INDUSTRIAL PROCESS

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SESSION 10 PETROLEUM AND ORGANIC COMPOUNDS

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Petroleum and organic compounds

The nature of an organic molecule means it can be transformed at the molecular level to create a range of products.

- <u>Cracking (chemistry)</u> the generic term for breaking up the larger molecules.
- <u>Alkylation</u> refining of crude oil
- <u>Burton process</u> cracking of hydrocarbons
- <u>Cumene process</u> making phenol and acetone from benzene
- Friedel-Crafts reaction, Kolbe-Schmitt reaction
- Olefin metathesis, Thermal depolymerization
- <u>Transesterification</u> organic chemicals
- Raschig process part of the process to produce nylon
- Oxo process Produces aldehydes from alkenes.
- Polymerisation .

Cracking (chemistry)

In <u>petroleum geology</u> and <u>chemistry</u>, **cracking** is the process whereby complex organic <u>molecules</u> such as <u>kerogens</u> or heavy <u>hydrocarbons</u> are broken down into simpler molecules such as light hydrocarbons, by the breaking of <u>carbon</u>carbon <u>bonds</u> in the precursors. The <u>rate</u> of cracking and the end products are strongly dependent on the <u>temperature</u> and presence of <u>catalysts</u>. Cracking is the breakdown of a large <u>alkane</u> into smaller, more useful <u>alkanes</u> and <u>alkenes</u>. Simply put, hydrocarbon cracking is the process of breaking a long-chain of hydrocarbons into short ones.

More loosely, outside the field of petroleum chemistry, the term "cracking" is used to describe any type of splitting of molecules under the influence of heat, catalysts and solvents, such as in processes of <u>destructive distillation</u> or <u>pyrolysis</u>.

Fluid catalytic cracking produces a high yield of <u>gasoline</u> and <u>LPG</u>, while hydrocracking is a major source of jet fuel, <u>Diesel fuel</u>, <u>naphtha</u>, and LPG.[[]



Refinery using the Shukhov cracking process, Baku, Soviet Union, 1934.

History and patents

Among several variants of thermal cracking methods (variously known as the "<u>Shukhov cracking process</u>", "<u>Burton cracking process</u>", "Burton-Humphreys cracking process", and "Dubbs cracking process") <u>Vladimir Shukhov</u>, a Russian engineer, invented and patented the first in 1891 (Russian Empire, patent no. 12926, November 27, 1891).^[11] One installation was used to a limited extent in Russia, but development was not followed up. In the first decade of the 20th century the American engineers <u>William Merriam Burton</u> and Robert E. Humphreys independently developed and patented a similar process as U.S. patent 1,049,667 on June 8, 1908. Among its advantages was the fact that both the condenser and the boiler were continuously kept under pressure.^[2]

In its earlier versions however, it was a batch process, rather than continuous, and many patents were to follow in the USA and Europe, though not all were practical.^[11] In 1924, a delegation from the American <u>Sinclair Oil Corporation</u> visited Shukhov. Sinclair Oil apparently wished to suggest that the patent of Burton and Humphreys, in use by Standard Oil, was derived from Shukhov's patent for oil cracking, as described in the Russian patent. If that could be established, it could strengthen the hand of rival American companies wishing to invalidate the Burton-Humphreys patent. In the event Shukhov satisfied the Americans that in principle Burton's method closely resembled his 1891 patents, though his own interest in the matter was primarily to establish that "the Russian oil industry could easily build a cracking apparatus according to any of the described systems without being accused by the Americans of borrowing for free".[3]

At that time, just a few years after the <u>Russian Revolution</u>, Russia was desperate to develop industry and earn foreign exchange, so their oil industry eventually

did obtain much of their technology from foreign companies, largely American.^[3] At about that time however, <u>fluid catalytic cracking</u> was being explored and developed and soon replaced most of the purely thermal cracking processes in the fossil fuel processing industry. The replacement was however not complete; many types of cracking, including pure thermal cracking, still are in use, depending on the nature of the feedstock and the products required to satisfy market demands. Thermal cracking remains important however, for example in producing naphtha, gas oil, and coke, and more sophisticated forms of thermal cracking have been developed for various purposes. These include <u>visbreaking</u>, <u>steam cracking</u>, and <u>coking</u>.^[4]

Chemistry

A large number of <u>chemical reactions</u> take place during the cracking process, most of them based on <u>free radicals</u>. <u>Computer simulations</u> aimed at modeling what takes place during steam cracking have included hundreds or even thousands of reactions in their models. The main reactions that take place include:

Initiation

In these reactions a single molecule breaks apart into two free radicals. Only a small fraction of the feed molecules actually undergo initiation, but these reactions are necessary to produce the free radicals that drive the rest of the reactions. In steam cracking, initiation usually involves breaking a <u>chemical</u> <u>bond</u> between two carbon atoms, rather than the bond between a carbon and a <u>hydrogen</u> atom.

 $CH_3CH_3 \rightarrow 2 CH_3 \bullet$

Hydrogen abstraction[

In these reactions a free radical removes a hydrogen atom from another molecule, turning the second molecule into a free radical.

 $CH_3 \bullet + CH_3 CH_3 \rightarrow CH_4 + CH_3 CH_2 \bullet$

Radical decomposition[

In these reactions a free radical breaks apart into two molecules, one an alkene, the other a free radical. This is the process that results in alkene products.

 $CH_3CH_2 \bullet \rightarrow CH_2 = CH_2 + H \bullet$

Radical addition[edit]

In these reactions, the reverse of radical decomposition reactions, a radical reacts with an alkene to form a single, larger free radical. These processes are involved in forming the aromatic products that result when heavier feedstocks are used.

 $CH_{3}CH_{2}\bullet + CH_{2}=CH_{2} \rightarrow CH_{3}CH_{2}CH_{2}CH_{2}\bullet$

Termination[

In these reactions two free radicals react with each other to produce products that are not free radicals. Two common forms of termination are recombination, where the two radicals combine to form one larger molecule, and *disproportionation*, where one radical transfers a hydrogen atom to the other, giving an alkene and an alkane.

 $CH_3 \bullet + CH_3 CH_2 \bullet \rightarrow CH_3 CH_2 CH_3$

 $CH_3CH_2\bullet + CH_3CH_2\bullet \rightarrow CH_2=CH_2 + CH_3CH_3$

Example: cracking butane[

There are three places where a butane molecule (CH₃-CH₂-CH₂-CH₃) might be split. Each has a distinct likelihood:

• 48%: break at the CH_3 - CH_2 bond.

CH₃* / *CH₂-CH₂-CH₃ Ultimately this produces an alkane and an <u>alkene</u>: CH₄ + CH₂=CH-CH₃

• 38%: break at a CH_2 - CH_2 bond.

CH₃-CH₂* / *CH₂-CH₃ Ultimately this produces an alkane and an <u>alkene</u> of different types: CH₃-CH₃ + CH₂=CH₂

• 14%: break at a terminal C-H bond

 $\rm H/CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ Ultimately this produces an alkene and hydrogen gas: CH_2=CH-CH_2-CH_3 + H_2

Cracking methodologies

Thermal methods[

Thermal cracking was the first category of hydrocarbon cracking to be developed. Thermal cracking is an example of a reaction whose energetics are dominated by <u>entropy</u> (Δ S°) rather than by <u>enthalpy</u> (Δ H°) in the Gibbs Free Energy equation Δ G°= Δ H°-T Δ S°. Although the bond dissociation energy D for a carbon-carbon single bond is relatively high (about 375 kJ/mol) and cracking is highly endothermic, the large positive entropy change resulting from the fragmentation of one large molecule into several smaller pieces, together with the extremely high temperature, makes T Δ S° term larger than the Δ H° term, thereby favoring the cracking reaction.

Thermal cracking

Modern high-pressure thermal cracking operates at absolute pressures of about 7,000 kPa. An overall process of disproportionation can be observed, where "light", hydrogen-rich products are formed at the expense of heavier molecules which condense and are depleted of hydrogen. The actual reaction is known as <u>homolytic fission</u> and produces <u>alkenes</u>, which are the basis for the economically important production of <u>polymers</u>.

Thermal cracking is currently used to "upgrade" very heavy fractions or to produce light fractions or distillates, burner fuel and/or <u>petroleum coke</u>. Two extremes of the thermal cracking in terms of product range are represented by the high-temperature process called "steam cracking" or <u>pyrolysis</u> (ca. 750 °C to 900 °C or higher) which produces valuable <u>ethylene</u> and other feedstocks for the petrochemical industry, and the milder-temperature <u>delayed coking</u> (ca. 500 °C) which can produce, under the right conditions, valuable <u>needle coke</u>, a highly crystalline petroleum coke used in the production of <u>electrodes</u> for the <u>steel</u> and <u>aluminium</u> industries.

The first thermal cracking method, the <u>Shukhov cracking process</u>, was invented by Russian engineer <u>Vladimir Shukhov</u>, in the Russian empire, Patent No. 12926, November 27, 1891.^[5]

<u>William Merriam Burton</u> developed one of the earliest thermal cracking processes in 1912 which operated at 700–750 °F (371–399 °C) and an absolute pressure of 90 psi (620 kPa) and was known as the <u>Burton process</u>. Shortly thereafter, in 1921, <u>C.P. Dubbs</u>, an employee of the <u>Universal Oil Products</u> Company, developed a somewhat more advanced thermal cracking process which operated at 750–860 °F (399–460 °C) and was known as the <u>Dubbs</u> process.¹⁶¹ The Dubbs process was used extensively by many <u>refineries</u> until the early 1940s when catalytic cracking came into use.

Steam cracking

Steam cracking is a <u>petrochemical</u> process in which saturated <u>hydrocarbons</u> are broken down into smaller, often unsaturated, hydrocarbons. It is the principal industrial method for producing the lighter <u>alkenes</u> (or commonly <u>olefins</u>), including <u>ethene</u> (or <u>ethylene</u>) and <u>propene</u> (or <u>propylene</u>). Steam cracker units are facilities in which a feedstock such as naphtha, liquefied petroleum gas (LPG), <u>ethane</u>, <u>propane</u> or <u>butane</u> is thermally cracked through the use of steam in a bank of pyrolysis furnaces to produce lighter hydrocarbons. The products obtained depend on the composition of the feed, the hydrocarbon-to-steam ratio, and on the cracking temperature and furnace residence time.^[2]

In steam cracking, a gaseous or liquid hydrocarbon feed like <u>naphtha</u>, <u>LPG</u> or <u>ethane</u> is diluted with steam and briefly heated in a furnace without the presence of oxygen. Typically, the reaction temperature is very high, at around 850°C, but the reaction is only allowed to take place very briefly. In modern cracking furnaces, the residence time is reduced to milliseconds to improve yield, resulting in gas velocities faster than the <u>speed of sound</u>. After the cracking temperature has been reached, the gas is quickly quenched to stop the reaction in a transfer line <u>heat exchanger</u> or inside a quenching header using quench oil.

The products produced in the reaction depend on the composition of the feed, the hydrocarbon to steam ratio and on the cracking temperature and furnace residence time. Light hydrocarbon feeds such as <u>ethane</u>, LPGs or light <u>naphtha</u> give product streams rich in the lighter alkenes, including ethylene, propylene, and <u>butadiene</u>. Heavier hydrocarbon (full range and heavy naphthas as well as other refinery products) feeds give some of these, but also give products rich in <u>aromatic hydrocarbons</u> and hydrocarbons suitable for inclusion in <u>gasoline</u> or <u>fuel oil</u>.

A higher cracking temperature (also referred to as severity) favors the production of <u>ethene</u> and <u>benzene</u>, whereas lower severity produces higher amounts of <u>propene</u>, C4-hydrocarbons and liquid products. The process also results in the slow deposition of <u>coke</u>, a form of <u>carbon</u>, on the reactor walls. This degrades the efficiency of the reactor, so reaction conditions are designed to minimize this. Nonetheless, a steam cracking furnace can usually only run for a few months at a time between de-cokings. Decokes require the furnace to be isolated from the process and then a flow of steam or a steam/air mixture is passed through the furnace coils. This converts the hard solid carbon layer to

carbon monoxide and carbon dioxide. Once this reaction is complete, the furnace can be returned to service.

Catalytic methods

The catalytic cracking process involves the presence of <u>acid catalysts</u> (usually solid acids such as <u>silica-alumina</u> and <u>zeolites</u>) which promote a heterolytic (asymmetric) breakage of bonds yielding pairs of <u>ions</u> of opposite charges, usually a <u>carbocation</u> and the very unstable <u>hydride anion</u>. Carbon-localized free radicals and cations are both highly unstable and undergo processes of chain rearrangement, C-C scission in position <u>beta</u> as in cracking, and <u>intra-</u> and <u>intermolecular</u> hydrogen transfer. In both types of processes, the corresponding reactive intermediates (radicals, ions) are permanently regenerated, and thus they proceed by a self-propagating chain mechanism. The chain of reactions is eventually terminated by radical or ion recombination.

Fluid Catalytic cracking

Main article: Fluid catalytic cracking



Schematic flow diagram of a fluid catalytic cracker

Fluid catalytic cracking is a commonly used process, and a modern oil refinery will typically include a <u>cat cracker</u>, particularly at refineries in the US, due to the high demand for <u>gasoline</u>.^{[81[9][10]} The process was first used around 1942 and employs a powdered <u>catalyst</u>. During WWII, in contrast to the Axis Forces which suffered severe shortages of gasoline and artificial rubber, the Allied Forces were supplied with plentiful supplies of the materials. Initial process implementations were based on low activity <u>alumina</u> catalyst and a reactor where the catalyst particles were suspended in a rising flow of feed hydrocarbons in a <u>fluidized bed</u>.

Alumina-catalyzed cracking systems are still in use in <u>high school</u> and <u>university</u> <u>laboratories</u> in experiments concerning alkanes and alkenes. The catalyst is usually obtained by crushing <u>pumice</u> stones, which contain mainly <u>aluminium</u> <u>oxide</u> and <u>silica</u> into small, porous pieces. In the laboratory, aluminium oxide (or porous pot) must be heated.

In newer designs, cracking takes place using a very active <u>zeolite</u>-based catalyst in a short-contact time vertical or upward-sloped pipe called the "riser". Pre-heated feed is sprayed into the base of the riser via feed nozzles where it contacts extremely hot fluidized catalyst at 1,230 to 1,400 °F (666 to 760 °C). The hot catalyst vaporizes the feed and catalyzes the cracking reactions that break down the high-molecular weight oil into lighter components including LPG, gasoline, and diesel. The catalyst-hydrocarbon mixture flows upward through the riser for a few seconds, and then the mixture is separated via <u>cyclones</u>. The catalyst-free hydrocarbons are routed to a main <u>fractionator</u> for separation into fuel gas, LPG, gasoline, <u>naphtha</u>, light cycle oils used in diesel and jet fuel, and heavy fuel oil.

During the trip up the riser, the cracking catalyst is "spent" by reactions which deposit coke on the catalyst and greatly reduce activity and selectivity. The "spent" catalyst is disengaged from the cracked hydrocarbon vapors and sent to a stripper where it is contacts steam to remove hydrocarbons remaining in the catalyst pores. The "spent" catalyst then flows into a fluidized-bed regenerator where air (or in some cases air plus <u>oxygen</u>) is used to burn off the coke to restore catalyst activity and also provide the necessary heat for the next reaction cycle, cracking being an <u>endothermic reaction</u>. The "regenerated" catalyst then flows to the base of the riser, repeating the cycle.

The gasoline produced in the FCC unit has an elevated <u>octane rating</u> but is less chemically stable compared to other gasoline components due to its <u>olefinic</u> profile. Olefins in gasoline are responsible for the formation of <u>polymeric</u> deposits in storage <u>tanks</u>, fuel ducts and <u>injectors</u>. The FCC LPG is an important source of <u>C</u>₃-C₄ olefins and <u>isobutane</u> that are essential feeds for the <u>alkylation</u> process and the production of polymers such as <u>polypropylene</u>.

Hydrocracking[

Hydrocracking is a catalytic cracking process assisted by the presence of added <u>hydrogen</u> gas. Unlike a <u>hydrotreater</u>, where hydrogen is used to cleave C-S and C-N bonds, hydrocracking uses hydrogen to break C-C bonds (hydrotreatment is conducted prior to hydrocracking to protect the catalysts in a hydrocracking).

The products of this process are <u>saturated hydrocarbons</u>; depending on the reaction conditions (temperature, pressure, catalyst activity) these products range from <u>ethane</u>, LPG to heavier hydrocarbons consisting mostly of

<u>isoparaffins</u>. Hydrocracking is normally facilitated by a bifunctional catalyst that is capable of rearranging and breaking <u>hydrocarbon chains</u> as well as adding hydrogen to <u>aromatics</u> and <u>olefins</u> to produce <u>naphthenes</u> and <u>alkanes</u>.

The major products from hydrocracking are jet fuel and <u>diesel</u>, but low sulphur naphta fractions and LPG are also produced.^[11] All these products have a very low content of <u>sulfur</u> and other <u>contaminants</u>.

It is very common in Europe and Asia because those regions have high demand for diesel and <u>kerosene</u>. In the US, fluid catalytic cracking is more common because the demand for <u>gasoline</u> is higher.

The hydrocracking process depends on the nature of the feedstock and the relative rates of the two competing reactions, hydrogenation and cracking. Heavy aromatic feedstock is converted into lighter products under a wide range of very high pressures (1,000-2,000 psi) and fairly high temperatures (750°-1,500° F), in the presence of hydrogen and special catalysts.

The primary function of hydrogen is, thus: a) If feedstock has a high paraffinic content, the primary function of hydrogen is to prevent the formation of polycyclic aromatic compounds. b) Reduced tar formation c) Reduced Impurities d) Prevent buildup of coke on the catalyst. e) High cetane fuel is achieved.

Alkylation

Alkylation is the transfer of an <u>alkyl</u> group from one <u>molecule</u> to another. The alkyl group may be transferred as an alkyl <u>carbocation</u>, a <u>free radical</u>, a <u>carbanion</u> or a <u>carbene</u> (or their equivalents).^[11] **Alkylating agents** are widely used in chemistry because the alkyl group is probably the most common group encountered in organic molecules.^[Citation needed] Many biological target molecules or their synthetic precursors are composed of an alkyl chain with specific <u>functional groups</u> in a specific order. Selective alkylation, or adding parts to the chain with the desired functional groups, is used, especially if there is no commonly available biological precursor. Alkylation with only one carbon is termed <u>methylation</u>.

In oil refining contexts, **alkylation** refers to a particular alkylation of <u>isobutane</u> with <u>olefins</u>. For upgrading of <u>petroleum</u>, alkylation produces synthetic C_7-C_8 alkylate, which is a premium blending stock for gasoline.^[2]

In medicine, alkylation of <u>DNA</u> is used in <u>chemotherapy</u> to damage the DNA of cancer cells. Alkylation is accomplished with the class of drugs called <u>alkylating</u> <u>antineoplastic agents</u>.



Benzene Friedel-Crafts alkylation.

Burton process

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The **Burton process** is a <u>thermal cracking</u> process invented by <u>William Merriam</u> <u>Burton</u> and <u>Robert E. Humphreys</u>, each of whom held a Ph.D. in chemistry from Johns Hopkins University. The process they developed is often called the Burton process. More fairly, though, it should be known as the Burton-Humphreys process, since both men played key roles in its development. This issue was settled in court, although the decision gave primary recognition to Burton.^[1]

The process uses the destructive distillation of crude oil heated in a still under pressure. In this revolutionary still, different products emerging from a bubble tower at different temperatures and pressures. Of critical importance, the use of these stills more than doubled the production of gasoline from most kinds of oil. The first large-scale use of these towers began with the decision by Standard Oil of Indiana to build 120 stills for an appropriation of \$709,000, authorized in 1911.^[2] This decision was taken just as the US Supreme Court ordered the dissolution of the <u>Standard Oil Trust</u>.

This thermal cracking process was <u>patented</u> on January 7, 1913 (Patent No. 1,049,667). The first <u>thermal cracking</u> method, the <u>Shukhov cracking process</u>, was invented by <u>Vladimir Shukhov</u> (Patent of <u>Russian empire</u> No. 12926 on November 27, 1891). While the Russians contended that the Burton process was essentially a slight modification of the Shukhov process, Americans refused to concede and the Burton-Humphreys patent remained in use. Ultimately, this process contributed to the development of petrochemicals.^[3]

In 1937 the Burton process was superseded by <u>catalytic cracking</u>, but it is still in use today to produce <u>diesel</u>.

Cumene process

The **cumene process** (**cumene-phenol process**, **Hock process**) is an <u>industrial process</u> for developing <u>phenol</u> and <u>acetone</u> from <u>benzene</u> and <u>propylene</u>. The term stems from <u>cumene</u> (isopropyl benzene), the intermediate material during the process. It was invented by Heinrich Hock in 1944^{[11][2]} and independently by R. Ūdris and P. Sergeyev in 1942 (USSR).^[3]

This process converts two relatively cheap starting materials, <u>benzene</u> and <u>propylene</u>, into two more valuable ones, <u>phenol</u> and <u>acetone</u>. Other reactants required are <u>oxygen</u> from air and small amounts of a <u>radical initiator</u>. Most of the worldwide production of phenol and <u>acetone</u> is now based on this method. In 2003, nearly 7 million tonnes of phenol was produced by the cumene process.^[4] In order for this process to be economical, there must also be demand for the <u>acetone</u> by-product as well as the <u>phenol</u>.



Technical description[

Benzene and propylene are compressed together to a pressure of 30 <u>standard</u> <u>atmospheres</u> at 250 °C (482 °F) in presence of a <u>catalytic Lewis acid</u>. <u>Phosphoric</u> <u>acid</u> is often favored over <u>aluminium halides</u>. Cumene is formed in the gasphase <u>Friedel-Crafts alkylation</u> of benzene by propylene:



Cumene is oxidized in air which removes the tertiary <u>benzylic</u> hydrogen from cumene and hence forms a cumene <u>radical</u>:



This cumene radical then <u>bonds</u> with an oxygen molecule to give cumene <u>hydroperoxide</u> radical, which in turn forms <u>cumene hydroperoxide</u> $(C_6H_5C(CH_3)_2$ -O-O-H) by abstracting benzylic hydrogen from another cumene molecule. This latter cumene converts into cumene radical and feeds back into subsequent chain formations of cumene hydroperoxides. A pressure of 5 atm is used to ensure that the unstable peroxide is kept in liquid state.

Friedel-Crafts reaction

(

The **Friedel–Crafts reactions** are a set of <u>reactions</u> developed by <u>Charles Friedel</u> and <u>James Crafts</u> in 1877 to attach substituents to an <u>aromatic ring</u>.^[11] There are two main types of Friedel–Crafts reactions: <u>alkylation</u> reactions and <u>acylation</u> reactions. Both proceed by <u>electrophilic aromatic substitution</u>. The general reaction scheme is shown below.



Several reviews have been written.

Friedel-Crafts alkylation[

Friedel–Crafts alkylation involves the alkylation of an <u>aromatic ring</u> with an <u>alkyl</u> <u>halide</u> using a strong <u>Lewis acid</u> catalyst.^[6] With anhydrous <u>ferric chloride</u> as a <u>catalyst</u>, the alkyl group attaches at the former site of the chloride ion. The general mechanism is shown below.^[7]



This reaction has one big disadvantage, namely that the product is more <u>nucleophilic</u> than the reactant due to the electron donating alkyl-chain. Therefore, another hydrogen is substituted with an alkyl-chain, which leads to overalkylation of the molecule. Also, if the chloride is not on a <u>tertiary carbon</u> or secondary carbon, <u>carbocation rearrangement reaction</u> will occur. This reactivity is due to the relative stability of the tertiary and secondary <u>carbocation</u> over the primary carbocations.^[2]

<u>Steric hindrance</u> can be exploited to limit the number of alkylations, as in the *t*-butylation of 1,4-dimethoxybenzene.

Kolbe–Schmitt reaction

The Kolbe-Schmitt reaction or Kolbe process (named after <u>Hermann Kolbe</u> and <u>Rudolf Schmitt</u>) is a <u>carboxylation chemical reaction</u> that proceeds by heating sodium phenolate (the <u>sodium</u> salt of <u>phenol</u>) with <u>carbon dioxide</u> under pressure (100 <u>atm</u>, 125 °C), then treating the product with <u>sulfuric acid</u>. The final product is an <u>aromatic</u> hydroxy <u>acid</u> which is also known as <u>salicylic acid</u> (the precursor to <u>aspirin</u>).^[1112113]



By using <u>potassium hydroxide</u>, <u>4-hydroxybenzoic acid</u> is accessible, an important precursor for the versatile <u>paraben</u> class of <u>biocides</u> used e.g. in personal care products.

Reaction mechanism[

The Kolbe–Schmitt reaction proceeds via the nucleophile addition of a phenoxide, classically <u>sodium phenoxide</u> (NaOC₆H₅), to carbon dioxide to give the salicylate. The final step is reaction of the salicylate with acid to form the desired salicylic acid.



Olefin metathesis



Olefin metathesis is an <u>organic reaction</u> that entails the redistribution of fragments of <u>alkenes</u> (olefins) by the scission and regeneration of carboncarbon <u>double bonds</u>.¹¹¹ Catalysts for this reaction have evolved rapidly for the past few decades. Because of the relative simplicity of olefin metathesis, it often creates fewer undesired <u>by-products</u> and <u>hazardous wastes</u> than alternative organic reactions. For their elucidation of the reaction mechanism and their discovery of a variety of highly efficient and selective catalysts, <u>Yves Chauvin</u>, <u>Robert H. Grubbs</u>, and <u>Richard R. Schrock</u> were collectively awarded the 2005 <u>Nobel Prize in Chemistry</u>.¹²

Transesterification

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In <u>organic chemistry</u>, **transesterification** / trænz ɛstərifi keɪʃən/ is the process of exchanging the organic group R" of an <u>ester</u> with the organic group R' of an alcohol. These reactions are often <u>catalyzed</u> by the addition of an <u>acid</u> or <u>base</u>

catalyst. The reaction can also be accomplished with the help of enzymes (biocatalysts) particularly lipases (E.C.3.1.1.3).



Transesterification: alcohol + ester \rightarrow different alcohol + different ester

Strong acids catalyse the reaction by donating a <u>proton</u> to the <u>carbonyl</u> group, thus making it a more potent <u>electrophile</u>, whereas bases catalyse the reaction by removing a proton from the alcohol, thus making it more <u>nucleophilic</u>. Esters with larger alkoxy groups can be made from methyl or ethyl esters in high purity by heating the mixture of ester, acid/base, and large alcohol and evaporating the small alcohol to drive equilibrium.

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Mechanism[edit]

In the transesterification mechanism, the carbonyl carbon of the starting ester $(RCOOR^1)$ undergoes nucleophilic attack by the incoming alkoxide (R^2O^-) to give a tetrahedral intermediate, which either reverts to the starting material, or proceeds to the transesterified product (RCOOR²). The various species exist in equilibrium, and the product distribution depends on the relative energies of the reactant and product.



Applications[edit]

Polyester production[edit]

The largest scale application of transesterification is in the synthesis of <u>polyesters</u>.^[11] In this application diesters undergo transesterification with diols to form macromolecules. For example, <u>dimethyl terephthalate</u> and <u>ethylene glycol</u> react to form <u>polyethylene terephthalate</u> and <u>methanol</u>, which is evaporated to drive the reaction forward.

Methanolysis and biodiesel production[edit]

The reverse reaction, methanolysis, is also an example of transesterification. This process has been used to recycle polyesters into individual monomers (see <u>plastic recycling</u>). It is also used to convert fats (<u>triglycerides</u>) into <u>biodiesel</u>. This conversion was one of the first uses. Transesterified <u>vegetable oil</u> (<u>biodiesel</u>) was used to power heavy-duty vehicles in South Africa before <u>World War II</u>.

It was <u>patented</u> in the US in the 1950s by <u>Colgate</u>, though <u>Biolipid</u> transesterification may have been discovered much earlier. In the 1940s, researchers were looking for a method to more readily produce <u>glycerol</u>, which was used to produce <u>explosives</u> for World War II. Many of the methods used today by producers and home brewers have their origin in the original 1940s research.

Raschig process

The **Raschig process** is a <u>chemical process</u> for the production of <u>hydroxylamine</u>, developed by German chemist <u>Friedrich Raschig</u>. The main step in this process, patented by Raschig in 1887, is the reduction of <u>nitrite</u> with <u>bisulfite</u> towards hydroxylamine di<u>sulfonate</u>, which is hydrolysed to <u>hydroxylammonium sulfate</u>.^[11] Most of the hydroxylamine produced is used in the manufacture of <u>caprolactam</u>, the precursor to the polymer <u>Nylon 6</u>.^[2]

The commercially used Raschig process consists of the following steps:^[2]

- <u>ammonium carbonate</u> solution is prepared by reacting ammonia, carbon dioxide and water
- an alkaline solution of <u>ammonium nitrite</u> is formed by reacting ammonium carbonate solution with <u>nitrogen oxides</u>
- ammonium nitrite is converted to hydroxylamine disulfonate with <u>sulfur</u> <u>dioxide</u>
- hydroxylamine disulfonate is hydrolysed to hydroxylammonium sulfate

Hydroformylation

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(Redirected from Oxo process)

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Hydroformylation of an Alkene (R1 to R3 organyl groups (i. e. Alkyl- or Aryl group) or hydrogen).

Hydroformylation, also known as **oxo synthesis** or **oxo process**, is an important <u>homogeneously catalyzed</u> industrial process for the production of <u>aldehydes</u> from <u>alkenes</u>.^[1] This chemical reaction entails the addition of a <u>formyl</u> group (CHO) and a <u>hydrogen</u> atom to a carbon-carbon double bond. This process has undergone continuous growth since its invention in 1938: Production capacity reached 6.6×10⁶ tons in 1995. It is important because the resulting aldehydes are easily converted into many secondary products. For example, the resulting aldehydes are hydrogenated to <u>alcohols</u> that are converted to <u>plasticizers</u> or <u>detergents</u>. Hydroformylation is also used in <u>specialty chemicals</u>, relevant to the <u>organic synthesis</u> of <u>fragrances</u> and natural products. The development of hydroformylation, which originated within the German coal-based industry, is considered one of the premier achievements of 20th-century industrial <u>chemistry</u>.

The process typically entails treatment of an <u>alkene</u> with high pressures (between 10 to 100 <u>atmospheres</u>) of <u>carbon monoxide</u> and hydrogen at temperatures between 40 and 200 °C. Transition metal <u>catalysts</u> are required.

Polymerization



An example of **alkene polymerization**, in which each <u>styrene</u> monomer's double bond reforms as a single bond plus a bond to another styrene monomer. The product is <u>polystyrene</u>.

IUPAC definition

polymerization: The process of converting a <u>monomer</u> or a mixture of monomers into a <u>polymer</u>. ^[11]

In <u>polymer chemistry</u>, **polymerization** is a process of reacting <u>monomer</u> <u>molecules</u> together in a <u>chemical reaction</u> to form <u>polymer</u> chains or threedimensional networks.^{[2][3][4]} There are many forms of polymerization and different systems exist to categorize them.