Hydrogen Energy: Production, Storage, Transportation and Safety
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Lecture - 10
Autothermal Reforming

In the earlier classes we have seen in detail the Process of Steam Methane Reforming and also we have seen the Method of Partial Oxidation. In today's class we will learn about the Autothermal Reforming method which is the third method for hydrogen production from hydrocarbons.

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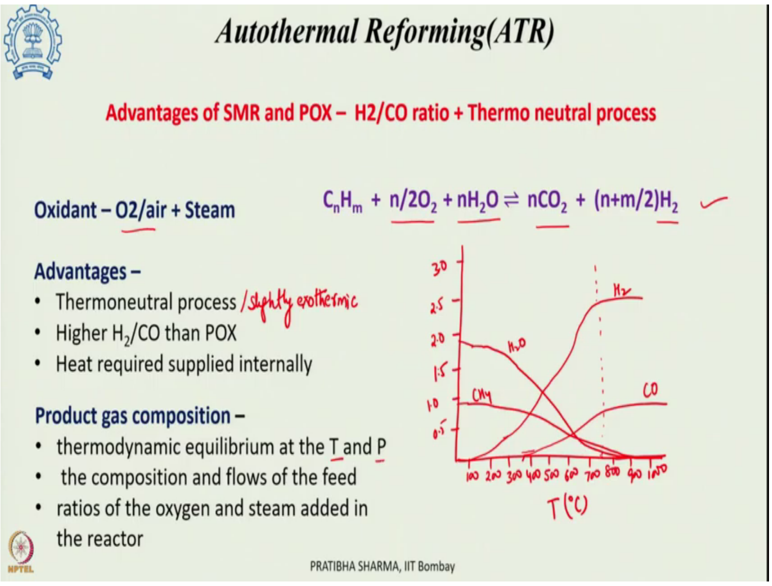

Autothermal Reforming(ATR)

Advantages of SMR and POX – H2/CO ratio + Thermo neutral process

Oxidant – O2/air + Steam

$C_nH_m + n/2O_2 + nH_2O \rightleftharpoons nCO_2 + (n+m/2)H_2$ ✓

Advantages –

- Thermoneutral process / slightly exothermic
- Higher H_2/CO than POX
- Heat required supplied internally

Product gas composition –

- thermodynamic equilibrium at the T and P
- the composition and flows of the feed
- ratios of the oxygen and steam added in the reactor

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Now, this autothermal reforming is a mix of both the processes we have learnt i.e., steam reforming as well as partial oxidation and it carries the advantages of both like steam methane reforming it has higher hydrogen to carbon monoxide ratio, but it was endothermic. So, that was a disadvantage that it required large amount of fuel for providing the heat of the reaction.

Partial oxidation which was an exothermic reaction so, as such no externally heated fuel no external heating was required, but the process had lower H_2 by CO ratio. So, the advantage of partial oxidation that it was an exothermic process is being carried in auto thermal reforming at the same time and at the higher H_2 by CO ratio which is an advantage of SMR is also being carried in the auto thermal reforming.

Now, if we see the oxidant used which is oxygen or air along with steam. So, if it is any of the hydrocarbon then the hydrocarbon undergoes partial oxidation as well as there is a steam oxidant, so that it gets converted into carbon monoxide and hydrogen. Now, the process being either it can be a thermoneutral process wherein the entire heat of reaction which is required for the endothermic reaction is met by the exothermic reaction heat produced or it can be either slightly exothermic.

Now, slightly exothermic because it can also take care of the exothermic reactions which are going on in the auto thermal reformer, can also take care of the losses which are occurring in the reformer, at the same time it has a higher hydrogen to carbon monoxide ratio as compared to the partial oxidation. And the heat which is required can be supplied internally rather than externally which was in the case of steam reforming reaction.

The product gas that we will get after an auto thermal reformer; however, it will depend on several things like what are the exit temperature and pressure, what is the thermodynamic equilibrium composition of the various constituents, what is the composition as well as flow of the reactants, the feed as well as the oxidant, the ratios involved of the oxygen and steam which are used in the reactor.

Now, if we quickly have a look at the equilibrium thermodynamic compositions, then we can see that the compositions may vary based on the temperatures, roughly making that scale here, so this is a temperature in degree centigrade and we can have the moles. Now, this is roughly around that 750 degree centigrade that the amount of hydrogen we get is it rises and it goes to about 2 and half moles amount of water steam and it is being used in the process as such forming the desired products.

The methane which is the reactant here is being consumed in the process. So, roughly these are the equilibrium composition how does this vary. So, this is how the steam is being consumed, methane reactant being consumed in the process and carbon monoxide is being formed. So, all these depends upon what is the temperature inside the reactor, what is the pressure inside the reactor, so this is CO which is being formed in the process.

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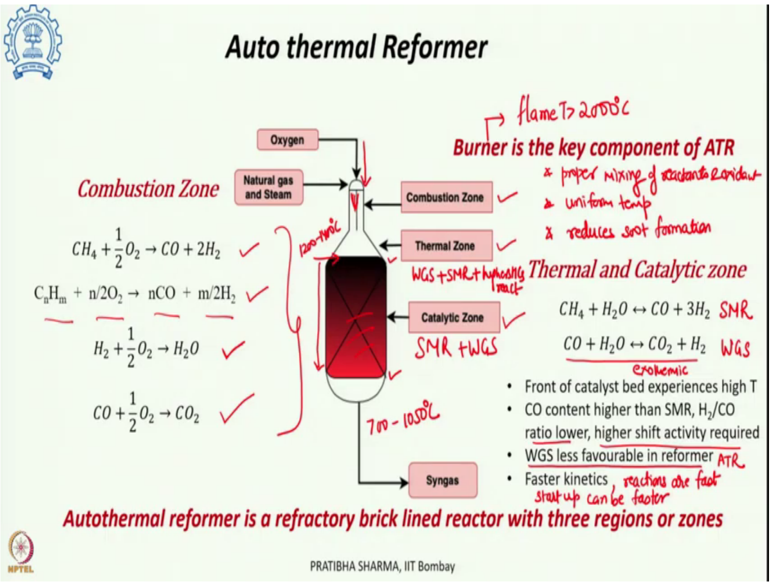

Auto thermal Reformer

Combustion Zone

$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$ ✓

$C_nH_m + n/2O_2 \rightarrow nCO + m/2H_2$ ✓

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ ✓

$CO + \frac{1}{2}O_2 \rightarrow CO_2$ ✓

→ flame T > 2000°C

Burner is the key component of ATR

- proper mixing of reactants & oxidant
- uniform temp
- reduces soot formation

Thermal and Catalytic zone

$CH_4 + H_2O \leftrightarrow CO + 3H_2$ SMR

$CO + H_2O \leftrightarrow CO_2 + H_2$ WGS

exothermic

- Front of catalyst bed experiences high T
- CO content higher than SMR, H_2/CO ratio lower, higher shift activity required
- WGS less favourable in reformer ATR
- Faster kinetics, reactions are fast start up can be faster

Autothermal reformer is a refractory brick lined reactor with three regions or zones

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Now, auto thermal reformer actually is a type of reactor which has to sustain very high temperatures than pressures, because partial oxidation as well as reforming both the processes are occurring in the same reactor. In Auto thermal reformer, there are three regions to mention; region one is the combustion zone, then there is a thermal zone and then followed by a catalytic zone. The oxygen as well as natural gas and steam are fed into the burner region and this is the key component of the auto thermal reformer and it serves several purposes.

So, the burner provides proper mixing of the reactants and oxidant, it also provides uniform temperature, it results into uniformity in the temperature across the region. If it is uniform mixing then it will reduce the soot formation and a proper burner design is very important in auto thermal reformer. It should be such that there should not be any backflow or back firing from the core of the flame towards the burner side neither the combustion gases should flow back towards the burner so, as to cause burner damage. So, a properly designed burner can ensure safe operations at the same time can increase the life of the burner.

Now, this is the burner region, wherein we have a flame then combustion reaction that is the partial combustion of methane, if it is methane as the feedstock or if it is any of the other higher hydrocarbon then it is partial oxidation occur. So, methane reacting with half O_2 giving syngas and higher hydrocarbons again undergoing partial oxidation to produce syngas in the process.

Other than that in the combustion zone there may be other reactions that can occur and in that process we can see hydrogen is being consumed. So, hydrogen here reacts to form water i.e. at this temperature it will be steam or so carbon monoxide can also undergo oxidation to produce carbon dioxide in the process and all these reactions occur in the combustion zone. The burner has a turbulent diffusion flame and that the temperatures at core of flame are very high, it is higher than even 2000 degree centigrade temperature could be even greater than 2000 degree centigrade.

Now, after this combustion region with the required heat in the thermal region there are other reactions that occur and these reactions are either water gas shift reaction combined with steam methane reforming and if these are higher hydrocarbons then the pyrolysis reactions can also occur of the higher hydrocarbons in the thermal zone.

So, in the thermal zone various gas phase homogeneous reactions occur including steam methane reforming, water gas shift as well as various hydrocarbons undergoing several reactions in the thermal zone. That is followed by a catalytic zone, wherein again the steam methane reforming as well as water gas shift reactions takes place these are heterogeneous reactions that occur in the catalytic zone and water gas shift these are heterogeneous reactions occurring in the catalytic zone.

Now, things to be noted here are at the top of the auto thermal reformer the temperature which is experienced by the catalytic bed. So, this is the catalytic zone in this zone this is the catalytic bed. So, the temperature in this region which is experienced by the catalyst is very high 1200 to 1400 degree centigrade because that is following the thermal zone which is an integral part of the combustion zone. Now at these temperatures the catalyst which is used has to be highly stable enough. So, it should be thermally and mechanical stable to be integrated in that particular temperature range.

However, as we go down across the bed the temperature will decrease, because in the catalytic bed the steam methane reforming reaction will occur which is an endothermic reaction and towards the end the temperature of the syngas will be lower. So, it could be somewhere between 700 to 1050 degrees centigrade. So, in the catalyst bed top temperature is higher towards the end of the catalyst bed the temperature is lower.

So, a high temperature gradient is experienced by the catalyst bed, at the same time we can see since there is a combustion reaction occurring in the combustion zone the amount of carbon monoxide content in the auto thermal reformer will be higher than the steam methane reformer, at the same time since CO content is higher.

So, H_2 by CO ratio will be lower in case of auto thermal reformer. If CO content is higher; that means, there is a requirement of high water gas shift activity, but at the same time what we observe is that the water gas shift is an exothermic reaction and it is favoured at a lower temperature.

But the temperature inside the auto thermal reformer is higher as such the water gas shift reaction is less favourable in the ATR reformer; that means, the outlet syngas will have less amount of carbon dioxide as compared to that would have been from the SMR reformer, at the same time the temperatures involved are higher therefore, the reactions which are taking place in the reformer are fast. The kinetics of the reactions are faster as such if auto thermal reformer have a faster startup can be faster in case of ATR.

So, the entire reformer since it has to sustained under very high temperature pressure conditions this is made up of brick refractory brick lined reactor.

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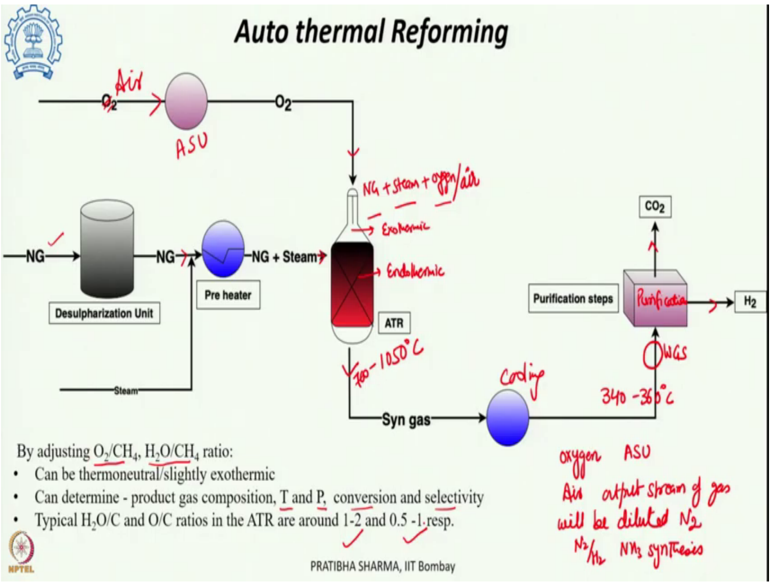

Auto thermal Reforming

By adjusting O_2/CH_4, H_2O/CH_4 ratio:

- Can be thermoneutral/slightly exothermic
- Can determine - product gas composition, T and P, conversion and selectivity
- Typical H_2O/C and O/C ratios in the ATR are around 1-2 and 0.5 -1 resp.

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Now, let us look at the complete process of auto thermal reformation, natural gas passes through the desulphurization unit. So, that the sulfur containing impurities can be removed from the natural gas, natural gas is then preheated with steam enters into the auto thermal reformer and oxygen. So, the natural gas, steam and oxygen enters into the auto thermal reformer, now it can be either oxygen or it can be air.

So, if oxygen is used in the auto thermal reformer; that means, air separation unit will be required for separating oxygen from the air. However, if air is directly used as an oxidant in that case the output stream of gas will be diluted with nitrogen. This gas can be depending upon what is the N_2 by H_2 ratio; this gas can be used for ammonia synthesis.

After it passes through the autothermal reformer the reactions that we have earlier seen, occurs inside the autothermal reformer, the syngas which is obtained after the ATR reformer has to undergo cooling, because the temperature here can be as high as 1050 degree centigrade, this has to be cooled down to the temperature which is required for water gas shift. So, roughly 340 to 360 degree centigrade, it has to undergo water gas shift reaction and followed by the purification step so, as to get hydrogen and carbon dioxide separately.

The important things here are that the ratio of steam to methane or oxygen air to methane can be adjusted, in such a way that the process can be made thermoneutral or slightly exothermic. Oxygen wherein in the beginning it will be an exothermic reaction in the catalyst bed there will be endothermic reactions that will occur. So, the overall process can be made thermoneutral by appropriate choice of O_2 by C_4 or steam to methane ratio.

The product gas composition as mentioned will be dependent on temperature, pressure, the conversion and selectivity of the process and the typical steam to carbon ratio or oxygen to carbon ratio which are used in the auto thermal reformer. Steam to carbon ratio of 1 to 2 and oxygen to carbon ratio of 0.5 to 1 in the process.

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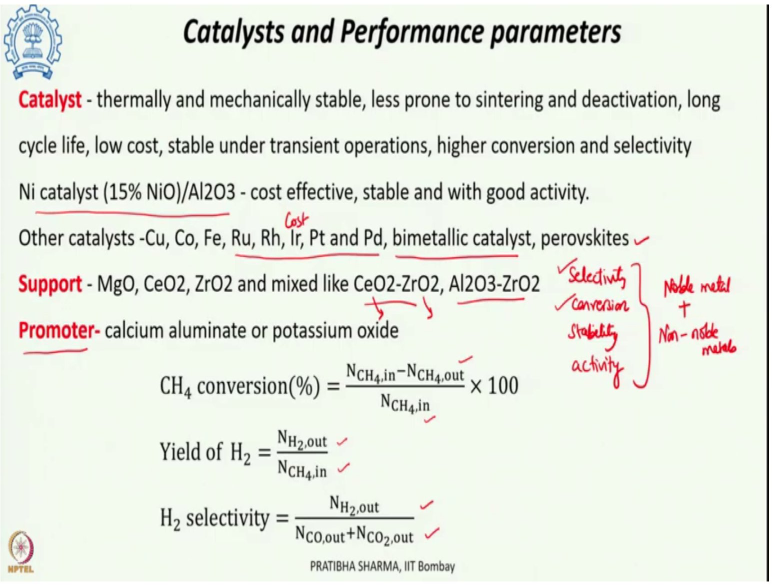

Catalysts and Performance parameters

Catalyst - thermally and mechanically stable, less prone to sintering and deactivation, long cycle life, low cost, stable under transient operations, higher conversion and selectivity

Ni catalyst (15% NiO)/Al2O3 - cost effective, stable and with good activity.

Other catalysts -Cu, Co, Fe, Ru, Rh, Ir, Pt and Pd, bimetallic catalyst, perovskites ✓

Cost

Support - MgO, CeO2, ZrO2 and mixed like CeO2-ZrO2, Al2O3-ZrO2

Promoter- calcium aluminate or potassium oxide

✓Selectivity
✓Conversion
Stability
activity

Noble metal
+
Non-noble metals

$$CH_4 \text{ conversion}(\%) = \frac{N_{CH_4,in} - N_{CH_4,out}}{N_{CH_4,in}} \times 100$$

$$\text{Yield of } H_2 = \frac{N_{H_2,out}}{N_{CH_4,in}}$$

$$H_2 \text{ selectivity} = \frac{N_{H_2,out}}{N_{CO,out} + N_{CO_2,out}}$$

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Now, since the process has more of CO_2 there are combustion products and the conversion and selectivity can also be selectively preferred towards the desired H_2 by CO ratio using the appropriate catalyst support and promoters. Catalyst we have seen earlier, the requirements for these catalyst are that they should be thermally and mechanically stable, they should not provide higher conversion and selectivity. They should be less prone to sintering and deactivation, should have low cost, long cycle life all these are requirements from the catalyst.

The most widely used one is again same as was used in case of steam methane reforming nickel on alumina support this is used because it is cost effective, it is stable and it has good activity. Other than nickel the other transition metal catalyst could also be used, copper, cobalt, iron, they have also been used as a catalyst. Non noble, non-transition metal, the noble metal catalyst have a better conversion, they have a better selectivity at the same time they are less prone to sintering as well as deactivation, but the cost is the major challenge while using noble metal.

As such the two can be combined to form a bimetallic catalyst wherein a certain amount of non-transition metal elements like the noble metals can be used along with the transition metal elements. So, all the three purpose can be met at the same time getting a better selectivity, conversion of the reactants, having a better stability towards deactivation and coking and the most important having a good activity. So, combining both i.e., small amount of noble metal catalyst with a non-noble metal catalyst can be used. Other than the transition metal and noble metal catalyst perovskites are also being used as catalyst.

There are various supports that can be used like magnesium oxide, cerium oxide, zirconium oxide and these can be mixed together. So, like alumina on alumina and zirconia when they are used in that case they have a better stability as well as better conversion. Zirconia that provides good conversion, they provide a little basicity of the support also, reduces coke formation, ceria that provides a higher thermal stability. So, that way these can be mixed with these oxides so, as to act as a support.

And support serves various purpose here like it can stabilize the catalyst, it can provide the required surface area, it can provide the dispersion of the catalyst, it could reduce the coking and sintering by having an interaction with the catalyst, it could provide the required basicity. So, there are several purpose that support can do here.

A small quantity of promoter can also be added and that reduces the coke deposition like the calcium aluminate or potassium oxide. And these numbers of parameters that we have mentioned here like selectivity conversion can be defined as the number of moles for example, for methane conversion number of moles of methane which was act in the reactant side minus the amount of methane which was unreacted to the amount of methane in the feedstock.

Same way we can define the yield of the amount of hydrogen we have got as against the amount of reactant feedstock and selectivity of the desired product as against the other undesirable products.

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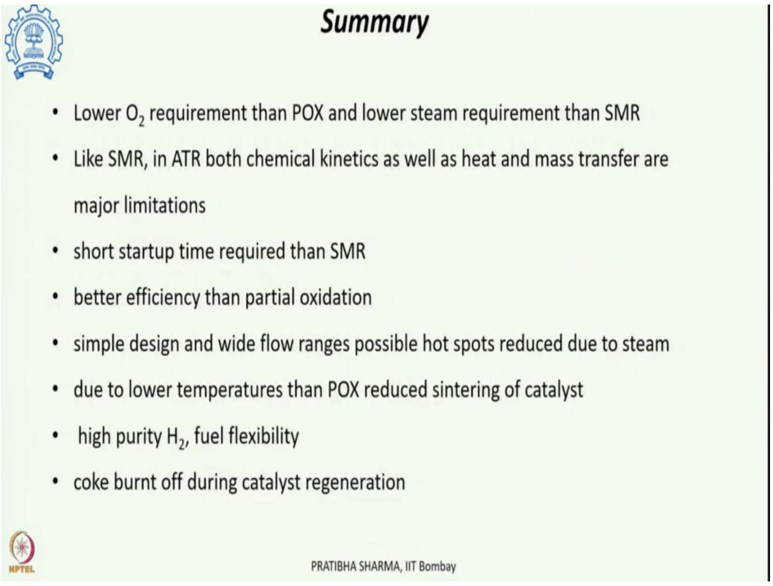

Summary

- Lower O_2 requirement than POX and lower steam requirement than SMR
- Like SMR, in ATR both chemical kinetics as well as heat and mass transfer are major limitations
- short startup time required than SMR
- better efficiency than partial oxidation
- simple design and wide flow ranges possible hot spots reduced due to steam
- due to lower temperatures than POX reduced sintering of catalyst
- high purity H_2, fuel flexibility
- coke burnt off during catalyst regeneration

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To summarize this particular ATR section let us see that, what are the differences of this as against the other two processes. Auto thermal reformer like the partial oxidation requires oxygen if it is to be used for applications wherein pure hydrogen is required or where it is that methanol synthesis process where the oxygen is used and we do not want the outlet stream to be diluted with nitrogen.

At the same time the requirement of oxygen in partial oxidation is higher as against the auto thermal reforming process and similarly for auto thermal reforming the requirement of steam is lower than the steam methane reforming process. Again the ATR process here in the chemical kinetics as well as both the heat and mass transfer, they are the major limiting factors deciding the overall process.

Compared to steam methane reforming since there are no external heat exchange required i.e., the energy or heat which is required for the reaction is provided within the reactor and the startup time which is required is much shorter compared to the steam methane reforming process. It has a better efficiency compared to the partial oxidation, because the energy or heat which is produced in the exothermic reaction is being used in the endothermic reaction. So, the thermal efficiencies are comparatively better than the partial oxidation.

The design of the auto thermal reformer is comparatively simpler, there are different ranges in which we can produce H_2 by CO, there are various wide flow ranges which are possible. At the same time since we are using steam, the possibility of hotspot formation inside the reformer is reduced. The temperatures which are encountered in the auto thermal reformer are lower than the partial oxidation and as such the problem of sintering is lowered in auto thermal reforming process. And, we can use other fuels also and can get high purity hydrogen and the coke which is formed can be burned off during the catalytic regeneration.

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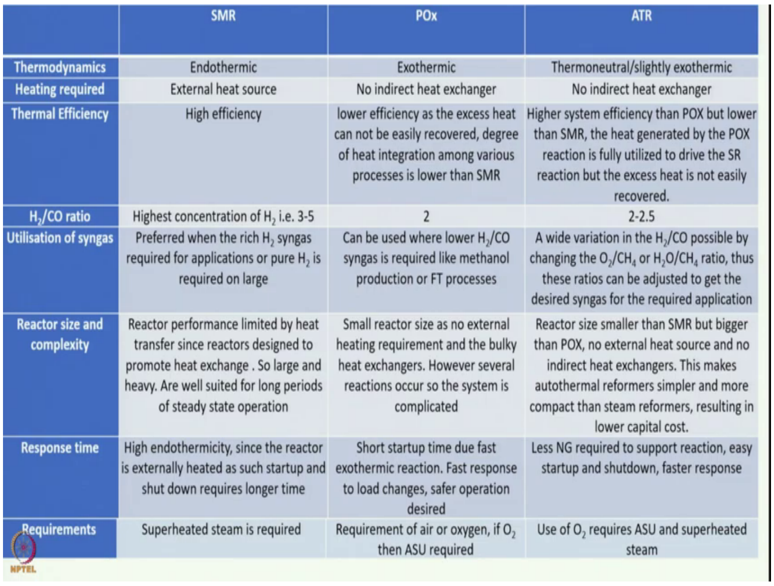

	SMR	POx	ATR
Thermodynamics	Endothermic	Exothermic	Thermoneutral/slightly exothermic
Heating required	External heat source	No indirect heat exchanger	No indirect heat exchanger
Thermal Efficiency	High efficiency	lower efficiency as the excess heat can not be easily recovered, degree of heat integration among various processes is lower than SMR	Higher system efficiency than POX but lower than SMR, the heat generated by the POX reaction is fully utilized to drive the SR reaction but the excess heat is not easily recovered.
H_2/CO ratio	Highest concentration of H_2 i.e. 3-5	2	2-2.5
Utilisation of syngas	Preferred when the rich H_2 syngas required for applications or pure H_2 is required on large	Can be used where lower H_2/CO syngas is required like methanol production or FT processes	A wide variation in the H_2/CO possible by changing the O_2/CH_4 or H_2O/CH_4 ratio, thus these ratios can be adjusted to get the desired syngas for the required application
Reactor size and complexity	Reactor performance limited by heat transfer since reactors designed to promote heat exchange . So large and heavy. Are well suited for long periods of steady state operation	Small reactor size as no external heating requirement and the bulky heat exchangers. However several reactions occur so the system is complicated	Reactor size smaller than SMR but bigger than POX, no external heat source and no indirect heat exchangers. This makes autothermal reformers simpler and more compact than steam reformers, resulting in lower capital cost.
Response time	High endothermicity, since the reactor is externally heated as such startup and shut down requires longer time	Short startup time due fast exothermic reaction. Fast response to load changes, safer operation desired	Less NG required to support reaction, easy startup and shutdown, faster response
Requirements	Superheated steam is required	Requirement of air or oxygen, if O_2 then ASU required	Use of O_2 requires ASU and superheated steam

Now, let us compare all the three processes that we have learnt so far. The steam methane reforming process, partial oxidation and auto thermal reforming based on several parameters. If we consider the thermodynamics of the process, then steam methane reforming was an endothermic process, partial oxidation was an exothermic process, auto thermal reforming is either a thermoneutral or it can be made slightly exothermic so as to encompass the losses also that are occurring in the reactor.

In terms of heating requirement in SMR the reformer which are filled with catalyst tubes are externally heated and in partial oxidation there is no such indirect heating involved, the heat of the reaction which is required for the endothermic reaction is being generated within the reactor itself and same is for auto thermal reforming.

The thermal efficiency with the use of several heat exchangers is higher in case of steam methane reforming, but in partial oxidation there are exothermic reactions occurring and it is very difficult to recover the excess heat which is obtained in the process. So, the degree of heat integration among the various processes is not like it was in case of steam methane reforming. In auto thermal reforming comparatively the system efficiency is higher than partial oxidation, because the heat produced is utilized by the reaction within the reactor, but at the same time the other reaction heat cannot be completely recovered. So, the excess heat which is being produced cannot be recovered in the process.

If we compare in terms of hydrogen to CO ratio it is highest in case of SMR it can go 3 to 5, in partial oxidation 2 in fact, less than 2 and for ATR this can vary depending upon the steam to feedstock ratio, steam to carbon ratio or steam to oxygen to carbon ratio. So, this can be 2 to 2.5 or it can be more wide range we can get compared to partial oxidation this is higher, but compared to steam methane reforming this is lower.

Now, this method of steam methane reforming is preferred in case where we require hydrogen rich syngas or the processes where we want pure hydrogen, we can separate out the other impurities from the hydrogen in the purification steps and then we can get pure hydrogen or in processes where this H_2 by CO ratio required is higher there we can use the syngas.

In partial oxidation since the H_2 by CO ratio is lower, this would be preferred for processes where this is ideal ratio for methanol's production or for other liquid fuels production. In ATR this ratio can be changed and it can be adjusted as per the desired application.

If we see the reactor size and complexity, since reactor performance is limited by heat transfer and reactor is designed so as to have heat exchange. So, these reactors are usually bulky and heavy; however, they are suited for long periods of steady state operation.

For partial oxidation the reactor size is small, there is no external heating requirement in the process and there are no bulky heat exchangers. So, these are much more compact in size, but at the same time these are complicated because there are several reactions which are highly exothermic. So, it has to be operated within the explosive limit that we need to be careful.

ATR reactor is comparatively smaller than the steam methane reforming, but it is bigger than the partial oxidation. There are no external heat sources or heat exchangers or indirect heat exchangers and that makes them simpler and compact than the steam reformer and that results in a lower cost, these are simpler as well as these are compact.

If we compare on the basis of the response time, since the process in SMR is of highly endothermic. So, the reactor is externally heated. So, it requires a long time for starting it up or shutting it down. So, these are not meant for dynamic operations and very faster operations, short startup time is observed in case of partial oxidation as well as auto thermal reforming.

In steam methane reforming superheated steam is required, in partial oxidation air or oxygen is required, if oxygen is to be used then air separation unit has to be added and same is we thought for auto thermal reformer.

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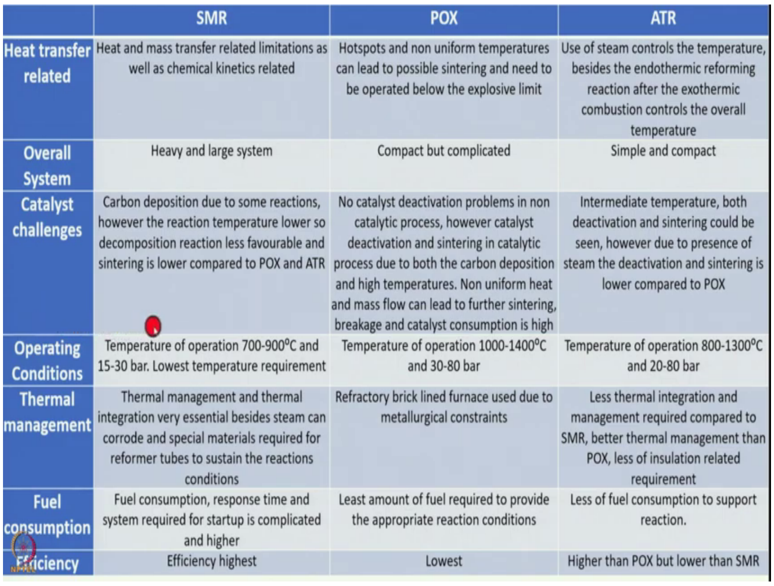

	SMR	POX	ATR
Heat transfer related	Heat and mass transfer related limitations as well as chemical kinetics related	Hotspots and non uniform temperatures can lead to possible sintering and need to be operated below the explosive limit	Use of steam controls the temperature, besides the endothermic reforming reaction after the exothermic combustion controls the overall temperature
Overall System	Heavy and large system	Compact but complicated	Simple and compact
Catalyst challenges	Carbon deposition due to some reactions, however the reaction temperature lower so decomposition reaction less favourable and sintering is lower compared to POX and ATR	No catalyst deactivation problems in non catalytic process, however catalyst deactivation and sintering in catalytic process due to both the carbon deposition and high temperatures. Non uniform heat and mass flow can lead to further sintering, breakage and catalyst consumption is high	Intermediate temperature, both deactivation and sintering could be seen, however due to presence of steam the deactivation and sintering is lower compared to POX
Operating Conditions	Temperature of operation 700-900°C and 15-30 bar. Lowest temperature requirement	Temperature of operation 1000-1400°C and 30-80 bar	Temperature of operation 800-1300°C and 20-80 bar
Thermal management	Thermal management and thermal integration very essential besides steam can corrode and special materials required for reformer tubes to sustain the reactions conditions	Refractory brick lined furnace used due to metallurgical constraints	Less thermal integration and management required compared to SMR, better thermal management than POX, less of insulation related requirement
Fuel consumption	Fuel consumption, response time and system required for startup is complicated and higher	Least amount of fuel required to provide the appropriate reaction conditions	Less of fuel consumption to support reaction.
Efficiency	Efficiency highest	Lowest	Higher than POX but lower than SMR

There is a limitation in steam methane reforming that is heat and mass transfer limitations as well as the chemical kinetics based limitations. In partial oxidation these limitations are comparatively less if it is non-catalytic partial oxidation, if it is catalytic partial oxidation, then since the temperatures are high in case of partial oxidation, there could be hotspots, non uniform temperature distributions inside catalyst could get sintered because of that high operational temperatures. This can be controlled with the use of steam in case of auto thermal reformer.

Overall system is large for steam methane reforming, compact for partial oxidation but it is complicated and simple and compact for auto thermal reforming. There are several catalyst related challenges like carbon deposition, in case of steam methane reforming, but these are comparatively much less than the other two processes because the reactions which produce carbon they either dominate at the very low temperature regime or these are not much favourable in the temperature in which the reformer works operates.

Non catalytic partial oxidation there is no catalyst deactivation problem, but in catalytic partial oxidation both the problems related to deactivation and sintering are there and non uniform heating and mass flow rate can lead to even catalyst sintering, breakage and consumption. In auto thermal reforming these challenges are sort of intermediate, deactivation and sintering is there, but due to presence of steam that deactivation can be reduced and sintering is lower than the partial oxidation.

So, the temperatures and pressures like 700 to 900 degree 15 to 30 bar for steam methane reforming, for partial oxidation 1000 to 1400 degree centigrade, 30 to 80 bar pressure, for auto thermal reforming 800 to 1300 degree centigrade 20 to 80 bar.

Thermal management is required in case of steam methane reforming and special tube materials is required and there are metallurgical challenges, steam can also corrode they have to bear the high temperatures and pressure. However, here in both the processes refractory brick line furnaces are being used.

Fuel consumption is high in steam methane reforming, response time is higher, startup is complicated; however, the amount of fuel which is required for providing the appropriate reaction conditions is lower in case of partial oxidation and auto thermal reforming.

So, comparing everything we can see that the efficiency is highest in steam methane reforming, it is lowest in partial oxidation and intermediate between partial oxidation and steam methane reforming in the auto thermal reformer. So, we have seen all the three processes which are used for hydrogen production from the hydrocarbons and we have compared each of these.

Thank you.