

CHAPTER II

LITERATURE REVIEW

Jet fuel or aviation turbine fuel is a specialized type of petroleum-based fuel designed for use in aircraft powered by gas-turbine engines. It is generally of a higher quality than fuels used in less critical applications, such as heating or road transport, and often contains additives to reduce the risk of icing or explosion due to high temperatures, among other properties.

This fuel is colorless to straw-colored in appearance. The most commonly used fuels for commercial aviation are Jet A and Jet A-1, has a carbon number distribution between about 8 and 16, which are produced to a standardized international specification. The other jet fuel commonly used in civilian turbine-engine powered aviation is Jet B (C₅ - C₁₅) which is rarely used except in very cold climates to prevent ice buildup inside the fuel tanks.

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

Conventional petroleum-based jet fuels are not renewable and generate a considerable amount of particulate and gaseous pollutants. Thus, it is important to find an alternative aviation fuel that is renewable and environmentally benign. Recently vegetable oil is receiving increasing attention as an environmental friendly and promising source of energy to replace the petroleum based fuel.

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

2.1 Hydrotreated Renewable Jet Fuel

Hydrotreated renewable jet fuel is a renewable fuel that can be used instead of jet fuel derived from petroleum. Similar to biodiesel, hydrotreated renewable jet fuel is made from sustainable sources such as vegetable oils, sugars, animal fats and even waste biomass, and it can be used in existing jet engines without modification. Among the vegetable oils, sources are soybean, canola, palm, jatropha, and rapeseed. Hydrotreated renewable jet fuel usually blends with petroleum-based Jet A/Jet A-1 fuel to meet the suitable jet fuel specifications.

2.2 Raw Materials for Hydrotreated Renewable Jet Fuel Production

Typical feedstocks for biofuels are vegetable oils with high energy contents. The intention is to use vegetable oils directly as fuel. However, the use of unmodified vegetable oils as the fuel is not efficient because of their high viscosity. Although there are a number of vegetable oils available as feedstock, including soybean, palm, sunflower, safflower, cottonseed, rapeseed and peanut oils have been proven to have the potential to produce alternative fuels. In developing countries, especially those in the Asian sub-continent, the production of edible vegetable oils is not sufficient, and so it is essential to use non-edible oil sources. Rapeseed and sun-flower oils are the main feedstocks used in Europe for biofuel. Palm and coconut oils are mainly used in the tropics, and soybean oil is used in United States. The advantages of these oil seeds are their abundant oil content, better adaptation to growing conditions, regular maturation periods, low maintenance and formation of eco-friendly waste during oil extraction.

Jatropha is a non-edible plant because of the presence of phorbol esters and can grow in infertile soil. The jatropha plant is cultivated mostly in Central and South America, Africa and Asia. Jatropha oil possesses a high kinematic viscosity, flash point, ignition point and solidifying point compared to conventional fuels.

Palm oil is widely used edible oil. Therefore, its utilization in fuel generation is not favored. Palm oil is mainly produced in Malaysia, and the Malaysian Palm Oil Board (MPOB) performed systematic studies on the production and evaluation of

alternative fuel from palm oil and palm oil derivatives. Malaysia plans to reduce its crude oil imports by promoting the use of palm oil for fuel production.

Sunflower seed oil is also edible oil in high demand, which has 40 - 50% oil content. The largest producers of sunflower oil are the Ukraine, the EU-27, the Russian Federation, Argentina and Turkey. Sunflowers only require a very short growing period compared to other oil crops, but the total worldwide production of sunflower oil is only 8% compared to the large production of soybean seed (55%), rapeseed (14%) and cottonseed (10%).

Rapeseed oil, also known as canola oil, is the most widely use feedstock for bio fuel generation. The main producers of rapeseed are China, Canada, India and Northern Europe. They produce 7 - 10 million tons of canola seed per year. Canada exports 3 - 4 million tons of the seed and 800,000 t of canola oil per year.

The merits and demerits of feedstocks that affect biofuel production showed in Table 2.1 (Mohammad *et al.*, 2013).

Table 2.1 Characteristics of the potential feedstocks used for biofuel production

Feedstocks	Advantages	Disadvantages
Sunflower	<ul style="list-style-type: none"> - More tolerant to low temperatures - Can grow in a wide range of soil types - Can be cultivated as a rotational crop 	<ul style="list-style-type: none"> - Edible oil - Quality of oil depends on weather conditions and agricultural practices
Rapeseed	<ul style="list-style-type: none"> - Less used for food purposes - Can grow on most soil types - Can be cultivated over a wide range of temperatures 	<ul style="list-style-type: none"> - Requires good drainage - Easily attacked by diseases
Palm	<ul style="list-style-type: none"> - Large scale production - Long life span - Less affected by climate - Harvest throughout the year 	<ul style="list-style-type: none"> - Edible oil - Limited regional range due to high rainfall need - Grow mostly in rain forest regions
Soybean	<ul style="list-style-type: none"> - Need optimum temperature - Minimum water supply for growth - Large scale production 	<ul style="list-style-type: none"> - Edible oil - Requires extensive land and uses of pesticides
Camelina	<ul style="list-style-type: none"> - Need less water and fertilizer to grow - Short growing season - Can be grown as rotation crop for wheat - By-product can be fed to animals 	<ul style="list-style-type: none"> - Edible oil - Depresses the growth of nearby plants
Jatropha	<ul style="list-style-type: none"> - Wide range of climatic suitability - Large land volumes in subtropical regions - Land use change can be carbon positive - Non-edible oil - Long lifetime and less water consume - Draught resistant 	<ul style="list-style-type: none"> - No compatible production

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', R'', and R''', which may be the same or different.

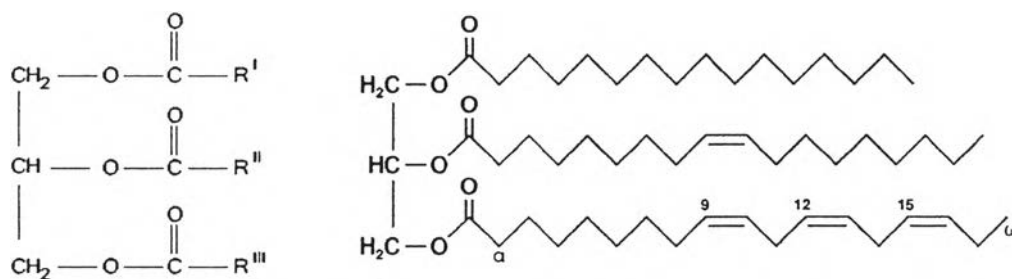


Figure 2.1 Example of a chemical structure of unsaturated fat triglyceride.

Some physical properties of the most common fatty acids present in vegetable oils and animal fats are listed 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. 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 2.2 Selected properties of some common fatty acids (Gerhard *et al.*, 1997)

Trivial (Systematic) name ^a ; 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	250.5 ¹⁰⁰	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°)
Stearic acid (Octadecanoic acid); 18:0	284.48	71	360	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 (mmHg) at which the boiling point was determined.

Table 2.3 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

2.2.1 Jatropha Oil

In 2012, Gong and co-workers studied hydrotreating of jatropha oil over alumina based catalysts. In this work, hydrotreatment of nonedible jatropha oils over PtPd/Al₂O₃ catalyst and NiMoP/Al₂O₃ catalysts was investigated under conditions of 330 - 390 °C, 3 MPa and 2 h⁻¹ in a fixed-bed reactor. Liquid products had two clear and colorless phases of oil phase and water phase for reaction temperatures higher than 330 °C, whereas the liquid products became cloudy and contained a suspension of white crystals when the reaction temperature was lower than 330 °C (when the catalysts were inactive, the liquid products became cloudy and contained a suspension of white crystals). The oil phase, which was regarded as liquid hydrocarbon products, was separated and determined using the GC-MS technique. The composition distribution of the liquid hydrocarbon products was analyzed using GC-FID showed in Figure 2.2.

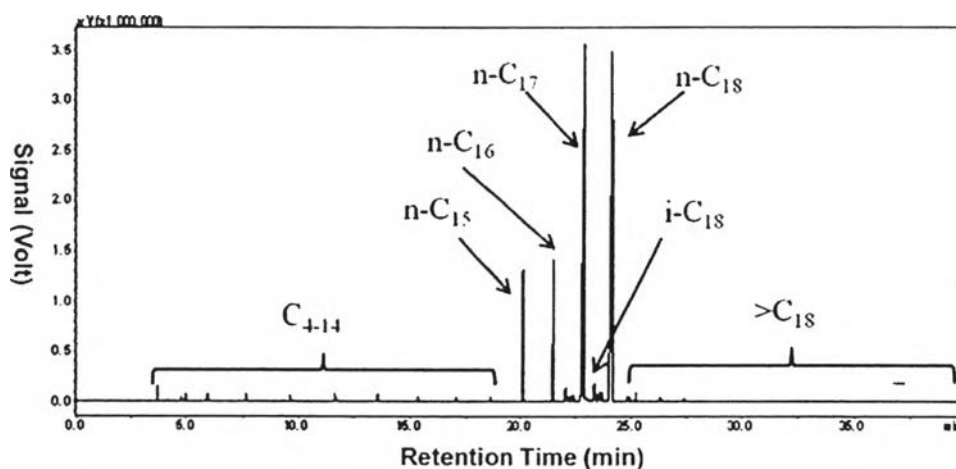


Figure 2.2 Typical chromatogram of the liquid hydrocarbon product.

The results of analysis show that the liquid hydrocarbon products represent a simple mixture containing mainly *n*-paraffins of C₁₅ - C₁₈. Aside from *n*-paraffins of C₁₅ - C₁₈, the liquid hydrocarbon products also contain small amounts of alkanes of C₄ - C₁₄ and *iso*-paraffins of C₁₅ - C₁₈, with trace amounts of cycloalkanes and aromatics of C₁₅ - C₁₈. Some oxygenates (e.g., fatty acid, fatty alcohol, monoglycerides, diglycerides) were found in some cases; the contents of the oxygenates were very low (<0.05%). These oxygenates are contained in C₁₈₊.

2.3 Hydrotreated Renewable Jet Fuel Production

2.3.1 Reaction for Hydrotreated Renewable Jet Fuel Production

Triglyceride conversions over hydrotreating catalysts in the presence of hydrogen have complex reaction pathways and consist of parallel and/or consecutive reaction steps, including saturation, cracking, decarboxylation, decarbonylation, and hydrodeoxygenation. A reaction pathway for conversion of tri-glycerides into alkanes is shown in Figure 2.3.

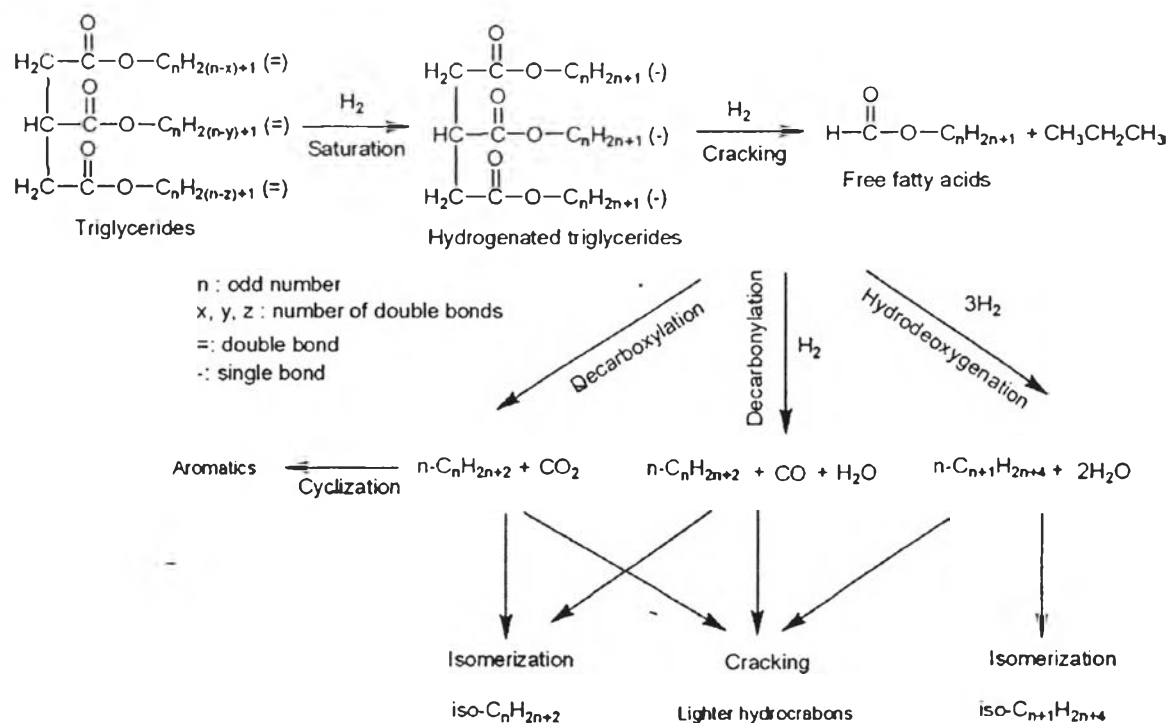
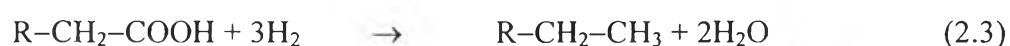
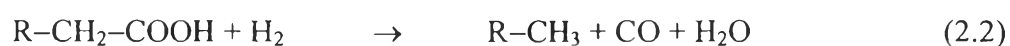
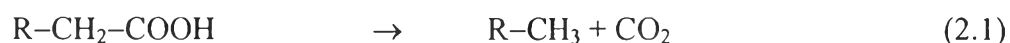


Figure 2.3 Reaction pathway for conversion of *tri*-glycerides to alkanes (Veriansyah *et al.*, 2012).

In the first step of this reaction pathway the triglyceride is hydrogenated, the double bonds that are present in the triglycerides are saturated with hydrogen. And then the hydrogenated triglyceride are broken down into various intermediates, including monoglycerides, diglycerides and free fatty acids, which is followed by the conversion of the intermediates into deoxygenated products. The formation of *n*-alkanes from free fatty acid can take place by one or a combination of three different pathways: decarboxylation, decarbonylation and hydrodeoxygenation.



Eqs. (2.1 - 2.3) show the different pathways for alkane production with carboxylic acids group in the free fatty acids as the reactant. We have used carboxylic acid to represent our feedstock and similar equations can be written for alkane production from *mono*-, *di*- or *tri*-glycerides. The decarboxylation pathway involves converting a carboxylic acid into a methyl group and CO₂ as shown in Eq. (2.1). No hydrogen is required to convert a carboxylic acid group to an alkane by the decarboxylation pathway. Carbon monoxide is produced by a decarbonylation pathway where the carboxylic group is reacted with hydrogen to produce a methyl group, CO and water as shown by Eq. (2.2). For the sunflower oil the decarbonylation and decarboxylation liquid alkane products are primarily *n*-C₁₇. The hydrodeoxygenation pathway involves converting the carboxylic acid with hydrogen to produce an alkane and water as shown by Eq. (2.3). This pathway involves bifunctional catalysis that contains sites for hydrogenation reactions (possibly NiMo sites) and for dehydration reactions (acid catalytic sites) (Huber *et al.*, 2007).

2.3.1.1 Hydrodeoxygenation

The aim of the hydrodeoxygenation process is to upgrade oil by removing the oxygen content as water to reduce the O/C ratio and simultaneously increase the H/C ratio. The process includes treatment of oil at high pressures and moderate temperatures over heterogeneous catalysts. The use of vegetable oils, mainly non-edible vegetable oils, as feedstock for the hydrodeoxygenation process is highly favorable because their hydrocarbon content is in the same range as that of fossil fuels, such as kerosene and diesel. The fatty acids in vegetable oils are composed of straight chains of carbon atoms, and hydrodeoxygenation produces *n*-alkanes as the primary product. The triglycerides in the vegetable oils are transformed into alkanes with water and propane as the by-products. Carbon dioxide or carbon monoxide is also obtained as a by-product when the reaction follows decarboxylation under hydrodeoxygenation conditions.

The rate of the hydrodeoxygenation reaction and its mechanism are influenced by the nature of feedstock used. Oxygen removal includes C–O bond hydrogenation, C–O bond rupture and C–C bond cleavage, and larger

hydrocarbons are selectively formed in the presence of a catalyst, which can cause C–O bond hydrogenation and C–O bond cleavage inhibiting C–C bond breaking.

The main factors that determine the selectivity of the reaction are the route of C–C and C–O bond cleavage and the extent of cleavage. The pathways for C–O bond cleavage were suggested to occur either through dehydrogenation to form surface-adsorbed species followed by direct cleavage catalyzed by metallic sites or via dehydration reactions catalyzed by acidic sites associated with the catalyst support (Mohammad *et al.*, 2013).

2.3.1.2 Hydrocracking

Hydrocracking is a catalytic chemical process used in petroleum refineries for converting the heavy hydrocarbon mixtures in petroleum crude oils to more valuable lower-boiling products by means of consecutive isomerization and cracking reactions. The process takes place in a hydrogen-rich atmosphere at elevated temperatures (260 - 425 °C) and pressures (35 - 200 bar).

Hydrocracking processes are capable of processing a wide variety of feedstocks of different characteristics to produce a broad range of products. Hydrocracking is suited for the production of high-value middle distillates. They can be designed and operated to maximize the production of gasoline blending component, jet fuel or diesel oil.

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 *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 *et al.*, 2009).

Reaction pathway of the *n*-alkane is first isomerized into its monobranched isomers and subsequently into *di*- and *tri*-branched isomers. According to the Figure 2.4, the cracking products are formed mainly through β -scission of *di*- and *tri*-branched isomers since they can crack through a more energetically favourable β -scission mode-not allowed for the monobranched and linear molecules (Calemma *et al.*, 2000).

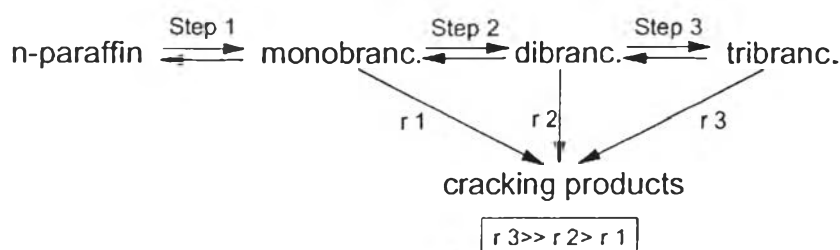


Figure 2.4 Reaction scheme for the formation of feed isomers and cracked products (Calemma *et al.*, 2000).

2.3.1.3 Hydroisomerization

Hydroisomerization reaction is an important process in petroleum refining, mainly used for producing high quality fuels. Hydroisomerization of light hydrocarbons is applied for improving the octane number of gasoline blending, while hydroisomerization of long-chain alkanes can be employed for improving the low-temperature properties of middle distillates (e.g., jet fuels and diesels) (Zhijian *et al.*, 2009).

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 *et al.*, 1998).

Biodiesel, an alternative diesel additive made from renewable sources, has problems associated with their cloud points when used in colder climate. One method of improving the cloud point of biodiesel is hydroisomerization which

branches the saturated portion of the biodiesel and lowers the cloud point of the compound. Palmitic acid methyl ester, which is the major saturated fatty acid in vegetable oils, is hydroisomerized with a 5 g kg^{-1} Pt impregnated beta zeolite catalyst at reaction conditions 200 - 285 °C and 1.0 - 4.0 MPa H_2 pressure. FTIR and GC/MS analyses confirmed the branching and the identity of the reaction products. The cloud point of the material was lowered from 30 °C to 20 °C under reaction conditions of 285 °C and 4.0 MPa H_2 pressure at the yield of 42% after 16 h. This study reports the hydroisomerization reaction being successful in branching the starting material in order to lower the cloud points of methyl esters (Reaume and Ellis, 2012).

2.3.1.4 Hydrogenation

Hydrogenation is the chemical reaction that results from the addition of hydrogen. The process is usually employed to saturate organic compounds. 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. 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 *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.

2.3.1.5 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 *et al.*, 1932).

2.3.2 Catalyst for Hydrotreated Renewable Jet Fuel Production

Catalysis is essential to modern energy conversion, chemicals manufacture, and environmental technology. From the start, oil refining and bulk chemicals manufacture have relied largely on the application of catalysts.

Depending on the needs and feedstock characteristics, Hydrocracking and hydroisomerization are performed over a wide range of catalysts developed for specific applications. The catalysts used are bifunctional, that is they are characterized by the presence of acidic sites which provide the isomerization/cracking function and metal sites with hydrogenation–dehydrogenation function (Calemma *et al.*, 2000).

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 (Kuznetsov, 2003).

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. Since during hydroconversion processes, both

cracking and isomerization always occur simultaneously, are two competing reaction via the same carbonium intermediate species (Calemma *et al.*, 2000).

In the early 1960s, jet fuel supply to China was cut off from abroad due to political situations, and faced an urgent need for producing jet fuels on that timed technologies. Lin, Zhang, and Liang succeeded in producing low-freezing jet kerosines from straight-run paraffinic kerosene fractions via hydroisomerization. The core of the paraffinic hydrocarbon hydroisomerization process was developing an adequate catalyst. A large number of studies on reaction mechanisms have elucidated that the isomerization of straight chain paraffins proceeds via intermediate steps of carbonium ion formation, and these steps can be realized only on dual-functional catalysts, i.e., catalysts comprising both metal components and acidic components.

Lin, Zhang, and co-workers, based on the summarizing of a great number of reported data, were able 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. These hybridizing effects can be illustrated schematically in Figure 2.5 (Zhijian *et al.*, 2009).

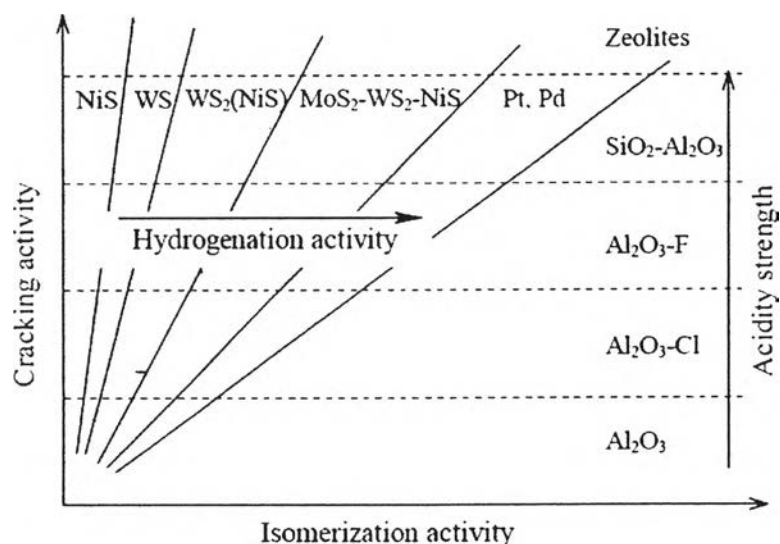


Figure 2.5 Schematic illustration of the dependence of hydroisomerization and hydrocracking activity on the interaction between the metal and the acidic components (Zhijian *et al.*, 2009).

2.3.2.1 Metals

Different metals such as Pt, Pd, Ni, Co, Mo, their oxides, and sulfides serve as the hydrogenating/dehydrogenating components. But the most commonly used metals are Pt, Pd or bimetallic system (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. Bifunctional catalysts are loaded with a noble metal (Pt or Pd) which shows a considerably higher selectivity for hydroisomerization with respect to non-noble transition metals such as Ni, Co, Mo and W (Calemma *et al.*, 2000).

There is evidence that the rate of the alkane hydrocracking and isomerization is dependent on the activity of metallic function. For example, the alkane hydroconversion over the catalysts with a high concentration of metallic components was significantly lower than that with less concentration. The drop in the *n*-hexane isomerization activity was observed when the contents of Pt and Ni in the HY zeolite exceeded their optimum levels of 0.6 and 3.0%, respectively (Kuznetsov, 2003).

In 2001, Ali and co-workers did research on topic hydroisomerization, hydrocracking and dehydrocyclization of *n*-pentane and *n*-hexane using *mono*- and *bi*-metallic catalysts on γ -Al₂O₃ support and promoted with fluorine. The hydroconversion activities and selectivities of monometallic catalyst on acidic support (0.35 wt.% Pt/Al₂O₃, 0.35 wt.% Ir/Al₂O₃, 0.35 wt.% Rh/Al₂O₃, 0.35 wt.% Re/Al₂O₃ and 0.35 wt.% U/Al₂O₃) and bimetallic catalyst on acidic support 0.35 wt.% Pt/Al₂O₃ promoted by addition of a second metal such as Ir, Rh, Re or U to form adducts (1:1) have been 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 activities and selectivities of monometallic catalyst on acidic support 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 Brønsted ones. The activity and selectivity sequences for isomerization is Pt > Ir > Rh and for hydrocracking Rh > Ir > Pt for *n*-pentane and *n*-hexane (Ali *et al.*, 2001).

From the above literatures review, using Pt as metal of catalyst is a good way to obtain high activity of isomerization and moderate activity of hydrocracking for hydrotreated renewable jet fuel fraction. Therefore, Pt will be used as metals loaded on Y-zeolite for this present study.

The conversion of *n*-octane over a series of monofunctional HY zeolites, which differed with the contents of Na and over the bifunctional Pt/HY zeolites differed with the contents of Pt, was studied by Kuznetsov in 2003. HY zeolites with different quantities of Na were prepared according to by repeated treatment of a commercial NaY zeolite with 0.1 N solutions 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 2.4 Selectivity of *n*-octane hydroconversion over different bi-functional Pt/HY0.9 catalysts (Kuznetsov, 2003)

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

In Table 2.4, the data on the selectivity of the *n*-octane hydroconversion depending on the activity of metallic function are shown. As the hydrogenation activity increases the selectivity shifts from the predominant cracking (82.2%) to predominant isomerization into branched octanes (80.6%), the latter representing methylheptane isomers mainly. The distribution in the C₃ - C₅ cracked fraction was perfectly symmetrical with respect to the number of carbon atoms, almost equimolar amounts of C₃ and C₅ hydrocarbons were produced indicating a simple cracking of C₈H₁₈ molecules by a carbenium ion mechanism. Hydrogenolysis and oligomeric cracking to C₁ - C₂ and C₆ - C₇ were insignificant over all the catalysts.

2.3.2.2 Acidic Support

Typical acidic supports are as follows:

- 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)
- silicoaluminophosphates (SAPO 11, SAPO 31, SAPO 41)

(Calemma *et al.*, 2000).

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 7.4 Å pore diameter. It thermally decomposes at 793°C (Htay and Oo, 2008).

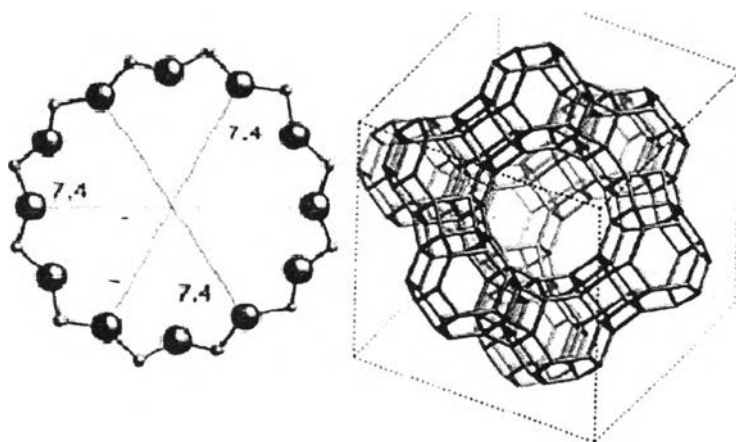


Figure 2.6 Schematic diagram of HY zeolite (Castano *et al.*, 2007).

HY zeolite has wider pores compared to other zeolites. However, diffusion transfer inside the pores is supposed to affect fast chemical reactions of highly reactive olefins over both the metallic and the acidic sites. On the other hand, the high acid density of zeolite Y facilitates the deposition of carbon in its channels, especially on its external surface, which causes a blockage of the channels and an untimely deactivation of the catalyst in the catalytic cracking (Zhang *et al.*, 2010).

In 1998, Souverijns and co-workers 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 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. But on Pt/H-ZSM-22, the cracked products are higher in the range of lighter components.

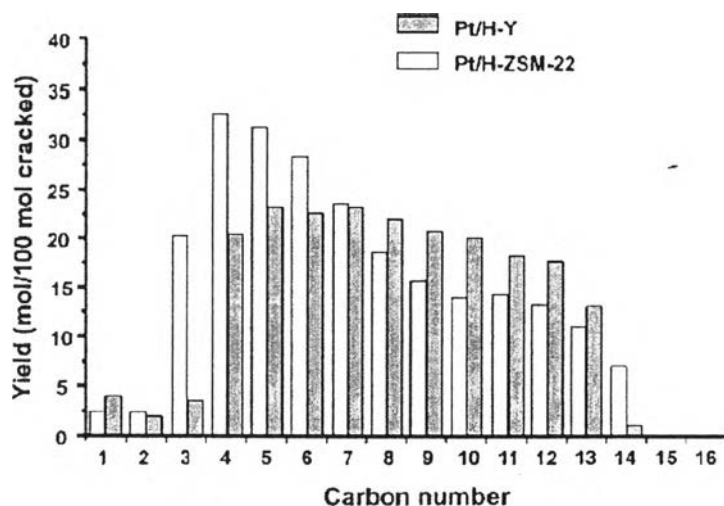


Figure 2.7 Yield of cracked product fractions per carbon number at 25% cracking yield of n -C₁₇ on Pt/H-Y and Pt/H-ZSM-22 (Souverijns *et al.*, 1998).

2.3.3 Effect on Hydrotreated Renewable Jet Fuel Production

2.3.3.1 Effect of Operating Conditions

In 2009, Rossetti and co-workers studied the hydrocracking of long chain linear paraffins. The hydrocracking reactivity of two model compounds, namely $n\text{-C}_{16}\text{H}_{34}$ ($n\text{-C}_{16}$) and $n\text{-C}_{28}\text{H}_{58}$ ($n\text{-C}_{28}$), was investigated on a $\text{Pt}/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst. Conversion and products distribution have been determined under a wide range of operating conditions (*i.e.* pressure: 20 - 80 bar; temperature: 270 - 330 °C; weight hourly space velocity: 0.33 - 1.0 h^{-1} ; $\text{H}_2/n\text{-paraffin}$ feeding ratio 0.05 - 0.15 wt/wt). The effect of the four main operating parameters, *i.e.* temperature, pressure, $\text{H}_2/n\text{-paraffin}$ ratio and contact time, on conversion and selectivity has been checked following a factorial experimental plan.

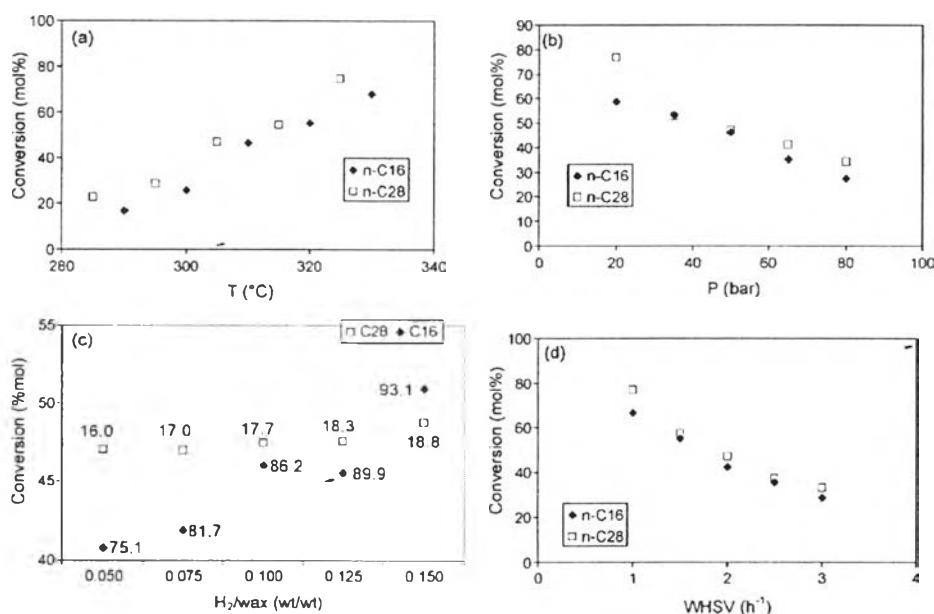


Figure 2.8 Dependence of conversion of $n\text{-C}_{16}$ and $n\text{-C}_{28}$ on the operating parameters: (a) temperature, (b) total pressure, (c) $\text{H}_2/n\text{-paraffin}$ ratio and (d) space velocity. The numbers on Figure 2.8c represent the percentage of evaporated wax (Rossetti *et al.*, 2009).

Summarizing, the dependence of conversion on the above reported parameters can be sketched as follows: (i) the higher the conversion, the lower is the amount of intermediate molecular weight products, indicating the

presence of consecutive cracking reactions; (ii) a temperature increase brings about an increase of conversion, due to kinetic reasons; (iii) conversion decreases with increasing pressure, due to the increase of hydrogen partial pressure; (iv) an increase of WHSV means a decrease of contact time and has a negative effect on conversion; (v) the H_2/n -paraffin ratio affects the liquid-vapor equilibrium of the reacting mixture. A high H_2/n -paraffin ratio (*i.e.* higher hydrogen concentration) increases the degree of vaporization of light species and causes a higher concentration of the heavier species in the liquid phase. The latter being more reactive, the conversion increases. This effect was much more evident for n -C₁₆ than for n -C₂₈.

2.3.3.2 Effect of Hydrotreated Feedstocks

In 2004, Salazar-Sotelo and co-worker studied effect of hydrotreating FCC feedstock on product distribution. In this work, two commercial catalysts, which exhibit different properties and production objectives, were used to convert two FCC feedstocks, typical and hydrotreated. Hydrotreating of FCC feedstock decreases hetero compounds that contain sulfur and nitrogen. However, there are other more important effects such as decreasing yield to dry gases and cyclic oils at constant conversion. The significant increase in the value of the product with increasing severity is mainly due to the increase in the gasoline production, as consequence of more efficient catalyst-to-oil interaction that leads to higher conversion. Coke yield decreases also.

2.3.3.3 Effect of Chain Length of Feedstocks

The hydroisomerization and hydrocracking of n -hexadecane (C₁₆H₃₄), n -octacosane (C₂₈H₅₈) and n -hexatriacontane (C₃₆H₇₄) on a 0.3% platinum/amorphous silica-alumina (MSA/E) catalyst was investigated in a stirred microautoclave at 345, 360 and 380 °C and between 2 and 13.1MPa hydrogen pressure. For each n -paraffin, the reaction pathway and the kinetic parameters were determined. The results were used to elucidate the effect of chain length and operating conditions on isomerization and cracking selectivity. The conversion of the n -paraffins leads to the formation of a mixture of the respective isomers, as the main product, together with cracking products. At every temperature, the *iso*-alkane/ n -alkane ratio of cracking products increased considerably with increasing

conversion degree. At the same conversion level, higher reaction temperatures lead to cracking products characterized by a lower *iso*-alkane/*n*-alkane ratio. The hydroisomerization selectivities showed a decrease as a function of chain length and with increasing conversion levels (Calemma *et al.*, 2000).

In addition, another research about the hydrocarbon effect of chain length was studied by Debrabandere and Froment in 1997 on topic influence of the hydrocarbon chain length on the kinetics of the hydroisomerization and hydrocracking of *n*-paraffins. The product distributions obtained by hydrocracking of several *n*-paraffins were determined on a Pt/US–Y catalyst in a gas phase reactor with complete internal mixing. The experimental results indicate that the components of the mixtures react independently: they only influence each other by competitive physisorption. Reactivity and strength of adsorption in the zeolite pores increase with chain length of the paraffins. At higher temperatures and lower pressures, the product distribution is no longer a unique function of conversion. The hydrocracking is no longer 'ideal'. The isomerization conversion decreases with increasing temperature and decreasing pressure. The longer the chain length, the more important this phenomenon. It is attributed to a relative decrease in the rate of hydrogenation, compared to the rate of the carbenium ion reaction.

2.3.3.4 *The Mechanism of Hydrocracking of Paraffins*

In 1993, Sie studied acid-catalyzed cracking of paraffinic hydrocarbons. The principle focus of research is evidence for the protonated cyclopropane mechanism from hydrocracking/hydroisomerization experiments. The analysis of the data obtained in the hydroisomerization/hydrocracking studies with normal paraffin feeds with the following additional points of correspondence between mechanistic predictions and actual experience: the almost zero production of C₁ and C₂ in hydrocracking; the relatively low production of fragments with carbon numbers of 3 and N - 3, if N is the carbon number of the feed paraffin; the almost equimolar distribution of fragments with intermediate carbon numbers, except with C₇ as feed (as shown in Figures 2.9 and 2.10); the tendency of *n*-C₇, to cleave into equimolar amounts of propane and isobutane; the high degree of branching obtainable in the fragments of hydrocracking of a linear feed paraffin; the extraordinarily high degree of branching in the fraction of carbon number N - 3; the

predominance of 2-methylalkanes among the monobranched isomers as well as that of 2, x-dimethylalkanes among the dibranched isomers in the product of hydrocracking; the fast increase of reactivity for hydrocracking for paraffins with increasing carbon number above 7; the striking difference in reactivity between hexane and heptane and the deviating product pattern obtained when hexane is cracked at all; the remarkable difference between the easiness of achieving highly selective isomerization of C_5 - and C_6 paraffins, and the difficulty to isomerize C_{7+} paraffins without concurrent cracking.

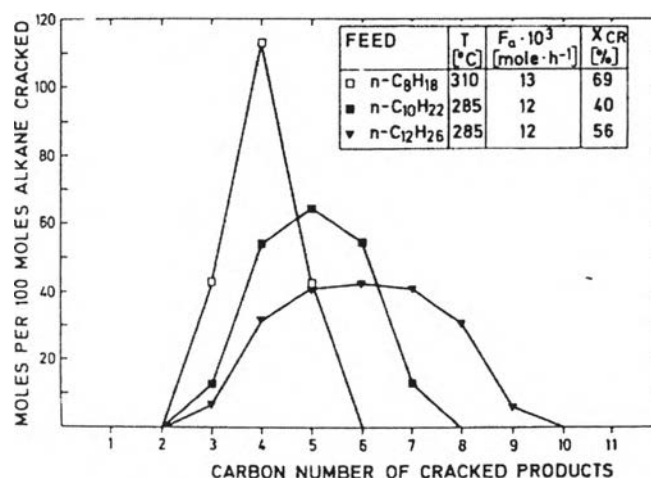


Figure 2.9 Hydrocracking of *n*-alkanes with an even carbon number. Distribution of the cracked product (Weitkamp, 1975).

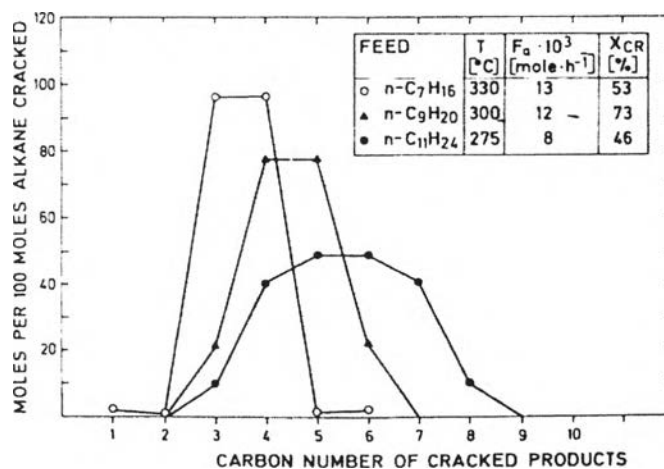


Figure 2.10 Hydrocracking of *n*-alkanes with an odd carbon number. Distribution of the cracked product (Weitkamp, 1975).