Hydrogen Energy: Production, Storage, Transportation and Safety

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Lecture - 42
Hydrogen Liquefaction

In the previous class we have seen compressed hydrogen tanks. Depending upon what material, they are made up of they were divided into type I, type II, type III and type IV tanks. Type I were all metallic, type II with an inner metallic liner and hoop wrapped with fiber resin composite, type III where there is metallic liner and a fully wrapped fiber resin composite and the type IV tank which had an inner polymer liner with an outside carbon fiber composite.

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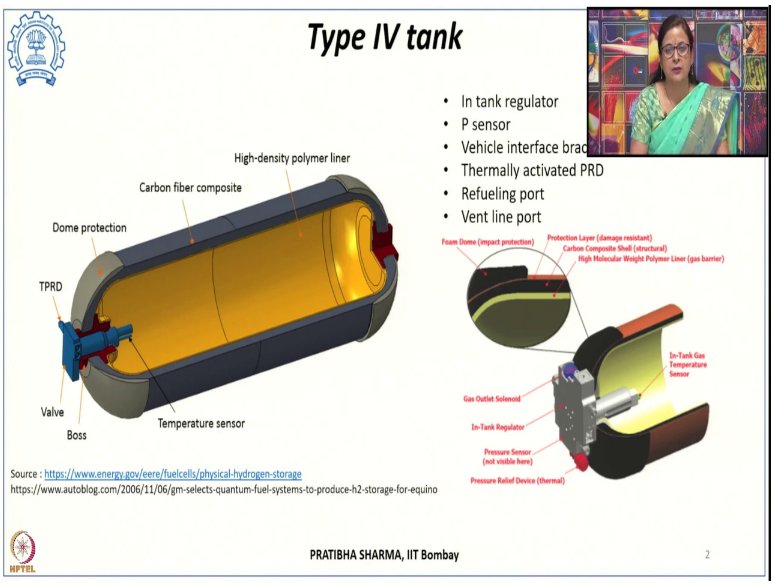

Type IV tank

- In tank regulator
- P sensor
- Vehicle interface brac
- Thermally activated PRD
- Refueling port
- Vent line port

Source : https://www.energy.gov/eere/fuelcells/physical-hydrogen-storage
https://www.autoblog.com/2006/11/06/gm-selects-quantum-fuel-systems-to-produce-h2-storage-for-equino

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So, this is what we have seen in the previous class. In a type IV tank this is an inner liner which provides the gas tightness as well as reduces the permeability. Then there is a carbon fiber composite. There is a carbon fiber wrapping and thereafter a resin. Now, this composite provides strength to the tank against the environmental challenges.

Now, this tank other than the carbon fiber and liner. There are other components like a port which is having a boss here. A port which has a valve and then there are several other accessories, which are there in with the tank. This is like the in tank regulator then there are pressure sensors to measure the pressure. Then there is interfacing with the refueling station for filling in. At the same time for dispensing for releasing the hydrogen for the utilization purpose.

Then there are thermally activated pressure relief devices. So, refueling port, vent line port. So, all these accessories are there, other than the remaining accessories outside the tank. Which are like the tubings, other valves, flow regulators. So, all these are the components of the type IV tank.

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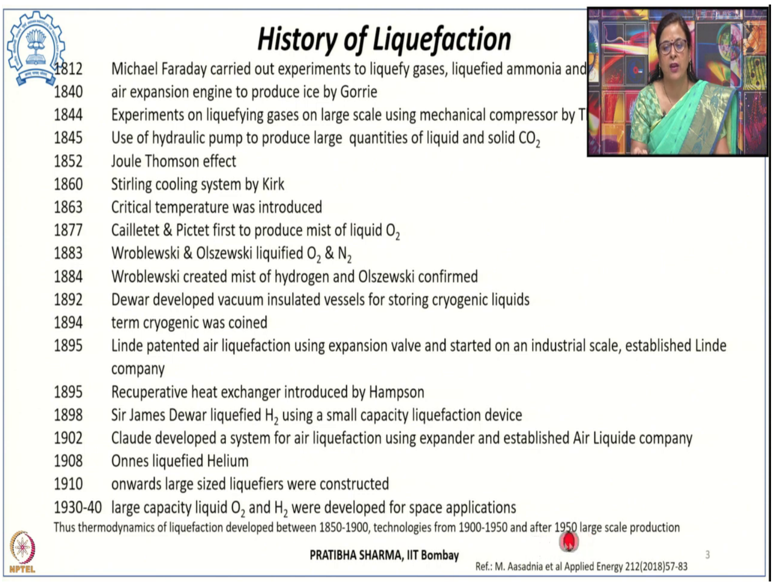

History of Liquefaction

1812	Michael Faraday carried out experiments to liquefy gases, liquefied ammonia and
1840	air expansion engine to produce ice by Gorrie
1844	Experiments on liquefying gases on large scale using mechanical compressor by T
1845	Use of hydraulic pump to produce large quantities of liquid and solid CO_2
1852	Joule Thomson effect
1860	Stirling cooling system by Kirk
1863	Critical temperature was introduced
1877	Cailletet & Pictet first to produce mist of liquid O_2
1883	Wroblewski & Olszewski liquified O_2 & N_2
1884	Wroblewski created mist of hydrogen and Olszewski confirmed
1892	Dewar developed vacuum insulated vessels for storing cryogenic liquids
1894	term cryogenic was coined
1895	Linde patented air liquefaction using expansion valve and started on an industrial scale, established Linde company
1895	Recuperative heat exchanger introduced by Hampson
1898	Sir James Dewar liquefied H_2 using a small capacity liquefaction device
1902	Claude developed a system for air liquefaction using expander and established Air Liquide company
1908	Onnes liquefied Helium
1910	onwards large sized liquefiers were constructed
1930-40	large capacity liquid O_2 and H_2 were developed for space applications

Thus thermodynamics of liquefaction developed between 1850-1900, technologies from 1900-1950 and after 1950 large scale production

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So, today we will look at the liquefied hydrogen storage. Now, by liquefied hydrogen storage we mean like the temperatures are in the cryogenic range. Now, the cryogenic term itself was coined from a Greek term and; that means, ice cold. Now, here the temperatures are below minus 150 degree centigrade and the gas in the process the gas at ambient conditions is cooled down to temperatures, which are cryogenic temperature and at ambient pressure.

Now, if we look briefly on to the history of liquefaction. It started way back in 1812, when Michael Faraday he carried out certain small scale experiments in a test tube to experiment with the different gases to liquefy them. And he was successfully able to liquefy ammonia and carbon dioxide. In 1840, Gorrie he was able to produce ice by means of air expansion engine.

In 1844, there were experiments being carried out on large scale for liquefying gases and that was Thilorier and he used mechanical compressor for this purpose. In 1845 with the use of hydraulic pump large quantities of liquid and solid carbon dioxide was produced. Now, the major landmark in the history of liquefaction was the invention of Joule Thomson effect, that was in 1852. Thereafter Kirk, he came up with the stirling cooling system in 1860, 1863 was another landmark when critical temperature was introduced at that time.

Thereafter 1877, Pictet and Cailletet they individually were able to produce mist of liquid oxygen. This was not completely liquefied, which was later on completely liquefied in 1883 by Wroblewski and Olszewski and they liquefied oxygen and nitrogen. So, Wroblewski he liquefied and Olszewski he confirmed that liquefaction by the process which was given by him. In 1884, Wroblewski he created mist of hydrogen.

And again he confirmed. It was another landmark that was in 1892, when Dewar he developed he vacuum insulated vessels for storing cryogenic liquid. And thereafter came the term 1894, the cryogenic term was coined. In 1895 Linde, he patented the air liquefaction using expansion valve and then he started producing the various gases at industrial scale.

He also established the well known company for liquefaction Linde. In 1895 started the recuperating heat exchangers and that was first time introduced by Hampson. In 1898 Sir James Dewar he liquefied hydrogen and that was in a very small capacity liquefaction device. In 1902, Claude he developed a system which was for air liquefaction and that used expanders.

And he also established a company which is now also known as Air Liquide. In 1908 Onnes he first time liquefied helium. In 1910, onwards there were large size liquefiers which were constructed. And thereafter applications where large capacity of liquid hydrogen and oxygen is used were developed, after 1930.

So, we can say that in the period 1850 to 1900, the thermodynamics of liquefaction was developed. While in the period 1900 to 1950, the various technologies for liquefactions were developed and there after started the large scale production of these liquefied gases. So, this is how the cryogenics liquefaction of various gases have advanced in past.

Now, coming back to liquefaction of hydrogen. In liquefying hydrogen there are several challenges involved.

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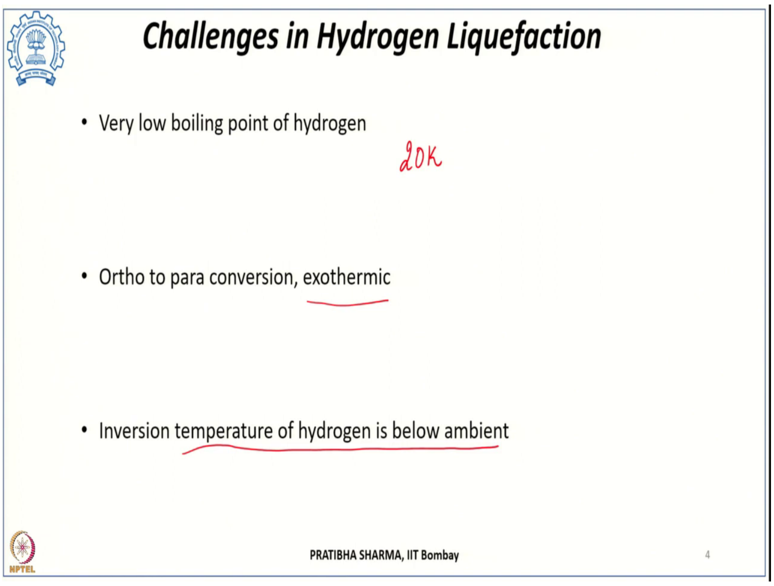

Challenges in Hydrogen Liquefaction

- Very low boiling point of hydrogen

20K

- Ortho to para conversion, exothermic
- Inversion temperature of hydrogen is below ambient

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The first and foremost is we know that and we have also seen thermodynamics of hydrogen liquefaction in earlier classes. That the liquefaction of hydrogen can be done by reducing its temperature to 20K (minus 253 degree centigrade) and this is a very low temperature for liquefaction. Requires a lot of energy.

The another challenge is ortho to para conversion. And this conversion has to be occur and at the same time this conversion is exothermic. So, we have to also remove the heat of conversion from the process of liquefaction. And the third major challenge that lies is that the inversion temperature of hydrogen is below ambient temperature. This we have earlier seen when we have studied the thermodynamics of expansion. The Joule Thomson effect, what is the Joule Thomson coefficient when it is positive.

Then if it is positive, in that case with the reduction of pressure temperature also reduces; that means, with expansion cooling is observed, if it is negative reverse of it happens; that means, if the expansion occurs or pressure reduction then temperature will increase. Joule Thomson coefficient which is negative at ambient temperature. And in order to cool it down we have to cool down below the inversion temperature. So, as to use the throttling process. So, these are the three major challenges which are observed in hydrogen liquefaction.

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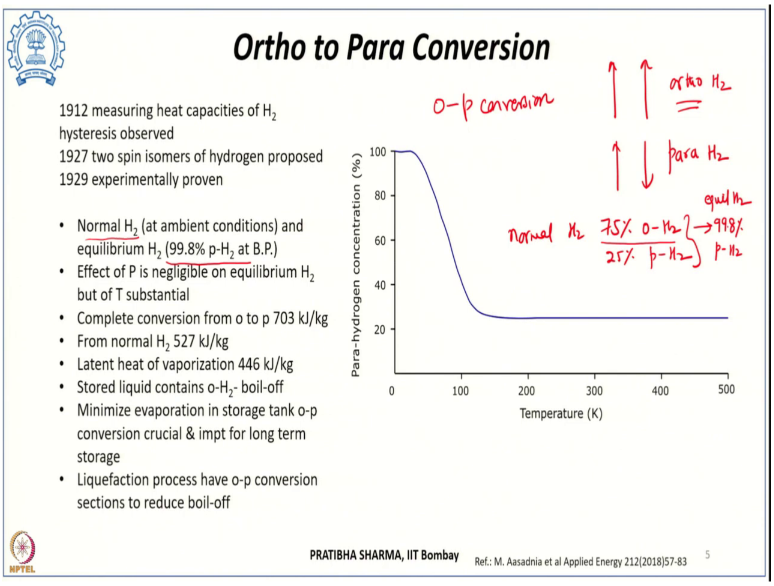

Ortho to Para Conversion

1912 measuring heat capacities of H_2
hysteresis observed
1927 two spin isomers of hydrogen proposed
1929 experimentally proven

- Normal H_2 (at ambient conditions) and equilibrium H_2 (99.8% p-H_2 at B.P.)
- Effect of P is negligible on equilibrium H_2 but of T substantial
- Complete conversion from o to p 703 kJ/kg
- From normal H_2 527 kJ/kg
- Latent heat of vaporization 446 kJ/kg
- Stored liquid contains o-H_2- boil-off
- Minimize evaporation in storage tank o-p conversion crucial & impt for long term storage
- Liquefaction process have o-p conversion sections to reduce boil-off

o-p conversion

$\uparrow\uparrow$ ortho H_2

$\uparrow\downarrow$ para H_2

normal H_2 $\left.\begin{matrix} 75\%\ o\text{-}H_2 \\ 25\%\ p\text{-}H_2 \end{matrix}\right\} \rightarrow 99.8\%\ p\text{-}H_2$ equil H_2

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Now, if we look these challenges one by one. The major challenge is the ortho to para conversion. Now, this was in 1912, that while measuring the heat capacity of hydrogen. It was observed that the warming and the cooling curve they have shown a hysteresis. And that hysteresis it was proposed in 1927, that it was arising because of the two different spin isomers of hydrogen.

And this presence of these two spin isomers was experimentally proven in 1929. Now, what this conversion is what these spins are. So, if the two spins, the nuclear spins, protons spins are parallel. Then it is ortho hydrogen if; however, the two spins are anti parallel, then it is para hydrogen. Now, there is a difference in the calorimetric properties of ortho hydrogen and para hydrogen.

At the same time the energy levels of these two isomers are also different. So, ortho hydrogen is an excited state. It is in a higher energy state compared to the para hydrogen. So, when we are liquefying hydrogen this conversion which occurs ortho to para hydrogen. That extra amount of energy is released in the process just to explain in more detail.

The normal hydrogen which is at the ambient normal temperature pressure condition. It consists of 75 percent of ortho hydrogen and 25 percent of para hydrogen. However during liquefaction at the boiling temperature.

At the boiling point of 20K the equilibrium composition of hydrogen is 99.8 percent of para hydrogen and the remaining is ortho hydrogen and that is the equilibrium composition at its boiling point; that means, if we are reducing the temperature of hydrogen. In that case the ortho hydrogen which was 75 percent under normal condition has to convert in such a way that we get 99.8 percent of para hydrogen from the normal hydrogen. That is the equilibrium hydrogen.

Now, in this conversion process since ortho hydrogen is its in higher energy state. So, the excess energy is released thus the process is exothermic process. So, this release or this conversion of ortho to para hydrogen. This is an exothermic process and that heat which is released that needs to be removed during the liquefaction process. Now, if we see the concentration of para hydrogen with temperature. We can see that it has a very strong dependence on temperature; however, it has negligible dependence on pressure.

So, there is a strong dependence on temperature. Specifically, we can see in this region, but no pressure dependence. Now, when we want complete conversion of hydrogen from the ortho to para. So, from complete ortho to complete para conversion that releases heat that releases energy approximately 703 kilo joule per kg; however, normal hydrogen which is 75 percent ortho, 25 percent para. When converts it into equilibrium hydrogen then the amount of heat which is released is 527 kilo joule per kg.

Now, we can see that both these energies are is higher than the latent heat of vaporization for hydrogen which is 446 kilo joule per kg. Now; that means, when we are converting, when we are liquefying, when we are reducing the temperature of hydrogen this amount of heat which is released in this ortho to para conversion is sufficient enough to evaporate certain amount of liquid hydrogen as well.

So, because this latent heat of vaporization is less compared to the heat released during this process. Now, this process where in the stored liquid which contains ortho hydrogen and with the reduction of temperature. When it converts to para hydrogen causes evaporation of hydrogen this process is known as boil-off. And what is required is that this boil-off should be as low as possible.

So, we need to minimize this evaporation in the storage tank and thus we need to minimize this ortho para conversion which is very important, when we are considering long term storage. The reason being if at normal temperature pressure hydrogen if it is very fastly cooled in that case the hydrogen may convert or may liquefy, but then in that case the concentration will be again same as the normal hydrogen and when it is being stored at that temperature 20 kelvin then slowly this ortho to para conversion will occur will release heat and the liquid hydrogen will start to evaporate.

And that will be resulting in boil-off loss. Also we need to understand that ortho to para conversion this process is a very slow process. This is a second order reaction which takes place very slowly. And it can take about several days or a week time to convert without catalyst from ortho to para. Now, if we want to increase the rate of this conversion, we have to use a catalyst.

In the presence of catalyst depending upon what catalyst, what is the temperature, what is the pressure this conversion is a first order reaction; however, at the liquid hydrogen temperature at 20 kelvin this conversion is a zeroth order reaction and takes place very fast. So, once we have cooled down the system to liquid hydrogen temperature.

In that case this ortho to para conversion takes place very fast and is an exothermic reaction leading to boil off and that is not required, when we are storing hydrogen for long term. Because that will result into evaporation of hydrogen and then we will have to release that hydrogen which is evaporated. So, liquefaction process has ortho to para conversion and most of liquefaction cycles they have this ortho to para conversion systems and that reduces the boil-off.

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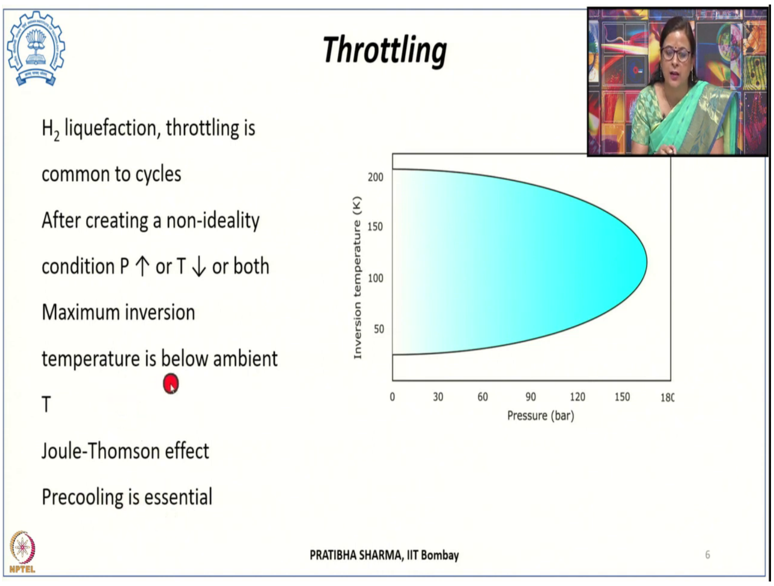

Throttling

H_2 liquefaction, throttling is common to cycles

After creating a non-ideality condition P ↑ or T ↓ or both

Maximum inversion temperature is below ambient T

Joule-Thomson effect

Precooling is essential

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Another important characteristic that we need to consider in liquefaction of hydrogen is throttling. Now, throttling we have studied in more detail. What is the Joule Thomson effect? What is the Joule Thomson coefficient? When is it positive? When it is negative? Now, important when we are liquefying hydrogen is; the throttling which is common to most of the cycle and this is created after we create a sort of non ideality and this non ideality condition is carried out by either increasing the pressure by compressing or lowering down the temperature.

That is pre cooling or it can be done using both. Now, the problem with gas like hydrogen is its inversion temperature is below ambient. And if we want to get the maximum cooling effect we have to cool it down below the maximum inversion temperature. So, that we can get a maximum cooling benefit. As such because of this inversion temperature being below ambient pre cooling of the gas becomes essential. So, that it can be cooled down before throttling below its inversion temperature.

And then only we will be able to get a cooling effect on expansion. So, pre cooling becomes essential, because of the negative inversion temperature of hydrogen above the ambient temperature.

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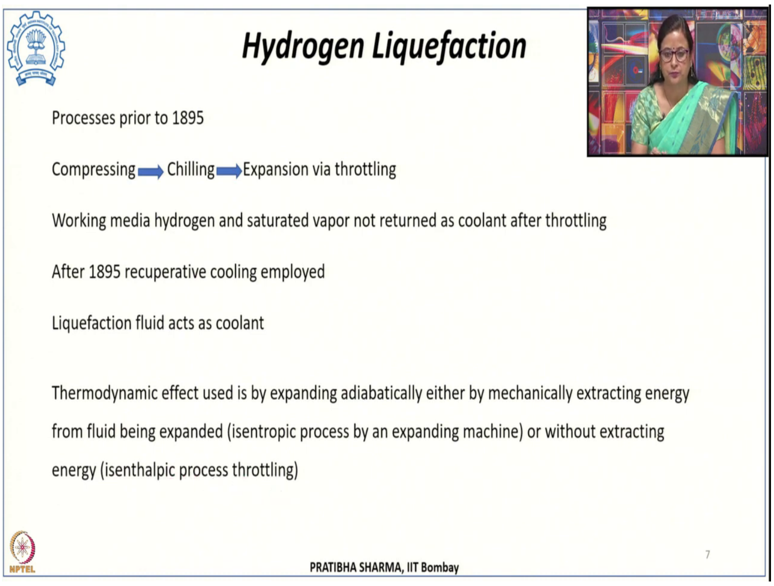

Hydrogen Liquefaction

Processes prior to 1895

Compressing ➡ Chilling ➡ Expansion via throttling

Working media hydrogen and saturated vapor not returned as coolant after throttling

After 1895 recuperative cooling employed

Liquefaction fluid acts as coolant

Thermodynamic effect used is by expanding adiabatically either by mechanically extracting energy from fluid being expanded (isentropic process by an expanding machine) or without extracting energy (isenthalpic process throttling)

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If we look at the hydrogen liquefaction process. Then before 1895, the process which was considered was compression followed by chilling, reduction in the temperature and finally, an expansion by means of throttling. So, prior to 1895, this was the process flow that was followed. Here in the working media used to be hydrogen and the saturated vapor was not returned as a coolant after the throttling.

So, after the throttling process that we will see in the subsequent slides. That after the throttling a certain amount of liquid will be obtained; however, vapor will be at a lower temperature. So, that vapor which was formed after throttling, that was not returned back as a coolant into the stream. But after 1895, the recuperative cooling was employed and here the liquefaction fluid that was itself acting as a coolant. Now, if we look at the process thermodynamics we have also studied earlier.

The thermodynamic effect which is used for expanding is that we do an adiabatic expansion. So, if you look at the complete process. It should be an isothermal compression and an adiabatic expansion. So, expansion is adiabatic, now this adiabatic expansion can be done either by mechanically extracting the energy from the fluid which is being expanded. So, the fluid which is being expanded from there the energy is extracted mechanically, then the process is isentropic process.

And the component used is an expanding machine or an expander or an expanding device; however, if this extraction is not done. So, without extracting the energy in that case the process is isenthalpic and that is what happens in the throttling process.

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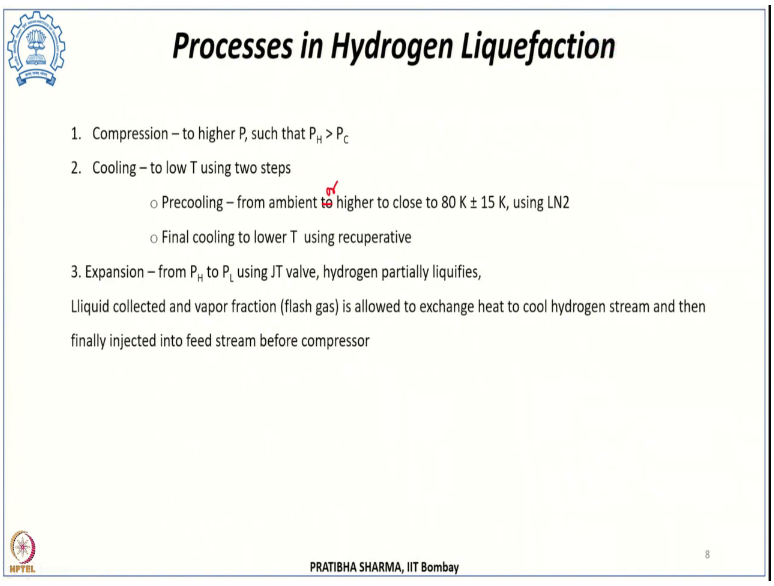

Processes in Hydrogen Liquefaction

1. Compression – to higher P, such that $P_H > P_C$
2. Cooling – to low T using two steps
    - Precooling – from ambient ~~to~~ or✓ higher to close to 80 K ± 15 K, using LN2
    - Final cooling to lower T using recuperative

3. Expansion – from P_H to P_L using JT valve, hydrogen partially liquifies,

Lliquid collected and vapor fraction (flash gas) is allowed to exchange heat to cool hydrogen stream and then finally injected into feed stream before compressor

So, if we quickly see what are the processes or what are the steps that occurs in hydrogen liquefaction is; first of all since finally, we have to do an expansion. We have to increase the pressure so, as to expand. So, first step involved is a compression step. Where the gaseous hydrogen is compressed to a higher pressure. This higher pressure should be such that it should be higher than the critical pressure.

Thereafter once compression is done, cooling is carried out to reduce its temperature. Now, this cooling can be done in two steps first is a pre-cooling. So, from the temperature ambient or after the compression. It will be at a higher temperature. So, from the ambient or to a higher temperature we have to cool it down to 80 K or slightly higher or lower temperature.

Depending upon that depends on several other parameters; that means, liquid nitrogen cooling is done which is also known as pre cooling. The another step could be a final cooling. So, this is at a temperature which is much lower than the liquid nitrogen temperature and that can be achieved using recuperating cooling where the vapor after throttling itself acts as a coolant.

And finally, the step involved is an expansion step where the gas which is at a higher pressure P_H it is expanded to P_L using the Joule Thomson valve. In this process the hydrogen partially gets liquefied and that amount which is getting liquefied is collected. So, the liquid hydrogen in this process, which is obtained can be collected the remaining which is in the vapor form or the vapor fraction of the gas which has got liquefied or the flash gas also known as flash gas.

This is allowed to exchange heat in a heat exchanger. In such a way that it cools down the hydrogen stream. In a heat exchanger and finally, it is again fed back to the mainstream to the feed stream before compressor. So, in general these are the three major steps which occurs in hydrogen liquefaction. Now, there are several ways of doing that, there are several components which can be used depending upon what are their energy consumption.

We can have even to reduce their energy consumption. We can have complicated cycles. We can have cascading, hybridization. So, we will see all those cycles now.

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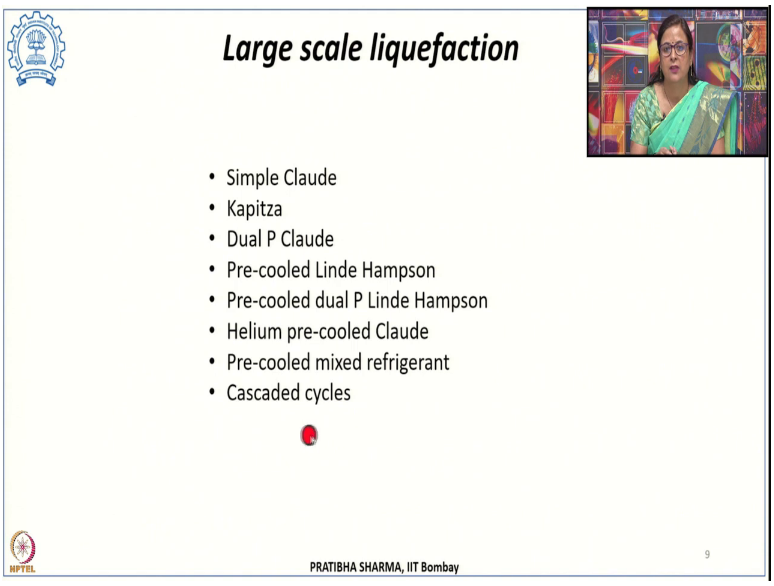

Large scale liquefaction

- Simple Claude
- Kapitza
- Dual P Claude
- Pre-cooled Linde Hampson
- Pre-cooled dual P Linde Hampson
- Helium pre-cooled Claude
- Pre-cooled mixed refrigerant
- Cascaded cycles

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So, for large scale liquefaction. The well known cycles are: the simple Claude process, Kapitza process, which is a modification, it can be a dual pressure Claude process, it can be pre cooled Linde Hampson cycle or it can be pre cooled dual pressure Linde Hampson cycle, it could be helium pre cooled Claude cycle or a pre cooled mixed refrigerant cycle or cascaded cycle. So, these are several options depending upon what are the components used they are. In fact, classified into these type of liquefaction methods.

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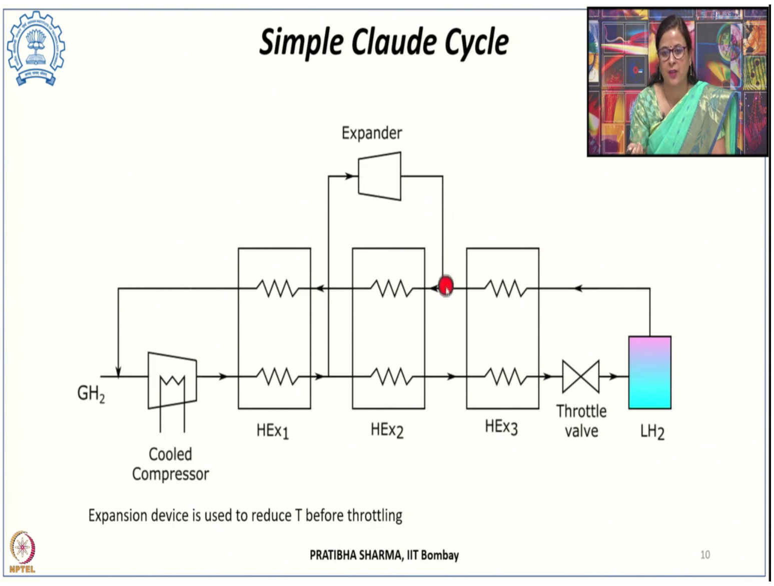

Simple Claude Cycle

Expansion device is used to reduce T before throttling

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Starting with the simple Claude cycle. Here, if we see how the liquefaction occurs. The gaseous hydrogen it is compressed in a cooled compressor. So, there is an inter cooling involved in the compressor. So, this gaseous hydrogen undergoes compression. Then it goes through a series of heat exchangers. Such that its temperature reduces.

Finally, it undergoes throttling. Now, between one of the heat exchangers is an expander or an expanding device. So, what happens is the part of the compressed gas, it goes through an expanding device reducing its temperature and that gas which is cooled then mixes with the hydrogen stream returning hydrogen stream. In that way the temperature of the gas further cools down.

Now, this expander or this expanding device cannot condense, because if it condenses then that is detrimental for the hardware. So, it only lowers down the temperature of the gas. Now, in this process compressed gas passes through a number of heat exchangers reducing its temperature below the inversion temperature, which is the requirement for the throttling process.

Once its temperature reduces below the inversion temperature. It passes through a throttle valve undergoes expansion, such that certain amount of a small amount of liquid is or gas gets liquefied or liquid hydrogen is obtained. Now, in this vessel the liquid hydrogen is collected while the gas which is not liquefied or is still in the vapor form or the vapor fraction of this gas is further recirculated back through these heat exchangers.

So, that it can reduce the temperature of the feed gas stream to the throttle process. Now, once it has exchanged its heat with the feed gas. Finally, it is fed back before the compressor. So, this is how the process takes place. Now, this expansion device which is used before the throttling process is to reduce the temperature of the gas.

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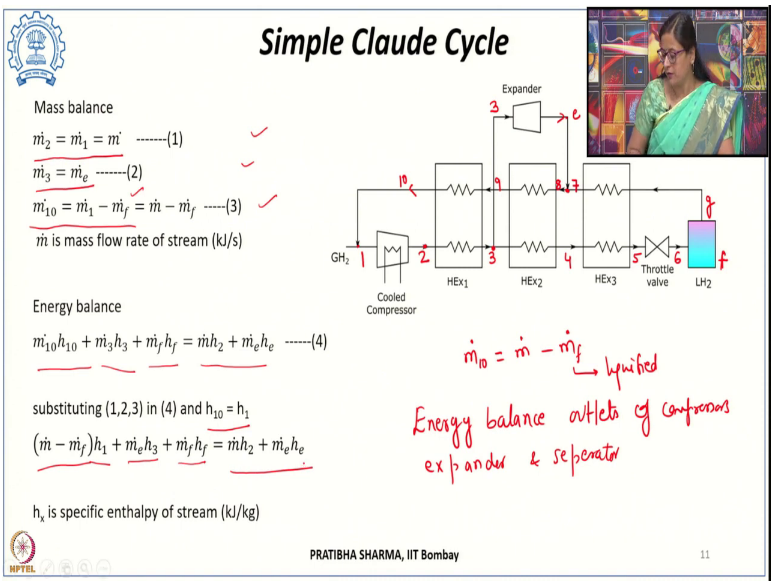

Simple Claude Cycle

Mass balance

$\underline{\dot{m}_2 = \dot{m}_1 = \dot{m}}$ -------(1) ✓

$\underline{\dot{m}_3 = \dot{m}_e}$ -------(2) ✓

$\underline{\dot{m}_{10} = \dot{m}_1 - \dot{m}_f} = \dot{m} - \dot{m}_f$ -----(3) ✓

$\dot{m}$ is mass flow rate of stream (kJ/s)

Energy balance

$\underline{\dot{m}_{10}h_{10}} + \underline{\dot{m}_3 h_3} + \underline{\dot{m}_f h_f} = \underline{\dot{m}h_2 + \dot{m}_e h_e}$ ------(4)

substituting (1,2,3) in (4) and $\underline{h_{10} = h_1}$

$\underline{(\dot{m} - \dot{m}_f)h_1} + \underline{\dot{m}_e h_3} + \underline{\dot{m}_f h_f} = \underline{\dot{m}h_2 + \dot{m}_e h_e}$

h_x is specific enthalpy of stream (kJ/kg)

$\dot{m}_{10} = \dot{m} - \underset{\to \text{liquified}}{\dot{m}_f}$

Energy balance outlets of compressors expander & seperator

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Now, if we see thermodynamics of this simple Claude cycle. Now, we can do the energy and mass balance. Considering the different points, we can do the mass balance of the control volumes. So, the gas it enters into the compressor, leaves the compressor, goes into the heat exchanger and the same goes into the expander. After the heat exchanger 2, after the heat exchanger 3 goes to the throttle valve. Certain amount of the gas gets liquefied, the remaining still is in the vapor form that again goes back to the heat exchanger.

Now, this at this point it gets mixed with the gas, which is coming from the expander. And as such this is 0.89 and finally, 10. Now, if we write a mass balance for the control volume at steady state. So, at this point after the compressor $\dot{m}_2 = \dot{m}_1$ and let us say it is $\dot{m}$. This is the 1st equation at 3. This is same as me dot after the expanding device after the expander.

Now, the gas which is at the exit at 10, $\dot{m}_{10}$ is it this is $\dot{m}_1$, which is entering and some amount which has already been liquefied. So, $\dot{m}_{10} = \dot{m} - \dot{m}_f$. So, the amount which gets liquefied is subtracted. And this is $\dot{m} - \dot{m}_f$, because $\dot{m}_1$ is same as $\dot{m}$. Now, $\dot{m}$ is in general represented for the mass flow rate of stream ‘x’ and this is expressed in kilo joules per second.

Same we can write the energy balance, energy balance between the different outlets. So, the energy balance is written at the outlet us of compressor, expander. Considering the different components compressor, heat exchangers, expander and separator. So, the energy balance is $\dot{m}_{10}h_{10} + \dot{m}_3h_3 + \dot{m}_fh_f = \dot{m}h_2 + \dot{m}_eh_e$.

Now, if we substitute these values for $\dot{m}_{10}$ it is $(\dot{m} - \dot{m}_f)h_1$, because h_{10} is h_1. Considering $h_{10} = h_1$. So, this is $\dot{m}_{10}h_{10}$, which is $(\dot{m} - \dot{m}_f)h_1$, $\dot{m}_3$ is $\dot{m}_e$. So, $(\dot{m} - \dot{m}_f)h1 + \dot{m}eh3 + \dot{m}_f h_f = \dot{m}h_2 + \dot{m}_e h_e$. So, this is the energy balance. Where h is specific enthalpy of the stream.

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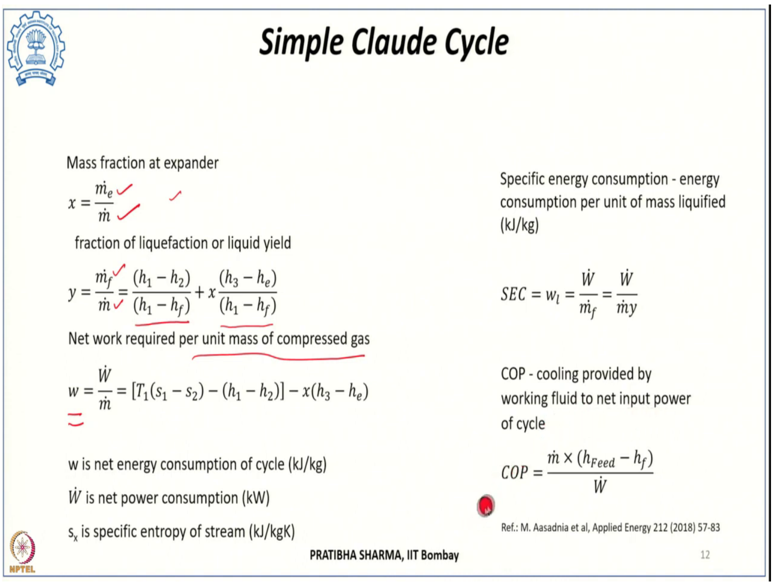

Simple Claude Cycle

Mass fraction at expander

$$x = \frac{\dot{m}_e}{\dot{m}}$$

fraction of liquefaction or liquid yield

$$y = \frac{\dot{m}_f}{\dot{m}} = \frac{(h_1 - h_2)}{(h_1 - h_f)} + x\frac{(h_3 - h_e)}{(h_1 - h_f)}$$

Net work required per unit mass of compressed gas

$$w = \frac{\dot{W}}{\dot{m}} = [T_1(s_1 - s_2) - (h_1 - h_2)] - x(h_3 - h_e)$$

w is net energy consumption of cycle (kJ/kg)

$\dot{W}$ is net power consumption (kW)

s_x is specific entropy of stream (kJ/kgK)

Specific energy consumption - energy consumption per unit of mass liquified (kJ/kg)

$$SEC = w_l = \frac{\dot{W}}{\dot{m}_f} = \frac{\dot{W}}{\dot{m}y}$$

COP - cooling provided by working fluid to net input power of cycle

$$COP = \frac{\dot{m} \times (h_{Feed} - h_f)}{\dot{W}}$$

Ref.: M. Aasadnia et al, Applied Energy 212 (2018) 57-83

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Now, if we see how much is the mass fraction at the expander. So, the mass fraction at the expander which is 'e' which is exiting from the expander. In that case the ratio is $\dot{m}_e/\dot{m}$. And the amount of which get liquefied or the liquid yield is given by $\dot{m}_f/\dot{m}$. And that is $(h1-h2)/(h1-hf) + x$, the mass fraction at expander times $(h3-he)/(h1-hf)$.

We can also calculate the net work which is required per unit mass of the compressed gas. And this is the net worth or the net energy consumption in the cycle w. Which is expressed in kilo joules per kg and this is given by the net power, consumption in the cycle divided by the mass flow rate. And that is equal to temperature $[T1(s1-s2) – (h1-h2)] – x(h3-he)$. Where the 's' is standing for specific entropy of the stream x and that is kilo joule per kg kelvin.

We can also calculate the specific energy consumption. Which is expressed as the energy consumed divided by the mass which gets liquefied. So, the energy consumption per unit mass liquefied it is in kilo joules per kg. This is $\dot{W}/\dot{m}_f$ and that is $\dot{W}/\dot{m}y$ from this expression, $\dot{m}_f$ is $y\dot{m}$. So, the specific energy consumption is the net power consumption divided by $y\dot{m}$.

So, the y is the fraction which got liquefied and the mass flow rate. We can also find the coefficient of performance that is the cooling which is provided by the working fluid to the net input power in the cycle. So, that is the COP and that is given by ṁ times, the enthalpy of the feed minus h_f of the liquefied hydrogen divided by the net power consumption.

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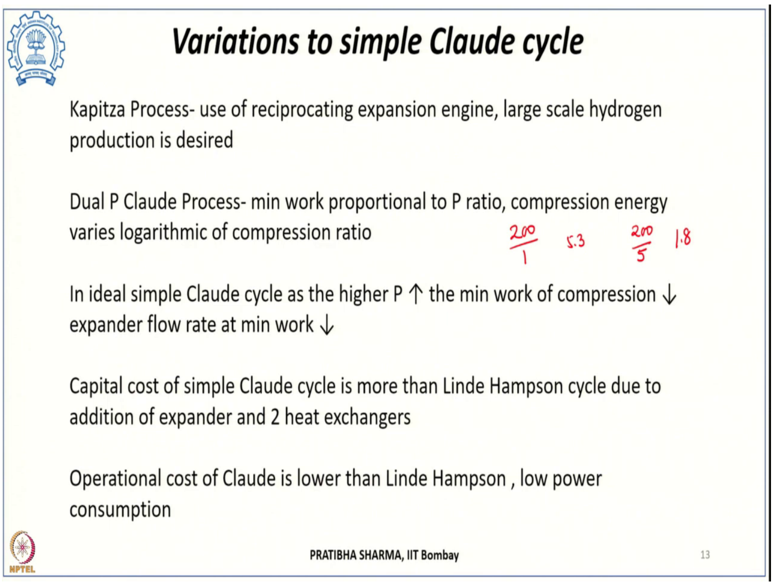

Variations to simple Claude cycle

Kapitza Process- use of reciprocating expansion engine, large scale hydrogen production is desired

Dual P Claude Process- min work proportional to P ratio, compression energy varies logarithmic of compression ratio

$\frac{200}{1}$ 5.3 $\frac{200}{5}$ 1.8

In ideal simple Claude cycle as the higher P ↑ the min work of compression ↓ expander flow rate at min work ↓

Capital cost of simple Claude cycle is more than Linde Hampson cycle due to addition of expander and 2 heat exchangers

Operational cost of Claude is lower than Linde Hampson , low power consumption

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Now, this was the thermodynamics or the energy consumption in a simple Claude cycle. There are several variations to the simple Claude cycle. The variation to simple Claude cycle is the Kapitza process wherein we can use reciprocating expansion engines instead of the instead of that expander. So, that expander is in fact, the reciprocating expansion engine and this particular process is specially used when large scale hydrogen production is required.

We can also have dual pressure Claude process. So, instead of compression to 1 pressure before a throttling. We can have 2 pressure levels or 2 compressors being added. This is because the minimum work is proportional to pressure ratio. So, minimum work in compression that is proportional to the pressure ratio and not the pressure difference in the cycle

Now, we know also know that the compression energy this varies with the logarithmic of the compression ratio. For example, if it is a simple Claude cycle with a primary compressor with a compressor having a compression ratio of 200:1. We can get the logarithmic value of 5.3 as a compression energy. So, that logarithmic term is 5.3; however, if we use a dual pressure cycle or a dual pressure Claude process then this compression ratio there are 2 compressors.

So, the main compressor that will have a compression ratio of 200:5. And that can reduce the logarithmic term to 1.8 and that clearly shows the improvement in the performance and the energy consumption reduction. Now, in an ideal simple Claude cycle the pressure as it increases. The minimum work of compression that reduces and as we know because it is proportional to the pressure ratio.

And then the expander flow rate is corresponding to the minimum work that also reduces, but the major problem with the Claude process is, because we are using several components. There is an expander which is being used there are several heat exchangers being used. In fact, 2 heat exchanger in the simple Claude process. That adds up to the capital cost of the simple Claude cycle.

So, the next cycle we will see will be the Linde Hampson cycle. Which compared to the Claude cycle has a lower capex capital investment, but compared to Claude cycle it has a higher operational cost. So, operational cost of Claude is lower compared to the Linde Hampson, the reason being the lower power consumption in the Claude process.

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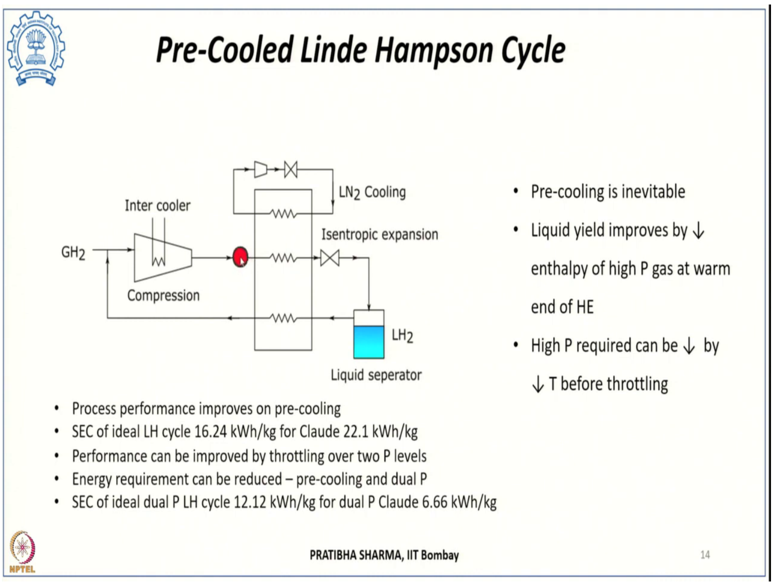

Pre-Cooled Linde Hampson Cycle

- Pre-cooling is inevitable
- Liquid yield improves by ↓ enthalpy of high P gas at warm end of HE
- High P required can be ↓ by ↓ T before throttling

- Process performance improves on pre-cooling
- SEC of ideal LH cycle 16.24 kWh/kg for Claude 22.1 kWh/kg
- Performance can be improved by throttling over two P levels
- Energy requirement can be reduced – pre-cooling and dual P
- SEC of ideal dual P LH cycle 12.12 kWh/kg for dual P Claude 6.66 kWh/kg

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So, we have seen that in the Claude cycle there is a expander or an expanding device which is used, but the Linde Hampson cycle that has a pre cooling step, which is by means of liquid nitrogen. And this pre cooling step is introduced the reason, because the inversion temperature of hydrogen is below the ambient temperature. So, that becomes inevitable.

So, it can be either by means of an expander which is done in case of the Claude cycle while in case of pre cooled Linde Hampson cycle. This is by means of a liquid nitrogen system through a heat exchanger the hydrogen is being cooled. Now, in the addition of this pre cooling not only reduces the temperature of hydrogen below its inversion temperature, but it also improves the yield of liquid which we are getting.

So, the yield of liquid hydrogen which is being collected. This is because it decreases in fact, the enthalpy of high pressure gas at the warm end of the heat exchanger. So, this reduces the enthalpy of the gas, which is entering into the heat exchanger by cooling that. And also the high pressure which is required. The requirement of high pressure can still be reduced.

If we cool it down we pre cool it using a liquid nitrogen network and this can be done by reducing the temperature before it undergoes the throttling. So, inclusion of this liquid nitrogen cooling has several benefit. It reduces hydrogen gas temperature below its inversion temperature, it reduces the enthalpy of the gas entering in the heat exchanger.

At the same time it reduces the pressure requirement before throttling. Now, the pre cooled Linde Hampson cycle is where the gaseous hydrogen it gets compressed in a cool compressor. Once it is compressed it passes through a heat exchanger wherein its temperature is dropped below the inversion temperature by means of liquid nitrogen cooling. After that it is throttled through a Joule Thomson valve, undergoes an isentropic expansion.

In this process some amount of liquid hydrogen is formed which is being collected. The remaining which is still in the vapor form that is allowed to exchange heat or that itself acts as a coolant, cooling down the inlet hydrogen gas stream from the compressor to the throttle valve. So, in the way back to the compressor that passes through the heat exchanger and undergoes or it acts as a coolant for the feed gas to the throttle valve.

After this heat exchanger it is fed back to the compressor. So, this is the simple pre cooled in Hampson cycle. Now, performance wise this precooling improves the performance of the entire process and we have seen the various reasons why it improves the performance. Now, if we compare the Claude cycle with the Linde Hampson cycle the specific energy consumption for an ideal Linde Hampson cycle is 16.24 kilowatt hour per kg.

But for Claude cycle it is 22.1 kilowatt hour per kg. So, it is less in case of Linde Hampson cycle. Now, this performance can further be improved if instead of one stage compression if we include 2 pressure levels before throttling. So, by we can have 2 pressure levels included and then it becomes dual pressure pre cooled Linde Hampson cycle. And the energy requirement can be reduced not only by means of pre cooling, but by increasing one more component the one more compressor and then we can have dual pressure levels included.

Now, if we consider that dual pressure ideal Linde Hampson cycle, then the specific energy consumption it reduces to 12.12 kilowatt hour per kg of liquid hydrogen being produced. While if the same we apply to dual pressure we apply to the Claude process. It reduces to 6.66 kilowatt hour per kg.

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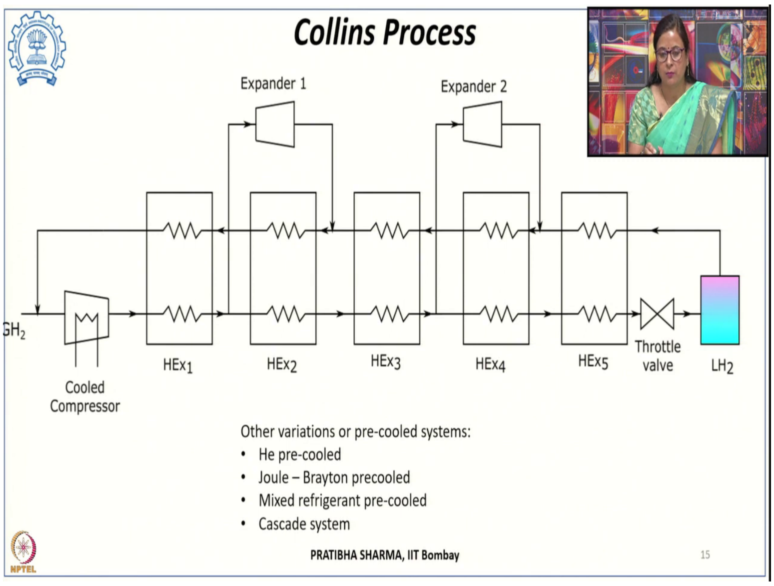

Collins Process

Other variations or pre-cooled systems:
- He pre-cooled
- Joule – Brayton precooled
- Mixed refrigerant pre-cooled
- Cascade system

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There are many other cycles which are possible. There are several other variations like one of the variation is Collins process. Wherein we have further added one more expander and then there are several a series of heat exchangers which have been employed in the process.

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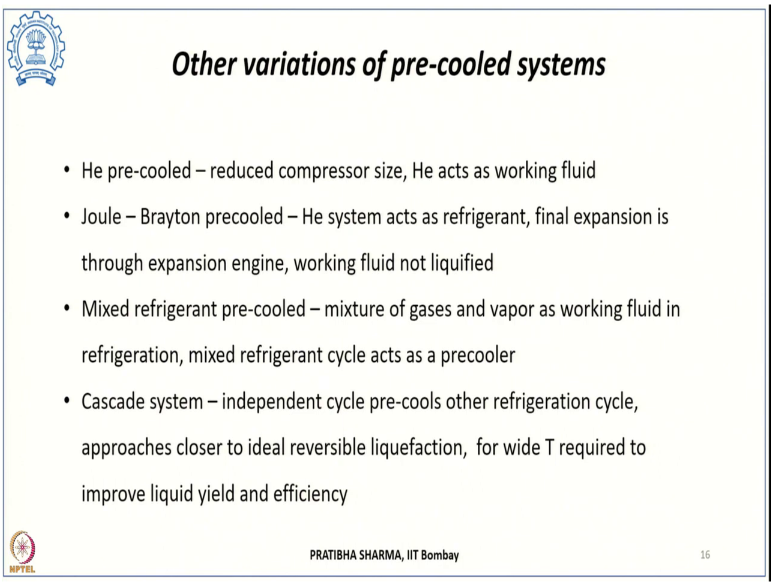

Other variations of pre-cooled systems

- He pre-cooled – reduced compressor size, He acts as working fluid
- Joule – Brayton precooled – He system acts as refrigerant, final expansion is through expansion engine, working fluid not liquified
- Mixed refrigerant pre-cooled – mixture of gases and vapor as working fluid in refrigeration, mixed refrigerant cycle acts as a precooler
- Cascade system – independent cycle pre-cools other refrigeration cycle, approaches closer to ideal reversible liquefaction, for wide T required to improve liquid yield and efficiency

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Now, other variations for the pre cooled system there are many variations possible one is like helium pre cooled. Now, we know that the major component of the cost is also a compressor in the liquefaction system. Higher the size of compressor which is being used higher will be the cost associated. Now, in order to reduce the size of compressor then the flow rate will also reduce the pressure will also reduce. And that can still work well if we use helium for pre cooling. So, that helium acts as a working fluid here.

And the cycle becomes helium pre cooled cycle. Another possibility is the Joule Brayton pre cooled cycle. Where again the helium system it acts as a refrigerant. While the final expansion this is done by means of an expansion engine. And this working fluid this is not liquefied; however, its temperature is reduced to below the hydrogen temperature. Another possibility is with the use of different refrigerants and then we can have mixed refrigerant pre cooled cycle

So, there can be mixtures of gases and vapors, which acts as working fluid in the refrigeration cycle. Now, this mixed refrigerant cycle that acts as a pre cooler for the expansion for the remaining cycle or we can super impose or we can have a hybrid. So, we can have a cascaded system. Where in different independent cycles they pre cool the other refrigeration cycle and with this particular system it approaches very close to the ideal reversible liquefaction process reducing net amount of energy consumption

But as we keep on adding the different components the complexity of the entire process increases. And this cascaded system is especially important when we have to use it for wide temperature range and there it improves not only the yield of the liquid which we are getting, but also it improves the efficiency.

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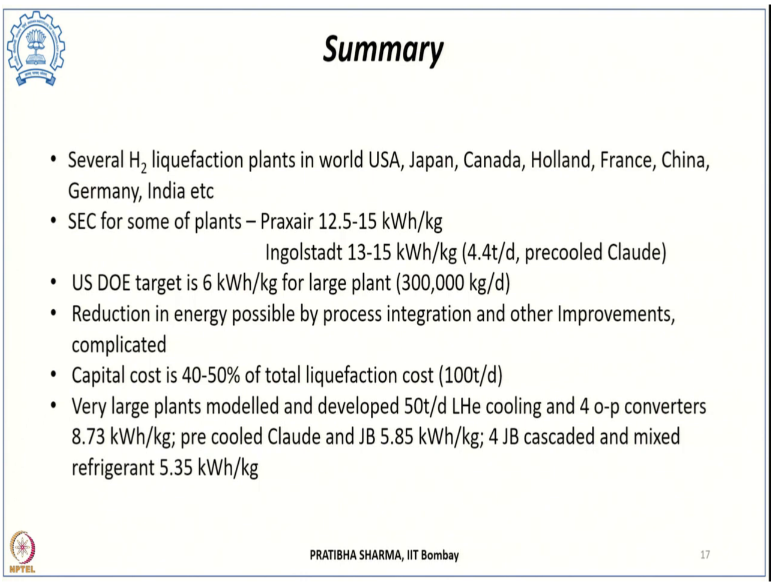

Summary

- Several H_2 liquefaction plants in world USA, Japan, Canada, Holland, France, China, Germany, India etc
- SEC for some of plants – Praxair 12.5-15 kWh/kg
  Ingolstadt 13-15 kWh/kg (4.4t/d, precooled Claude)
- US DOE target is 6 kWh/kg for large plant (300,000 kg/d)
- Reduction in energy possible by process integration and other Improvements, complicated
- Capital cost is 40-50% of total liquefaction cost (100t/d)
- Very large plants modelled and developed 50t/d LHe cooling and 4 o-p converters 8.73 kWh/kg; pre cooled Claude and JB 5.85 kWh/kg; 4 JB cascaded and mixed refrigerant 5.35 kWh/kg

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So, to summarize this part there have been several hydrogen liquefaction plants, which are operational in the world these are located in various regions its in USA, Japan, Canada, Holland, France, China, Germany, India. Now, if we see some of these representative examples like the one which is at being installed by Praxair, this is having a specific energy consumption between in the range of 12.5 to 15 kilowatt hour per kg.

Another one in Germany Ingolstadt that has 13 to 15 kilowatt hour per kg of specific energy consumption the plant that has about 13.5 that is 4.4 tons per day of liquid hydrogen being produced and it operates on the principle of pre cooled Claude cycle. This specific energy consumption is still very high. The USDOE targets are to achieve a specific energy consumption of 6 kilowatt hour per kg for a large sized plant of 300000 kg of hydrogen liquefaction per day.

And still it is way far off compared to the plants which are operational today. So, we have requirement to reduce the specific energy consumption, because the liquefaction is highly energy intensive process. We have to reduce the energy requirement and that can be carried out by several process integrations and many improvements in the cycle, but with integration processing integration including more and more components to reduce the specific energy consumption the entire cycle becomes more and more complicated.

Out of the total liquefaction cost considering a size of 100 tons of liquefaction per day about 40 to 50 percent is the capital cost of the capital cost involved in the plant. So, there have been improvements there have been models where in large size plants have been modeled and also developed like a size of 50 tons per day with liquid helium cooling and that had 4 ortho to para converter systems, which has reduced the specific energy consumption to 8.73 kilowatt hour per kg.

Another one which is being modeled is pre cooled Claude and Joule Brayton cycle and that has a specific energy consumption of 5.85 kilowatt hour per kg. So, as we are looking at the reduction in the specific energy consumption the process gets more and more complicated. Then four Joule Brayton cycles being cascaded together and then use the mixed refrigerant cycle as well for the refrigeration and that reduces the specific energy consumption to 5.35 kilowatt hour per kg.

So, the major challenges which we can see with the liquefaction processes the high capital cost, the high specific energy consumption, boil off losses inversion temperature of hydrogen which is. In fact, lower than the ambient temperature conversion from ortho to para all these lead to a complicated hydrogen liquefaction process.

Thank you.