

Chemical Technology
Prof. Indra D. Mall
Department of Chemical Engineering
Indian Institute of Technology, Roorkee

Module - 7
Petrochemical
Lecture - 3
Recovery of Chemicals from FCC and Steam Cracking

We are discussing the module 7 of the organic chemical technology course, and in the module 6 we discuss about the petroleum refinery and the FCC. In the lecture 2 of the module 7, we discuss about the naphtha and gas cracker, because the next lecture will be the recovery of the C₄ and C₅ gases from the FCC and the cracker plant. Actually you see the, I am not I have already discuss in detail about the FCC in the module 6.

What are the products we are getting? What are the development that has taking place in case of the your FCC, how the changes are taking place, the now the FCC that is being operated in propylene mode, and even the recovery of the C₃ gases propylene from the FCC that will be discuss while discussing the propylene, and the module 6 module 7 and the substance lecture. So, I am not going to discuss here the C₃ only here what will be discussing in this lecture that is the recovery of the chemicals from FCC and steam cracker C₄ and C₅ gases.

(Refer Slide Time: 01:57)

Coverage of Lecture

- Introduction
- Upgrading of C₄ and C₅ Cuts
- Typical Compositions of C₄ and C₅ Fractions
- Product profile of C₄ and C₅ Hydrocarbons
- Processing of C₄ and C₅ Cut From Steam Cracker And FCC
- Separation of Butadiene , Isobutylene, Butenes
- Isoprene and Cyclopentadiene
- Oxygenates from C₄ and C₅ cut (MTBE, ETBE, TAME)

This will be the coverage of the lecture introduction of the why we are going for the recovery of the C 4 C 5 gases, what is the importance of these C 4, C 5 hydrocarbon upgrading of the C 4 and C 5 cuts. Because how to separate from these, because many of the fraction, which you are getting here hydrocarbon they are having the close boiling point. How to because this was only became possible with the development of the adsorption technology, in the development of the some of the solvents. Otherwise earlier it was the separation was also difficult of the close boiling component. Similarly, in the C 5 also the same problem was there.

So, typical composition of the C 4 and C 5 fraction because many of the products which are getting from the C 4 and C 5, they are very important valuable petro-chemical feedstock. So, we will be discussing detail about the product profile of the C 4 and C 5 hydrocarbon then the processing of the C 4 C 5 cut from the steam cracker and the FCC. Separation of the butadiene isobutylene and butenes these are the 3 very important raw material, which you are getting from the C 4 C 5 cut for the organic chemical industry, or the petro-chemical industry isoprene and cyclopentadiene that the from the C 5.

(Refer Slide Time: 04:28)

Introduction

- 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.

Another very important is steam and the L D A actually, starting making the M T B E or E T B E or the T A M E, that was the, oxygenates from the C 4 and C 5 cut. And especially, the M T B E, and as I discussed earlier that there was some problem in case of the M T B E leakage of the M T B and as M T B is hydric carsinic. Then the in some of

the develop country they have there is ban in the use of the M T B as oxynate, but the, but at the same thing M T B, which you are getting that can be cracked to get a isobutylene for the synthetic rubber because a pure isobutylene that you can get. Ethyl tersebutaethyl again that is one of the here, instead of methanol that we are using ethanol or the team that is what we are getting from the C 5 steam of the cracker plant.

With the rising demand of the ethylene and the propylene, there has been a tremendous growth in the steam cracking of the hydrocarbon during the last 4 decades. And as I told you that the now the FCC that is the integral part of the any refinery, you cannot imagine a refinery with the FCC or the hydro cracker. So, FCC soap with the coming and the, with the requirement of the propylene, we are going to have more and more FCC in the in the gasoline as well as the propylene more.

(Refer Slide Time: 05:59)

Introduction

- FCC (fluid catalytic cracking) has been also 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. Now FCC are being operated in propylene mode.

So, the even the steam cracking because just to meet the requirement of the rising population, which is going to be seven billion world population 1.3 around 1.2 plus in India, so how to meet that requirement under the various chemical. So, the steam cracker and the FCC they are playing very important role and lot of the development that has taken place, and new furnishes new cracker plant, and new because the there was also one of the constant during the initial stages that was the supply. The especially, the natural gas, ethane, propane supply that was the problem in the initial stage, but now we

cannot afford to lose the natural, and all the natural gas that is being that has to be utilize. So, the more and more cracker plant based on the, your gas cracker plants are coming.

FCC has been also developed into a major upgrading process, in the petroleum refinery as I told you for the conversion of the heavy fuel oil into more valuable products ranging from light olefines to naphtha and middle distillate. Now, FCC are being operated in the propylene modes. This already I had discuss about the how the changes that is taking place in the FCC, even changing in the raw material which are taking. Now, you are talking about resin residue FCC also. So, the even the product which will be getting that will also vary depending upon the operation of the FCC and the feedstock.

(Refer Slide Time: 06:41)

Upgrading of C₄ and C₅ Cuts

- 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 important source of feedstock for butadiene, oxygenates, synthetic rubber, chemical intermediates finding wide application in organic chemical industry.

So, the large amount of C₄ and C₅ compound a produce along with the production of the ethylene in the steam cracker, and the gasoline in the FCC. So, the this because the as I told you during the fluid catalytic cracking although, a rare most of the refinery they are operating the gasoline mode and the propylene that was less, but now we are that is the propylene that is going as high as ever 15 percent, 15 to 20 percent or high it may be 25 percent. So, the now the large amount of the C₄ and C₅ compound they are available from these plants. C₄ and C₅ steams are important source of feedstock for butadiene oxygenates synthetic rubber, chemical intermediates which are finding wide application in the organic chemical industry.

(Refer Slide Time: 07:43)

Introduction

- With increasing demand of C_5 hydrocarbons and oxygenates, upgrading of C_4 and C_5 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.

With the increase in demand of C_5 hydrocarbons and oxygenates upgrading of C_4 and C_5 steam from steam crackers, and the FCC that the catalytic cracker is important to the economic performance of the above process. It also provides the rich resource of reactive molecules, which forms the backbone of the synthetic rubber industry, as I told you the isobutylene or the butadiene or the isoprene, which you are getting from the naphtha cracker.

(Refer Slide Time: 08:18)

Introduction

The quantity and composition of the C_4 and C_5 stream depends on the severity of the steam cracker operation and feedstock being processed.

The quantity and composition of the C 4 and C 5 steam depends on the severity of the steam cracker, operation and the feedstock being processed. As I told you I discuss while discussing the naphtha cracking, the product steam which you are getting that will totally depend upon the type of the feedstock. Let me clear here two things about the regarding the C 4 and C 5 steam, you must know about the difference between the C 4 C 5 steam of the FCC and the C 4 C 5 steam of the cracker plant.

What is happening in case of the C 4 and C 5 of the FCC, we do not have the butadiene fraction that is very negligible amount is there, but in case of the cracker, naphtha cracker we are having lot of the butadiene, especially in the naphtha cracker, so the wherever you are having naphtha, as I told you the 52 percent of the feedstock is through the naphtha cracker.

And still most of the, your cracker plant they earlier based on the naphtha feed, but some of the now the gas base cracker plants are also coming. So, the, whatever the product we are getting that will be different in the composition your butadiene fraction will be only in the naphtha crackers, not in the FCC. And rest of the processing steam which you are having for up gradation they are almost similar.

(Refer Slide Time: 10:06)

Typical Compositions of C₄ Fractions

Component	FCC	Steam Cracking
Isobutane	37	2
Isobutene	15	26
1-Butene	12	14
1,3-Butadiene	0.5	3
2-Butene	11	4
2-Butene	12	5
Cis-2-Butene	11	4

This is the typical composition which I was telling that the in case of the, your, here you see the butadiene percentage that is there in the butadiene, isobutadiene, isobutene, 1 butene, 2 butene for the butenes are there.

(Refer Slide Time: 10:29)

Upgrading OF C₄ And C₅ Cuts	
Typical C ₅ cuts from steam cracking contain	
C ₄	(1%)
n-pentene	(26%)
isopentane	(24%)
n-pentenes	(4.5%)
butenes	(12%)
methyl cyclopentenes	(1.5%)
isoprene	(13.5%)
pentadiene (piperylene)	(9.0%)
cyclopentadiene	(7.5%)
C ₆ ⁺	(1%)

[Chauvel & Lefebvre, 1989].

This is the typical composition of the steam cracking from the C 5 fraction that we are having, and here you see these isoprene and the cyclopentadiene these are the two very valuable products there. This is not butene here, but that will be then means that will be the isoamylene, which are from the amylenes which are using so that is there.

(Refer Slide Time: 10:59)

C₅ Cuts From Steam Cracker And FCC
The C ₅ cuts from steam cracker and FCC can be processed for recovery of valuable C ₅ chemicals. Steam cracker C ₅ cuts contain unsaturated hydrocarbons that can be upgraded, particularly isoprene and cyclopentadiene , as they are present in reasonably high concentration when naphtha feedstock is used.

So, the C 5 cuts from the steam cracker and FCC can be processed for recovery of the valuable C 5 chemicals, steam cracker C 5 cuts contain unsaturated hydrocarbons that

can be upgraded, particularly the isoprene and cyclopentadiene as they are present in reasonable high concentration when naphtha feedstock is used.

(Refer Slide Time: 11:25)

Typical C₅ Cuts From Steam Cracking

- Typical C₅ cuts from steam cracking contain C₄ (1%), n-pentene (26%), isopentane (24%), n-pentenes (4.5%), methyl butenes (12%), cyclopentenes (1.5%), isoprene (13.5%), pentadiene (piperylene) (9.0%), cyclopentadiene (7.5%), C₆⁺ (1%)

Source: Chauvel & Lefebvre, 1989.

(Refer Slide Time: 12:10)

Product profile of butadiene

SB rubber (emulsion/solution)	ABS resins
SB latex (carboxylated)	MBS resins
SB latex (non-carboxylated)	Adiponitrile, HMD, caprolactam
Polybutadiene rubber	Ethylidene norbornene
Nitrile rubber	Lauryl lactum
Nitrile latex	Cyclo-octadiene
Pyridine vinyl SB rubber	1,4-butanediol
SBS/SEBS elastomers	Tetrahydrofuran
Styrene monomer	Sulpholane
n-octanol	1-Octene
Telomers	Specialities

This is the typical composition of the C 5 cuts and here you see the percentage of the isoprene around 13 percent. So, that will variant to 13 percent that may be there pentadiene is also the cyclopentadiene is also because now, there is a solvent that we are using the cyclopentadiene the solvent that we are using, so the importance of the cyclopentadiene at the same time iso. This I was telling they are in the butene that is the,

that was the methyl butene not the butene C 4, but there was methyl butene which we are using for making of the steam.

These are the, we can see the broad range of the product, you are making from the butadiene and the so for the development of the synthetic rubber is concern, that was only because of the availability of the butadiene, and the S B R that is the styrene butadiene rubber. So, that is the still the major portion of the rubber that is from the synthetic styrene butadiene rubber. And so the butadiene that has played very important role in the overall economy of the cracker plant, where you are heading the naphtha cracker because lot of the butadiene that is available.

So, these are the some of the products because in case of the here you the both the S B R that you can make different grade of the S B R that can be there, poly butadiene rubber because now, the many of the petro-chemical complexes instead of going for S B R because if you are going for S B R. Then you need the ethyl benzene ethyl benzene to styrene. So, they are making the poly butadiene even the Haldia they are making the poly not only that Reliance Hazira, they are making the poly butadiene. Even some other plants are also having the poly butadiene.

Nitrile rubber, nitrile mean the combination of the styrene acronitrile rubber that you are having, pyridine vinyl rubber S B S, S E B S elastomer, styrene monomer, n octanol, A B S resin, M B S resin, adiponitrile. This is the one of the very important outlet for the hexamethylene diamine and adiponitrile in the manufacture of the nylons 66, where you are you need the hexa methylene diamine, and the adipic acid for making the nylons salt and then which is the polymerized to nylon 66.

Then the ethylene norbornene lauryl lactum cyclo octadiene 1 4 betanediol, this is also very important. Tetrahydrofuran sulfolane, 1 octane and other specialties these are the some of the major outlet for the butadiene. Similarly, the butene 1 because the butene 1 that is also one of the very important feedstock and especially, when you are having the L L D P comonomer 1 butene you are using. And some of the actually, the where plants they are making the butene 1 from other sources. So, butene 1 that is both the butenes are available that you can separate the butane.

(Refer Slide Time: 14:46)

Product Profile of Butene-1

LLDPE comonomer (1-butene) Amorphous PAOs
HDPE comonomer (1-butene)
n-Butylene oxide
n-Butyl mercaptan
Specialities
1-Polybutene

H D P E comonomer, n butylene oxide, n butyl mercaptan specialties chemicals 1 polybutene. So, these are the some of the product of the butene 1.

(Refer Slide Time: 14:59)

Product Profile of Mixed Butylenes

- 2-Butanol C4 polygasoline
- Methyl ethyl ketone
- 2-Propyl heptanol
- Maleic anhydride
- Higher oxo alcohols
- C4 alkylate
- Propylene (via 2-butene)

Then the mixed butylenes 2 butanol, C 4 pyrolysis gasoline, methyl ethyl ketone, 2-propyl heptanol, maleic anhydride, higher oxo alcohols, C 4 alkylate, propylene because the C 4 steam which I have I discuss while discussing the petroleum refinery, I told you the alkalates are they are going to be important part of the reformulated gasoline. And

already other developed country in other are the some of the Middle East country, they are already having the alkylation plant they are.

And the about I think it is around 10 to 12 percent of the total gasoline from alkylation process, so the C 4 C 5 ice that is going to play a very important role. Similarly, the other com your isobutylene which I told you that is very important isobutylene that you can go for the manufacture of M T B, E T B, polybutylenes, these are the three major apart from the long list is there.

(Refer Slide Time: 16:10)

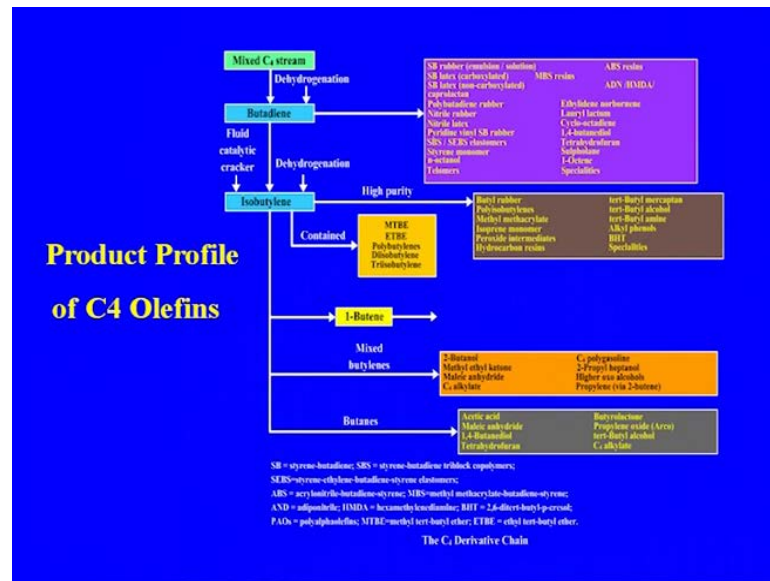
Product Profile of Isobutylene	
Butyl rubber	tert-Butyl mercaptan
Polyisobutylenes	tert-Butyl alcohol
Methyl methacrylate	tert-Butyl amine
Isoprene monomer	Alkyl phenols
Peroxide intermediates	BHT
Hydrocarbon resins	Specialities
MTBE,ETBE,Polybutylenes,Diisobutylene Triisobutylene	

(Refer Slide Time: 16:29)

Product Profile	
Acetic acid	Butyrolactone
Maleic anhydride	Propylene oxide
1,4-Butanediol	tert-Butyl alcohol
Tetrahydrofuran	C ₄ alkylate

Butyl rubber, polyisobutylenes, methyl methacrylate, isoprene monomer which you are getting peroxide intermediate that you have having, and triisobutylene, mercaptan butyl alcohol and some of the specialty di isobutylene. This is the product profile of butene acetic acid, malcic anhydride, 1,4-butanol, butyrolactone, propylene oxide, tertile butyl alcohol.

(Refer Slide Time: 16:41)



This is the complete list of the product which I discuss there the mix C 4 steam butadiene isobutylene M T B, E T B 1 butene the mix butene and butanes. So, all these products already I have discussed separately in detail, and the various product valuable product which you are getting from the C 4 steam. Now, let us discuss we have discussed about the C 4 steam of the various product, which you are getting from the C 4 steam, as I told you the one of the very important.

(Refer Slide Time: 17:22)

Product Profile Of C₅ Hydrocarbon

Isoprene

Synthetic rubber Poly isoprene and Butyl rubber
(substitute for natural rubber), fine chemicals

2 methyl butene 1(2 MB₁) 2 methyl butene -2 (2 MB₂)

Synthetic masks,

Amyl benzene hydrogen peroxide catalyst

2,4 diamyl phenol-photographic colour complex

Pinadone crop protection, chemicals pharmaceuticals

Amylenes: Tertiary amyl methy ether(TAME)

Pentenenes: organic synthesis, polymerisation inhibitor

Product the hydrocarbon C 5 hydrocarbon that you are getting that is the isoprene, and these are the some of the major usage of the isoprene. Another very important constituent of the C 5 steam is the 2 methyl butane, and 2 methyl butane, 1 and 2 methyl butene 2 these are the 2 actually, the hydrocarbon that we are using for making of the tame. Synthetic mask that is also we are using amyl benzene, hydrogen this iso amylenes that we call the amylenes hydrogen peroxide catalyst 2, 4 dimethyl phenol photographic color complex, pinadone which you are getting.

(Refer Slide Time: 18:22)

Product Profile of C₅ Hydrocarbon

Cyclopentadiene

Chlorinated hydrocarbon,

Hexachlorocyclopentadiene agrochemicals

Cyclonephthatriene, cyclopentane

Elastomers, pharmaceuticals,

Crop protection chemicals

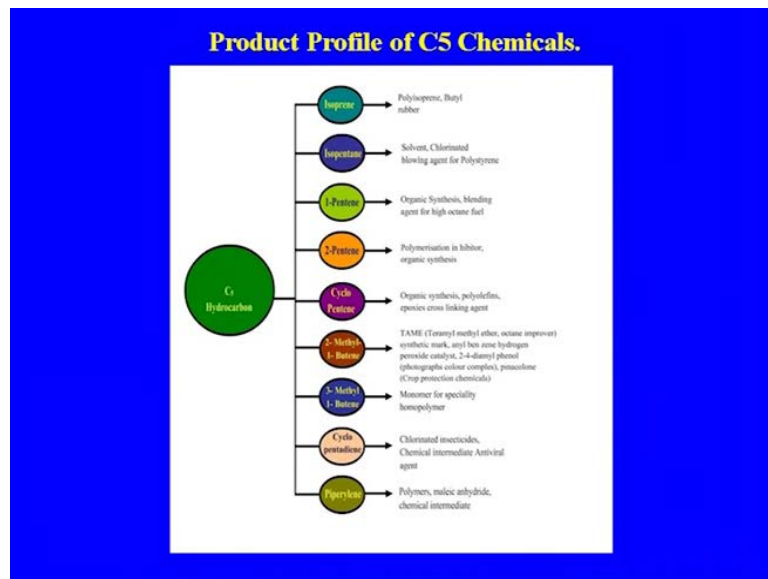
flame retarder (chloroendic acid)

polyesters, medicines, perfumes.

Piperylene: Polymers, Maleic anhydride

There the crop protection chemicals, pharmaceutical industry amylenes. Tertiary amyl methyl which you are dealing that the, this is the amylene then tame you are getting pentenes, organic synthesis and the polymerization inhibitor. Cyclopentadiene that you are making the chlorinated hydrocarbon, hexachloro pentadiene, agro chemical. Then the cyclonephthatriene, cyclopentane, elastomere pharmaceuticals crop protection, flame retarder and then the, another important product you are getting piperylene for the polymers and the maleic anhydride.

(Refer Slide Time: 18:50)



This is the complete list of the C 5 for hydrocarbons already I discuss that the from the isoprene, what are the based product we are getting and the these are various actually, the major product derived from these hydrocarbon which you are getting from the C 5 steam. Now, let us discuss the processing of the C 4 steam because you are getting C 4 and C 5 of course. So, let us discuss for the C 4 cut from the steam cracker because in normal the C 4 that has to be separated from the C 5, the C 4 cut from the FCC and the cracker plant.

(Refer Slide Time: 19:33)

Processing Of C₄ Cut From Steam Cracker And FCC

There is not much difference in the processing of C₄ streams after the recovery of butadiene from the steam cracker and C₄ streams from the FCC.

There is not much difference in the as I told you, in the processing of the C₄ steam after the recovery of the butadiene, because the butadiene is only present in case of the naphtha cracker plant not in case of the FCC. So, after the extraction of the butadiene, the other steam which is left the processing scheme is same whether, it is from FCC or it is from the naphtha cracker.

(Refer Slide Time: 20:05)

Processing of C₄ Cut From Steam Cracker And FCC

C₄ stream Butadiene from C₄ stream of naphtha cracker/ gas cracker is first recovered, followed by separation Isobutylene, isobutane, butane, butane-1 and butene-2 from C₄ stream/ FCC and cracker using various process like etherification, hydrolusis, cracking, adsorption distillation

C₄ steam butadiene from C₄ steam of the naphtha cracker, and the gas cracker is first recovered. It is more in the it is hire in the naphtha cracker gas cracker, it is left followed

by separation of the isobutene because first stage is the separation of the butadiene from the other C₄ means, the isobutylene isobutene butane, butane 1, butene 2 from C₄ steam FCC. And cracker using various process like etherification, hydrolysis, cracking adsorption, hydro isomerization all those that you are using for the separation of the various steam. And adsorption is also because the, you see the olex process, for the separation of the some of the close boiling point, olefins that we are having incase of the separation of the butene 1.

(Refer Slide Time: 21:05)

Butadiene

Butadiene is important raw material for production of a larger number of synthetic rubber and polymers such as styrene butadiene rubber (SBR), poly butadiene, chloroprene rubber, nitrile rubber, acrylonitrile butadiene styrene plastic.

(Refer Slide Time: 21:20)

Butadiene

Other fastest growing use of butadiene is in the manufacture of adiponitrile used in the manufacture of Nylon66, Steam cracker and catalytic dehydrogenation of butenes are the two major sources of butadiene.

Butenes can be recovered from C₄ stream or produced by dehydrogenation of butanes.

Butadiene is the important raw material for the production of large number of the synthetic rubber, and the polymer such as styrene butadiene. Already I have discussed about the various outlet of the butadiene. Other fastest growing use of the butadiene is in the manufacture of adiponitrile, and the hexa methane, which I told you in the manufacture of nylon 66 because nylon 66 and nylon 6 are the two major synthetic fiber, which are playing very important role in using the conventional cotton because the incase of the tire cut lining, we are using the nylon 66, which is having the high melting point then the nylon 6.

So, the steam cracker and catalytic dehydrogenation of the butenes are the two major source of the other source of the butadiene. Butenes can be recovered from the C 4, or produced by dehydrogenation of the butanes because the butane is also the problem that is the, and that is why the even the butanes which are there that can be use for making some of the valuable products. So, let us discuss about the butadiene, what are the sources of the butadiene here I am discussing butadiene, the butadiene one of the important chemical. And so the, we are instead of discussing separately I am discussing in this chapter.

(Refer Slide Time: 22:33)

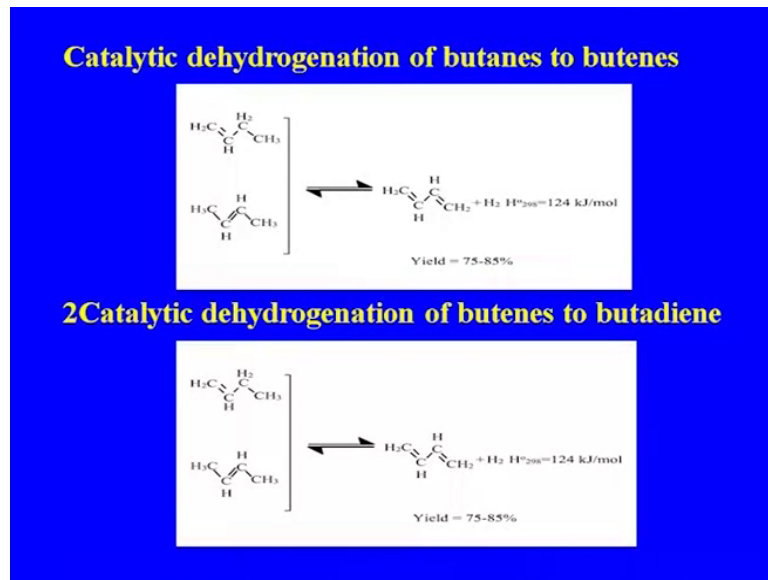
Butadiene

- Steam cracking of naphtha.
- Catalytic dehydrogenation of butenes.
- Catalytic dehydrogenation of butanes.
- Dehydrogenation-dehydration of ethanol (molasses route).

The sources are steam cracking of naphtha other sources are also there because you see the cracker steam cracker that is not very old, so the earlier also the butadiene available and as we are long back. We started in Bareilly that was the synthetic and chemicals parade

were there as we are that was started long back, before coming of the your cracker plant. So, catalytic dehydrogenation of butanes catalytic dehydrogenation of butanes dehydrogenation and dehydration of the ethanol. This was the process that was being used for the butadiene earlier, when the, it was not available from the cracker plant.

(Refer Slide Time: 23:14)



This is the actually the reaction that is taking place in case of the catalytic dehydrogenation of the butanes to butenes, 2 catalytic dehydrogenation of butenes to butadiene this is also, sorry this is also butadiene. Now, let us discuss about the separation of the butadiene from the other C 4 fraction.

(Refer Slide Time: 23:38)

Butadiene Separation

Separation of Butadiene from C₄ Cuts

- Selective hydrogenation of feedstock to remove acetylene compounds: 0.5-1.106 Pa, 10-60°C
- Catalyst palladium
- Extraction by cuprous ammonium salts
- Absorption of butenes 10 to 50 times less.
- Preliminary absorption of acetylenic compound by 20%. Weight solution of ammonium acetate and desorption at 65°C followed by desorption of acetylene compounds at 90°C. Absorption/desorption for butadiene removal.

So, first stage is the selective hydrogenation of the feedstock to remove acetylene compound, which is not needed in case of the when you are using the butadiene for the synthetic rubber in the polymerization that is undesirable part. Here the catalyst as we discussed there in case of the naphtha cracker also, peridium catalyst very commonly in the hydrogenation reaction. Then the next step is the extraction of the butadiene. So, we are having the two methods when the extraction by cupra, cuprous ammonium salts are the distillation using the dimethyl formal anhydride, other solvents are also available.

The absorption of butenes tend to 15 times less than the butadiene. So, the, because butenes they are having the close boiling to the butadiene. So, preliminary absorption of acetylene compound by 20 percent weight solution of ammonia acetate, and the desorption at the 65 degree centigrade followed by the desorption of the acetylene compound. So, the separation that takes place, and absorption desorption for butadiene removal. These are the some of the steps involved in case of the extraction process. Now, let us discuss about the extractive distillation part of the butadiene separation.

(Refer Slide Time: 25:06)

Butadiene Separation

Extractive distillation

Various solvents used are acetonitrile (Shell), furfural (Phillips), dimethyl acetamide (Nippon Zeon), N-methylpyrrolidone (BASF), dimethyl acetamide (Union Carbide)

Process steps: Extractive distillation of acetylenic compounds and extraction of butadiene and separation of other C4 hydrocarbons

Various solvents used are aceto-nitrile because different with the continuous development there has been in case of the solvent also because the phenol, furfural all these were the initial solvent that was available, but with the coming of the manufacture of the dimethyl acetamide, dimethyl formaldehyde that is being used. So, the lot of the changes that has taking place in case of the, your solvent extraction processes. Here the process steps the extractive distillation of acetylenic compounds, and extraction of butadiene and separation of the other C 4 hydrocarbon, this is the process that we are using in case of the.

(Refer Slide Time: 25:55)

Polymerisation Grade Butadiene

1,3 Butadiene % min	99.6%
Butenes ppm max	4000
Methacetylenes ppm. max.	25
Vinyl acetate ppm max	200
C ₅ dimers ppm max	2000
Carbonyl compounds (as aldehyde) max.	50
tert-butyl catechol	100-200
Inhibitor (p-tert-butyl catechol)	200
Non-volatile residue ppm	2000

This is the requirement of the butane butadiene for the polymerization grade. So, the impurity that has to be removed. Now, let us discuss about the isobutene isobutene which is present because after this separation of the butadiene from the cracker plant, that can be combine with the FCC. How? Because this is how the integration of the refinery and the petro-chemical that may be there. So, the from the cracker which you are getting the C 4 after separation of the butadiene, that can be combine with the C 4 fraction of the refinery. And then the further processing that can be done or depending upon the situation it can be separately process in the refinery, or in the your the cracker plant.

(Refer Slide Time: 26:50)

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, ETB, alkylation, polymer gasoline.

So, the isobutylene is present in the C 4 steam of the naphtha cracker, and FCC major application of the isobutene is in the manufacture of the gasoline bending components such as M T B E, E T B alkylation. As I told you the in alkylation use of the isobutylene, as the alkylation that is it has very high scope polymer gasoline that you are getting means, the (()) part which I discuss while discussing the petroleum refinery, the polymerization part.

(Refer Slide Time: 27:26)

Isobutylene

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.

The polymer grade isobutylene can be made by cracking M T B E, or manufacture of poly isobutylene because you see the here what we are getting the isobutene, in case of the polymer grade in the pure of form. So, M T B E which you are getting then that can be cracked and then you can get back the isobutylene. So, isobutylene use in the manufacture butyl rubber, which is made by the copolymerization of isobutylene in the small amount of isoprene.

(Refer Slide Time: 28:01)

Isobutylene From C₄ Stream

First iso butylenes 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 Butane:- isobutylene can be also produced from butane by isomerisation using zeolite Ferrierite (zeolite of medium pore size)

Isobutylene from the C₄ steam cracker first isobutylene is converted to M T B E by etherification, and recovered by cracking of M T B E to get polymer grade isobutylene as I told you. So, either suppose the incase of the after the etherification M T B E direct it can go to the gasoline to, or further it can be cracked to get the isobutylene. It is also obtain by hydrogenation of the isobutylene containing the steam, and then cracking because the isobutylene containing steam that will be hydrogenation.

And after hydrogenation then the again cracking will get back the isobutylene. So, these two roots are available. So, isomerisation of the butane, isobutylene can be also produced from the butane by isomerisation using zeolite. So, this is the separate steam it is not connected with the recovery part, but the as the butane is available. So, butane that can be use for making of the, this is another route that you can get the isobutylene. As I discuss about the importance of the butane 1.

(Refer Slide Time: 29:19)

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 and separation of isobutylene and final y separation by adsorption technology (Olex process) or hydroisimerisation and finally distillation

Butene 1 is a comonomer in the production of the low density, poly ethylene and the high density poly ethylene. Butene 1 can be separated C₄ steam of the cracker after extraction of butadiene and separation of the isobutylene, after the remaining fraction of the C₄ steam that will be use for the separation of the butene 1.

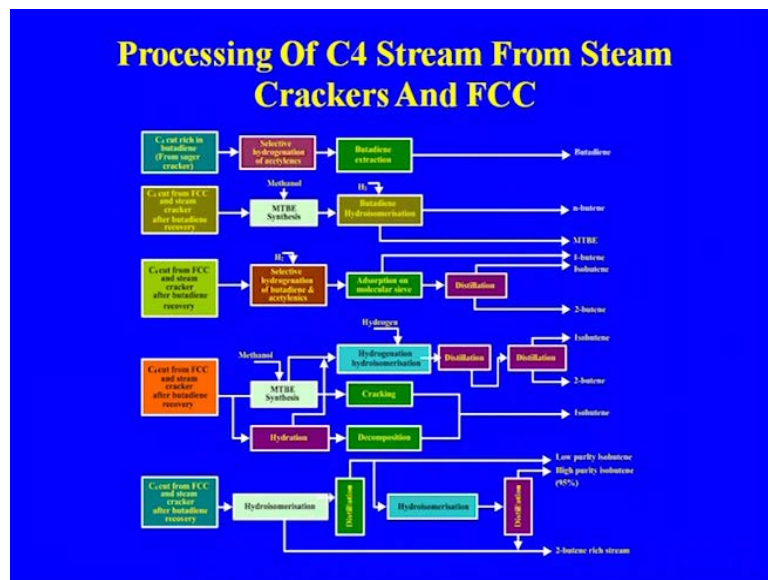
(Refer Slide Time: 29:52)

Butene -2

- Separation of 2-butene involves hydroisomerisation and subsequent distillation for separation of isobutene and 2-butene rich cut.

Separation of the 2 butene involves hydro isomerisation, and subsequent distillation for separation of the isobutene and the 2 butene rich cut.

(Refer Slide Time: 30:04)



This is the complete process that you are having the different cuts, and it is going for the selective hydrogenation of acetylene and then the butadiene extraction. And finally, will be getting the butadiene then the steam from where that can be combine with the C 4 cut from the FCC. Then it will go to the M T B E and M T B E then either by cracking to get

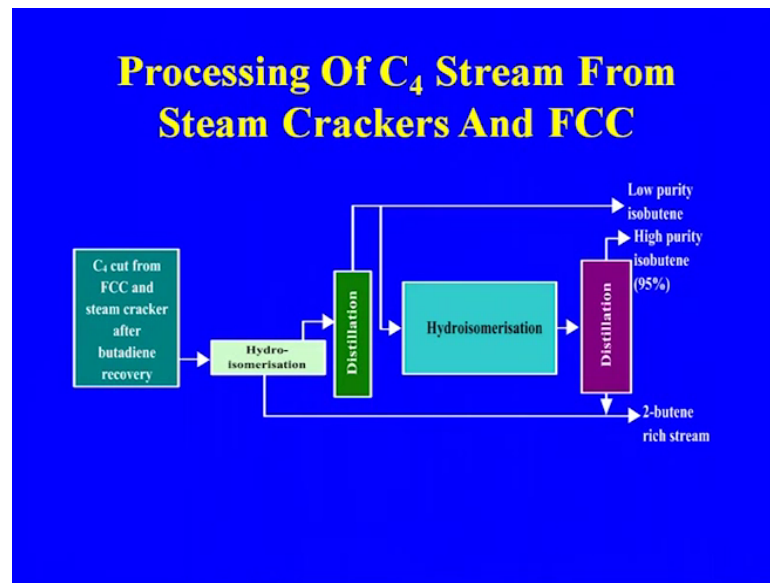
the M T B E, or it will go the your hydro isomerisation process. So, let us discuss in detail about this steam.

So, this is the you see the similarly, here you can go selective hydromerisation adsorption on the molecular sieve distillation for the separation of isobutene, and 2 butene here the cracking M T B E or it will go for the for the separation. Similarly, methanol M T B E that you are if you interested in the M T B E and isobutylene, then methanol the cracking oil which I told you the process hydration. Hydration, and then the decomposition then you can get the pure isobutylene of the polymer grade. So, this is the process that you getting then the hydro isomerisation and the finally, the, you will be getting the various steam of the highly pure steam of the isobutene and the 2 butene.

So, various actually the options are there for separating depending upon the requirement, as in the many of some of the refinery industry take. In the case of the Reliance for they are doing they are making the tame from the C 5 steam, they are not going for the further all in case of the or you see the Bhadodra they are making the M T B E, but as I told you the there has M T B E is very corsogenic. So, M T B E asses it is having it is not having so importance as it used to be earlier, but defiantly if you want to make the isobutylene.

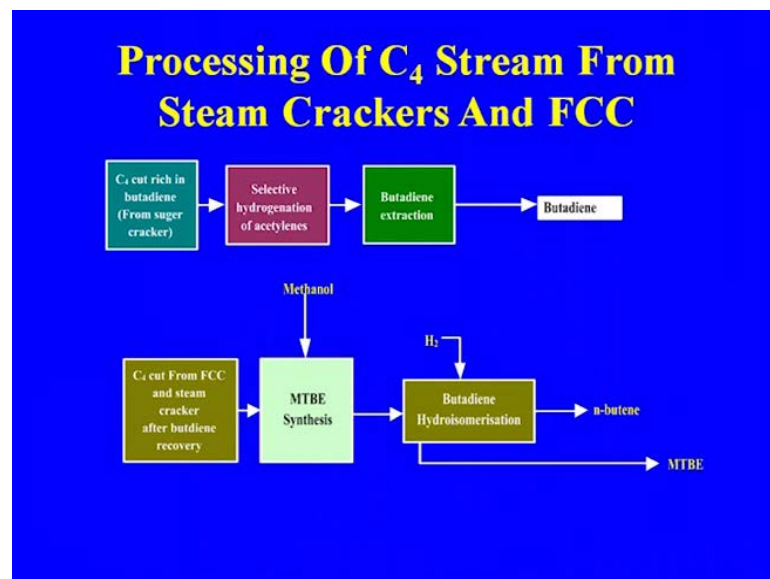
So, the isobutylene that can be separated or butene 1 there are the routes are also for making the butene 1 because in the in the petro-chemical complexes, they are making from other route the butene 1 because that is there requirement, but that can be separated because lab to add more and more units for the separation of the these C 4 gases, or the C 5 gases.

(Refer Slide Time: 32:46)



So, this was I was telling the normally what is happening, you will have to combine these steam C₄ stream after separation of the butadiene, or the butane. And then it will go to the final separation of the various product, low purity isobutene, high purity isobutylene. So, hydro isomerisation is there. So, this is the, a process that can be use for the 2 butene.

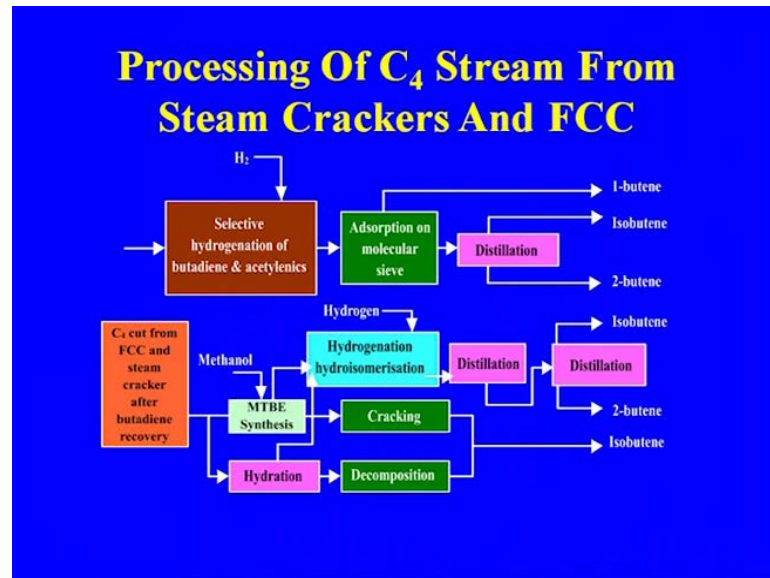
(Refer Slide Time: 33:12)



Similarly, this was the, this is the process which I discuss about the butadiene that is selective hydrogenation of the ethylene butadiene extraction, and then the butadiene.

Then the C 4 cut of the FCC and the steam cracker that will go to the M T B E synthesis butadiene hydro isomerisation, which may be their present. So, n butene will be getting and then the M T B E here M T B E rich steam that will be getting.

(Refer Slide Time: 33:43)



Similarly, this is the another steam that which I was telling common it may be cracking or it may be the decomposition after the M T B E synthesis or the hydrogenation then you can get the isobutene of the polymer grade. These are the other steam that you are getting separation of the 2 butene. Similarly, here the adsorption molecular c because this was the process developed by the E O P L O X process for the separation from butene using the zeolite adsolvent, and it will go to the further distillation then the steam that will contain the isobutene and 2 butene, so any of the combination that may be there in this processing of the C 4 steam. Now, let us discuss the up gradation of the C 5 cut for the recovery of the C 5 chemicals, which I present in the cracker plant or naphtha cracker especially.

(Refer Slide Time: 34:43)

Upgrading Of C₅ Cut For Recovery Of C₅ Chemicals

The naphtha steam cracker C₅ stream is rich resource of olefins and diolefins which can be upgraded to produce elastomers resins and valuable chemical intermediates.

Important C₅ diene and olefins: Isoprene, cyclopentadiene, piperylene, iso amylene, Dicyclopentadiene, Pentene-1

In naphtha steam cracker C₅ stream is rich resource of olefins and diolefins, which can be upgraded to produce elastomers resins and the valuable chemical intermediate. Important C₅ dienes and olefins are isoprene cyclopentadiene, piperylene, iso amylene, dicyclopentadiene and the pentene 1. Because in case of the cyclopentadiene, what you are doing we are first of all converting the dicyclopentadiene and then again disectomy converting the cyclopentadiene. So, I will be discussing now.

(Refer Slide Time: 35:23)

Upgrading Of C₅ Cut For Recovery Of C₅ Chemicals

- The C₅ cuts from steam cracker and FCC can be processed for recovery of valuable C₅ chemicals.
- Steam cracker C₅ cuts contain unsaturated hydrocarbons that can be upgraded, particularly isoprene, pentadiene and cyclopentadiene, as they are present in reasonably high concentration when naphtha feedstock is used.

The C 5 cuts from the steam cracker and the FCC can be process for recovery of the valuable C 5 chemicals steam cracker, C 5 cuts contain unsaturated hydrocarbon that can be upgraded. Particularly the isoprene, and the pentadiene, and the cyclopentadiene as they are present in the reasonably high concentration when naphtha feedstock is used.

(Refer Slide Time: 35:50)

Upgrading Of C₅ Cuts

- Cyclopentadiene is easily dimerised to higher boiling dicyclopentadiene and separated from C₅ stream by simple distillation. Dicyclopentadiene can be cracked to get cyclopentadiene

Cyclopentadiene is easily dimerised to higher boiling dicyclopentadiene, and separated from the C 5 stream by simple distillation because here also the problem of the close boiling point fraction are there. So, the both the combination at the fractionation and the adsorption process are the distillation that we are using here, we are using the liquid extension are extracted distillation using some of the solvent. To cyclopentadiene is easily dimerised to higher boiling dicyclopentadiene, and then it is separated after making of the, and the C 5 steam by simple distillation. Dicyclopentadiene which I told you can be cracked to get back cyclopentadiene, which is having the more value than the dicyclopentadiene.

Then after the separation of these cyclopentadiene, isoprene is separated by extractive distillation from cyclopentadiene free C 5 steam using dimethylformamide because dimethylformamide. Now, the solvent which were not earlier available now the many of the fertilizer plant they are making, the dimethylformamide from the synthesis gas. So, with the availability the D M F even in case of the acrylic fiber also, for the as it saw for the in the disphenic the D M F that is being used.

(Refer Slide Time: 37:21)

Upgrading Of C₅ Cuts

- Distillation remove light acetylenes from the isoprene – priperylene which is further seperated by fractionation
- Isoprene is separated by extractive distillation from cyclopentadiene free C₅ stream using DMF
- Ispoprene 99%, Piperylene 6—75%

So, distillation remove the light acetylenes from the isoprene priperylene which is further separated by fractionation. So, after the extractive distillation we are separating the isoprene, and then the iso pripilene and priperylene fraction again they are separated from the light, and then this steam isoprene and priperylene steam again further separated by distillation. So, isoprene 99 percent priperylene around 75 percent that you are getting purity, this is 60 not 60 to 75 percent. Now, the as I told you the one of the very important product which you are getting from the C₄ C₅ steam that was the that is the M T B E tame and the E T B.

(Refer Slide Time: 38:20)

Oxygenates From Refinery C₄ And C₅ Stream

Several oxygenated fuel components have figured prominently in refinery reformulated gasoline planning. Methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME) and ethyl tertiary butyl (ETB) ether.

So, several oxygenated fuel components have figured prominently and refinery reformulated gasoline, gasoline planning. Especially, with the phasing out of the tetra ethyl and methyl tertiary butyl ether that will play important role, and with the availability of the alcohol also, you can go for the ethyl tertiary butyl ether. And already we discuss in case of the while discussing the petroleum refinery model 6.

The properties of the various oxygenate which you are getting, the octane number improvement in the octane number then the oxygen contain. So, all those thing that already I have discussed here I am not going only the process, how we are making the process these oxygen that will be discussing. So, the M T B E tertiary amyle methyl tame which you called in a ethyl E T B these are three major oxygenate which you are producing from the C 4 and C 5 steam.

(Refer Slide Time: 39:26)

Oxygenates from refinery C₄ and C₅ stream

- All oxygenated fuels reduce hydrocarbons in the automobile exhaust. MTBE was considered one of the most important oxygenates used in the production of lead free gasoline and was used produced on a large scale throughout the world.

All oxygenated fuels reduce hydrocarbons in the automobile exhaust. M T B E was considered as one of the most important oxygenates use in the production of the lead free gasoline, which I told. And was used produce on a large scale throughout the world, but without after the environment constant the problem with the carcinogenic nature of the M T B E they are in banned. So, the again the units are change, changing from the M T B E to other products variable product, but let us discuss the process.

(Refer Slide Time: 40:03)

Methyl Tertiary Butyl Ether (MTBE)

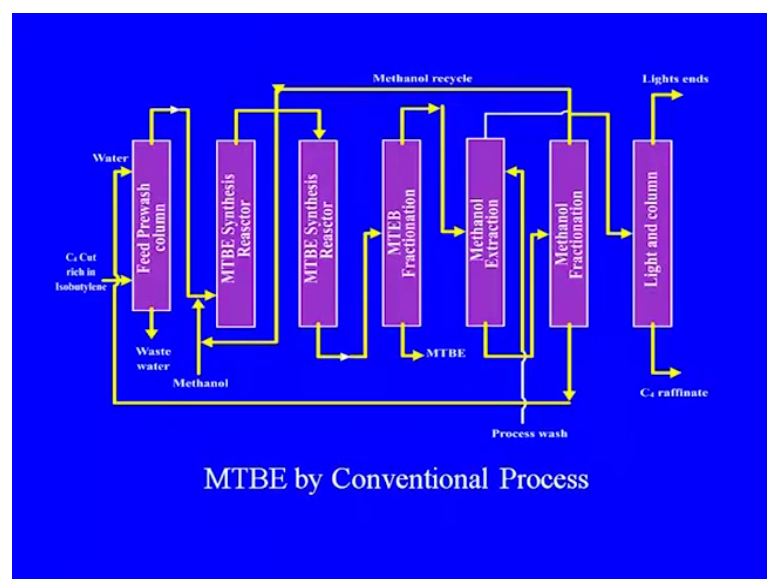
MTBE which is made by etherification of C4 gases from cracker and FCC is also used for production of polymer grade isobutylene for synthetic rubber by cracking.

Conventional process

Reactive Distillation process

MTBE which is made etherification of C4 gases from the cracker, and FCC is also used for the production of the polymer grade isobutylene, which we discuss while discussing the separation of the various C4 gases from the FCC and the cracker plant. There are processes by which the MTBE is made one is the conventional process one stage process and the reactive distillation process, where the reactor followed by reactive distillation column where both the reaction and distillation simultaneously take place. So, the finishing stage you can say the finishing reactive distillation unit is there, and so this both the processes that have been used for making of the MTBE.

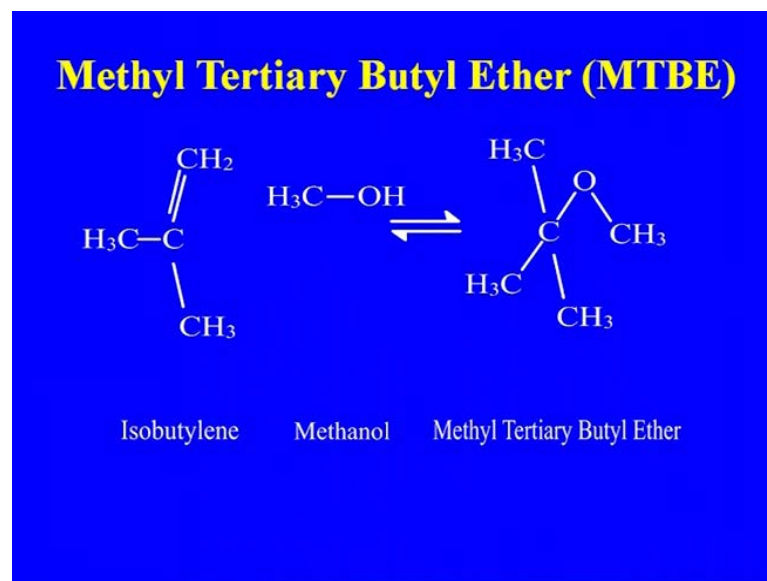
(Refer Slide Time: 40:53)



This is the process that you are getting here c four this is the by the conventional process after the methanol that is you are having one reactor, but in case of the, your this is the your feed preparation part. This is the M T B E synthesis where methanol that is being added by etherification, then M T B E reactor that is going two reactors are there then the fractionation.

In case of the two stage process we are having the reactive distillation part also then M T B E fractionation, you are separating the M T B E then the methanol un reacted methanol that is separated and that is again recycle to the reactor. So, this is the process there is not much different between the reactive distillation only the presence that is better, we are having the finishing stage reactor distillation also there that is the different. Similar process also the same type of the flow diagram is also for making the tame.

(Refer Slide Time: 42:03)



This is the reacting that is taking place, the isobutylene and the methanol that is reacted and we are getting the methyl tertiary butyl ether.

(Refer Slide Time: 42:19)

Ethyl Tertiary Butyl Ether (ETBE)

ETBE is made by etherification of isobutylene with ethanol similar to MTBE.

Isobutylene + Ethanol



Now, let us discuss about the ethyl tertiary butyl ether because ethanol because of the problem in case of the M T B E, and due to availability of the ethanol from the molasses route, or some other route because the both the routes are there. You can get from the ethylene to ethanol or ethanol to ethylene. So, ethanol that can be, but we are not making, but that can be made with the, from the ethylene and then it can be used for the, your etherification, with the isobutylene and for making of the ethyl tertiary butyl ether.

(Refer Slide Time: 43:19)

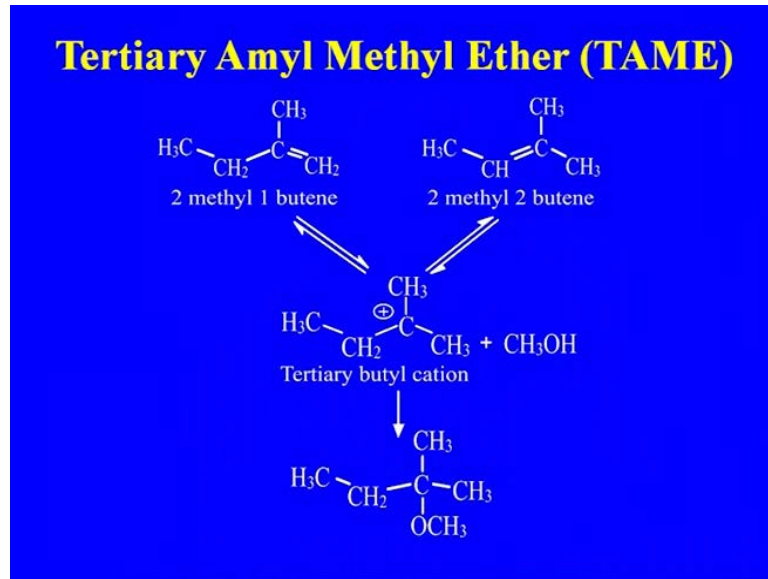
Tertiary Amyl Methyl Ethane(TAME)

TAME is produced by etherification of Isoamylene. Isoamylene can be recovered from C₅ stream of steam crackers.

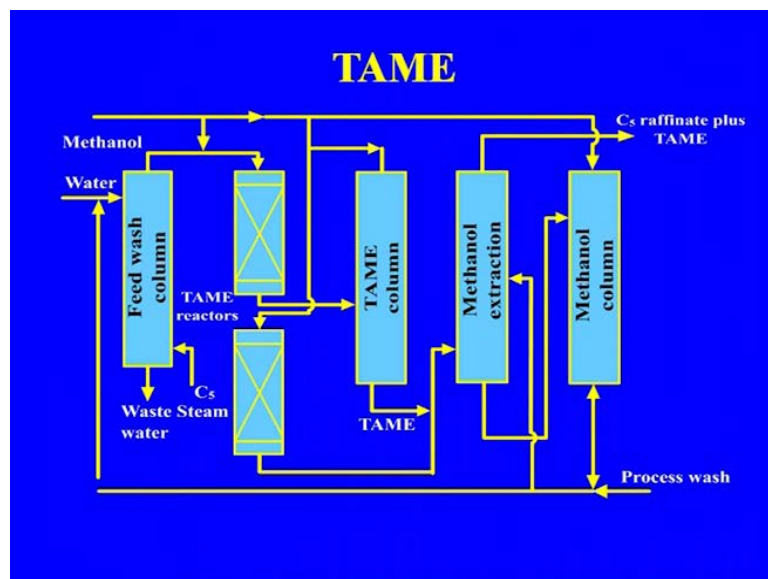
Two reactive components of iosmaylenes are 2-Methyl butene-1 and 2-Methyl butene-2. catalytic distillation process is used for the manufacture of TAME

This is a very good oxygenate and that be use although it is not being manufacture in India, but in the future you may have E T B also. Now, comes the tame tertiary amyl methyl ether that is produced by etherification. Of isoamylene which is present in the C 5 steam and isoamylene can be recovered from the C 5 steam of the steam cracker, or the FCC because you see the reliance Jamnagar refinery they are making the tame.

(Refer Slide Time: 44:03)



(Refer Slide Time: 44:19)



And the C 5 steam they are using for making of the etherification they are doing the combine steam C 4 C 5 that is going for a etherification. So, 2 reactive components of

the isoamylene, 2 methyl butene 1 and 2 methyl butene 2 there which are participating the reaction, and the catalytic distillation process use for manufacture of the tame. So, actually this is the reaction that is taking place to M T B E your butene 1 M B 1, and M B 2 and that is going to after the etherification you will getting the tertiary butyl.

This is the process actually the we are getting in case of the tame manufacture methanol and the water feed pre wash section, which is the tame flow diagram as it was in case of the your M T B E. So, then it will go to the tame reactors and then separation of the tame that will take place here, it is not combine it is you are getting the tame from here and the rest of the it is going un react for the separation of the your this is tame, and the from this, that is going to the for the separation of the tame, and at the same time methanol from where it is recycled to the system. From where it is not it is coming from this, it is coming from this and it is going to the tame column.

So, this was about the recovery of the chemicals C 4 C 5 steam from the FCC and the cracker plant because that is one of the important source of the feedstock, for the synthetic rubber industry and some of the value added product. So, the in fisher we may have some of the processing steam, which I discuss in the refinery although presently we are only having the, your M T B E, or the tame and the separation of the butadiene that is may practice.

In case of the petro-chemical complexes, but the in the future because you see the whole processing steam that is very complicated. So, definitely that will act to the cost, but in the future because we are going for the more and more economy and the, for the upgradation of the processes. So, definitely the recovery part of the C 4 and C 5 that will play important role.

The next lecture will be discussing about the some of the steam that you are getting. Because you see the any refinery complex petro-chemical that have the three major section that may be cracker plant, that may be the synthesis gas part synthesis gas means, it may be the nitrogen and hydrogen or C O N H 2, or it may be the your aromatic plant. So, the will next lecture will be discussing about the synthesis gas manufacture. What are the various products from the synthesis?

And then the importance of the even the C O 2, C O each actually component of the synthesis gas they are very important and at the same time. What is happening in case of

the synthesis with the coming of the new G T L technology, or methanol to propylene technology synthesis gas that is going to play a very important role? So, the next lecture will be on the methane and the synthesis gas.