

## CHAPTER II

### THEORETICAL CONSIDERATION

#### Waxes [13, 16-19]

Wax usually refers to a substance that is a plastic solid at ambient temperature and, on being subjected to moderately elevated temperatures, becomes a low viscosity liquid. Because it is plastic, wax usually deforms under pressure without being heated. The chemical composition of waxes is complex: they usually contain a broad variety of molecular weight species and reactive functional groups, although some classes of mineral and synthetic waxes are totally hydrocarbon compounds.

#### A. Natural waxes

##### 1. Insect and animal waxes

Beeswax is secreted by bees and used to construct the combs in which bees store their honey. The wax is harvested by removing the honey and melting the comb in boiling water; the melted product is filtered and cast into cakes. The yellow beeswax cakes can be bleached with oxidizing agents, e.g., peroxide or sunlight, to white beeswax, a product much favored in the cosmetic industry. Beeswax is used widely in applications associated with the human body because it is safe to ingest in limited quantities and to apply to the skin.

## 2. Vegetable Waxes

The aerial surfaces of almost all multicellular plants are covered by a layer of wax. Vegetable waxes include candelilla, carnauba, japan wax, ouricury wax, Douglas-fir bark wax, rice-bran wax, jojoba wax, castor wax, and bayberry wax.

## 3. Mineral waxes

Mineral waxes include montan wax, peat waxes, ozokerite and ceresin waxes, and petroleum waxes. A paraffin wax is a petroleum wax consisting principally of normal alkanes. Paraffin, microcrystalline, and semimicrocrystalline waxes may be differentiated using the refractive index of the wax and its congealing point as determined by ASTM D 938. Typical physical properties of petroleum waxes are listed in Table 2.1

Petroleum wax is outstanding as a cost-effective moisture and gas barrier; thus, food packing is the largest market for petroleum waxes. Much of the petroleum wax produced is food-grade quality, although such quality may well be used in non-food-grade applications to simplify inventorying.

### B. Synthetic waxes

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

### Petroleum waxes [13, 16-22]

Petroleum waxes are substances which are solid at normal temperature. Paraffin and microcrystalline waxes in their pure form consist of

only solid hydrocarbons. Petrolatum, in contrast to the other two waxes, contains both solid and liquid hydrocarbons. Petrolatum is semi-solid at normal temperature and is quite soft compared to the other two waxes.

Waxes are normally associated with lubricating oils and during separation a certain amount of oil remains with the wax. Paraffin wax is separated essentially oil-free when crystallized from the oil. Microcrystalline waxes, on the other hand, tend to hold oil with unusual retentivity during separation. Microcrystalline wax is normally obtained associated with a large proportion of oil and it is from this product, called crude petrolatum, that microcrystalline wax is obtained by deoiling.

It is difficult to make a sharp division between petrolatums and microcrystalline waxes. In fact petrolatum may be considered as a soft-type microcrystalline wax. The difference between these two classes may be mainly a question of oil content. In actual practice, with increasing oil content, products varying in consistency from a tough wax to soft petrolatum can be obtained.

It has been confirmed by various compositional studies that commercial paraffin waxes consist largely of normal paraffins or straight chain hydrocarbons with some amount of iso-paraffins or branched chain hydrocarbons. Cyclic compounds are present in only minute quantities in paraffin waxes. Microcrystalline waxes, on the other hand, consist mainly of iso-paraffins and naphthenes (cyclic paraffins) with small amounts of paraffins and alkylated aromatics.

In general, microcrystalline waxes are higher in molecular weight than paraffin waxes. Paraffin waxes normally consist of hydrocarbons having average molecular weight in the range of 360 to 420 with individual components varying from 275 to 425. On the other hand, microcrystalline waxes usually consist of hydrocarbons having average molecular weight in the range of 575 to 700 although individual components may vary from 400 to 850.

Table 2.1 presents the comparison between paraffin wax and microcrystalline wax.

**Table 2.1** Typical physical properties of petroleum waxes

Property	Paraffin	Microcrystalline
Flash point, °C	204, min.	260, min.
Viscosity at 98.9 °C, mm <sup>2</sup> /s(SUS)	4.2-7.4(40-50)	10.2-25(60-120)
Melting range, °C	46-68	60-93
Refractive index at 98.9 °C	1.430-1.433	1.435-1.445
Average molecular weight	350-420	600-800
Carbon atom per molecule	20-36	30-75
Crystals	plates	needles
Other physical aspects	friable to crystalline	ductile-plastic to tough-brittle

### Constituents of crude oils [2, 13, 16, 20-23]

Of the more than 500 identified compounds found in petroleum, most are in the paraffin, naphthene (alicyclic), or aromatic groups of organic compounds and all could be derived through organisms. Because aromatics are least abundant, most petroleum is either paraffin base (low density or light), or naphthene base (high density, heavy, or asphaltic), or mixed base.

The general similarity of the composition and nature of petroleum constituents to the basic structural elements of compounds occurring in organisms is a major reason for believing petroleum originates from buried sedimentary organic matter derived from biopolymers. These biopolymers produced by plants and animals (lignin, carbohydrates, lipids, and proteins) undergo diagenesis—biological, physical, and chemical alteration of organic matter prior to a pronounced effect of heat to lead to complex geopolymers known collectively as kerogen, which are the main organic constituents of ancient sediments. Two main types of kerogen are recognized, a 'coal-like' type which does not contribute to petroleum and a 'sapropelic' type which does. Thermal conversion of sapropelic kerogen into oil and gas occurs as the temperature rises during burial of sediments.

Physically, crude oil can vary from a light, mobile, straw-colored liquid containing a large proportion of easily distillable material to a highly viscous, semi-solid black substance from which very little material can be moved by distillation before the onset of thermal decomposition. Densities generally lie in the range 0.79 to 0.95 g/cm<sup>3</sup> under surface conditions, and viscosities vary widely, from about 0.7 centipoise to more than 42000 centipoise. In general, crude oils are flammable under ambient conditions and their odors can vary from an almost pleasant aromatic bouquet to the distinctly unpleasant smell often associated with sulfur derivatives. Despite the wide differences in the physical aspects of different crude oils, their ultimate or elemental compositions are remarkably consistent; thus the values of the percentages by weight of the elements present in a 'crude' fall within the narrow limits quoted in Table 2.2.

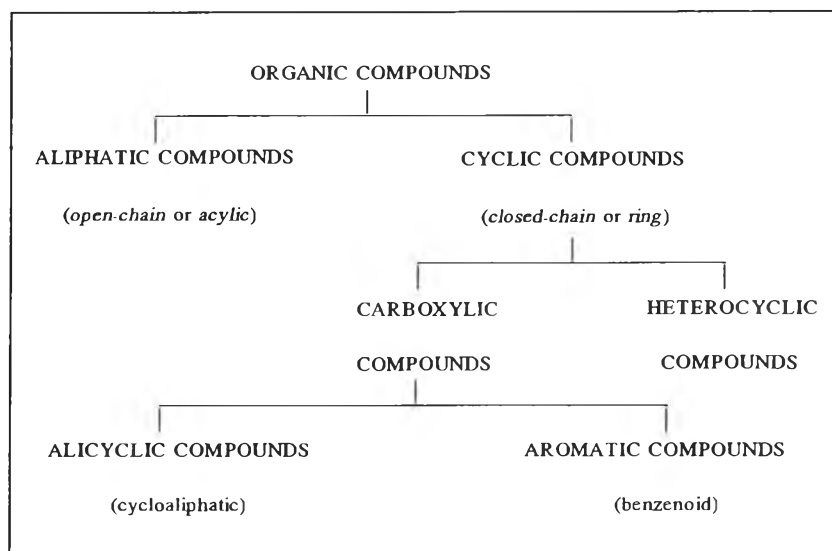
**Table 2.2** Elemental composition / %wt. ranges for crude oils

Carbon	83.9-86.8
Hydrogen	11.0-14.0
Sulfur	0.06-8.00
Nitrogen	0.02-1.70
Oxygen	0.08-1.82
Metal	0.00-0.14

As indicated by the analytical data listed in Table 2.2, The main constituents of crude oils are hydrocarbons, i.e. compounds composed solely of hydrogen (H) and carbon (C), and these can account for over 75 percent of the material. Of the other elements present, sulfur (S), nitrogen (N), and oxygen (O) appear as heteroatoms in hydrocarbon derivatives, some of which occur as petroporphyrins, i.e. complexes involving traces of metals [notably vanadium (V), and nickel (Ni)] present in petroleum. Metals may also be combined as salts of carboxylic acids, but much remains to be learned about the structural affiliations of metallic and metalloidal elements in crude oil. Inorganic sulfur can be present as the element or as hydrogen sulfide (H<sub>2</sub>S) dissolved in the oil. Heavy crude of the younger formations, for instance Venezuelan crude, have a low hydrocarbon content of the order of 35 to 38 percent, the remainder comprising compounds with molecules containing at least one heteroatom. Non-hydrocarbon components are concentrated mainly in the heavy residues from the distillation of crude.

The types of carbon compound (organic compound) present in crude oil are defined and exemplified. Readers are reminded that organic compounds

may be classified according to the basic scheme set out below. All the classes shown are present in petroleum.



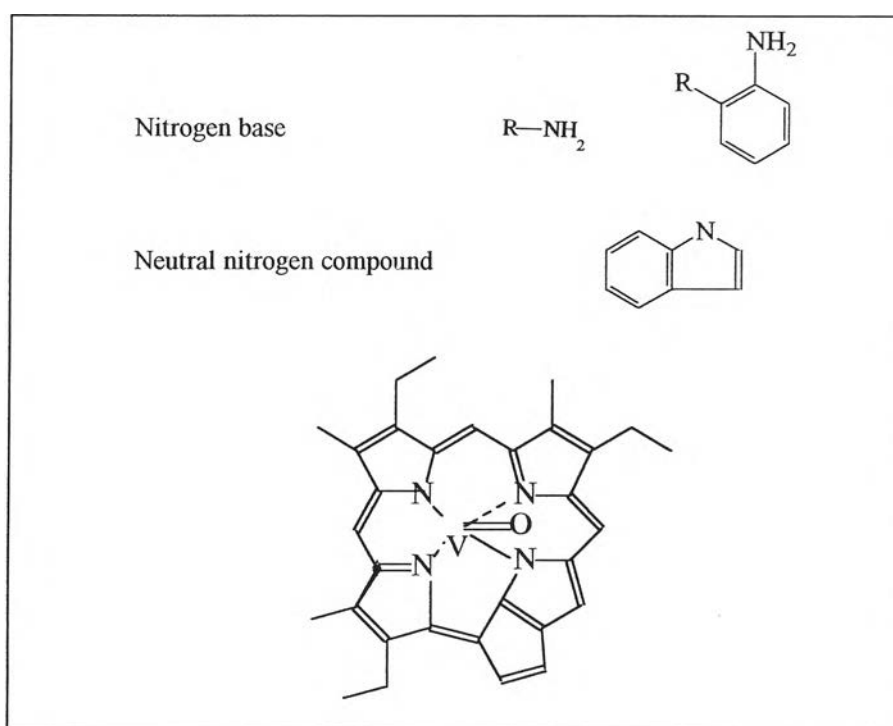
### A. Hydrocarbons

The principal types of hydrocarbon present in crude oils are normal, branched, or cyclic *saturated hydrocarbons*, *aromatic hydrocarbons* or compounds with molecular structures associating *both* these basic types. *Unsaturated hydrocarbons*, such as alkenes (aliphatic olefins), appear to be present in trace amounts—if at all. Types and general structures of hydrocarbons found in crude oil are shown in Table 2.3.

### B. Nonhydrocarbons

Crude oils contain appreciable amounts of organic compounds with structures incorporation one or more (the same or different) atoms of sulfur, nitrogen, or oxygen in addition to carbon and hydrogen. Some of these are associated with metals such as vanadium and nickel, i.e. they are



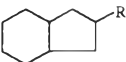

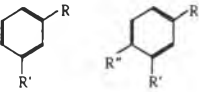


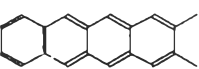
organometallic in nature. As a class, these organic nonhydrocarbon components are distributed throughout the whole boiling range of a crude oil, but appear mainly in the heavier distillation fractions and the nonvolatile residue. Although the concentration of nonhydrocarbons in any fraction may be relatively small, their influence can be important; for example, acidic components such as thiol and carboxylic acids promote corrosion of metal equipment; catalysts in the refining process are seriously deactivated by sulfur compounds; trace metals (V, Ni) become deposited on and passivate and/or poison catalysts employed in desulfurization or catalytic cracking of heavy distillates. The color and odor of crude oil stems mainly from the NSO compounds that are concentrated in the lubricating oil ( $C_{26}$ - $C_{40}$ ) and residuum ( $>C_{40}$ ; asphaltic bitumen) fractions. Examples of nonhydrocarbon compounds are shown in Figure 2.1 and Table 2.4.



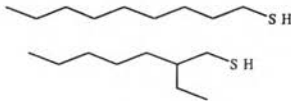
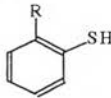


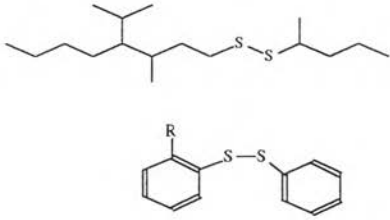
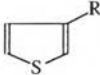
**Figure 2.1** Types of nitrogen compounds in crude oil



**Table 2.3** Type and structure of hydrocarbon in crude oil

Type	Structure
<b>Normal paraffins</b> (straight chain)	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\dots$
<b>Iso-paraffins and branched paraffins</b>	$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\dots \\   \\ \text{CH}_3 \end{array}$ $\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_2-\dots \\   \\ \text{CH}_3 \end{array}$
<b>Cycloparaffins</b>	
Alkylcyclopentane	
Alkylcyclohexane	
Bicycloparaffin	
<b>Aromatics</b>	
Alkylbenzene	
Dialkylbenzene and trialkylbenzene	
Alkyl naphthalene	
Aromatic cycloparaffin	
Polynuclear aromatics	

**Table 2.4** Types of sulfur compounds in crude oils.

Type	Structure	
Hydrogen sulfide	$H_2S$	
Mercaptans		
Aliphatic	$R-S$	
Aromatic		
Sulfides		
Aliphatic	$R-S-R$	
Cyclic		
Disulfides	$R-S-S-R$	
Polysulfides	$R-(S)_n-R$	
Thiophenes		

Refining process [2, 14-17, 21-28]

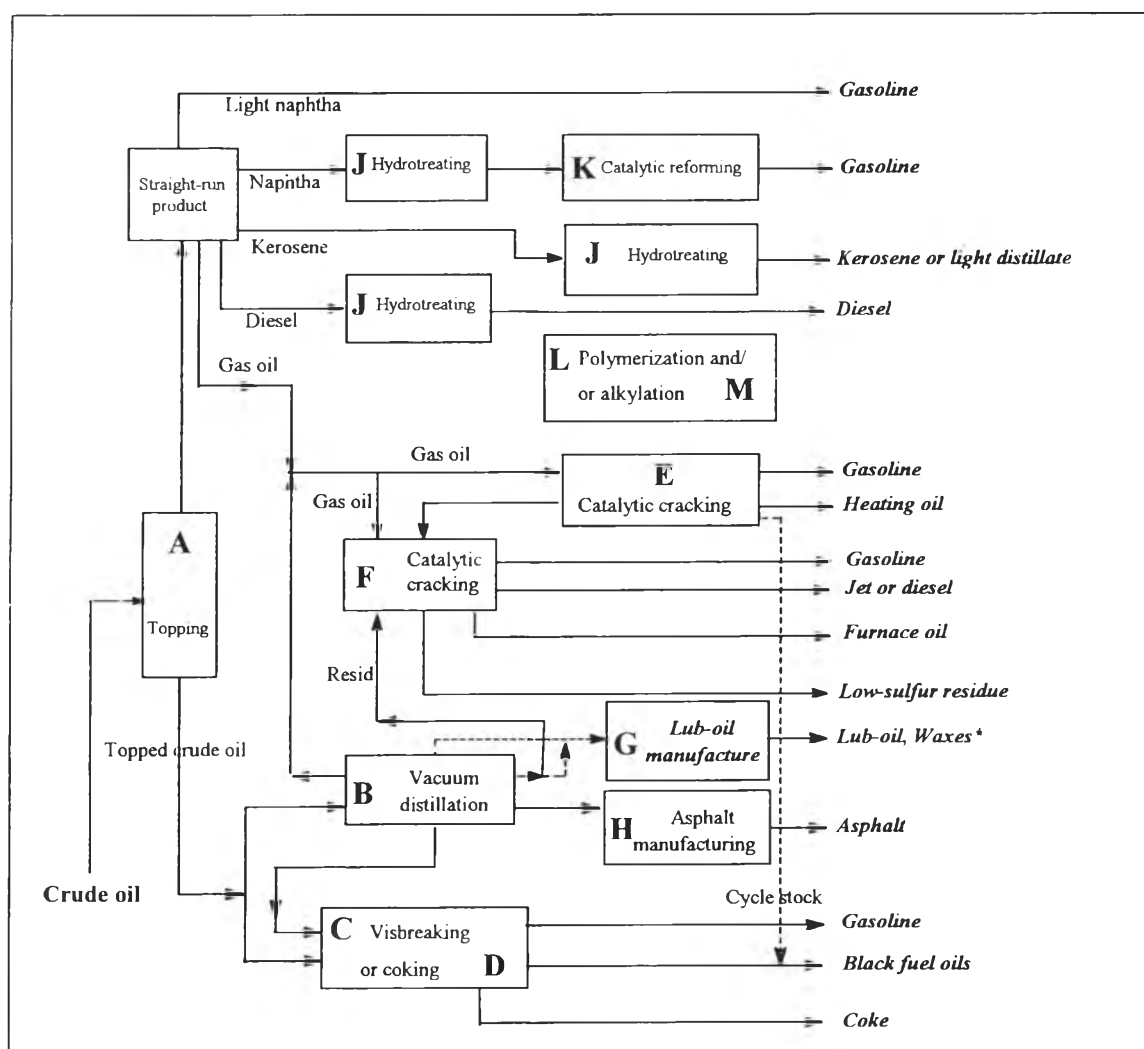
Crude oils are found in a variety of types ranging from light colored oils, consisting mainly of gasoline, to black, nearly solid asphalts. Crude are highly complex mixtures containing many individual hydrocarbons. These range from methane, the main constituent of natural gas, with one carbon atom, to compounds containing 50 or more carbon atoms.

The boiling range of the products increases roughly with an increase in the number of carbon atoms as shown in Table 2.5

**Table 2.5** Petroleum fractions

Products	Boiling range (°F)	API
Gas, light ends	C <sub>1</sub> - C <sub>4</sub>	-
Light naphtha	50-200	70
Heavy naphtha	200-375	53
Kerosene	375-450	43
Diesel, heating oil	450-550	37
Atmospheric gas oil	550-650	32
Reduced crude loss, slop	650+	
Light vacuum gas oil	650-750	30
Heavy vacuum gas oil	750-1,000	23
Residuum	1,000+ (large molecule)	

The heavier asphaltic materials cannot be vaporized because they decompose when heated above the normal distillation temperatures and their molecules either “crack” to form gas, gasoline and lighter fuels or unite to form higher molecular weight molecules. These latter materials result in carbonaceous residues called “coke”. Crude oils also contain varying amounts of compounds of sulfur, nitrogen, oxygen, various metals such as vanadium and nickel, water, and salts. A simplified “over view” of petroleum refinery operations is shown in Figure 2.2.



**Figure 2.2** Basic refinery operations

In general, when a lubricating base oil is produced from crude oil, the crude oil is first subjected to atmospheric distillation, and the resulting residual oil is further subjected to vacuum distillation to separate the various lubricating oil fractions by vacuum distillation of the residual oil. The vacuum distillation residual oil is subjected to solvent deasphalting, thereby removing asphalt contents and obtaining a heavy lubricating oil fraction (bright stock). The bright stock and other lubricating oil fractions of various viscosities are further subjected to solvent refining, hydrofinishing, dewaxing and similar steps to produce the lubricating base oil of interest.

Hydrocracking and hydroisomerization processes are to produce lubricating base oil of high viscosity index. In the hydrocracking process a vacuum gas oil fraction, a bright stock, waxes of various types, or a mixture thereof is subjected to hydrocracking under high temperature and high pressure conditions in the presence of a catalyst, and a high viscosity index base oil is produced from the resulting oil. In the hydroisomerization process, the conditions and catalyst are selected so that the feedstock is primarily isomerized with substantial retention of molecular weight and minimum hydrocracking to products of lower molecular weight. The advantage of the hydroisomerization process resides in the increased yield and stability of the oil as compared to other upgrading dewaxing processes which convert wax to light products. Slack waxes are isomerized and processed into high viscosity index and very low pour point lube base stock oils.

In the case of the catalytic isomerization of slack wax, it is necessary to carry out a pretreatment for the removal of nitrogen and sulfur components by including a hydrofinishing step prior to the isomerization step, because the isomerization catalyst is likely to undergo deterioration due to nitrogen and sulfur compounds contained in the slack wax.

### Fang refinery

For over 30 years, Fang refinery has been in operation under the supervision of the Defense Energy Department (DED), ministry of Defense. All of its crude supplies come from the nearby Fang basin area where production level is now at 1,500 barrels per day. This crude oil is fed into the refinery which runs at a capacity of 1,000 barrels per day. The process consists of several operation units including Topping distillation unit, Vacuum distillation unit, Gasoline treating unit, Gasoline blending unit, Power unit, and Facilities unit

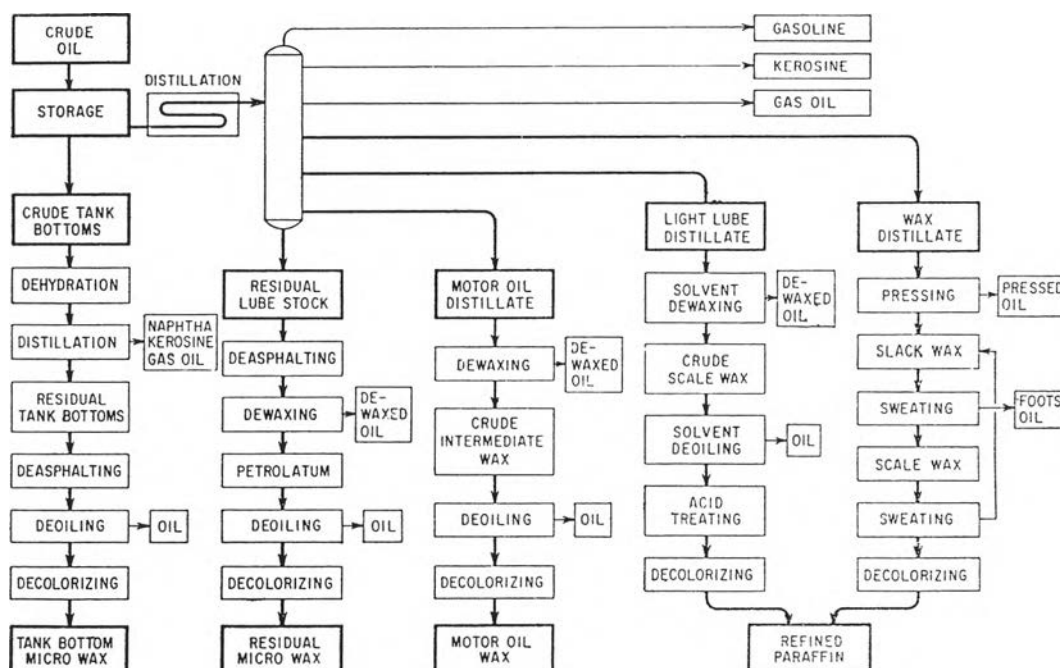
Once crude oil from Mae Soon Luang is shipped to Fang refinery, the water will be separated in the separation unit where treat-O-lite is used as emulsifier. After that, the crude is pumped through a preheat exchanger and its temperature raised to about 120°C by heat exchange with hot oil from the vacuum tower. It is then further heated to 430°C in an atmospheric heater and charged to the atmospheric fractionators. The liquids withdrawn from this tower will contain straight run oil, kerosene and diesel. Reduced crude from the bottom of the atmospheric tower is sent to the vacuum heater and its temperature raised to 365 °C prior to charging a vacuum tower where it is separated into light distillate, heavy distillate and heavy fuel oil. The refinery products consist of straight run oils 6 %, diesel 26 %, light distillate 17 %, heavy distillate 14 %, and heavy fuel oil 37 %.

### Manufacture and classification of petroleum waxes [13, 16, 18, 22]

A schematic representation of the basic routes by which petroleum waxes are produced from crude oil is shown in Figure 2.3

The manufacture of petroleum waxes is closely related to the manufacture of lubricating oils. After the low boiling fractions of the crude petroleum, gasoline, kerosene, etc., have been removed, the reduced crude contains lubricating oils, waxes, and asphalt. The distillation of this reduced crude gives the following fractions:

1. Light lube wax distillate.
2. Heavy wax distillate.
3. Residue.



Flow diagram of wax production at a petroleum refinery.

**Figure 2.3** Flow diagram of wax production at a petroleum refinery.

The light lube distillate is also called pressable wax distillate as the wax contained in it can be removed by filter pressing after chilling. The wax contained in light lube distillate is paraffinic in nature. The heavy distillate is also called motor oil distillate and contains a large percentage of wax which, though commonly included in microcrystalline waxes, falls between the true paraffin and true microcrystalline wax. The residue consists of high viscosity oil and microcrystalline wax along with a significant amount of asphalt, if the crude is of naphthenic or mixed base. The next operation is separating the wax from lubricating oil. This operation is called dewaxing.

The different routes by which separation is accomplished have given rise to two waxes classifications namely paraffin waxes and microcrystalline waxes.

### 1. Paraffin waxes

Paraffin waxes are mixtures of saturated paraffinic hydrocarbons (alkanes), straight-chain or normal alkanes being the major component of the mixtures, with varying proportions of paraffins having a degree of branching in their chains (iso-alkanes) present, together with a small cycloalkanes content. The chain length of the individual alkanes ranges from about 18 carbon atoms to about 45, the higher the average molecular weight of the alkane mixtures, the higher the proportion of iso-alkane likely to be present.



## Grades of paraffin wax

Paraffin wax is solid in various grades with the difference from one to another being in their melting points. Generally, each grade covers a 2 °C range of melting points, for example 54-56 °C. Melting points are given by either of two accepted standards: American melting point (AMP) or ASTM melting point, which is often called English melting point (EMP).

The most familiar types of paraffin wax on the market are refined and crude scale waxes.

### a) Refined wax

Refined wax has a melting point range of 47-68°C, a color (Saybolt chronometer scale) +21 or lighter, and an oil content of 0.5 %wt or less. At ordinary temperatures, refined waxes are hard and are frequently brittle. On heating they become progressively softer and more plastic until they finally melt to the thin clear liquid. The presence of a small proportion of oil, due to insufficient refining, greatly affects certain properties. Such wax easily discolors when exposed to light. With as little as 0.5 % oil content, the mechanical strength is much reduced and becomes mealy or easily crushed to fine powder.

### b) Crude scale wax

Crude scale wax has a melting point range of 47-57 °C, a color darker than +21 (Saybolt chronometer scale) and an oil content of about 0.6-3 %. It is not entirely stable in color even when bleached, nor is it free from taste and odor.

Crude scale wax is sold in two forms: white and yellow. They are similar except for one additional step in the refining procedure of

bleaching the yellow wax to produce white wax. Most crude scale wax sold in the market is the white type.

## 2. Microcrystalline waxes

Microcrystalline waxes also are mixtures of saturated alkanes, but with a much greater preponderance of branched-chain or cyclic molecules. The carbon atom content per molecule can vary from the mid-thirties to well over eighty, the average molecular weight thus being much higher than in the case of the distillate waxes. The complex branched-chain structures prevent any degree of close packing and microcrystallization, giving rise to the original name of *amorphous* waxes, and later, rather more accurately, to the current nomenclature of microcrystalline waxes.

The microcrystalline waxes on the market are often designated by their method of preparation and physical properties. For example, the name petrolatum wax\* applies to a microcrystalline wax refined from petroleum stock. Usually sticky wax of about 68-77 °C melting point, and a penetrometer value of more than 25 is implied. The wax that are much harder, more oil free, of higher melting point (82-90 °C), and which have a penetrometer value of less than 25, are known as petroleum ceresins#.

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\* Petrolatum or crude petrolatum wax, as it is also called, contains more than 10 per cent oil it is obtained from the acid-treated petrolatum stock containing a fairly high percentage of wax, by treatment with naphtha and centrifugation to removed excess oil.

# This is also wax of fine crystalline structure, which varies in color from dark brown to white. Unlike the petrolatum waxes it is hard and brittle; this constitutes the main difference between these two groups. Petroleum ceresins have molecular weights ranging from about 450-1000 Daltons and melting points range from 70 to 105 °C.

## Purification of waxes [4-6, 17]

The waxes obtained by solvent dewaxing processes contain about 30-35 percent oil. They are brown in color and for further uses must be purified by deoiling and decolorizing. The purification of waxes can be performed in two ways

### 1. Physical treatment

#### 1.1 Solvent extraction

Purification is carried out by solvent deoiling to give waxes with less than 0.3 percent of oil

#### 1.2 Adsorbent material treatment

Adsorbent materials (such as bauxite, Fuller's earth, bentonite, synthetic aluminum silicate, activated charcoal and/or activated adsorbent) are used for removal of, or the reduction in, color and color-forming bodies, aromatic content, sulfur, nitrogen, combined oxygen, trace metals and other undesirable materials present in the waxes. After adsorbent material treatment, the waxes exhibit improved odor and color characteristics.

### 2. Chemical treatment

#### 2.1 Acid treatment

Sulfuric acid is the most often used for purification of waxes in order to reduce their carbinizable matter content. The reactions of sulfuric acid are complex. The undesirable components to be removed are generally present in small amounts; large excesses of acid are required for efficient removal, which may cause marked changes in the remainder of the hydrocarbon mixture.

Paraffinic and naphthenic hydrocarbons in their pure forms are not attacked by concentrated sulfuric acid at the low temperature and during the short time, but solution of light paraffins and naphthenes in the acid sludge can occur.

## 2.2 Catalytic-type hydrogen treatment

Catalytic-type hydrogen treatment is the modern procedure for purification of waxes. Catalysts in this treatment comprise transition metal group VIB and group VIII B on particular solid adsorbent carrier such as alumina or silica. The products obtained from this procedure have excellent color, odor, and stability.

The most generally accepted procedure for purification of waxes has consists of subjecting the waxes to a sweating or solvent deoiling step to reduce the oil content of the waxes. The partially deoiled waxes are then treated with sulfuric acid and thereafter are contacted with an adsorbent material.

### Solvent dewaxing [20, 23]

The original dewaxing method involved cooling the waxy oil and filtering. Pressure of up to 20 bar could be applied to the wax cake to force out the oil. Filtration efficiency could be greatly improved by diluting the oil with a solvent such as naphtha, but selectivity to removal was reduced.

Improved solvent systems have been developed to give better dewaxing performance and important factors in the choice of solvent are

- Good solubility of oil in the solvent and low solubility of wax in the solvent.
- Small temperature difference between the dewaxing temperature and the pour point of the dewaxed oil.
- Minimum solvent/oil ratio.
- Formation of large wax crystals which are easily filtered.
- Ease of solvent recovery (i.e. low boiling point).

- Desirable properties (such as stability, safety, low toxicity, ease of handling, and cost).

Solvents used in commercial processes include propane, methyl isobutylketone, and mixed solvents such as methyl ethyl ketone/toluene or methylene chloride/dichloromethane. The use of a mixture of solvents gives better control of the oil solubility and wax crystallization properties than the use of a single solvent.

After the separation operation, wax is fully refined to white wax. The important properties of white wax are shown in Table 2.6 and 2.7.

**Table 2.6** Properties of paraffin wax [18]

Properties	Values
Melting point, °C	47-68
Needle Penetration, at 25 °C	10-20
Oil content, %wt	<0.5
Viscosity, at 98.9 °C (i) cSt.	2.4-5.7
(ii) SUS	35-45
Flash Point, °C	175-235
Specific gravity, at 100 °C	about 0.75
Refractive index, at 100 °C	1.430-1.433
Contraction from 5 °C above to 25 °C below m.p., %	13.5-14.5
Flexibility at low temperature	Zero
Adhesion or laminating strength	Zero
Properties when mixed with petroleum oil,	
(i) Ductility	low
(ii) Staining or bleeding	high

**Table 2.7** Properties of Microcrystalline Waxes [18]

Properties	Values
Melting Point, °C	5-96
Needle Penetration, at 25 °C	5-50
Oil content, %wt	2-15
Viscosity, at 98.9 °C (i) cSt.	9-25
(ii) SUS	50-100
Flash Point, °C	230-315
Specific gravity, at 100 °C	about 0.80
Refractive index, at 100 °C	1.435-1.445
Contraction from 5 °C above to 25 °C below m.p., %	
Flexibility at low temperature	Zero
Adhesion or laminating strength	Zero
Properties when mixed with petroleum oil,	
(i) Ductility	low
(ii) Staining or bleeding	high

**Base oil composition, properties, and structure relationship [2]**

The petroleum fraction used as lubricant generally contains compounds containing 18 or more carbon atoms. The lubricating base oil fraction is a complex mixture consisting primarily of five characteristic classes: paraffin naphthenes, condensed naphthenes, aromatic naphthenes, naphthalenes (two ring aromatics), and multiple ring aromatics.

Moreover, it also contains small amounts of heterocyclic compounds containing sulfur and nitrogen atoms (e.g. thionaphthene, indole, quinoline, and carbazoles) and various oxygen compounds including naphthenic acids which account for most of the chemically bound oxygen in petroleum fractions.

Using products contained these compounds without prior treatment present corrosion problem and pollute the environment.



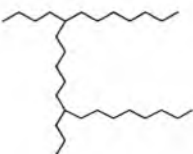
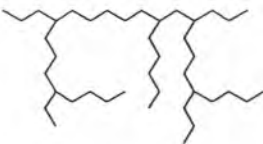
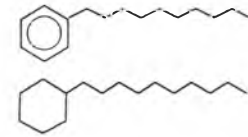
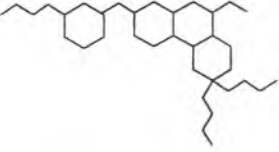

Alkanes, alicyclics, and aromatics of the same molecular weight have markedly different physical and chemical properties. Physical characteristics will affect the viscometrics of the lubricant, and the chemical properties relate to the stability of each class to oxidation and degradation while in use. is also very important. The effect of different types of compounds on the lubricating oil's properties can be seen in Table 2.6.

Table 2.6 shows qualitatively that the highly desirable structures for lubricant base oils are the highly branched isoparaffin and monocyclic hydrocarbons, whether saturated or not, with long aliphatic chains and preferably six carbon atoms in the ring.

The linear alkanes (normal paraffins) have good viscosity/temperature characteristics but their high melting points cause them to crystallize out of solution as wax. On the other hand, branched-chain paraffins are not waxy and have good stability and viscosity/temperature properties.

Alicyclics and aromatics have rather higher densities and viscosities for their molecular weights compared to the alkanes. They tend to have low melting points and so do not contribute to wax. However, their viscosity/temperature characteristics and oxidation stability are in general rather poor. Single ring alicyclics or single ring aromatics with long alkyl side chains, in contrast, share many properties with branched alkanes and can in fact be very desirable base oil components.

**Table 2.8** Lubricating oil properties of some typical hydrocarbon structures

Structures	VI	Freezing point	Resistance to oxidation	Value as base oil
Linear paraffin 	Very high	High	Good	Nil
Isoparaffin with linear chain 	High	Medium	Good	Medium
Isoparaffin with isomerized chains 	High	Low	Good	High
Highly substituted isoparaffin 	Medium	Low	Good	Medium
Single ring with long aliphatic chain 	High	Low	Good	High
Polycondensed naphthenes 	Low	Low	Medium	Nil
Polycondensed aromatics 	Very low ( < 0 )	Low	Weak	Nil



### Hydrotreating process [2, 23]

Despite the intensive series of process steps carried out so far, trace impurities may still be present in the products and a finishing step is needed to correct problems such as:

- poor color
- poor oxidation or thermal stability
- poor emulsification properties
- poor electrical insulating properties

These undesirable components tend to be nitrogen-, oxygen-, or, to a lesser extent, sulfur-containing molecules.

In the past, selective adsorbents such as clay or bauxite were used to remove impurities, but these processes were messy and give waste disposal problems. Today hydrofinishing has almost completely taken over.

Hydrofinishing is different from all the processes steps used so far because it is not a physical separation procedure. It depends on the selective, catalyzed hydrogenation of the impurities to form harmless products and is carried out under relatively mild conditions. Hydrofinishing should be effective at removing organonitrogen molecules because they are largely responsible for poor color and poor stability of base oils. At the same time it should not remove organosulfur molecules because they tend to impart natural oxidation stability to the products. The finishing process is usually called a hydrotreating process because it uses hydrogen and catalyst for removing impurities and converting unsaturated hydrocarbons to saturated hydrocarbons.

The types of reactions that occur in the catalytic hydrogenation process are :

- Hydrogenation of aromatics and other unsaturated molecules
- Ring-opening, especially of multiple ring molecules
- Cracking to lower molecular weight products

- Isomerization of alkanes and alkyl side chains
- Desulfurization
- Denitrogenation
- Reorganization of reactive intermediates, e.g. to form trace of stable polycyclic aromatics.

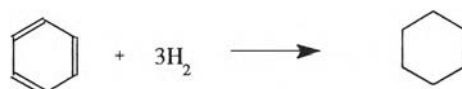
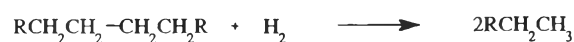
### Reactions [16,25-28]

The finishing process or hydrotreating process of petroleum and its fractions comprises a wide assortment of reactions involving all the components present in the complex mixture. The typical reactions of hydrotreating are shown in Figure 2.4.

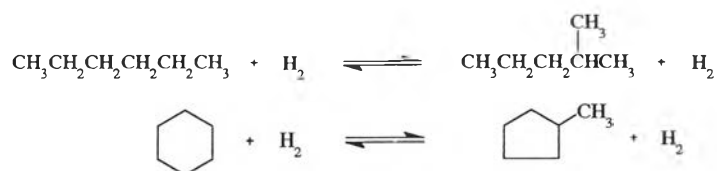
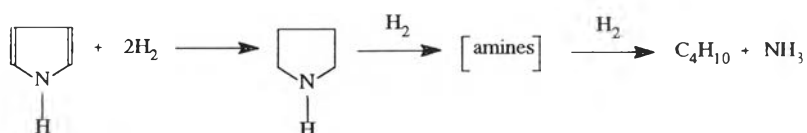
Petroleum fractions may contain large quantities of sulfur and nitrogen compounds. Using these products without prior treatment not only presents corrosion problems but also pollutes the environment. In addition, sulfur and nitrogen compounds poison many catalysts used in petroleum processing. Hydrotreatment of these fractions eliminates or reduce sulfur and nitrogen compounds to an acceptable level. Hydrotreatment may also be necessary to saturate olefinic compounds present in some cracked fractions. Olefinic compounds are known to be precursors of coke formation, which is responsible for deactivating valuable catalysts. Although many reactions take place during hydroprocessing of petroleum fractions, hydrodesulfurization and hydrodenitrogenation reactions are probably the most important ones. The process used for this purpose is usually called hydrodesulfurization.

**Saturation** : Olefinic bonds

## : Aromatic bonds

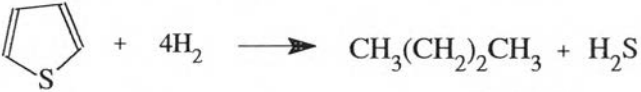
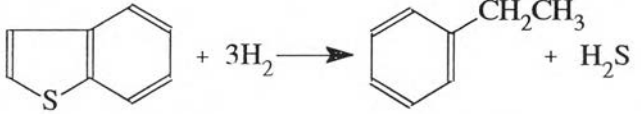
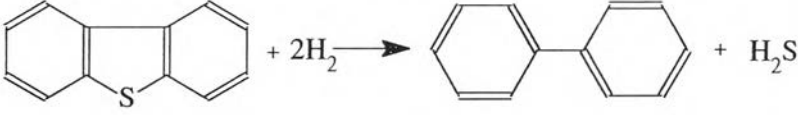
**Hydrocracking** : Paraffins**Hydrocracking** : Dealkylation

## : Ring open

**Hydroisomerization** : Paraffins and naphthenes**Hydrodesulfurization****Hydrodenitrogenation****Figure 2.4** Typical reactions in hydrotreating process

### A. Hydrodesulfurization [6, 14-16, 25, 26, 29, 30]

Hydrodesulfurization or hydrogenolysis of sulfur compounds produces a hydrocarbon and hydrogen sulfide. The most important classes of organic compounds found in petroleum fractions are mercaptants, sulfides, disulfides, thiophenes, benzothiophenes and dibenzothiophenes. The following are examples illustrating some of the reactions of these compounds during hydrodesulfurization.

Sulfur Class	Reaction
<i>Mercaptans</i>	$R-SH + H_2 \longrightarrow RH + H_2S$
<i>Sulfides</i>	$R-S-R + H_2 \longrightarrow 2RH + H_2S$
<i>Disulfides</i>	$R-S-S-R + 3H_2 \longrightarrow 2RH + 2H_2S$
<i>Thiophene</i>	 $\text{C}_4\text{H}_4\text{S} + 4H_2 \longrightarrow CH_3(CH_2)_2CH_3 + H_2S$
<i>Benzothiophene</i>	 $\text{C}_{10}\text{H}_8\text{S} + 3H_2 \longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 + H_2S$
<i>Dibenzothiophene</i>	 $\text{C}_{12}\text{H}_8\text{S} + 2H_2 \longrightarrow \text{C}_6\text{H}_5\text{C}_6\text{H}_5 + H_2S$

#### 1. Hydrodesulfurization catalysts

In general, any hydrogenation catalyst may be employed for the hydrodesulfurization of petroleum fractions. In the patent literature, such catalysts are often classified broadly on the basis of the Periodic Table. Thus,

one patent indicates that suitable compositions contain oxides or sulfides of Group IIB to VIIB, preferably of Group VIB and preferably in conjunction with metals of Group VIIIB or heavy metals of Groups IB and IIB or their oxide or sulfides. Typical carriers for such catalysts are indicated to be activated charcoal, Fuller's earth, Florida earth, silica gel, alumina, pumice, bauxite, and burnt fire clay. A basic US patent describes Group VIB metal (molybdenum, tungsten, and chromium) compounds which may be admixed with substances which may or may not have hydrogenating properties such as iron or nickel or cobalt or their compounds, or alumina, zinc oxide, magnesia, or calcium carbonate. Another general classification indicates catalytic agents to include oxides or other compounds of the related metals which possess their differentiating electron in the "second from the outermost shell" (shell immediately beneath the outer shell). Metals which are included are scandium, titanium, *vanadium*, *chromium*, manganese, *iron*, *cobalt*, *nickel*, copper, zinc, yttrium, zirconium, niobium, *molybdenum*, ruthenium, rhodium, palladium, silver, cadmium, lanthanum, hafnium, tantalum, *tungsten*, rhenium, osmium, iridium, *platinum*, gold, mercury, actinium, thorium, and uranium. With the exception of copper, zinc, silver, cadmium, gold, and mercury, these elements are of the transition type characterized by the fact that the outer two or three electron shells are complete. Copper, silver and gold in their polyvalent states also belong to the transitional class.

Obviously such broad classifications as given above are of sufficient scope to include materials of little value, or which have value only as promoters, and to cover substances which may only function as carriers. On the basis of frequency of mention in representative patent and other literature and of activity, italicized members of the latter classification above, when used alone or in certain combinations, assume the most important positions. The catalyst normally contains an element of group VIA, such as Mo or W and an element of group VIIIA, such as Co or Ni. The combinations of oxides or

sulfides of cobalt and molybdenum or of sulfides of nickel and tungsten are used most frequently in commercial applications. Supported or unsupported combinations of cobalt oxide and molybdenum oxide may be mixtures of these compounds and/or cobalt molybdate. All such compositions are referred to as cobalt molybdate on alumina support (CoMo/alumina) according to the most common commercial hydrodesulfurization catalyst usage.

Pier and co-workers introduced the sulfur resistant hydrogenation catalyst CoMoS/Al<sub>2</sub>O<sub>3</sub>, NiMoS/Al<sub>2</sub>O<sub>3</sub> and NiWS/Al<sub>2</sub>O<sub>3</sub>. The CoMoS/Al<sub>2</sub>O<sub>3</sub> catalyst appeared to be the most suitable catalyst for hydrodesulfurization and NiMoS/Al<sub>2</sub>O<sub>3</sub> for hydrodenitrogenation.

## 2. Hydrodesulfurization mechanism [32, 33]

The most common commercial hydrodesulfurization catalyst is CoMo/alumina. It is commonly accepted that the catalytically active centers are located on the molybdenum species, while the cobalt species acts as promoter. Synergy between these two species has been explained several ways. Delmon (1979) proposed the concept of remote control with the activation of active sites by spill-over hydrogen. In the highly active Co-Mo-S phase; the promotion is associated with an increase in electron density on molybdenum species while the promoter stabilizes the dispersion of very small particles of MoS<sub>2</sub>. In spite of these different opinions, some agreement on certain aspects of the catalyst's activity exists. The first aspect agreed upon is the necessity of intimate contact between both molybdenum and cobalt species. The second aspect is the nature of the active sites, which can be varied by catalyst support and the preparation and pretreatment of the catalyst. Variation in the nature of active sites may give different adsorption, reaction, and desorption rates.

The remote control concept distinguishes between the role of two types of species on the catalyst. One is active in creating spill-over hydrogen and the other in catalyzing the reactions. The spill-over hydrogen is created on the former phase (donor) and then migrates to the latter phase (acceptor), where different types of active sites are created by the spill-over hydrogen. The donor is much less active than the acceptor in catalyzing reactions. Without the spill-over hydrogen from the donor, the potentially active sites on the acceptor cannot be transformed into sites active in the reactions. For CoMo/alumina catalyst, the cobalt sulfide phase acts as the donor of spill-over hydrogen, while the molybdenum sulfide phase acts as the acceptor. The activation of the catalyst consists of three steps:

(1) generation of spill-over hydrogen on cobalt sulfide phase.

Spill-over hydrogen has been commonly accepted to be atomic hydrogen formed by dissociative adsorption of molecular hydrogen. The atomic hydrogen may be ionic, radical or bounded hydrogen, depending upon the circumstances. The hydrogen in gas phase is first dissociatively adsorbed on the cobalt sulfide phase. Then spills over to the catalyst support and to the nearby molybdenum sulfide phase. This step is considered to be intrinsically much slower than the adsorption step and its rate determines the rate of generation of spill-over hydrogen.

(2) migration of spill-over hydrogen from the cobalt sulfide phase to the molybdenum sulfide phase.

Spill-over hydrogen formed on the cobalt sulfide phase can migrate to the molybdenum sulfide phase. The driving force for this migration is the concentration difference of spill-over hydrogen between the two phases. The mass transfer rate also depends on the interfacial surface area of the two phases. The latter is a function of the dispersions of the cobalt and molybdenum sulfide phases and the degree of contact between the two phases. The dispersion is reflected in the surface area and the degree of contact is

reflected in the size of interfacial area per unit product of unit surface areas. Therefore, the interfacial surface area between cobalt and molybdenum sulfide phases is proportional to the product of both unit surface areas and the unit interfacial area.

(3) activation of the molybdenum sulfide phase by the spill-over hydrogen.

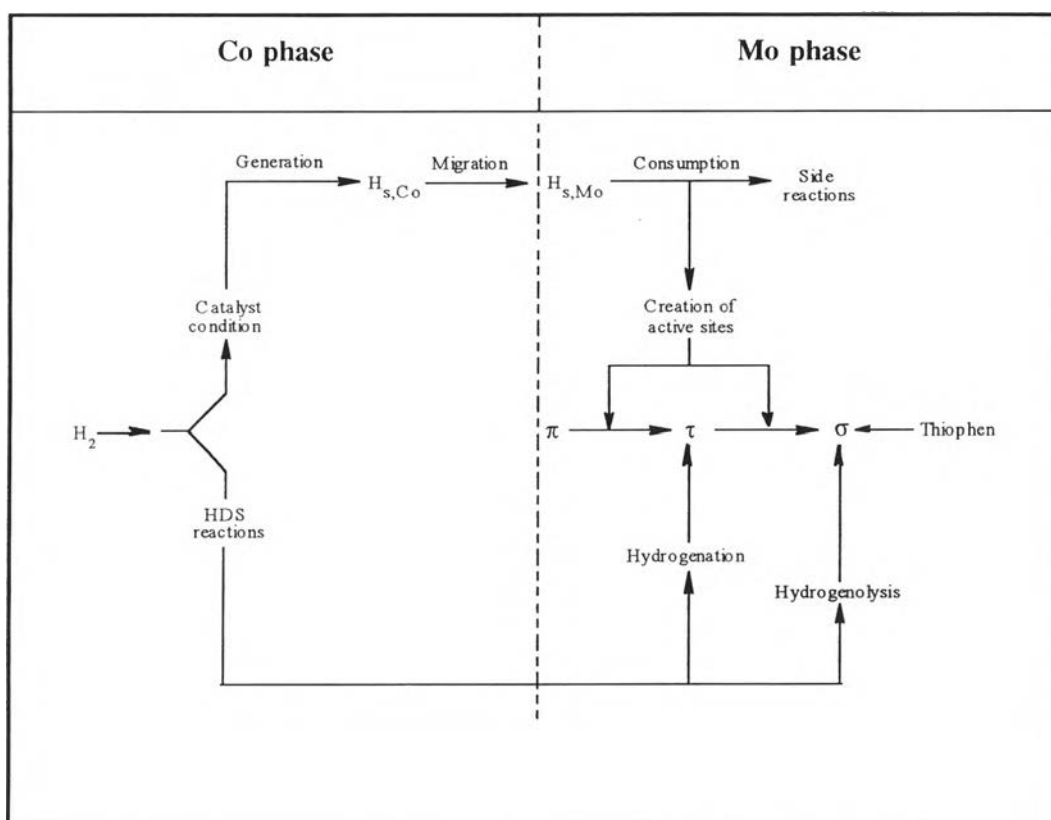
Spill-over hydrogen on the molybdenum sulfide phase may be involved in various types of reactions. First, it is needed in the creation of hydrogenation (weakly reduced) sites and hydrogenolysis (strongly reduced) sites. In this mechanism, unreduced, weakly reduced, and strongly reduced sites are represented by  $\pi$ ,  $\tau$ , and  $\sigma$ , respectively. The  $\tau$  and  $\sigma$  sites are created by the reaction of  $\pi$  and  $\tau$  sites, respectively, with spill-over hydrogen on the molybdenum sulfide phase. During the site conversion, sulfide atom of the molybdenum sulfide phase are rearranged and may be rejected into the gas phase as hydrogen sulfide.

The rates of hydrogenolysis and hydrogenation on this catalyst are a function of the number and type of active sites generated by the spill-over hydrogen under reaction conditions.

The three types of sites occurring on the molybdenum sulfide during hydrodesulfurization are unreduced, weakly reduced, and strongly reduced sites. Before the reduction by spill-over hydrogen, the unreduced site is only potentially active in the hydrodesulfurization reactions. It can be weakly reduced to a site, active in hydrogenation only, or strongly reduced to a site, active in hydrogenolysis.

The flow diagram of the overall mechanism, including the generation, migration, and consumption of spill-over hydrogen, the creation and interconversion of active sites and the hydrogenolysis and hydrogenation, is presented in Figure 2.5





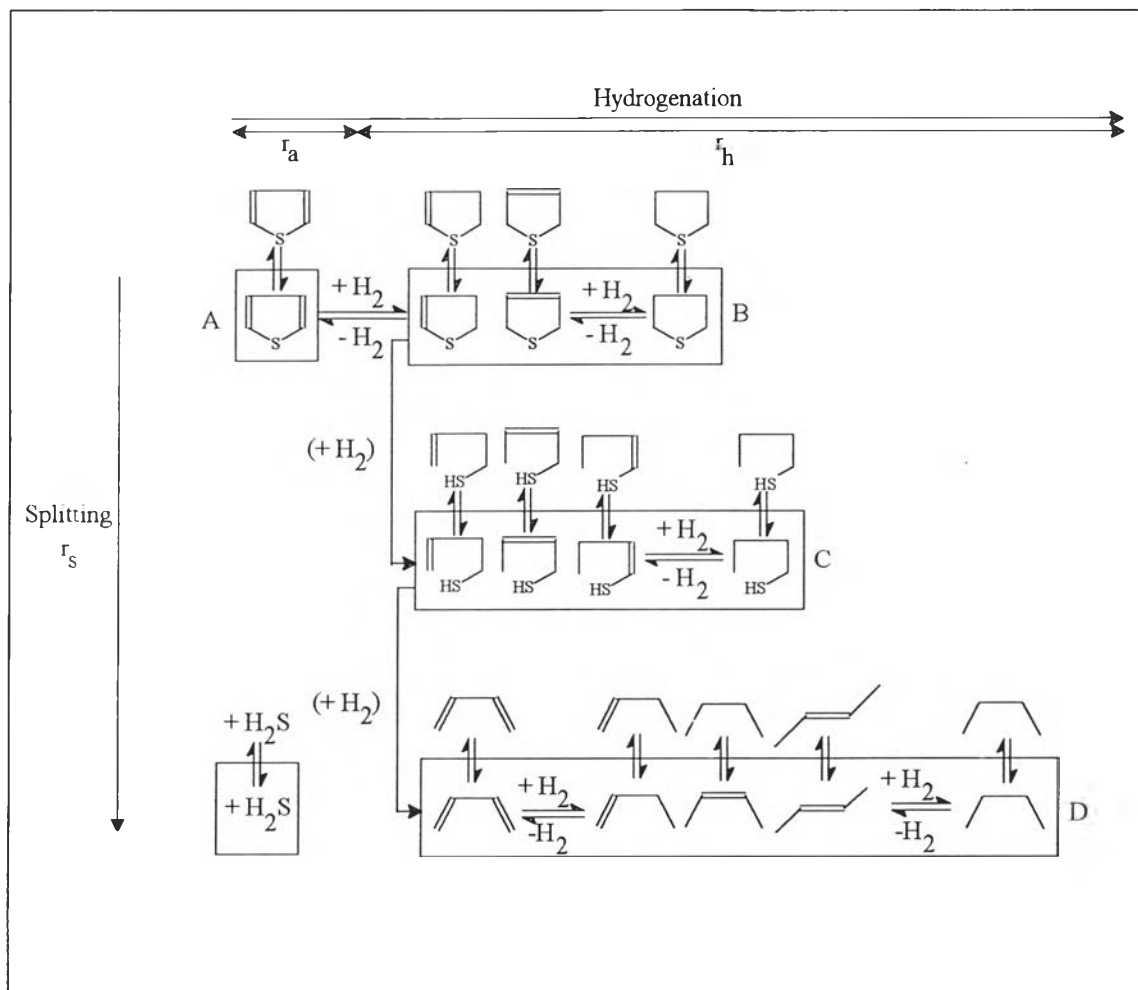
**Figure 2.5** Flow diagram of the overall mechanism, including both the conditioning of catalyst and the hydrodesulfurization reaction

The mechanism of hydrogenolysis of sulfur compounds can be explained in two different ways. In thiophene and its derivatives, the sulfur atom is part of the conjugated system of  $\pi$ -electrons and the molecule behaves like an aromatic hydrocarbon. The adsorption on the catalyst surface must be realized through the  $\pi$ -electrons and is therefore weak. By addition of one or more hydrogen atoms to the ring, the free electron pairs of the sulfur atom allow a coordinative bond to the surface, which results in weakening of the two C-S bonds. These two bonds are split in two separate steps. As intermediate species with a single C-S bond must be considered, corresponding in the case

of thiophene to butanethiol or butenethiol. The type of substances appearing subsequently in hydrodesulfurization of heteroaromatic sulfur compounds are the hydrocarbons. The catalyst support plays an important role in the catalyst activity. It influences the dispersion and contract of cobalt and molybdenum sulfide phases and may interact with the cobalt and molybdenum sulfide phases. Spill-over hydrogen may be consumed on the catalyst support through the recombination and desorption of spill-over hydrogen. This phenomenon is assumed to be proportional to the total surface area of catalyst support.

Thus, we have four distinct groups of compounds in the reaction scheme for hydrodesulfurization, which will be denoted A-D (Figure 2.6). Firstly is the starting compound containing, sulfur in the aromatic ring (A: thiophene, benzothiophene and dibenzothiophene), secondly, the cyclic, non-aromatic intermediates with two C-S bonds (B), thirdly, the intermediates with one C-S bond (C), and fourthly, the hydrocarbon plus hydrogen sulfide (D). It is evident that the progress of the reaction towards the final products is achieved by a number of hydrogenation and hydrogenolytic steps; moreover, the splitting of the C-S bond by acid-catalyzed elimination of hydrogen sulfide has to be considered.

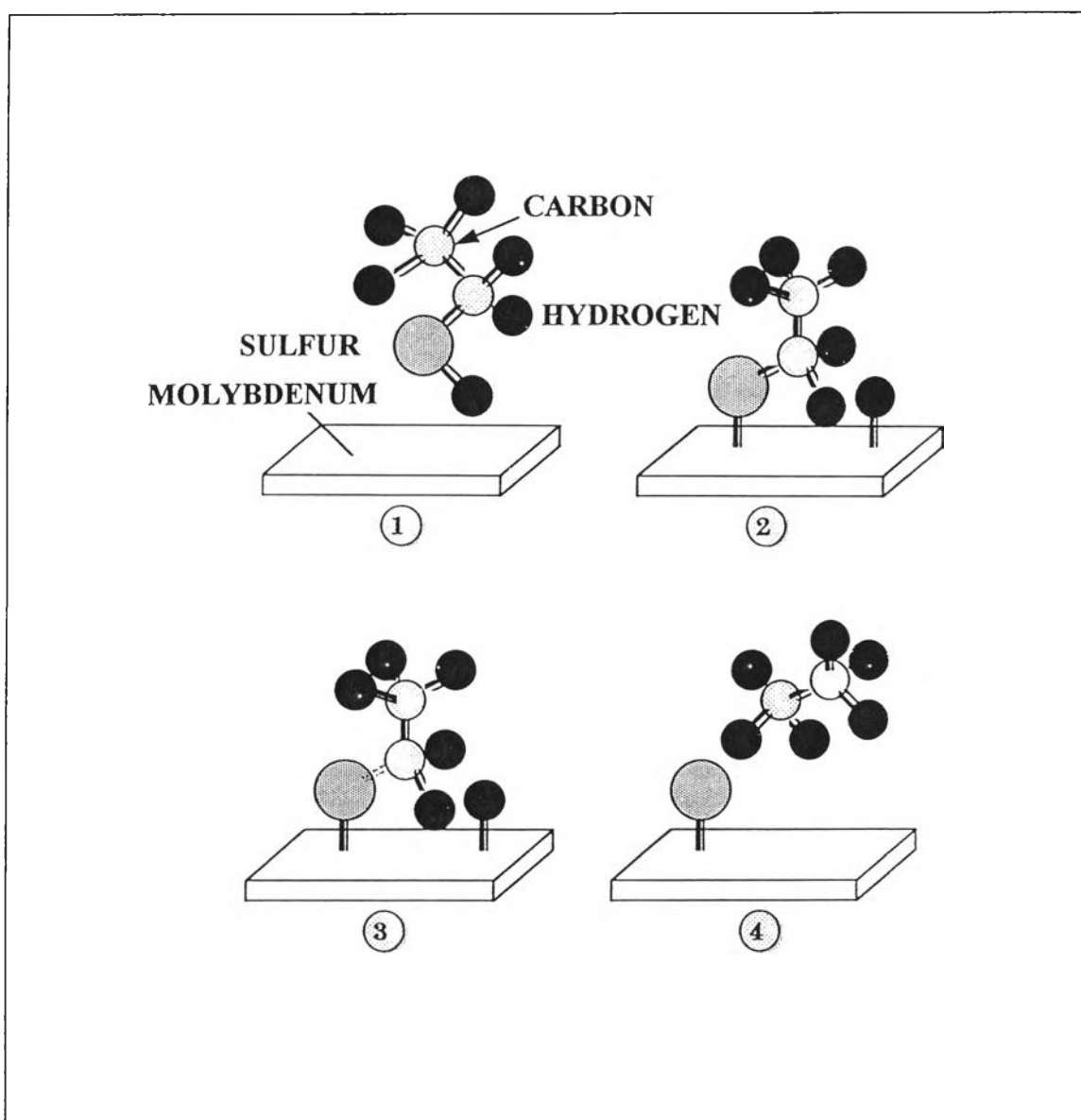
In Figure 2.6, the compounds enclosed in boxes are regarded as adsorbed, the compounds above them are in the bulk phase. The species within each segment are related by their principal structural feature and their interconversion by hydrogenation-dehydrogenation is possible; however, an equilibrium between them is, in general, not established. Whereas all hydrogenation and adsorption steps are reversible, the splitting of the C-S bonds is considered irreversible under the condition of the hydrodesulfurization process.



**Figure 2.6** Hydrodesulfurization mechanism of Thiophene [24]

Another mechanism describes the hydrodesulfurization of sulfide or thiol compounds which are not unsaturated or aromatic sulfur compounds, such as diethyl sulfide and ethanethiol. The first step of hydrodesulfurization is the cleavage of the sulfur-hydrogen bond. This step occurs very rapidly and is favored because both sulfur and hydrogen form strong bonds to the molybdenum surface. In subsequent steps the carbon-sulfur bond must break, and one carbon-hydrogen bond is either formed or broken to yield hydrocarbon products from thiol or sulfide compounds. For example,

ethanethiol bind to the catalyst as illustrated in Figure 2.7, breaking the sulfur-hydrogen bond and becoming ethyl thiolate ( $\text{CH}_3\text{CH}_2\text{S}^-$ ). The carbon-sulfur bond is broken next. Finally, the formation of a carbon-hydrogen bond yields ethane, whereas the breaking of such a bond leads to ethylene.



**Figure 2.7** The steps in desulfurization of thiol on molybdenum [33]

By using this general model and information about the strength of the carbon-sulfur bond [33] have been able to predict the rate of reaction and the type of products formed during desulfurization on molybdenum surfaces. Surface bound carbon and gaseous hydrogen—the undesirable products, are formed at a rate that depends largely on whether a carbon-hydrogen bond can be broken before the breaking of the carbon-sulfur bond. According to fundamental principles of chemistry, therefore, the fraction of thiol intermediates that lead to useful hydrocarbons is proportional to the rate of carbon-sulfur bond breaking relative to the rate of carbon-hydrogen bond breaking.

Hence, the prediction that thiols with low carbon-sulfur bond strengths, that is high rates of carbon-sulfur bond breaking, will yield a large fraction of hydrocarbons.

#### B. Hydroisomerization [2, 9-12, 16, 23, 25, 26]

Another variant of the severe hydrotreatment process is the substitution of wax for lube distillate as feedstock. The wax recovered from conventional solvent dewaxing units is essentially a pure alkane feedstock containing a high proportion of linear alkanes. With this type of feedstock and under appropriate operating conditions, the isomerization reaction can be made to predominate over cracking reactions. Unconverted wax can be removed by conventional methods to yield a base oil that is exclusively composed of isoalkanes. A comparison of some of these base fluid properties is shown in Table 2.9.

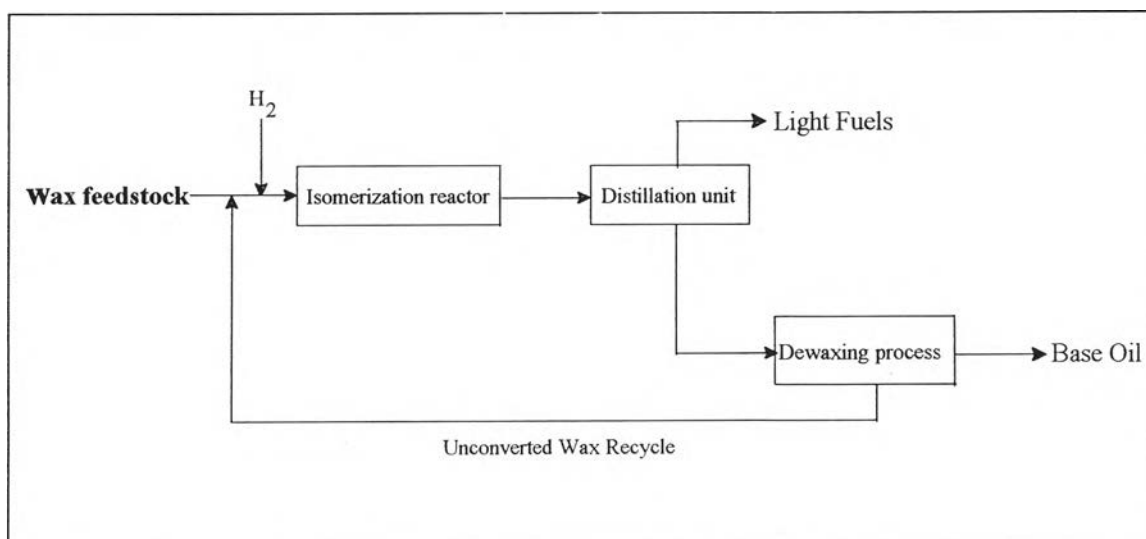
Synthetic polyalphaolefins are composed of a very limited number of branched alkane isomers, all having the same molecular weight and all completely wax-free. The wax isomerization product has a wider spread of isomers and covers a broad band of different molecular weights. It also

contains some wax so these products can not match the low temperature properties of the polyalphaolefins.

**Table 2.9** Base fluid comparisons [23]

	Solvent refined	Hydrocracked	Wax isomerized	Polyalphaolefin
Viscosity at 100 °C (cSt)	5.2	5.6	5.0	5.8
Viscosity index	98	12.5	146	137
Pour point (°C)	-15	-15	-18	-60

A process flow scheme for making these base oils is shown in Figure 2.8. The wax feedstock reacts over a catalyst in a hydrogen atmosphere but, despite control of conditions to favor isomerization, a significant amount of cracking to light products is inevitable. The products are separated by distillation and the lube boiling range material is conventionally dewaxed. It is possible to recycle the unconverted wax to increase the overall base oil yield.



**Figure 2.8** Scheme for producing wax isomerized base oils.

Waxes from dewaxing conventional hydrocarbon oils are commonly called slack waxes and usually contain an appreciable amount of oil. The oil content of these slack waxes can range anywhere from 0 to 45 % or more, but usually are in the 5 to 30 % range. The waxes are divided into two categories: (1) light paraffinic waxes boiling in the range about 300 °-580 °C and (2) heavy microcrystalline waxes having a substantial fraction (> 50 %) boiling above 600 °C.

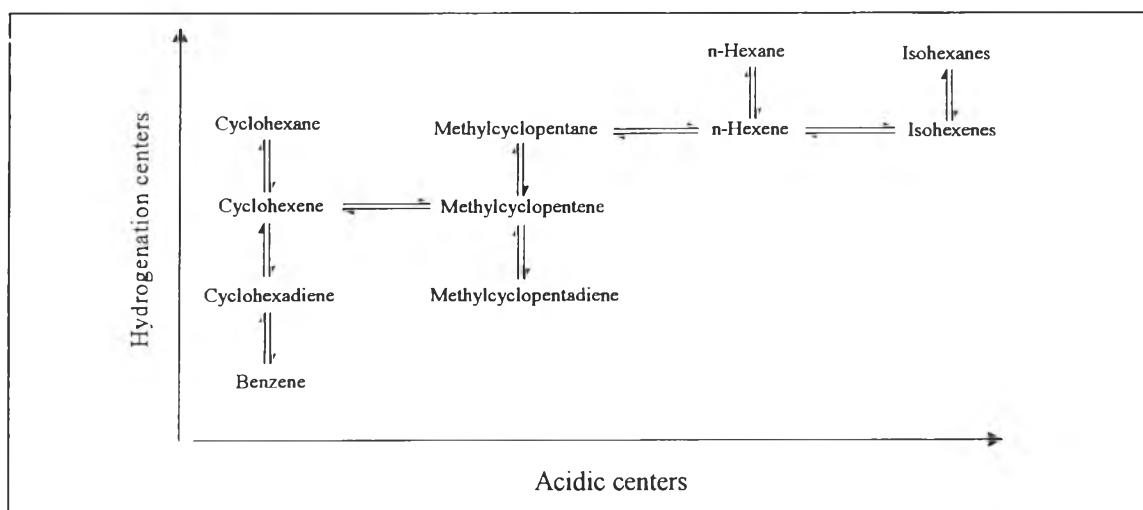
Isomerization is conducted over a catalyst containing a hydrogenation metal component typically one from Group VI or Group VIII or mixtures thereof. The order of preference is platinum supported on a halogenated refractory metal oxide support, preferred noble group VIII B metal, preferred over other group VIII B metals. The catalyst typically contains from 0.04-5.0 %wt. metal, preferably 0.1-1.0 %wt. metal, most preferably 0.2-0.6 % wt. metal. The refractory metal oxide support is typically a transition, e.g. gamma or beta alumina, and the halogen is most usually fluorine. Preferred catalysts are presented in many patents.

As one would expect, isomerization catalysts are susceptible to deactivation by the presence of heteroatom compounds [22] (i.e. N or S compounds) in the wax feed so care must be exercised to remove such heteroatom material from the wax feed charges. In such cases subjecting the waxes to very mild hydrotreating may be sufficient to insure protection for the isomerization catalyst. On the other hand waxes obtained from natural petroleum sources contain quantities of heteroatom compounds as well as appreciable quantities of oil which contain heteroatom compounds. In such instances the slack waxes should be hydrotreated to reduce the level of heteroatom compounds to the level commonly accepted in the industry as tolerable for feeds to be exposed to isomerization catalysts. Such levels will typically be a nitrogen content of about 1 to 5 ppm and a sulfur content of about 1 to 20 ppm, preferably 2 ppm or less nitrogen and 5 ppm or less sulfur.

Similarly such slack waxes should be deoiled prior to hydrotreating to an oil content in range of 0-35% oil, typically 5-25% oil. The hydrotreating step will employ a typical hydrotreating catalyst such as Co/Mo, Ni/Mo, or Ni/Co/Mo on alumina under standard, commercially accepted conditions.

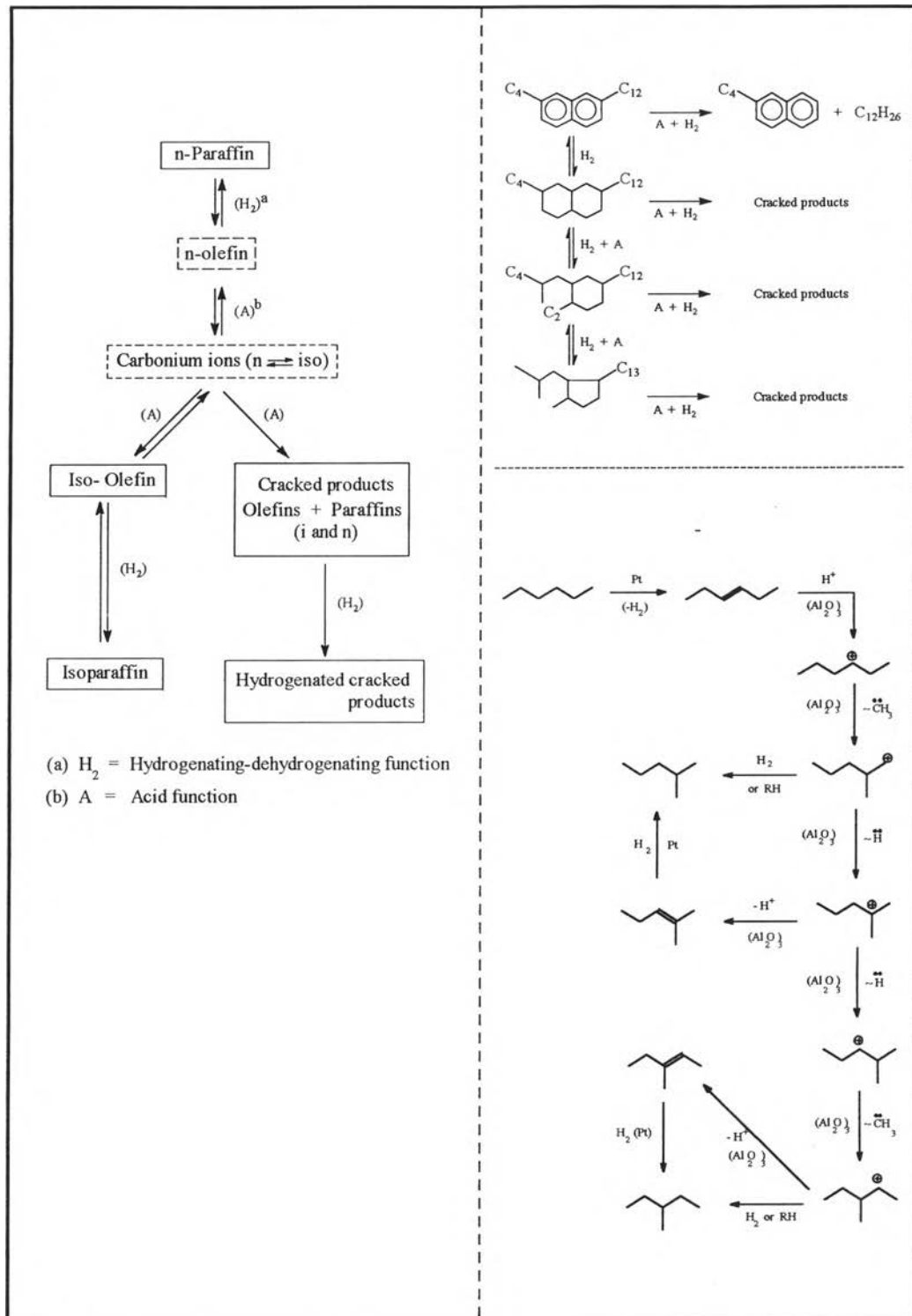
### Hydroisomerization reaction and mechanism [16, 25-26, 28]

The hydroisomerization catalyst is a type of bifunctional catalyst. Thus, the reactions require two different functions: (1) a metal catalyzes dehydrogenation of paraffins into olefins and naphthenes into aromatics; it also catalyzes hydrogenation of iso-olefins and contributes to dehydrocyclization and isomerization, and (2) an acid function provided by the support catalyzes isomerization, cyclization, and hydrocracking through a carbonium-ion mechanism. The two functions interact through the olefins, which are the key intermediates in the reaction network. The original statement of a reaction scheme for this reactions is shown in Figure 2.9 and the reaction mechanism for bifunctional catalyst is shown in Figure 2.10.



**Figure 2.9** Reaction network for bifunctional catalysis of C<sub>6</sub> hydrocarbons





**Figure 2.10** Reaction mechanism for bifunctional catalyst

## Methods of testing petroleum waxes [13, 16]

The most commonly used tests are as follows:

### 1. Melting point and setting point

#### a) IP 55, ASTM D 87, ISO 3841

Molten wax is allowed to cool in an apparatus while the temperature is recorded at frequent intervals, the point at which the temperature remains within a range of 0.1 °C for one minute being taken setting point. This is the one cooling curve method. This method is not suitable for microcrystalline or intermediate waxes, or blends of paraffin waxes with these or many additives.

b) The congealing point of petroleum wax or petrolatum (IP 76, ASTM D 938, ISO 2207)

The congealing point of petroleum wax or petrolatum is determined by applying a drop of molten wax to the thermometer bulb, and noting the temperature at which it congeals when the thermometer is rotated under standard cooling conditions. This method is suitable for waxes and blends. Some anomalous results can be obtained when materials of widely differing viscosities and setting point are mixed.

c) The drop melting point of wax or petrolatum (IP 33, ASTM D 127, ISO 6244)

The drop melting point of wax or petrolatum is determined by recording the temperature at which a drop of the sample falls from the bulb of a thermometer when heated under standard conditions. Anomalous results are obtained on blends when materials of widely differing melting or setting points or viscosities are mixed.

## 2. Viscosity (IP 71, ASTM D 445, ISO 3140)

The viscosity of molten petroleum wax is a measure of its normal-nonnormal composition, and important in many packaging applications. The classical U-tube kinematics viscosity method is utilized by this method, and is suitable for all waxes and low viscosity blends.

For much higher viscosity blends of petroleum waxes with polymeric and resinous additives, some mechanical rotational method such as described by ASTM D 2669 is desirable.

## 3. Oil content (IP 158, ASTM D 721, ISO 2908)

This standard test method is based on dissolving the oil-containing wax in a specified solvent and cooling to an arbitrary chosen low temperature at which the insoluble material is defined as wax and the soluble portion as oil.

There is a good deal to say for employing this test at temperatures higher than the stipulated minus 32 °C, since the proportion of components of a petroleum wax which are liquid or semi-solid at ambient or near ambient temperature has a considerable bearing on the characteristics and applications of that wax.

In a distillate wax, too high an oil content will give a greasy texture to the wax surface, impair its tensile strength, scuff resistance, seal strength potential, staining propensity, color stability.

Whilst the IP 158 type test remains the standard test for waxes of unknown oil content, wide line nuclear magnetic resonance (NMR) techniques calibrated by IP 158 are being used increasingly for routine control of specific refinery wax streams.

#### 4. Penetration (ASTM D 1321, ISO 3992, IP in preparation)

The needle penetration of petroleum waxes is the distance in units of 1/10 mm to which a standard needle penetrates into the sample under fixed conditions of load, time and temperature. It is an indication of the hardness of the wax, but is of doubtful value in the case of very hard waxes where the precision of the method approaches the level of the readings obtained.

If the test is carried out over a temperature range, from 15 to 50 °C for example, a temperature against penetration curve can be plotted which can be a valuable guide to the staining ('bleeding') potential of the wax and wax blend, to its temperature resistance, and hence to its performance in heat-seal and packaging applications.

#### 5. Color (IP 196, ASTM D 1500, IP 17, ASTM D 156)

Several methods are available for measuring color, some of which are listed above. All are based on comparing in the molten state, by transmitted light, the colored glasses of varying intensity and hue. All such measurements are subjective, and values obtained by the different methods cannot be correlated exactly, though approximate conversions are possible.

#### 6. Odor and taste

Waxes to be used in the food packing industry must be free from any odor or taste which could transfer itself to the foodstuff to a degree detectable by the consumer, and whilst there is a standard odor test for petroleum waxes (IP 185, ASTM D 1833), There is no recognized test for taste.

Most users of wax in the food packaging industry use their own highly specific odor and taste tests employing panels of skilled operators.

### Industrial uses of petroleum wax [16, 18, 19, 22]

The use of petroleum waxes, including paraffin, are listed in Table 2.10 together with the amounts of wax used. The largest use is in the field of paper coating, which accounts for 58.1% of the total usage. Fully refined wax, which may be mixed with microcrystalline wax, is used for food containers and wrapping. Other wax-coated paper includes dynamite wrapping and building paper.

Paraffin is also used as a liner for kegs. It is usually blended with microcrystalline wax for greater toughness. Candles are another important application of paraffin. Paraffin has important uses in pharmaceutical and cosmetic, material such as creams, emollients, lipsticks, and ointments. It is used in electrical insulation, both for its moisture-proofing properties and its high dielectric strength. In rubber compounding, paraffin will blend only to a certain extent with rubber. The excess migrates to the surface of the rubber, forming a layer which protects against sunlight deterioration. Paraffin, usually a white crude scale grade, is used in matches to aid ignition. A high melting, fully refined paraffin wax is used in polishes, but it is less important than natural waxes such as carnauba, since its film is softer and less lustrous. Paraffin is used in dental materials, particularly for impressions.

Other uses include the manufacture of crayons and colored pencils, the coating oranges to prevent dehydration, and depletion of poultry by wax dipping. In this last application the poultry carcass, after rough plucking, is dipped into a wax bath, which is basically paraffin wax plus additives. When this coating has hardened, it is easily removed, along with the hair and small features. Paraffin wax is also used to manufacture chlorinated paraffins.

**Table 2.10** Consumption of petroleum wax in the United States

Use	Consumption	
	Short tons	Percentage of total
Sanitary containers	98,000	28.4
Waxed wrappers	103,000	29.7
Candles	26,000	7.5
Drugs, cosmetics, chemicals	20,000	5.8
Electrical goods	2,000	0.6
Textiles	2,000	0.6
Rubber	2,700	0.8
Matches	2,200	0.6
Miscellaneous(pyrotechnics, adhesives, crayons, polishes, paint removers, metal castings, etc.)	90,000	26.0
Total US Consumption	346,900	100