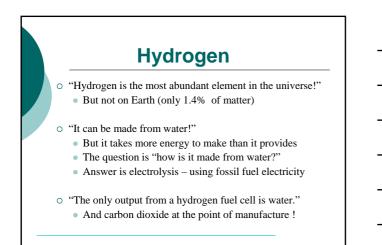


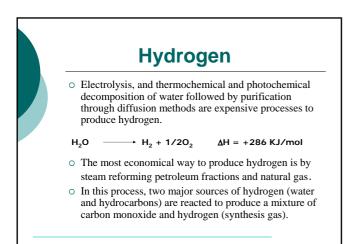
INTRODUCTION

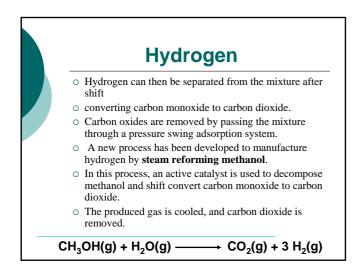
- From natural gas, crude oils, and other fossil materials such as coal, few intermediates are produced that are not hydrocarbon compounds.
- The important intermediates discussed in this chapter are hydrogen, sulfur, carbon black, and synthesis gas.
- $\,\circ\,$ Synthesis gas consists of a mixture (H₂,CO) obtainable from more than one source.
- Naphthenic acids and cresylic acid, which are extracted from certain crude oil fractions, are briefly reviewed at the end of the chapter.

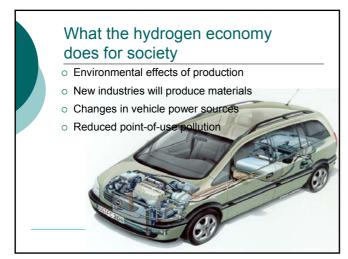
Hydrogen

- $\circ~$ The lightest element in the known universe.
- Water, natural gas, crude oils, hydrocarbons, and other organic fossil materials are major sources of hydrogen.
- A versatile fuel.
- Chemically, hydrogen is a very reactive element.
- $\circ~$ Occurs only with some other elements on earth
 - Free hydrogen exists on the sun.









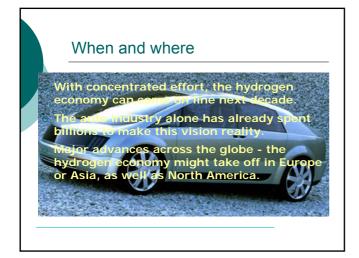
Many significant accomplishments...

o Fuel cells have improved by orders of magnitude

- Doubling of solid phase hydrogen storage capacity
- Expanding options to make, store and use hydrogen
- Vehicle material content becomes ever more sophisticated

...but challenges remain

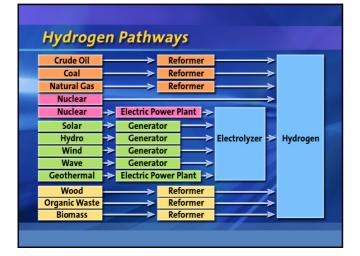
- Reduce the cost of fuel cells while improving durability.
- Reduce cost, and improved function of storage.
- Establish a production and delivery infrastructure nationwide/worldwide.
- Establish the nanotech industry on a scale to serve the energy and transportation industries.



Hydrogen production

- Currently done by steam reforming hydrocarbons, but diverse options exist
- Clean production options may use nanoscale technology
- Current cost is too high, and supply only meets current needs
- Advances could be used now









o A manufactured fuel - not a naturally occurring one

- o U.S. hydrogen production (40 megatons/yr)
 - Mostly from fossil fuels (96%)

 Natural gas (48%), oil (30%), coal (18%)
 4% from mostly coal generated electricity
- Pollutants from producing hydrogen
 Carbon dioxide
 - Other gases from fossil fuel based hydrogen

SULFUR

- Most industrial processes that involve H₂S containing streams utilize the Claus process for the recovery of sulphur to minimize SOX emissions.
- $\circ~$ The Claus process requires partial combustion of $\rm H_2S$ to form SO_2.
- Elemental sulfur is recovered by reacting the remaining H₂S with SO₂; for optimum operation, the composition of the gases must be maintained such that the H₂S / SO₂ ratio is 2:1.

USES OF SULFUR

- Sulfuric acid production.
- Flower sulfur is used in match production and in certain pharmaceuticals.
- o Sulfur is also an additive in high pressure lubricants.
- Sulfur asphalt pavements. Sulfur can replace 30-50% of the asphalt in the blends used for road construction.
- Road surfaces made from asphalt-sulfur blends have nearly double the strength of conventional pavement.
- o Such roads are more resistant to climatic conditions.

USES OF SULFUR

• The impregnation of concrete with molten sulfur is another potential large sulfur use.

- Concretes impregnated with sulfur have better tensile strength and corrosion resistance than conventional concretes. Sulfur is also used to produce phosphorous pentasulfide, a precursor for zinc dithiophosphates used as corrosion inhibitors.
- Sulfur reacts with nitrogen to form polymeric sulfur nitrides (SNX) or polythiazyls.

THE CLAUS PROCESS

- This process includes two main sections: the burner section with a reaction chamber that does not have a catalyst, and a Claus reactor section.
- In the burner section, part of the feed containing hydrogen sulfide and some hydrocarbons is burned with a limited amount of air.

THE CLAUS PROCESS

 The two main reactions that occur in this section are the complete oxidation of part of the hydrogen sulfide (feed) to sulfur dioxide and water and the partial oxidation of another part of the hydrogen sulfide to sulfur.

 $\circ\;$ The two reactions are exothermic:.

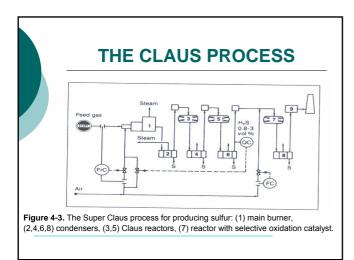
$$H_2S + 3/2O_2 \longrightarrow SO_2 + H_2O_2$$

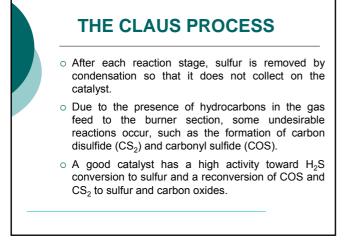
$$3H_2S + 3/2O_2 \longrightarrow 3/x S_x + 3H_2O$$

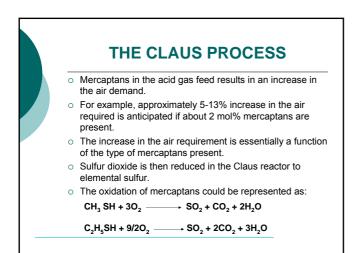


- In the second section, unconverted hydrogen sulfide reacts with the produced sulfur dioxide over a bauxite catalyst in the Claus reactor.
- Normally more than one reactor is available. In the Super-Claus process, three reactors are used. The last reactor contains a selective oxidation catalyst of high efficiency. The reaction is slightly exothermic:

 $2 H_2S + SO_2 \longrightarrow 3/x S_x + 2 H_2O$







SULFURIC ACID (H₂SO₄)

- Sulfuric acid is the most important and widely used inorganic chemical.
- Sulfuric acid is produced by the contact process where sulfur is burned in an air stream to sulfur dioxide, which is catalytically converted to sulfur trioxide.
- $\circ~$ The catalyst of choice is solid vanadium pentoxide $(V_2O_5).$
- The oxidation reaction is exothermic, and the yield is favored at lower temperatures.

SULFURIC ACID (H₂SO₄)

 $SO_2(g) + 1/2O_2(g) \longrightarrow SO_3(g)$ $\Delta H = -98.9 \text{ KJ}$

- The reaction occurs at about 450°C, increasing the rate at the expense of a higher conversion.
- To increase the yield of sulfur trioxide, more than one conversion stage (normally three stages) is used with cooling between the stages to offset the exothermic reaction heat.
- $\circ~$ Absorption of SO_3 from the gas mixture exiting from the reactor favors the conversion of SO_2.



- The absorbers contain sulfuric acid of 98% concentration which dissolves sulfur trioxide. The unreacted sulfur dioxide and oxygen are recycled to the reactor.
- The absorption reaction is exothermic, and special coolers are used to cool the acid:

 $SO_3(g) + H_2O(1) \longrightarrow H_2SO_4(1)$

Uses of Sulfuric Acid

o Sulfuric acid is primarily used to make fertilizers.

 It is also used in other major industries such as detergents, paints, pigments, and pharmaceuticals.

CARBON BLACK

- Carbon black is an extremely fine powder of great commercial importance, especially for the synthetic rubber industry.
- The addition of carbon black to tires lengthens its life extensively by increasing the abrasion and oil resistance of rubber.
- Carbon black consists of elemental carbon with variable amounts of volatile matter and ash. There are several types of carbon blacks, and their characteristics depend on the particle size, which is mainly a function of the production method.

CARBON BLACK

- Carbon black is produced by the partial combustion or the thermal decomposition of natural gas or petroleum distillates and residues.
- Petroleum products rich in aromatics such as tars produced from catalytic and thermal cracking units are more suitable feedstocks due to their high carbon/hydrogen ratios.
- These feeds produce blacks with a carbon content of approximately 92 wt%.

CARBON BLACK

 Coke produced from delayed and fluid coking units with low sulfur and ash contents has been investigated as a possible substitute for carbon black.

 Three processes are currently used for the manufacture of carbon blacks. These are the channel, the furnace, and the thermal processes.

CARBON BLACK THE CHANNEL PROCESS

 $\circ\;$ No more than 5% of the blacks are produced via this Process.

- In this process, the feed (e.g., natural gas) is burned in small burners with a limited amount of air.
- Some methane is completely combusted to carbon dioxide and water, producing enough heat for the thermal decomposition of the remaining natural gas.
- Channel black is characterized by having a lower pH, higher volatile matter, and smaller average particle size.

 $\begin{array}{c} \mathsf{CH}_4 + 2\mathsf{O}_2 & \longrightarrow & \mathsf{CO}_2 + 2\mathsf{H}_2\mathsf{O} & \Delta\mathsf{H} = \textbf{-799} \ \mathsf{KJ} \\ \mathsf{CH}_4 & \longrightarrow & \mathsf{C} + \mathsf{H}_2 & \Delta\mathsf{H} = \textbf{+} \ 92\mathsf{KJ} \end{array}$

CARBON BLACK THE FURNACE BLACK PROCESS

- The feed is first preheated and then combusted in the reactor with a limited amount of air.
- The hot gases containing carbon particles from the reactor are quenched with a water spray and then further cooled by heat exchange with the air used for the partial combustion.
- The type of black produced depends on the feed type and the furnace temperature.
- The average particle diameter of the blacks from the oil furnace process ranges between 200-500 Å, while it ranges between 400-700 Å from the gas furnace process.

CARBON BLACK THE THERMAL PROCESS

- In this process, the feed (natural gas) is pyrolyzed in preheated furnaces lined with a checker work of hot bricks.
- The pyrolysis reaction produces carbon, which collects on the bricks. The cooled bricks are then reheated after carbon black is collected.
- The average particle diameter from this process is large and ranges between 1800 Å for the fine thermal and 5000 Å for medium thermal black.

CARBON BLACK PROPERTIES AND USES

- The important properties of carbon black are particle size, surface area, and pH.
- These properties are functions of the production process and the feed properties.
- Channel blacks are generally acidic, while those produced by the Furnace and Thermal processes are slightly alkaline.
- The pH of the black has a pronounced influence on the vulcanization time of the rubber. (Vulcanization is a physicochemical reaction by which rubber changes to a thermosetting mass due to cross-linking of the polymer chains by adding certain agents such as sulfur.)
- The basic nature (higher pH) of furnace blacks is due to the presence of evaporation deposits from the water quench.

CARBON BLACK PROPERTIES AND USES

- Thermal blacks, due to their larger average particle size, are not suitable for tire bodies and tread bases, but they are used in inner tubes, footwear, and paint pigment.
- Gas and oil furnace blacks are the most important forms of carbon blacks and are generally used in tire treads and tire bodies.
- Carbon black is also used as a pigment for paints and printing inks, as a nucleation agent in weather modifications, and as a solar energy absorber.
- About 70% of the worlds' consumption of carbon black is used in the production of tires and tire products.
- Approximately 20% goes into other products such as footwear, belts, hoses, etc. and the rest is used in such items as paints, printing ink, etc.

SYNTHESIS GAS

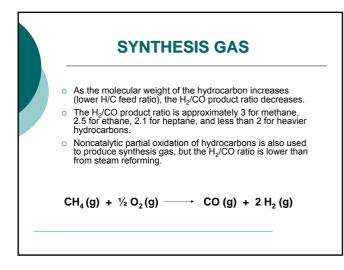
- Synthesis gas generally refers to a mixture of carbon monoxide and hydrogen. The ratio of hydrogen to carbon monoxide varies according to the type of feed, the method of production, and the end use of the gas.
- There are different sources for obtaining synthesis gas. It can be produced by steam reforming or partial oxidation of any hydrocarbon ranging from natural gas (methane) to heavy petroleum residues.
- A major route for producing synthesis gas is the steam reforming of natural gas over a promoted nickel catalyst at about 800°C.

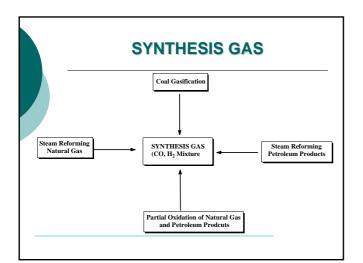
SYNTHESIS GAS

$CH_4(g) + H_2O(g) \longrightarrow CO + 3 H_2(g)$

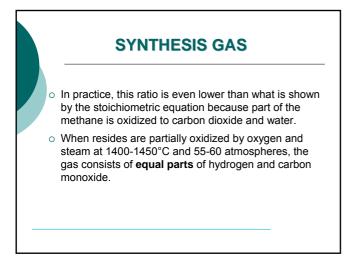
- This route is used when natural gas is abundant and inexpensive, as it is in Saudi Arabia and the USA.
- In Europe, synthesis gas is mainly produced by steam reforming naphtha. Because naphtha is a mixture of hydrocarbons ranging approximately from C5-C10, the steam reforming reaction may be represented using n-heptane.

 $CH_3(CH_2)_5CH_3 + 7 H_2O(g) \longrightarrow 7 CO(g) + 15 H_2(g)$









SYN"		313	GAS		
Composition of synthesis	Table gas fro		m reforr	ning natu	ural gas
and parti	al oxida	ation of	fuel oil		
		Volume	% dry s	sulfur fre	е
	со	H ₂	CO ₂	$N_2 + A$	CH₄
Steam reforming natural gas	15.5	75.7	8.1	0.2	0.5
oleann reionning natural gas					
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.

USES OF SYNTHESIS GAS

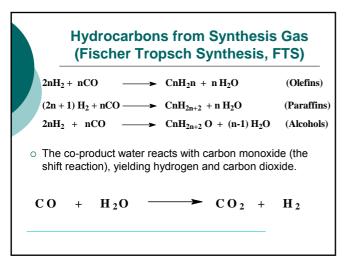
- The hydroformylation reaction (Oxo synthesis) is based on the reaction of synthesis gas with olefins for the production of Oxo aldehydes and alcohols.
- Synthesis gas is a major source of hydrogen, which is used for producing ammonia.
- Ammonia is the host of many chemicals such as urea, ammonium nitrate, and hydrazine. Carbon dioxide, a by-product from synthesis gas, reacts with ammonia to produce urea..



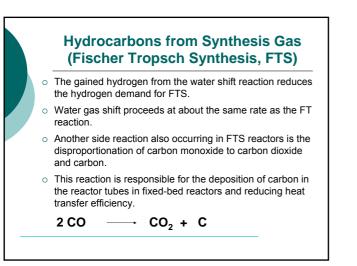
- Most of the production of hydrocarbons by Fischer Tropsch method uses synthesis gas produced from sources that yield a relatively low H₂/CO ratio, such as coal gasifiers. This, however, does not limit this process to low H₂/CO gas feeds.
- The process of obtaining liquid hydrocarbons from coal through FTS is termed indirect coal liquefaction.
- It was originally intended for obtaining liquid hydrocarbons from solid fuels.



- However, this method may well be applied in the future to the manufacture of chemicals through cracking the liquid products or by directing the reaction to produce more olefins.
- $\circ\;$ The reactants in FTS are carbon monoxide and hydrogen.
- The reaction may be considered a hydrogenative oligomerization of carbon monoxide in presence of a heterogeneous catalyst.







Hydrocarbons from Synthesis Gas (Fischer Tropsch Synthesis, FTS)

- Fischer Tropsch Synthesis is catalyzed by a variety of transition metals such as iron, nickel, and cobalt.
- $\circ\;$ Iron is the preferred catalyst due to its higher activity and lower cost.
- Nickel produces large amounts of methane, while cobalt has a lower reaction rate and lower selectivity than iron.
- By comparing cobalt and iron catalysts, it was found that cobalt promotes more middle-distillate products.
- In FTS, cobalt produces hydrocarbons plus water while iron catalyst produces hydrocarbons and carbon dioxide.
- It appears that the iron catalyst promotes the shift reaction more than the cobalt catalyst.

Hydrocarbons from Synthesis Gas (Fischer Tropsch Synthesis, FTS)

Two reactor types are used commercially in FTS, a fixed bed and a fluid-bed.

The **fixed-bed** reactors usually run **at lower temperatures to avoid carbon deposition** on the reactor tubes. Products from fixed-bed reactors are characterized by **low olefin content**, and they are generally heavier than products from fluid-beds.

- Heat distribution in **fluid-beds**, however, is better than fixedbed reactors, and fluid-beds are generally operated at higher temperatures.
- Example: Synthol fluid-bed reactor. Products are characterized by having more olefins, a high percent of light hydrocarbon gases, and lower molecular weight product slate than from fixed bed types.

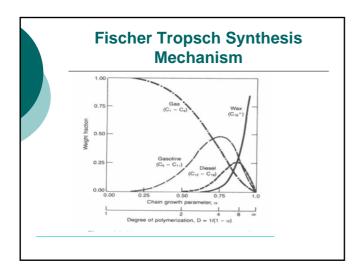
Hydrocarbons from Synthesis Gas (Fischer Tropsch Synthesis, FTS)

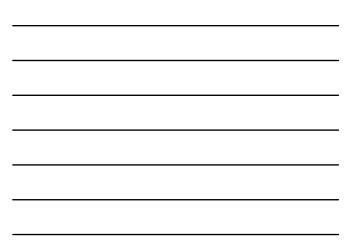
Table 4-3 Typical analysis of products from Fischer-Tropsch fixed and fluid bed reactors

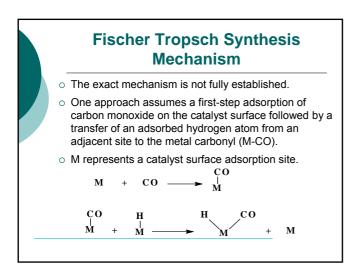
Conditions		Fixed-Bed	Fluid-Bed
Temperature ran	ge °F	425-450	625-650
Conversion %	-	65	85
H ₂ /CO ratio		1.7	2.8
Products %			
Hydrocarbon Gases C1-C4		21.1	51.0
	C5-C,12	19.0	31.0
	C13-C 18	15.0	5.0
	C19-C31, (Heavy oil)	41.0	6.0
Oxygenates		3.9	7.0

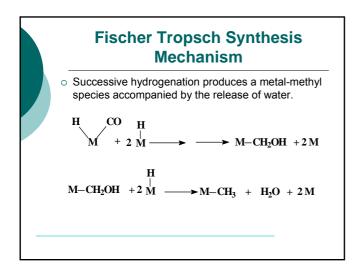
Fischer Tropsch Synthesis Mechanism The FTS mechanism could be considered a simple polymerization reaction, the monomer being a C1 species derived from carbon monoxide. This polymerization follows an Anderson- Schulz-Flory distribution of molecular weights.

- This distribution gives a linear plot of the logarithm of yield of product (in moles) versus carbon number.
- $\circ~$ Under the assumptions of this model, the entire product distribution is determined by one parameter, $\alpha,$ the probability of the addition of a carbon atom to a chain.

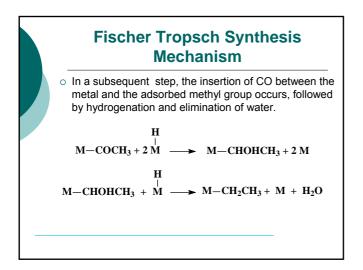




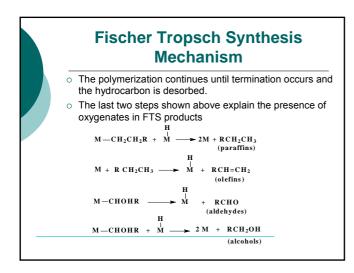




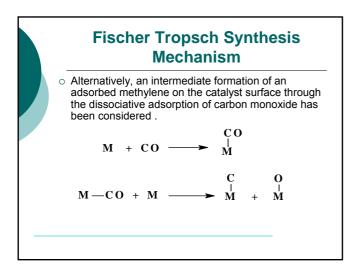




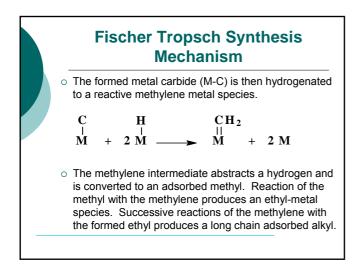




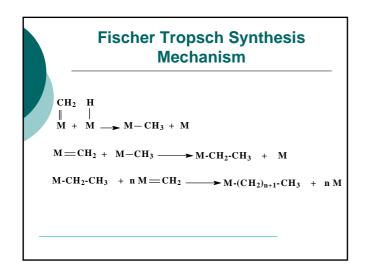


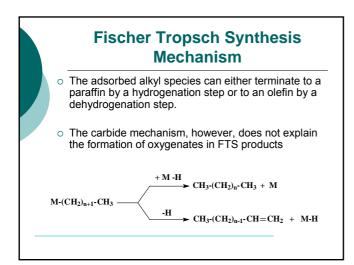


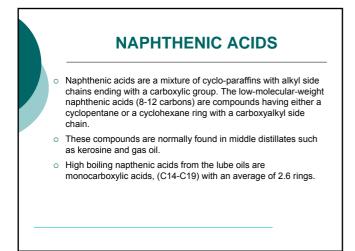






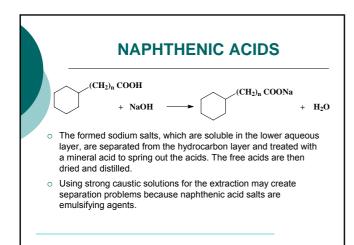






NAPHTHENIC ACIDS

- Naphthenic acids constitute about 50 wt% of the total acidic compounds in crude oils.
- Naphthenic-based crudes contain a higher percentage of naphthenic acids. Consequently, it is more economical to isolate these acids from naphthenic-based crudes.
- The production of naphthenic acids from middle distillates occurs by extraction with 7-10% caustic solution.



USES OF NAPHTHENIC ACIDS AND THEIR SALTS

- $\circ\;$ Free naphthenic acids are corrosive and are mainly used as their salts and esters.
- The sodium salts are emulsifying agents for preparing agricultural insecticides, additives for cutting oils, and emulsion breakers in the oil industry.
- Calcium naphthenate is a lubricating oil additive, and zinc naphthenate is an antioxidant.
- Lead, zinc, and barium naphthenates are wetting agents used as dispersion agents for paints.



- Some oil soluble metal naphthenates, such as those of zinc, cobalt, and lead, are used as driers in oil-based paints.
- Among the diversified uses of naphthenates is the use of aluminum naphthenates as gelling agents for gasoline flame throwers (napalm).
- Manganese naphthenates are well-known oxidation catalysts.

CRESYLIC ACIDS

- Cresylic acid is a commercial mixture of phenolic compounds including phenol, cresols, and xylenols.
- Cresylic acid constitutes part of the oxygen compounds found in crudes that are concentrated in the naphtha fraction obtained principally from naphthenic and asphaltic-based crudes.
- Phenolic compounds, which are weak acids, are extracted with relatively strong aqueous caustic solutions.
- Originally cresylic acid was obtained from caustic waste streams that resulted from treating light distillates with caustic solutions to reduce H₂S and mercaptans.

CRESYLIC ACIDS

- Currently, most of these streams are hydrodesulfurized, and the product streams practically do not contain phenolic compounds.
- Cresylic acid is still obtained to a lesser extent from petroleum fractions, especially cracked gasolines, which contain higher percentages of phenols. It is also extracted from coal liquids.
- Strong alkaline solutions are used to extract cresylic acid. The aqueous layer contains, in addition to sodium phenate and cresylate, a small amount of sodium naphthenates and sodium mercaptides.
- The reaction between cresols and sodium hydroxide gives sodium cresylate.

Table 4-5 Properties of Phenol, Cresols and Xylenols ²⁶						
Name	Formula	Mp(°C)	BP(°C)	204/4°C	pK a	K _a x 10 ⁻¹
Phenol	Ô	42.5	182	1.0722	10.0	1.1
C resols O-Cresol	СН,	31	191	1.02734	10.2	0.63
m-Cresol	Сп.	11	202	1.0336	10.1	0.98
p-C resol	OH C	35.5	2 0 2	1.0178	10.17	0.67
Xylenols	сн он сн,					
2,4-Dimethylphenol	он сност,	26	211	0.9650		
2,5-Dimethylphenol	он Сн ₃ Сн,	75	212			
3,4-Dimethylphenol	он	62.5	2.25	0.983		
3.5.Dimethylphenol	сн 💭 н,	68	219.5	0,9680		

CRESYLIC ACIDS

Mercaptans in the aqueous extract are oxidized to the disulfides, which are insoluble in water and can be separated from the cresylate solution by decantation.

 $2 \text{ RSH} + \frac{1}{2} \text{ O}_2 \longrightarrow \text{ R-S-S-R} + \text{ H}_2 \text{ O}$

- Free cresylic acid is obtained by treating the solution with a weak acid or dilute sulfuric acid.
- $\,\circ\,$ Refinery flue gases containing ${\rm CO_2}$ are sometimes used to release cresylic acid.

CRESYLIC ACIDS

Aqueous streams with low cresylic acid concentrations are separated by adsorption by passing them through one or more beds containing a high adsobent resin.

- $\circ~$ The resin is regenerated with 1% sodium hydroxide solution.
- The extraction of cresylic acid does not create an isolation problem with napthenic acids which are principally present in heavier fractions.
- Naphthenic acids, which are relatively stronger acids (lower pKa value), are extracted with less concentrated caustic solution.

USES OF CRESYLIC ACIDS

- Cresylic acid is mainly used as degreasing agent and as a disinfectant of a stabilized emulsion in a soap solution.
- Cresols are used as flotation agents and as wire enamel solvents.
- Tricresyl phosphates are produced from a mixture of cresols and phosphorous oxychloride. The esters are plasticizers for vinyl chloride polymers.
- $\circ\;$ They are also gasoline additives for reducing carbon deposits in the combustion chamber.