



Al-Mustaqbal University

College of Engineering and Engineering Technologies

Department of Chemical Engineering and Petroleum Industries

Name of the substance: Chemicals from petroleum

Lecture number: Four

Lecture title :

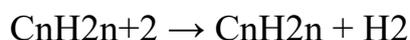
- Primary Petrochemicals (Part 2)
- Derivatives Syn gas derivatives
 - Ethlene derivatives

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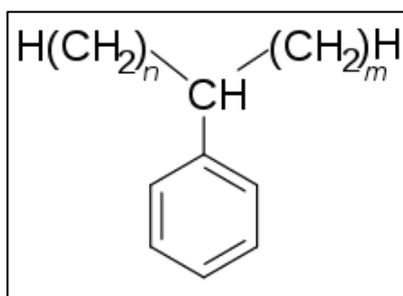
Linear alkylbenzene(LAB)

Linear alkylbenzenes (sometimes also known as LABs) are a family of organic compounds with the formula $C_6H_5C_nH_{2n+1}$. Typically, n lies between 10 and 16, although generally supplied as a tighter cut, such as C12-C15, C12-C13 and C10-C13, for detergent use. The C_nH_{2n+1} chain is unbranched. They are mainly produced as intermediate in the production of surfactants, for use in detergent. Since the 1960s, LABs have emerged as the dominant precursor of biodegradable detergents.

Production : Hydrotreated kerosene is a typical feedstock for high purity linear paraffins (n-paraffins), which are subsequently dehydrogenated to linear olefins:



Alternatively, ethylene can be oligomerized (partially polymerized) to produce linear alkenes. The resulting linear mono-olefins react with benzene in the presence of a catalyst to produce the LABs. Hydrogen fluoride (HF) and aluminium chloride ($AlCl_3$) are the two major catalysts for the alkylation of benzene with linear mono-olefins. The HF-based process is commercially dominant; however, the risk of releasing HF (a poisonous substance) into the environment became a concern particularly after the Clean Air Act Amendment. In 1995, a solid catalyst system (the DETAL process) became available. The process eliminates catalyst neutralization and HF disposal. Consequently, most LAB plants built since then have utilized this process.



Hydrogen production:

Hydrogen production is the family of industrial methods for generating hydrogen gas. There are four main sources for the commercial production of hydrogen: natural gas, oil, coal, and electrolysis of water; which account for 48%, 30%, 18% and 4% of the world's hydrogen production respectively.[1] Fossil fuels are the dominant source of

industrial hydrogen .As of 2020, the majority of hydrogen (~95%) is produced by steam reforming of natural gas and other light hydrocarbons, partial oxidation of heavier hydrocarbons, and coal gasification .Other methods of hydrogen production include biomass gasification and methane pyrolysis. Methane pyrolysis and water electrolysis can use any source of electricity including renewable energy.

The production of hydrogen plays a key role in any industrialized society, since hydrogen is required for many chemical processes. In 2020, roughly 87 million tons of hydrogen was produced[6] worldwide for various uses, such as oil refining, in the production of ammonia through the Haber process, and in the production of methanol through reduction of carbon monoxide. The global hydrogen generation market was valued at US\$155 billion in 2022, and expected to grow at a compound annual growth rate of 9.3% from 2023 to 2030

Steam reforming:

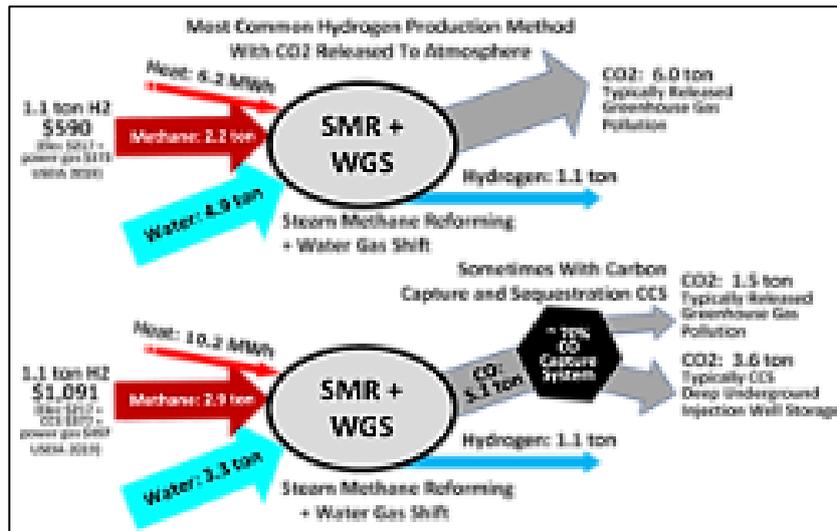
Steam reforming or steam methane reforming (SMR) is a method for producing syngas (hydrogen and carbon monoxide) by reaction of hydrocarbons with water. Commonly natural gas is the feedstock. The main purpose of this technology is hydrogen production. The reaction is represented by this equilibrium:



The reaction is strongly endothermic ($\Delta H_{SR} = 206 \text{ kJ/mol}$)

Hydrogen produced by steam reforming is termed 'grey hydrogen' when the waste carbon monoxide is released to the atmosphere and 'blue hydrogen' when the carbon monoxide is (mostly) captured and stored geologically. Zero carbon 'green' hydrogen is produced by thermochemical water splitting, using solar thermal, low- or zero-carbon electricity or waste heat, or electrolysis, using low- or zero-carbon electricity. Zero carbon emissions 'turquoise' hydrogen is produced by one-step methane pyrolysis of natural gas.

Steam reforming of natural gas produces most of the world's hydrogen. Hydrogen is used in the industrial synthesis of ammonia and other chemicals

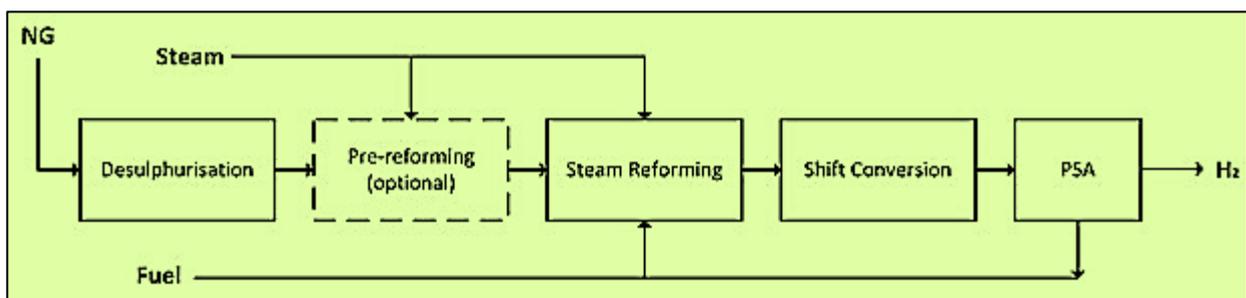


Illustrating inputs and outputs of steam reforming of natural gas, a process to produce hydrogen and CO₂ greenhouse gas that may be captured with CCS

Reactions:

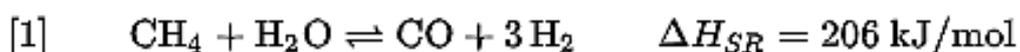
Steam reforming reaction kinetics, in particular using nickel-alumina catalysts, have been studied in detail since the 1950s.

Pre-reforming: The purpose of pre-reforming is to break down higher hydrocarbons such as propane, butane or naphtha into methane (CH₄), which allows for more efficient reforming downstream.

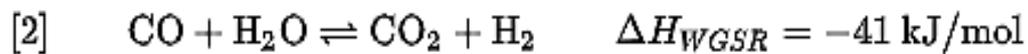


Depiction of the general process flow of a typical steam reforming plant. (PSA = Pressure swing adsorption, NG = Natural gas)

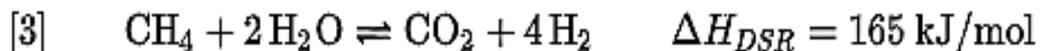
Steam reforming: The name-giving reaction is the steam reforming (SR) reaction and is expressed by the equation



Via the water-gas shift reaction (WGSR), additional hydrogen is released by reaction of water with the carbon monoxide generated according to equation [1]:



Some additional reactions occurring within steam reforming processes have been studied. Commonly the direct steam reforming (DSR) reaction is also included



As these reactions by themselves are highly endothermic (apart from WGSR, which is mildly exothermic), a large amount of heat needs to be added to the reactor to keep a constant temperature. Optimal SMR reactor operating conditions lie within a temperature range of 800 °C to 900 °C at medium pressures of 20-30 bar.[8] High excess of steam is required, expressed by the (molar) steam-to-carbon (S/C) ratio. Typical S/C ratio values lie within the range 2.5:1 - 3:1

Polonium(PO):

Polonium is a chemical element with the symbol Po and atomic number 84. A rare and highly radioactive metal with no stable isotopes, polonium is a chalcogen and chemically similar to selenium and tellurium, though its metallic character resembles that of its horizontal neighbors in the periodic. Due to the short half-life of all its isotopes, its natural occurrence is limited to tiny traces of the fleeting polonium-210 (with a half-life of 138 days) in uranium ores, as it is the penultimate daughter of natural uranium-238. Though longer-lived isotopes exist, such as the 125.2 years half-life of polonium 209, they are much more difficult to produce. Today, polonium is usually produced in milligram quantities by the neutron irradiation of bismuth. Due to its intense radioactivity, which results in the radiolysis of chemical bonds and radioactive self-heating, its chemistry has mostly been investigated on the trace scale only.

Polonium was discovered in July 1898 by Marie Skłodowska-Curie and Pierre Curie, when it was extracted from the uranium ore pitchblende and identified solely by its strong radioactivity: it was the first element to be so discovered. Polonium was named after Marie Curie's homeland of Poland. Polonium has few applications, and those are

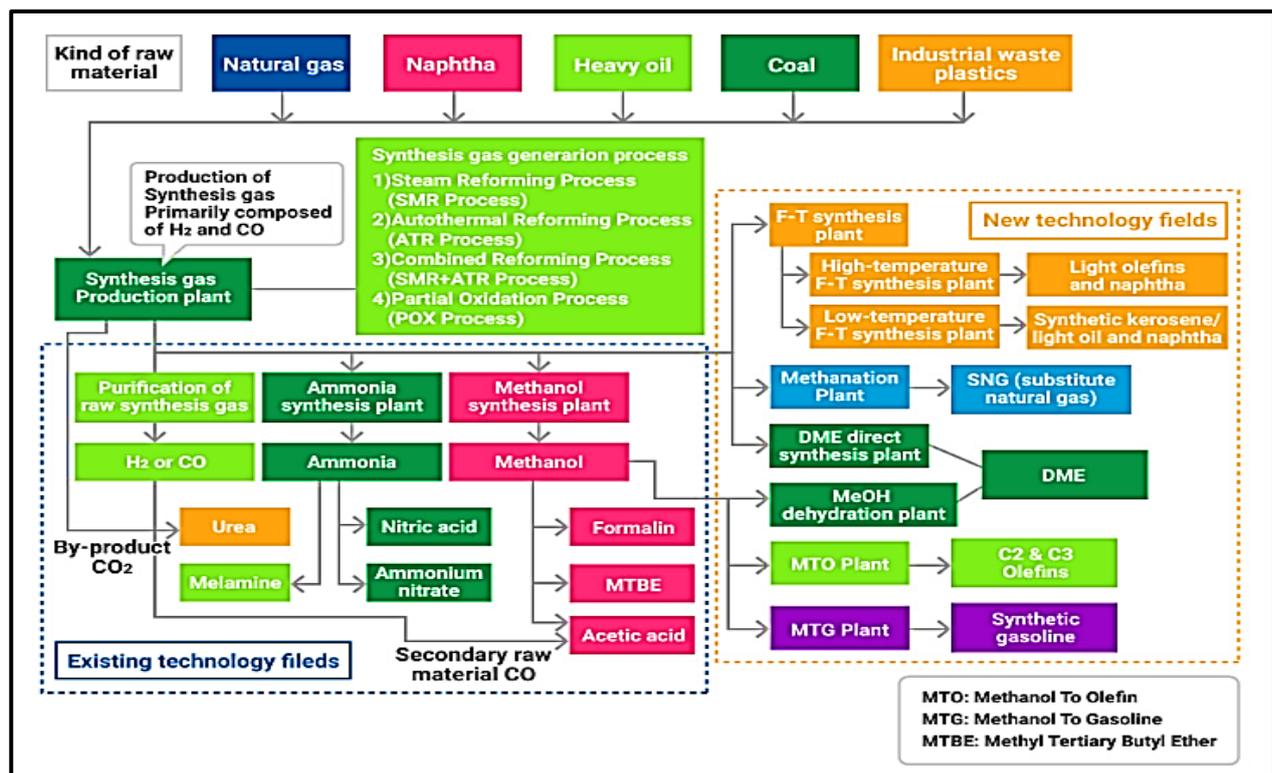
related to its radioactivity: heaters in space probes, antistatic devices, sources of neutrons and alpha particles, and poison. It is extremely dangerous to humans.



Synthesis Gas and Derivatives

Synthesis gas (Syngas) is the generic term for raw gas produced from feedstock hydrocarbon and consists of hydrogen (H_2) and carbon monoxide (CO) as primarily components and carbon dioxide (CO_2), methane (CH_4), etc. as remaining components.

It is also the generic term for raw gases used for the synthesis of ammonia, methanol, and oxo alcohol or the production of hydrogen. In addition to the application to these existing technology field, the application to the new energy related technology field, such as Gas-to-Liquid (GTL) which is based on Fischer Tropsch process, dimethylether (DME), or substitute natural gas (SNG).

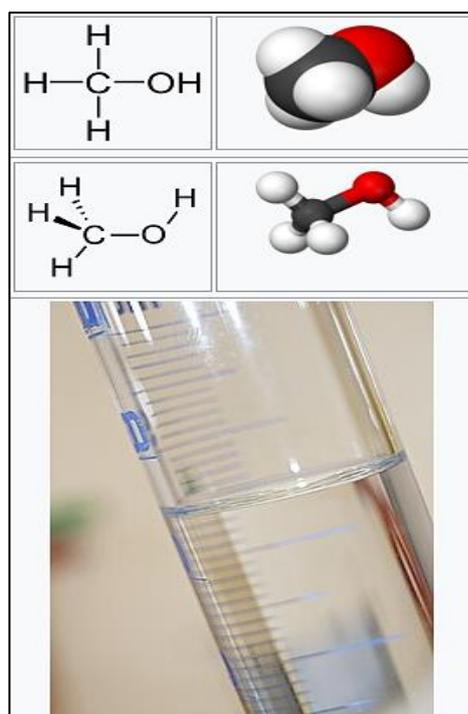


Quite wide range of hydrocarbon starting from natural gas (composed mainly of methane), LPG/naphtha, residual oil, coal till industrial waste plastic can be used as feed stock for production of synthesis gas.

1- Methanol:

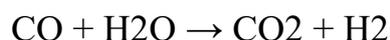
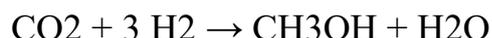
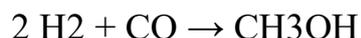
Methanol is an important primary chemical product, used as a chemical feedstock for production of a range of important industrial chemicals, primarily acetic acid, formaldehyde, methyl methacrylate and methyl tertiary-butyl ether (MTBE). Methanol is also used directly as a fuel or in fuel blends (e.g. in M85 consisting of 85% methanol and 15% gasoline). As fuel, methanol can be used to fire rapid-start utility peak-shaving combustion turbines; to substitute for or blend with gasoline to power vehicles; to be converted to gasoline via the ExxonMobil methanol-to-gasoline (MTG) process; or to be converted to dimethyl ether (DME) to power diesel engines.

Most methanol is made from syngas. About 55-65% of global methanol production uses natural gas feedstock, about 30-35% uses coal, with the rest using coking gas and other feedstocks. (Alvarado M. Methanol Industry Overview, 35th World Methanol Conference, Berlin, Germany 2017). In 2021, worldwide methanol production reached 107 million metric tons.



Process Chemistry

Catalytic conversion of hydrogen (H₂) and carbon monoxide (CO) from coal-derived syngas into methanol can be done with conventional gas-phase processes, or with a liquid phase methanol (LPMEOH™) process developed by Air Products and Chemicals. The reactions of interest are:



All three reactions are highly exothermic. The conventional commercial gas-phase process carries out the conversion in fixed-bed reactors at high pressure. Depending on the catalyst supplier, the synthesis reaction is normally carried out at about 600 to 1,700 psig and 400 to 600°F. Substantial process gas recycle of H₂ rich gas moderates the temperature rise across the adiabatic reactor. CO concentration at the reactor inlet is normally limited to about 10-15%, after dilution with recycled H₂.

Catalyst systems used for methanol synthesis are typically mixtures of copper, zinc oxide, alumina and magnesia. Recent advances have also yielded a possible new catalyst composed of carbon, nitrogen, and platinum. This catalyst is based on an earlier catalyst created by Dr. Roy Periana of the Scripps Research Institute. This newer catalyst is a solid material that is suspended in sulfuric acid to aid in the catalysis. The material is easily recyclable as it can be filtered from the acid.

2- Acetic acid:

Also known as ethanoic acid, with the formula CH₃COOH, it is an organic chemical compound and an organic carboxylic acid that gives vinegar its sour taste and pungent odor. Pure, water-free acetic acid (glacial acetic acid: so called because it freezes if the air temperature drops below 16.8 °C) is a colorless liquid that absorbs water from the surrounding atmosphere (hygroscopicity), and freezes below 16.7 °C into colorless solid crystals. Acetic acid is corrosive, and its vapor causes irritation to the eyes, dryness and burning of the nose, and congestion of the throat and lungs. It is a weak acid because under standard conditions of temperature and pressure the dissociated acid exists in equilibrium with the undissociated form in the form of aqueous solutions, in contrast to strong acids, which dissociate completely



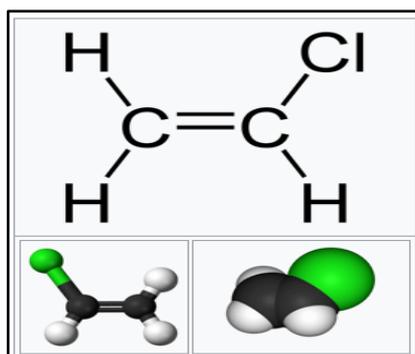
Ethlene derivatives

- 1- Vinyl chloride M
- 2- Ethylene oxide
- 3- Ethylene glycol
- 4- MEA
- 5- DEA&TEA

Vinyl chloride M:

Vinyl chloride is an organochloride with the formula $H_2C=CHCl$. It is also called vinyl chloride monomer (VCM) or chloroethene. This colorless compound is an important industrial chemical chiefly used to produce the polymer, poly(vinyl chloride) (PVC).

Vinyl chloride monomer is among the top twenty largest petrochemicals (petroleum-derived chemicals) in world production. The United States remains the largest vinyl chloride manufacturing region because of its low-production-cost position in chlorine and ethylene raw materials. China is also a large manufacturer and one of the largest consumers of vinyl chloride. Vinyl chloride is a flammable gas that has a sweet odor and is carcinogenic. It can be formed in the environment when soil organisms break down chlorinated solvents. Vinyl chloride that is released by industries or formed by the breakdown of other chlorinated chemicals can enter the air and drinking water supplies. Vinyl chloride is a common contaminant found near landfills.



Uses: Vinyl chloride, also called vinyl chloride monomer (VCM), is exclusively used as a precursor to PVC. Due to its toxic nature, Until 1974, vinyl chloride was used in aerosol spray propellant. Vinyl chloride was briefly used as an inhalational anaesthetic, in a similar vein to ethyl chloride, though its toxicity forced this practice to be abandoned.



Vinyl Chloride



WHAT:

Vinyl chloride was a common ingredient used in cosmetic products, refrigerants and household aerosols in the United States. It is also used to make polyvinyl chloride (PVC).

FOUND:

Vinyl chloride can be found near manufacturing plants, hazardous waste sites and landfills. Traces of vinyl chloride can be found in products that are made using PVC.

SCIENCE:

Vinyl chloride became classified as a human carcinogen after various studies demonstrated toxic effects in humans and animals.

TOP TIP:

Limit use of PVC plastic containers and food packaging, as they may have traces of vinyl chloride. Industrial workers in close contact with vinyl chloride should use respirators and wear protective clothing.

Production: To give a sense of scale, globally approximately 40 million tonnes of PVC resin are produced per year, requiring a corresponding amount of vinyl chloride monomer

Ethylene oxide:

Ethylene oxide is an organic compound with the formula C_2H_4O . It is a cyclic ether and the simplest epoxide: a three-membered ring consisting of one oxygen atom and two carbon atoms. Ethylene oxide is a colorless and flammable gas with a faintly sweet odor. Because it is a strained ring, ethylene oxide easily participates in a number of addition reactions that result in ring-opening. Ethylene oxide is isomeric with acetaldehyde and with vinyl alcohol. Ethylene oxide is industrially produced by oxidation of ethylene in the presence of a silver catalyst.

The reactivity that is responsible for many of ethylene oxide's hazards also makes it useful. Although too dangerous for direct household use and generally unfamiliar to consumers, ethylene oxide is used for making many consumer products as well as non-consumer chemicals and intermediates. These products include detergents, thickeners, solvents, plastics, and various organic chemicals such as ethylene glycol, ethanolamines, simple and complex glycols, polyglycol ethers, and other compounds. Although it is a vital raw material with diverse applications, including the manufacture of products like polysorbate 20 and polyethylene glycol (PEG) that are often more effective and less toxic than alternative materials, ethylene oxide itself is a very hazardous substance. At room temperature it is a very flammable, carcinogenic, mutagenic, irritating, and anaesthetic gas.

Ethylene oxide is a surface disinfectant that is widely used in hospitals and the medical equipment industry to replace steam in the sterilization of heat-sensitive tools and equipment, such as disposable plastic syringes. It is so flammable and extremely explosive that it is used as a main component of thermobaric weapons; therefore, it is commonly handled and shipped as a refrigerated liquid to control its hazardous nature

