

SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF CHEMICAL ENGINEERING
COURSE MATERIAL

PETROLEUM AND PETRO CHEMICAL TECHNOLOGY

UNIT V

SCH1308

UNIT V CHEMICALS FROM HIGHER ALKANES

1.0 Cracking of naphtha and gas for the production of ethylene, propylene

1.1 Isobutylene

1.2 Butadiene

1.3 Synthetic fibers.

1.0 Cracking of naphtha and gas for the production of ethylene, propylene

Olefins are major building blocks for petrochemicals. Because of their reactivity and versatility, olefins especially the light olefins like ethylene, propylene, butenes, butadiene, etc., there has been tremendous growth in the demand of the olefins. Olefins are finding wide application in the manufacture of polymers, chemical intermediates, and synthetic rubber. Ethylene itself is basic building block for large number of petrochemicals and is quoted as king of chemicals.

The steam cracker remains the fundamental unit and is the heart of any petrochemical complex and mother plant and produces large number of products and byproducts such as olefins - ethylene, propylene, butadiene, butane and butenes, isoprene, etc., and pyrolysis gasoline. The choice of the feedstock for olefin production depends on the availability of raw materials and the range of downstream products. Naphtha has made up about 50-55 percent of ethylene feedstock sources since 1992.

Modern ethylene plants incorporate following major process steps : cracking compression and separation of the cracked gas by low temperature fractionation. The nature of the feed stock and the level of pyrolysis severity largely determine the operating conditions in the cracking and quenching section. Various steps involved in the pyrolysis of naphtha and separation of the products are discussed below. In case of gas cracking separation of ethane and propane from natural gas is involved. Flow diagram for pyrolysis of naphtha is given in
FIGURE BLOW

Hot Section

It consists of convection zone and radiant zone. In the convection zone, hydrocarbon feed stock is preheated and mixed with steam and heated to high temperature. In the convection zone the rapid rise in temperature takes place and pyrolysis reaction takes place. The addition of dilution steam enhances ethylene yield and reduces the coking tendency in the furnace coils. The production of the pyrolysis reaction consists of a wide range of saturated and unsaturated hydrocarbons.

Quench Section

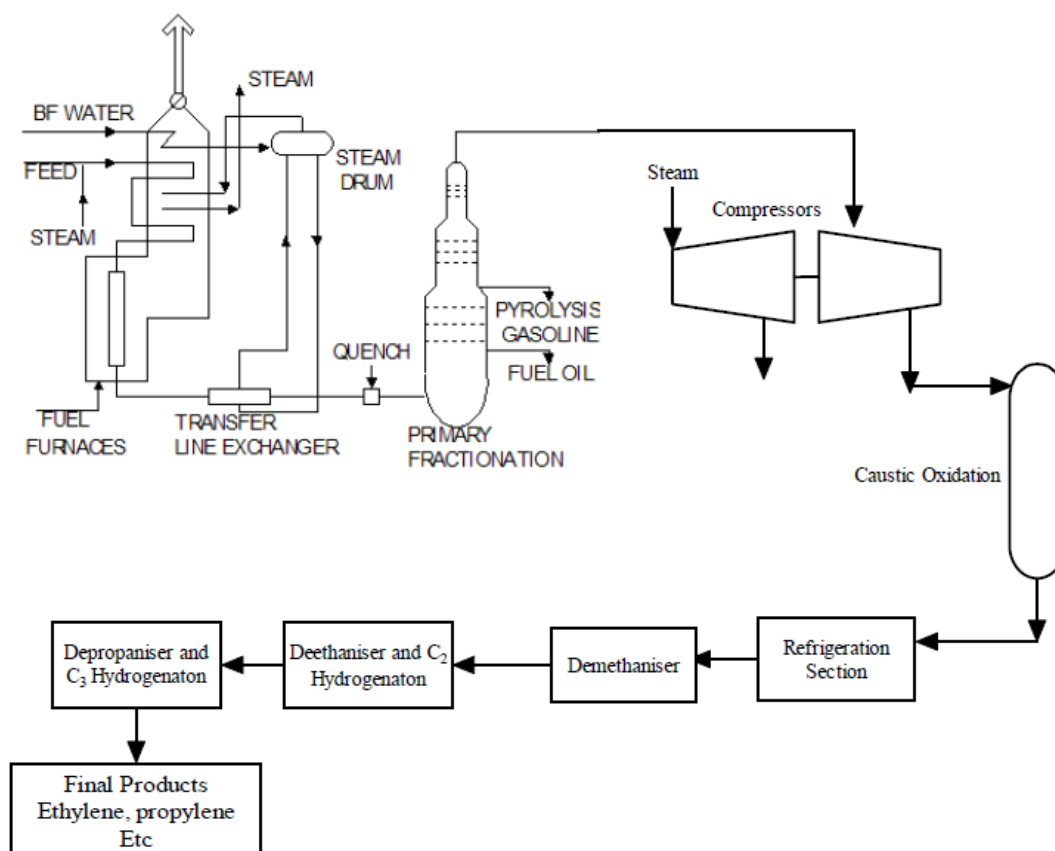
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To avoid subsequent reaction the effluent are fixed in their kinetic development by sudden quench first by indirect quench by water to 400 – 450 °C in transfer line exchanger or quench boiler. This is a large heat exchanger that is a bundle of metal tubes through which the gases pass and around which is circulated water under pressure. The hot water produced is used to generate steam for use in the plant. In the next step the quench is done by heavy product of pyrolysis.



Typical Naphtha Cracker Plant

HOT SECTION

Convection Zone Feed stock is pyrolysed and the effluent conditioned

Radiation Zone The product formed are separated and purified

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Quench To avoid subsequent reaction the effluents are fixed in their kinetics development by sudden quench.

I Indirect Indirect quench by water to 400-500°C generation of high pressure steam

II Direct Direct quench by heavy residue by-product of pyrolysis
Primary Fractionation Column Separation of light products of pyrolysis as top and bottom as pyrolysis product

Compression Compression of light products
Caustic Scrubbing and Drying Scrubbing with caustic followed by molecular sieve adsorption to remove sulphur compounds, mercaptan, etc.

Cold Section

After compression, caustic scrubbing and drying the light effluents enter the cold section of the unit which performs the separation of (i) hydrogen to various concentration (ii) ethylene containing 99.4 percent (iii) 95 percent propylene (iv) A C₄ cut containing 25-50 percent butadiene (v) pyrolysis gasoline which is rich in aromatic hydrocarbons. The complexity of the separation section of a cracker increases markedly as the feed changes from ethane.

COLD SECTION ☐ Hydrogen separation

☐ Ethylene separation 99.9 percent

☐ Propylene separation

☐ A C₄ cut containing 25-50 percent butadiene

☐ Complementary fraction of pyrolysis gasoline rich in aromatic hydrocarbons

Demethaniser Methane condensed at top around – 100°C pressure 32 Pa

Deethaniser Separation of C₂ cut; (Ethane and ethylene)

Acetylene eliminated by selective hydrogenation Catalyst : Palladium or Nickel 40-80°C, 3 kPa

Separation of Ethylene Ethylene is fractionated and unreacted ethane recycled

Depropaniser C₃ cut from bottom of deethaniser is fractionated.

C₃ cut from top of depropaniser is selectively hydrogenated to remove methyl acetylene and propadiene.

Propylene content 95 percent.

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Removal of propane from propylene Separation in supplementary column for more pure propylene.
Separation in supplementary column for more pure propylene

Debutaniser Separation of C4 stream from C5+ stream

REACTIONS IN STEAM CRACKING

The reactions involved in thermal cracking of hydrocarbons are quite complex and involve many radical steps. The thermal cracking reaction proceeds via a free radical mechanism. Two types of reactions are involved in the thermal cracking (i) primary cracking where the initial formation of paraffin and olefin takes place (ii) secondary cracking reaction where light products rich in olefins are formed. The total cracking reactions can be grouped as follows:

- ☐ Initiation reaction.
- ☐ Propagation reaction.
- ☐ Addition reaction.
- ☐ Isomerization reaction.
- ☐ Termination reaction.
- ☐ Molecular cyclization reaction

OPERATING VARIABLES OF STEAM CRACKING

The main operating variables in the pyrolysis of hydrocarbon are composition of feed stock, reaction temperature, residence time, hydrocarbon partial pressure and severity.

Composition of Feed Stock

Naphtha are mixture of alkane, cycloalkanes, and aromatic hydrocarbons depending on the type of oil from which the naphtha was derived. The group properties of these components greatly influence the yield pattern of the pyrolysis products. A full range naphtha boiling range approximately 20 to 200°C would contain compound, with from 4-12 carbon atoms. Short naphtha boiling point range from 100-140°C and long chain naphtha boiling point lies around 200-220°C. The steam cracking of the naphtha yields wide variety of products, ranging from hydrogen to highly aromatic heavy liquid fractions. The thermal stability of hydrocarbons increases in the following order: paraffins, naphthenes, aromatics. Yield of ethylene as well as that of propylene is higher if the naphtha feed stock is rich in paraffins. It may be seen that relative production of ethylene decreases as the feed stock becomes heavier. The percentage of pyrolysis gasoline C5-

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200°C cut increases. Simultaneously butadiene yield varies slight with feed stock in the treatment of liquid petroleum fractions.

With the rising demand of ethylene and propylene, there has been a tremendous growth in the steam cracking of hydrocarbons during the last four decades. Similarly, FCC (Fluid Catalytic Cracking) has developed into a major upgrading process in the petroleum refinery industry for the conversion of heavy fuel oil into more valuable products ranging from light olefins to naphtha and middle distillate. Large amounts of C₄ and C₅ compounds are produced along with the production of ethylene in steam cracking and gasoline in FCC. C₄ & C₅ streams are an important source of feedstock for synthetic rubber and many chemicals.

With increasing demand of C₅ hydrocarbons and oxygenates, upgrading of C₄ and C₅ streams from steam crackers and catalytic cracker is important to the economic performance of the above processes. It also provides a rich resource of reactive molecules, which forms the backbone of the synthetic rubber industry. The quantity and composition of the C₄ and C₅ stream depends on the severity of the steam cracker operation and feedstock processed.

FLUID CATALYTIC CRACKING

Fluid catalytic cracking (FCC) converts low value crude oil into a variety of higher value products which include gasoline, diesel, heating oil and valuable gases containing LPG, propylene and C₄ and C₅ gases. Various products from fluid catalytic cracking and their uses are given in Table FCC units are versatile and can be operated in three main modes which are aimed at maximizing middle distillate, gasoline, or olefins respectively by means of the adequate combination of various parameters such as catalyst type, catalyst to oil ratio, rise of outlet temperature and recycle of fractionators bottom. FCC is the second largest source of propylene supplied for petrochemical application.

Conventional FCC 4-7% propylene and 1-2 % Ethylene

High Severity FCC: 10% propylene

Petro FCCTM (UOP): Ethylene 6%, Propylene 20-22%, Higher aromatics (18%) in Naphtha

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Higher C₄₋₈ olefins yield which can be cracked to yield lower olefins by Total

Petrochemicals ATOFINA/UOP Olefin cracking Process

Although FCC is an important petroleum refining process, however, FCC gases have now become important petrochemical feedstock for production of LPG that can be converted to aromatics and C₃, C₄, & C₅ hydrocarbons, i.e. propylene, butene, isobutene, pentene, etc.

Product distribution from FCC depends

- Reactor temp
- Feed preheat temperature
- Catalyst activity
- Catalyst circulation rate
- Catalyst activity
- Recycle rate

Various Petroleum Products from FCC and their uses

Product	Composition and Uses
Light gases	Primarily H ₂ , C ₁ and C ₂ s, ethylene can be recovered
LPG	C ₃ s and C ₄ s containing light olefins suitable for alkylations
Gasoline	C ₅ + high octane component for gasoline pool or light fuel
Light cycle oil (LCO)	Blend component for diesel or light fuel
Heavy cycle oil (HCO)	Fuel oil or cutter oil
Clarified oil	Carbon black feedstock
Coke	Used in regenerator to provide the reactor heat demand

Propylene Recovery from FCC: FCC gases has important source of propylene from refinery and now FCC units are being operated both in gasoline mode and propylene mode. Details of propylene from FCC are given in Lecture 5 Module 6. Propylene from FCC may be as

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high as 25% with new FCC based propylene technologies. increased production of olefins from FCC units has been achieved through changes in operations, base cracking catalyst and additive catalysts and in hardware designs [Teng and Xie, 2006]

UPGRADING OF C₄ and C₅ Streams

C₄ and C₅ Streams from Steam Cracker and FCC contains C₄ and C₅ hydrocarbons recovery of which has become important steps for improving the overall economy of these processes. Some of the important C₄ streams from Cracker and FCC butadiene (from cracker plant only), butene-1, 2-butane, isobutylene, mixed n-butene, isobutene. C₄ stream of steam cracker contains appreciable amount of butadiene which is being recovered from naphtha cracker plants. Typical composition of C₄ stream of naphtha cracker and FCC is given Table M-VII 3.3. The distribution product will depend on the feed stock, cracking severity and catalyst in case of FCC

1.1 ISOBUTYLENE

Isobutylene is present in the C₄ stream naphtha cracker and FCC. Major application of isobutene is in the manufacture of gasoline blending component such as MTBE, ETBE, alkylation, polymer gasoline. Polymer grade isobutylene can be made by cracking MTBE or for manufacture of polyisobutylene. Isobutylene is used in manufacture butyl rubber which is made by copolymerization of isobutylene with small amount of isoprene.

Various Routes for Isobutylene

Extraction of C₄ cuts from steam cracking / FCC: Isobutylene is separated from C₄ cuts from naphtha cracker after extraction of butadiene and from FCC gases after propylene recovery. First isobutylenes is converted to MTBE by etherification and the recovered by cracking of MTBE to get polymer grade isobutylene it is also obtained by hydration of isobutylene containing stream and then cracking.

Isomerisation of Butene: isobutylene can be also produced from butane by isomerisation using

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zeolite ferrierite (zeolite of medium pore size) [Maulijanet al.2001]

Dehydrogenation of Isobutene:

BUTENE -1

Butene-1 is co-monomer in the production of low density polyethylene and high density polyethylene. Butene-1 can be separated from C4 stream of cracker after extraction of butadiene SHB-CB process: This process selectively hydrogenate the butadiene in the C4 cut by converting it to butane-1 and butane-2. Acetylenes and dienes are likewise hydrogenated. If the process is optimized to produce butane-1, about 60% of butadiene is converted to butane-1. The process is operated in the liquid phase mild temperatures and moderate pressures.

UPGRADING OF C₅ CUTS

The steam cracker C5 stream is a rich resource of olefins and diolefins which can be upgraded to produce elastomers, resins and fine chemical intermediates. In steam crackers during cracking process along with ethylene, propylene, C4 stream, aromatics and pyrolysis gasoline are also formed. Apart from aromatics, Pyrolysis gasoline stream also contains C5 stream [Morgan,1996]. The quantity and composition of the stream depend on the nature of the cracked product and severity of cracker operation C5 stream.

1.2 Butadiene and Benzene Manufacture

Introduction

In this lecture, we present the process technologies associated to Butadiene and Toluene.

Butadiene manufacture is considered using n-Butane as the feed stock.

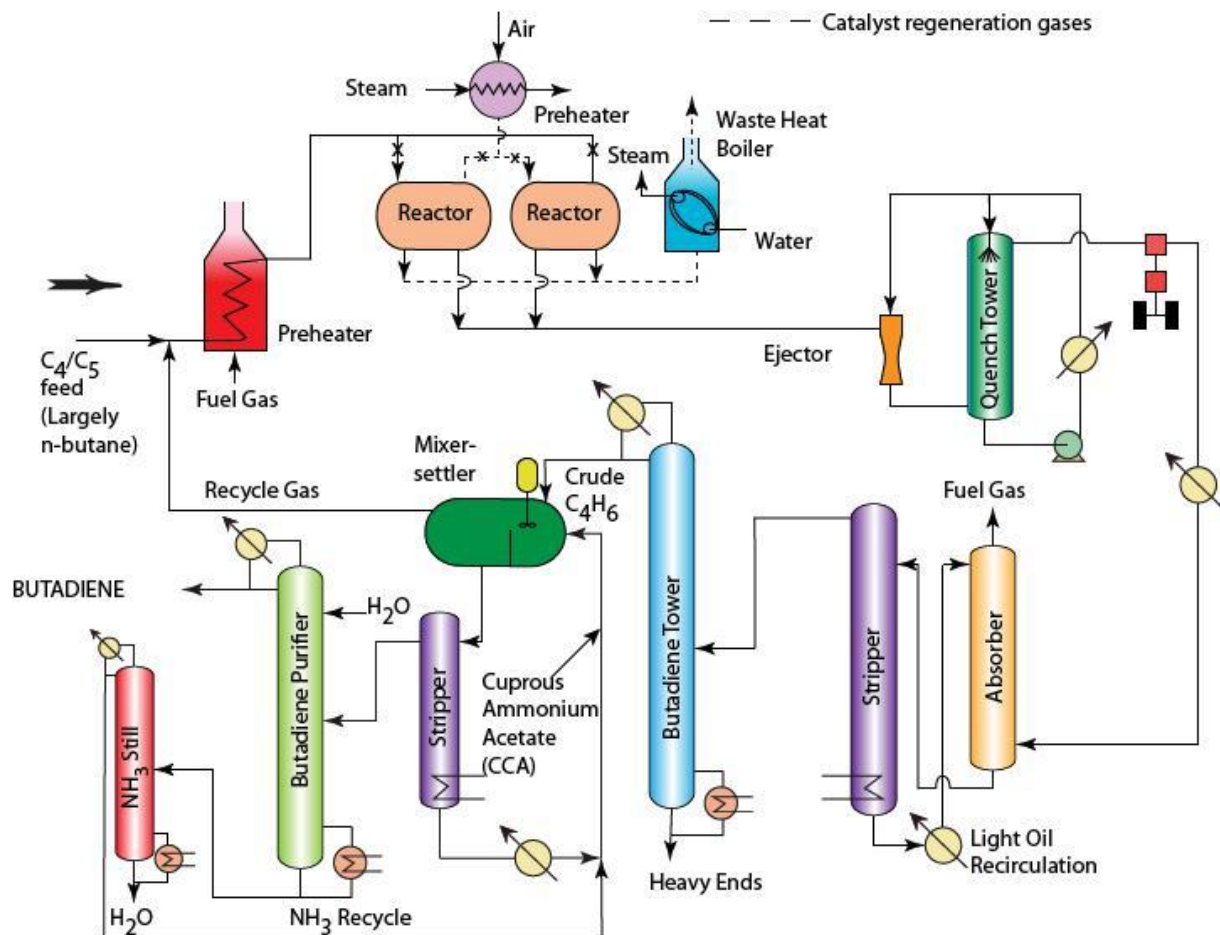
Benzene process technology refers to the famous hydrodealkylation process that uses toluene as the feed stock.

We first present the process technology associated to Butadiene.

Butadiene

Reactions

Feed stock: n-Butane with some isopentane from refinery processes.



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Flow sheet of Butadiene manufacture

- The process technology for Butadiene manufacture consists of a reactor-separator-recycle system.

The separation network is extremely complex and involves quenching, absorption, distillation and extractive distillation process.

First, the feed stock is pre-heated in a furnace along with unreacted gases that have been recovered in the process using the separator network.

After pre-heating in a furnace to desired temperature, the gases enter the catalytic packed bed reactors loaded with the catalyst.

After the specified residence time, the product is withdrawn and the feed to the unit is stopped. The product withdraw and stoppage of the feed flow to the reactor unit is carried out using valves.

The coked catalyst is subjected to combustion using pre-heated air. Air pre-heating is done using steam in an extended area heat exchanger equipment. Therefore during regeneration, another set of valves operate to allow the pre-heated air in and enable the product withdrawal after the combustion.

The pre-heated air not only removes the coke as CO_2 but increases the reactor temperature to 650°C .

The flue gases are sent to a waste heat recovery boiler so as to generate steam from water.

The entire operation of a feed entry, product withdrawal, pre-heated air entry and combustion gases withdrawal from the packed bed reactor corresponds to one single cycle.

Since the above operation is a batch operation, to make the operation continuous in accordance to the separation network, two reactors are used and these reactors are operated in cyclic fashion i.e., when the first reactor is subjected to reaction, the second reactor is subjected to catalyst regeneration and vice-versa.

The hot reactor outlet gases are sent to a quenching operation where light gas oil is used to quench the gases using a recirculating quenching tower.

After product gases from the quenching tower are compressed and cooled to enter an absorber

In this absorber, naphtha is used as an absorbent to absorb all hydrocarbons except fuel gas.

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The absorbent + hydrocarbons enter a stripper that produces fresh naphtha and hydrocarbon mixture. The hydrocarbon mixture consists of unreacted feed stock and butadiene and some heavy ends.

This mixture now enters a fractionator to separate the crude butadiene and heavy ends.

The crude butadiene consists of butadiene and unreacted feed stock i.e., n-butane and isopentane. The separation of n-butane, other hydrocarbons with butadiene is one of the difficult separations and they cannot be separated using ordinary distillation. Therefore, a complicated route of separation is followed next that involves azeotropic distillation using ammonia.

The crude butadiene is mixed with ammoniated cuprous ammonium acetate solution in a mixer settler. This solution is generated by absorbing ammonia into fresh cuprous ammonium acetate solution.

The ammoniated cuprous ammonium acetate is sent to a mixer settler unit where the butadiene dissolves in the ammoniated solution. The gas from the mixer settler unit is recycled to mix with the feed stock and enter the pre-heater.

The ammoniated cuprous ammonium acetate solution is thereby stripped to separate butadiene + ammonia from the ammonium acetate solution. The regenerated fresh solvent is allowed to absorb NH_3 and thereby enter the mixer-settler unit.

The ammonia + butadiene mixture enters a fractionator fed with water. Here, water interacts with ammonia and generates the ammonium hydroxide product as the bottom product and butadiene is obtained as the top product.

The ammonia solution is subjected to stripping to separate water and ammonia. The water is recycled back to the butadiene purifier and ammonia is allowed to get absorbed into the fresh cuprous ammonium acetate solution.

This process is not followed in India. In India, it is manufactured from ethanol by catalytic cracking at $400\text{--}450^\circ\text{C}$ over metal oxide catalyst.

1.3 Synthetic fibers

Synthetic fibers and synthetic fabrics consist of bulk fibers, yarns, woven cloth or other textile products manufactured from **polymer**-based materials such as polyamide (**nylon**), polyester, aramid, or other spun thermoplastics. The end-product is the form of the fiber/fabric when manufacturing is complete.

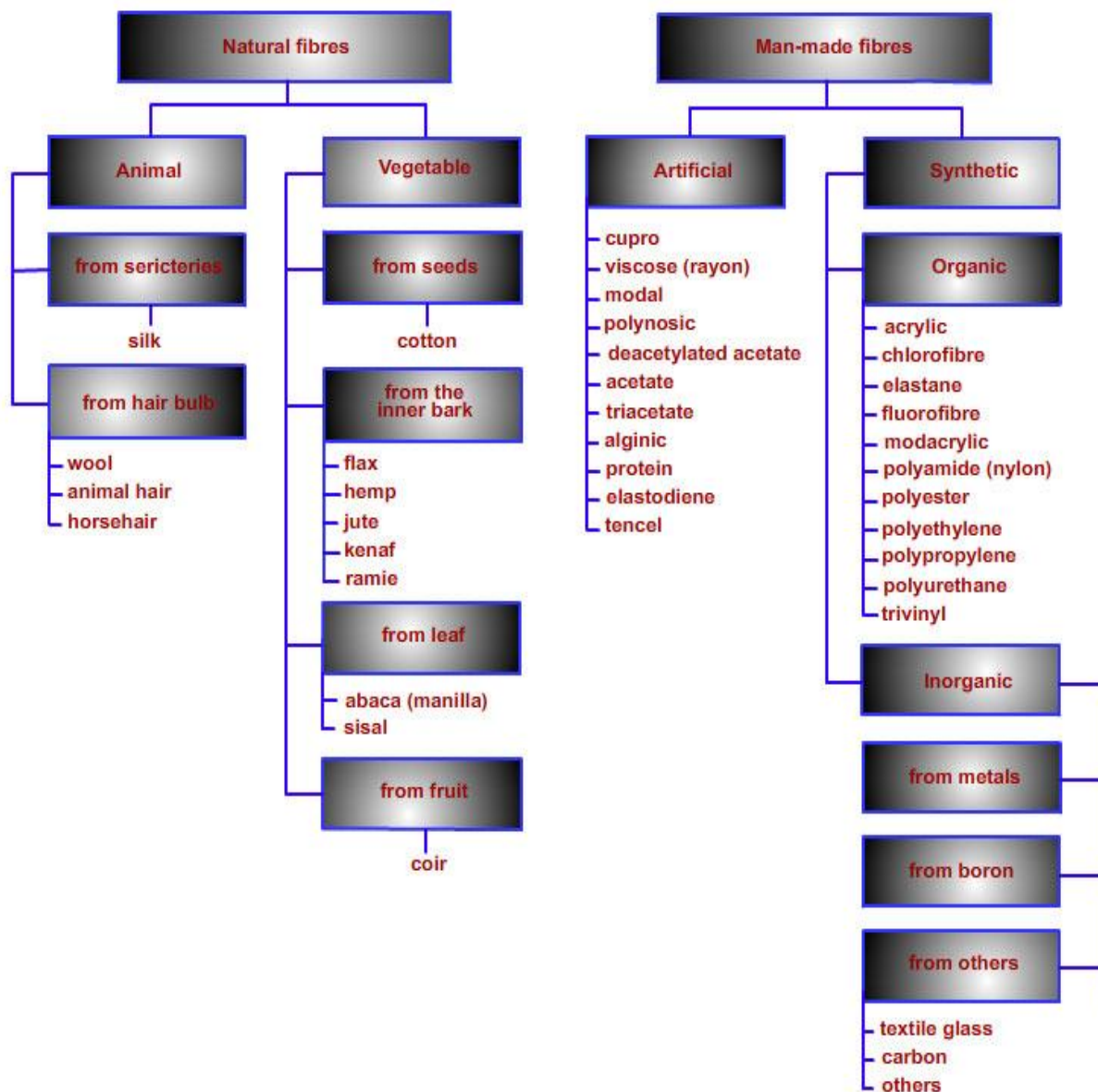
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Classification of fibres



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