# Petrochemicals

- **Petrochemicals** are chemical products made from raw materials of petroleum or other hydrocarbon origin.
- Although some of the chemical compounds that originate from petroleum may also be derived from coal and natural gas, petroleum is the major source.

# Petrochemicals

- Petroleum is the biggest and cheapest source of hydrocarbons which can be converted to a number of organic compounds
- All such organic chemicals which have been derived from petroleum are known as petrochemicals

# Petrochemicals

| Hydrocarbon | Types of Compounds obtained |
|---|---|
| Methane | Halogen derivatives, Methanol, Formaldehyde, Formic Acid, Dimethyl Ether, Methyl esters, Acrylonitrile, Freon etc |
| Ethane | Ethyl Chloride, Ethyl Bromide, Acetic Acid, Nitroethane, Acetaldehyde, Ethyl ester, Ethers, Acetic Anhydride, Ethylene, Acetylene etc |
| Ethylene | Ethanol, Ethylene oxide, Glycol, Halogen derivatives, Vinyl chloride, Glyoxal, Acrylic acid, Butadiene, Acetaldehyde, Acetic acid etc |
| Propane | Halogen derivatives, Propanol, Propionic acid, Acetone, Propene, Nitropropane, Propyl ether etc |
| Propene | Allyl chloride, Allyl alcohol, Glycerol, Acetone, Mesityl chloride, Propylene oxide, Acrolein, Diacetone alcohol, Propylene glycol etc. |

# Petrochemicals

| Hydrocarbon | Types of Compounds obtained |
|---|---|
| Butane | Butene, Butadiene, Thiophene etc |
| Butene | Butanol, Butadiene, Methylethyl ketone, iso-octane etc. |
| Pentanes | Amyl alcohol, Amyl halide, Amines etc |
| N-Hexane | Benzene, Gammexane, DDT etc. |
| N-Heptane | Toluene, Benzoic acid, Saccharin etc. |
| Cycloalkanes | Benzene, Toluene, Xylene, Adipic acid etc. |
| Benzene & toluene | Benzyl halides, Benzyl alcohol, Benzoic acid, Benzaldehyde, TNT, Chloramin-T, Phthalic acid, tere phthalic acid etc. |

# Petrochemicals

- Almost every type of chemical having industrial application is now obtained from petroleum source.
- These petrochemicals serve as raw materials for many more derivatives and compounds of industrial use.

# Petrochemicals

- Allows conversion of crude oil & gas into products
- Petrochemicals are main building blocks for manufacturing all base chemicals & most consumer goods

## Synthetic fuel

- **Synthetic fuel** or **synfuel** is any liquid fuel obtained from coal, natural gas, or biomass.
- It can sometimes refer to fuels derived from other solids such as oil shale, tar sand, waste plastics, or from the fermentation of biomatter.
- It can also (less often) refer to gaseous fuels produced in a similar way.

## Synthetic fuel

- Depending on the initial feedstock, the process of producing synfuels is often referred to as
  - Coal-To-Liquids (CTL),
  - Gas-To-Liquids (GTL)
  - Biomass-To-Liquids (BTL),
- Many current projects are also now combining coal and biomass feedstocks, creating hybrid synthetic fuels loosely categorized as
  - Coal and Biomass To Liquids (CBTL).
- Synthetic crude may also be created by upgrading bitumen (a tar like substance found in tar sands), or synthesizing liquid hydrocarbons from oil shale and synthesis gas: a mixture of carbon monoxide and hydrogen.

## Synthetic fuel

- An important consideration for synthetic petrol is the availability of starting material.
  - It should be readily available
  - It should be low priced
- The most common raw material fulfilling these conditions is COAL
- Two common methods for obtaining synthetic petrol are
  - **Bergius Process**
  - **Fischer-Tropsch process**

## Bergius process

- The **Bergius Process** is a method of production of liquid hydrocarbons for use as synthetic fuel by hydrogenation of high-volatile bituminous coal at high temperature and pressure. It was first developed by Friedrich Bergius in 1913.

## Bergius Process

- The Bergius process was used for the production of synthetic gasoline in Germany during World War II
- Towards the end of WWII most of the fuel consumed by the German forces was produced in this way.
- At present there are no plants operating the Bergius Process or its derivatives commercially.
- The largest demonstration plant was the 200 ton per day plant at Bottrop, Germany, operated by Ruhrkohle, which ceased operation in 1993.
- There are reports of the Chinese company constructing a plant with a capacity of 4 000 ton per day. It was expected to become operational in 2007, but there has been no confirmation that this was achieved.

## Bergius Process

- The coal is finely ground and dried in a stream of hot gas.
- The dry product is mixed with heavy oil recycled from the process.
- Catalyst is typically added to the mixture.
- A number of catalysts have been developed over the years, including
  - tungsten or molybdenum sulfides,
  - tin or nickel oleate,
- Alternatively, iron sulphides present in the coal may have sufficient catalytic activity for the process, which was the original Bergius process.

## Bergius Process

- The mixture is pumped into a reactor. The reaction occurs at between 400 to 500 °C and 200 to 250 atmosphere pressure. The reaction produces heavy oils, middle oils, gasoline, and gases. The overall reaction can be summarized as follows:

$$nC + (n+1)H_2 \longrightarrow C_nH_{2n+2}$$

## Bergius Process

- The immediate product from the reactor must be stabilized by passing it over a conventional hydrotreating catalyst.
- The product stream is high in naphthenes and aromatics, low in paraffins and very low in olefins.
- The different fractions can be passed to further processing (cracking, reforming) to output synthetic fuel of desirable quality.
- If passed through a process such as Platforming, most of the naphthenes are converted to aromatics and the recovered hydrogen recycled to the process.
- The liquid product from Platforming will contain over 75% aromatics and has a RON of over 105.

## Fischer-Tropsch Process

- The **Fischer-Tropsch process** (or Fischer-Tropsch Synthesis) is a catalyzed chemical reaction in which synthesis gas (syngas), a mixture of carbon monoxide and hydrogen, is converted into liquid hydrocarbons of various forms.
- The most common catalysts are based on iron and cobalt, although nickel and ruthenium have also been used.
- The principal purpose of this process is to produce a synthetic petroleum substitute, typically from coal, natural gas or biomass, for use as synthetic lubrication oil or as synthetic fuel. This synthetic fuel runs trucks, cars, and some aircraft engines.

## Fischer-Tropsch Process

History

- Since the invention of the original process by the German researchers Franz Fischer and Hans Tropsch, working at the Kaiser Wilhelm Institute in the 1920s, many refinements and adjustments have been made,
- The term "Fischer-Tropsch" now applies to a wide variety of similar processes
  - **Fischer-Tropsch synthesis** or
  - **Fischer-Tropsch chemistry**.
- Fischer and Tropsch filed a number of patents, e.g. US patent no. 1,746,464, applied 1926, published 1930.
- The process was invented in petroleum-poor but coal-rich Germany in the 1920s, to produce liquid fuels. It was used by Germany and Japan during World War II to produce *ersatz* fuels. Germany's synthetic fuel production reached more than 124,000 barrels per day (19,700 $m^3$/d) from 25 plants ~ 6.5 million tons in 1944.

## Fischer-Tropsch Process

- The Fischer-Tropsch process involves a variety of competing chemical reactions, which lead to a series of desirable products and undesirable byproducts.
- The most important reactions are those resulting in the formation of alkanes. These can be described by chemical equations of the form:

$$(2n+1)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O$$

  - where 'n' is a positive integer.
- The simplest of these (n=1), results in formation of methane, which is generally considered an unwanted byproduct
  - particularly when methane is the primary feedstock used to produce the synthesis gas

## Fischer-Tropsch Process

- Process conditions and catalyst composition are usually chosen, so as to favor higher order reactions (n>1) and thus minimize methane formation.
- Most of the alkanes produced tend to be straight-chained, although some branched alkanes are also formed.
- In addition to alkane formation, competing reactions result in the formation of **alkenes**, as well as **alcohols** and other oxygenated hydrocarbons. Usually, only relatively small quantities of these non-alkane products are formed, although catalysts favoring some of these products have been developed.
- Another important reaction is the water gas shift reaction:

$$H2O + CO \rightarrow H2 + CO2$$

- Although this reaction results in formation of unwanted $CO_2$, it can be used to shift the $H_2$:CO ratio of the incoming Synthesis gas. This is especially important for synthesis gas derived from coal, which tends to have a ratio of ~0.7 compared to the ideal ratio of ~2.

## Fischer-Tropsch Process

- Generally, the Fischer-Tropsch process is operated in the temperature range of 150-300°C (302-572°F).
- Higher temperatures lead to faster reactions and higher conversion rates, but also tend to favor methane production.
- As a result the temperature is usually maintained at the low to middle part of the range.
- Increasing the pressure leads to higher conversion rates and also favors formation of long-chained alkanes both of which are desirable.
- Typical pressures are in the range of one to several tens of atmospheres. Chemically, even higher pressures would be favorable, but the benefits may not justify the additional costs of high-pressure equipment.
- A variety of synthesis gas compositions can be used. For cobalt-based catalysts the optimal $H_2$:CO ratio is around 1.8-2.1. Iron-based catalysts promote the water-gas-shift reaction and thus can tolerate significantly lower ratios. This can be important for synthesis gas derived from coal or biomass, which tend to have relatively low $H_2$:CO ratios (<1).

## Fischer-Tropsch Catalysts

- A variety of catalysts can be used for the Fischer-Tropsch process
- The most common are the transition metals cobalt, iron, and ruthenium.
- Nickel can also be used, but tends to favor methane formation.
- Cobalt seems to be the most active catalyst, although iron also performs well and can be more suitable for low-hydrogen-content synthesis gases such as those derived from coal due to its promotion of the water-gas-shift reaction.
- In addition to the active metal the catalysts typically contain a number of promoters, including potassium and copper, as well as high-surface-area binders/supports such as silica, alumina, or zeolites.

## Synthesis gas production

- The initial reactants (synthesis gases) used in the Fischer-Tropsch process are hydrogen gas ($H_2$) and carbon monoxide (CO). These chemicals are usually produced by one of two methods:
  - 1. The partial combustion of a hydrocarbon:
    - $C_nH_{(2n+2)} + ½\, nO_2 \rightarrow (n+1)H_2 + nCO$
      - When n=1 (methane), the equation becomes
      - $2CH_4 + O_2 \rightarrow 4H_2 + 2CO$
  - 2. The gasification of coal, biomass, or natural gas:
    - $CH_x + H_2O \rightarrow (1+0.5x)H_2 + CO$
      - The value of "x" depends on the type of fuel. For example, natural gas has a greater hydrogen content (x=2 to x=4) than coal (x<2).
    - The energy needed for this endothermic reaction is usually provided by the (exothermic) combustion of oxygen and the hydrocarbon source.

## Fischer-Tropsch Process

- The mixture of carbon monoxide and hydrogen is called synthesis gas or syngas. The resulting hydrocarbon products are refined to produce the desired synthetic fuel.
- The carbon dioxide and carbon monoxide is generated by partial oxidation of coal and wood-based fuels. The utility of the process is primarily in its role in producing fluid hydrocarbons from a solid feedstock, such as coal or solid carbon-containing wastes of various types. Non-oxidative pyrolysis of the solid material produces syngas which can be used directly as a fuel without being taken through Fischer-Tropsch transformations. If liquid petroleum-like fuel, lubricant, or wax is required, the Fischer-Tropsch process can be applied.

## Fischer-Tropsch Process

- The synthetic petroleum or a mixture of hydrocarbon obtained by this process is subjected to fractional distillation to obtain petrol and other fractions.
- The yields of petroleum are similar to those obtained by the Bergius process but the overall yield of petrol is slightly higher in this process