

CHAPTER II

THEORETICAL CONSIDERATION

2.1 Wax [3-9]

Wax usually refers to a substance that is a plastic solid at ambient temperature with a relatively low melting point, and capable of softening when heated and hardening when cooled. It is insoluble in water and combustible. Because it is plastic, wax usually deforms under pressure without being heated. The chemical composition of wax is complex. It usually contains a broad variety of molecular weight species and reactive functional groups. Wax is used as a generic classification of many materials that are either natural or synthetic and of petroleum, mineral, vegetable or animal origin.

Waxes are usually classified by their sources as natural or synthetic waxes. The waxes obtained from natural sources include animal waxes, vegetable waxes and petroleum waxes. These waxes are sometimes classified by their chemical composition with the animal, vegetable and some mineral (i.e. montan) referred to as ester waxes and the petroleum waxes and some mineral waxes (i.e. ozokerite and ceresin) referred to as hydrocarbon waxes. Sometimes synthetic waxes are also classified in this manner.

2.1.1 Petroleum waxes [4,5]

Petroleum waxes are essentially saturated hydrocarbon mixtures obtained from the refining of crude waxes from petroleum. They are classified into paraffin and microcrystalline waxes.

1. Paraffin wax

Paraffin wax is obtained from the distillation of crude oil. The distillate is solvent extracted to remove oil. The resulting wax is decolorized by hydrogenation and bauxite filtration. Paraffin waxes consist mainly of straight-chain, saturated hydrocarbons. The molecular weights of paraffin waxes range from 280 to 560 (C_{20} to C_{60}).

2. Microcrystalline wax

Microcrystalline waxes are produced by deoiling the petrolatums or greases obtained by dewaxing deasphalted residual lube stocks or by deoiling the deasphalted tank bottoms that settle out during the storage of crude oil. These waxes are referred to as microcrystalline because the crystals are much smaller than those of paraffin wax. The molecular weight of microcrystalline waxes range from 450 to 800 (C_{35} to C_{60}).

Petroleum waxes are used in laminations and coating for food packaging applications. Other applications include hot-melt adhesives, printing inks, protective coatings, molded products and antichecking waxes for automobile tires.

2.1.2 Animal waxes [4,5]

Animal waxes may be of insect or mammalian origin. The most important commercial animal waxes are beeswax and wool grease.

Beeswax

After the honey has been recovered, crude beeswax is separated from the honeycomb by melting the comb in boiling water and skimming off the crude wax. The crude wax can be decolorized or further refined by filtration with diatomaceous earth or activated carbon, or by bleaching with peroxide.

2.1.3 Vegetable waxes [4,5]

Vegetable waxes are obtained either from leaves and stems or from fruits and seeds. Candelilla and Carnauba waxes are obtained from the leaves and stems of the Candelilla plant and the Carnauba palm. These two waxes are the most important commercial vegetable waxes.

2.1.4 Mineral waxes [4,5]

Mineral waxes are obtained from fossil remains such as lignite, bitumens, peat and shale, excluding the waxes derived from petroleum. The most important mineral wax is montan wax. Its main components are nonglyceride esters of carboxylic acids, alcohols, acids, resins and hydrocarbons.

2.1.5 Synthetic waxes [4,5,6]

Synthetic waxes include polyethylene wax, Fischer-Tropsch waxes, chemically modified hydrocarbon waxes and substituted amide waxes.

Polyethylene waxes

Polyethylene with molecular weight of 1,200-2,000 has the properties of high molecular weight hydrocarbon waxes. They have a melting point range of 70-120 °C and needle penetration at 25 °C of 0.5-10 (ASTM D 5).

2.2 Hydroisomerization reaction and bifunctional catalyst [6,10,11,12]

The hydroisomerization catalyst is a type of bifunctional catalyst. Thus the reaction consist of two different functions :

(1.) metal functionality which catalyzes hydrogenation-dehydrogenation reactions. The metal could be platinum, palladium or nickel

(2.) an acidic or hydrocracking functionality provided by the support which catalyzes isomerization reactions. This could be alumina or silica-alumina.

These catalysts (Second generation) supplanted the Friedel-Crafts systems (First generation). It can eliminate many of the shortcomings of the First generation, such as poor on-steam efficiency and high costs. The reaction mechanism for a bifunctional catalyst is shown in Figure 2.1.

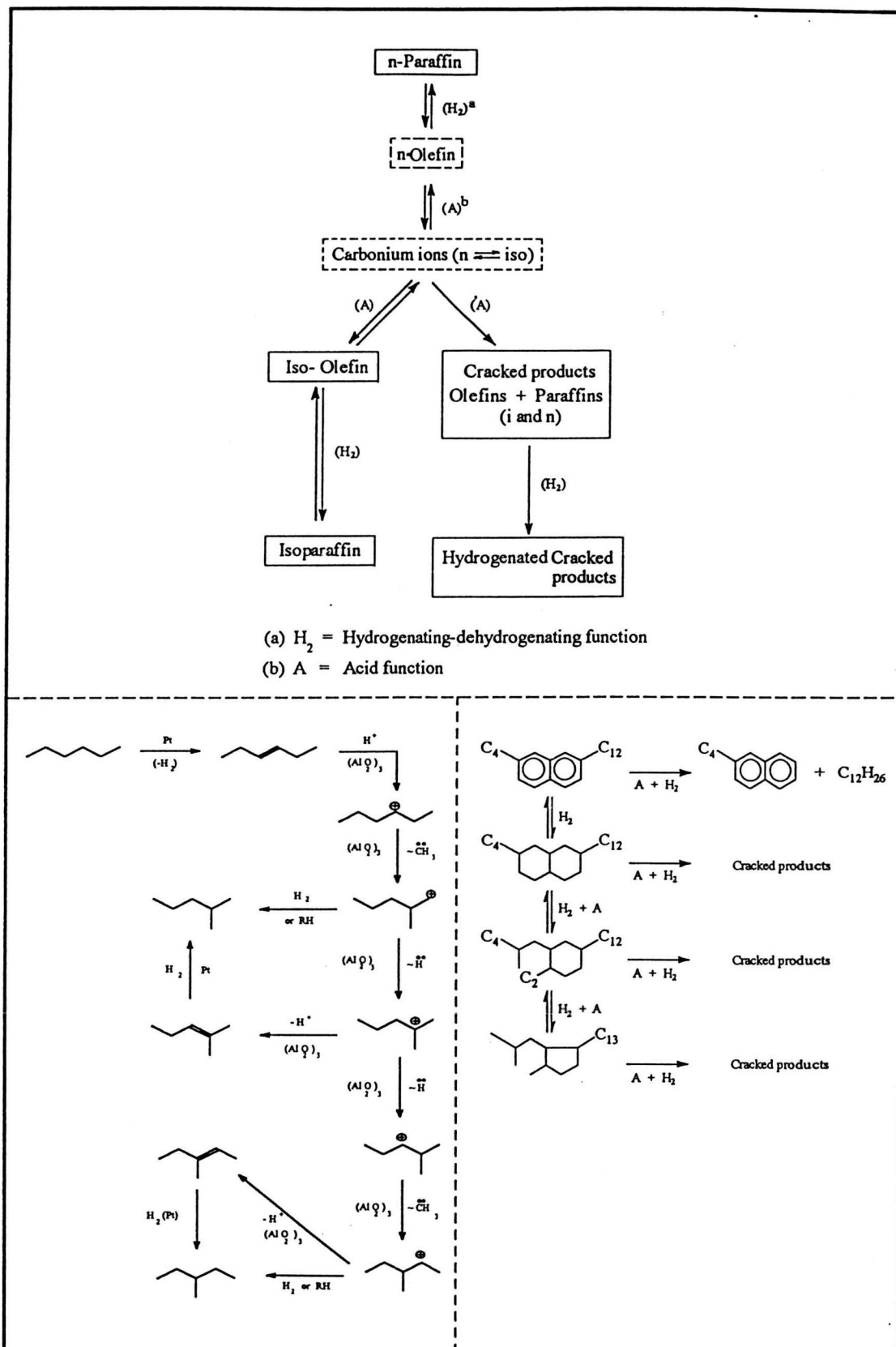


Figure 2.1 Reaction mechanism for bifunctional catalysts

The two functions interact through the olefins, which are the key intermediates in the reaction network. In the first reaction in the pathway, n-paraffin is rapidly dehydrogenated on the metal surface, the resulting n-olefin is easily protonated by the acidic sites on the support to give a carbonium ion, which can then isomerize and desorb iso-olefin which migrates to the metal function, where it can be absorbed and hydrogenated to give an iso-paraffin. Alternatively, the secondary carbonium ion can react to form cracked products (iso or n-olefins and paraffin), which can react further to form hydrogenated cracked products.

Isomerization can also occur on a pure platinum surface, but the rates are slow compared with those of dual-function catalysts, so the contribution of the metal induced isomerization route is probably minor.

Later, catalysts with greatly enhanced acidity, were prepared by treating a platinum-alumina composite with polyhalides, such as carbon tetrachloride, chloroform, methylene chloride, aluminium chloride or by impregnation of the platinum-alumina catalysts with monohalide, such as fluoride (from ammonium fluoride solution). The halogen most usually fluorine, acts as a promoter by increasing the acidity of the acidic function. The processes that use these high acidity catalysts are collectively called "Third generation". These three catalyst types are represented in Table.2.1

Table 2.1 Three Generations of Paraffin Isomerization Catalysts

Order of Generations	Type of Catalysts
1. First Generation	Friedel-Crafts Catalysts $\text{AlCl}_3 + \text{Hydrocarbon complex}$ AlCl_3 on Bauxite or Al_2O_3 $\text{AlCl}_3 + \text{SbCl}_3 + \text{HCl}$ $\text{AlBr}_3 + \text{HBr}$
2. Second Generation	Hydroisomerization Catalysts Platinum on Al_2O_3 Platinum on $\text{Al}_2\text{O}_3/\text{SiO}_2$ Platinum on $\text{Al}_2\text{O}_3/\text{B}_2\text{O}_3$ Platinum on Y-type Zeolite Platinum on Mordenite
3. Third Generation	Hydroisomerization Catalysts Platinum on Al_2O_3 reacted with organic chlorides Platinum-Fluoride on Al_2O_3 Platinum-Chloride on Al_2O_3

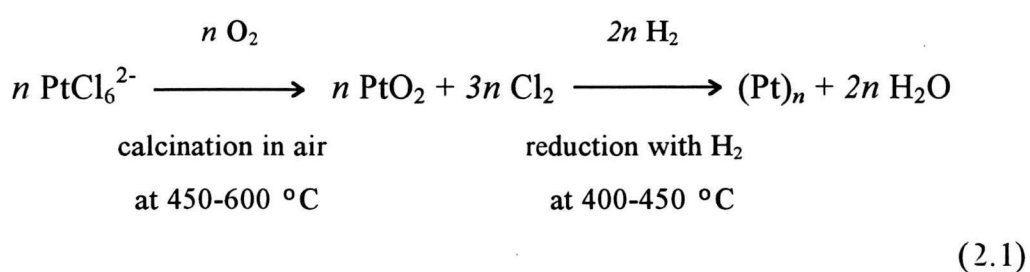
2.2.1 Preparation and structure of bifunctional catalysts [14,21]

Alumina-supported platinum is one of the most frequently used catalysts in isomerization, hydrogenation and dehydrogenation processes. Platinum is the metal of choice because it is the only one that has activity for the desired reactions without being more than moderately active

activity for the desired reactions without being more than moderately active for undesired reactions such as hydrogenolysis of paraffins. Alumina is the support of choice because it is inexpensive and easy to aggregate with platinum to maintain a high metal dispersion.

One common method of preparing the bifunctional catalysts involves impregnation of alumina with an aqueous solution of chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$). The catalyst typically contains from 0.1-5.0 %wt metal, preferably 0.1-1.0 % wt metal, most preferably 0.2-0.6 %wt. After impregnation the samples are usually dried and then calcined at temperatures between 450 to 600 °C. Other catalysts have been considered. Among these are certain metal oxides on alumina e.g. chromia (chromium oxide) and molybdena (molybdenum oxide). However, these catalysts are much less active than the platinum on alumina catalysts.

The preparation of platinum metal impregnated on alumina can be represented as the hexachloroplatinate ion being the precursor which does not react with the support (equation 2.1).



2.2.2 Metallic component

On the metallic component (usually platinum), hydrocarbons can undergo hydrogenation or dehydrogenation reactions in

catalysts are more active in hydrogenation-dehydrogenation reactions. Table 2.2 gives a comparison of the activities of some catalysts in the dehydrogenation of cyclohexane.

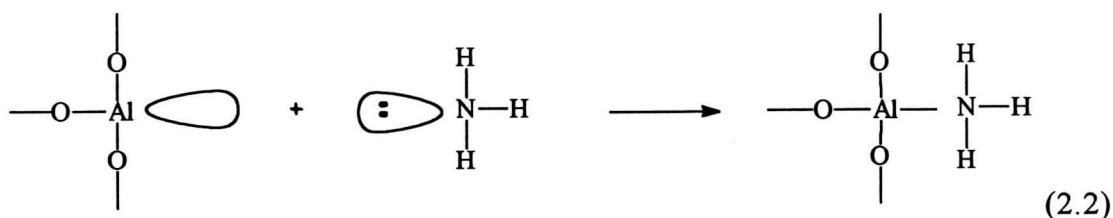
Table 2.2 Rate of the Dehydrogenation of Cyclohexane over different catalysts (temperature 427 °C, pressure 7 atm)

Catalyst	Dehydrogenation activity, mmoles benzene / g of catalyst \times sec ⁻¹
34% Cr ₂ O ₃ on Al ₂ O ₃	0.5
10% Mo ₂ O ₃ on Al ₂ O ₃	3
5% Ni on Al ₂ O ₃	13
5% Co on Al ₂ O ₃	13
0.5% Ir on Al ₂ O ₃	190
1% Pd on Al ₂ O ₃	200
5% Ni on SiO ₂	320
1% Rh on Al ₂ O ₃	890
0.5% Pt on Al ₂ O ₃	1,400-4,000

2.2.3 Acidic component

The alumina support used in bifunctional catalysts has been shown to be acidic in nature. The acidic properties are really demonstrated by the affinity of these solids for adsorption of basic compounds, such as ammonia, trimethylamine and pyridine. In the case of structure, the aluminium atom is not completely coordinated. It is bonded to three oxygen atoms instead of four. The aluminium atom has six valence electrons instead of the maximum eight. It therefore has the potential of accepting a pair of electrons from another species to complete a stable octet.

The reaction between alumina and a basic compound, ammonia, is shown in equation 2.2



Treatment of alumina with halogens, such as chloride or fluoride tends to make the acidic properties of alumina more pronounced, in the sense that it increases the activity of alumina for the catalysis of typical acid catalyzed reaction, such as the skeletal isomerization and various cracking reactions of hydrocarbons. The enhancement of acidic properties can be attributed to the halogens having higher donor ability of the oxygen, chloride and fluoride atoms.

2.3 Diesel Fuels [9, 33-37]

The basic requirement of a diesel fuel is that it must ignite spontaneously and burn satisfactorily under the conditions existing in the combustion chamber. It must be suitable for handling by the injection equipment and must be adaptable to convenient handling at all stages from the refinery to the engine fuel tank, without suffering degradation and without harming any surface which it may normally contact.

Conventional diesel fuels are distillates with a boiling range of about +300 °F to +700 °F (149 °C to 371 °C), obtained by the distillation of crude oil. They are predominantly straight - run fractions that contain the

greatest amount of normal paraffins and naphthenes, and the least amount of isoparaffins and aromatics. Normal paraffins and naphthenes have superior diesel ignition qualities, but they have the disadvantages of higher pour points than isoparaffins and aromatics.

2.3.1 General Characteristics of Diesel Fuels

A. Viscosity

Viscosity (ASTM D 445), described as a measure of a liquid's resistance to flow, is usually measured by recording the time required for a given volume of a fuel at a constant temperature to flow through a small orifice of standard dimensions. The viscosity of diesel fuel is important primarily because of its effects on the handling of the fuel by the pump and injector system. It decreases with increasing temperature and increases with large increasing pressure. The extent of the viscosity change depends on the crude source of the oil and the molecular weights of the constituent components.

The instrument used to determine the viscosity of an oil is called a viscometer. In general two types are used: the Saybolt and kinematic viscometers. Kinematic viscosity is the more common and is measured by the time required for a given volume of an oil at a specified temperature to flow through a capillary tube under gravitational force. Test temperatures are usually 40 and 100 °C, and the viscosity is measured in centistokes.

B. Specific Gravity

Specific gravity (ASTM D 1298) is defined as the ratio of the mass of a given volume of product to the mass of an equal volume of water, usually at 60 °F for each. The density is the absolute value and can be

expressed as lb/gal or lb/ft³ in Imperial units or as kg/m³ in the SI system of units.

In the petroleum industry the API gravity scale is almost universally used as the measure of the density of a petroleum product. API gravity is an arbitrary scale, calibrated in degrees and related to the specific gravity by

$$\text{API gravity (degrees)} = \frac{141.5}{\text{specific gravity at } 60/60^\circ\text{F}} - 131.5$$

The higher the specific gravity or density, the lower the API gravity. Water, by definition, has an API gravity of 10°. The specific gravity (or API) is an important parameter which is sometimes used to indicate crude oil quality. A low density crude (high API) has a higher percentage of the more valuable light and middle distillate oils.

C. Color Test

The color test is performed by following the ASTM D 1500 method. It is a guide to the presence of contaminants or to the degree of deterioration in storage. It is also an indication of the intensity of refining. Absence of color (water white) is important in certain applications such as in textile machinery lubrication to avoid indelible staining of the textile. Absence of color is also important to users of waxes, petrolatums, and white oils where extremely high purity is required.

D. Pour point

The pour point (ASTM D 97) of a fuel is an indication of the lowest temperature at which the fuel can be pumped. As the oil is chilled, it

eventually reaches a point where it will no longer flow under the influence of gravity. Fuel and, in particular waxy fuels, will in some circumstances flow below their tested pour point. This condition is brought about either by the thickening that always accompanies a reduction in temperature or by crystallization of wax dissolved in the oil, restricting the flow of the liquid portion.

E. Flash point

The flash point is a measurement of the flammability of a petroleum product. The flash point is the temperature at which enough vapor is produced to be burned in an instantaneous flash when exposed to a source of ignition. Normally, this test is used to determine the storage and operating temperatures and the type of storage that will preclude the possibility of a fire.

The flash point of a diesel fuel has no relation to its performance in an engine nor to its auto ignition qualities. In practice, flash point is important primarily from a fuel handling stand point. Too low a flash point will cause fuel to be a fire hazard, subject to flashing and possible continued ignition and explosion. In addition, a low flash point may indicate contamination by more volatile and explosive fuels, such as gasoline.

F. Sulfur Content

A fuel sulfur content above 0.4 percent is generally considered as medium or high, whereas fuel sulfur content below 0.4 percent is considered low. Summer grades of commercially available diesel are commonly in the 0.2 to 0.5 percent sulfur range. Winter grades often have less than 0.2 percent sulfur. Some slow- or medium- speed engines in

stationary service are desired to operate on heavy fuels, which have sulfur contents up to 1.25 percent or even higher.

Diesel - engine crankcase oils are formulated to combat various levels of fuel sulfur content. If the engine builders recommended crankcase oil quality and oil change intervals are followed, there should be no concern with the effects of fuel sulfur.

The presence of sulfur compounds in the fuel is undesirable because of their corrosive action. They burn to form SO_2 and SO_3 which may react with water to form sulfurous and sulfuric acid. Acid formation is a more serious problem for engines operating either intermittently or at low temperature. Removal of sulfur compounds by chemical treatment increases the cost of the fuel. The production of straight - run fuels low in sulfur is limited by the availability of low sulfur crude.

G. Distillation

Distillation characteristics are measured using a procedure (ASTM D 86) in which a sample of the fuel is distilled and the vapor temperatures are recorded for the percentages of evaporation or distillation throughout the range.

In general the distillation range should be as low as possible without adversely affecting the flash point, burning quality, heat content or viscosity of the fuel. If the 10 percent point is too high, poor starting may result. An excessive boiling range from 10 percent to 50 percent evaporated may increase warm - up time. A low 50 percent point is desirable in preventing smoke and odor. Low 90 percent and end points tend to ensure low carbon residuals and minimum crankcase dilution.

H. Cetane Index

Since the determination of cetane number by engine testing requires special equipment, as well as being time consuming and costly, alternative methods have been developed for calculating estimates of cetane number. The calculations are based upon equations involving values of other known characteristics of the fuel.

One of the most widely used methods is based on the Calculated Cetane Index formula. This formula represents a method for estimating the cetane number of distillate fuels from API gravity and mid-boiling point. The index value as computed from the following formula is designated as a Calculated Cetane Index (CCI, ASTM D 976).

$$\begin{aligned} \text{CI} = & 97.833 (\log T)^2 + 2.2088G \log T + 0.01247G^2 \\ & - 423.51 \log T - 4.7808G + 419.59 \end{aligned}$$

where

G = API gravity

T = midboiling point in °F

= distillation temperature for 50 percent recovery at a pressure of 1 atm when determined by ASTM D 86 or ASTM D 158

Since the formula is complicated in its manipulation, a nomograph based on the equation has been developed for its solution.

2.4 Literature reviews [38-46]

Earlier studies on methods for improving wax to higher value product can be found in the following patent literature.

Cody, Hamner, Sawyer and Schorfheide reported an improved wax isomerization catalyst [38]. This catalyst was prepared by a process involving the step of depositing a hydrogenation metal component on a refractory metal oxide support followed by halogenation using an acidic halogen source. Following halogenation, the catalyst was crushed to expose inner surfaces of the prepared catalyst particles and sized to a particle of 1/32 inch across its longest continuous cross-sectional dimension.

Five catalysts were produced in different ways and contacted with wax. Comparisons of these five catalysts on oil yields showed good selectivity when the low pH fluoriding media was used. Sized catalyst always improve selectivity and the catalyst can be sized before fluoriding.

To summarize, it is clear that this sized catalyst is preferred for use in an isomerization process.

Hamner, Sawyer and Boucher studied a hydroisomerization for producing middle distillate fuel products from paraffin waxes such as slack wax and Fischer - Tropsch wax [39]. The catalyst employed was a fluorided Group VIII metal on alumina. A series of runs were made with different fluorided platinum on alumina catalysts to determine the effect of the catalyst and feed conversion levels on the selective conversion of petroleum slack wax to middle distillate fuel products.

In these runs, the slack wax feed was separately contacted with hydrogen over three different catalysts at constant conditions of feed rate, pressure and hydrogen addition. Three catalysts were prepared in a similar manner except calcination temperature and halogenated supported solution. It was seen that the catalyst calcined at a temperature of 750 °F and contacted with hydrogen fluoride solution was effective for the production of middle distillate. In addition, on comparing Pt/F on alumina with Pt on zeolite beta catalyst, Pt/F on alumina catalyst gives a much higher yield of middle distillate.

In conclusion, the platinum fluoride alumina catalyst of this invention is much more efficient at converting paraffinic wax to middle distillate material.

Cody and Brown studied isomerization of waxes which were obtained from dewaxing hydrocarbon oils by small particle low fluoride content catalyst [40]. Waxes were isomerized into oils by contacting the wax under isomerization conditions and in the presence of hydrogen with an isomerization catalyst comprising a noble Group VIII metal on a small particle size refractory metal oxide support having a low total fluoride content catalyst. The oil from the process had boiling range in the lube oil boiling range.

Five catalysts were prepared and compared for wax isomerization. These catalysts had different fluorided content and different alumina particle size.

From the results of isomerizing the wax using the five catalysts, it is clear that isomerization using a catalyst having low fluoride content and small particle size is superior to isomerization using a catalyst having high fluoride content or large particle size. In addition, three catalysts were prepared to show that catalysts fluorided using aqueous NH_4 solutions and having noble Group VIII metal are preferred.

Hamner and Sawyer prepared a catalyst useful for hydroisomerizing and hydrocracking a Fisher - Tropsch wax to liquid hydrocarbons [41]. The catalyst is a fluorided platinum on alumina.

Two catalysts were prepared. The only difference between them was that one had been heated in air at 400 °C for 1 hr after drying. This treatment resulted in a reduction of the hydrate level and produced a higher yield of oil boiling in the 370 °C+ range as compared to the yield obtained using the other.

In addition, it can be seen that the severe activation conditions to be responsible for subsequently increasing the surface fluorine level.

Cody, Hamner and Schorfheide studied a method for the production of lube oil base stocks or blending stocks [42]. Isomerization was done over isomerization catalysts containing a hydrogenating metal component on a fluorided alumina or material containing alumina.

From this it was seen that even for isomerates obtained by isomerizing waxes from a natural petroleum source, the ability to dewax the isomerate to the desired low pour point of at least about $-21\text{ }^{\circ}\text{C}$ is dependent upon the level of conversion. Low conversion levels produce isomerate which cannot be dewaxed to a low target pour point using conventional dewaxing solvents under typical dewaxing filter temperature conditions.

Wachter, Cody, Hamner and Achia produced lube base oils by isomerization of waxes over isomerization catalysts containing a hydrogenating metal component, most preferably platinum, on a halogenated refractory metal oxide support [43]. The refractory metal oxide support is typically on alumina and the halogen is fluorine.

It is apparent that at low levels of wax conversion and when using typical dewaxing solvents under standard conditions (filter temperature $-22\text{ }^{\circ}\text{F}$), a low yield of dewaxed oil having an unsatisfactory pour point is produced. Lower filtration temperatures would produce the desired pour point but would produce an even lower dewaxed oil yield.

Hamner, Boucher and Wachter studied the hydroisomerization of Fisher - Tropsch wax by first hydrotreating the wax under severe conditions and then hydroisomerizing the hydrotreated wax in the presence of hydrogen on a particular fluorided Group VIII metal on alumina catalyst [44]. The

hydroisomerate is then dewaxed to produce a lubricating oil having a high viscosity index and a low pour point.

A series of catalysts were prepared in the same manner except in the calcination catalyst. The results showed that platinum agglomeration increases exponentially with the drying/calcination temperature.

Cody and Brown upgraded waxy distillates and raffinates by a process comprising the steps of hydrotreating the waxy oil under conditions which convert less than 20% of the feed into products boiling lower than the feed to reduce the sulfur and nitrogen content of the oil, followed by hydroisomerizing the hydrotreated waxy oil to reduce the wax content and increase the viscosity index [45].

Two catalysts were prepared. One had a low fluorine content and another had high fluorine. The results demonstrated that low fluorine level Al_2O_3 -based catalysts are excellent "raffinate isomerization" catalysts. Preferred catalysts for raffinate isomerization, therefore, are Al_2O_3 -based catalysts comprising Group VIII metals or Group VIII/Group VI combinations and containing less than 2 %F, preferably 0.2 to 1.5 wt %F. The preferred fluoriding media is aqueous NH_4F .

Degnan and Landis described a process for hydroisomerizing petroleum wax or synthetic paraffin wax with a particular catalyst [46]. The catalysts are comprised of a hydrogenating component and a layered titanate. The hydrogenating components are Group VIII metal such as Pt. The layered titanate contained an interspathic polymeric oxide such as silica. The process produced the low pour point necessary for valuable high viscosity index products.

The study compared the activity of Pt/Silicotitanate and Pt/ SiO_2 - Al_2O_3 catalyst on the basis of the reactor temperature required to obtain a given

pour point of 650 °F+ fraction. It can be seen that the Pt/Silicotitanate catalyst is approximately 25 °F more active than the Pt/SiO₂-Al₂O₃ catalyst.