Lecture 2

Raw Material For Organic Chemical Industries
LECTURE 2
RAW MATERIAL FOR ORGANIC CHEMICAL INDUSTRIES

INTRODUCTION
Chemical process industry play an important role in the development of a country by providing a wide variety of products, which are being used in providing basic needs of rising population which is 6.4 billion globally and 1.2 billion in India in 2012. Chemical process industries uses raw material derived from petroleum and natural gas, salt, oil and fats, biomass and energy from coal, natural gas and a small percentage from renewable energy resources.
Although initially manufacture of organic chemicals initially started with coal and alcohol from fermentation industry, however later due to availability of petroleum and natural gas dominated the scene and now more than 90% of organic chemicals are produced from petroleum and natural gas routes. However, rising cost of petroleum and natural gas and continuous decrease in the reserves has spurred the chemical industry for alternative feedstock like coal, biomass, coal bed methane, shale gas, sand oil as an alternate source of fuel and chemical feedstock.

ENERGY RESOURCES
Energy play vital role an important role for the development of any country and to meet the challenges due to increasing population it has become one of the very important to optimize its use and look for alternative energy resources. Coal remains the dominant source of energy meeting 52.4% of India’s prime energy needs while oil and natural gas met 41.6% of energy requirement in 2008-09. Power sector accounted for 77% of the non-coking coal off-take. As per planning commission projections till 2032, coal will continue to have a dominant share meeting over 50% of primary commercial requirement [Dutta, 2011].
World and India Energy consumption scenario is given in Figure M-I 2.1 [Hindu Industrial directory, 2007]. The world energy consumption had projected to increase by 58% over a 24 year period from 2001 to 2025. The total energy use projected to grow from 404 in 2001 to 640
quadrillion BTU in 2025 [Energy outlook, 2003]. India’s requirement for fossil fuels by 2030 is estimated by various agencies is in the range of 337 to 462 million tones of oil, 99 to 184 million tones oil equivalent of gas and 602 to 954 million tones of coal Indian energy’s [Hindu industrial directory, 2007].

![Indian Energy Scenario](image)

**World 74.5 Bnbbl OE**

**India 2.7 Bnbbl OE**

*Figure M-I 2.1: Indian Energy Scenario*

Sources: Hindu industrial directory, 2007

**RAW MATERIALS FOR ORGANIC CHEMICAL INDUSTRIES**

Although initially manufacture of organic chemicals initially started with coal and alcohol from fermentation industry, however later due to availability of petroleum and natural gas dominated the scene and now more than 90% of organic chemicals are produce from petroleum and natural gas routes. However, rising cost of petroleum and natural gas and continuous decrease in the reserves as spurred the chemical industry for alternative feedstock like coal, biomass, coal bed methane, shale gas, sand oil as alternate source of fuel and chemical feedstock. Table M-I 2.1 gives the details of raw materials for chemical process industries. Raw materials for chemical industries are classified as primary raw materials and basic intermediates. Although major organic chemicals are produced from petroleum feed stock, however alternative raw materials are available which are getting attention. Detail of feedstock for organic chemical industries is
shown in Figure M-I 2.2. Table M-I 2.2 shows the details of natural gas and petroleum fractions as petrochemicals feedstock. Alternative Routes to Principal Organic Chemicals is given Table M-I 2.3

**Table M-I 2.1: Raw Material for Chemical Process Industries**

**Primary Raw Materials:**

<table>
<thead>
<tr>
<th>Gaseous</th>
<th>Natural gas, condensate, refinery gases, coal Bed methane, gas hydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquids</td>
<td>Naphtha, kerosene, gas oil, middle distillates</td>
</tr>
<tr>
<td>Solids</td>
<td>Coal, coke, wax, residues</td>
</tr>
<tr>
<td>Oils and fats</td>
<td>Tallow and coconut oil, palm oil and other oil</td>
</tr>
<tr>
<td><strong>Biomass</strong></td>
<td>Alcohol, paper, energy,</td>
</tr>
<tr>
<td><strong>Salt</strong></td>
<td>Chlorine, caustic soda, soda ash</td>
</tr>
<tr>
<td><strong>Sulphur</strong></td>
<td>Sulphuric acid, fertilizer,</td>
</tr>
<tr>
<td><strong>Lime stone</strong></td>
<td>Cement, lime</td>
</tr>
</tbody>
</table>

**Basic Intermediates:**

<table>
<thead>
<tr>
<th>Paraffins</th>
<th>Methane, propane, butane and higher hydrocarbons</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ethylene, propylene, butadiene, alcohol, vinyl chloride</td>
</tr>
<tr>
<td><strong>Olefins and derivatives</strong></td>
<td>Ethylene, propylene, butadiene, alcohol, vinyl chloride</td>
</tr>
<tr>
<td><strong>Aromatics</strong></td>
<td>Benzene Toluene Ethyl benzene, Xylenes, Naphthalene</td>
</tr>
</tbody>
</table>

**Secondary Intermediates:**

Monomer: Caprolactam, adipic acid, hexamethylene diamine, terephthalic acid and acrylonitrile for synthetic fibres, intermediates for dye stuff industry and pesticides.
Figure M-I 2.2: Feed Stock for Organic Chemical Industries
Table M-I 2.2: Natural Gas and Petroleum Fractions as Petrochemicals Feedstock

<table>
<thead>
<tr>
<th>Petroleum Fractions and Natural Gases</th>
<th>Source</th>
<th>Composition</th>
<th>Intermediate Processes</th>
<th>Intermediate Feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery Gases</td>
<td>Distillation, catalytic cracking, catalytic reforming</td>
<td>Methane, ethane, propane, butane, BP upto 25 °C</td>
<td>Liquefaction, cracking</td>
<td>LPG, ethylene, propylene, butane, butadiene.</td>
</tr>
<tr>
<td>Naphtha</td>
<td>Distillation and thermal &amp; catalytic cracking, visbreaking</td>
<td>C(<em>4)-C(</em>{12}) hydrocarbon, BP 70 - 200 °C</td>
<td>Cracking, reforming, alkylation, disproportionation, isomerisation</td>
<td>Ethylene, propylene, butane, butadiene, benzene, toluene, xylene</td>
</tr>
<tr>
<td>Kerosene</td>
<td>Distillation and secondary conversion processes</td>
<td>C(<em>9)-C(</em>{10}) hydrocarbon, BP 175-275 °C</td>
<td>Fractionation to obtain C(<em>{10})-C(</em>{14}) range hydrocarbon</td>
<td>Linear n C(<em>{10}) - n C(</em>{14}) alkanes</td>
</tr>
<tr>
<td>Gas Oil</td>
<td>Distillation of crude oil and cracking</td>
<td>C(<em>{10})-C(</em>{25}) hydrocarbons BP 200-400 °C</td>
<td>Cracking</td>
<td>Ethylene, propylene, butadiene, butylenes</td>
</tr>
<tr>
<td>Wax</td>
<td>Dewaxing of lubricating oil</td>
<td>C(<em>8)-C(</em>{56}) hydrocarbon</td>
<td>Cracking</td>
<td>C(<em>6)-C(</em>{20}) alkanes</td>
</tr>
<tr>
<td>Pyrolysis Gasoline</td>
<td>Ethylene cracker</td>
<td>Aromatic, alkenes, dienes, alkanes, cycloalkane</td>
<td>Hydrogenation distillation, extraction, crystallisation, adsorption</td>
<td>Aromatics</td>
</tr>
<tr>
<td>Natural Gases &amp; Natural Gas Condensate</td>
<td>Gas fields and crude oil stabilisation</td>
<td>Hydrogen, methane, ethane, propane, pentane, aromatics</td>
<td>Cracking, reforming, separation</td>
<td>Ethylene, propylene, LPG, aromatics, etc.</td>
</tr>
<tr>
<td>Petroleum Coke</td>
<td>Crude oil</td>
<td>Carbon</td>
<td>Residue upgradation processes, gasification</td>
<td>Carbon electrode, acetylene, fuel</td>
</tr>
</tbody>
</table>

Table M-I 2.3: Alternative Routes to Principal Organic Chemicals

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Petroleum Source</th>
<th>Alternate Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>Natural gas, Refinery light gases (de-methaniser overheads)</td>
<td>Coal, as by-product of separation of coke oven gases (1920-30) or of coal hydrogenation (1930-40)</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Methane Light liquid hydrocarbons</td>
<td>From coal via water gas (1910-20)</td>
</tr>
<tr>
<td>Methyl alcohol</td>
<td>Methane Light liquid hydrocarbons</td>
<td>From coal via water-gas (1920-30); from methane (from coal) by methane-stream and methane oxygen processes (1930-40)</td>
</tr>
<tr>
<td>Ethylene</td>
<td>Pyrolysis of gaseous liquid hydrocarbons</td>
<td>Dehydration of ethyl alcohol (original route). By-product in fractional distillation of coke oven gas (1925-35). Hydrogenation of acetylene (1940-45)</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Ethane</td>
<td>Calcium carbide (original process). methane from coal by partial combustion and by arc process (1935-45)</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>Ethylene</td>
<td>From ethylene made as above (1925). In America, from coal via carbon-monoxide and formaldehyde (1935-40)</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>Synthetic ethyl alcohol ,</td>
<td>Fermentation of molasses (original route)</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>Co-product of paraffin gas oxidation. Direct oxidation of ethylene</td>
<td>Fermentation of ethyl alcohol, or acetylene from carbide (1900-10)</td>
</tr>
<tr>
<td>Acetone</td>
<td>Propylene</td>
<td>Wood distillation (original process). Pyrolysis of acetic acid (1920-30) or by acetylene-stream reaction (1930-40)</td>
</tr>
<tr>
<td>Glycerol</td>
<td>Propylene</td>
<td>By-product of soap manufacture (original process)</td>
</tr>
<tr>
<td>Butadiene</td>
<td>2-Butenes Butane Synthetic ethyl alcohol By-product of ethylene by pyrolysis of liquid hydrocarbons</td>
<td>Ethyl alcohol (1915); acetaldehyde via 1:3-butandiol (1920-30); acetylene and formaldehyde from coal via 1:4-butandiol (1940-45); from 2:3-Butandiol by fermentation (1940-45)</td>
</tr>
<tr>
<td>Aromatic hydrocarbons</td>
<td>Aromatic-rich and naphthenic-rich fractions by catalytic reforming and direct extraction or by hydro-alkylation</td>
<td>By-products of coal-tar distillation</td>
</tr>
</tbody>
</table>

Source: Masood, R. “Role of Raw material in Petrochemical industry” Chemical Industry news, July 2002
 ROUTES TO PRODUCE CHEMICALS

- Steam Reforming and Partial Oxidation (Synthesis gas (CO+H₂ and H₂& N) to produce synthesis gas
- Cracking and Pyrolysis to olefins (C₂H₄, C₃H₆, C₄H₈ and olefins)
- By-products (Pyrolysis gasoline and Higher liquids, Gas condensate) for aromatics
- Catalytic Reforming to produce mainly BTX from naphtha.
- Dehydrogenation of Paraffin (Paraffin: ethane, paraffin) to produce olefin
- Petrocoke and Biomass gasification
- GTL (Gas to liquid), MTO (Methanol to Olefin),
- Coal to liquid fuel and coal to chemicals
- Dehydrogenation (olefin) and alkylation (alkylate) from kerosene for LAB
- Saponification of oil and fats and recovery of chemical from glycerin

 NATURAL GAS AS CHEMICAL FEED STOCK

- Chemicals from methane
- Chemicals from C₂ – C₄
- C₅+ (natural gasoline)
- Methane/total natural gas

 ROUTES FOR NATURAL GASES AS CHEMICAL FEED STOCK

- Cracking of natural gas to olefins, C₄ and C₅ chemicals
- Steam reforming and Partial oxidation for synthesis gas
  - Conventional steam reforming
  - Partial oxidation (POX)
  - Catalytic partial oxidation (CPO)
  - Combined reforming
  - Combined reforming with performer
  - Gas-heating reforming (GHR)
  - Auto-thermal reforming
  - Combined auto-thermal reforming (CAR)
  - Kellogg heat reforming exchanger system (KRES)
- Cyclar process: For production of aromatics from natural gas (Propane and butane)
- Oxidative coupling of methane (natural gas) to olefins

**NAPHTHA AS CHEMICAL FEED STOCK**

Naphtha is the most versatile chemical feedstock and its use depends on composition, boiling range, end use market requirements. Naphtha remains prominent feedstock (52%) for olefin production from steam cracker. Feedstock of olefins is shown in Figure M-I 2.3. Catalytic reforming of naphtha produces aromatics which is important chemical feed stock for organic chemical industries for producing synthetic fibre, pesticides explosive, dyes intermediate, plasticizer, solvent etc. Some of the routes for conversion of naphtha to petrochemicals are

**Steam reforming/ Partial oxidation of naphtha:** For production of synthesis gas and derivatives

**Cracking of naphtha:** For production of olefins, C4 and C5 hydrocarbons, pyrolysis gasoline for aromatic production

**Catalytic reforming of naphtha:** For production of aromatics- benzene, toluene, xylenes,

![Production by Feedstock](image)

*Figure M-I 2.3: Olefin Feed Stock*


**KEROSENE AS FEED STOCK FOR LAB**

**n-Paraffins from SR Kerosene :** n-Paraffins are extracted using adsorptive separation by molecular sieves. These paraffins are excellent feedstock for LAB. Various steps involved are:

**Kerosene Pre-fractionation:** To tailor the kerosene to desired carbon range
**Hydrotreatment:** To remove sulfur, nitrogen and olefins and oxygenates which might poison the Molex adsorbent.

**ALTERNATE FEED STOCK FOR CHEMICAL INDUSTRY**
In view of dwindling fossil fuel sources and increasing cost of crude and volatile market oil, there is tremendous activity all over world to utilize alternative feedstock’s alternative feedstock includes biomass and algae, coal, petrocoke, waste plastic for production of synthesis gas, olefin, methanol, ethanol and derivatives, naphtha.

**BIOMASS**
Biomass resources like crop residues, forage, grass, crops, wood residues, forest residues, short rotation energy crops and cellulosic components of municipal solid waste can be use as alternative feedstock for production of synthesis gas, ethanol, and naphtha through FT process. Alternative energy resources will play a growing role and biofuels mainly ethanol are expected to grow rapidly, reaching about 2% of total liquid supplies by 2030 [Singh et al., 2008]. Some of the routes for conversion of biomass to heat & power, transport fuels, bioethanol is given in Figure M-I 2.4 [Banerjee et al., 2011].

The constantly depleting resources of conventional energy and the steeply escalating price of fossil fuels have led to the need of alternate energy sources. Second generation production of bioethanol production is gaining increasing impetus due to abundant availability, high cellulose d hemicelluloses content of lingo-cellulose materials [Tuil et al., 2008]. Biotechnological route for bioethanol production utilizing lingo cellulose material involves delignification, sacchification and fermentation. The most common process of bioethanol production from sacchified lingo cellulosics involves hydrolysis of cellulose and fermentation in the same reactor [Lo, 2009]. Options for Conversion of Biomass to Fuel and Power and Chemical feed stock is given in Figure M-I 2.5.
Figure M-I 2.4: Biomass Conversion Technologies for Chemical Production
Source: Journal of the Petrotech Society, January 2007, p.37

Figure M-I 2.5: Options for Conversion of Biomass to Fuel and Power and Chemical feed stock
Sources: Mark et al., 2011
ETHANOL

There are three types of feedstocks for ethanol production [Tuli et al. 2008]

_Sugars:_ Molasses, cane sugar, beat sweet sorghum and fruits

_Starches:_ Corn, wheat, rice, potatoes, cassava, sweet potatoes etc

_Lignocellulosic:_ Straw, bagasse, other agricultural residues, wood, energy crops

_Algae:_ Ethanol production

Biomass can be also used a feedstock for methanol production and hydrogen through synthesis gas produced from biomass gasifiers.

**Ethanol from Algae**

Direct to Ethanol technology, a novel technology developed by Algenol is in Pilot plant testing at Dow Chemical’s Freeport, Texas to produce ethanol by photosynthesis from CO2, H2O and sunlight instead of producing carbohydrates [Dutta, 2011]

**COAL**

Coal is another promising feed stock as huge amount of coal reserves is available in India and other part of the world. Based on the production of coal gasification unit it will be possible to to produce large number of chemicals. Possibility Coal as a source of petrochemicals, which again explored all over the world [Handa and Ganesh, 2010]

Coal was the original feed stock for production of large number of chemicals through coke oven plants, synthesis gas from gasification, acetylene fro calcium carbide route. However, due to availability of petroleum based raw material presently more than 90% of chemicals are produce from petroleum and natural gas. Due to volatile market of crude oil and dwindling petroleum resources, coal is emerging as alternative feedstock for chemical industry as huge coal reserves are available all over the world. Various routes for utilization of coal as chemical feedstock and fuel are [Duchesne, 2011, Patil, 2009, Furimsky, 1999]:

- Gasification
- Coal to fuel through FT process
- Coal to methanol technology, Liquid phase Methanol process from coal (LPMEOH™)
- Methane to MTO plus Olefin cracking process (OCP)
• Coal to Olefin technology
• Coal to Plastic technology

PETROCOKE

Due to the use of heavy crude oil, huge amount of petrocoke is being produce from the thermal cracking process in the refinery. Although petrocoke is being used as fuel in cement industry however it can be a promising raw material for production of synthesis gas, hydrogen, methanol through petrocoke gasification. Through FT synthesis the synthesis gas can be converted to fuel also. Utilization of petrocoke offers an alternative to handle high sulfur and metal containing residues in a refinery with value addition. Reliance is already in process of implementing petrocoke gasification to utilize its petrocoke.

REFERENCES

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