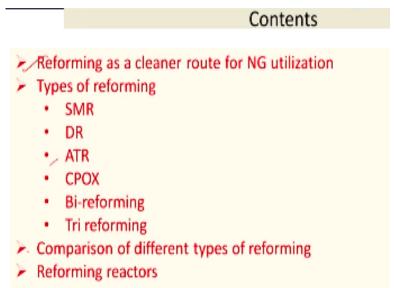
Technologies for Clean and Renewable Energy Production Prof. Prasenjit Mondal Department of Chemical Engineering Indian Institute of Technology – Roorkee

Lecture - 22 Syngas Production from Natural Gas

Hi friends, now we will discuss on the topic gaseous fuels, syngas production from natural gas. In the previous class, we have seen that natural gas can be used conventionally for the heat application or it can be used in power plant for electricity production. We have also discussed that this can be converted to syngas and then syngas to different types of chemicals including hydrogen. So if we can do it, then we can reduce emission level due to the utilization of syngas.

In this class, we will be focusing on how the natural gas can be converted to syngas, later next we will discuss how the syngas can be converted to liquid fuel and also how we can get hydrogen from natural gas.

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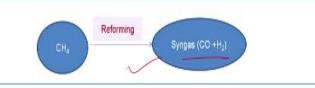


So the contents of this class is your reforming as a cleaner route for natural gas utilization; then types of reformers or reforming that is SMR, dry reforming, ATR, CPOX, bi-reforming tri-reforming, etc.; and then comparison of different types of reforming; and then reforming reactors.

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Reforming as a cleaner route for NG utilization
 In reforming process natural gas is converted to H₂ and CO containing syngas by means of an exothermic or endothermic reaction depending on the chemical process selected to perform the process
 It is normally a catalytic process

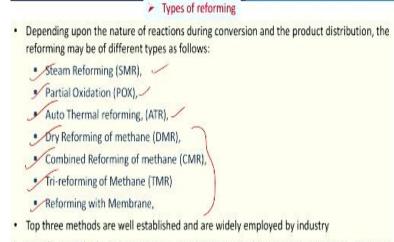
- The elimination of oxygen from the initial fuel mixture improves the overall system efficiency by minimizing energy losses from catalytic combustion.
- The product can be used for different applications such as heat, steam, liquid fuels and chemical synthesis



If we see the reforming, that means that it will be reformed the molecules, the methane will be converted to other molecules. In this process, the syngas is produced, hydrogen and CO containing syngas by the thermal process, it may be exothermic or endothermic, both reactions take place in this and depending upon the nature of reforming process, the del H value changes. Normally it is a catalytic process, but without catalyst also the reforming can take place, and if we use catalyst, we will get better performance.

What is happening by this process, we can eliminate the oxygen from the initial fuel mixture that improves the overall system efficiency by minimizing energy losses from catalytic combustion. This product which we are getting that syngas, this will be used for heat application, for steam generation and for different types of chemical synthesis. So that is the major advantage of this process for the conversion of natural gas to syngas and then syngas to other chemicals. So this is our reforming process, CH₄ will be reformed to CO+H₂, that is called syngas.

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 Last four methods are innovations to minimize greenhouse gases emissions, minimize energy consumption and improve the reforming process yields

Then we can get different types of reforming process as you have mentioned and the most important are steam reforming, then partial oxidation, auto thermal reforming, then dry reforming or combined reforming of methane that is called bi-reforming, then tri-reforming of methane, and reforming with membrane. So these are the different types of reforming processes available in literature and some of these are applied in commercial scale and some of these are still under development stage.

The first 3 are mostly used in industry. Other these are under development and demonstration scale and these will be having better feature for the control of carbon dioxide.

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Operating conditions, reactions and products	SM	Catalysts Can occur without catalyst but requires
• $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$ • $SMR1, \Delta H_{298} = 206.2 \text{ kJ/mol}$ • $CH_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4H_2(g)$ • $SMR2, \Delta H_{298} = 164.7 \text{ kJ/mol}$ • $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$ • $WGSR, \Delta H_{298} = -41.5 \text{ kJ/mol}$ • $H_2/CO \text{ ratio } \in 3-5$		very high temperature Modern steam reforming catalyst uses nickel on ceramic support with or without promoters or stabilizers Precious metals offers alternative to nickel Supports must be strong, inert, thermally and chemically stable
 Temperature: 700-850 °C 	Re	quirements:
 Pressure 15-30 bar 	0	High geometric surface area
	0	High heat transfer coefficient
 Larger amount of CO₂ emissions 	0	Low pressure drop
 Expensive method for producing H 	2 0	Less carbon deposition

Now we will see what SMR is, that is steam methane reforming. So in this case, we will be using methane and steam as a reacting agent and the reaction will be CH_4+H_2O both remain

in gas phase, it will give us CO and $3H_2$. So, this one SMR1. In this reaction, we can get 206.2 kilojoule/mol energy, this energy is required, that is endothermic process. Then another reaction may take place, CH_4+2H_2O that is CO_2+4H_2 , so carbon monoxide can be produced, carbon dioxide also can be produced and here 164.7 kilojoule/mol energy is required for this reaction.

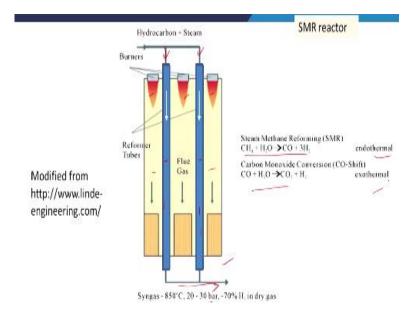
Then we can get water-gas-shift reaction in the reforming reactor also, that is CO which is produced here that can also react with H_2O which is available in the reactor and then converts to CO_2+H_2 , so this reaction is exothermic. So overall, it is endothermic reaction. Then another important feature is that H_2/CO ratio, this H_2 and CO which is available in syngas, the ratio of these 2 components are very very important because this will decide the suitability of the syngas for its downstream applications.

Different downstream applications require different ratio of H_2 is to CO. So in this case, we can get this ratio as 3-5, so the very high ratio we can get with respect to other reforming and the temperature requirement is 700-850 degree centigrade and pressure is 15-30 bar. So, this is a commercial process and in this process catalyst is normally used. If we do not use catalyst, then also we will get some syngas formation, but basically nickel or on ceramic support, this catalyst nickel based catalyst on ceramic support with or without some promoter or stabilizers these catalysts have been used in the SMR process.

The precious metals offers alternative to the nickel and supports may be strong, inert, thermally and chemically stable. So these are the catalyst for this reaction. It requires high geometric surface area, high heat transfer coefficient, low pressure drop, and less carbon deposition. So during this process, carbon deposition takes place and the catalyst should have that property where the low carbon deposition will be achieved.

This process we will discuss in detail because we see here hydrogen is maximum. So if we want to get hydrogen from the syngas, the steam reforming may be one of the important process or route and we will discuss in next class in more detail.

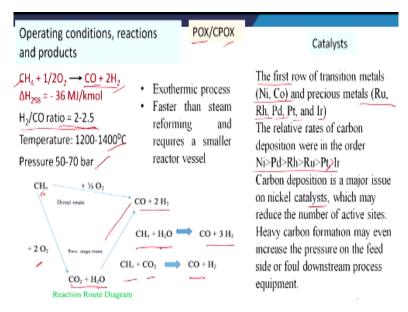
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Now we will see some aspect of the SMR reactor. So here is the SMR reactor schematic say. So we have these are the tubes that is called reformatives. So from this, we are putting natural gas and steam, both natural gas and steam. So, then high temperature will be provided in this reactor, these are the tubes through, inside of the tube we are having the hydrocarbon and steam, outside we are having high temperature by burning some fuel gas.

So here, the burners are there, so high temperature is generated, and there will be some reforming reactions inside the tube and we will get the product from the bottom of this tubular reactor or tubes of the reformer. The syngas we can get 850 degree centigrade, 20-30 bar, and 70% hydrogen in dry gas. So this is the steam reforming reactor and these are the reactions already we have discussed, endothermic and exothermic reactions, both are available during the process, and overall it is endothermic reaction.

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Next, we are coming to partial oxidation, that is POX, and catalytic partial oxidation CPOX. So these methods is also used largely and here as you see partial oxidation so you will be providing less amount of oxygen. So CH_4 will be converted to $CO+2H_2$ that is the required in syngas. So then here we can get H_2/CO ratio 2-1.5 and temperature is higher 1200-1400 degree centigrade and then pressure 50-70 bar.

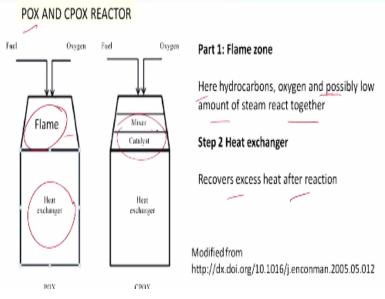
So here, methane will be partially converted to this one, that is one reaction; another it is possible methane is reacting with 2O₂, then it is CO_2+H_2O , then CO_2+H_2O further it can give up CO+2H₂. Other reactions which can take place here CH₄ +H₂O which is produced in this H₂ can react with the methane also and it can give CO+3H₂ and CH₄+CO₂ which generated this reaction that can also give a CO+H₂ so that is why we can get H₂/CO ratio as equal 2-2.5 and this is exothermic process and faster than steam reforming and requires a smaller reactor vessels.

So advantage of this, we do not need to give much external energy for this reactions. Then if we see the catalyst part, then also we will see that the first row of transition metals nickel and cobalt and precious metals ruthenium, rhodium, palladium, platinum, and iridium those are used as a catalyst for this reaction and the relative rates of carbon depositions are in the order, that is nickel greater than palladium greater than ruthenium, then it is greater than Ru, and then it is greater than Pt, so this is greater than iridium okay.

So carbon deposition is a major issue on nickel catalyst which may reduce the number of active sites. So heavy carbon formation may give increase in the pressure on the feed side

that is the pores will be blocked and more pressure drop will get during the reactions and in the reactor.

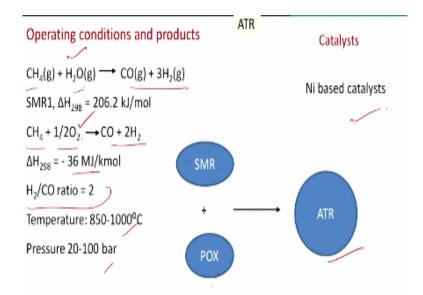
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So we will see the reactor configurations. So we will be having 2 zones in this case. The first is your flame zone and another is your heat exchanger zone. So flame zone means here hydrocarbons, in our case methane, then oxygen, those will be combusted and possibly low amount of steam react together. So here, some reaction takes place and then CO and H_2 form here and then at high temperature we recover excess heat.

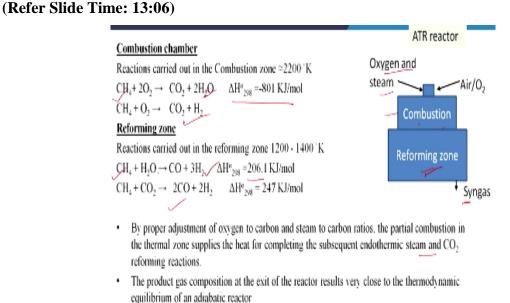
So, this is the features of this, but this is for POX, but if we use CPOX, then we can have some catalyst layer here at the first flame and then we will be having some catalyst here, so catalyst will help the reactions. So conversion of the process will be more than the POX.

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Then we are going to ATR, auto thermal reforming. So in this case, we use steam and oxygen, so steam and oxygen, so the reactions are the methane plus steam then will be $CO+3H_2$, it will give also $CH_4+1/2O_2$, then it is $CO+2H_2$ and then this is the heating value - 36 megajoule per kilo mol and overall it is endothermic process. H₂/CO ratio here we can get around 2 and temperature is 850-1000 degree centigrade and pressure is 20-100 bar.

So what we see here are 2 types of reactions. So this reaction is basically for SMR and this reaction is for partial oxidation. So SMR plus partial oxidation basically gives us ATR and nickel based catalyst had been used for this reforming process.



If we see the reactor configurations, as you have discussed the first the hydrocarbon or methane will be combusted and may use some oxygen and steam here and then some reforming reactions will take place in this zone. Now catalyst will be available here and then we will get syngas. So the reactions already we have discussed that CH_4+O_2 this will be there and then deforming will be taking place CH_4 + this H_2 which is forming this and CH_4+CO_2 , then we can get this one. So this is the basics of the ATR process.

So by proper adjustment of oxygen and steam to carbon ratios, the partial combustions in the thermal zone supplies the heat for completing the subsequent endothermic steam and CO_2 reforming reactions, that is 2 reactions which we are getting, this heat generated, that is used in the second case.

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Operating conditions and productsDRMCatalysts $CH_4(g) + CO_2(g) \longrightarrow 2CO(g) + 2H_2(g)$
 $\Delta H_{298} = 247$ kJ/molNi based catalysts are commonly used H_2/CO ratio = 0.4 - 1.5Temperature: 630-850°CPressure 1-20 bar

Presence of CO₂ gives rise to more chances of carbon formation on catalyst surface due to production of CO and consumption of H₂ via reaction

 $CO_2 + H_2 \leftrightarrow CO + H_2O$; $\Delta H_{298}^{\circ} = 41 \text{ kJ/mol}$

Development of active catalytic materials, but with a very low coke formation rate, either on the catalysts or in the cold zones of the reactor is the main challange.

Next we are coming to DRM, that is dry reforming of methane. So dry reforming means there will be no steam use, obviously carbon dioxide is used for the reforming purpose. So reaction is methane + carbon dioxide $2CO+2H_2$ in gaseous phase and this is our ΔH 247 kilojoule/mol, so endothermic reaction again, and your temperature 630-850 degree centigrade and pressure 1-20 bar and here the H₂/CO ratio is less, 0.4-1.5 and here we can get nickel based catalysts are used widely.

The presence of CO_2 gives rise to more chance of carbon formation, so as we are using carbon dioxide as the reactant for the reforming process, the carbon deposition is more in this type of reforming process and that is the major disadvantage of dry reforming and that is the more challenging part also and that is why it has not got industrial application yet. Then efforts are on to improve this process, how to reduce the carbon deposition in DRM.

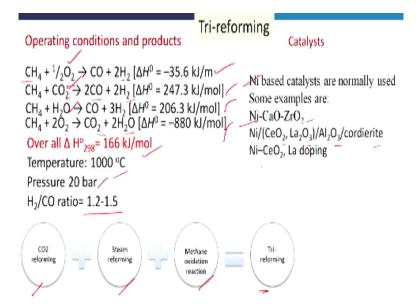
Development of active catalyst materials but with a very low coke formation rate, either on the catalyst or in the cold zones of the reactor is the main challenge just we have discussed. (Refer Slide Time: 15:45)

Operating conditions and products	Bi reforming	Catalysts
$\begin{array}{l} CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g) \\ \DeltaH_{258} = 206.2 \text{ kJ/mol} \\ CH_4(g) + 2H_2O(g) \longrightarrow CO_2(g) + 4H_2(g) \\ \DeltaH_{258} = 164.7 \text{ kJ/mol} \\ CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g) \\ \DeltaH_{258} = -41.5 \text{ kJ/mol} \\ CH_4(g) + CO_2(g) \longrightarrow 2CO(g) + 2H_2(g) \\ \DeltaH_{258} = 247 \text{ kJ/mol} \\ Overall \DeltaH^\circ_{298k} = -41.2 \text{ KJ/mol} \\ H_2/CO \text{ ratio} = 2 \\ Temperature: 700-950 \ ^\circC \\ Pressure: \ 10-30 \text{ bar} \end{array}$	Nano-comp convention	atalysts are commonly used posite Ni/ZrO ₂ , is superior to al Ni/ZrO ₂ and Ni/Al ₂ O ₃ terms of catalytic activity and

Then we are coming to bi-reforming, then in this case we will be using 2 reforming agents, so here methane plus steam and then carbon monoxide. So here, we will be having methane plus steam $CO+3H_2$, $\Delta H = 206.2$ kilojoule/mol, then CH_4 + steam, this reaction can also take place and then the ΔH is this one and $CO+H_2O$ that can give us CO_2+H_2 and other reactions which is taking place here CH_4+CO_2 it is giving us $2CO+2H_2$. So in this case, we can use carbon dioxide and steam as a reactant for the reforming process.

Overall is -41.2 kilojoule/mol and H_2 /CO ratio is 2 and temperature 700-950 degree centigrade and pressure 10-30 bar. So one of the important advantage of this process is that it can use carbon dioxide as a reacting agent. So it helps to reduce the carbon emission and increase the carbon footprint. Here also, nickel based catalysts are used and nano-composite that is nickel zirconium oxide is superior to conventional nickel zirconium oxide, that means efforts are on to increase superior quality catalyst using nano-particles for this particular process.

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Then we will discuss the tri-reforming. So here, we will be using 3 agents; oxygen, carbon dioxide, and steam for the conversion of the methane, that is why it is tri-reforming. So major reactions are here; $CH_4+1/2O_2$, $CO+2H_2O$, this is your ΔH value and then CH_4+CO_2 it will give us $2CO+2H_2$ and then this is del H value, and CH_4+H_2 , it will give H_2O , it will give $CO+3H_2$ with this heating value and CH_4+2O_2 , CO_2+2H_2O , heating value is this one. So overall heating value 166 kilojoule/mol and temperature 1000 degree centigrade, and pressure 20 bar, hydrogen to carbon monoxide ratio 1.2-1.5.

So here, we are getting tri-reforming, that is carbon dioxide reforming, steam reforming, and methane oxidation reactions. So these are the features of tri-reforming and catalysts are basically nickel-based catalyst and some examples are given here, nickel, calcium oxide, zirconium; nickel, cerium oxide, lanthanum oxide and aluminum and corderite; nickel ceria and then lanthanum doping. So these are some example of this catalyst used in this reaction. (**Refer Slide Time: 18:44**)

Comparison of different reforming					
Type of reforming	Reforming reactants	Operating conditions	CH ₄ Conv.(%)	- Advantages	Disadvantages
Steam Reforming	CH₄, H₂O	700-850 °C 15-30 bar	65 - 95	Heat recovery from flue gas. Lowest process temperature requirement.	Endothermic reactions The product gas has a $H_2/C0$ ratio of 3. Steam corrosion problems. Costs in handling excess H_2O .
Partial Oxidation	CH4, O2	1000-1450 °C 30-85 bar	95 - 100	No direct heat exchanger is needed. More compact then steam reformer. Low reformer vessel cost.	High cost of air separation unit. Poor heat recovery.

Now we will compare different type of reforming processes. So steam reforming, partial oxidation and then bi-reforming and ATR we will discuss. So here are reforming reactants as we have discussed, operating conditions we have discussed, methane conversions we will see here how it changes and all of these are having some advantage and some disadvantage, so that part we will see here.

So steam reforming gives us 65-95% of methane conversion, partial oxidation 95-100%, and then it gives auto thermal 95-100%, and dry reforming 70-96%. So these are different methane conversions reported in literature. Advantage as you have discussed that the steam reforming can give us maximum H_2 /CO ratio, so when we are interested to get hydrogen from the syngas, then this process will prefer. Steam as you are using steam, it may induce some corrosion problems also and that is its disadvantage.

Similarly for partial oxidation, high cost of air separation units, we have to separate the oxygen from the air, so that increases the cost for the process and no direct heat exchanger is needed and more compact than steam reforming and low reformer vessel cost, so these are the advantage of this partial oxidation.

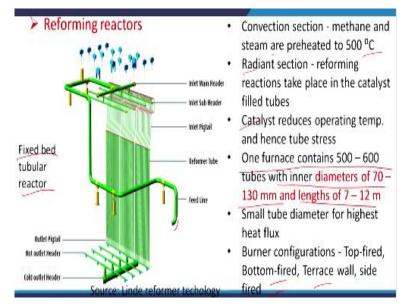
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Comparison of different reforming						
Type of reforming	Reforming reactants	Operating conditions	CH ₄ Conv.(%)	Advantages	Disadvantages	
Auto- thermal Reforming	CH ₄ , H ₂ O, O ₂	850–1300 °C 20–100 bar	95 - 100	All heat needed is supplied by partial oxidation. No direct heat exchanger is needed. More compact then steam reformer.	High cost of air separation unit. Oxygen added lowers the H ₂ /CO ratio in the product gas.	
Dry reforming	CH₄, CO₂	640-1073 °C 1-10 bar	70 - 96	Conversion of greenhouse gas into fuel/syngas. Specific ratio of CH_4 , H_2O , and CO of 3:2:1 can produce a gas mixture with essentially a 2:1 ratio of H_2 to CO_2 .	Consumes 1.6 times more energy than steam reforming.	

Similarly auto thermal process, we have high cost of air separation unit. Advantage is all heat needed is supplied by partial oxidation and then that heat is used for reforming, so more compact than steam reformer. Then dry reforming as you have discussed that it uses carbon dioxide, so that is the major advantage of this process and conversion of greenhouse gas into fuel or to syngas.

Specific ratio of methane, steam, and carbon monoxide 3:2:1 can produce a gas mixture with essentially a 2:1 ratio of hydrogen and CO₂, so this is required for liquid fuel synthesis, methanol synthesis, etc. So that is the advantage of this process, but if we can develop suitable catalyst and coke deposition problem can be reduced, so this process can be attractive, but this is the challenge for the process.

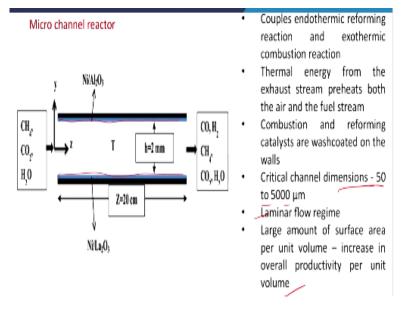
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Now we will see the reforming reactors. So different types of reactor configurations or reactor types have been used, out of those fixed bed tubular reactor this is mostly used in commercial scale for larger reformer units. We see here feed inlet, it goes here and then it goes through this tube as we have discussed in the previous slide, so these are the tubes through which the feed hydrocarbon and other reactants goes through. Then after reforming, it is going for as a product.

So in this case, the tubular reactors, in the tubes in this reactor, the reforming reaction takes place and the temperature is given by the combustion of another fuel gas at the outside of the tubes. So in commercial scale if we see, one furnace contains 500-600 tubes with inner diameter of 70-130 millimeter and length of 7-12 meter and conversion section methane and steam are preheated to 500 degree centigrade.

Then there are some radiant sections and catalytic sections and the catalyst used for the conversions of the methane to syngas, it is top fired, it can be bottom fired, it can be terrace wall, side fired. So, the feed can be at the top, bottom, or side of the wall, anywhere it can be done.



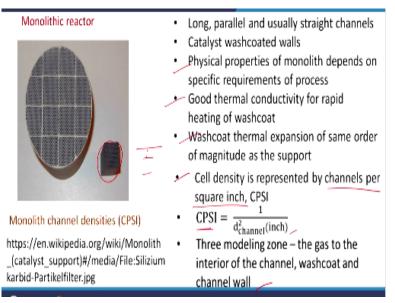
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Then we are coming to microchannel reactor. So because of the latest development on this technology on this reactor part, if we use the microchannel, then the performance or economics of the process can be improved because it reduces the mass and heat transfer limitation. So if you can reduce the diameter of this, it is almost similar to say tubular reactor, but if we can reduce the diameter very, very small and then we can coat some catalyst inner

part of this tube, so very small diameter and the inner side coating or washcoating of the catalyst, so that will increase the performance of the reactor and this is a microchannel reactor.

Here, critical channel dimension we see 50 to 5000 micrometer. So, we had 70 millimeter, here we are having 50 to 5000 micrometer. So because of the reductions of this tube size, the performance increases because of the reduction in different mass and heat transfer losses. Here also, it is laminar flow regime and large amount of surface area per unit volume increase the overall productivity per unit volume. So, you can get more productivity per unit volume in this reactor.

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Then another development is monolithic reactor. So, it is like say honeycomb structure we can say. These are the number of comb or circular or the square shaped channels are made and this is a honeycomb like structure. So, it is also similar to the microchannel, here also we can put catalyst loading inside and washcoating and only the improvement in the design is available in this case and long parallel and usually straight channels and catalyst washcoated walls.

Physical properties of monolith depend on specific requirements of process and good thermal conductivity for rapid heating and of washcoat. Washcoat thermal expansion of same order of magnitude as the support. Cell density here, what is the cell density, where you see here in this case, so number of cells are there, so that is CPSI that is channels per square inch, that is very important that will decide the dimensions of the channels also, so that influences the

performance of the process and CPSI is $1/d^2_{channel}$ in inch.

So 3 modeling zone, the gas to the in interior of the channel, washcoat, and channel wall; so these are 3 parts, this one, this one and in between.

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Reactor type	Operating conditions	Catalyst used	Advantages	Disadvantages	Reference
Fixed bed	700-950 °C	Regular/	High production capacity.	Less heat transfer	Froment and
tubular	10-25 bar	irregular		efficiency (50% heat loss in	Bischoff, 1990
reactor	-	packing		flue gas).	
1		materials. E.g. raschig rings.		Larger footprint Catalyst deactivation starts at 700 °C.	

Comparison of different reactor types

Now, comparison of different reactor types. If we compare the fixed bed and tubular 700-950 degree centigrade, 10-25 bar, and regular/irregular packing materials, raschig rings are used, high production capacity it has, less heat transfer efficiency as you are talking about the limited sense is reduced by the reductions of the diameter of the tubes, and then larger footprint and catalyst deactivation starts at 700 degree centigrade okay.

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Reactor type	Operating conditions	Catalyst used	Advantages	Disadvantages	Reference
Micro- channel reactor	860-900 °C 15 bar	Wash- coated	Uniform temperature Low rate of excess air (25%) reduces the cost of blowers or compressors. Thermal losses below 5% for scaled-up plant. Low NO _x (<10 ppm) emission.	Requires advance technology for fabrication. Small capacity. Many reactors can be arranged in parallel for high throughput.	A.Y. Tonkovich et al., 2004
Mono- lithic reactor	860-900 ⁴⁴ C 15 bar ⁄	Wash- coated	Low pressure drop. Good mass transfer interphase. Good thermal and mechanical properties. Simpler scale-up due to specific geometries.	Ceramic monoliths have poor thermal conductivity, hence metal monoliths are preferred. Lower specific surface when compared with random packing reactors that may lead to lower reaction rate.	Chen et al, 2008

Then we see microchannel. The temperature is given here that is 15 bar and 860-900 degree

centigrade, the washcoated catalyst, uniform temperature, low rate of excess air, reduces the cost of blower or compressors, their requirement reduces, and then thermal losses below 5% for scaled-up plant, and then it requires advanced technology. This technology is not very matured, some plants have come up and it is still development stage and it is having small capacity also and many reactors can be arranged in parallel for high throughput.

The monolithic, also the similar operating conditions it is having and same type of catalyst is also used. It has also similar properties, low pressure drop, good mass transfer interphase, good thermal and mechanical properties, simpler scale up due to specific geometries. These are the disadvantages that the ceramic monoliths have poor thermal conductivity, hence metal monoliths are preferred. Up to this in this class. Thank you very much for your patience.