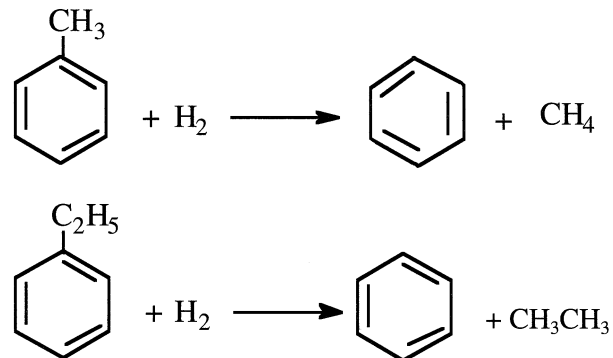


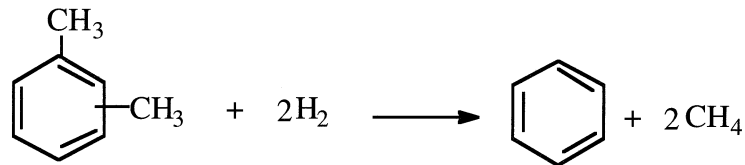
# Lecture Seven

## Hydrodealkylation Process

This process is designed to hydrodealkylate methylbenzenes, ethylbenzene and  $C_9^+$  aromatics to benzene. The petrochemical demand for benzene is greater than for toluene and xylenes. After separating benzene from the reformat, the higher aromatics are charged to a hydrodealkylation unit. The reaction is a hydrocracking one, where the alkyl side chain breaks and is simultaneously hydrogenated. For example, toluene dealkylates to methane and benzene, while ethylbenzene produces ethane and benzene. In each case one mole of  $H_2$  is consumed:



Consuming hydrogen is mainly a function of the number of benzene substituents. Dealkylation of polysubstituted benzene increases hydrogen consumption and gas production (methane). For example, dealkylating one mole xylene mixture produces two methane moles and one mole of benzene; it consumes two moles of hydrogen.



Unconverted toluene and xylenes are recycled.

## Hydrotreatment Processes

Hydrotreating is a hydrogen-consuming process primarily used to reduce or remove impurities such as sulfur, nitrogen, and some trace metals from the feeds. It also stabilizes the feed by saturating olefinic compounds. Feeds to hydrotreatment units vary widely; they could be any petroleum fraction, from naphtha to crude residues. The process is relatively simple: choosing the desulfurization process depends largely on the feed type, the level of impurities present, and the extent of treatment needed to suit the market requirement.

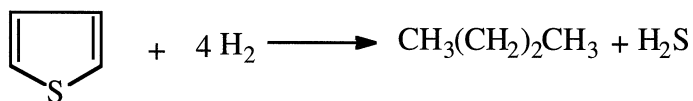
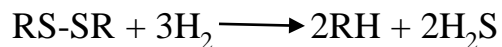
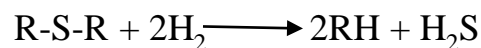
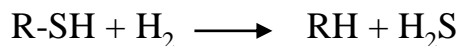
In this process, the feed is mixed with hydrogen, heated to the proper temperature, and introduced to the reactor containing the catalyst. The conditions are usually adjusted to minimize hydrocracking. Typical reactor temperatures range from 260 to 425°C. Hydrogen partial pressure and space velocity are important process variables. Increasing the temperature and hydrogen partial pressure increases the hydrogenation and hydrodesulfurization reactions. Lower space velocities are used with feeds rich in polyaromatics. Total pressure varies widely—from 100 to 3,000 psi—depending on the type of feed, level of impurities, and the extent of hydrotreatment required.

### **Hydrotreatment Catalysts and Reactions**

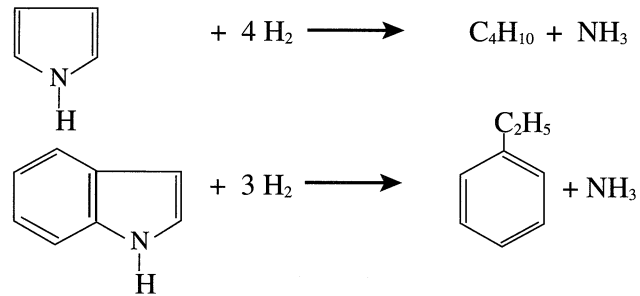
Catalysts used in hydrotreatment (hydrodesulfurization, HDS) processes are the same as those developed in Germany for coal hydrogenation during World War II. The catalysts should be sulfur-resistant. The cobalt-molybdenum system supported on alumina was found to be an effective catalyst.

The catalyst should be reduced and sulfided during the initial stages of operation before use. Other catalyst systems used in HDS are NiO/MoO<sub>3</sub> and NiO/WO<sub>3</sub>. Because mass transfer has a significant influence on the reaction rates, catalyst performance is significantly affected by the particle size and pore diameter.

Reactions occurring in hydrotreatment units are mainly hydrodesulfurization and hydrodenitrogenation of sulfur and nitrogen compounds. In the first case H<sub>2</sub>S is produced along with the hydrocarbon. In the latter case, ammonia is released. The following examples are hydrodesulfurization reactions of some representative sulfur compounds present in petroleum fractions and coal liquids.



Examples of hydrodenitrogenation of two types of nitrogen compounds normally present in some light and middle crude distillates are shown as follows:



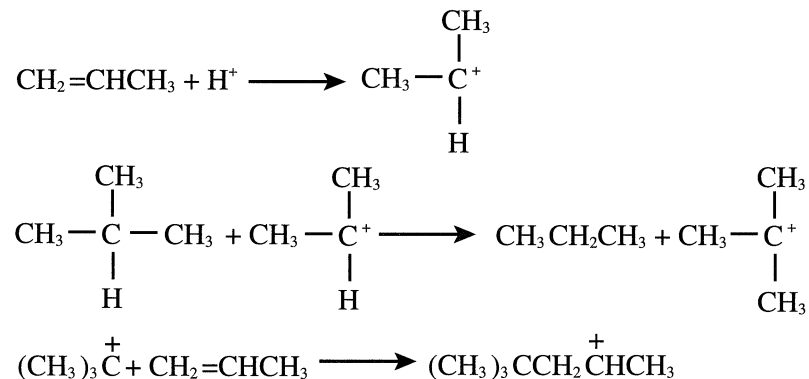
## Alkylation Process

Alkylation in petroleum processing produces larger hydrocarbon molecules in the gasoline range from smaller molecules. The products are branched hydrocarbons having high octane ratings.

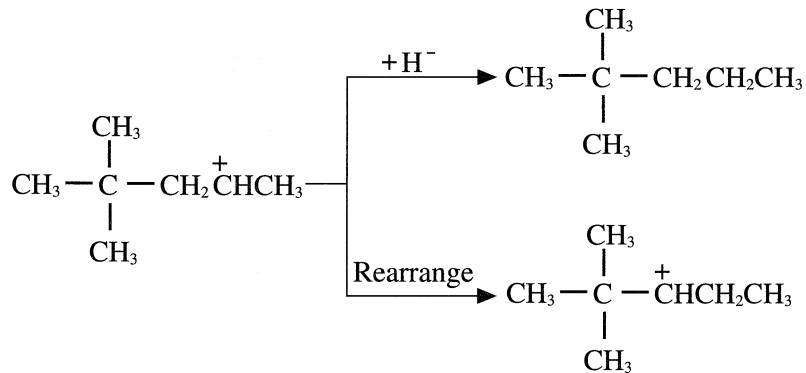
The term alkylation generally is applied to the acid catalyzed reaction between isobutane and various light olefins, and the product is known as the alkylate. Alkylates are the best of all possible motor fuels, having both excellent stability and a high octane number.

Either concentrated sulfuric acid or anhydrous hydrofluoric acid is used as a catalyst for the alkylation reaction. These acid catalysts are capable of providing a proton, which reacts with the olefin to form a carbocation.

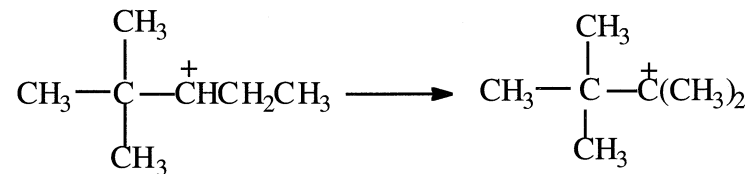
For example, when propene is used with isobutane, a mixture of C<sub>5</sub> isomers is produced. The following represents the reaction steps:



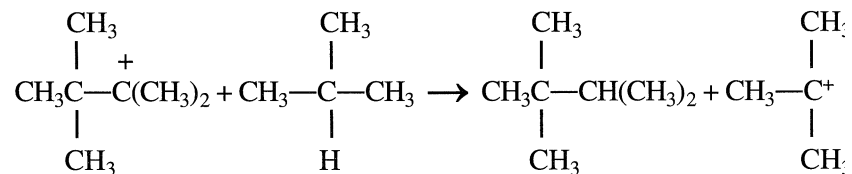
The formed carbocation from the last step may abstract a hydride ion from an isobutane molecule and produce 2,2-dimethylpentane, or it may rearrange to another carbocation through a hydride shift.



The new carbocation can rearrange again through a methide/hydride shift as shown in the following equation:



The rearranged carbocation finally reacts with isobutane to form 2,2,3-trimethylbutane.



The final product contains approximately 60–80% 2,2-dimethylpentane and varying amounts of 2,2,3-trimethylbutane and 2-methylhexane.

The primary process variables affecting the economics of sulfuric acid alkylation are the reaction temperature, isobutane recycle rate, reactor space velocity, and spent acid strength. To control fresh acid makeup, spent acid could be monitored by continuously measuring its density, the flow rate, and its temperature. This can reduce the acid usage in alkylation units.

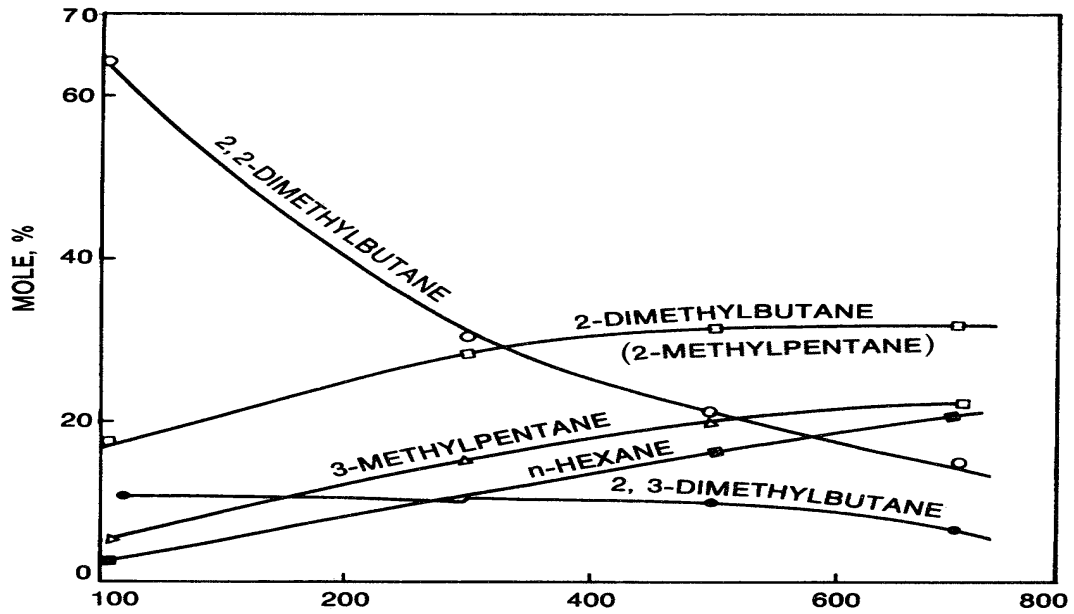


The presence of impurities such as butadiene affects the product yield and properties. Butadiene tends to polymerize and form acid-soluble oils, which increases acid makeup requirements. For every pound of butadiene in the feed, ten pounds of additional make-up acid will be required.

## **Isomerization Process**

Isomerization is a small-volume but important refinery process. Like alkylation, it is acid catalyzed and intended to produce highly-branched hydrocarbon mixtures. The low octane  $C_5/C_6$  fraction obtained from natural gasoline or from a light naphtha fraction may be isomerized to a high octane product.

Dual-function catalysts activated by either inorganic or organic chlorides are the preferred isomerization catalysts. A typical catalyst is platinum with a zeolite base. These catalysts serve the dual purpose of promoting carbonium ion formation and hydrogenation-dehydrogenation reactions. The reaction may start by forming a carbocation via abstraction of a hydride ion by a catalyst acid site. Alternatively, an olefin formed on the catalyst surface could be protonated to form the carbocation. The carbocation isomerizes by a 1,2-hydride/methide shift as mentioned earlier. Figure 3-10 shows the vapor phase equilibrium of hexane isomers.

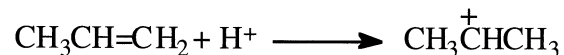


**Figure 3-10.** Vapor phase equilibrium for hexanes.

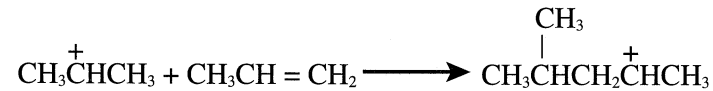
## Oligomerization of Olefins (Dimerization)

This process produces polymer gasoline with a high octane. Dimerization was first used (1935) to dimerize isobutylene to diisobutylene, constituted of 2,4,4-trimethyl-1-pentene (80%) and 2,4,4-trimethyl-2-pentene (20%). Both phosphoric and sulfuric acid were used as catalysts. At present, the feedstock is either a propylene-propane mixture or propylene-butane mixture where propane and butane are diluents. The product is an olefin having a high octane number. When propylene is used, a trimer or a tetramer is formed. The polymerization reaction is highly exothermic, so the temperature has to be controlled. The presence of propane and butane in the mixture acts as a heat sink to absorb part of the reaction heat. Typical reaction conditions are 170–250°C and 25–100 atm.

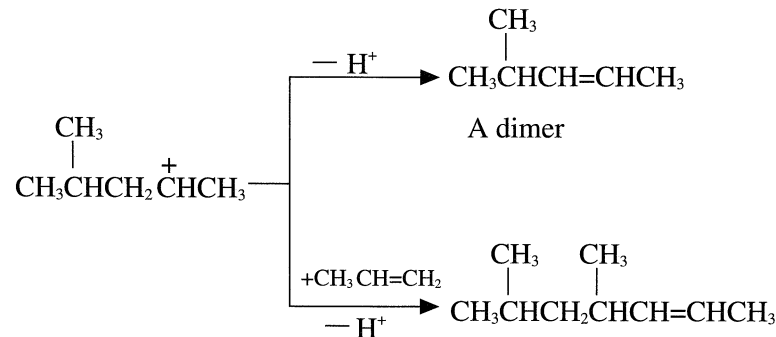
The polymerization reaction starts by protonating the olefin and forming a carbocation. For example, protonating propene gives isopropyl carbocation. The proton is provided by the ionization of phosphoric acid:



The next step is the reaction of the carbocation with the olefin (propene or butene).



The newly-formed carbocation either eliminates a proton and forms a dimer or attacks another propene molecule and eliminates a proton, giving the trimer.



Further protonation of the trimer produces a C<sub>9</sub> carbocation which may further react with another propene molecule and eventually produce propylene tetramer.

The product is a mixture of dimers, trimers, tetramers, and pentamers having an average RON (Research Octane Number) = 95. Table 3-14 shows the analysis of feed and products from dimerization of propylene.

**Table 3-14**  
**Typical feed and products from the dimerization of propylene**

	Vol. %	Total	wt %	Total
<b>Feed</b>				
Propylene	71	-	-	-
Propane	29	100	-	-
<b>Products</b>				
LPG				
Propylene	4.2	-	-	-
Propane	34.6	-	-	-
Isohexanes	61.2	100	-	-
Isohexenes	-	-	92.0	-
Isononenes	-	-	6.5	-
Heavier	-	-	1.5	100

## CHAPTER FOUR

### Nonhydrocarbon Intermediates

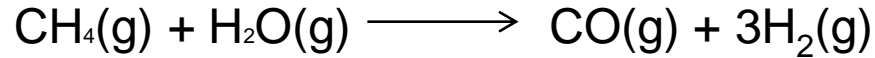
#### SYNTHESIS GAS

Synthesis gas generally refers to a mixture of carbon monoxide and hydrogen. The ratio of hydrogen to carbon monoxide varies according to the type of feed, the method of production, and the end use of the gas.

During World War II, the Germans obtained synthesis gas by gasifying coal. The mixture was used for producing a liquid hydrocarbon mixture in the gasoline range using Fischer-Tropsch technology. Although this route was abandoned after the war due to the high production cost of these hydrocarbons, it is currently being used in South Africa, where coal is inexpensive .

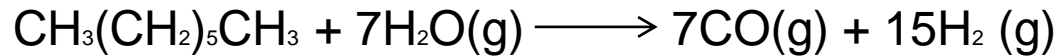
There are different sources for obtaining synthesis gas. It can be produced by steam reforming or partial oxidation of any hydrocarbon ranging from natural gas (methane) to heavy petroleum residues. It can also be obtained by gasifying coal to a medium Btu gas (medium Btu gas consists of variable amounts of CO, CO<sub>2</sub>, and H<sub>2</sub> and is used principally as a fuel gas). Figure 4-5 shows the different sources of synthesis gas.

A major route for producing synthesis gas is the steam reforming of natural gas over a promoted nickel catalyst at about 800°C:

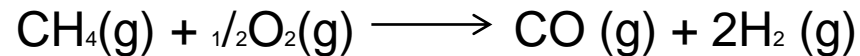
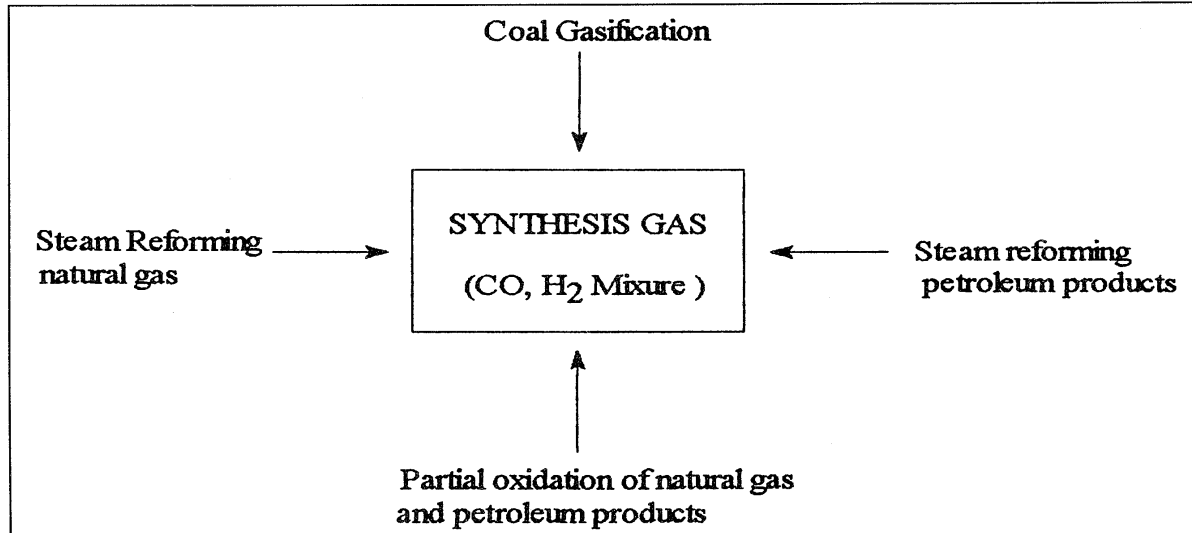


This route is used when natural gas is abundant and inexpensive, as it is in Saudi Arabia and the USA.

In Europe, synthesis gas is mainly produced by steam reforming naphtha. Because naphtha is a mixture of hydrocarbons ranging approximately from  $\text{C}_5$ - $\text{C}_{10}$ , the steam reforming reaction may be represented using n-heptane:



As the molecular weight of the hydrocarbon increases (lower H/C feed ratio), the  $\text{H}_2$  /CO product ratio decreases. The  $\text{H}_2$  /CO product ratio is approximately 3 for methane, 2.5 for ethane, 2.1 for heptane, and less than 2 for heavier hydrocarbons. Noncatalytic partial oxidation of hydrocarbons is also used to produce synthesis gas, but the  $\text{H}_2$  /CO ratio is lower than from steam reforming:



In practice, this ratio is even lower than what is shown by the stoichiometric equation because part of the methane is oxidized to carbon dioxide and water. When resids are partially oxidized by oxygen and steam at 1400–1450°C and 55–60 atmospheres, the gas consists of equal parts of hydrogen and carbon monoxide. Table 4-2 compares products from steam reforming natural gas with products from partial oxidation of heavy fuel oil.



**Table 4-2**

**Composition of synthesis gas from steam reforming natural gas and partial oxidation of fuel oil**

Process	Volume % dry sulfur free				
	CO	H <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub> +A	CH <sub>4</sub>
Steam reforming natural gas	15.5	75.7	8.1	0.2	0.5
Partial oxidation- heavy fuel oil	47.5	46.7	4.3	1.4	0.3

## **USES OF SYNTHESIS GAS**

Synthesis gas is an important intermediate. The mixture of carbon monoxide and hydrogen is used for producing methanol. It is also used to synthesize a wide variety of hydrocarbons ranging from gases to naphtha to gas oil using Fischer Tropsch technology. This process may offer an alternative future route for obtaining olefins and chemicals. The hydroformylation reaction (Oxo synthesis) is based on the reaction of synthesis gas with olefins for the production of Oxo aldehydes and alcohols.

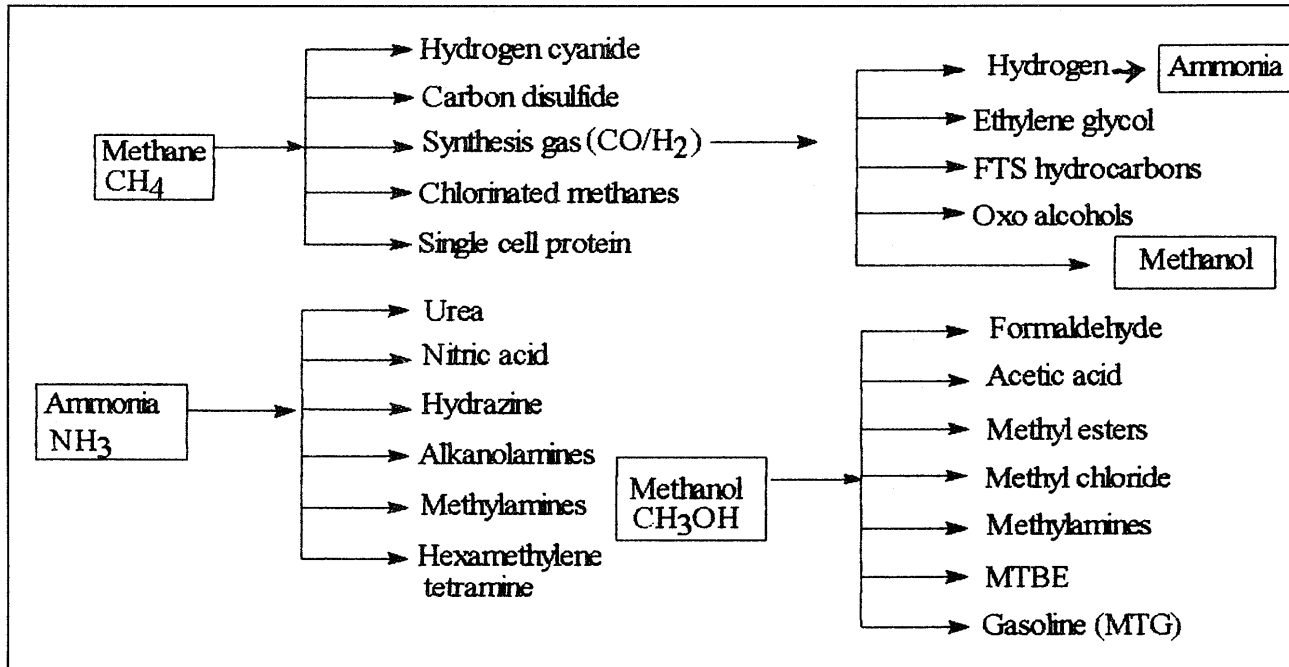
Synthesis gas is a major source of hydrogen, which is used for producing ammonia. Ammonia is the host of many chemicals such as urea, ammonium nitrate, and hydrazine. Carbon dioxide, a by-product from synthesis gas, reacts with ammonia to produce urea.

## CHAPTER FIVE

### Chemicals Based on Methane

#### INTRODUCTION

As mentioned in Chapter 2, methane is a one-carbon paraffinic hydrocarbon that is not very reactive under normal conditions. Only a few chemicals can be produced directly from methane under relatively severe conditions. Chlorination of methane is only possible by thermal or photochemical initiation. Methane can be partially oxidized with a limited amount of oxygen or in presence of steam to a synthesis gas mixture. Many chemicals can be produced from methane via the more reactive synthesis gas mixture. Synthesis gas is the precursor for two major chemicals, ammonia and methanol. Both compounds are the hosts for many important petrochemical products. Figure 5-1 shows the important chemicals based on methane, synthesis gas, methanol, and ammonia.



**Figure 5-1.** Important chemicals based on methane, synthesis gas, ammonia, and methanol.

## SYNTHESIS GAS (STEAM REFORMING OF NATURAL GAS)

Synthesis gas may be produced from a variety of feed stocks. Natural gas is the preferred feedstock when it is available from gas fields (non-associated gas) or from oil wells (associated gas).

The first step in the production of synthesis gas is to treat natural gas to remove hydrogen sulfide. The purified gas is then mixed with steam and introduced to the first reactor (primary reformer). The reactor is constructed from vertical stainless steel tubes lined in a refractory furnace. The steam to natural gas ratio varies from 4–5 depending on natural gas composition (natural gas may contain ethane and heavier hydrocarbons) and the pressure used.

A promoted nickel type catalyst contained in the reactor tubes is used at temperature and pressure ranges of 700–800°C and 30–50 atmospheres, respectively. The reforming reaction is equilibrium limited. It is favored at high temperatures, low pressures, and a high steam to carbon ratio. These conditions minimize methane slip at the reformer outlet and yield an equilibrium mixture that is rich in hydrogen.

The product gas from the primary reformer is a mixture of  $H_2$ ,  $CO$ ,  $CO_2$ , unreacted  $CH_4$ , and steam.