



CHAPTER II

LITERATURE REVIEW

Jet fuel is a type of aviation fuel designed for use in aircraft powered by gas-turbine engines. The most commonly used fuels for commercial aviation are Jet A and Jet A-1(C₈-C₁₆) which are produced to a standardised international specification. The only other jet fuel commonly used in civilian turbine-engine powered aviation is Jet B(C₅-C₁₅) which is used for its enhanced cold-weather performance.

Jet fuel is a mixture of a large number of different hydrocarbons. The range of their molecular weights or carbon numbers is restricted by the requirements for the product, for example, freezing point or smoke point.

Since the jet fuel prices depend on petroleum prices which are unstable and unpredictable, jet fuel derived from biomass (or bio-jet fuel) becomes an interesting solution.

In this section, basic overviews of bio-jet fuel production in term of chemical reaction, types of catalysts, processing condition and production process are described.

2.1 Bio-jet Fuel

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 bio-jet fuel production. Among the vegetable oils, sources are soybean, canola, palm, jatropha, and rape. Bio-jet fuel usually blends with petroleum-based Jet A/Jet A-1 fuel and 50 percent sustainable biofuels. The advantage of bio-jet fuel over petroleum-based jet fuel is renewable. Moreover, the raw materials e.g. jatropha and palm oil can be grown locally.

2.2 Raw Materials in Bio-jet Fuel Production

Vegetable oils are considered as raw materials for bio-jet fuel production because they are broadly available from a variety of sources, and they are renewable.

The examples of vegetable oils used in bio-jet fuel production are palm oil, sunflower oil, corn oil, coconut oil, jatropha oil, olive oil, canola oil, cottonseed oil, castor oil, soybean oil, etc. There are many benefits of bio-jet fuel including domestic available feedstock, decreased greenhouse gas emissions, decreased dependence on fossil fuels, improvement of rural economies and increased national security. (Huber, G.W. *et al.*, 2007)

Both vegetable oils and animal fats are composed of molecules called triglycerides. Fat generally refers to the triglycerides in solid form at room temperature, whereas oils are liquid at room temperature. The molecule of triglyceride is composed of three long-chain fatty acids of 8 to 22 carbons attached to a glycerol backbone. The chemical structure of a triglyceride is shown in Figure 2.1 where R_1 , R_2 , and R_3 , which may be the same or different, represent long chain fatty acids which are mostly palmitic, stearic, oleic, linoleic, and linolenic acids.

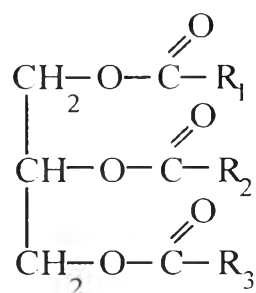


Figure 2. 1 A chemical structure of triglyceride.

Some physical properties of the most common fatty acids present in vegetable oils and animal fats are listed in Table 2.1. Besides these fatty acids, numerous other fatty acids occur in vegetable oils and animal fats, but their abundance usually is considerably lower. Table 2.2 summarizes the fatty acid composition of some vegetable oils. The fatty acids which are commonly found in vegetable oils are stearic, palmitic, oleic, linoleic and linolenic acids. Vegetable oils contain free fatty acids (generally 1 to 5%), phospholipids, phosphatides, carotenes, tocopherols, sulphur compounds and traces of water.

Table 2.1 Selected properties of some common fatty acids (Gerhard *et al.*, 1997)

| Trivial (Systematic) name ; Acronym ^b | MW | m.p. (°C) | b.p. ^c (°C) | Formula | Heat of Combustion (kg-cal/mole) |
|--|--------|--------------|---------------------------|--|--|
| 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 ¹⁰ | 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°) |
| Stearic acid (Octadecanoic acid); 18:0 | 284.48 | 71 | 360d | 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 cis 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 2.2 Fatty acid composition in vegetable oils (Fangrui *et al.*, 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 |

2.3 Bio-jet Fuel Production

2.3.1 Reaction for Bio-jet Fuel Production

Catalytic hydrocracking is an essential process in refinery for the conversion of middle and heavy distillates and residuals into more valuable products. Moreover, it is easy to equilibrate the supply and demand of fuels such as gasoline, diesel and jet fuel (Munoz Arroyo, J.A *et al.*, 2000). Therefore, the main process of bio-jet fuel production is also catalytic hydrocracking. Especially the branching isomerization, hydrogenation and hydrodeoxygenation are desirable to improve the quality of bio-jet fuel.

2.3.1.1 Hydrocracking

Hydrocracking is a hydrogen-consuming reaction that leads to higher gas production and lower liquid yield. This reaction is favored at high temperatures and high hydrogen partial pressure. Figure 2.2 represents a hydrocracking reaction:

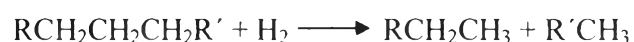


Figure 2.2 Schematic of hydrocracking reaction.

The hydrocracking behavior of an alkane depends primarily on the degree of branching of the carbon skeleton and on the relative positions of the branching along the main carbon chain. The degree of branching of a carbon skeleton is obtained when considering that each tertiary and quaternary carbon atom introduces one and two branching, respectively (Souverijns, W. *et al.*, 1998).

The process of cracking vegetable oils or animal fatties takes place in two stages. The first stage, known as primary cracking, is characterized by the formation of acid species through the decomposition of triacylglyceride molecules which occurs through the breakage of C–O bonds within the glyceride part of the triacylglyceride chain. The second stage is characterized by the degradation of the acids produced in the first stage leading to the formation of hydrocarbons with properties similar to those of petroleum products. This stage is called secondary cracking (Prado, C.M.R. *et al.*, 2009)

Hydrocracking of used cooking oil for biofuels production was studied by Bezergianni, S. *et al.*, 2009. This work considers several parameters for evaluating the effectiveness of this technology, mainly hydrocracking temperature, liquid hourly space velocity (LHSV) and days on stream (DOS). For all experiments used the same sulfided commercial NiMo catalyst hydrocracking catalyst and feedstock. Experiment was conducted at various conditions, i.e. reactor temperatures 350, 370, and 390°C, system pressure 2,000 psig (14 MPa), liquid hourly space velocity (LHSV) 1.5 h⁻¹, and H₂-to-liquid feed ratio (H₂/oil) of 6,000 scfb (1.068 nm³/m³). In the case of effect of reaction temperature, higher reaction

temperature leads to a higher gasoline fraction that indicated hydrocracking activity rises with increasing reaction temperature. Kerosene/jet and naphtha selectivity was also found to increase with reaction temperature. Saturation of double bonds decreases with reaction temperature due to catalyst activity was primarily driven towards cracking or other reactions rather than saturation. For the effect of liquid hourly space velocity (LHSV), increasing of LHSV caused less cracking and smaller production of the lighter products which were kerosene/jet and naphtha because molecule of feed had smaller residence time to react with catalyst.

In 2009, Bezerigianni, S. *et al.* studied the catalytic hydrocracking of fresh and used cooking oil. This work compared the product yields and quality of hydrocracking fresh and used cooking oil. Both experimental runs employed the same commercial hydrocracking catalyst and were conducted at the same conditions, i.e. reactor temperatures 350, 370, and 390°C, system pressure 2,000 psig (13,789.5 kPa), liquid hourly space velocity (LHSV) 1.5 h⁻¹, and H₂-to-oil feed ratio (H₂/oil) of 6,000 scfb (1068 nm³/m³). Cracking, heteroatom removal and saturation reaction mechanisms were evaluated for both feedstock types and for three typical hydrocracking temperatures (350 °C, 370 °C, and 390 °C). The results showed that both feedstocks were able to give high diesel yields with smaller kerosene/jet and gasoline/naphtha yields. As temperature increases, diesel selectivity increases for both feedstock types. However, the used oil feedstock was converted to higher kerosene/jet and naphtha selectivity at low temperatures (350 °C) and lower at the highest hydrocracking temperature (390 °C). In terms of heteroatom removal, nitrogen was the most easily removed element in both used and fresh cooking oil. Finally a large degree of saturation was achieved via hydrocracking of both oils, which was not favored by temperature. It could be expected as saturation is a competing reaction to the cracking one.

2.3.1.2 Hydroisomerization

Isomerization of *n*-alkanes is applied for improving the octane number of gasoline fractions, the low-temperature properties of jet and diesel fuels, and for the synthesis of lubricants. Branching isomerization of *n*-alkanes can be achieved with bifunctional heterogeneous catalysis, using noble metal containing acid zeolite catalysts working in hydrogen atmosphere. For instance, platinum on

mordenite is used to isomerize C_5/C_6 alkane streams to boost the octane number (Souverijns, W. *et al.*, 1998).

2.3.1.3 Hydrogenation

Hydrogenation is the chemical reaction that results from the addition of hydrogen. The process is usually employed to saturate organic compounds. The process typically constitutes the addition of pairs of hydrogen atoms to a molecule.

Unsaturated fatty acids may be converted to saturated fatty acids by the relatively simple hydrogenation reaction. Recall that the addition of hydrogen to an alkene (unsaturated) results in an alkane (saturated).

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 the 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 (Jovanovic, D.S. *et al.*, 2000).

Catalytic hydrogenation is widely applied for the reduction of a variety of functional groups. It has been and will continue to be a very substantial market for platinum group metal (pgm) catalysts as they tend to be more active for a given transformation than their base metal equivalents (Nishimura, S. *et al.*, 2001).

2.3.1.4 Hydrodeoxygenation

Hydrodeoxygenation is a process by which a feedstock that contains double bonds and oxygen moieties is converted to hydrocarbons by saturation of the double bonds and removal of oxygen. The hydrodeoxygenation of vegetable oils produces alkanes with carbon atom equivalent to the fatty acid chains, although the exact nature of the product mix depends on reaction conditions. The straight-chain alkanes can undergo isomerization and cracking for production of fuels more suitable for aviation purposes (Gerhard Knothe *et al.*, 2010).

The deoxygenation reaction may be carried out in the presence of homogeneous or heterogeneous catalysts under controlled hydroprocessing conditions, known as hydrotreating or hydrocracking processes.

There are several possible reaction pathways for the production of straight-chain hydrocarbons, shown in Figure 2.3. Fatty acids can be directly decarboxylated or decarbonylated. Direct decarboxylation removes the undesired oxygen by releasing carbon dioxide and producing aliphatic hydrocarbon chains with one carbon atom less than in the original feed, while direct decarbonylation removes the undesired oxygen by forming carbon monoxide and water, as explained by reactions I and II. Moreover, the fatty acid can be deoxygenated by adding hydrogen leading to a production of straight-chain hydrocarbons and undesired oxygen will be removed through the formation of water, as explained by reactions III (Murzin D.Yu. *et al.*, 2007).

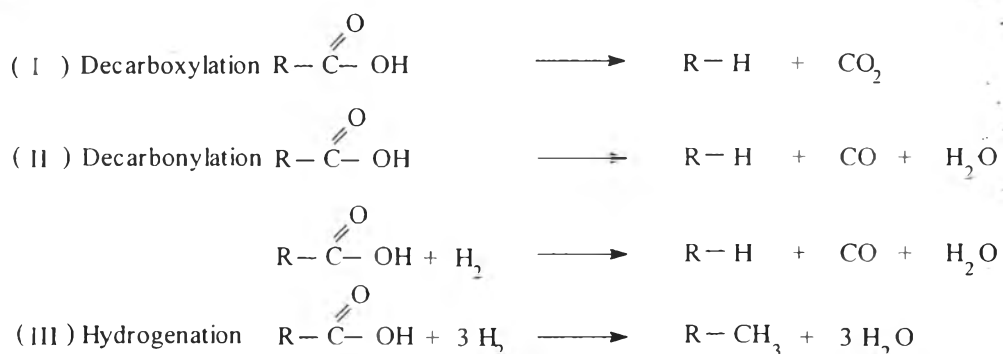


Figure 2.3 The possible liquid-phase reaction pathways for production of straight chain hydrocarbons from fatty acids.

In addition to the liquid-phase reactions, the water gas shift and methanation reactions are occurred with a number of carbon monoxide, carbon dioxide, hydrogen, and water formed during decarbonylation/decarboxylation reaction. The water-gas-shift reaction may balance the concentrations of CO and CO₂, while methanation reaction of fatty acids gives methane and water.

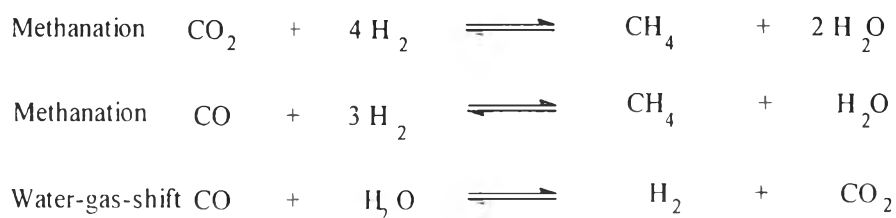


Figure 2.4 Gas phase reactions of CO or CO₂ with H₂ or H₂O.

The influence of hydrogen partial pressure on the conversion and products distribution on the deoxygenation of stearic acid, ethyl stearate, and tristearine, over palladium supported on activated carbon to produce diesel fuel-like hydrocarbons was studied. The experiments were done at temperature ranging from 300 to 360 °C and overall pressure of 17-40 bar in a conventional Parr autoclave (300 ml) operating in a semi-batch mode. Different reaction atmospheres, e.g. helium (He), hydrogen (H₂), 5% hydrogen in argon (5%H₂/Ar) mixture, were applied. The results showed that all the three reactants were converted to the same final products, n-heptadecane, with high selectivity. The presence of hydrogen in the reaction atmosphere particularly diminished the undesired products such as unsaturated C17 and aromatic hydrocarbons (Dmitry Yu. Murzin *et al.*, 2005)

2.3.1.5 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 hydrogenation, where hydrogen is added to the molecule, without cleaving bonds. Usually hydrogenolysis is conducted catalytically using hydrogen gas (Connor, R. *et al.*, 1932). The following represents a hydrogenolysis reaction:

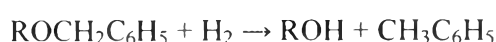


Figure 2.5 Schematic of hydrogenolysis reaction.

2.3.2 Catalyst for Bio-jet Fuel Production

2.3.2.1 Hydroisomerization and Hydrocracking

Both hydrocracking and hydroisomerization always occur simultaneously, the term hydroisomerization is used to indicate a situation where isomerization predominates over hydrocracking, while the opposite holds for the term hydrocracking. Depending on the needs and feedstock characteristics, hydrocracking and hydroisomerization are performed over many types of catalysts developed for many specific applications. The typical catalysts for the hydroisomerization are bifunctional catalysts consisting of acidic sites providing the isomerization/cracking function and metal sites providing the hydrogenation–dehydrogenation function (Calemma, V. *et al.*, 2000).

The typical acidic supports used are amorphous oxides or mixtures of oxides (i.e. HF-treated Al_2O_3 , $\text{SiO}_2\text{–Al}_2\text{O}_3$, $\text{ZrO}_2/\text{SO}_4^{2-}$), zeolites (Y, beta, mordenite, ZSM-5, ZSM-22) or silicoaluminophosphates (SAPO 11, SAPO 31, SAPO 41).

The most commonly used metals are Pt, Pd or bimetallic systems (i.e. Ni/Co, Ni/W, Ni/Mo, W/Mo in the sulfided form). The latter are mainly used for feedstocks with a high concentration of sulphur. The balance between the acidity of the support concentration of acidic sites and their strength and the hydro/dehydrogenation activity of the metal are of primary importance in determining the selectivity for hydroisomerization and distribution of cracking products (Calemma, V. *et al.*, 2000).

According to the classic mechanism, the skeletal isomerization and hydrocracking of alkanes over bifunctional catalysts occur through a set of parallel and consecutive steps involving dehydrogenation of the alkane molecule over the metallic site to produce the respective olefin which is highly reactive for carbenium ion conversion and rapidly isomerizes and/or cracks into two smaller olefins over the acidic sites. The cracked and isomerized olefinic intermediates are hydrogenated at the final step. However, there is evidence that the rate of the alkane hydrocracking and isomerization is dependent on the activity of metallic function (Kuznetsov, P.N. *et al.*, 2003).

The isomerization of *n*-alkane over metal-loaded solid acid catalysts is generally believed to proceed via a classical bifunctional mechanism. The *n*-alkane molecules are dehydrogenated at the metal particles to the *n*-alkene molecules which migrate to the acid sites where they are protonated to form carbenium ions. The carbenium ions rearrange to form isocarbenium ions which then convert to isoalkene molecules. The isoalkene molecules shuttle back to the metal sites and are rehydrogenated there to produce the isoalkane (Ali, A-G.A. *et al.*, 2001).

In 2000, Calemma, V. *et al.* studied the hydroisomerization and hydrocracking of *n*-hexadecane, *n*-octacosane and *n*-hexatriacontane on a 0.3% Pt/amorphous SiO₂-Al₂O₃(MSA/E) catalyst. The catalytic experiments were conducted in a stirred microautoclave at 345, 360 and 380 °C and between 2 and 13.1 MPa hydrogen pressure. The results were used to explain the effect of chain length and operating conditions on isomerization and cracking selectivity. The result showed that the selectivity for hydroisomerization decreased with increasing length of paraffin chain as shown in Figure 2.6.

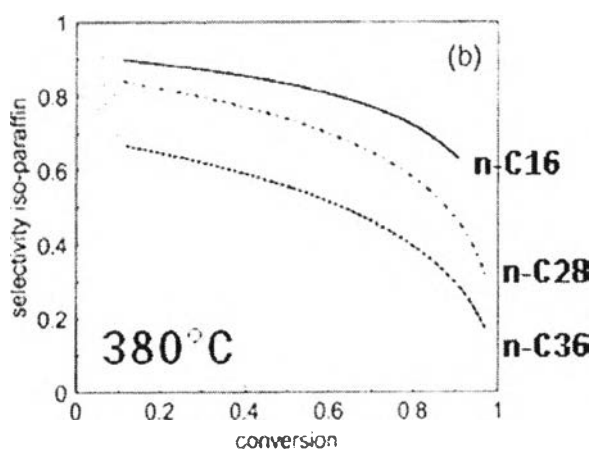


Figure 2.6 First-order plots for the selectivity of feed isomers corresponding to 380°C.

In case of study effect of hydrogen pressure, hydrogen pressure affects the rate of hydroisomerization/hydrocracking of *n*-paraffin inversely because it will reduce the steady state concentration *n*-alkenes and secondary

carbenium ions, the main species which involve in limiting step (rearrangement of the secondary carbenium) with a consequent decrement of the limiting step rate.

As shown in Figure 2.7, the limiting step is the rearrangement of the secondary carbenium. Moreover, three factors may contribute to the high hydroisomerization selectivity shown by the Pt/MSA/E catalyst: a mild Brønsted acidity, a very high surface area and a narrow distribution of pores in the mesopore region (Calemma, V. *et al.*, 2000).

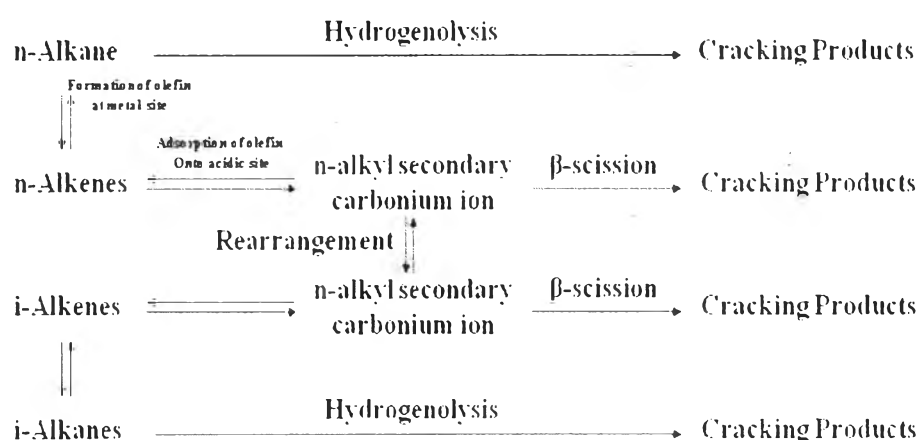


Figure 2.7 Reaction scheme for hydroisomerization and hydrocracking of *n*-alkanes on bifunctional catalysts (V.Calemma *et al.*, 2000).

In 1998, Souverijns, W. *et al.* studied the hydrocracking of isoheptadecanes on Pt/H-ZSM-22 and Pt/H-Y. The catalytic experiments were conducted in a tubular downflow reactor. The catalysts were activated in situ in the reactor by a calcination under flowing oxygen at 673 K, followed by a reduction under flowing hydrogen at the same temperature. The *n*-C17 and hydrogen partial pressures at the entrance of the reactor were 900 Pa and 350 kPa, respectively. The constant space time, W/F_0 is equal to 0.5 h kg mol⁻¹. The results from catalyst characterizations showed that on Pt/H-Y, the most cracked products have carbon numbers in the range from C4 to C13. On Pt/H-ZSM-22, the cracked products are higher in the range of lighter components.

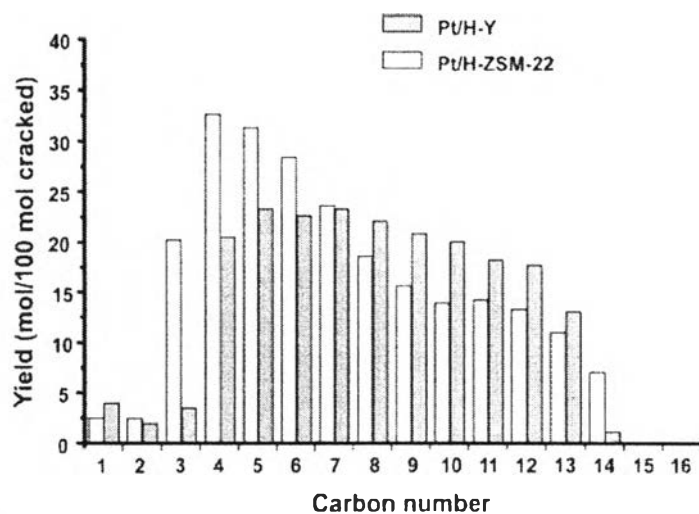


Figure 2.8 Yield of cracked product fractions per carbon number at 25% cracking yield of *n*-C17 on Pt/H-Y and Pt/H-ZSM-22 (Souverijns, W. *et al.*, 1998).

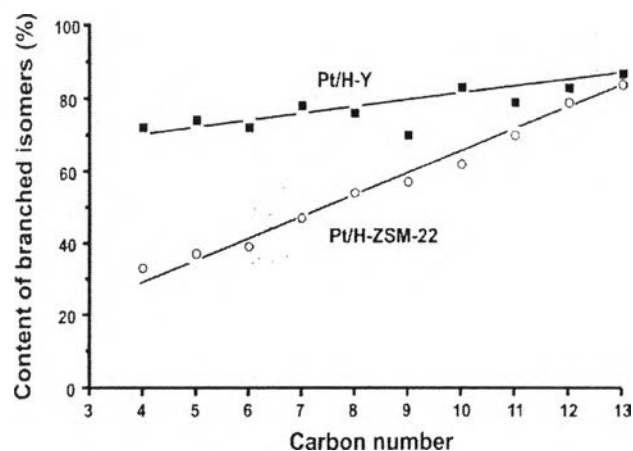


Figure 2.9 Content of branched products in the cracked product fractions at 10% cracking yield of *n*-C17 on Pt/H-ZSM-22 and Pt/H-Y. (Souverijns, W. *et al.*, 1998).

The content of branched isomers in the cracked product fractions increases with increasing carbon number of the fraction. The content of branched isomer fragments in the cracked product fractions on Pt/H-Y is higher than Pt/H-ZSM-22. Content of branched products in the cracked product fractions at 10% cracking yield of *n*-C17 on Pt/H-ZSM-22 and Pt/H-Y is shown in Figure 2.9. In

2000, Park, K-C *et al.* studied the hydroisomerization of n-hexadecane on bifunctional platinum catalysts supported on ZSM-5, ZSM-22, SAPO-11, Al-MCM-41, H-Y and H- β . The results from catalyst characterizations showed that the Pt/ZSM-5, Pt/ZSM-22 and Pt/H- β catalysts showed higher hydrocracking activity due to their strong acid sites, while the Pt/SAPO-11, Pt/Al-MCM-41 and Pt/H-Y catalysts with moderate acid strength showed better isomerization selectivity.

Hydrocracking and isomerization of n-paraffin are also investigated by Munoz Arroyo, J.A. *et al.* A mixture of n-paraffins was hydrocracked over a Pt/ZSM-22 and a Pt/USY zeolite catalyst in a three phase reactor with internal mixing operated under industrially relevant conditions. The result showed that the isomerization products obtained from the n-paraffin mixture and the hydrotreated gasoil on Pt/USY is higher than on Pt/ZSM-22. On Pt/ZSM-22, the formation of highly branched alkanes is difficult because of sterical hindrance so the cracked products obtained on Pt/ZSM-22 contain a high amount of linear paraffins. Distribution of cracked products in the hydrocracking, a central cracking and formation of C5 and C6 products can be observed on Pt/USY. On Pt/ZSM-22 the formation of C3 is much more pronounced, and the maximum is rather at C4 and C5. The content of branched cracked products observed on Pt/USY higher than Pt/ZSM-22. Figure 2.10 shows distribution of cracked products in the hydrocracking as a function of carbon number at yield of 15%.

These days zeolites are desired catalysts. Zeolites are natural minerals that are mined in many parts of the world. Most zeolites used commercially are synthetically produced. In hydrocarbon conversion catalysis, these structures of principal interest are the large pore zeolites, type X, Y, L, omega and mordenite. Today, Y zeolite is used commercially as catalyst in petroleum refinery because of its high concentration of active acid sites, its high thermal stability and high size selectivity. Y zeolite is a synthetic analog to the mineral faujasite and crystallizes with cubic symmetry. It has crystal sizes in the approximate range of 0.2-0.5 μm and 12 member ring with 7.4Å pore diameter. It thermally decomposes at 793°C (Htay, M.M., and Oo, M.M.. 2008).

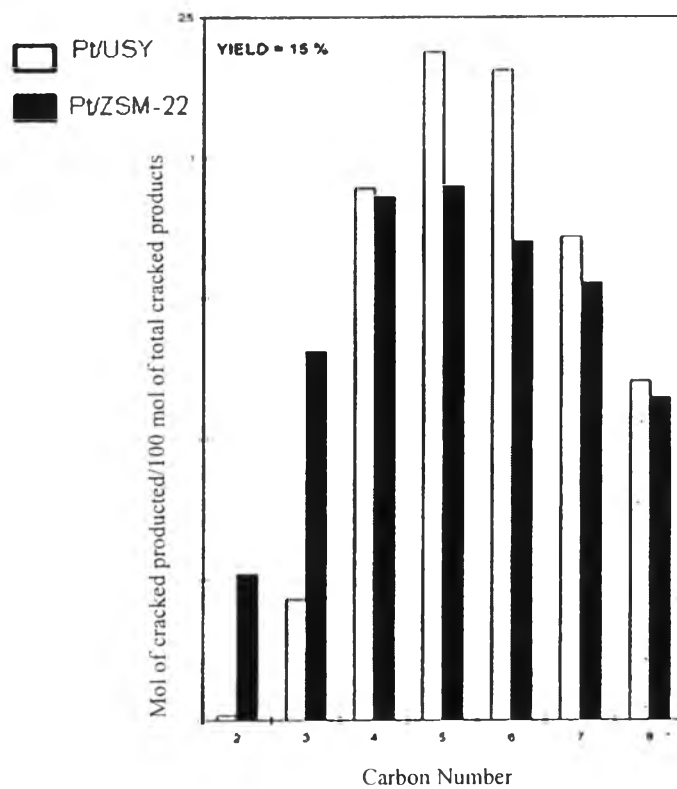


Figure 2.10 Distribution of cracked products in the hydrocracking as a function of carbon number at yield of 15 (Munoz Arroyo, J.A. *et al.*, 2000).

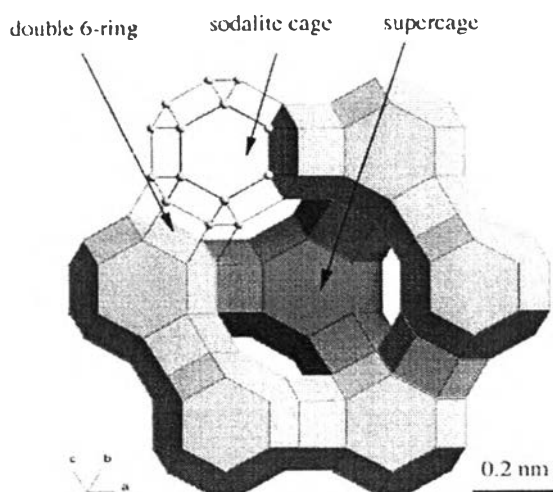


Figure 2.11 Structure of Y zeolite

(<http://www.rsc.org/ej/JM/2000/b002473m/b002473m-f1.gif>).

In 2001, Ali, A-G.A. *et al.* studied hydroisomerization, hydrocracking and dehydrocyclization of *n*-pentane and *n*-hexane using mono- and bimetallic catalysts on γ -Al₂O₃ support and promoted with fluorine. This work studied for the conversion of *n*-pentane and *n*-hexane at different temperatures of 300–500°C, except for Rh catalysts (from 150 to 500°C) in the presence of H₂ atmosphere, 0.049 mol/h. The results from catalyst characterizations showed that the overall activity of Pt, Ir and Rh/Al₂O₃ increases with increasing the reaction temperature up to 500°C. This behavior may be due to the increase of acidity by the conversion of Lewis acid sites to the Brönsted ones. The activity sequences for isomerization is Pt > Ir > Rh, for hydrocracking Rh > Ir > Pt, and for dehydrocyclization Pt > Ir > Rh for *n*-pentane and *n*-hexane. For Pt/Al₂O₃, it may be concluded that incorporation of 3.0 wt.% fluorine enhances the selectivity for hydroisomerization greater than hydrocracking and dehydrocyclization. For Ir/Al₂O₃, the hydroisomerization selectivity increased on the fluorinated catalyst. The selectivity of fluorinated Rh/Al₂O₃ is highly directed towards hydrocracking.

In 2001, Ali, L.I. *et al.* studied the hydroconversion of *n*-paraffins in light naphtha using Pt, Ir, Rh, Re, and U supported on Al₂O₃ catalysts promoted with noble metals and/or chlorine. In this work studied hydroconversion of *n*-pentane and *n*-hexane was in a pulsed micro-reactor system at a temperature range of 300–500 °C, except for Rh/Al₂O₃ (150–500 °C). In case of monometallic catalysts, they also found that the most active catalysts for hydroisomerization, hydrocracking and hydrogenolysis are Pt, Ir and Rh, respectively. Nevertheless Re and U are found inactive.

From the above literatures review, using Pt and Ir as metal of catalyst is a good way to obtain high activity of isomerization and moderate activity of hydrocracking, respectively for jet fuel fraction. Therefore, Pt and Ir will be used as metals supported on Y-zeolite as we proposed before for this present study. Moreover, for F-promoted γ -Al₂O₃ exhibited a better selectivity to hydroisomerization which can improve octane number of jet fuel. Therefore, γ -Al₂O₃ promotion with F⁻ ions will be also used as a catalyst support in this study.

2.3.2.2 Hydrodeoxygenation

The deoxygenation of stearic acid over the heterogeneous catalysts for production of biodiesel was investigated by Dmitry Yu. Murzin *et al.*, (2006). A variety of metal (Pd, Pt, Ru, Mo, Ni, Rh, Ir, and Os) supported on Al₂O₃, Cr₂O₃, MgO, and SiO₂, as well as activated carbons were studied. The deoxygenation experiment were carried out in a semi batch reactor under constant overall pressure and temperature at 600 kPa and 300°C, respectively. In case of noncatalytic deoxygenation, it was found that less than 5% of stearic acid was converted within 6 h of reaction and the main products formed were linear C17 hydrocarbons. The heterogeneous catalytic deoxygenation of stearic acid achieved with high activity and selectivity to n-heptadecane (n-C17), desired product. The catalyst screening showed that the reaction can be effectively performed over palladium and platinum supported on activated carbons. Furthermore, the gas phase analysis indicated that the decarboxylation reaction was more preferably over the Pd/C catalyst, as the decarbonylation was more preferably over the Pt/C catalyst.

2.3.2.3 An Innovative Technology for Converting any Renewable Oil into High-Value Biofuels (Patent-pending Technology “Centia™”)

Diversified Energy Corporation (DEC) and North Carolina State University (NCSU) are developing a patent-pending technology for converting oils derived from any triglyceride feedstock (agriculture crops, animal fats, algae, energy crops, waste greases, etc.) to high value biofuels. The technology, termed Centia™ (a derivation of “green power” in Latin), consists of three steps as shown in Figure 2.12 to produce biogasoline, Jet A-1/JP-8 (aviation fuel), and renewable diesel.

Centia™ also provides flexibility in the type of biofuel produced. One excellent target market is the aviation industry because of its economic sensitivity to crude oil prices and the current lack of bio-based fuel alternatives.

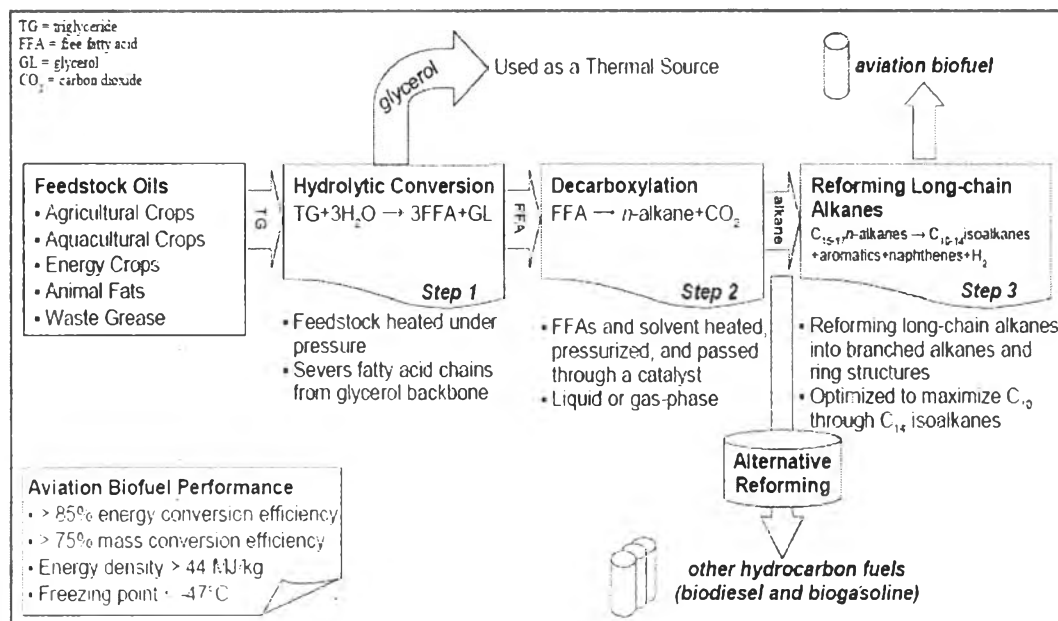


Figure 2.12 3-Step Centia™ Biofuels Process.

Table 2.3 Centia™ Project Team

| Team Member | Specialty/Experience |
|-----------------------------------|--|
| Diversified Energy Corporation | <ul style="list-style-type: none"> • Program Management • Systems Engineering • Commercialization • Economics |
| North Carolina State University | <ul style="list-style-type: none"> • Catalyst Scaling and Commercialization • Principal Subcontractor • Key Technology Holder |
| BASF | <ul style="list-style-type: none"> • Catalyst Development |
| Lauren Engineers and Constructors | <ul style="list-style-type: none"> • Fuel Qualification • Proven Alternative Fuels Work |
| Turner Engineering | <ul style="list-style-type: none"> • Specialized Engineering and Biofuels Development • Systems Engineering |
| Southwest Research Institute | <ul style="list-style-type: none"> • Fuel Plant Design and Construction • Fuel Plant O&M |
| Chambers Process Engineering | <ul style="list-style-type: none"> • Systems Engineering • Practical Process Engineering |

2.3.3 Catalyst Deactivation

The mechanisms of catalyst deactivation can be grouped into six intrinsic mechanisms of catalyst decay (Bartholomew *et al.*, 2001):

1. poisoning
2. fouling
3. thermal degradation
4. vapor compound formation accompanied by transport
5. vapor–solid and/or solid–solid reactions
6. attrition/ crushing

The causes of deactivation are basically three-fold: chemical, mechanical and thermal. Each of the six basic mechanisms is defined briefly in Table 2.4.

Table 2.4 Mechanisms of catalyst deactivation

| Mechanism | Type | Brief definition/description |
|---------------------------------------|------------|---|
| Poisoning | Chemical | Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction |
| Fouling | Mechanical | Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores |
| Thermal degradation | Thermal | Thermally induced loss of catalytic surface area, support area, and active phase–support reactions |
| Vapor formation | Chemical | Reaction of gas with catalyst phase to produce volatile compound |
| Vapor–solid and solid–solid reactions | Chemical | Reaction of fluid, support, or promoter with catalytic phase to produce inactive phase |
| Attrition/crushing | Mechanical | Loss of catalytic material due to abrasion Loss of internal surface area due to mechanical-induced crushing of the catalyst particle |

2.3.4 Prevention of Catalyst Deactivation

As the catalyst is the heart of a process, it is necessary to keep it working for as long as it is possible. Though some catalysts may be regenerated through burning (or washing with solvents) of the coke or poison, frequent regeneration entail loss of productivity and a slow decline in the performance of the catalyst with each regeneration. It is necessary, therefore, to maximize the cycle

length (active period) of the catalyst before resorting to regeneration. The prevention of catalyst deactivation will depend on the identification of the reasons for deactivation. Some typical reasons for deactivation and methods for prevention of catalyst activity loss are presented in Table 2.5.

Table 2.5 Methods for prevention of catalyst deactivation

| Cause | Solutions |
|-------------------------|--|
| Poisoning | Purify feed; use guard beds; use additives which selectively react with/deactivate the poison; change reaction conditions |
| Coking | Avoid coke precursors in feed; avoid free radical reaction; avoid free space; passivate metal surfaces; add water, hydrogen; use shape selective zeolites; add promoters; change operating conditions. |
| Sintering | Use promoters/stabilizers; lower reaction temperature; avoid specific impurities |
| Loss of catalytic phase | Avoid impurities which cause volatilization; alter operating conditions; add promoters |
| Mechanical failure | Improve mechanical strength of catalyst; alter reaction conditions; improve catalyst formation |