Al-Mustaqbal University

College of Engineering and Engineering Technologies

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Introduction

natural gas and crude oils are the main sources for hydrocarbon inter mediates or secondary raw materials for the production of petrochemicals. From natural gas, ethane and LPG are recovered for use as intermediates in the production of olefins and diolefins. Important chemicals such as methanol and ammonia are also based on methane via syn thesis gas. On the other hand, refinery gases from different crude oil processing schemes are important sources for olefins and LPG. Crude oil distillates and residues are precursors for olefins and aromatics via cracking and reforming processes.

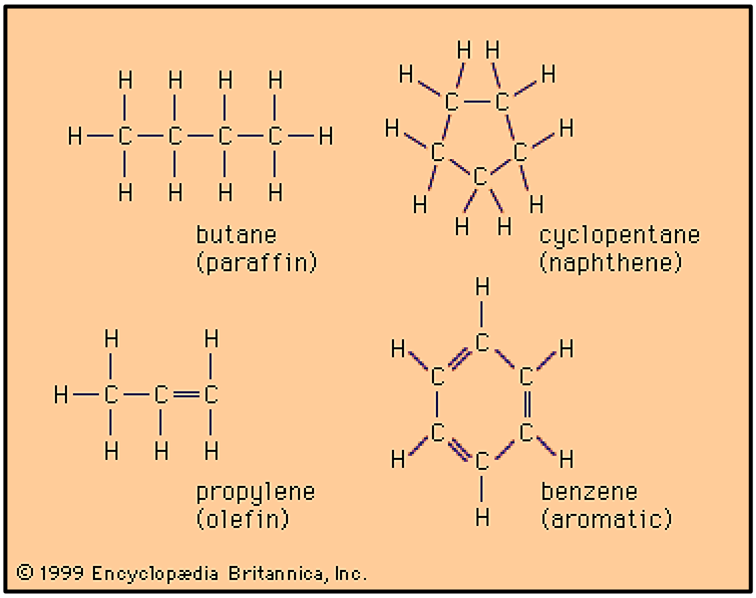
Olefin :

Olefin, also called alkene, compound made up of hydrogen and carbon that contains one or more pairs of carbon atoms linked by a double bond. Olefins are examples of unsaturated hydrocarbons (compounds that contain only hydrogen and carbon and at least one double or triple bond). They are classified in either or both of the following ways:

(1) as cyclic or acyclic (aliphatic) olefins, in which the double bond is located between carbon atoms forming part of a cyclic (closed-ring) or of an open-chain grouping, respectively .

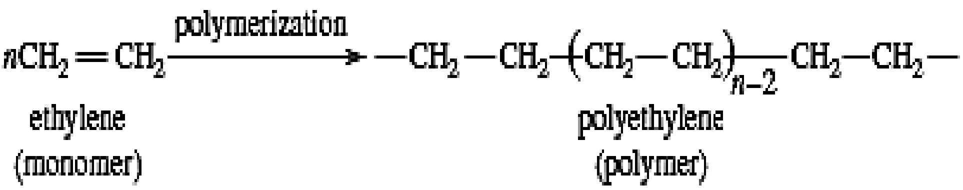
(2) as monoolefins, diolefins, triolefins, etc., in which the number of double bonds per molecule is, respectively, one, two, three, or some other number.

Acyclic monoolefins have the general formula C_nH_{2n}, C being a carbon atom, H a hydrogen atom, and n an integer. They are rare in nature but can be formed in large quantities through industrial processing. One of the first processes used to produce them, developed in the early 20th century, was thermal cracking (breaking down of large molecules) of petroleum oils to gasoline. Olefins later were also produced via fluid catalytic cracking, steam cracking, and hydrocracking.



hydrocarbon: Alkenes and alkynes

Beginning in the 1970s, so-called linear alpha olefins (LAOs; distinguished by the double bond occurring on the first, or alpha, carbon atom in the unbranched chain) were produced through polymerization (specifically, oligomerization) and olefin metathesis, which together formed the basis of the Shell higher olefin process (SHOP). In olefin oligomerization, the compounds are grown by combining lower-molecular-weight monoolefins, particularly ethylene, which is the simplest olefin. Olefin metathesis involves the exchange of chemical substituents with subsequent re-formation of double bonds. LAOs produced via oligomerization and olefin metathesis are used as starting materials for plastics (e.g., polyethylene), detergents, adhesives, and other products. Hence, lower monoolefins (other examples of which include propylene and butylene) are the basis for an extensive petrochemicals industry. Both ethylene and propylene, which are used as chemical feedstocks (to fuel large chemical reactions), occur naturally in the environment.



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Olefins containing two to four carbon atoms per molecule are gaseous at ordinary temperatures and pressure; those containing five or more carbon atoms are usually liquid at ordinary temperatures. Olefins are only slightly soluble in water.

Since the compound is unsaturated with respect to hydrogen atoms, the extra electrons are shared between carbon atoms forming double bonds in alkenes. Alkenes are also called Olefins because they form oily liquids on reaction with Chlorine gas.

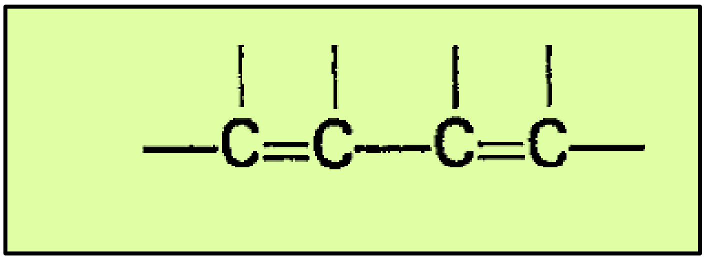
Olefins are widely used as raw materials in the manufacture of chemical and polymer products like plastic, detergent, adhesive, rubber, and food packaging. They consist of a group of chemicals: ethylene, propylene, and butadiene.

Examples of olefin compounds:

1-Nitro Compound , 2- Naphthalene , 3- Butane , 4-Lucite , 5- ethylene , 6- polyester , 7- resin , 8- Polyacrylonitrile:

Diolefins :

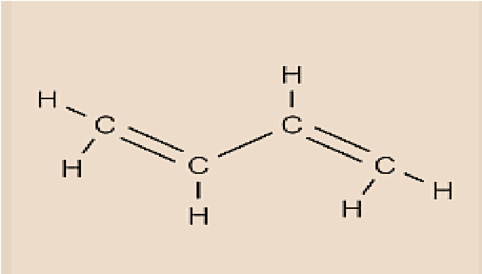
Diolefins are hydrocarbon compounds that have two double bonds. Conjugated diolefins have two double bonds separated by one single bond, the general formula CnH2n-2. Due to conjugation, these compounds are more stable than mono-olefins and diolefins with isolated double bonds. Conjugated diolefins also have different reactivities than monoolefins. The most important industrial diolefinic hydrocarbons are butadiene and isoprene.



Butadiene

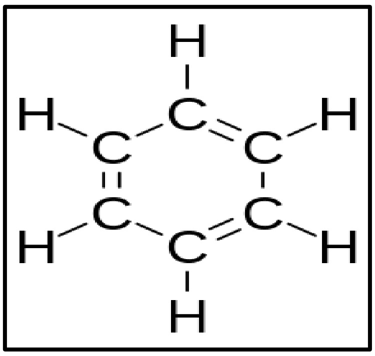
Butadiene is the raw material for the most widely used synthetic rubber, a copolymer of butadiene and styrene (SBR). In addition to its utility in the synthetic rubber and plastic industries (over 90% of butadiene produced), many chemicals could also be synthesized from butadiene.

Butadiene is obtained as a by-product from ethylene production. It is then . separated from the C4 fraction by extractive distillation using furfural Butadiene could also be produced by the catalytic dehydrogenation of butanes or a butane/butene mixture.



***Aromatic*:**

Aromatic compounds, also known as "mono- and polycyclic aromatic hydrocarbons", are organic compounds containing one or more aromatic rings. The word "aromatic" originates from the past grouping of molecules based on odor, before their general chemical properties were understood. The current definition of aromatic compounds does not have any relation with their odor.



2D model of a benzene molecule. The carbon "ring" is what makes benzene "aromatic".

Heteroarenes are closely related, since at least one carbon atom of CH group is replaced by one of the heteroatoms oxygen, nitrogen, or sulfur. Examples of non-benzene compounds with aromatic properties are furan, a heterocyclic compound with a five-membered ring that includes a single oxygen atom, and pyridine, a heterocyclic compound with a six-membered ring containing one nitrogen atom. Hydrocarbons without an aromatic ring are called aliphatic. Approximately half of compounds known in the year 2000 are described as aromatic to some extent.

Aromatic compounds play key roles in the biochemistry of all living things. The four aromatic amino acids histidine, phenylalanine, tryptophan, and tyrosine each serve as one of the 20 basic building-blocks of proteins. Further, all 5 nucleotides (adenine, thymine, cytosine, guanine, and uracil) that make up the sequence of the genetic code in DNA and RNA are aromatic purines or pyrimidines. The molecule heme contains an aromatic system with 22 π-electrons. Chlorophyll also has a similar aromatic system.

Aromatic compounds are important in industry. Key aromatic hydrocarbons of commercial interest are benzene, toluene, ortho-xylene and para-xylene. About 35 million tonnes are produced worldwide every year. They are extracted from complex mixtures obtained by the refining of oil or by distillation of coal tar, and are used to produce a range of important chemicals and polymers, including styrene, phenol, aniline, polyester and nylon.

Benzene ring model:

Benzene, C_6H_6 is the least complex aromatic hydrocarbon, and it was the first one named as such. The nature of its bonding was first recognized by August Kekulé in the 19th century. Each carbon atom in the hexagonal cycle has four electrons to share. One goes to the hydrogen atom, and one to each of the two neighboring carbons. This leaves one electron to share with one of the two neighboring carbon atoms, thus creating a double bond with one carbon and leaving a single bond with the other, which is why some representations of the benzene molecule portray it as a hexagon with alternating single and double bonds.

Other depictions of the structure portray the hexagon with a circle inside it, to indicate that the six electrons are floating around in delocalized molecular orbitals the size of the ring itself. This represents the equivalent nature of the six carbon-carbon bonds all of bond order 1.5; the equivalency is explained by resonance forms. The electrons are visualized as floating above and below the ring, with the electromagnetic fields they generate acting to keep the ring flat.

General properties of aromatic hydrocarbons:

1-They display aromaticity

2-The carbon-hydrogen ratio is high

3-They burn with a strong sooty yellow flame because of the high carbon–hydrogen ratio

4-They undergo electrophilic substitution reactions and nucleophilic aromatic substitutions

Separation Aromatics:

One of the most used processes to separate these aromatic compounds is liquid-liquid extraction, due to the fact that it can be used for a wide range of aromatic concentration in the mixture.

Fragrance extraction refers to the separation process of aromatic compounds from raw materials, using methods such as distillation, solvent extraction, expression, sieving, or enfleurage. The results of the extracts are either essential oils, absolutes, concretes, or butters, depending on the amount of waxes in the extracted product.

To a certain extent, all of these techniques tend to produce an extract with an aroma that differs from the aroma of the raw materials. Heat, chemical solvents, or exposure to oxygen in the extraction process may denature some aromatic compounds, either changing their odour character or rendering them odourless, and the proportion of each aromatic component that is extracted can differ

1-Maceration/solvent extraction

Certain plant materials contain too little volatile oil to undergo expression, or their chemical components are too delicate and easily denatured by the high heat used in steam distillation. Instead, the oils are extracted using their solvent properties.

A- Organic solvent extraction

Organic solvent extraction is the most common and most economically important technique for extracting aromatics in the modern perfume industry. Raw materials are submerged and agitated in a solvent that can dissolve the desired aromatic compounds. Commonly used solvents for maceration/solvent extraction include hexane, and dimethyl ether.

In organic solvent extraction, aromatic compounds as well as other hydrophobic soluble substances such as wax and pigments are also obtained. The extract is subjected to vacuum processing, which removes the solvent for re-use. The process can last anywhere from hours to months. Fragrant compounds for woody and fibrous plant materials are often obtained in this matter as are all aromatics from animal sources. The technique can also be used to extract odorants that are too volatile for distillation or easily denatured by heat. The remaining waxy mass is known as a concrete, which is a mixture of essential oil, waxes, resins, and other lipophilic (oil-soluble) plant material, since these solvents effectively remove all hydrophobic compounds in the raw material. The solvent is then removed by a lower temperature distillation process and reclaimed for re-use.

Although highly fragrant, concretes are too viscous – even solid – at room temperature to be useful. This is due to the presence of high-molecular-weight, non-fragrant waxes and resins. Another solvent, often ethyl alcohol, which only dissolves the fragrant low-molecular weight compounds, must be used to extract the fragrant oil from the concrete. The alcohol is removed by a second distillation, leaving behind the absolute. These extracts from plants such as jasmine and rose, are called absolutes.

Due to the low temperatures in this process, the absolute may be more faithful to the original scent of the raw material, which is subjected to high heat during the distillation process.

B- Supercritical fluid extraction

Supercritical fluid extraction is a relatively new technique for extracting fragrant compounds from a raw material, which often employs supercritical CO_2 as the extraction solvent. When carbon dioxide is put under high pressure at slightly above room temperature, a supercritical fluid forms (Under normal pressure CO_2 changes directly from a solid to a gas in a process known as sublimation.) Since CO_2 in a non-polar compound has low surface tension and wets easily, it can be used to extract the typically hydrophobic aromatics from the plant material. This process is identical to one of the techniques for making decaffeinated coffee.

In supercritical fluid extraction, high pressure carbon dioxide gas (up to 100 atm.) is used as a solvent. Due to the low heat of process and the relatively unreactive solvent used in the extraction, the fragrant compounds derived often closely resemble the original odour of the raw material. Like solvent extraction, the CO_2 extraction takes place at a low temperature, extracts a wide range of compounds, and leaves the aromatics unaltered by heat, rendering an essence more faithful to the original. Since CO_2 is gas at normal atmospheric pressure, it also leaves no trace of itself in the final product, thus allowing one to get the absolute directly without having to deal with a concrete. It is a low-temperature process, and the solvents are easily removed. Extracts produced using this process are known as CO_2 extracts.

C- Ethanol extraction

Ethanol extraction is a type of solvent extraction used to extract fragrant compounds directly from dry raw materials, as well as the impure oils or concrete resulting from organic solvent extraction, expression, or enfleurage. Ethanol extracts from dry materials are called tinctures, while ethanol washes for purifying oils and concretes are called absolutes.

The impure substances or oils are mixed with ethanol, which is less hydrophobic than solvents used for organic extraction, dissolves more of the oxidized aromatic constituents (alcohols, aldehydes, etc.), leaving behind the wax, fats, and other generally hydrophobic substances. The alcohol is evaporated under low-pressure, leaving behind absolute. The absolute may be further processed to remove any impurities that are still present from the solvent extraction.

Ethanol extraction is not typically used to extract fragrance from fresh plant materials; these contain large quantities of water, which will be extracted into the ethanol, although this is sometimes not a concern.

2- Distillation

Distillation is a common technique for obtaining aromatic compounds from plants, such as orange blossoms and roses. The raw material is heated and the fragrant compounds are re-collected through condensation of the distilled vapor. Distilled products, whether through steam or dry distillation are known either as essential oils or ottos.

Today, most common essential oils, such as lavender, peppermint, and eucalyptus, are distilled. Raw plant material, consisting of the flowers, leaves, wood, bark, roots, seeds, or peel, is put into an alembic (distillation apparatus) over water.

A- Steam distillation

Steam from boiling water is passed through the raw material for 60–105 minutes, which drives out most of their volatile fragrant compounds. The condensate from distillation, which contain both water and the aromatics, is settled in a Florentine flask. This allows for the easy separation of the fragrant oils from the water as the oil will float to the top of the distillate where it is removed, leaving behind the watery distillate. The water collected from the condensate, which retains some of the fragrant compounds and oils from the raw material, is called hydrosol and is sometimes sold for consumer and commercial use. This method is most commonly used for fresh plant materials such as flowers, leaves, and stems. Popular hydrosols are rose water, lavender water, and orange blossom water. Many plant hydrosols have unpleasant smells and are therefore not sold.

Most oils are distilled in a single process. One exception is Ylang-ylang (Cananga odorata), which takes 22 hours to complete distillation. It is fractionally distilled, producing several grades (Ylang-Ylang "extra", I, II, III and "complete", in which the distillation is run from start to finish with no interruption.

*B- **Dry distillation***

Also known as rectification, the raw materials are directly heated in a still without a carrier solvent such as water. Fragrant compounds that are released from the raw material by the high heat often undergo anhydrous pyrolysis, which results in the formation of different fragrant compounds, and thus different fragrant notes. This method is used to obtain fragrant compounds from fossil amber and fragrant woods (such as birch tar) where an intentional "burned" or "toasted" odour is desired..

3- Expression

Expression as a method of fragrance extraction where raw materials are pressed, squeezed or compressed and the essential oils are collected. In contemporary times, the only fragrant oils obtained using this method are the peels of fruits in the citrus family. This is due to the large quantity of oil is present in the peels of these fruits as to make this extraction method economically feasible. Citrus peel oils are expressed mechanically, or cold-pressed. Due to the large quantities of oil in citrus peel and the relatively low cost to grow and harvest the raw materials, citrus-fruit oils are cheaper than most other essential oils to the extent that purified limonene extracted from these fruit is available as an affordable naturally-derived solvent. Lemon or sweet orange oils that are obtained as by-products of the commercial citrus industry are among the cheapest citrus oils.

Expression was mainly used prior to the discovery of distillation, and this is still the case in cultures such as Egypt. Traditional Egyptian practice involves pressing the plant material, then burying it in unglazed ceramic vessels in the desert for a period of months to drive out water. The water has a smaller molecular size, so it diffuses through the ceramic vessels, while the larger essential oils do not. The lotus oil in Tutankhamen's tomb, which retained its scent after 3000 years sealed in alabaster vessels, was pressed in this manner.

4- Enfleurage

Enfleurage is a process in which the odour of aromatic materials is absorbed into wax or fat, which is then often extracted with alcohol. Extraction by enfleurage was commonly used when distillation was not possible because some fragrant compounds denature through high heat. This technique is not commonly used in modern industry, due to both its prohibitive cost and the existence of more efficient and effective extraction methods.

Syngas

- Syngas, or synthesis gas, is a mixture of hydrogen and carbon monoxide, in various ratios. The gas often contains some carbon dioxide and methane. It is principally used for producing ammonia or methanol. Syngas is combustible and can be used as a fuel. Historically, it has been used as a replacement for gasoline, when gasoline supply has been limited; for example, wood gas was used to power cars in Europe during WWII (in Germany alone half a million cars were built or rebuilt to run on wood gas).

- Syngas is ***used*** as a source of hydrogen as well as a fuel. It is also used to directly reduce iron ore to sponge iron. Chemical uses include the production of methanol which is a precursor to acetic acid and many acetates; liquid fuels and lubricants via the Fischer–Tropsch process and previously the Mobil methanol to gasoline process; ammonia via the Haber process, which converts atmospheric nitrogen (N_2) into ammonia which is used as a fertilizer; and oxo alcohols via an intermediate aldehyde.

- Synthesis gas (syngas) can be ***produced*** from a number of carbon feedstocks. Traditionally, it has been produced from natural gas or coal, depending on the availability and cost of the natural gas or coal and the end use of the syngas.

- The mixture of CO (carbon monoxide) and H_2 (hydrogen gas) is known as 'water gas'. Since this mixture is used in the synthesis of methanol and many hydrocarbons, it is also ***known as 'syngas'.***

- syngas is 30 to 60% carbon monoxide (CO), 25 to 30% hydrogen (H_2), 0 to 5% methane (CH_4), 5 to 15% carbon dioxide (CO_2), plus a lesser or greater amount of water vapor, smaller amounts of the sulfur compounds . This can vary significantly depending on the feedstock and the gasification process involved

- The cleaning system downstream of the gasifier removes the contaminants using several techniques: oil scrubbing is used to remove tars, sulfur compounds are removed via solid-phase adsorption and ammonia is removed by water scrubbing.

- Due to the fact that syngas is mainly composed of hydrogen and carbon monoxide, which are both flammable gases and the latter of which is also toxic, its uncontrolled release can pose a serious hazard.