


Hydrogen Energy: Production, Storage, Transportation and Safety
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Lecture - 35
Thermodynamics of Hydrogen Compression Part - 2

In the earlier class, we have seen the fundamentals of hydrogen compression and expansion. And, also we have seen the work we can calculate for compression using the different state equation or different state variables. Now, there are two different ways of calculating the work of Hydrogen Compression.

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Work for Hydrogen Compression

State variables used for calculating the compression work – simplest method, indirect method

Calorific equation of state used, accurate method, direct method, involves calculating calorific values


$$W_{\text{isentropic}} = (h_2 - h_1) - q_{12} \quad \text{No heat is removed}$$


$$W_{\text{isentropic}} = (h_2 - h_1) = \underline{h(s_2, p_2)} - \underline{h(s_1, p_1)} = \underline{h(p_2)} - \underline{h(p_1)}$$

$$W_{\text{isothermal}} = (h_2 - h_1) - T(s_2 - s_1) \quad \text{Heat is removed, T remains constant}$$

$$= \underline{[h(T, p_2) - h(T, p_1)]} - T \underline{[s(T, p_2) - s(T, p_1)]}$$

Very little deviation – direct and indirect methods, deviation increases with increasing compression ratio
 Deviations between ideal (underpredicts $W_{\text{compression}}$) and real gas behaviors large for higher compression ratios





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One is using the state variables using the state equations. And, if we use that for calculating the compression work, this is the simplest method for calculation and this is also known as an indirect method. However, if instead of state equation if we use calorific equation of state to calculate the work of hydrogen compression, this method is a direct method.

And it is a more accurate method to find out the work of compression. In this method which is also known as direct method, we have to calculate the calorific values. Now, again if we consider the compression process or the compression to be approximated by either an isothermal or an isentropic process then we can calculate using this direct method the work of compression.

Like if we consider the process to be an isentropic process, such that there is no heat exchange or heat is not being removed from the process. In that case, we can write the work of compression as $(h_2 - h_1)$ - the heat exchanged in the process, but since this is 0. So, the isentropic work can be written as the difference in the enthalpies; the specific enthalpies of the two states where the pressure has changed from pressure initial pressure p_1 to a final pressure p_2 , but since it is an isentropic process the entropy remains constant.

Let the constant entropy be s . So, the isentropic work which is the difference in the enthalpies is given by the difference in the enthalpies when the entropy is same for the process s in the state when the pressure is p_2 minus the enthalpy where the entropy is s and the pressure is p_1 . So, it is the difference in the entropies in the state with entropy s and pressure p_2 minus that in the state when the entropy is ' s ' and pressure is p_1 . This is considering the process of compression to be approximated by isentropic process.

However, if the process is considered to be isothermal that is if as we compress we remove the heat which is being generated in the process such that the temperature remains constant or if the process is considered to be an isothermal process, the temperature will remain constant. And in that case, the work of compression considering again the calorific equation of state and the calorific values is given by the difference in the enthalpies in the two states minus the constant temperature and the difference of the entropies in state 1 and state 2.

Thus we can rewrite this expression as, since the temperature remains constant an enthalpy is a function of both temperature and pressure the enthalpy of the gas in a state where the temperature is T and pressure is p_2 minus enthalpy when the temperature is T and pressure is p_1 minus the temperature T times the difference in the entropies in the two states; when the temperature is T pressure p_2 and temperature T and pressure p_1 .


So, this is how we can calculate using the direct method the isentropic and isothermal work of compression. Now, if we calculate this say for real gases it is found that there is very little deviation whether we use indirect method using the state variable or equation of state or whether we use the calorific equation of state and calculate using the direct method the deviation is very little.

But this deviation is found to increase with the increasing compression ratio. As p_2 by p_1 increases as the outlet pressure or the delivery pressure gets higher compared to the inlet

pressure or the suction pressure, this deviation between the two methods using which we calculate the work of compression it increases.

It is observed that, if we consider the gas to be ideal gas and do the calculation using this method or if we consider the gas as a real gas between the two compressions works the difference is large for higher compression ratio. What is observed is, if we consider it to be an ideal gas then using that model it under predicts the work of compression.

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Isenthalpic and isentropic Expansion

Similar equations (direct or indirect) for expansion, difference is now $p_2 < p_1$

Isenthalpic expansion (JT or throttle valve)
Isentropic expansion (in a turbine)

Using indirect method, final T


$$T_2 = T_1 + \left[\frac{\mu(T_1, p_1) + \mu(T_2, p_2)}{2} \right] (p_2 - p_1)$$

Using direct method, enthalpy constant then final T

$$h(T_1, p_1) = h(T_2, p_2)$$

$$T_2 = f(h, p_2)$$

Pressure difference important when isenthalpic process and compression ratio for isentropic process
Very little deviation –direct and indirect methods
Deviations between ideal and real gas behaviors large for higher compression ratios


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We can other than compression we can also consider the expansion. And, now expansion will become important when we will consider the liquefaction of hydrogen or when we will consider the liquid state storage of hydrogen. So, the equations which we have used earlier whether it is using the direct method or whether it is using the indirect method, can still be applied for expansion as well.

The difference will be now this is an expansion. So, there will be a pressure drop as such the outlet pressure or the delivery pressure is lower compared to the inlet pressure or the suction pressure. So, the condition that we will be using will be p_2 less than p_1 . Now, when we consider the expansion of the gas, there can be two ways in which we can expand. So, there can be two thermodynamic processes which can be used to approximate the actual expansion.

One possibility is we can consider it to be an isenthalpic expansion. And, this is considered when we are expanding it through a Joule Thomson or a throttle valve. Other possibility is we

can consider or approximate the actual process by means of an isentropic thermodynamic process. So, it can be an isentropic expansion. This is considered when the expansion is done using a turbine.

Now, if we consider the indirect method as we have learnt in the previous class. In that case, during the expansion the final temperature attained by the gas can be obtained using this indirect method as this is T_1 initial temperature plus the Joule Thomson coefficient the average value of the Joule Thomson coefficient.


Considering the pressure steps the difference of the pressure p_2 minus p_1 in the two different state, where the temperature in the initial state was T_1 , pressure was p_1 . In the final state temperature was T_2 and the pressure was p_2 . So, the Joule Thomson coefficient has been averaged over these two states and it is being multiplied by the pressure difference during the expansion process. We can also use direct method to calculate the final temperature.

Now, in isenthalpic process we know that the enthalpy remains constant. So, in the state 1, when it is a function of temperature T_1 , p_1 , the enthalpy in this state remains same in the second state which is a function of T_2 and p_2 . So, in the final state. So, the two enthalpies are same because it is an isenthalpic process being considered. So, we can find out the final temperature attained using this direct method and this will depend upon the enthalpy of the process and the final pressure or the delivery pressure.

When we consider the process to be an isenthalpic process the pressure difference p_2 minus p_1 becomes important; however, when we consider it to be an isentropic process then the compression ratio p_2 by p_1 becomes more important that needs to be considered again the deviations between both the two methods whether it is a direct method or an indirect method the deviation is very less.

However, huge deviation is obtained when we consider the gas to be ideal or a real gas. And this specifically is higher for higher compression ratios when the p_2 by p_1 is high.

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Hydrogen Storage Process

Considering the law of mass conservation: filling
 $x=1, y=0$
discharge
 $x=0, y=1$

$$\frac{dm_s}{dt} = V_s \frac{d\rho_s}{dt} = x \frac{dm_{in}}{dt} - y \frac{dm_{out}}{dt}$$

Energy balance for the storage system

$$\frac{dU_s}{dt} = x \left(h_{in} \frac{dm_{in}}{dt} \right) - y \left(h_{out} \frac{dm_{out}}{dt} \right) + z \left(\frac{dQ}{dt} \right)$$

$$U_s = m_s u_s$$

$$\frac{dU_s}{dt} = \left(u_s \frac{dm_s}{dt} \right) + \left(m_s \frac{du_s}{dt} \right)$$

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One time rate of change should be known
Two ways to solve-
1. Mass or volume flow rate
2. Change of one state variable is known e.g. P

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Now, this is the background which we required the amount of work the various thermodynamic quantities that we have learned so far to model a hydrogen storage process. Now, if we consider a hydrogen storage process if we want to model it, in that case what we need to consider is the conservation of energy and conservation of mass. So, to model the process of hydrogen storage we can write down the law of conservation of mass as dm_s/dt where m_s is the mass of hydrogen being stored in the storage system.

So, this provides us the mass rate of flow in the inside the storage system. And that is equal to $V_s(dp_s/dt)$. V_s is actually the geometric volume of the storage tank, dp_s is the change in the rate of change in the density of the storage. And that is equal to a coefficient $x(dm_{in}/dt)$ - another coefficient $y(dm_{out}/dt)$. So, this is the mass entering (dm_{in}/dt) per unit time.

Rate of rate at which mass leaves dm_{out}/dt the storage unit. These coefficient x and y these are used to demonstrate whether it is a filling process or whether it is a removal process or withdrawal process. If it is a filling process then $x=1$ and $y=0$; however, during the discharge process or delivery process $x=0$ and $y=1$.

Similarly, we can consider the energy balance for the storage system. So, the rate of change of the internal energy of inside the storage unit (dU_s/dt) is given by the exponent x the specific enthalpy entering into the system, the rate of change of mass flow rate entering into the system minus the exponent y the specific enthalpy leaving out or the entire term which

corresponds to the component which is leaving out, the enthalpy associated and the rate of change of mass that is leaving out of the system.


Something which is entering in and then the term which is corresponding to that leaving out plus another coefficient which is z times the rate of heat exchange dQ/dt . Now, this total energy or the total internal energy can be written as mass in the storage system times the specific internal energy in the storage system. So, U_s capital U is the total internal energy, m is the corresponding mass, small u is the specific internal energy

Now, using this if we differentiate we can write this as $dU_s/dt = u_s \times (dm_s/dt) + m_s \times (du_s/dt)$.

Now, if we want to solve this expression we need to know at least one rate of change. So, either we need to know the mass flow rate or the volume flow rate that is the mass volume flow rate of the gas entering in and leaving into the storage system and depending upon what time rate of change we know that could be the controlling equation in that case.

The second option to solve this is we need to know the change of one state variable for example, when it is expansion or compression how the pressure increases or what is the inlet pressure and the outlet pressure. So, the change in one of the state variable need to be known in order to solve this.

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Hydrogen Storage Process

$$m_s(t) = V_s \rho_s(t) = m_s(t=0) + \dot{m}_{in} t - \dot{m}_{out} t \quad \text{---(2)} \quad \begin{matrix} t=0 \\ m_s(t=0) \end{matrix}$$


Considering a constant mass flow rate

$$\frac{du_s}{dt} = \frac{[h_{in} \dot{m}_{in} - h_{out} \dot{m}_{out}] - u_s (\dot{m}_{in} - \dot{m}_{out}) + z \dot{Q}(t)}{m_s(t=0) + \dot{m}_{in} t - \dot{m}_{out} t}$$

For constant enthalpy and no heat exchange, during filling

$$\frac{du_s}{dt} = \frac{[h_{in} \dot{m}_{in}] - u_s (\dot{m}_{in})}{m_s(t=0) + \dot{m}_{in} t}$$

$$u_s = \frac{[h_{in} \dot{m}_{in}] t + m_s(t=0) u_s(t=0)}{m_s(t=0) + \dot{m}_{in} t}$$



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Now, we can solve this; for example, considering the first method if we know the mass flow rate or volume flow rate let us consider the mass flow rate to be constant. So, the mass in the

storage system this is nothing but the volume times the density. And this can be expressed as the initial mass at T equal to 0, what was the mass if it is at the time of filling or at the time of delivery what was the initial mass plus the exponent x times \dot{m}_{in} the mass flow rate entering minus the exponent $y \times \dot{m}_{out}$ the mass leaving and then t .

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Hydrogen Storage Process

Considering the law of mass conservation:


$$\frac{dm_s}{dt} = V_s \frac{d\rho_s}{dt} = x \frac{dm_{in}}{dt} - y \frac{dm_{out}}{dt}$$

Energy balance for the storage system

$$\frac{dU_s}{dt} = x \left(h_{in} \frac{dm_{in}}{dt} \right) - y \left(h_{out} \frac{dm_{out}}{dt} \right) + z \left(\frac{dQ}{dt} \right)$$

$U_s = m_s u_s$

$$\frac{dU_s}{dt} = \left(u_s \frac{dm_s}{dt} \right) + \left(m_s \frac{du_s}{dt} \right)$$



fill
discharge
 $x=0, y=1$

$\frac{du_s}{dt} = \frac{1}{m_s} \left(\frac{dU_s}{dt} \right)$
(2) (1)

One time rate of change should be known
Two ways to solve-
1. Mass or volume flow rate
2. Change of one state variable is known e.g. P

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Now, if we consider a constant mass flow rate in the earlier equation. So, if the mass flow rate is considered to be constant this term will turn out to be 0. And, if this term turns out to be 0, we can calculate the change in the specific time rate of change of the specific internal energy as $(1/m_s) \times dU_s/dt$. Now, this dU_s/dt . This can be obtained from first equation and this m_s can be obtained from equation number 2.


So, this is equation number 2. So, d/dt of specific internal energy stored inside the storage system considering a constant mass flow rate can be obtained as $h_{in} x \dot{m}_{in} - h_{out} y \dot{m}_{out}$ minus the specific internal energy $u_s x \dot{m}_{in} - y \dot{m}_{out} + z Q \dot{t}$. Now, this z quantity for diathermal it can be 1; for adiabatic this can be 0. And this is divided by the m_s term.

So, m_s at t equal to 0 plus $x \dot{m}_{in} t - y \dot{m}_{out} t$. Now, if we consider the enthalpy to be constant and if there is no heat exchange then this term will also be 0, and in that case considering filling.

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Hydrogen Storage Process



$$m_s(t) = V_s \rho_s(t) = m_s(t=0) + x\dot{m}_{in}t - y\dot{m}_{out}t \quad (2)$$

Considering a constant mass flow rate

$$\frac{du_s}{dt} = \frac{[h_{in}x\dot{m}_{in} - h_{out}y\dot{m}_{out}] - u_s(x\dot{m}_{in} - y\dot{m}_{out}) + z\dot{Q}(t)}{m_s(t=0) + x\dot{m}_{in}t - y\dot{m}_{out}t}$$

For constant enthalpy and no heat exchange, during filling

$$\frac{du_s}{dt} = \frac{[h_{in}\dot{m}_{in}] - u_s(\dot{m}_{in})}{m_s(t=0) + \dot{m}_{in}t}$$

$x=1, y=0$

Integrating this eq

$$u_s = \frac{[h_{in}\dot{m}_{in}]t + m_s(t=0)u_s(t=0)}{m_s(t=0) + \dot{m}_{in}t}$$

$u_s(t=0)$ specific internal energy at $t=0$

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So, for filling x is equal to 1 and y is equal to 0, we can rewrite this expression as du_s/dt is $(h_{in}\dot{m}_{in} - u_s\dot{m}_{in})/(m_s(t=0) + \dot{m}_{in}t)$. Now, integrating this equation with respect to time, we can get the value of specific internal energy. And that is given by $h_{in}\dot{m}_{in} \times t + m_s(t=0) \times u_s(t=0)$.

So, u_s at t equal to 0 is specific internal energy at initial state energy at the initial state or the at the initial time of filling divided by $m_s(t=0) + \dot{m}_{in}t$. Now, while considering this equation we have assumed that there is no heat exchange in solving this equation.

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Hydrogen Storage Process



If consider heat exchange by the system

$$\dot{Q} = U_{ht}A_{ht}(T_{surr} - T_s)$$

$$R_{ht} = \frac{1}{U_{heat\ tr}A_{heat\ tr}}$$

U_{ht}
 A_{ht}
 T_{surr}
 T_s

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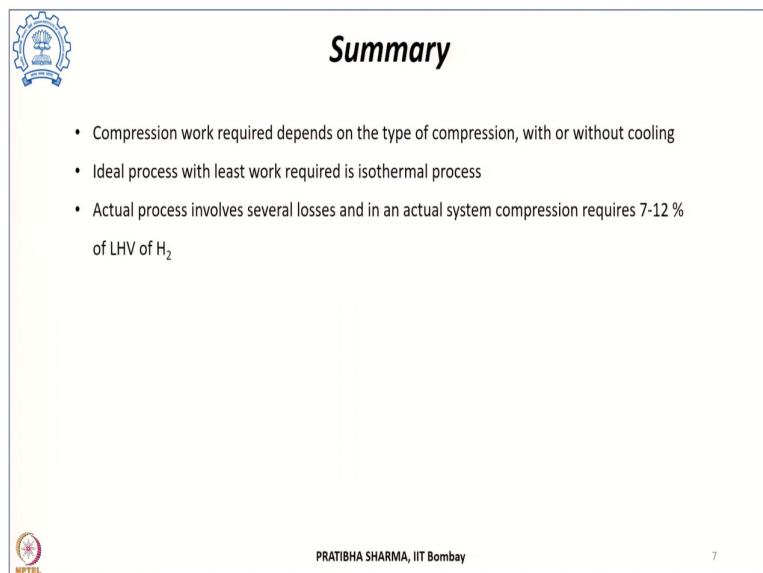
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We can also consider that if the system exchanges heat with the surrounding. So, if this term is non zero in that case we can also find out the heat exchanged by the system which is \dot{Q} . And that is given by the overall heat transfer coefficient U_{ht} is the overall heat transfer coefficient, A is the area for heat exchange, T is the T surrounding temperature, and this is the storage system temperature.

And using, we can also find out the thermal resistance for the storage system as 1 upon the heat transfer coefficient and the area of heat transfer coefficient. So, this is how we can model a hydrogen storage process.

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Summary

- Compression work required depends on the type of compression, with or without cooling
- Ideal process with least work required is isothermal process
- Actual process involves several losses and in an actual system compression requires 7-12 % of LHV of H_2

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To summarize this part, we have seen that the compression work it depends upon which type of compression we are using, whether we are including cooling or whether we are not including cooling. So, accordingly the process can be either it can be isothermal or it can be isentropic. We know that the ideal process is when it is considered as an isothermal process.

So, the work required is least in that case. In an actual system, there are several losses involved. And, if we account for those losses it is observed that the actual compression work it requires 7 to 12 percent of the lower heating value of hydrogen or 7 to 12 percent of the energy content of the stored hydrogen in the hydrogen storage system, it goes for compression.

Also we have modeled the hydrogen storage process considering the different state equations, and we have also considering the calorific equations. And then we have seen how we can include the heat transfer also with the surroundings in the today's class.

Thank you.