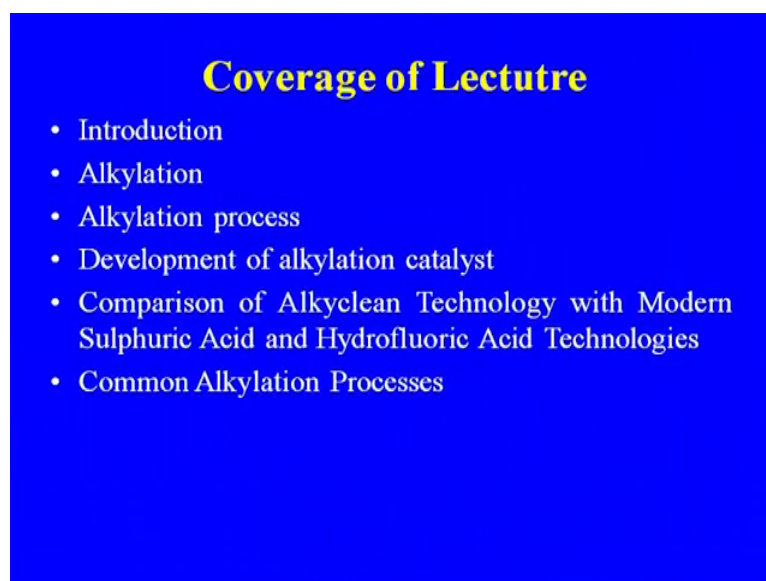


**Chemical Technology**  
**Prof. Indra D. Mall**  
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**Indian Institute of Technology, Roorkee**

**Module - 6**  
**Petroleum Refinery**  
**Lecture - 7**  
**Alkylation Isomerisation and Polymerization**

We are discussing the module 6 of the Chemical Technology course, which is dealing with the Petroleum Refinery process. In the lecture 6, we discuss about the catalytic reforming process, which is one of the very important unit of the any refinery that is for the improvement of the octane number of the low octane naphtha. Some of the other processes that has been developed and that is been used in the refineries to improve the octane number of the some of the feed low octane feeds to high octane gasoline. So, the among these processes Alkylation, Isomerisation and Polymerization, especially the oligomerisation that is very important part in case of the refinery operation.

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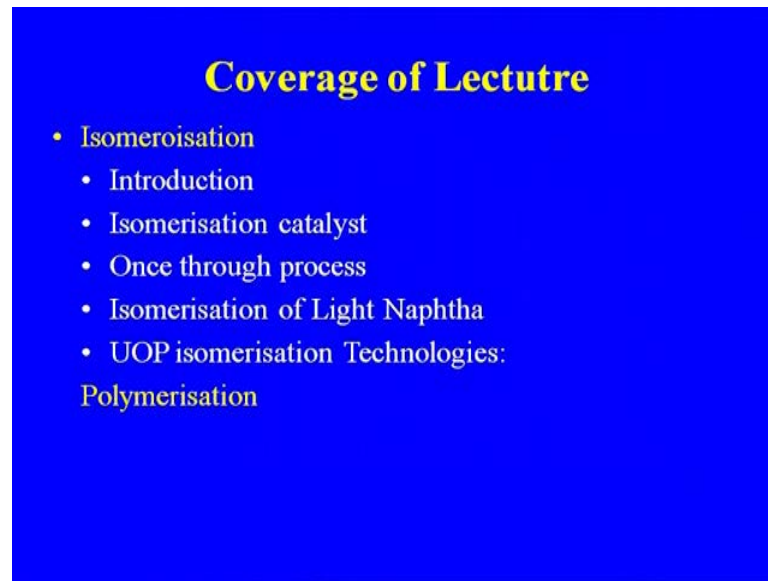


**Coverage of Lectutre**

- Introduction
- Alkylation
- Alkylation process
- Development of alkylation catalyst
- Comparison of Alkyclean Technology with Modern Sulphuric Acid and Hydrofluoric Acid Technologies
- Common Alkylation Processes

Coverage of the lecture that will be the introduction alkylation, alkylation process, development of the alkylation catalyst, comparison of the alkylation technology with modern sulphuric acid and hydrofluoric acid, common alkylation processes.

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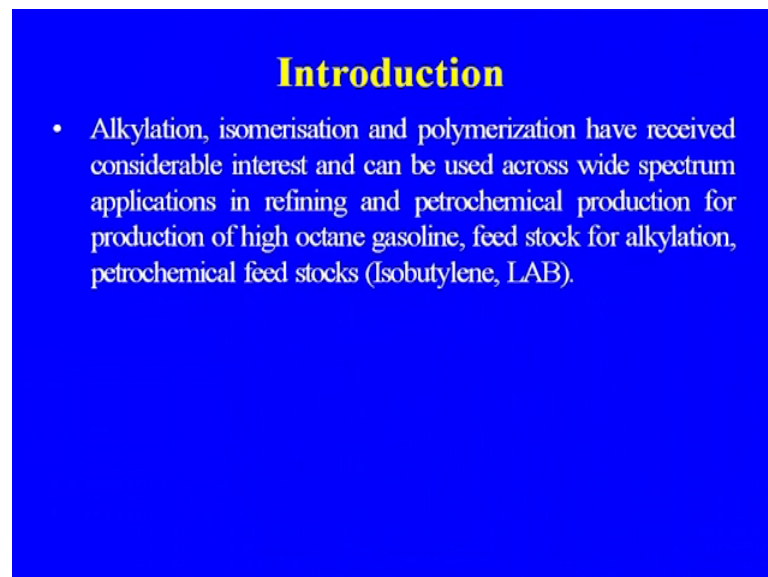


**Coverage of Lectutre**

- Isomeroisation
  - Introduction
  - Isomerisation catalyst
  - Once through process
  - Isomerisation of Light Naphtha
  - UOP isomerisation Technologies:
- Polymerisation

Then the isomerisation that will left the again introduction, isomerisation catalyst, once through process, isomerisation of the light naphtha, UOP isomerisation technologies and then the polymerization. Some of the technology, which are available in case of the polymerisation or aluminisation, which I told you for improving the octane number.

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**Introduction**

- Alkylation, isomerisation and polymerization have received considerable interest and can be used across wide spectrum applications in refining and petrochemical production for production of high octane gasoline, feed stock for alkylation, petrochemical feed stocks (Isobutylene, LAB).

Alkylation isomerisation and polymerization have received considerable interest and can be used across wide spectrum of application in refining and the petrochemical production or production of the high octane gasoline. Feed stock for the alkylation, petrochemical

feed stock just like the isobutylene or linear alkyl benzene were also we are using the alkylation process.

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**Table 10.1 Alkylation, Isomerisation and Polymerization**

	Feed stock	Source	Process	Typical product	Application
Alkylation	Petroleum gas Olefins Isobutane	Distillation, cracking Catalytic or hydro cracking Isomerisation	Unification	High octane gasoline	Gasoline pool

This is the how the alkylation, I will be discussing in detail, what are the feed and other thing alkylation isomerisation let us discuss for the alkylation. This is the petroleum gas olefin isobutene, distillation, cracking, source and then the process unification, type of the product high octane gasoline, application gasoline pool.

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**Table 10.1 Alkylation, Isomerisation and Polymerization**

	Feed stock	Source	Process	Typical product	Application
Isomerisation	n-Butane n-pentane n-hexane	From various refinery processes	Rearrangement	Isobutene Isopentane isohexane	Alkylation Gasoline pool Gasoline pool

Similarly, the isomerisation feed stock n butane, normal pentane, normal hexane source from the various refinery processes. Process rearrangement typical product yield that will be the isobutylene, isopentane, isohexane and the application that is the alkylation of the that will go to the gasoline pool.

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**Table 10.1 Alkylation, Isomerisation and Polymerization**

	Feed stock	Source	Processes	Typical product	Application
Polymerization	Light Olefins (ethylene, propylene, Butylenes)	Various Refinery processes	Unification	High octane naphtha Petrochemical feed stocks LPG	Gasoline pool

Polymerization light olefins that will be the C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub> various refinery processes. Because, this process that has become important with the coming of the more and more FCC and generation of more or lighter effluent that lighter, it will that can be used in these processes for up gradation of the octane number. So, the unification process typical product high octane naphtha petrochemical feed and application is the gasoline pool.

Now let us discuss the about the alkylation alkylation is important unit in the refinery to upgrade light olefins and isobutene into highly value gasoline component. Light olefins are produced mainly by catalytic cracking, which you are getting from the the FCC gases, which you are recovering now. And the now there has been lot of emphasis emphasis in the refinery to separate the various useful component of the C<sub>4</sub> because C<sub>3</sub> propylene you were recovering.

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## Alkylation

- Alkylation is important unit in refinery to upgrade light olefins and isobutane into highly valued gasoline component
- Light olefins are produced mainly by catalytic cracking
- Alkylate is one of the best gasoline blend because of high octane

But, now there has been continuous increasing in the refining to recover the C 4 components of the F C C gases. Alkylate is one of the best gasoline blend, because of the high octane number. So, the in future refinery what we will see because we cannot totally depend up on the either crude oil distillation or the only the catalytic cracking or the or the catalytic reforming process. But, that will be the blame, because the gasoline pool will be getting a blend of the various ah high octane gasoline, if you are getting from the various conversion process.

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## Future Refinery

- Reformulated Gasoline blend of product from
- Alkylation, Isomerisation
- Catlytic Reforming
- FCC and Hydrocracker
- Polymerisation
- and
- Oxygenates

So, reformulated gasoline blend of the product from alkylation isomerisation catalytic reforming FCC and hydrocracker polymerization and plus addition of the oxygenates. So, that will be the reformulated gasoline in the future, because here also oxygenate means addition of the methanol or addition of the alcohol. So, that will increase the total, if you increase in the output of the refinery and at the same time better octane number.

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### **Alkylation**

- Alkylation process, which was commercialized in 1938, since then there has been tremendous growth in the process.
- In US and Europe about alkylate is about 11-12 % and 6 % in the gasoline pool respectively.

So, alkylation process, which was commercialized in 1938, since then there has been tremendous growth in the process. In US and Europe about alkylate is about 11 to 12 percent, that is going to the gasoline pool and 6 percent in the 11 to 12 from the US and 6 percent in the Europe country. But, still in India we do not have the alkylation process in most of the refinery, I think the need refinery in Bhatinda that might have the alkylation unit one of the major constraint in the alkylation process in the availability of the alkylation.

Because, this is we will be discussing about the catalysts, what are the catalysts that we are using and the development of the changing the catalytic use of the sulphuric acid, so hydrochloric acid, solid is there. These are the some of the development that are taken place in case of the alkylation and in the future alkylation process that is going to play very important role in an increasing the octane number and at the same time enhancing the production of the gasoline.

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### **Alkylation**

- Alkylate is a key component in reformulated gasoline.
- Alkylation processes are becoming important due to growing demand for high octane gasoline and requirement of low RVP, low sulphur, low toxics.

Alkylate is a key component in the reformulated gasoline, alkylation process are becoming important due to growing demand for high octane gasoline and requirement of the low re vapour pressure, low sulphur and the low toxicity. Alkylate is an ideal blend stock to meet these requirement, the process of alkylation different iso paraffin's using olefins, were developed during 30s using aluminium chloride catalyst. However, the catalyst was later replaced by sulphuric acid and hydrofluoric acid.

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### **Alkylation**

- The process of HF alkylation produces high octane blend stock for isoparaffin ( mainly isobutane) and olefin (propylene, butylene and amylenes) to meet all the criteria of reformulated gasoline.
- Replacing high risk toxic liquid acids, such as hydrofluoric acid(HF) and sulphuric acid with solid acid catalysts was challenging goal isoparaffin alkylation technology.

First it was the hydrofluoric and because of some problem, this will be discussing about the when, we will compare the these sulphuric acid to hydrofluoric acid and again because in case of the hydrofluoric acid lot of the corrosion problem was there. So, now, the shift in the catalyst from H F to solid acid catalytic that is there.

Alkylation of the C 5 cut from the F C C can significantly reduce the R V P of the finished gasoline pool. The process of hydrofluoric alkylation because that was the earlier alkylation process that was being used and still that is being used in many refinery the process of hydrofluoric acid H F alkylation produces high octane blend stock for iso paraffin.

Mainly isobutene and olefin, propylene, butylenes and amylene to meet all the criteria of the reformulated gasoline, replacing high risk toxic liquid acids such as hydrofluoric acid and then sulphuric acid which is solid acid catalyst was the challenging goal iso paraffin alkylation technology and this has the major development in case of the catalyst. The shifting from sulphuric acid to hydrofluoric acid and from hydrofluoric acid to solid acid catalytic.

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### **Alkylation**

- Alkylation is Environmentally safer routes to maximise C5-C7 alkanes from C3- C4 olefine and iosbutane feed for reformulated gasoline blend stock.
- Development of non-hazardous solid acid catalyst is the driving force for more environmentally safe alkylation units all over the world

So, alkylation why, we are alkylation is environmentally safer routes to maximize C 5 C 7 alkanes from C 3 C 4 olefin and iso butane feed for reformulated gasoline blend stock. Development of the non hazardous solid acid catalyst is the driving force for more environmentally, safe alkylation units all over the world. And now they slowly mills are



shifting from the they are changing, they are going for the solid acid catalyst alkylation process.

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### **Alkylation**

Although butylenes alkylation is one of the most commonly used process, however, alkylation of amylenes obtained from C<sub>5</sub> fraction of FCC can be another route to increase the availability of alkylate.

Butylenes alkylation is one of the most commonly used process. However, alkylation of the amylenes because the C 5 part as I told you, the now the more and more interest is for the recovery of the C 4 and C 5 gases from the refinery. Because, C 4 what we are doing in some of the refinery M T B isobutene, that is going. They are using for making the M T B methyl tert-butyl ethyl, which is being used as a oxygenate, but as I told you earlier also, now there is the ban on use of the M T B in many of the developmentry. So, now, what they have shifted to the team, but alkylation of the amylenes obtained from the C 5 fraction of F C C can another route to increase the availability of the alkylate. Because, C 5 still, we are not doing the alkylation, that is going to the, a stem manufacturing. C 5 alkylate, amylene alkylation has 2 fold advantage. It increase the volume of the alkylate available, while decreasing the Reid vapour pressure and olefinic content of the gasoline blend stocks.

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## Alkylation

C<sub>5</sub> alkylate: Amylene alkylation has two fold advantage: It increase the volume of alkylate available while decreasing Reid vapor pressure and olefinic content of gasoline blend stocks

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## Alkylation Process

- The reaction involved in aliphatic alkylation consist of conversion of isobutane and butylenes to iso octanes using HF catalyst.
- The side reaction results in increased iso butane consumption increased acid consumption increased acid soluble formation, equipment handling and for the corrosion problem .

The reaction involved in the alkylation consist of conversion of the Isobutene and isobutylene to iso octane using H F catalyst or solid acid catalyst whatever the catalyst. That, we are using the side reaction which are taking place that results in increased, iso butane consumption, increase acid consumption, increase acid soluble formation, hydrocarbons, equipment handling and corrosion problem.

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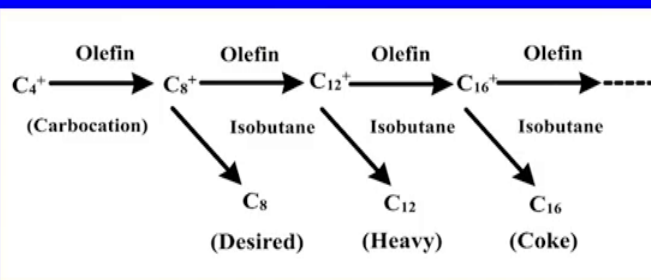
## Process

- The key factors to be controlled in alkylation process are
- Maintaining proper composition of reaction mixture which include isobutene olefins and the HF acid.
- Maintaining the proper reaction environment which includes adequate contacting, controlled temperature, freedom from surges.
- Making a proper separation of the reactor effluent into its various components.

The key factors to be controlled in your alkylation process are maintaining proper composition of the reaction mixture, which include isobutene isobutene and olefins and the H F acid. Maintaining the proper reaction environment, which includes the adequate contacting, control temperature freedom from surges, making a proper separation of the reactor effluent into various component.

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## Isoparaffin Alkylation Mechanism



This is the reaction, which is taking place in case of the iso paraffin alkylation. So, these are the this is the desired reaction and this is the because the your paraffins and the olefin

that you are getting alkylation. So, these are the some of the un desirable part, that is taking place in case of the alkylation process.

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**Process**

- Some of the other side reaction is the formation of paraffin which boils above and below the desired product. Impurities in the feed acid and normal operating practices all can contribute to additional side reactions

$$i-C_4H_{10} + C_4H_8 \longrightarrow C_8H_{18}$$

Some of the other side reaction is the formation of the paraffin, which boils above and below the desired product impurities in the feed acid and normal operating practices, all can contribute to the additional side reactions. So, let us discuss now the, because as I told the number of the alkylation process, that has been developed depending up on the catalyst that is being used.

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**Common Alkylation Processes**

CONOCO Phillips process (ReVAP process): Alkylation of propylene, butylenes, pentenes and isobutane to high quality motor fuel using HF catalyst.

The CONOCO Phillips process that is the alkylation of the propylene, butylenes, pentanes and isobutene to high quality motor fuel using hydrofluoric acid catalyst.

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### Common Alkylation Processes

**UOP Alkylene™** : UOP Alkylene process is based on solid catalyst (HAL-100) for alkylation of light olefins and isobutane to form a complex mixture of isoalkanes which are highly branched trimethylpentanes (TMP) that have high octane blend values of approximately 100.

U O P alkylene, T M U O P alkylene process is based on the solid acid catalyst for alkylation of the light olefins. Because, this is the same while discussing the L A B, we discussed the solid acids catalyst now the alkylation process for the l a b manufacture is based on the solid acid catalyst. Similarly in, case of the refinery also the future refinery that is not going to use the H F.

But, they are going to use solid acid catalyst for alkylation. So, this is the development of the catalyst that has been developed by the U O P. So, the process of the U O P alkylene T M, they uses the solid acid catalyst for alkylation of the light olefins and isobutene to form a complex mixture of iso alkanes, which are highly branched tri-methyl pentanes, that have octane blend values of the approximately 100.

So, this is what our interest is to have highly branch paraffins U O P as earlier the process of H F was also there. So, U O P H F process alkylation of the iso butane with a light olefins, propylene, butylenes and amylenes to produce branch chain paraffinic paraffin fuel using hydrofluoric acid catalyst that was the more than 100 commercial process.

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### **Common Alkylation Processes**

UOP HF Alkylation Process: Alkylation of isobutane with light olefins (propylene, butylenes and amylenes to produce branched chain paraffinic fuel) using hydrofluoric acid catalyst. More than 100 commercial process.

Because, most of the process which, we have earlier started alkylation process in refinery that was based on the H F, but because of the highly corrosive nature of the H F and the cost involved, now the new refinery ordinary refinery also they are shifting because the environmental constraint that is also one of the problem. So, they are shifting from H F to solid acid catalyst.

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### **Common Alkylation Processes**

AlkylClean solid Acid alkylation technology (ABB Lummus global): The alkylation process uses a robust zeolite solid acid catalyst formulation coupled with a novel reactor processing scheme to yield a high quality alkylate product. The catalyst contains no halogen

A B B as lumus global the alkylation process uses a robust, zeolite solid acid catalyst formulation coupled with a novel reactor processing scheme to yield a high quality alkylate product. The catalyst contain no halogen.

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### **Common Alkylation Processes**

**Exxon Alkylation:** Alkylation of propylene, butylenes and perylene with isobutene in the presence of sulphuric acid catalyst using auto-refrigeration.

**Products:** a low sensitivity, highly iso, low RVP, high octane gasoline blend stock paraffinic.

Exxon alkylation process alkylation of the propylene butylenes, perylenes with the isobutene in the presence of sulphuric acid catalyst using auto refrigeration, product a low sensitivity highly iso low R V P high octane gasoline blend stock. But, only problem here in case of the is of the sulphuric acid.

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### **Common Alkylation Processes**

**Stratco INC:** Alkylation of propylene, butylenes and amylenes with isobutane using strong sulfuric acid to produce high octane branched chain hydrocarbons using effluent refrigeration alkylation process.

Stratco I N C that process alkylation of the propylene, butylenes and amylenes with isobutene using strong sulphuric acid to produce high octane branch chain hydrocarbons. Using the effluent refrigeration alkylation process, because that is also one of the requirement of the process low temperature.

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<b>Comparison of Alkylation Technologies</b>			
Parameter	Modern sulphuric acid technology	Modern hydrofluoric acid technology	Alkyclean
Base condition	C4 feed stock	C4=feed stock	C4=fedstock
Product RON	95	95	95
Product MON	Base	Base or better	Base or better
Alkylate yield	Base	BASE	90% of base
Total installed cost	Base	85% OF BASE	50% of base

These are the some of the comparison of the parameters base condition product R O N product motor octane, gasoline, alkylate yield and the total installed. If you compare with the modern sulphuric acid technology, modern hydrofluoric acid and the alkyclean the solid acid catalyst the product M O N and there is not much difference in the this is going the criteria.

Because when, we are using an catalyst the now the environmental for corrosion for these are also coming the picture the total cost. So, the product is it is the product in case of the modern hydrofluoric acid is the better M O N best or better than this alkylate base 90 percent of the base ninety percent of the base total install cost here, it is more than this this sulphuric acid, when we are using the catalyst. Total install cost in case of the hydrofluoric acid less.



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<b>Comparison of Alkylation Technologies</b>			
Parameter	Modern sulphuric acid technology	Modern hydrofluoric acid technology	Alkyclean
Total installed cost, including OSBL(regeneration, facilities, and/or safety installations)	Base	Less	None

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<b>Comparison of Alkylation Technologies</b>			
Parameter	Modern sulphuric acid technology	Modern hydrofluoric acid technology	Alkyclean
ASO yield	Base	Less	None
Equipment maintenance	High	High	Much lower
Corrosion problems	Yes	Yes	Higher

ASO yield base less none equipment high high much lower, that is the one of the major advantage in case of the a solid acid catalyst corrosion problems. So, the equipment maintenance that is very high in case of the in these 2 sulphuric acid and the hydrofluoric acid catalytic histology and that is the reason, why we are going for solid acid catalyst.

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<b>Comparison of Alkylation Technologies</b>			
Parameter	Modern sulphuric acid technology	Modern hydrofluoric acid technology	Alkyclean
Reliability and on stream factor	Base	Base	Match FCC or better/shorter

Reliability and on the stream factor so, match F C C or the better shorter.

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<b>Comparison of Alkylation Technologies</b>			
Parameter	Modern sulphuric acid technology	Modern hydrofluoric acid technology	Alkyclean
Safety	Unit specific safety precautions as well as transport precautions unit specific precautions	C safety precautions required that extend throughout refinery very specific	No special precautions other than those for any refinery process unit

Safety unit specific safety precautions as well as transport precautions unit is specific is there because depending up on the unit. C safety precautions required that extend curve output of the refinery very specific, because we have the highly corrosion nature and safety part that is no special precautions, that is the one of the again advantage in that these of the solid acid catalyst.

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Param-eter	Modern sulphuric acid technology	Modern hydrofluoric acid technology	Alkyclean
Catalyst	H <sub>2</sub> SO <sub>4</sub>	HF	Zeolite
Environmental	Significant waste streams generated	Significant waste streams generated	No emissions to air, water, or ground

Catalyst we have the zeolite, catalyst that is we are using in one and significant waste streams that is produced here. Actually, if you compare with the H F and H<sub>2</sub>SO<sub>4</sub> amount of the H F required, if you compare with the H<sub>2</sub>SO<sub>4</sub>, that is much less than what we are using in case of the sulphuric acid alkylation and this is this was the one of the reason for shifting from sulphuric acid to hydrofluoric acid alkylation.

So, in case of the solid acid catalyst no emission to air water or ground. This was about the alkylation process importance of the alkylation process and as I told you the now the engine refinery is also as we are not having the alkylation isomerisation already they have it. So, more and more alkylation may come in the future and with the development of the solid acid catalyst. Now it is it will be easier to go for the alkylation then the problem of the sulphuric acid handling corrosion are the alkylation of the.

So, the isomerisation part again the just like the alkylation part, isomerisation part that is also playing very important role now in the refinery as a measure conversion process for improvement of the octane number. Because, the that is the stream which we are getting product from the refinery they are low octane number product. So, how to improve, so that is one step in case of the improvement of the octane number, that is the isomerisation part.

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## Isomerisation

- Petroleum fractions contain significant amounts of n-alkanes and the isomerisation of alkanes into corresponding branched isomers is one of the important process in refining.
- The highly branched paraffins with 7-10 carbon atoms would be the best to fulfill the recent requirements of the reformulated gasoline.

So, petroleum fractions contain significant amounts of normal alkenes and the isomerisation of the alkenes into corresponding branch isomers is one of the important process in case of the petroleum refining. The highly branched paraffin with 7 to 10 carbon atoms would be the best to fulfil the recent requirements of the reformulated gasoline.

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## Isomerisation

### Driving Force for Light Paraffin isomerisation

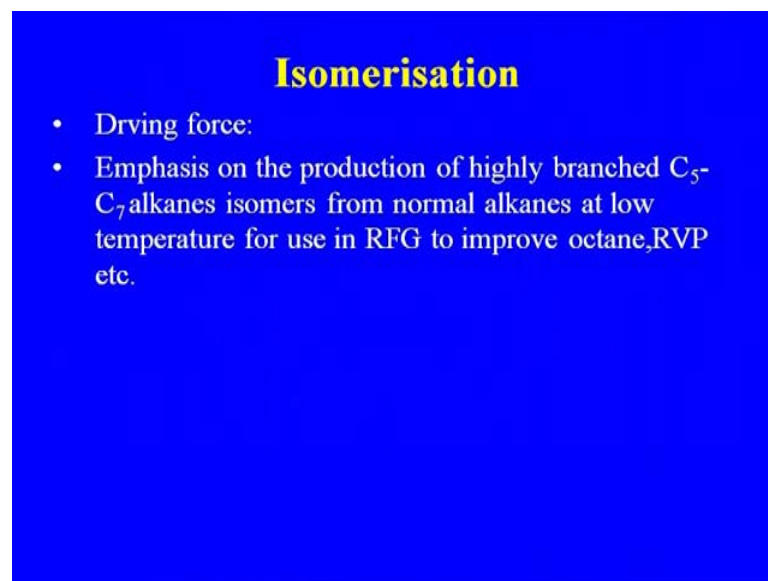
- ❖ Recent trend sho isomeristion could be significant contributor to octane pool
- ❖ Offset octane loss from gasoline desulphurisation and aromatic reduction
- ❖ Benzene Management
- ❖ Increased LPG production

What are the driving force of the light paraffin isomerisation, because why they needs earlier, when it is where in, I mean in the Indian refinery, we are not having the

isomerisation. But, many of the now, new refineries they are going for the already some of the refinery already they are having the isomerisation unit. And they need refinery definitely they are going to have the isomerisation part. So, driving force for the light paraffin isomerisation.

Recent trend shows isomerisation could be significant contributor to octane number. Offset octane loss from gasoline desulphurization and aromatic reduction benzene management increase L P G production. Because, benzene reduction as per the U R O norms U R O pool will have to reduce the benzene content of the gasoline, that is one percent that is recommended and. So, the now they were going for the isomerisation that will be good actually the from the naphtha also, because naphtha isomerisation that is also being trend. So, that will go to the gasoline pool.

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**Isomerisation**

- Driving force:
- Emphasis on the production of highly branched C<sub>5</sub>-C<sub>7</sub> alkanes isomers from normal alkanes at low temperature for use in RFG to improve octane, RVP etc.

So, driving force emphasis on the production of highly branched C<sub>5</sub> C<sub>7</sub> alkenes isomers from the normal alkenes at low temperature for use in reformatting gasoline to improve the octane number and the R V P re vapour pressure. Because, the R V P is also included in the tenders and so, the R V P that has to be controlled.

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### **Isomerate as Percent of Gasoline**

- USA: widely implemented during lead phase out more than 8%
- Western Europe: widely implemented during Euro IV phase in
- India: New units have installed now isomerisation

Isomerate percent of the gasoline U S A widely implemented during the lead phase out more because they that was the period when the requirement how to improve the octane number. So, that was the tetra ethylene that was added.

But, because of the environmental problem that was phase out even indent refinery also be no more lead, we are using for the tetra ethylene for improving the octane number. So, that will be completely phase out all over the world because of the lead pollution. But, in case of the U S, they have gone for the implementation of the isomerisation processing the refinery and more than 8 percent of the gasoline pool.

They are getting from the as isomerate, which we are getting from the isomerisation, western Europe widely implemented during the Euro 4 phase in because the now they are all the even Indian refinery they are ready to provide the Euro 4 fuel some of the refinery. So, that is the how the things was the importance of, but Indian new units have installed now the isomerisation, but still there is lot of scope in going for the further to have the isomerisation process in the Indian refineries.

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### Isomerisation

- The production of paraffin based high octane gasoline blend stock, such as isomers from isomerisation of light and mid cut naphtha might be a key technology for gasoline supply to cope with future gasoline regulation.
- Light naphtha and paraffin isomerisation recognizes emerging technologies in order to boost octane in light gasoline fractions.

Now, let us discuss about the isomerisation, the production the paraffin based high octane gasoline blend stock such as isomers from isomerisation of light and mid cut naphtha might be a key technology for gasoline supply to cope with the future gasoline regulation, because we are producing low octane and the use, if it is going to the gasoline during, because our requirement may be...

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### Isomerisation

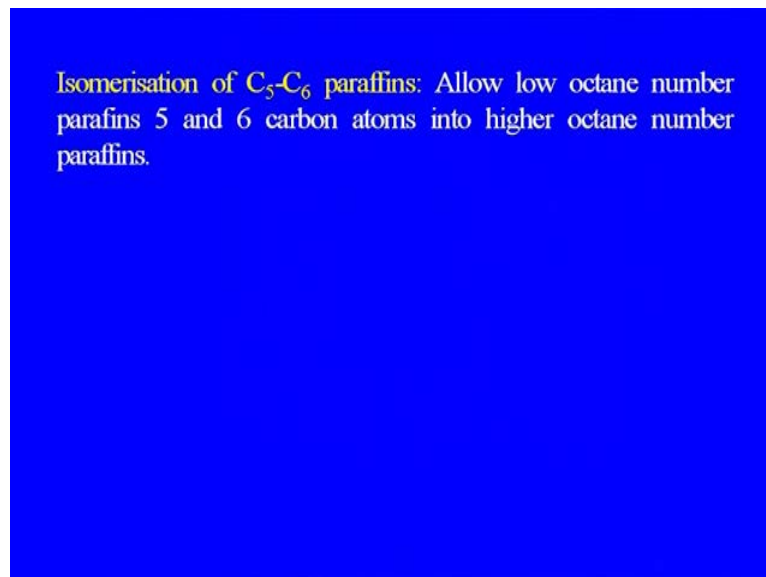
- Recent pricing trends show isomerisation could be a significant contributor to octane pool which will offset the loss from gasoline desulfurisation and aromatic reduction.
- Isomerisation involves
  - Isomerisation of Light paraffins
  - Isomerisation of C<sub>5</sub>-C<sub>6</sub> paraffins
  - Isomerisation of n-butane

Because more and more gas crackers also coming soon more and more naphtha will be available in the refinery and. So, this technology low octane naphtha to high octane

naphtha by isomerisation process definitely that will boost the economy of the refinery. So, light naphtha and the paraffin isomerisation recognize emerging technology in order to boost octane in the light gasoline fractions.

Recent price trends show isomerisation could be a significant contributor to octane pool, which will offset the loss from gasoline desulfurisation. And the aromatic reduction this is taking place, because now that has become the integral part desulfurisation for the removal of the what about the thesis of the sulphur is there. Because, to meet the requirement of 0.3 or 0.4 isomerisation involve isomerisation light paraffin isomerisation of the C<sub>5</sub>-C<sub>6</sub> paraffin isomerisation of the n butane.

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Isomerisation of the C<sub>5</sub>-C<sub>6</sub> paraffins allow low octane number paraffins 5 to 6 carbon atom into higher octane number paraffins. This is the advantage in case of the when, we are going for the isomerisation of the C<sub>5</sub>-C<sub>6</sub> n pentane isopentane n hexane to 2. Methyl pentane 2,2 methyl dimethyl butane, 2,3 butane isomerisation of n butane.



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n-pentane- isopentane:

- n-pentane to 2-methyl pentane, 3 methyl pentane ( low octane 75)
- 2,2 dimethyl butane, 2,3 dimethyl butane

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Isomerisation of n-Butane: To produce isobutene feed for alkylation or as source of isobutene dehydrogenation to manufacture MTBE.

To produce isobutene feed for alkylation or as source of isobutene dehydrogenation to manufacture of the M T B E. Isomerisation catalyst as it where, they having the continuous development in the isomerisation process also in the refinery.

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### **Isomerisation Catalyst**

- Two types of isomerisation catalyst, zeolite and chlorinated alumina, has been used.
- Zeolite catalyst requires higher temperatures and provide lower octane boost while chlorinated alumina's results in highest octane.

Two types of the isomerisation catalyst zeolite and the chlorinated alumina has been used and the zeolite catalyst requires higher temperature and provide lower octane boost, while chlorinated alumina result in highest octane.

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### **Isomerisation Catalyst**

- However, it has higher sensitivity to feed stock impurities requiring strict feed pretreatment to eliminate oxygen, water, sulphur and nitrogen is containing compounds.

However, it has higher sensitivity to feed stock impurity requiring strict feed pretreatment to eliminate oxygen, water, sulphur and nitrogen, containing compound.

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### Isomerisation Catalyst

- Zeolite
- Chlorinated alumina
- Zeolite catalyst requires higher temperatures and provide lower octane boost
- Chlorinated alumina's results highest octane, however, it has higher sensitivity to feed stock impurities requiring strict feed pretreatment to eliminate oxygen, water, sulphur and nitrogen containing compounds.

Isomerisation catalyst as it will be may be zeolite and may be chlorinated chlorinated alumina zeolite catalyst require higher temperature and provide lower octane boost chlorinated alumina result highest octane. However, it has a higher sensitivity to feed impurities. Isomerisation with light naphtha as I told you the some of the crude oil, which we are having the more paraffinic. So, the pertibute of the light naphtha, which is more paraffinic and the octane is low. So, many refinery, they have gone for isomerisation of the light naphtha to improve the octane number.

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### Isomerisation of Light Naphtha

- $C_5/C_6$  feed either from straight run crude distillation or from catalytic reformig
- *Reformate*: separated in lighter mostly benzene and heavier containing C7
- Catalyst: Zeolite or Pt on Chlorinated alumina.

C 5 C 6 feed either from straight run crude distillation or from the catalytic reforming that is going for the isomerisation process. So, reformate separated in lighter mostly benzene and heavier containing C 7 catalyst zeolite or platinum on chlorinated alumina.

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<b>Operating Condition</b>		
	Pt on Chlorinated Alumina	Pt on Zeolite
Temperature oC	120-180	250-270
Pressure	20-30	15-30
Space velocity h <sup>-1</sup>	1-2	1-2
H <sub>2</sub> /HC ratio	0.1-2	2-4
Product RON	83-84	78-80

Operating condition depending up on the type of the catalyst, we are having the temperature changing pressure is also space velocity hydrogen to have hydro carbon ratio and the product research octane number. Depending upon the type of the catalyst, the parameter slightly different from the parameters are there.

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- | <b>Once Through Process</b> |                              |  |
|-----------------------------|------------------------------|--|
| •                           | Recycle Process:             | Unconverted n-paraffins and any single branched isomers from double branched isomers |
| •                           | Recycling with Distillation: | Deisohexaniser   |
| •                           | Recycling with Adsorption:   | Adsorption on Molecular sieve: n-paraffins are adsorbed and separated by desorption  |

Process recycles process un converted normal paraffins and any single branched isomers from the double branched isomers. Recycling with the distillation deisohexaniser that is added recycling with the adsorption, adsorption on the molecular sieve n paraffins are adsorbed and separated by desorption. So, these are some of the actually, various type of the configuration that may be in case of the isomerisation process as I told you there has been continuous development in case of the catalyst. And the huge amount of the money in refinery that is being invested for improvement of the catalyst, which is either F C C catalyst or the your catalyst reforming catalyst or it may be isomerisation catalyst.

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<b>Isomerisation Catalyst</b>	
1st generation	Freidel and Crafts AlCl <sub>3</sub> catalysts, exhibit very high activity at low temp.980-100°C
2 <sup>nd</sup> generation	Metal/ support bifunctional catalyst essentially Pt/alumina sensitivity to poisons are less acute, however, require higher temperature (350-550)°C.

So, first generation catalyst the freidel and the freidel craft direction the aluminium chloride exhibit very high activity at low temperature metal support bifunctional catalyst. Essentially, platinum alumina sensitivity to poisons are less acute however, require higher temperature.

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<b>Isomerisation of Light Paraffins Catalyst</b>	
3 <sup>rd</sup> generation	Metal/support bifunctional catalysts with increased acidity by halogenation of the alumina support. Sensitive to poisons and need pretreatment, Corrosion problem. High activity at low temperature 120°C-to 160°C
4 <sup>th</sup> generation	Bifunctional zeolite catalysts, very resistant to catalyst poison and feed does not need pretreatment

Third generation metal support bifunctional catalyst with increased acidity by halogenations of the alumina support sensitive to poison and need pretreatment corrosion problem high activity at low temperature.

Fourth generation bi functional zeolite catalysts very resistant to catalyst poison and feed does not need in pretreatment. So, this is the actually, the changes that has taken place in the catalyst, which are used in case of the isomerisation process in all the catalyst one of the problem is the presence of the impurities in the feed stock.

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<b>UOP Butamar Process:</b>
<ul style="list-style-type: none"><li>• Catalyst: Pt/chlorintated Al<sub>2</sub>O<sub>3</sub></li><li>• Operating Condition: Temperature: 180-220 °C,</li><li>• Pressure : 15-20 bar</li><li>• Soace vel : 2h<sup>-1</sup></li><li>• H<sub>2</sub>/HC : 0.5 to 2</li></ul>

Now let us discuss some of the processes which are available in case of the isomerisation U O P butamar process. Catalyst platinum chlorinated almonia operating condition is 180 to 220 pressure 15 to 20 bar, space velocity 2 hour hydrogen to hydro carbon ratio 0.2 to 2.

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### **UOP isomerisation Technologies:**

- **Penex™** : Higher octane, higher product yields more than 120 licensed units
- **Par-Isom™**: UOP introduced par-ISOM™ in 1996 using zeolite chloride sulfate of zirconium catalyst.
- It is characterised by lower equipment cost, multiple catalyst approach.

Another development that has taken place in case of the U O P isomerisation technology that is the penex process. Higher octane higher product yields more than 120 licensed units whether penex and penex T M. So, this is the actually, the some of the development and here, you see the number of the refinery in other country. They are having the isomerisation as integral part, the par isomerisation U O P introduced the this process in 1996 using zeolite chloride sulphate of the zirconium catalyst. It is characterized by lower equipment cost and the multiple catalyst approach.

Now, they this was about the isomerisation part and the importance of the isomerisation in the refinery, where you can convert the low low oxygen hydro carbons to high octane hydro carbon. Now let us discuss about the polymerization part, because this is also one of the actually, do not be confuse with the polymerization, which we are using for the manufacture of the polymerization, it is mostly the part.

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## Polymerisation

- Polymerization processes have received considerable interest in petroleum refining because of the higher requirement of reformulated gasoline and phasing of MTBE. The process may be attractive in two main areas.

So, the polymerization process have received considerable interest in the petroleum refinery, because of the higher requirement of the reformulated gasoline and phasing out of the M T B E. Because, this problem I told you, I have been telling time to time because M T B E that came in a big way as a substitute for the tetra ethylate to increase the octane and at the same time.

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## Polymerisation

- Upgrading of  $C_2$  and  $C_3$  Temperature: 150-200°C, Pressure : 30-50bar, space velocity 0.3-0.5  $m^3/h$  per  $m^3$  cuts from catalytic cracking for oligmerization ethylene & propylene to olefinic gasoline.
- Producing high quality middle quality.

Because, the  $C_4$  gas is iso ethylene that was available from the F C C gases methanol was there number of methanol plant came just to supply the methanol to the M T B E



tank, but there was leakage in M T B E tank in U S and. So, the now there is ban, because M T B E is A I D card. So, many country developed country they have ban the manufacture of the M T B E. So, the process may be attractive into main areas, that the one in the from the petroleum and the another form the petro chemical part.

Upgrading of C 2 and C 3 temperature 150 to 200 degree centigrade pressure 30 to 50 bar space velocity 0.3 to 0.5. Catalytic cracking for oligmerisation ethylene, propylene to olefinic, gasoline producing high quality or the middle quality gasoline.

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## Oligmerisation

- Oligmerisation are getting importance in refinery in two main areas
- upgrading C2 and C3 cuts from catalytic cracking to olefinic gasoline
- Producing high quality distillates from light olefins.

Oligmerisation are getting importance in the refinery in 2 main area upgrading of C 2 and C 3 cuts from catalytic cracking to olefinic gasoline producing high quality distillates from light olefins. So, this is what happening in most of the oligmerisation process. So, some of the let us discuss some of the processes, which has been developing in case of the polymerisation and the oligmerisation process.

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### Industrial Processes

- UOP Catpoly Process: This process can transform propylene, butene or a mixture of both.
- IFPPolynaphtha Process: Process to convert  $C_3, C_4$  and  $C_5$  olefins into a gasoline cut.
- Dimersol Process: Convert  $C_2, C_3, C_4$  olefin to gasoline.

Industrial process that is U O P catpoly process, this process can transform propylene butane or a mixture of both to high octane gasoline I F P Poly naphtha process process to convert  $C_3, C_4$  and  $C_5$  olefins into a gasoline cut. So, then dimensional process convert  $C_3, C_4$  olefin to gasoline because in all the cases if you see that we are using  $C_3, C_4$  and  $C_5$  olefins this is available from the F C C gases and. So, that can be used for improving the octane number and that will be also, we can utilize this gases, which are still not being used in many of the refineries.

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### Industrial Processes

- Mobil olefin to Gasoline and Distllate(MOGD) : Light olefin  $C_3, C_4$  converted to olefinic product which is hydrogenated to go for diesel oil pool.

Mobil olefin to gasoline and distillate technology light olefin here again, we are using C<sub>3</sub> C<sub>4</sub> converted to olefinic product, which is hydrogenated to go for diesel oil pool. So, this is the about the alkylation about the polymerisation process alkylation process, which are using in the refinery.

So, the in the feature, because you see the both all the 3 process, they are going to play very important role in improving the octane number in improving the availability of the high octane gasoline. And at the same time utilization of the some of the gases and the low octane naphtha, which is more paraffinic. So, this is the reason, why they now the all the refinery, they are getting interest in isomerisation in alkylation process or in case of the alkylation.

Only constant in case of the lesser adopt adoptability in case of the your alkylation process major constant, which was there that was the acid catalyst, hydro fluoric acid alkylation. But, with the coming of the your solid acid catalytic definitely the problem that is going to be less at least. So, for the corrosion in the corrosion problem is there and that is the reason, why the now the more and more interest is for the alkylation processing same thing is in isomer.

So, this was about the in the next lecture, that is one of the very important part in case of the refinery operation and with the coming of the various norms extenders, which are changing time to time looking to the environmental condition desulfonation process. This is very important in the refinery and the desulfonation of the product recovery of the sulphur, because it is not only that desulfonation and the atmospheric recovery of the sulphur from the sulphur compound, which are removed during the process it may be process then the recovery of the sulphur from the class process.

So, this is has become again integral part of the refinery because if you want to meet the norms U R O 3 U R O 4 or it may be 3 or the U R O 4 norm. So, definitely will have to go for the. So, next lecture will be on the desulfonation of the there is and the at the same time. Because, you are also doing the hydro desulfonation process in the refinery for the removal of the sulphur compound already that part, we have discussed in the very section of the catalytic cracking or it may be the hydro cracker or the in case of the catalytic.

So, will be how we are, what are the stream for which the hydro desulfonation necessary then what are the desulfonation process in detail about the and the conventional class.

Further may be there being lot of improvement changing the class process and at the same time 1 another source at the loss of the sulphur in the waste water. That is also one of the major problems with the coming of the more and more sour gases, sour crude oil sorry, not gases.