternative to the extraction of petroleum. The industrial importance of the hydrogenation process dates from 1897, when Sabatier discovered that the introduction of a trace of nickel as a catalyst facilitated the addition of hydrogen to molecules of carbon compounds. The catalysts most commonly used for hydrogenation reactions are the metals nickel, platinum, and palladium and their oxides. For high-pressure hydrogenations, copper chromite and nickel supported on kieselguhr (loose or porous diatomite) are extensively used.

2.3.1.4 Hydrogenolysis

Hydrogenolysis is a chemical reaction whereby a carbon-carbon or carbon-heteroatom single bond is cleaved or undergoes "lysis" by hydrogen. The heteroatom may vary, but it usually is oxygen, nitrogen, or sulfur. A related reaction is hydro-genation, where hydrogen is added to the molecule, without

cleaving bonds. Usually hydrogenolysis is conducted catalytically using hydrogen gas (Connor *et al.*, 1932). Equation 2.4 represents a hydrogenolysis reaction:

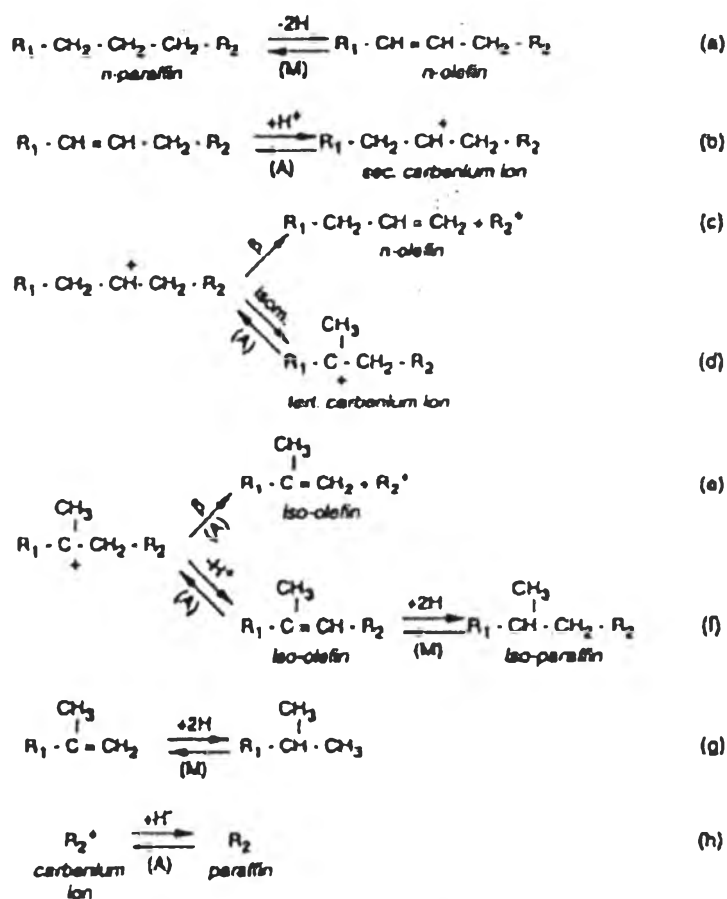


2.3.1.5 Reaction Mechanism of Bifunctional Hydrocracking Catalysts

The mechanisms of hydrocracking reaction are essentially the carbenium ion mechanism of catalytic cracking reaction both with that of hydrogenation and isomerization reaction. The mechanism of paraffin hydrocarbon over bifunctional amorphous catalysts was studied in 1960. The later studied were carried out mostly by using model compounds. Base on the pioneering work of Mills and Weisz, a carbenium ion mechanism was proposed, similar to that described for catalytic cracking, with additional hydrogenation and skeletal isomerization. More recent studies of *n*-paraffin hydroconversion over noble metal-loaded, zeolite-based catalysts have concluded that the reaction mechanism is similar to that proposed for amorphous, bifunctional hydrocracking catalysts. Hydrocracking of *n*-paraffins over a bifunctional catalyst goes through the following steps:

1. Adsorption of *n*-paraffins on metal sites
2. Dehydrogenation with formation of *n*-olefins
3. Desorption from metal sites and diffusion to acid sites
4. Skeletal isomerization and/or cracking of olefins on the acid sites through carbenium ion intermediates
5. Desorption of formed olefins from acid sites and diffusion to metal sites
6. Hydrogenation of these olefins (*n*- and *iso*-) on metal sites
7. Desorption of resulting paraffins

The elementary reactions corresponding to the reaction path described are shown in Equation 2.5. Product analysis has shown in (a) to (h) that whenever several reaction pathways are possible, the one leading to the formation and subsequent cracking of a tertiary carbenium ion is preferred (Equation (d) and (e) (Scherzer and Gruai, 1996).



β : beta scission, A: acid site, M: metal site

(2.5)

The hydrogenation-to-acidity ratio is significantly effect on the hydrocracking of paraffin. The *iso*-to-normal ratio in product paraffin increases with decreasing reaction temperature because the cracking rate of *iso*-paraffins increases faster than that of *n*-paraffins at higher temperature. This is illustrated by the hydrocracking of *n*-decane in Figure 2.1 The *iso*-to-normal ratio also increases when the catalyst contains a weak hydrogenation component and strong acid component. The higher *iso*-to-normal ratio is attributed to a higher rate of isomerization of olefinic intermediates at the strong acidic sites.

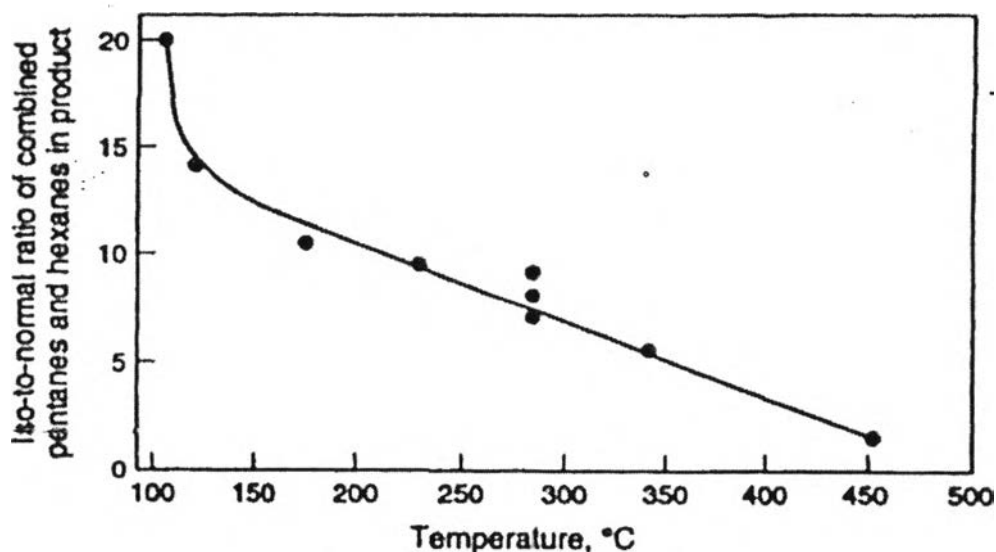


Figure 2.1 Effect of reaction temperature on iso-to-normal paraffin ratio in products obtained from hydrocracking of *n*-decane over strongly acidic catalyst (Scherzer Scherzer and Gruai, 1996).

Figure 2.2 shows the product distribution of *n*-hexadecane hydrocracking with catalysts having different hydrogenation components and different supports. A higher hydrogenation-to-acidity ratio in the catalyst was result in wider spread of products. Such hydrocracking is sometime called “ideal hydrocracking” and often results in higher liquid yields. In “Ideal hydrocracking,” the rate determining events (isomerization and β scission) occur at the acid site, whereas the metal sites serve only for rapid hydrogenation and dehydrogenation.

A high rate of desorption and hydrogenation of the primary cracking products before secondary cracking implied to the wide spread of products. The high rate of carbenium ion desorption is due to their displacement by *n*-olefins, whose steady state concentration is higher in the presence of strong hydrogenation/dehydrogenation component (competitive sorption/desorption). The strength of this component can influence the rate of desorption of tertiary carbenium ion and product distribution. Figure 2.2, the long-chain molecule tend to crack in or near the center because C_1 or C_2 hydrocarbons were not found in product.

On the other hand, the catalysts with low hydrogenation-to-acidity ratios, some of primary cracking reaction remains longer adsorbed at acid site and undergo secondary cracking. This results in higher yields in low molecular weight products (C_2-C_6). In low hydrogenation component, the secondary cracking reaction becomes more important and lead to high yield of low molecular weight products.

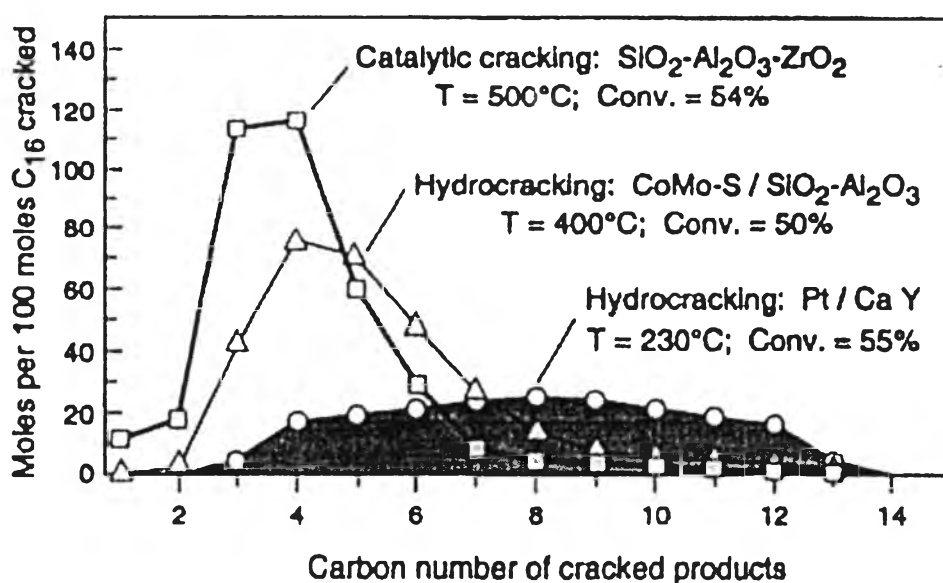


Figure 2.2 Effect of reaction temperature on isomerization and hydrocracking of n-tridecane over a Pt/CaY zeolite catalyst (Scherzer and Gruai, 1996).

2.3.2 Catalyst for Biojet Production

2.3.2.1 Bifunctional Catalyst

Many important hydrocarbon reaction such as paraffin cracking and isomerization, are catalyzed by material with acid properties. Some reactions require sites of stronger acidity than others, for example, in paraffin cracking, the required strength of the acid sites is stronger than that required for isomerization. When the metallic function is added to the acid function, a bifunctional catalyst is obtained. This catalyst presents in general a more beneficial behavior than the catalyst having only the acid function. The bifunctional metal-acid catalysts are

generally porous oxides with acid properties that have a small amount of a metal support on them. The acid function of support and the metal function may be tuned to promote the desired reaction selectivity by the addition of promoters.

The alternative bifunctional concept suggests that the initial activity of acidic components with strong acidity is high enough to activate an alkane molecule. The main problem associated with the use of strongly acidic catalysts is the fast deactivation by carbonaceous species generated from the olefinic precursors. The key role of metallic component in this bifunctional concept is to prevent poisoning and to maintain the performance of acid centers by means of hydrogen activation to hydrogenate the olefinic intermediates. For example, over the monofunctional H mordenite, the high catalytic activity for *n*-butane isomerization decreased drastically with time on stream. Deactivation was minimized by hydrogen and Pt loading that was thought to reduce the concentration of intermediate olefins in the zeolite pores. (Kuznetsov., 2003).

Zhan *et al.* summarized a great number of reported data to propose a series of rules that have proved to be versatile guidelines for the preparation of tailored hydroisomerization and hydrocracking catalysts for hydrocarbon processing. These rules were designated as the “hybridization rules of electronic and acidic interactions”, and the main points are as follows. (1) The metal (i.e., the electronic component) and the support (i.e., the acidic component) of the catalyst interact with each other to form a hybridized active center. The catalytic properties of the hybridized centers depend on the nature of the precursor components as well as the interaction between the two components. (2) The stronger the acidity of the support, the higher the cracking activity, and the lower the isomerization selectivity. However, by hybridizing the acidity of the support with the electronic action of the metal component, the hydrogenation activity will be strengthened, whilst the cracking activity will be weakened, and this hybridizing effect will in turn enhance the isomerization activity of the catalyst.

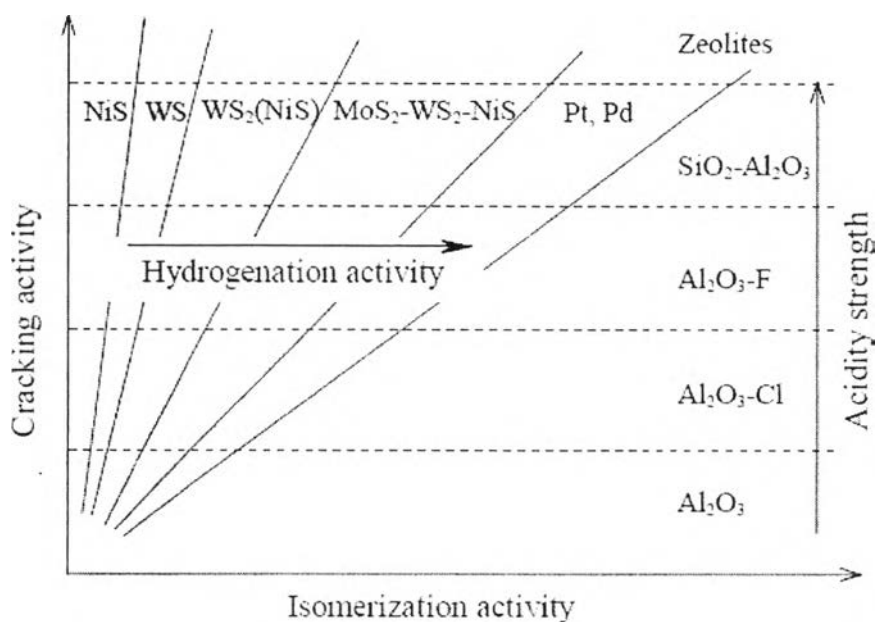


Figure 2.3 Schematic illustration of the dependence of hydroisomerization and hydrocracking activity on the interaction between the metal and the acidic components (Zhang *et al.*, 2010).

A long chain hydrocarbon from fluid phase enters the catalyst through physisorption to a metal function. On the metal function, the elimination of a single $\cdot\text{H}_2$ molecule takes place resulting in an olefin. This olefin is desorbed by the metal sites and chemisorbs on an acid site for protonation yielding a carbenium ion. This carbenium ion can isomerize through alkyl shift and/or protonated cyclopropane (PCP) and/or cyclobutane (PCP) branching. Cracking occurs through scission of the C-C bond in β -position of the charge-carrying carbon atom. (Borghet., 2010)

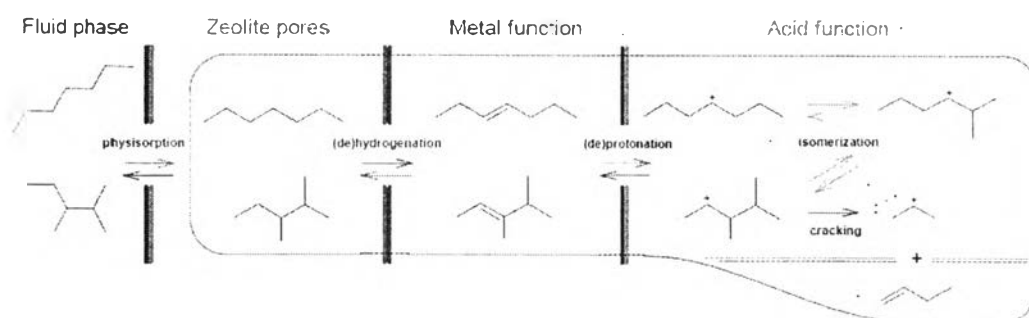


Figure 2.4 Bifunctional reaction mechanism of hydroconversion (Borgh., 2010).

2.3.2.2 Metal

Most industrial hydroisomerization catalysts are based on zeolites, which provide the acid function. As the hydrogenating-dehydrogenating function, several metals have been tested including Pt, Pd, Rh, Ir, Ru, Re and Ni, mostly associated with mordenite or CaY. Bifunctional catalysts, with both hydrogenating dehydrogenating and isomerization function have shown high efficiency in alkane hydroisomerization. Noble metal-zeolite catalysts especially Pt or Pd loaded Y mordenite and beta possess a high activity and selectivity for hydroisomerization of *n*-alkanes (De Lucas *et al.*, 2006).

Zhang *at el.* showed that the higher the acidity of the support, the more enhanced are the cracking reactions at the expense of the selectivity to hydroisomerization. They also suggest that metal sites and catalyst support interact forming a “hybrid” active site, which seems to enhance the hydrogenation activity constraining undesired cracking reactions.

An additional approach toward improved catalytic performance is to use catalysts either with weak acidity for suppressing the hydrocracking of multibranched alkyl carbenium ions or with high metal dispersion for enhancing the hydrogenation of desorbed multibranched alkenes. The balance between the two catalytic functions, i.e. the density and the strength of the Brönsted acid site (H⁺) and the amount and the dispersion of the metal is what determines the desired selectivity. When the hydrogenating function is highly active, the activity and

the selectivity of the bifunctional catalyst will depend only on the acidic function, which is the rate-limiting step in the absence of diffusion limitations. A decrease in acidity would decrease cracking, but also the global activity since the acidic step is rate limiting. Metal content in the hydroisomerization catalysts has also a crucial effect on the catalytic activity and selectivity. However, the optimum Pt content in the majority of modern industrial light naphtha hydroisomerization catalysts is in the range of 0.40 % (Elliopoulou *et al.*, 2013).

Park and Ihm, 2000 studied the bifunctional platinum (0.5 wt%) catalysts containing ZSM-5, ZSM-22, SAPO-11, Al-MCM-41, H-Y were tested for the hydroisomerization of *n*-hexadecane and compare their catalytic activities. The catalysts were dried at 110 °C in oven for 10 h and calcined at 320 °C for 2 h in air. The catalyst was carried out in batch reactor of 300 ml. A 0.5 g of catalyst was loaded in the reactor and hydrogen gas was introduced with 50 ml/min for 2 h. The reactor was cooled down to room temperature, fed with 50 ml of *n*-hexadecane and pressurized to 34.5 bars with hydrogen gas. The impeller was set at 1000 rpm. The reactor was heated at rate of 5 °C/min to 350 °C and the pressure was set to 103 bars. The liquid products were analyzed by gas chromatography, the results on Pt/H-Y from this experiment showed that the most cracked products (*n*-alkane) have carbon numbers in the range between C₄ and C₁₃ more than the isomerized products (*i*-alkane) for conversion 40 %.

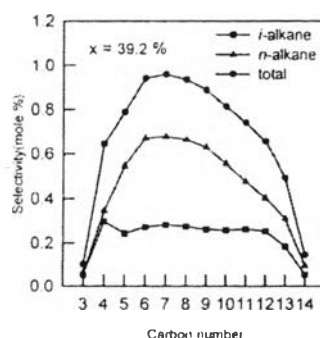


Figure 2.5 Molar distribution in the cracked products during *n*-hexadecane isomerization at 350 °C and 103 bar (Park and Ihm, 2000).

In 2003, Kuznetsov studied *n*-octane hydrocracking and hydroisomerization over Pt/HY zeolites which differ in the contents of Pt. HY zeolites with different quantities of Na were prepared by repeated treatment of a commercial NaY zeolite with 0.1 N solution of NH₄Cl + NH₄OH followed by calcination (between treatments) at 400 °C for 3 h. The HY zeolites produced were repeatedly treated with [Pt(NH₃)₄]Cl₂ solutions to prepare a set of Pt/HY samples with different Pt concentrations from 0.02 to 10.3 wt%. To produce fine metallic particles, Pt-loaded zeolites were treated at 350 °C in a dry air flow and then reduced by hydrogen in the catalytic reactor at 350 °C for 2 h before the catalytic tests.

Table 2.5 shows the data on the selectivity of the *n*-octane hydroconversion depending on the activity of metallic function. As increasing the content of Pt on HY zeolite that it give high selectivity of hydroisomerization. In the other hand increasing the content of Pt on HY zeolite, the cracking processes are decrease. When increasing in the hydrogenating activity of Pt component in Pt/HY0.9 catalysts improved greatly the selectivity to branched octanes. As few as 0.2–0.5 wt% of metallic Pt in HY0.9 zeolite are required to equilibrate the reaction of *n*-octane dehydrogenation.

Table 2.5 Selectivity of *n*-octane hydroconversion over different bifunctional Pt/HY0.9 catalysts (Kuznetsov., 2003)

Catalyst	Selectivity (%)			C ₃ /C ₅ molar ratio
	Cracking	Hydrogenolysis	Hydroisomerization	
0.02Pt/HY0.9	82.2	1.8	16.0	1.10
0.06Pt/HY0.9	66.9	1.2	31.8	1.06
0.2Pt/HY0.9	53.6	0.4	46.0	0.98
0.5Pt/HY0.9	54.5	0.8	44.8	0.97
1Pt/HY0.9	48.5	0.8	50.7	1.02
2Pt/HY0.9	33.2	0.6	66.2	1.03
8Pt/HY0.9	25.7	0.6	73.7	0.96
10Pt/HY0.9	20.6	0.5	80.6	0.96

Flow circulation unit, 300 °C, 0.18 MPa of H₂. H₂/C₈H₁₈ molar ratio = 16.

2.3.2.3 HY Zeolite

Zeolite-supported catalysts although less active, are characterized by their outstanding tolerance to feed poisons (sulfur and water) and therefore do not require feed pretreatment. Moreover, they are more resistant to the presence of aromatics, while they simultaneously have the advantage of a well-defined porous structure, which allows one to select the most suitable structure for the process. However, zeolite-based catalysts exhibit lower activity and thus the reaction must be performed at higher temperature (250 °C), favoring unwanted cracking side reactions. Great efforts have been directed to modify zeolite supports in these catalysts via strengthening or creating stronger acid sites, compared to the traditionally used alumina support, as well as modifying the metal sites via incorporating metallic promoters.

It is noteworthy that longer n-alkanes are more easily converted to *iso*-alkanes and/or cracked alkanes than shorter n-alkanes. Unfortunately, multibranched alkanes are susceptible to hydrocracking. If the pore size is made small enough to restrain multibranched *iso*-alkanes from being further converted at inner acidic site, the isomerization selectivity can be increased. Therefore, shape selectivity of zeolites is probably their most significant and advantageous property, which can be used to suppress the formation of multibranched *iso*-alkanes and thus inhibit hydrocracking reactions, finally improving isomerization selectivity. When referring to shape selectivity, we address the fact that the hydroisomerization performance of a zeolite depends on several parameters such as the zeolite topology, pore size, window size and dimensionality of the pore system (Iliopoulou *et al.*, 2013).

In 2014, Cheng *et al.* studied the optimizing catalysis conditions to decrease aromatic hydrocarbons and increasing alkanes for improve jet biofuel quality. Ni and Mo clusters supported on zeolites HZSM-5 and HY catalysts were prepared using a wetness impregnation method. The procedure used for synthesizing Ni (8 wt%)-Mo (12 wt%)/HY and Ni (8 wt%)-Mo (12 wt%)/HZSM5 catalysts were as follows: 2.37 g Ni(NO₃)₂·6H₂O and 1.32 g (NH₄)₆Mo₇O₂₄·4H₂O were dissolved in 10 ml deionized water. Then 4.8 g HY or HZSM-5 was added to the solution. The mixture was stirred for 6 h at ambient temperature and then dried in

an oven at 70 °C for 8 h. The catalyst was calcined in air at 550 °C (heating rate 5 °C/min) for 4 h and reduced in hydrogen (flow rate = 300 ml/min) at 500 °C (heating rate = 4 °C/min) for 4 h.

Zeolite HY exhibited higher alkane selectivity (40.3 %) while exhibiting lower aromatic hydrocarbon selectivity (23.8 %) than zeolite HZSM-5 (13.8 % and 58.9 %, respectively). The results indicated that jet fuel quality was noticeably improved by zeolite HY by increasing alkanes and decreasing aromatic hydrocarbons in jet fuel. The high alkane and low aromatic hydrocarbon selectivity of zeolite HY was attributed to its pore structure. Zeolite HY displayed 12-member ring pores with size of 0.74 nm and cages with size of 1.14 nm. Large molecules such as fatty acids were initially cracked into long carbon chain alkanes in the cages or on the outer surface. Then, the long carbon chain alkanes were able to diffuse after the crack or be further cracked into short carbon chain alkanes in the pores of zeolite HY. However, zeolite HZSM-5 contained only 10-member ring pores with size of 0.53 x 0.56 nm. Large molecules had to be pre-cracked into alkanes on the outer surface of zeolite HZSM-5 to gain access to the microspores. Given the small pore size of HZSM-5, the resulting alkanes were not able to diffuse until they were further cracked into aromatic hydrocarbons with shorter carbon chains (Cheng *et al.*, 2014).

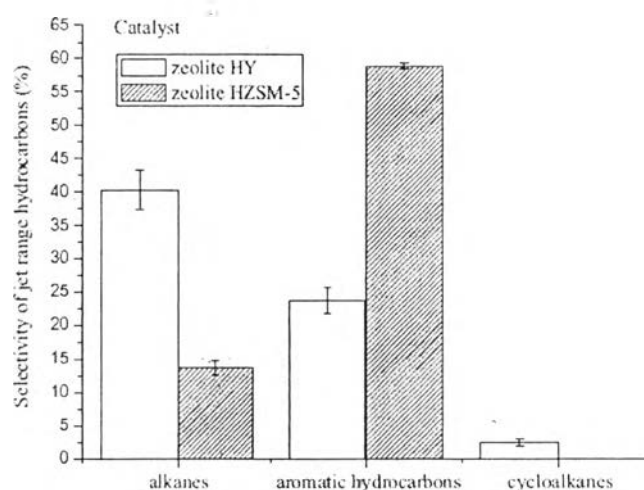


Figure 2.6 Selectivity of jet range (C8-C16) alkanes, aromatic hydrocarbons and cycloalkanes (Cheng. *et al.*, 2014).

2.4 Formulation of Catalyst

Most industrial zeolite based catalysts are in powder form and needs to be shaped into spheres, granules and extruded prior to their usage in commercial reactor in order to improve the mechanical properties of the catalyst particles, thus avoiding extremely high-pressure drops in fixed-bed reactors. It has been demonstrated that the binder is not active as a catalyst but could change the acid properties of a zeolite as a result of changes in the proton-exchange efficiency, trapping by the binder of coke precursors, and/or blocking of zeolite channels during the formulation process (De Lucas. *et al.*, 2006).

Extrusion is the most important shaping technique applied in the manufacturing of fixed-bed catalysts. Processed in pure form or with organic binders, zeolites as well as many other solid catalysts would not yield catalyst bodies of sufficient crush and attrition strength. In these cases, ceramic binders have to be added. Industrially used binders for zeolite extrudates are hydrous or hydroxidic forms of alumina or mixed silica-alumina. Upon calcination of the moist extrudates, interstitial and chemically bound water is removed, and aluminum hydroxides are transformed into γ or other Al_2O_3 oxide types. The mechanical strength is mostly provided through adhesive forces and additionally by crosslinking of some terminal hydroxyl groups between neighboring binder particles (Freiding *et al.*, 2007).

2.4.1 Binder

In general, extrudates are prepared with the addition of binder like alumina, bentonite, kaolin and attapulgite to improve the strength. However, addition of binder will influence the physicochemical property and catalytic performance of the catalyst to some degree.

Pseudo boehmite is an aluminum compound with the chemical composition $\text{AlO}(\text{OH})$. It consists of finely crystalline boehmite. However, the water content is higher than in boehmite. Pseudo boehmite is essentially finely crystalline boehmite which consists of the same or similar octahedral layers in the xz plane but lacks three-dimensional order because of a restricted number of unit cells in y direction. It consists of a significant number of crystallites which contain a single

unit cell along y or single octahedral layers. It contains more water which is commonly intercalated between octahedral layers, normally randomly arranged, but sometimes regularly. The water content consists of adsorbed and chemically bound water. The higher water content compared to boehmite can be explained by a smaller crystallite size. While boehmite consists of relatively long AlOOH chains that have terminal H_2O groups, the chains in pseudo boehmite are significantly shorter. This translates into significantly higher specific water content due to the terminal water groups.

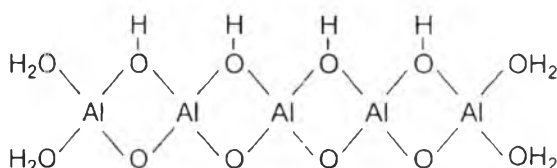


Figure 2.7 Structure of pseudo boehmite.

At higher temperatures pseudo boehmite is transformed to γ -alumina but the pore size distribution remains unchanged up to 1000 °C. At around 1100 °C however, specific area significantly decreases because of sintering related to a transformation to α - Al_2O_3 .

In 2013, enhanced production of high octane gasoline blending stock from methanol with improved catalyst life on nano-crystalline ZSM-5 catalyst was studied by Saxena and co-worker. This work two micro-crystalline (MZ) and nano crystalline (NZ) ZSM-5 samples with Si/Al ratio of 13 have been synthesized. All the synthesized samples were filtered and washed with de-ionized water, followed by drying at 100 °C and calcination at 500 °C for 4 h under vacuum. Shaping of all the zeolite powder samples are carried out by mixing an inert alumina binder, pseudo boehmite with zeolite: binder ratio of 3:2 by weight, followed by adding sufficient amount of 3 vol% glacial acetic acid for peptization. Wet extrusion of the resultant paste was carried out through a 2 mm diameter size metallic syringe for the formation of wet extrudates. The extrudates were allowed to get dry at room

temperature (25 °C) overnight and further dried at 100 °C for 7 h followed by calcination at 500 °C for 4 h.

The Hawarth-Koewazoe pore size distribution trends indicate the increase in pore volume is mainly due to the creation of mesopores of 200-500 Å diameters in NZ sample. The presence of mesopores in NZ catalyst also influenced the external surface area and the average pore diameter of the sample, which is almost doubled. The higher external surface area (as well as total surface area) and large number of strong acid sites present in NZ catalyst seems to provide higher reactivity (conversion) of methanol on this catalyst. The higher amount of strong acid sites along with high amount of mesopores present in this sample might have facilitated bulky hydrogen transfer reactions responsible for aromatic formation.

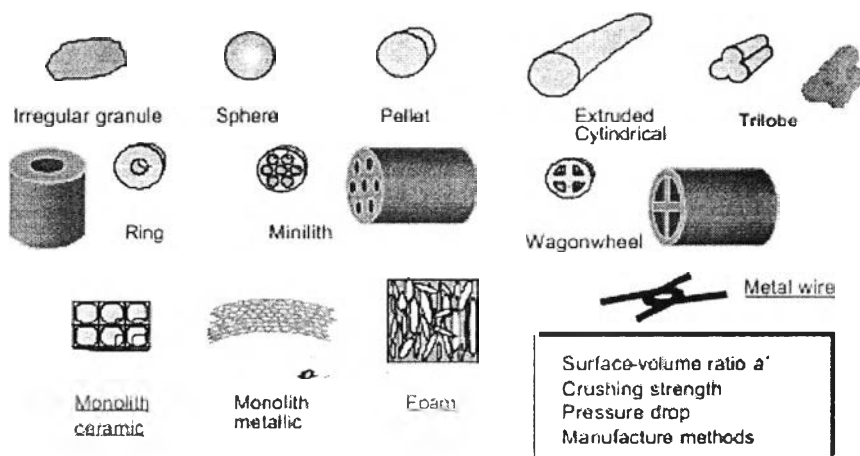


Figure 2.8 Structures of shaped catalysts.