Science and Technology of Polymers

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Lecture - 04
Polymer Raw Materials

Good morning, today we shall discus the raw materials requires for manufacture of polymers. If I ask you a question, what is the basic source of polymeric raw materials or raw materials for polymers, yes?

Naphtha

Naphtha, is that the basic source, crude oil? Again, no I cannot except that, is basic source is the plant kingdom. Plant kingdom is the basic source of raw materials all source of raw materials chemical chemical compounds, because this plant kingdom acts as a energy conversion unit, solar energy conversion unit it stores it stores the solar energy. That plants can be a major source of or the best source of this polymer raw materials.

Now, this petroleum, coal these are the fossil fuels, fossil of plant, plant fossils. There is some geothermal conversion under high temperature and pressure is a lot of chemical transformations occur in plant materials. You know what is the plant material the content carbohydrates, geologic materials and lignin’s compounds of carbon, hydrogen, oxygen along with certain minerals and other atoms elements of other atoms. The majority is the carbon, hydrogen and oxygen and little bit nitrogen.

For artificial manufacture of polymers, we take this petrochemicals or the petroleum as the basic source here. You may say the yes petroleum petroleum can be considered as a basic source, but the genesis of petroleum is from plant kingdom. Now, if you remove this lignin from wood, woody material of plants, how do you find? We find, we get cellulose and lignin, you can consider this lignin as a store house of plenty of chemical compounds. Today large number of chemical compounds chemicals available from well level manufacturers of chemicals. Suppliers of chemicals or traders of chemicals majority of those chemicals are made from this lignin through pyrolysis etcetera.

So, if there is no if if this petroleum reserve which exhausted, we have the plant system, from the plant system we can manufacture chemicals provided we have the abrogate technology. That is different aspect, we should not discus those things here. What I like to tell you that majority of the polymers artificial or synthetic polymers, those are manufactured from raw materials obtained from petroleum. Petroleum provides large number of petrochemicals, there are three major generations of petrochemicals; first generation of petrochemical, second generation of petrochemical, third general generation of petrochemical. Polymer is also a petro chemical.

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Polymer Raw Materials

PETROCHEMICALS

Polymers should also be considered as a petrochemical. S0o, let us see we we must we must have certain idea about this raw materials for the manufacture of this polymers. Think of polyethylene, polypropylene, polyvinylchloride, polystyrene, polyesters, polycarbonates, phenolic resins all these materials are obtained from this petroleum.

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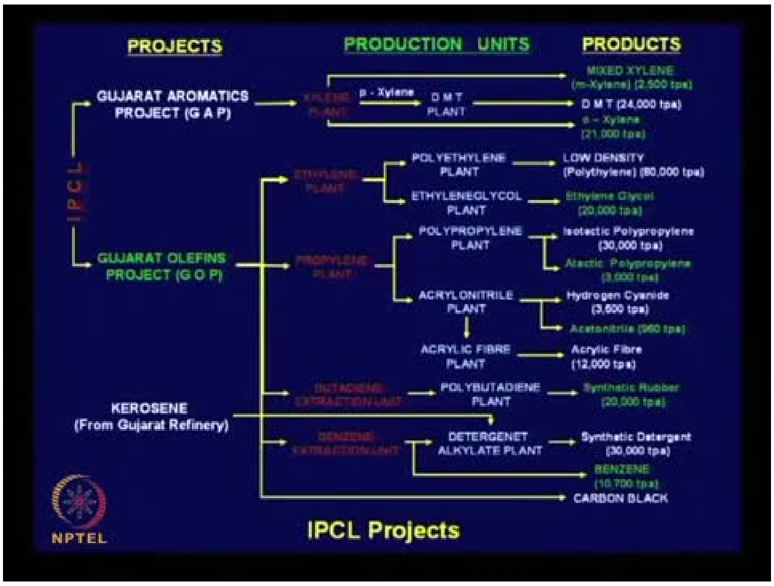

IPCL Projects

When we say in 1970’s actually in 1970’s, the first petrochemical complex was set by Indian petrochemical corporation of India at Madhudara, for manufacture of or cracking of naphtha, the refining of crude oil. Then cracking of naphtha, by cracking process different types of organic chemicals were manufactured. So, it gives a close view of different projects taking up by the IPCL that time and here you see different chemical compounds xylene, then polyethylene and these are the a polymers.

Actually the polyethylene, ethylene, xylene, propylene, butadiene, benzene and subsequently they are derivatives lead to large number of petrochemical products. You can get these things from any petrochemical book, the any chemical book you can see. I have taken, I had one book that is written that is known as the introduction to petrochemicals written by Shivakumar Mahiti and it is a small book, small book there are many books available in all library, you can go through to this things.

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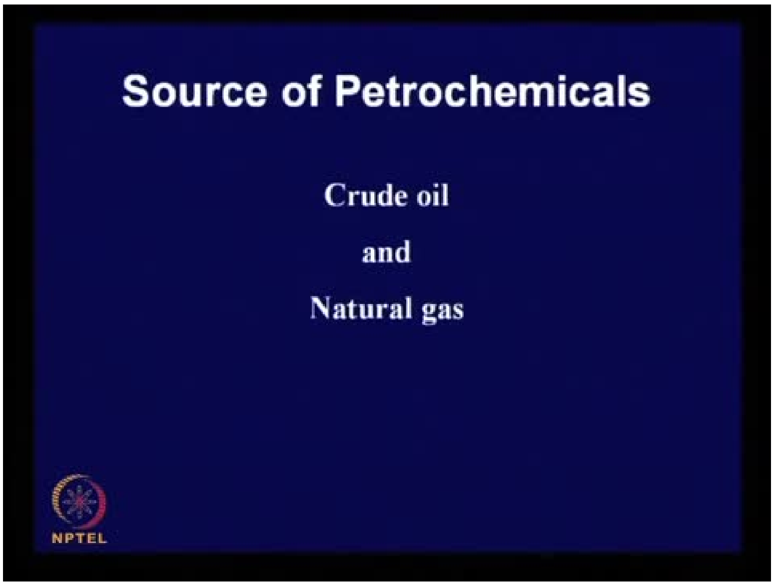

Source of Petrochemicals

Crude oil

and

Natural gas

Source of petrochemicals, the crude oil and natural gas, hydrocarbon materials and mostly those are saturated hydrocarbons.

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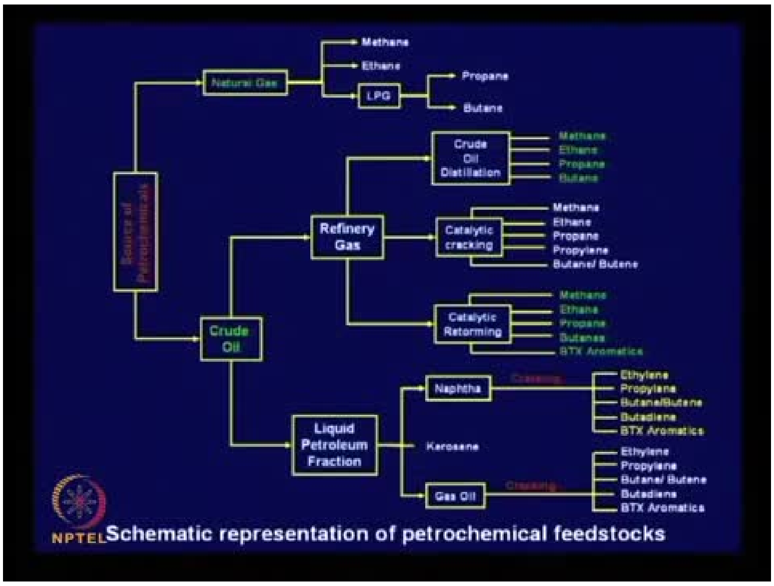

Schematic representation of petrochemical feedstocks

This source is schematic representation of petrochemical feedstock's. These are the varies petrochemicals here you see, we are mentioned here methane, ethane, propane, butane, propylene, butane, butane, btx, benzene, toluene, xylene, aerobatics etcetera. So, these are obtained from either crude oil or natural gas. These are praxinated from this we get LPG, liquefied petroleum gas, cooking gas. This contains propane propane and butane and from crude oil we get in the form of refinery gas or liquid petroleum fraction. So, there are two fractions gas and liquid fraction from the gas fraction we can get this methane, ethane, propane, butane etcetera.

By catalytic reforming, catalytic reforming means you see this is basically stretched hydrocarbons. This crude oil contains basically stretched in hydrocarbons. May be say number of carbon atoms from 2 2 or 3 2, 10 12 like this. From there are all source of petrochemical compounds, all source of chemical compounds, organic compounds are made by some reforming process known as cracking process. What is cracking process? Cracking means breaking, say if you are a stretched hydrocarbon, say suppose see C 5 hydrocarbon, 5 carbon atoms are saturated C 5 that means pentane or hexane or heptanes like that. Now, there the bonds present in the strechened carbon is carbon carbon single bond and carbon hydrogen single bond.

Now, when that is subjected to high energy environment might be thermal energy or some of other form of energy we should be technologically verbal. So, it is better to have thermal energy in presents or absents of catalyst. Those bonds can be broken in a closed chamber. So, once those bonds are broken that is that breaks by hemolytic session, you know what is hemolytic session.

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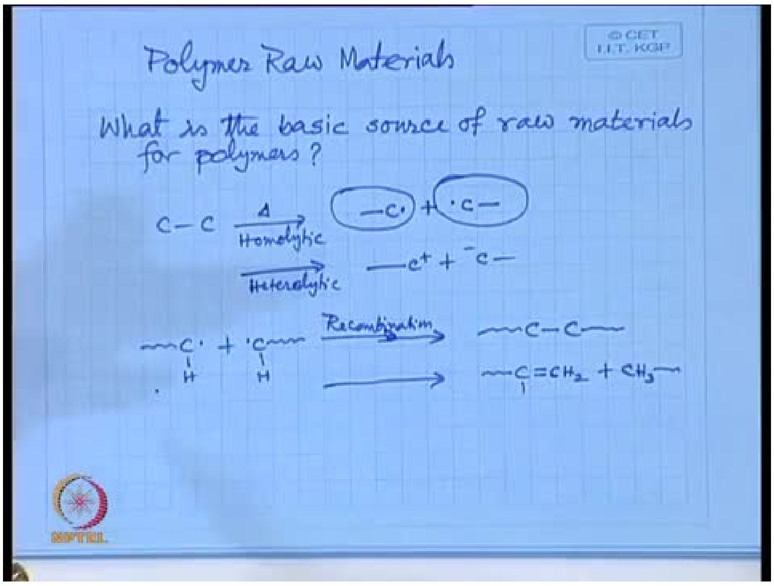

Polymer Raw Materials

What is the basic source of raw materials for polymers?

$$C-C \xrightarrow[\text{Homolytic}]{\Delta} \boxed{-C\cdot} + \boxed{\cdot C-}$$

$$\xrightarrow[\text{Heterolytic}]{} -C^{+} + {}^{-}C-$$

$$\sim\underset{H}{\underset{|}{C}}\cdot + \cdot\underset{H}{\underset{|}{C}}\sim \xrightarrow{\text{Recombination}} \sim C-C\sim$$

$$\longrightarrow \sim\underset{|}{C}=CH_2 + CH_3\sim$$

Suppose carbon carbon bond, if there is it breaks, it will break into two fragments having two firadicals on this own whole hydrolytic session. Heterolytic, I am not showing the other bonds, so Ketene Renan this will formed cracked. So, this is the basic principle of cracking. So, in a mixture what happens? See large number of molecules are there infinite number of molecules are there. So, there are collisions as well as thermal cracking thermal breaking into firadicals. It depends whether it will firadical or ionic that depends on the nature of a catalyst, which is used for such cracking operation.

So, once these are formed in large number, then they can collide with each other and recombine. So, the size of this radical may may not be equal to the size of this radical, one may content 2 carbon another may content 3 carbon or 4 carbon like this. So, after breaking they collide with each other and again they can form reform or again or or even they can abstract hydrogen atom from one the other radical, that is call disproportionation reaction.

So, what happens I am showing this way, recombination. They can reform or there are possibilities of say it has hydrogen it is also hydrogen so these hydrogen can be abstracted so if this hydrogen abstracted then some double bond will found warier unsaturated end and other thing will be other part will be saturated like this. So, depending on the the residual part hydrogen or other carbon, it will it can be methane or ethane or propane. This can be ethylene propylene like this, all right?

So, this is the things happen when their fraction or they are cracked. That means they are expose to high energy environment after that those are fractionated. So, after cracking what happens? We will have a mixture of different chemical compounds mixture of starting compound with the product compounds. Then it needs to be separated and purified isolated etcetera and that is done by fractionation, fractionalization or by other means of fractionation.

So, those are separated and purified and we can get pure methane we can get pure ethane or we can get pure ethylene. We can get pure propylene, all right? We can, we may need to go for other steps where with the help of catalyst and other regions. We can convert this ethane to ethylene like this or benzene or some other hydro your monomer compounds. So, those are there, so you can have close view of the different chemical organic compounds available from petrol crude oil or petroleum.

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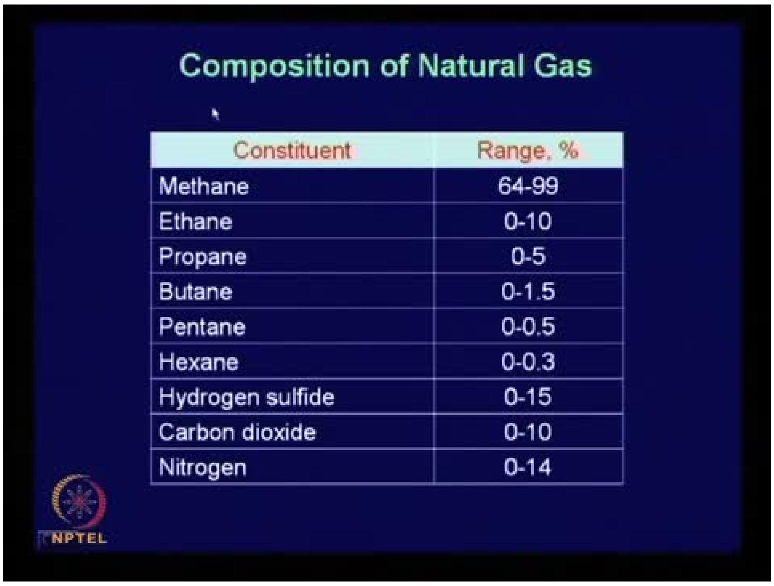

Composition of Natural Gas

Constituent	Range, %
Methane	64-99
Ethane	0-10
Propane	0-5
Butane	0-1.5
Pentane	0-0.5
Hexane	0-0.3
Hydrogen sulfide	0-15
Carbon dioxide	0-10
Nitrogen	0-14

Now, is this shows a basic composition of natural gas majority is methane and then ethane. So, others are very less some times and little bit of say hydrogen, sulfide, nitrogen. You know the source of sulfur sulfur is there. Also in plant in plant there is a sulfur, nitrogen, phosphorus. So, those can remain in the some compounds can be there of sulfur compounds, phosphorus compounds, nitrogen compounds can be there.

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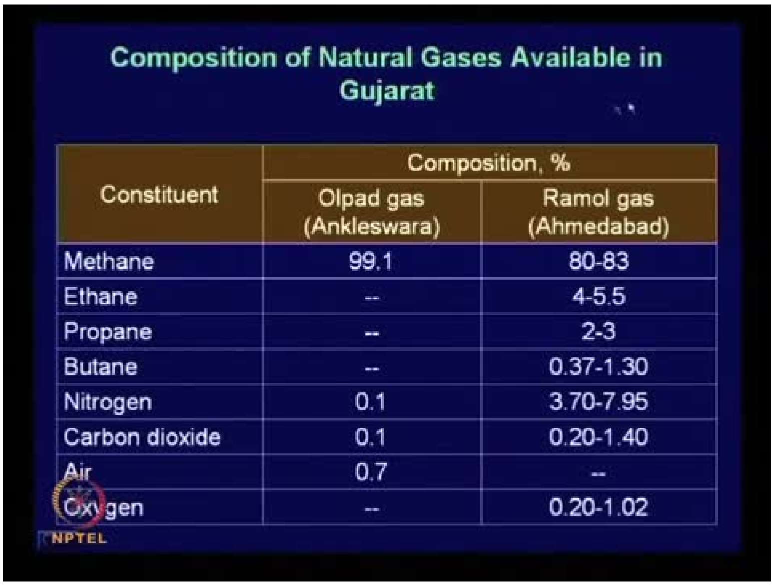

Composition of Natural Gases Available in Gujarat

Constituent	Composition, %	
	Olpad gas (Ankleswara)	Ramol gas (Ahmedabad)
Methane	99.1	80-83
Ethane	--	4-5.5
Propane	--	2-3
Butane	--	0.37-1.30
Nitrogen	0.1	3.70-7.95
Carbon dioxide	0.1	0.20-1.40
Air	0.7	--
Oxygen	--	0.20-1.02

Compositions of natural gas available from available in Gujrat. Actually this composition of natural gas varies from place to place site to site composition of crude oil varies from site to site aliphatic aromatic mixtures of this things as well as different hydrocarbons present over there.

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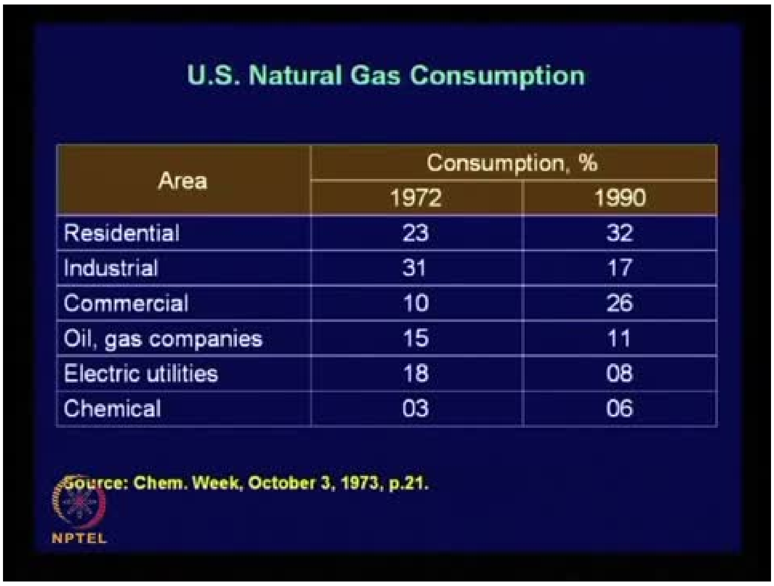

U.S. Natural Gas Consumption

Area	Consumption, %	
	1972	1990
Residential	23	32
Industrial	31	17
Commercial	10	26
Oil, gas companies	15	11
Electric utilities	18	08
Chemical	03	06

Source: Chem. Week, October 3, 1973, p.21.

I will go hurriedly today, I have to finish this, there are large number of slides. So, here you see US natural US natural gas consumption consumption consumption pattern is shown. This is owned statistics, you can said the recent or current statistics from your recent journals, so skip these things.

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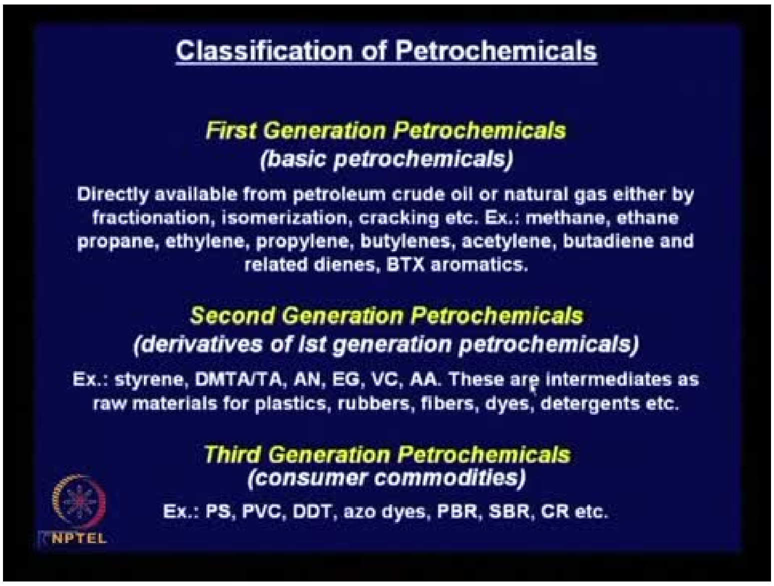

Classification of Petrochemicals

First Generation Petrochemicals
(basic petrochemicals)

Directly available from petroleum crude oil or natural gas either by fractionation, isomerization, cracking etc. Ex.: methane, ethane propane, ethylene, propylene, butylenes, acetylene, butadiene and related dienes, BTX aromatics.

Second Generation Petrochemicals
(derivatives of Ist generation petrochemicals)

Ex.: styrene, DMTA/TA, AN, EG, VC, AA. These are intermediates as raw materials for plastics, rubbers, fibers, dyes, detergents etc.

Third Generation Petrochemicals
(consumer commodities)

Ex.: PS, PVC, DDT, azo dyes, PBR, SBR, CR etc.

Classification of petrochemicals, as I told there are first generation petrochemicals known as basic petrochemicals, second generation petrochemicals known as derivatives, of first generation petrochemicals. So, from first generation petrochemicals one can get second generation petrochemicals, then third generation of petrochemicals are consumer commodities or products like which are we are using say polymers. Say propylene, a polypropylene, polyethylene, polyvinylchloride, polystyrene, these are third generation petrochemicals because these are chemical compounds made from petroleum.

So, second generation look at the first generation, examples are methane, ethane, propane, ethylene, propylene, butylene is in the monomeric form. Btx, aromatics, benzene, toluene, xylene, aromatics and second generation petrochemicals are styrene, dimethyl terephthalate, or tartaric acid, acronitile ethylene, glycol, vinyl chloride, acrylic acid, these are intermediates as raw materials for plastics, rubbers, fibers, dyes, detergents all these things.

Now, you understand majority of the chemical industries in a country, they have to depend on the availability of this crude oil. If there is you know sufficient crude oil because this sufficient, that crude oil goes for this petrochemical manufacture as well as for what? Fuels, petrochemicals are the fuels. Today people are, automobiles vehicles run by this gas gasses fuels. So, then third generation petrochemicals after obtaining this monomers from first generation petrochemicals or second generation petrochemicals, they are converted to polymers as third generation petrochemical materials.

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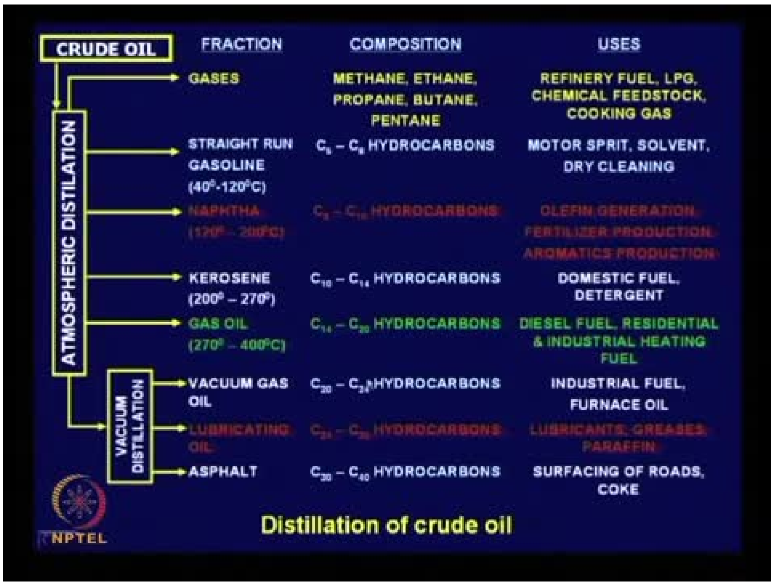

CRUDE OIL

ATMOSPHERIC DISTILLATION

VACUUM DISTILLATION

FRACTION	COMPOSITION	USES
GASES	METHANE, ETHANE, PROPANE, BUTANE, PENTANE	REFINERY FUEL, LPG, CHEMICAL FEEDSTOCK, COOKING GAS
STRAIGHT RUN GASOLINE (40°-120°C)	$C_5 - C_8$ HYDROCARBONS	MOTOR SPRIT, SOLVENT, DRY CLEANING
NAPHTHA (120° - 200°C)	$C_8 - C_{10}$ HYDROCARBONS	OLEFIN GENERATION FERTILIZER PRODUCTION AROMATICS PRODUCTION
KEROSENE (200° – 270°)	$C_{10} - C_{14}$ HYDROCARBONS	DOMESTIC FUEL, DETERGENT
GAS OIL (270° – 400°C)	$C_{14} - C_{20}$ HYDROCARBONS	DIESEL FUEL, RESIDENTIAL & INDUSTRIAL HEATING FUEL
VACUUM GAS OIL	$C_{20} - C_{24}$ HYDROCARBONS	INDUSTRIAL FUEL, FURNACE OIL
LUBRICATING OIL	$C_{24} - C_{30}$ HYDROCARBONS	LUBRICANTS, GREASES, PARAFFIN
ASPHALT	$C_{30} - C_{40}$ HYDROCARBONS	SURFACING OF ROADS, COKE

Distillation of crude oil

You see what a what one can get distillation of crude oil. If you go to some refinery, you will see huge distillation, distilleries, distillation plants huge atom huge structures are there. Thousands of tones of this your crude oil is used for cracking distillation separation, purification and conversion to different products. So, vacuum distillation or direct distillation fractionation. So, different fractions C 5 to C 8, C 8 to C 10, C 10 to C 14, C 14 to C 20, C 20 to C 24, C 24 to C 30, C thirty to C 40 and you see nature of their uses of these various fractions.

Now, for road surfacing or for coke you also depend on this petrochemicals crude oil high high boiling fractions, these are called high boiling fractions or residues. Those are high viscous materials, they are some binding capacity. They are some addition properties those are used for road surfacing etcetera. So, depending on the depending on the number of carbon atoms in the hydrocarbon chain, you see their uses are different because their boiling points are different. Tragily, boiling point increases from top to downwards.

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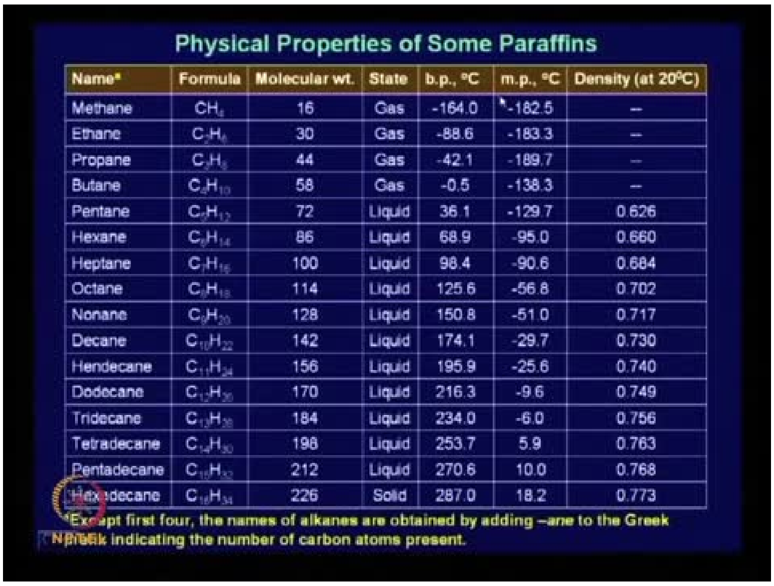

Physical Properties of Some Paraffins

Name*	Formula	Molecular wt.	State	b.p., °C	m.p., °C	Density (at 20°C)
Methane	CH_4	16	Gas	-164.0	-182.5	--
Ethane	C_2H_6	30	Gas	-88.6	-183.3	--
Propane	C_3H_8	44	Gas	-42.1	-189.7	--
Butane	C_4H_{10}	58	Gas	-0.5	-138.3	--
Pentane	C_5H_{12}	72	Liquid	36.1	-129.7	0.626
Hexane	C_6H_{14}	86	Liquid	68.9	-95.0	0.660
Heptane	C_7H_{16}	100	Liquid	98.4	-90.6	0.684
Octane	C_8H_{18}	114	Liquid	125.6	-56.8	0.702
Nonane	C_9H_{20}	128	Liquid	150.8	-51.0	0.717
Decane	$C_{10}H_{22}$	142	Liquid	174.1	-29.7	0.730
Hendecane	$C_{11}H_{24}$	156	Liquid	195.9	-25.6	0.740
Dodecane	$C_{12}H_{26}$	170	Liquid	216.3	-9.6	0.749
Tridecane	$C_{13}H_{28}$	184	Liquid	234.0	-6.0	0.756
Tetradecane	$C_{14}H_{30}$	198	Liquid	253.7	5.9	0.763
Pentadecane	$C_{15}H_{32}$	212	Liquid	270.6	10.0	0.768
Hexadecane	$C_{16}H_{34}$	226	Solid	287.0	18.2	0.773

*Except first four, the names of alkanes are obtained by adding –ane to the Greek prefix indicating the number of carbon atoms present.

You see physical proper, some physical properties of paraffin’s. These are known as paraffin’s. Methane, ethane, propane butane, these are hydrocarbon. Look at boiling points, very low temperature is required for cellu refine methane, minus 182, minus 183 like this. Then when the number of carbon atoms is more than actually these these are the melting point, while look at the boiling point, pentane. When the number of carbon atoms is regard more than 4 or 5, it becomes liquid otherwise it is gas. Paraffin wax paraffin wax its melting point actually it does not melt showing a sub melting point, say it is from 55 to 60, 65 70, 55 to 70 in this range, it melts because it contains a mixture of hydrocarbons, higher than C 30 or something like that.

So, those you can have some idea looking at these boiling points and the number of carbon atoms and carbon hydrogen ratio. This is most important thing carbon, hydrogen ratio the calorific value or the fuel value of a hydrocarbon depends on this carbon hydrogen ratio, because this combustion region oxidation process hydrocarbon reacts is oxygen for being carbon dioxide and water as well as releasing energy. Now, if if you just try to watch one phenomena that is there are some hydrocarbons, which bond without smoke some hydrocarbons are whilst burned with smoke or sooty flame sooty flame. Means there is some unbound carbon as smoke that from soot carbon particles that is due to the variation in ratio of the carbon to hydrogen atom.

Aromatic compounds when it bond it produces sooty flame produces soot where as lower hydrocarbons does not produce soot. There is complete combustion and conversion to water and carbon dioxide. Any way you just if you go through this data, this data you will have some idea. It may help you because if you want be a polymer expert, if you want to work in polymer industry, if you want understand the process over, then you must have some basic idea in these things.

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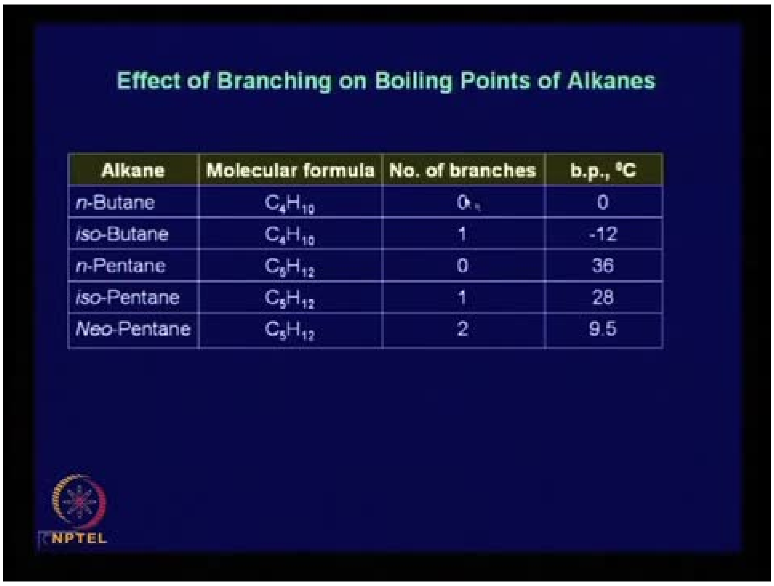

Effect of Branching on Boiling Points of Alkanes

Alkane	Molecular formula	No. of branches	b.p., °C
n-Butane	C_4H_{10}	0	0
iso-Butane	C_4H_{10}	1	-12
n-Pentane	C_5H_{12}	0	36
iso-Pentane	C_5H_{12}	1	28
Neo-Pentane	C_5H_{12}	2	9.5

Effect of branching on boiling points of alkanes. So, here you see effect of branching is there on boiling point effect of branching is there on the properties of polymers. That you can visualize you will see. Why I shall cover the structure properties of structure property relations of polymers, you will see the effect of branching effect of molecular weight effect of their morphology etcetera. All this things they have proponed influence on their properties were also the effect of branching is there on the boiling point as well as the melting point, number of branch length of branch etcetera.

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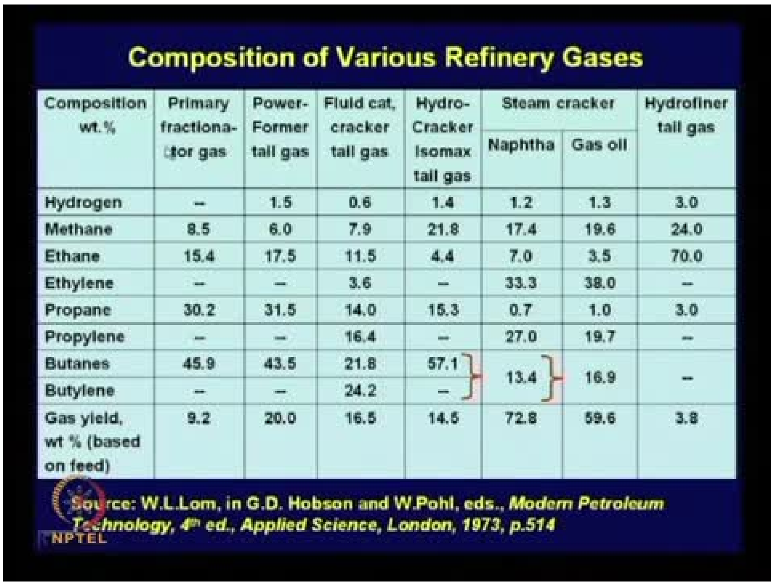

Composition of Various Refinery Gases

Composition wt.%	Primary fractionator gas	Power-Former tail gas	Fluid cat, cracker tail gas	Hydro-Cracker Isomax tail gas	Steam cracker		Hydrofiner tail gas
					Naphtha	Gas oil	
Hydrogen	–	1.5	0.6	1.4	1.2	1.3	3.0
Methane	8.5	6.0	7.9	21.8	17.4	19.6	24.0
Ethane	15.4	17.5	11.5	4.4	7.0	3.5	70.0
Ethylene	–	–	3.6	–	33.3	38.0	–
Propane	30.2	31.5	14.0	15.3	0.7	1.0	3.0
Propylene	–	–	16.4	–	27.0	19.7	–
Butanes	45.9	43.5	21.8	57.1	13.4	16.9	–
Butylene	–	–	24.2	–			
Gas yield, wt % (based on feed)	9.2	20.0	16.5	14.5	72.8	59.6	3.8

Source: W.L.Lom, in G.D. Hobson and W.Pohl, eds., *Modern Petroleum Technology, 4th ed., Applied Science, London, 1973, p.514*

This is composition of various refinery gases, primary fractionators gas, power former tall gas, fluid catalyst cracker tall gas, hydro cracker isomeric isomeric tall gas, steam cracker, naphtha, gas oil, hydro finer tall gas, so different fractions actually these are some technical terminologies, different fractions can be available and these are the compounds available from those different fractions. It may not be so important for you at this movement.

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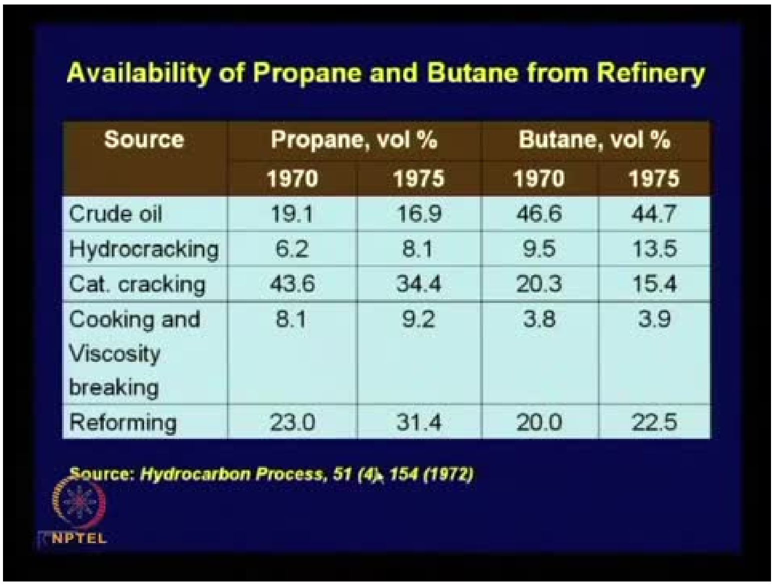

Availability of Propane and Butane from Refinery

Source	Propane, vol %		Butane, vol %	
	1970	1975	1970	1975
Crude oil	19.1	16.9	46.6	44.7
Hydrocracking	6.2	8.1	9.5	13.5
Cat. cracking	43.6	34.4	20.3	15.4
Cooking and Viscosity breaking	8.1	9.2	3.8	3.9
Reforming	23.0	31.4	20.0	22.5

Source: *Hydrocarbon Process, 51 (4), 154 (1972)*

But as a reference you can keep with you, any time it may be necessary. Availability of propane and butane from refinery. Propane volume or some statistical data is given over here propane, butane and source are the crude oil, hydro cracking process. Hydro cracking means cracking influence of steam. I will explain this hydro cracking process little later, what is hydro cracking, what is catalytic cracking etcetera. So, the from different processes we can get different percentage of hydrocarbons.

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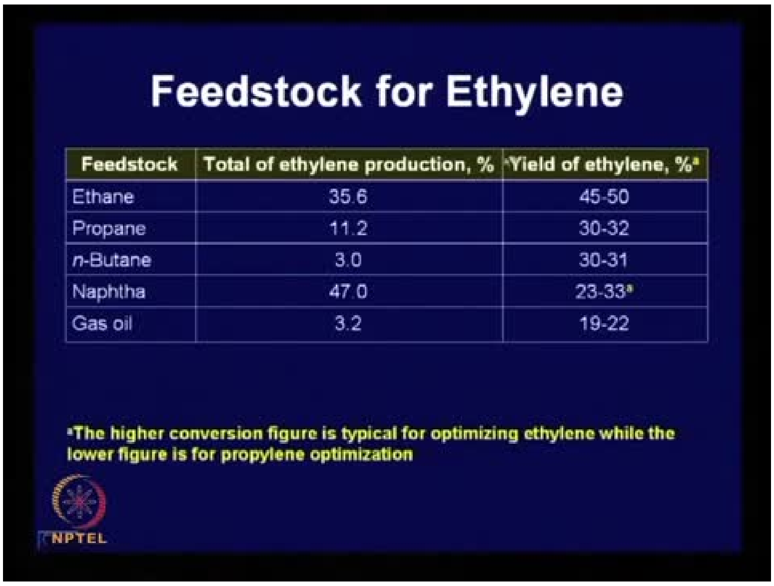

Feedstock for Ethylene

Feedstock	Total of ethylene production, %	Yield of ethylene, %[a]
Ethane	35.6	45-50
Propane	11.2	30-32
n-Butane	3.0	30-31
Naphtha	47.0	23-33[a]
Gas oil	3.2	19-22

[a] The higher conversion figure is typical for optimizing ethylene while the lower figure is for propylene optimization

Now, what is feedstock for ethylene? That means for manufacture of ethylene because ethylene ethylene is a basic again it is very important raw material for today is commodity polymers, olyethylene or polypropylene etcetera. So, for making the ethylene or production of ethylene monomer ,what feedstock's are taken for manufacture of this ethylene? These are ethane, propane, normal butane, naphtha, gas oil and in the of total ethylene production in percent from each of these and total yield of ethylene production from range range is given yield of ethylene percent, total ethylene and yield of ethylene.

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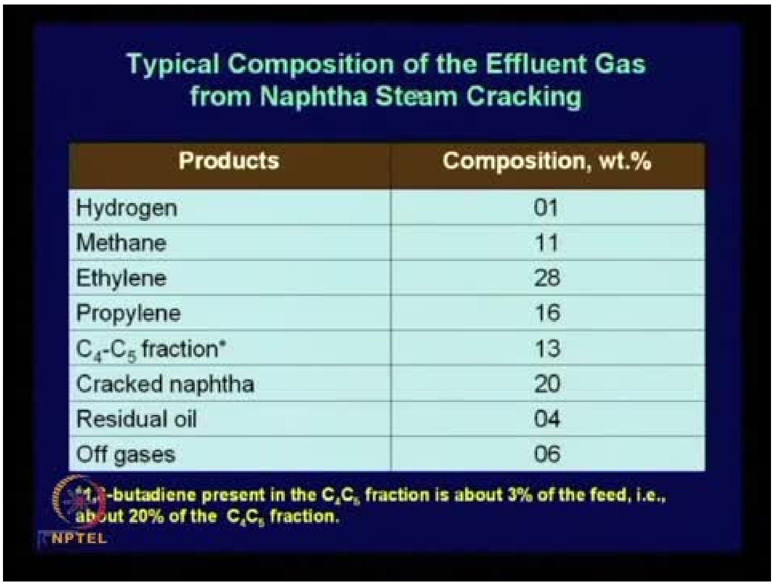

Typical Composition of the Effluent Gas from Naphtha Steam Cracking

Products	Composition, wt.%
Hydrogen	01
Methane	11
Ethylene	28
Propylene	16
C_4-C_5 fraction*	13
Cracked naphtha	20
Residual oil	04
Off gases	06

*1,3-butadiene present in the C_4C_5 fraction is about 3% of the feed, i.e., about 20% of the C_4C_5 fraction.

Typical composition of the effluent gas from naphtha steam cracking. In refineries we will find naphtha cracker, what is naphtha cracker? Naphtha is taken as the feedstock, then it is subjected to thermal cracking. Cracking means braking of hydrocarbon chains into smaller fragments that is call thermal cracking and that heat is supplied through steam high pressure steam, high temperature steam. You can have steam at 100 degree celsius, you can have steam at 150 degree celsius, you can have steam at steal at high temperature depending on the pressure of the steam.

Now, that is steam is mixed with this hydrocarbon gas, what happens? There is water vapor water molecules in the vapor page vapor state and hydrocarbon and thermal energy heat energy, so that heat energy if it is more than the bond energy of carbon, carbon bond energy, if it is more than the bond energy of carbon hydrogen bond energy, then those bonds into broken that is call cracking, okay?

Now, once as I means, once this bonds are bookend there is a possibility of of major possibility of recombination to get you back in the feedstock feed stock that means the starting material. Inorder to prevent that this steam is used it is, it acts as a diluents, understand? It acts as a diluents; that means if there is certain percentage of water vapor molecules are there, then when they come, when these spaces when these spaces comes closer to collide each other to the form the starting material that will be prevent. That means if in this space some water molecule comes in between these two, they will be prevented to collide with each other, rather this will collide with this water water vapor molecule and temperature is high.

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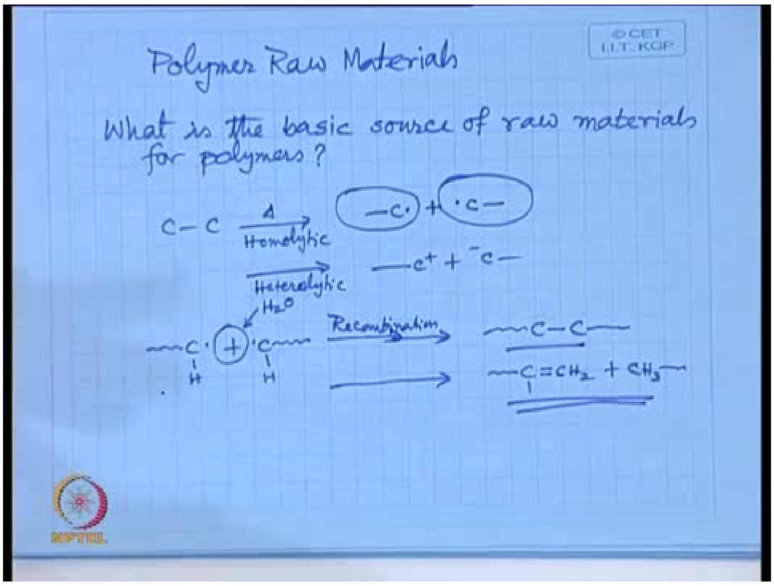

Polymer Raw Materials

What is the basic source of raw materials for polymers?

So, it can lead to this kind of reaction, in these products. This is the effect of dilution and that is the process and that principle has been develop to refine technology today, to get the specific products of ethylene products like ethylene or propylene like this, okay? So, typical composition of the effluent gas from naphtha steam cracking. So, this hydrogen, some hydrogen is also produced because hydrogen is broken carbon hydrogen born. Bond is broken to some active hydrogen atom will be produced.

They may combine to forms of hydrogen also. Again that may be, that will react with it react to form other compounds on; that mean that may add to the hydrocarbons, but some hydrogen atoms, hydrogen molecules will be there, methane, ethylene, propylene, C 4, C 5 fraction and cracked naphtha residual oil or gases, these are various components reduce during steam cracking.

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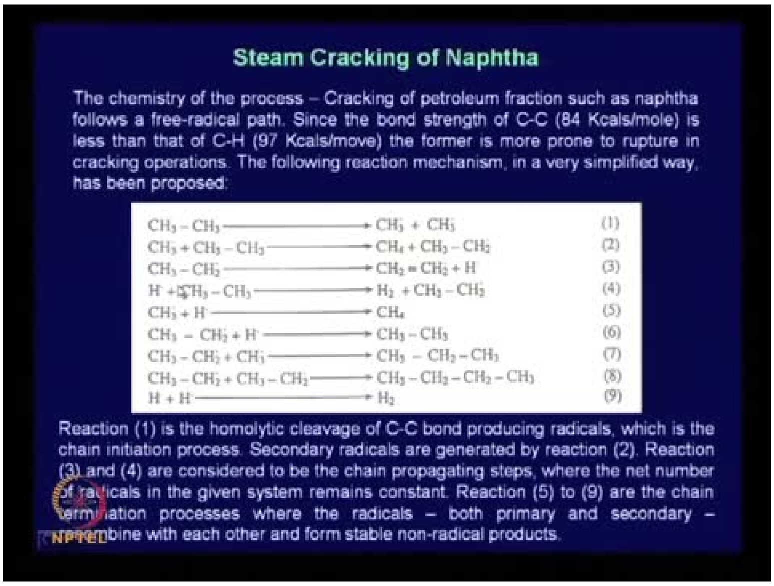

Steam Cracking of Naphtha

The chemistry of the process – Cracking of petroleum fraction such as naphtha follows a free-radical path. Since the bond strength of C-C (84 Kcals/mole) is less than that of C-H (97 Kcals/move) the former is more prone to rupture in cracking operations. The following reaction mechanism, in a very simplified way, has been proposed:

$$CH_3-CH_3 \longrightarrow CH_3^{\cdot} + CH_3^{\cdot} \quad (1)$$
$$CH_3^{\cdot} + CH_3-CH_3 \longrightarrow CH_4 + CH_3-CH_2^{\cdot} \quad (2)$$
$$CH_3-CH_2^{\cdot} \longrightarrow CH_2=CH_2 + H^{\cdot} \quad (3)$$
$$H^{\cdot} + CH_3-CH_3 \longrightarrow H_2 + CH_3-CH_2^{\cdot} \quad (4)$$
$$CH_3^{\cdot} + H^{\cdot} \longrightarrow CH_4 \quad (5)$$
$$CH_3-CH_2^{\cdot} + H^{\cdot} \longrightarrow CH_3-CH_3 \quad (6)$$
$$CH_3-CH_2^{\cdot} + CH_3^{\cdot} \longrightarrow CH_3-CH_2-CH_3 \quad (7)$$
$$CH_3-CH_2^{\cdot} + CH_3-CH_2^{\cdot} \longrightarrow CH_3-CH_2-CH_2-CH_3 \quad (8)$$
$$H^{\cdot} + H^{\cdot} \longrightarrow H_2 \quad (9)$$

Reaction (1) is the homolytic cleavage of C-C bond producing radicals, which is the chain initiation process. Secondary radicals are generated by reaction (2). Reaction (3) and (4) are considered to be the chain propagating steps, where the net number of radicals in the given system remains constant. Reaction (5) to (9) are the chain termination processes where the radicals – both primary and secondary – recombine with each other and form stable non-radical products.

Now, look at the as I was telling look at this reactions. If you look into this thing methane, ethane ethane CH3 CH3 saturated hydrocarbon. So, thermal cracking due to hemolytic session of this bond lead to this methyl radicals to methyl radicals. The high active an energetic high activity state. So, methyl radical will further collide with this ethane molecule plus ethane molecule forming. That means this methyl radical is snatch one hydrogen atom from this ethyl group forming methane as well as it will lead to an ethyl radical.

This ethyl radical can give up one hydrogen from this carbon forming. Actually this is wrong here, this is wrong here are forming an unsaturated molecule ethylene producing 1 hydrogen radical. So, this hydrogen radical can also lead to products like this and again it can lead to form methane. Again this hydrogen radical again combine with this thing giving back the starting ethane molecule. So, this way you see the random process, random reaction, random collision between these hydrocarbon molecules. Here only one spaces is shown ethane, if you go for cracking of natural gas, cracking of crude oil or some other feedstock, then there will be mixture of different hydrocarbon compounds differing in number of carbon atoms in the chain.

So, there will be mixture of products, what depending on the energy? Depending on the energy appears the temperature and the pressures of catalyst and all those things pressure temperature pressure catalyst. Those parameters control the percentage of products percentage of products. Say say this is, if this is the des most desired product the technologies would be such that maximum percentage of this will be produced along with with minimum percentage of other products. Then the product mixture, this is the product mixture should be subjected to fractionation, isolation, separation purification.

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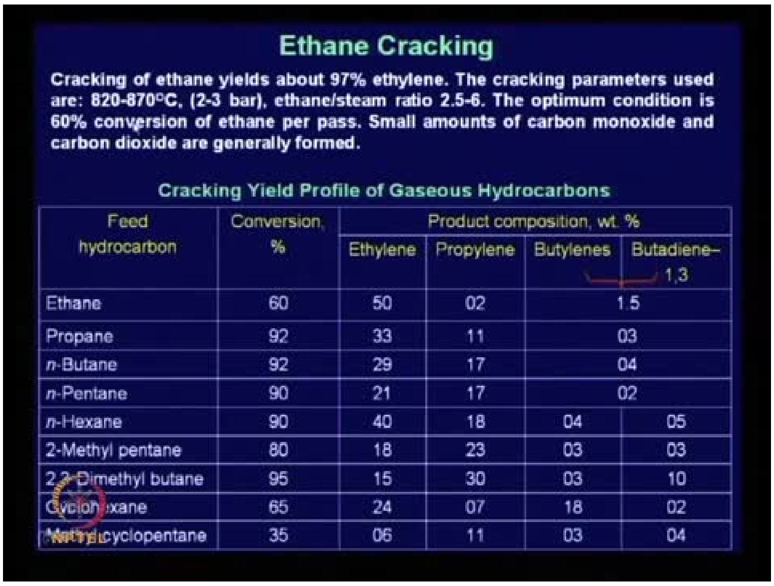

Ethane Cracking

Cracking of ethane yields about 97% ethylene. The cracking parameters used are: 820-870°C, (2-3 bar), ethane/steam ratio 2.5-6. The optimum condition is 60% conversion of ethane per pass. Small amounts of carbon monoxide and carbon dioxide are generally formed.

Cracking Yield Profile of Gaseous Hydrocarbons

Feed hydrocarbon	Conversion, %	Product composition, wt. %			
		Ethylene	Propylene	Butylenes	Butadiene–1,3
Ethane	60	50	02	1.5	
Propane	92	33	11	03	
n-Butane	92	29	17	04	
n-Pentane	90	21	17	02	
n-Hexane	90	40	18	04	05
2-Methyl pentane	80	18	23	03	03
2,2-Dimethyl butane	95	15	30	03	10
Cyclohexane	65	24	07	18	02
Methyl cyclopentane	35	06	11	03	04

You see cracking of ethane, it look at the temperature cracking of ethane yields about 97 percent of ethylene. The cracking parameters used are very high temperature this is a pressure ethane steam ration is 2.5 to 6. The optimum condition is 60 percent conversion of ethane per pass. That may be tubular reactor is circulating and this connected to separator also separator fractionator. So, per one pass it produces 60 percent ethane conversion of ethane to ethylene small amounts of carbon monoxide. Carbon dioxide are generally formed that is also possible, so you see product composition from this cracker you can take time later and go through in detail catalytic cracking.

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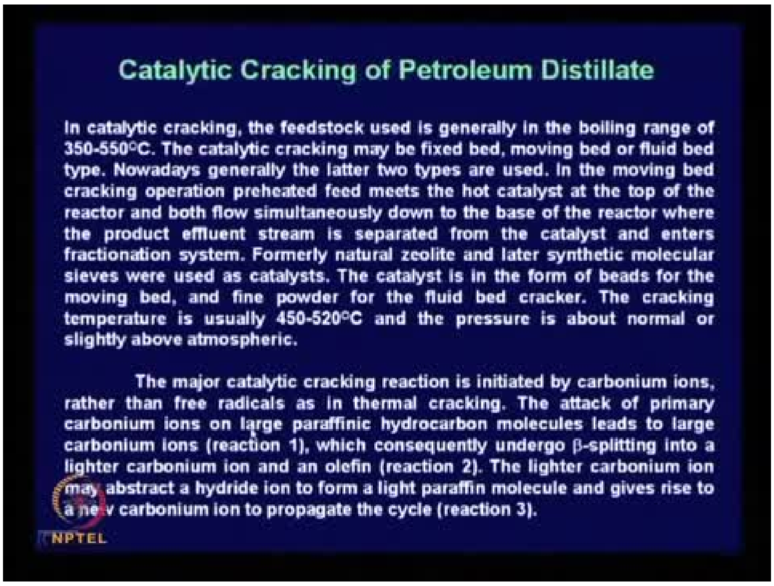

Catalytic Cracking of Petroleum Distillate

In catalytic cracking, the feedstock used is generally in the boiling range of 350-550°C. The catalytic cracking may be fixed bed, moving bed or fluid bed type. Nowadays generally the latter two types are used. In the moving bed cracking operation preheated feed meets the hot catalyst at the top of the reactor and both flow simultaneously down to the base of the reactor where the product effluent stream is separated from the catalyst and enters fractionation system. Formerly natural zeolite and later synthetic molecular sieves were used as catalysts. The catalyst is in the form of beads for the moving bed, and fine powder for the fluid bed cracker. The cracking temperature is usually 450-520°C and the pressure is about normal or slightly above atmospheric.

The major catalytic cracking reaction is initiated by carbonium ions, rather than free radicals as in thermal cracking. The attack of primary carbonium ions on large paraffinic hydrocarbon molecules leads to large carbonium ions (reaction 1), which consequently undergo β-splitting into a lighter carbonium ion and an olefin (reaction 2). The lighter carbonium ion may abstract a hydride ion to form a light paraffin molecule and gives rise to a new carbonium ion to propagate the cycle (reaction 3).

NPTEL

Now, this if you go to a once again to the previous slide this temperature is very high this high temperature and pressure may not be economically suitable, economically acceptable. That means the product of this cracker the cost of the product of this cracker will be high, if the cost of those products are high, then that means the cost of raw materials for polymer is high. So, here monomer and polymer from that monomer cannot compete in the market. Today entire globe is open.

There is open market now in India there are few polymer manufacturer petrochemical industries, they are manufacturing this polymers. Now, if some other manufacturer from other country they supply polymer to India, then in the Indian market if the imported product, imported polymer is available cheaper than our petrochemical industries should be shutdown. They convert many profit, so there is huge competition today because of very efficient catalysts developed for such cracking operations, refining operations.

That means your production cost of these raw materials for polymer should be as minimum as possible. If such high temperature and pressure is required for manufacture of those monomeric raw materials, then we cannot compete in the market with the cost of polymer with other manufacturers. So, this is the basic region, that is why if some catalyst you know the presence of a catalyst can decrease the activation energy of any reaction of any process. So, energy consumption thermal energy consumption during the production of these raw materials or during the production of this polymers is minimized, then there is huge saving of money.

So, cost of the raw material will be lower and that can fine competition in the market your product will be solved in the market, if we taking by the consumers customers. So, that is why the catalysts are used for this, catalytic cracking purpose and the cracking temperature is usually 450 to 520 degree celsius. Today I do not know the what what is the temperature modern, this is little old information.

Just you have to give you some idea. Since, I had this materials I am showing you there are recent book recent literatures available in the library, please go through it. There you will find the conditions of this cracking process, temperature pressure and the nature of catalyst, please go through those things.

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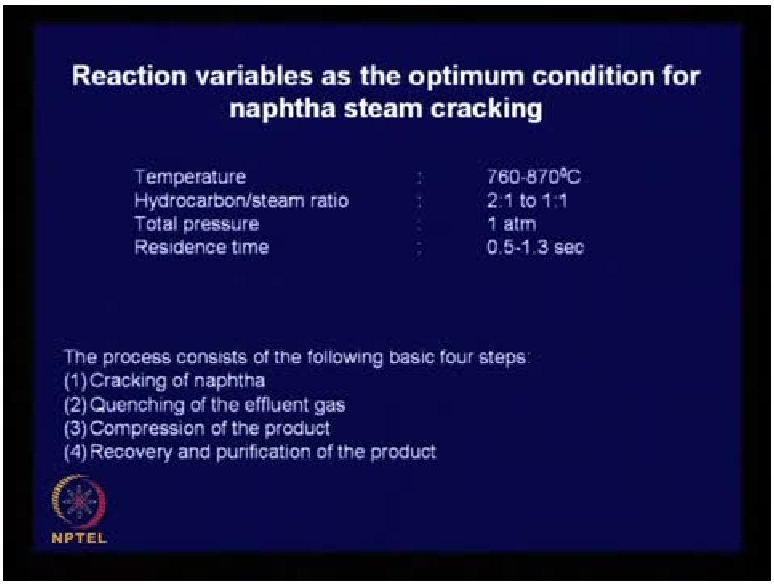

Reaction variables as the optimum condition for naphtha steam cracking

Temperature	:	$760-870^{\circ}C$
Hydrocarbon/steam ratio	:	2:1 to 1:1
Total pressure	:	1 atm
Residence time	:	0.5-1.3 sec

The process consists of the following basic four steps:
(1) Cracking of naphtha
(2) Quenching of the effluent gas
(3) Compression of the product
(4) Recovery and purification of the product

Reaction variables as the optimum condition for naphtha steam cracking, this steam cracking. There was I already shown to you, and look at the reactions came in catalytic cracking.

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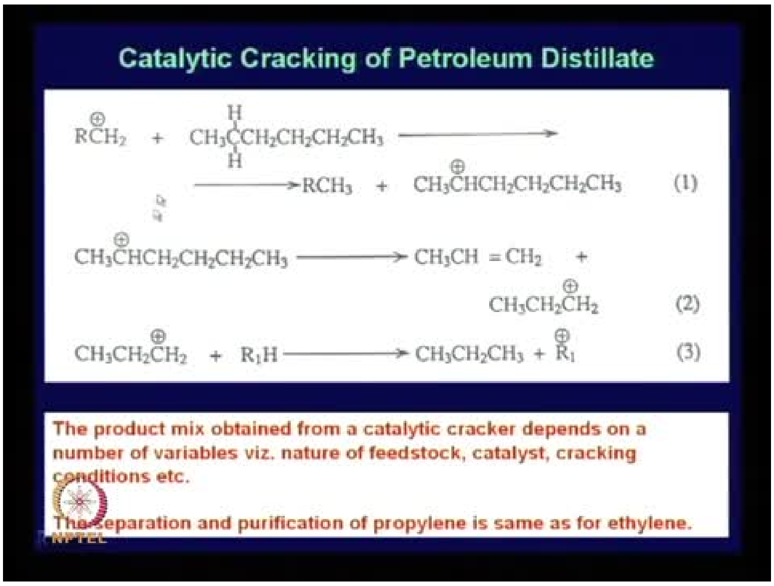

Catalytic Cracking of Petroleum Distillate

$$R\overset{\oplus}{C}H_2 + CH_3\overset{H}{\underset{H}{C}}CH_2CH_2CH_2CH_3 \longrightarrow RCH_3 + CH_3\overset{\oplus}{C}HCH_2CH_2CH_2CH_3 \quad (1)$$

$$CH_3\overset{\oplus}{C}HCH_2CH_2CH_2CH_3 \longrightarrow CH_3CH=CH_2 + CH_3CH_2\overset{\oplus}{C}H_2 \quad (2)$$

$$CH_3CH_2\overset{\oplus}{C}H_2 + R_1H \longrightarrow CH_3CH_2CH_3 + \overset{\oplus}{R}_1 \quad (3)$$

The product mix obtained from a catalytic cracker depends on a number of variables viz. nature of feedstock, catalyst, cracking conditions etc.

The separation and purification of propylene is same as for ethylene.

In the thermal cracking process, you saw the hemolytic session of this carbon carbon bonds leading to smaller fragments of monomers or other hydro smaller hydrocarbons. Here you see infligent of catalyst, this cracking process undergoes by ionic mints and that leads to this monomers like propylene or ethylene or other monomers. The product mixture obtained from a catalytic cracker depends on a number of variables namely nature of feedstock, nature of catalyst, cracking conditions etcetera. The separation and purification of propylene is same as for ethylene.

Again there is huge cost involved in separation of one particular product from a mixture of different hydrocarbons. How many of you have performed distillation of solvent in the laboratory. What operators is used? What set of what operators is there in that distillation setup? Soxhlet is not a distillation setup, soxhlet is a setup used for, who can say? Extraction, soxhlet is not a distillation setup. What is the principle of distillation? You take a solvent in a container, supply heat, it will start boiling, vapor will produced and at a particular pressure it will boil at a constant temperature.

So, due to boiling of those that liquid it produces vapor molecules and those vapor molecules need to be condensed. So, you must have a still distillation still or a container container where you have taken the liquid. That still is connected to a condenser, so vapor will be generated by supplying heat from the bottom of the still or container vapor will try to go out and passed through the condenser where some (( )) being continuously passed that coolant may be cold water chilled water or some gas also cold gas cold oil.

So, those vapor that vapor molecules will be condensed to form a liquid in if that means that is a fraction containing. That is the pure form of one particular fraction, which starts boiling at one fixed temperature and continues till the last stage of that compound is removed from the distillation still that is distillation process. Now, here many things are there those are chemical engineering aspects and unit operations. There is simple setup, I have told you simple distillation setup that contains a container connected to a condenser and a receiver. In the receiver that distillate is collected as a condensate.

Now, the efficiency of distillation efficiency, efficiency of distillation means at minimum energy consumption you have to separate or you have to distill a component in the form, in the pure form. Now, if that vapor is condensed properly, then distillation will be faster otherwise there will be it will go back to the still and it will be collected in the same container, rather than getting as a distillate. So, for that it needs high surface area of high condensing surface high condensing surface, so for those different types of different designs of condenser are available.

Anyway those who will be going for synthesis of chemical compounds or polymer materials, they will need this kind of distillation and again the distillation can be done at a lower temperature than the, than a normal boiling temperature, because because the there is a possibility of degradation. Thermal decomposition of the compound which you of the liquid of the solvent, which you want to distill or separate by fractionate.

So, distillation is a kind of fractionating process technique, fractionating technique fractionating and purification technique by which you can separate one particular pure component from a mixture. There are other techniques also as he told soxhlet soxhlet; that is used for sep also separation by extraction liquid, liquid extraction, solid liquid extraction all this things. So, there are various techniques or unit operations found in or or followed in chemical engineering. Those are necessary for our purpose.

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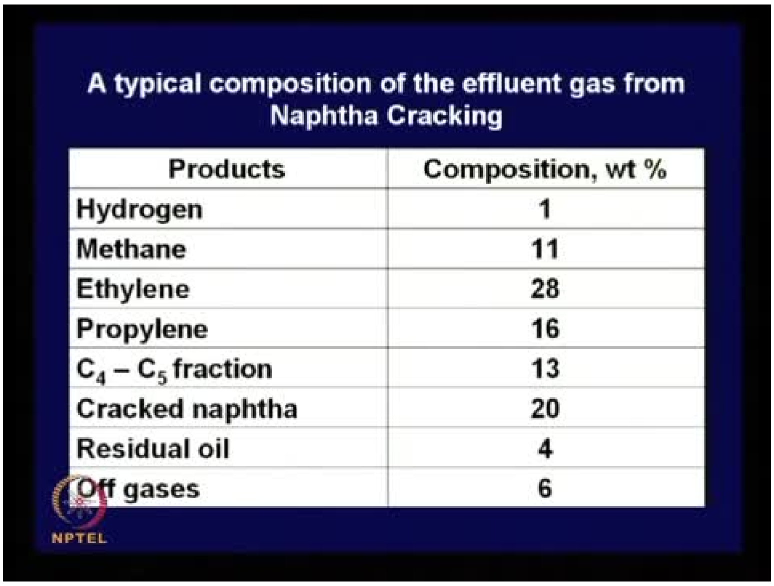

A typical composition of the effluent gas from Naphtha Cracking

Products	Composition, wt %
Hydrogen	1
Methane	11
Ethylene	28
Propylene	16
$C_4 - C_5$ fraction	13
Cracked naphtha	20
Residual oil	4
Off gases	6

Also here, a typical composition of the effluent gas from naphtha cracking you see.

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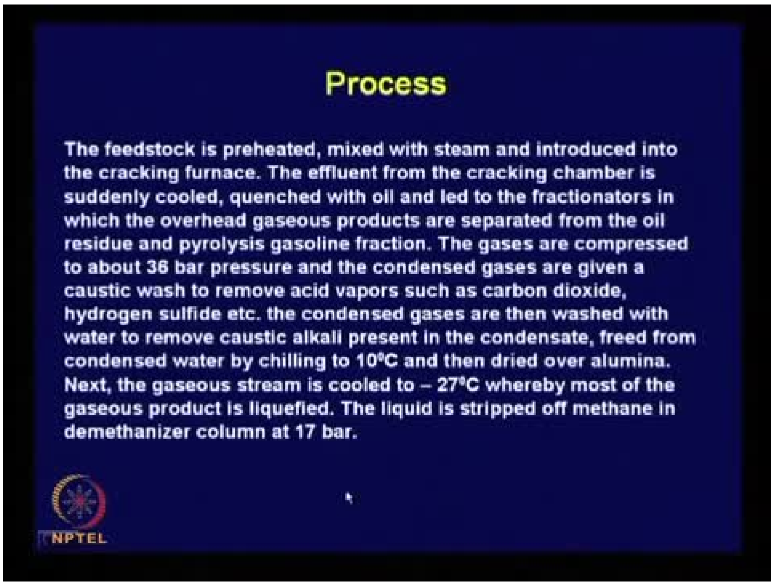

Process

The feedstock is preheated, mixed with steam and introduced into the cracking furnace. The effluent from the cracking chamber is suddenly cooled, quenched with oil and led to the fractionators in which the overhead gaseous products are separated from the oil residue and pyrolysis gasoline fraction. The gases are compressed to about 36 bar pressure and the condensed gases are given a caustic wash to remove acid vapors such as carbon dioxide, hydrogen sulfide etc. the condensed gases are then washed with water to remove caustic alkali present in the condensate, freed from condensed water by chilling to 10°C and then dried over alumina. Next, the gaseous stream is cooled to – 27°C whereby most of the gaseous product is liquefied. The liquid is stripped off methane in demethanizer column at 17 bar.

Of course, catalytic cracking process is there you read.

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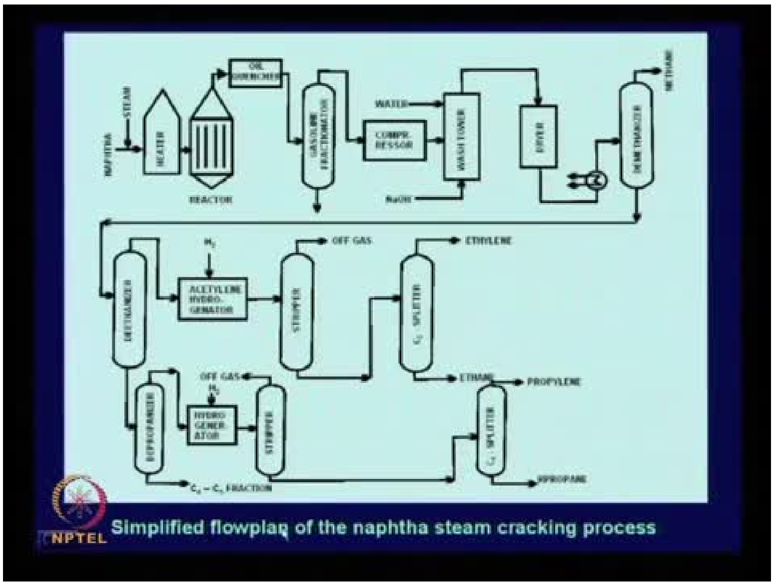

Simplified flowplaŋ of the naphtha steam cracking process

Now, simplified flow plan of the naphtha steam cracking process. Stephen? You are not getting Stephen? Are you getting into rest because you are from different subject? I know any of you feeling uneasy, feeling uneasy? Why?

Student: (( ))

No, it is not that you have to just remember everything from this, I am showing for your some exposure, for some exposure I am showing this things to you. It is necessary, it will be necessary in the next subsequent lectures. You will see some weapons will be there so i am showing the for your information. You see the naphtha steam cracker is a reactor by cracking of pressure is done. Then this fractionators, I was telling you then wash tower again this is a kind of purifier, then a drier, then demethanizer; that means some methane is removed and again from here it comes to the deethanizer, depropanizer, acetylene hydrogenator.

That means you see in a process after cracking, there are large number of order say few number say 5 or 6 compound mixtures are there. Mixture is there in the product steam from their you have to isolate one specific product, how to get these are the various techniques? Say methane is removed, ethane is removed, if you want say ethylene methane is removed, ethane ethane is removed, then if there is some acetylene actually by by hydrogenation of of acetylene hydrogenated.

So, various units are there, so and this product steam is passed through though all those things. Ultimately you can get propylene, ethylene and this something wrong it is be propane, the propane. Some mistake is there, it will propane. So, some propane, propylene and ethylene. You can get this schematic information we started with naphtha and steam feedstock some units it passes through some units. Ultimately you get these products. and these are the basic raw material these are the raw materials for making polymers.

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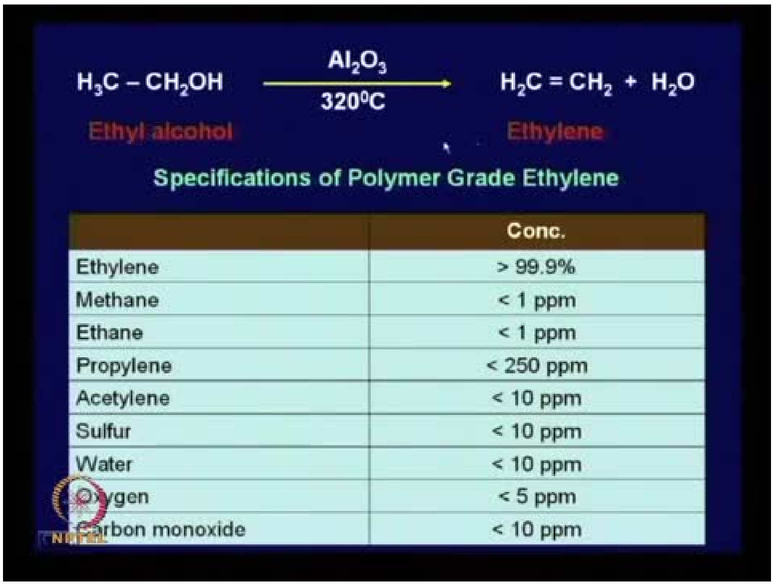

$$H_3C-CH_2OH \xrightarrow[320^0C]{Al_2O_3} H_2C=CH_2 + H_2O$$

Ethyl alcohol

Ethylene

Specifications of Polymer Grade Ethylene

	Conc.
Ethylene	> 99.9%
Methane	< 1 ppm
Ethane	< 1 ppm
Propylene	< 250 ppm
Acetylene	< 10 ppm
Sulfur	< 10 ppm
Water	< 10 ppm
Oxygen	< 5 ppm
Carbon monoxide	< 10 ppm

Again, if you want to make ethylene from ethanol, you can go for dehydration technique this is a specification specification of polymer grade, ethylene polymer grade. Ethylene means ethylene which is used for making manufacturing polyethylene ni99.9 percent purity of ethylene is there. The rest of the things are there, but in very low concentration 1 parts per million, 10 parts per million or 250 parts per million. Actually these influence the final properties of the polymer market.

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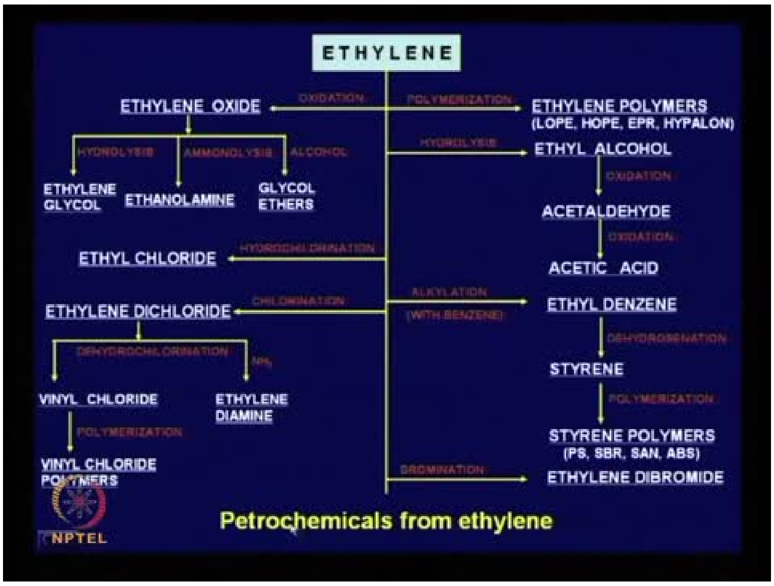

ETHYLENE

ETHYLENE OXIDE

OXIDATION

POLYMERIZATION

ETHYLENE POLYMERS
(LOPE, HOPE, EPR, HYPALON)

HYDROLYSIS

AMMONOLYSIS

ALCOHOL

ETHYLENE GLYCOL

ETHANOLAMINE

GLYCOL ETHERS

HYDROLYSIS

ETHYL ALCOHOL

OXIDATION

ACETALDEHYDE

OXIDATION

ACETIC ACID

ETHYL CHLORIDE

HYDROCHLORINATION

ETHYLENE DICHLORIDE

CHLORINATION

ALKYLATION
(WITH BENZENE)

ETHYL DENZENE

DEHYDROGENATION

STYRENE

POLYMERIZATION

STYRENE POLYMERS
(PS, SBR, SAN, ABS)

DEHYDROCHLORINATION

NH_3

VINYL CHLORIDE

ETHYLENE DIAMINE

POLYMERIZATION

VINYL CHLORIDE POLYMERS

BROMINATION

ETHYLENE DIBROMIDE

Petrochemicals from ethylene

Petrochemical, different petrochemicals from ethylene see different petrochemical from ethylene through derivatization through derivative formation can say, these are chemical process industries. Chemical process units various chemical process units leads to different products, if the source is ethylene. So, these are also raw materials. If you have ethylene, then from ethylene you can get other raw material means in the form of polymers through some chemical transformations. Chemical reactions can see can get styrene you can get phenylade, you can get vinyl chloride you can get ethylene diamine. So, you have the ethylene, if you have the ethylene pure ethylene at low cost you can have these plenty of raw materials.

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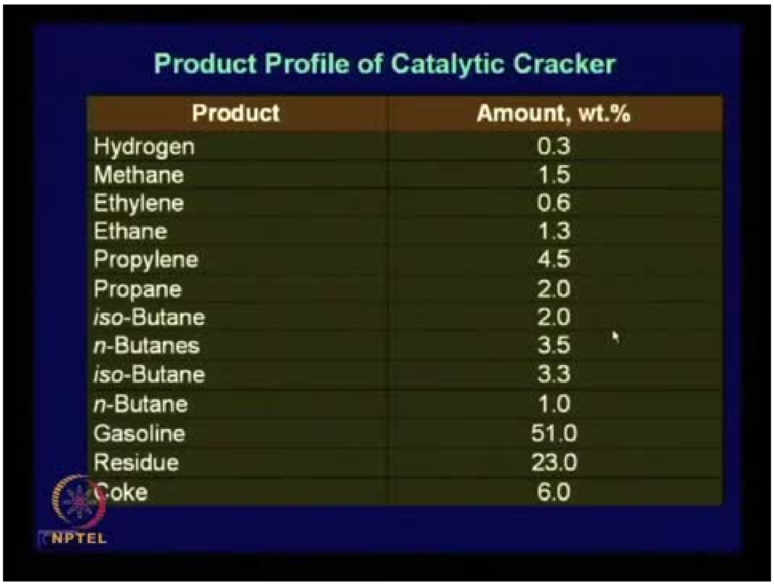

Product Profile of Catalytic Cracker

Product	Amount, wt.%
Hydrogen	0.3
Methane	1.5
Ethylene	0.6
Ethane	1.3
Propylene	4.5
Propane	2.0
iso-Butane	2.0
n-Butanes	3.5
iso-Butane	3.3
n-Butane	1.0
Gasoline	51.0
Residue	23.0
Coke	6.0

Product profile of catalytic cracker. Propylene, you see propylene 4.5 is not very high, then gasoline residue and coke. Why the cost of polymer is so high? 1 kg polymer, know what is the cost of polythene today? Yes please, Pradeepto? So, 70 to 80 rupees 1 kilogram. If you go to market for buying 1 bucket polyethylene bucket, how much they take say ten liter bucket, have not brought purchased? How much it cost?

Student: 50.

No it is more than 50. How much you paid?

Student: (( ))

Bit louder, 65, 70, 80, rupees 100 rupees, Yes you are you are right, 100 rupees. It depends on the manufacturer, quality etcetera. So, that is not 1 kg around, 250 grams, 250 grams or 500 grams or or or its under of 400 grams. So, if the raw material cost is your polymer cost is if there polymer 1 kg polymer is available in 75 rupees, how come that 300 gram bucket takes 80 rupees or 100 rupees from you? They are making huge profit, are they making huge profit? No, you to you have to add the process cost for manufacturing that bucket, that may not be again so high.

See, if 300 gram polymer, how much is the cost? 20 rupees, 25 rupees like that 20, 20, 25 rupees, so add process cost to it, another 15 rupees or 20, rupees so huge margin is there, huge profit is there. So, my my suggestion to you all of you instead of going for job, hunting for job you start one enterpreneurship of manufacturing buckets and supply to these hostels where you can make a profit of say 30 to 40 rupees per bucket, mugs, tubs and even your monofilament polyethylene polypropylene monofilament for making mosquito nets. How many of you have mosquito nets in your hostel? Only one? Be careful huge mosquito’s are there, so you should buy and that mosquito net is made for made of nylon, nylon nets you are using. Are you using nylon nets? Nylon nets what is the cost? What is the size?

Student: (( ))

3 by 5 and half or 6 feet, 3 by 6 they are taking 200 rupees. It is made of polyethylene monofilament, not nylon. Nylon at will be much your expansive than this one.

So, you manufacture polyethylene monofilament. So, do not ask for a job there are many other outlets of manufacturing plastic or polymeric products you can make capital investment, yes. Now, yes come who is who has told capital investment capital investment your friend is a quite rich person there, some friends there. Stephen is there, Stephen is quite rich. So, he can supply money.

Student: (( ))

Yes.

Student: (( ))

Imported plastic, why you are going for imported plastic? Better quality? Not necessary is always the imported plastic imported material are all better quality than the manufacture in India. Anyway, so these are I have given you a brief picture of this raw materials or this polymer manufacture.

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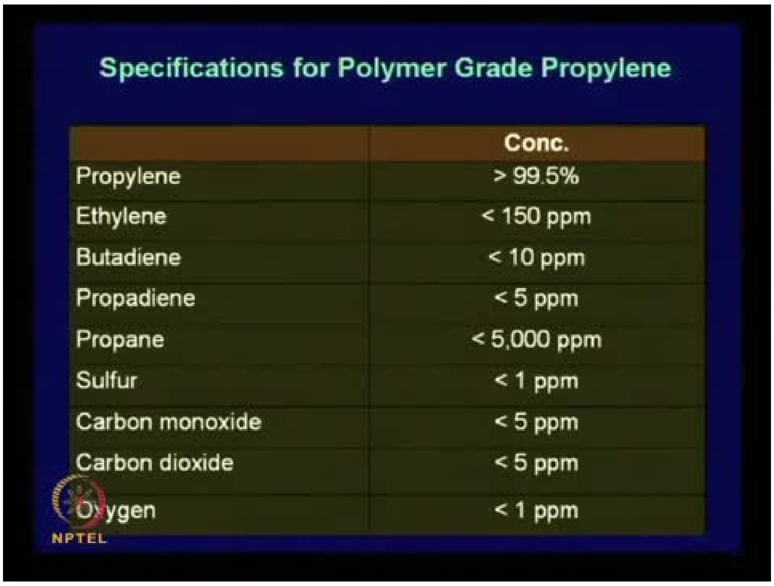

Specifications for Polymer Grade Propylene

	Conc.
Propylene	> 99.5%
Ethylene	< 150 ppm
Butadiene	< 10 ppm
Propadiene	< 5 ppm
Propane	< 5,000 ppm
Sulfur	< 1 ppm
Carbon monoxide	< 5 ppm
Carbon dioxide	< 5 ppm
Oxygen	< 1 ppm

Now if you have any question, queries please ask me, any queries after reading? That means am I to accept that you have (( )) your time in this class?

Student: No sir.

Then why after reading, why not immediately? Hammer the iron when while it is hot, is not it correct? I will forget you will also forget? Then you should immediately ask in the class sir, what is this, what is that, you have not explained that part clearly. Next day we shall start polymer synthesis.