Energy Conversion Technologies (Biomass And Coal)

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Lecture 19

Gasification

Good morning, everyone.

Welcome to the second lecture of the module 4. In this lecture we will discuss about the gasification process- upstream processing as well as the downstream processing. Also, the comparison of this conventional gasification with advanced gasification techniques such as sub or supercritical water gasification and plasma gasification process.

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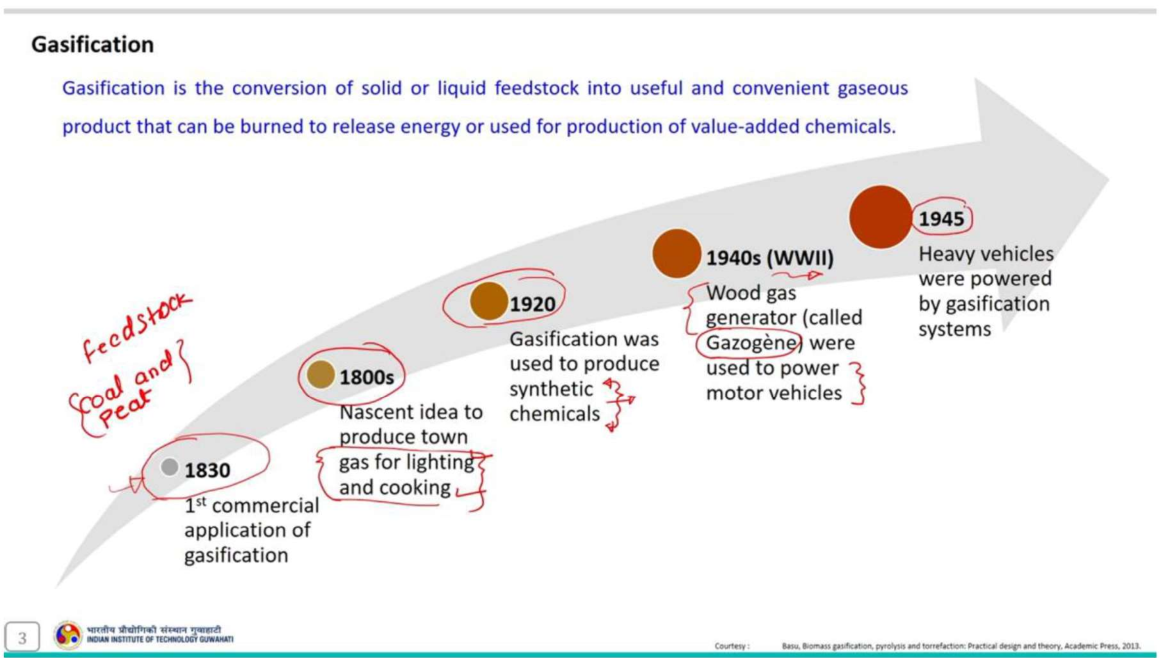

Gasification is the conversion of solid and liquid feedstock into useful and convenient gaseous products that can be burned to release energy or can be used as a feedstock, for the production of value-added chemicals. So, the gaseous product obtained after the gasification process can directly be burned to release the energy or can be processed further to produce value added chemicals. It is an established technology and the commercial application of which dates back to 1830. So, if you look at this particular chart here, it shows the first commercial application of the gasification dates back to 1830. And in the beginning years coal and peat were used as a feedstock material for the gasification process, feedstock material for gasification process. And in the 18th century, the nascent idea of the process was to produce town gas. And that is mainly for lighting and the cooking purpose. And around 1920, the major shift came in this field, when it was used to produce synthetic chemicals. So, this is a major shift happened in the gasification process here around 1920 when the production of gas was used to prepare or manufacture synthetic chemicals from the gasified product. And during World War II, biomass gasification system, it played a significant role when due to shortage of the petroleum, wood gas generator was used to produce gazogene. It is also called as a gazogene and the produced gazogene were used to power motor vehicles. And by 1945, even the heavy vehicles were powered by the gasification system.

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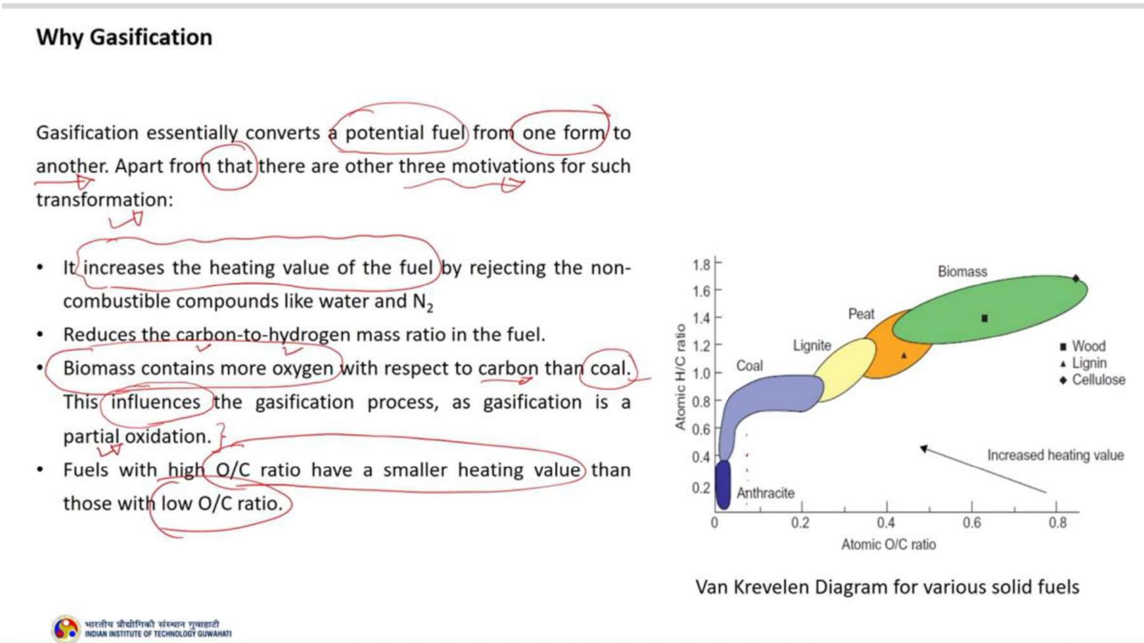

Now, why gasification? Because the gasification essentially converts potential fuel from one form to another. And apart from that, there are other three motivation for such transformation of energy from one form to the another. Because after gasification the product gas increases the heating value of a fuel by rejecting the non-combustible compounds such as water and the nitrogen. And it also reduces the carbon to hydrogen mass ratio in the fuel. Since biomass contain more oxygen in its composition with respect to the carbon than coal. Because as we discussed this concept in one of the lectures, the oxygen contained in the biomass is significantly higher than that of the coal. And this particular oxygen content in the biomass influences the gasification process as gasification is a partial oxidation process. And the heat release during this particular partial oxidation provides the thermal energy which is required for the gasification process as well. Fuels with high O/C ratio have a smaller heating value, and this concept we discussed in one of the lectures in the previous module, than those of the low O/C ratio, that you can see here from this chart as well. The low O/C ratio material has a relatively higher heating value than that of the high O by C ratio. Here the high heating value is relatively low for the biomass material, whereas for the coal and anthracite the high heating value is relatively high, but their O by C ratio is also relatively low.

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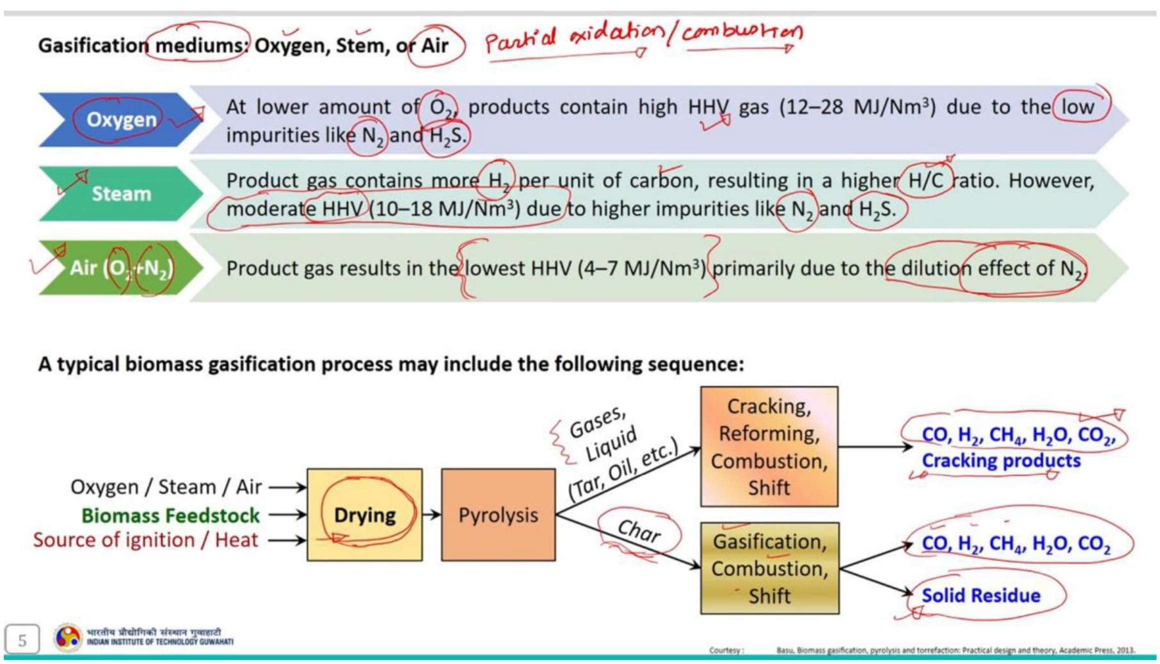

As discussed in the previous slide, gasification is a partial oxidation process or we also term it as a partial combustion process. Because the heat produced during this partial oxidation and combustion provides the thermal energy which is required for the gasification operation. the gasification is carried And because of that the gasification is carried out using different mediums that is either oxygen, steam or air. And when the oxygen is used as an oxidizing medium or sometime it is termed as a gasification medium as well. So, at low amount of oxygen the product contains high calorie value gas and that is mainly due to the low impurities like nitrogen and H_2S in the exhaust gas stream. That is the advantage of utilizing oxygen that is a pure oxygen as an oxidizing medium in the gasification process. And when the steam is used as a gasifying medium or oxidizing medium then the product gas contains more hydrogen per unit of the carbon resulting in higher H by C ratio. And as we know if the H by C ratio is higher for a specific fuel then its high reading value also known as a calorie value is relatively low.

And that is what happens in case of the steam as an oxidizing medium. Because it contains more hydrogen per unit of the carbon resulting in the higher H by C ratio. And because of this higher H by C ratio it gives a product gas which has relatively moderate heating value. And that is also mainly due to impurities like nitrogen and hydrogen sulphide in its composition. And when air is used as an oxidizing medium which is a mixture of oxygen and nitrogen then the product gas results in lowest calorie value gas and this is primarily due to dilution effect of nitrogen. So, as I mentioned at the beginning itself, that when the air is used it is a mixture of oxygen and nitrogen. So, 1 mole of oxygen carries around 3.76 moles of nitrogen and this nitrogen it remains unaffected during this gasification process and may impart dilution effect. And because of that it remains results in lowest calorie value gas when air is used as an oxidizing or the gasifying medium in the gasification process. So, a typical biomass gasification process may involve the following steps as shown here in this schematic. During the gasification process the biomass-based feedstock or fossil fuel-based feedstock once enter the gasifier it passes through the drying zone first, followed by the pyrolysis zone also called as a thermal decomposition zone where it gets converted into a gaseous and the liquid as well as the char as a product. The gases and the liquid products, that is in the form of tar and oil further undergoes the cracking, reforming, combustion, and shift reaction to produce the gaseous product along with the cracking products. Parallelly the char also undergoes the gasification, combustion, and shift reaction to produce this gaseous product and solid residue as a byproduct during this operation. This describes the conventional gasification process and how it takes place in the gasifier.

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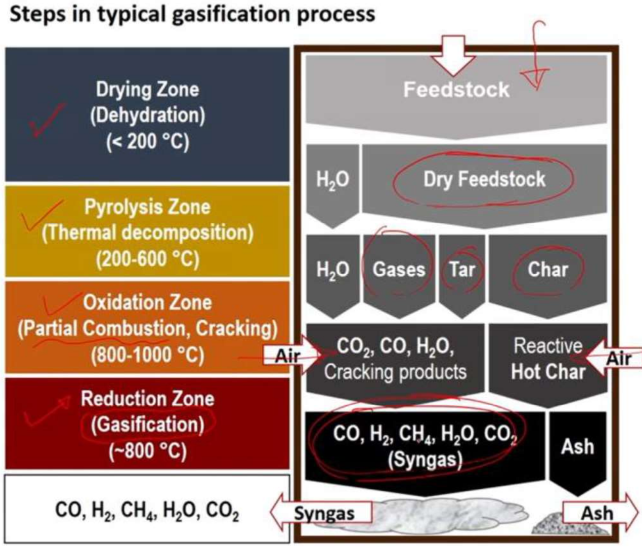
Steps in typical gasification process



- A downdraft gasifier typically involves four distinct zones (or steps):
  - ↦ Drying zone
  - ↦ Pyrolysis zone
  - ↦ Oxidation zone
  - ↦ Reduction zone
- Biomass first undergoes drying and then thermal degradation (or pyrolysis).
- The pyrolysis products (i.e., gas, char, and liquid) **inter-react** among themselves as well as with the gasifying medium (air/steam/oxygen) to form the final gasification products.

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Courtesy: Basu, Biomass gasification, pyrolysis and torrefaction: Practical design and theory, Academic Press, 2013.

The schematic shown here is a down draft gasifier typically involves the four distinct zone. As shown here in the schematic, that is drying zone, pyrolysis zone that is also termed as a thermal decomposition zone, oxidation zone that is also called as a partial combustion or oxidation zone and reduction zone that is mainly the gasification of the entire oxidized product is getting reduced here in the reduction zone to produce the synthesis gas, that is called as a syngas. So, in this case the biomass once enters the gasifier it undergoes drying operation first, where the most of the moisture present in the biomass gets removed. Followed by thermal degradation in the pyrolysis zone where it gets converted into a gaseous tar and char as a product. The pyrolyzed product interact among themselves as well as with the gasifying medium which is entering at this particular location in the gasifier to form final gaseous product. Which is mainly happening in the reduction zone here in the gasifier where the oxidized products are getting reduced in the reduction zone to produce synthesis gas along with the ash as a product.

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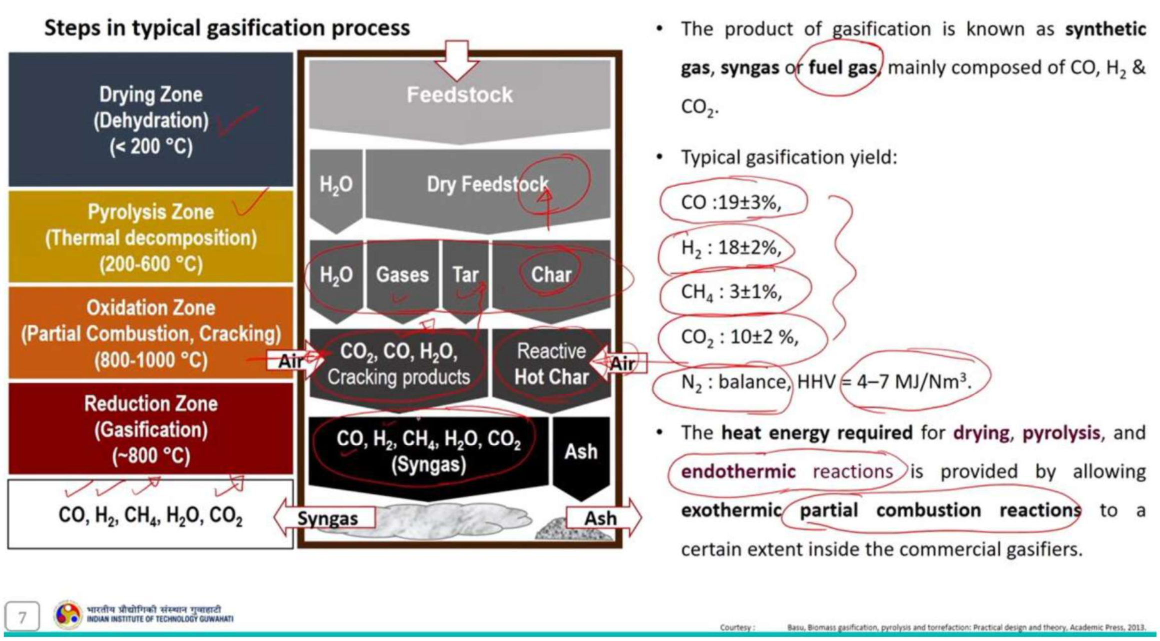

And this product of the gasification is known as a synthetic gas or syngas or sometime it also termed as a fuel gas, which is mainly composed of carbon monoxide, hydrogen and some stresses of methane along with the CO_2. The typical gasification yield CO the percentage is in between 19 plus-minus 3%, hydrogen around this much, methane as I mentioned, the traces of methane can be observed in the gasified product. That is around 3 percent and CO_2 is around 10 percent plus minus 2 and the remaining balance is nitrogen. And the high reading value for this composition of gas is around 4 to 7 mega joule per meter cube. And the heat energy which is required for this drying operation as well as for this pyrolysis operation and several other endothermic reactions which are occurring parallel in the gasifier is provided by allowing the exothermic partial combustion reaction to certain extent, inside the commercial gasifier and that is what I mentioned here.

This is a point where oxidizing medium either air, oxygen or steam is injected inside the gasifier to allow this partial combustion reaction to takes place, so that the thermal energy which is produced during this reaction will transfer to the upper zone here that is pyrolysis zone and the drying zone. As a result, the drying of the incoming material will take place in the continuous manner and after drying the specific temperature, which is maintained here. Which is responsible for the thermal decomposition of this particular dried feedstock which results into the formation of gases tar and char as a product. And these gases, liquid, tar and the char which are produced here which undergoes parallel oxidation and cracking operation here. Because here the gases and the tar undergo cracking and oxidation. Similarly, the reactive hot char also gets oxidized here in the presence of oxidizing medium. And after that is the reduction zone where these products are getting reduced to form carbon monoxide, hydrogen, traces of methane and CO_2 as a product along with solid residue as ash.

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Typical Gasification Reactions (Syngas Production)

SN	Reactions	Heat of Reaction	Reaction Type	
1	$C + CO_2 \rightleftharpoons 2CO$	+172 kJ/mol	Bourdouard	Endothermic
2	$C + H_2O \rightleftharpoons CO + H_2$	+131 kJ/mol	Water-gas or steam	Endothermic
3	$C + 2H_2 \rightleftharpoons CH_4$	– 74.8 kJ/mol	Hydrogasification	Exothermic
4	$C + ½ O_2 \rightarrow CO$	– 111 kJ/mol	Oxidation	Exothermic
5	$C + O_2 \rightarrow CO_2$	– 394 kJ/mol	Oxidation	Exothermic
6	$CO + ½O_2 \rightarrow CO_2$	– 284 kJ/mol	Oxidation	Exothermic
7	$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$	– 803 kJ/mol	Oxidation	Exothermic
8	$H_2 + ½O_2 \rightarrow H_2O$	– 242 kJ/mol	Oxidation	Exothermic
9	$CO + H_2O \rightleftharpoons CO_2 + H_2$	– 41.2 kJ/mol	Water-gas shift	Exothermic
10	$2CO + 2H_2 \rightleftharpoons CH_4 + CO_2$	– 247 kJ/mol	Methanation	Exothermic
11	$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	– 206 kJ/mol	Methanation	Exothermic
12	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	–165 kJ/mol	Methanation	Exothermic
13	$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	+ 247 kJ/mol	Dry Reforming	Endothermic
14	$CH_4 + H_2O \rightleftharpoons CO + 3H_2$	+ 206 kJ/mol	Steam Reforming	Endothermic
15	$CH_4 + ½O_2 \rightleftharpoons CO + 2H_2$	– 35.7 kJ/mol	Steam Reforming	Exothermic

The positive sign (+ Q kJ/kmol) of the reaction equations implies that heat is absorbed in the reaction. A negative sign (-Q kJ/kmol) means that heat is released in the reaction.

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Courtesy: Basu, Biomass gasification, pyrolysis and torrefaction: Practical design and theory, Academic Press, 2013.

And this table here it depicts the typical gasification reaction occurs in the gasifier. So, these first two reaction are basically the Bourdouard reaction and the water gas or steam reaction. Both these reactions are endothermic in nature, because the plus sign here it indicates heat is absorbed in the reaction and the negative sign here indicates the heat is released in the reaction. Followed by that is the hydrogasification and the oxidation reaction and these are mostly the exothermic reaction. Followed by water gas shift reaction and the methanation reaction and all these are exothermic in nature as a result the heat released during this particular reaction is used to balance the heat required for the endothermic reaction in the gasifier. Similarly, the reaction number 13 and the 14 basically are dry reforming and the steam reforming reaction, respectively. And both these reactions are again in the endothermic in nature. And last is the steam reforming reaction that is the exothermic reaction again. So, if you look at the reaction number 2, 13, 14 and 15 along with the reaction number 9 here, so this reaction mainly produces carbon monoxide and hydrogen as a product. Whereas reaction number 9 it produces carbon dioxide and hydrogen as a product. And most of the other reactions are either oxidation reaction or methanation reaction, which produces methane as a product here. And this produced methane is further undergoing this dry reforming and the steam reforming to produce carbon monoxide and hydrogen as a product. And that is the reason some stresses of methane still can be observed in the exhaust gas stream of the gasifier which remains unconverted.

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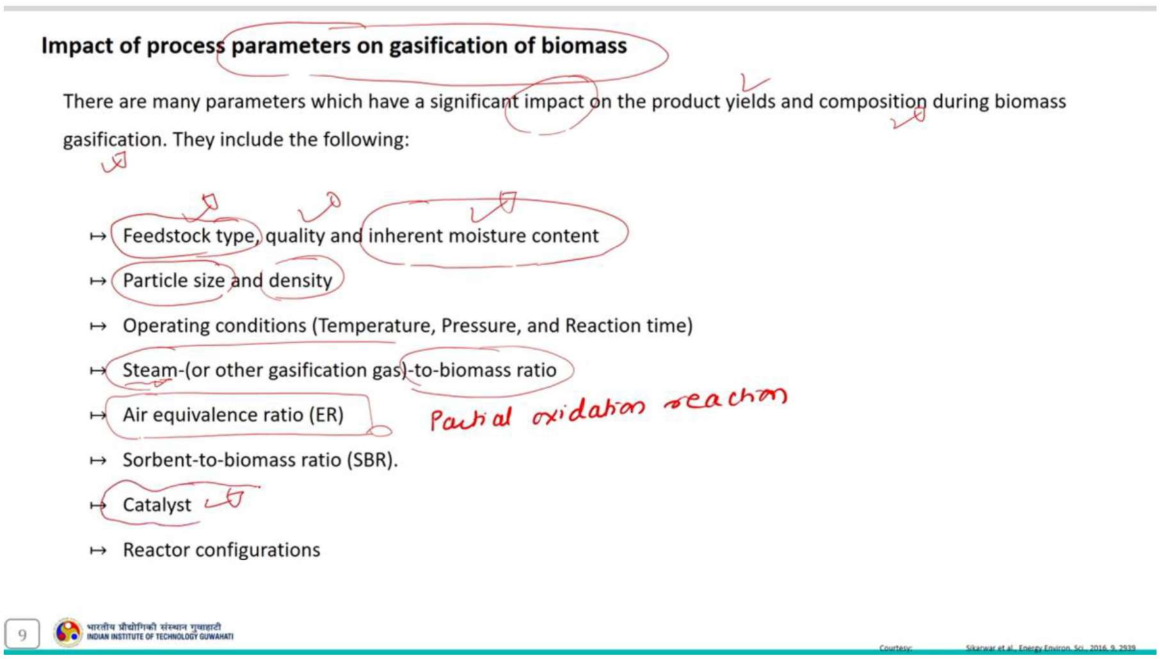

So, some parameters are quite influential in the gasification process, that is mainly of gasification of the biomass. And this particular parameter they have a significant impact on the product yields and composition during the biomass gasification process. And this parameter includes the feedstock type, quality and the inherent moisture content of the feedstock. Because if the feedstock is of high moisture content then most of the energy goes waste in removing the moisture from the feedstock. Which eventually results in reducing the product yield as well as reducing the quality of the product. And that is the reason some pre-treatment operations are essential in such kind of feedstock where the moisture content is sufficiently high or more than the required limit for the gasification process. The particle size and the density of the material is also crucial parameter during the gasification process. Operating conditions, such as temperature, pressure and the reaction time is also one of the important parameters in the gasification process followed by the steam to biomass ratio. If the gasification process is using steam as a medium then steam to gasification ratio need to be maintained properly inside the gasifier. If instead of steam air or the oxygen is being used so accordingly this particular ratio need to be maintained in the gasifier. Gasifier equivalence ratio is a very important parameter, that anyway we would be discussing in this particular lecture, and this need to be maintained to provide partial oxidation reaction in a gasifier. Similarly, sorbent to biomass ratio, the catalyst, if the gasification is carried out in presence of catalyst, then the percentage of catalyst is also important in the gasification process, followed by the reactor configuration.

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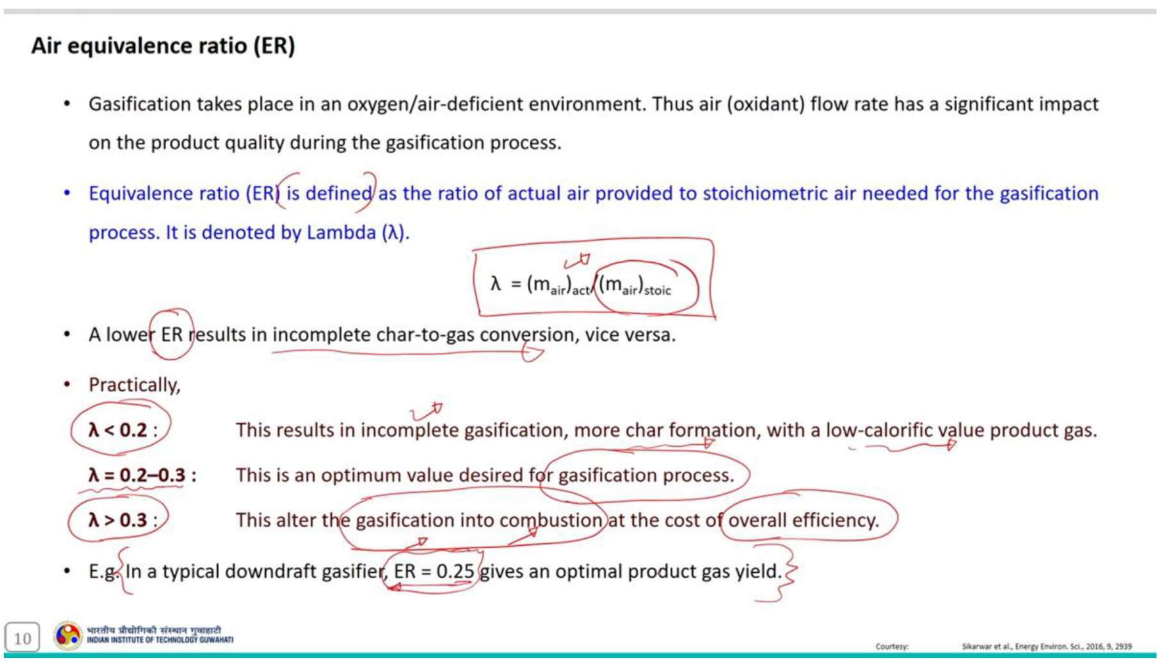

As I mentioned earlier the equivalence ratio is one of the important parameters in the gasification process because the gasification process is carried out in an oxygen or air deficient environment. And thus, air flow rate or the oxygen flow rate has a significant impact on the product quality during the gasification process. And this equivalence ratio here is defined as the ratio of actual air provided to stoichiometric air which is needed for the gasification process. And it is denoted by lambda. And this is the equation normally used for the equivalence ratio calculation. The lower equivalence ratio it results in the incomplete char to gas conversion and even it may happen vice versa also. Practically if lambda is less than 0.2 this results in incomplete gasification and may results in the more char formation with low calorific value product gas. If lambda is maintained between 0.2 to 0.3 this is an optimum value which is desired for the gasification process. And if it goes beyond that, if lambda is supposed greater than 0.3 then this alter the gasification into combustion at the cost of overall efficiency of the gasification process. Because in this case the air it is in the excess amount than required for the partial oxidation process to carry out in the gasification reaction. And this excess air may result into the conversion of most of the volatiles into CO_2 and as a result it may shift from gasification to combustion operation. In a typical downdraft gasifier, equivalence ratio of 0.25 it gives an optimum product gas yield. So, equivalence ratio of specific range needs to be maintained in the gasifier to achieve optimum product gas yield.

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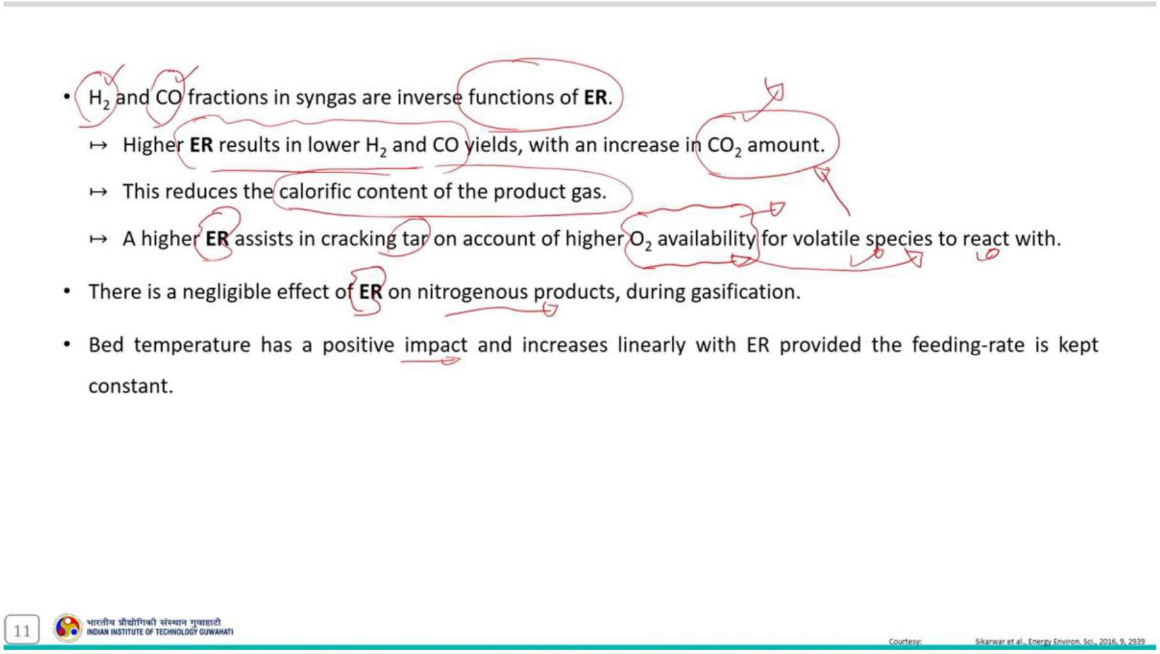

Similarly, this hydrogen and carbon monoxide which are the dominant gases in the product stream of the gasifier. So, this fraction in syngas are inverse function of ER that means equivalence ratio. Suppose if equivalence ratio is higher than it results in lower hydrogen and carbon monoxide yields with an increase in the carbon dioxide amount in the product stream. And this reduces ultimately the calorific value content of the product gas. Because here the percentage of carbon monoxide and hydrogen is less, whereas the percentage of carbon dioxide is relatively high, which eventually results into reducing the calorific value content of the product gas. A high equivalence ratio also assists in cracking tar on account of higher oxygen availability for the volatile species to react with. That means in this case if equivalence ratio is slightly higher then it may also assist in the cracking tar, because of the higher percentage of oxygen available during the gasification process. Apart from that this excess oxygen which is available in the gasification process also results into the conversion of this volatiles into the CO_2. And that is the reason why the CO_2 amount increases at higher ER ratio in the gasifier. There is a negligible effect of equivalence ratio on nitrogenous products during the gasification process. Similarly, the bed temperature has a positive impact and it increases linearly with the equivalence ratio provided the feeding rate is kept constant in the gasifier.

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Comparison of Gasification & Combustion

Criteria	Combustion	Gasification
Mechanism	Combustion breaks the chemical bonds to release the energy	Gasification packs energy into chemical bonds in the form of product gas.
Mechanism	Combustion oxidizes the hydrogen and carbon into water and carbon dioxide, respectively.	Gasification process adds hydrogen to and strips carbon away from the hydrocarbon feedstock to produce gases with a higher H/C ratio.
Gaseous products	Flue gas (CO_2, H_2O)	Fuel gas (CO, H_2, HC)
CO_2	Higher concentration	Lower concentration
SO_x & NO_x	Higher emissions	Lower emissions
Solid waste	Large amounts	Small amounts
Value added products	Not produced	Range of VAPs can be produced

Courtesy : Basu, Biomass gasification, pyrolysis and torrefaction: Practical design and theory, Academic Press, 2013.

This particular table here it depicts the comparison of the gasification and the combustion process as both these are the thermochemical conversion processes. So, as we know the combustion is carried out under the excess supply of oxygen, whereas the gasification is carried out under the partial supply of oxygen and that is also it is termed as a partial oxidation process. So, let us compare these two different thermochemical conversion processes in terms of their mechanism, product gas yield, as well as the other value-added product which can be produced from the exhaust stream of this particular processes. So, first let us discuss about the mechanism here. In case of combustion, it breaks down the chemical bond to release the energy so the chemical bond in the cellulose, hemicellulose and lignin breaks down to release the energy that is in the form of heat and along with that it also produces CO_2 and H_2O as a stable product. Whereas in case of gasification it packs the energy into chemical bonds in the form of product gas stream. And the product of gasification process includes carbon monoxide, hydrogen and hydrocarbon. So, during the gasification process this energy is packed into the chemical bonds of these particular gases that is also called as a fuel gas or the product gas. Another aspect of the combustion process is it oxidize the hydrogen and carbon into water and carbon dioxide as a stable product, as I just mentioned here. However, in case of gasification process it adds hydrogen too but strips carbon away from the hydrocarbon feedstock to produce gases with higher H by C ratio.

And that is the main difference between the combustion and the gasification process. The product obtained from the combustion process is a flue gas with CO_2 and H_2O in the product stream. Whereas gasification process produces fuel gas which also has a calorific value and it includes carbon monoxide, hydrogen and traces of other hydrocarbon gases. CO_2 concentration is higher in the combustion process whereas it is lower in the gasification process. SO_x and NO_x is higher here but lower in the gasification process. Solid waste it can handle large amount of solid waste, because it is a complete combustion process, so it can handle the large amount of solid waste. However, here it handles smaller amount of the solid waste, because we need to maintain the biomass to oxidizing medium ratio. So, based on that it can handle respective amount of the solid during the gasification process. Value added products are not produced during this particular combustion process, whereas the product which are obtained from the gasification process can further be processed to produce range of value-added products.

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Comparing conversion of different elements in Gasification & Combustion

Gasification	CO, Hydrocarbons	H_2	N_2	H_2S
	↑	↑	↑	↑
Elements	**C**	**H**	**N**	**S**
	↓	↓	↓	↓
Combustion	CO_2	H_2O	NO_x	SO_x

Courtesy : Basu, Biomass gasification, pyrolysis and torrefaction: Practical design and theory, Academic Press, 2013.

And this table here it depicts the comparison of conversion of the different elements in the gasification and the combustion operation. So, see here that is the carbon is converted into carbon monoxide and other hydrocarbon gases in the gasification process. Whereas in the combustion it is completely composite to produce carbon dioxide. H is getting converted to hydrogen here, whereas in case of combustion it produces H2O. Nitrogen it remains unaffected in the gasification process and it comes out as it is along with the exhaust gas stream. Whereas in case of combustion it gets converted into the NOx. Similarly, S that means the sulfur here converts into SOx whereas in case of gasification it forms hydrogen sulfide.

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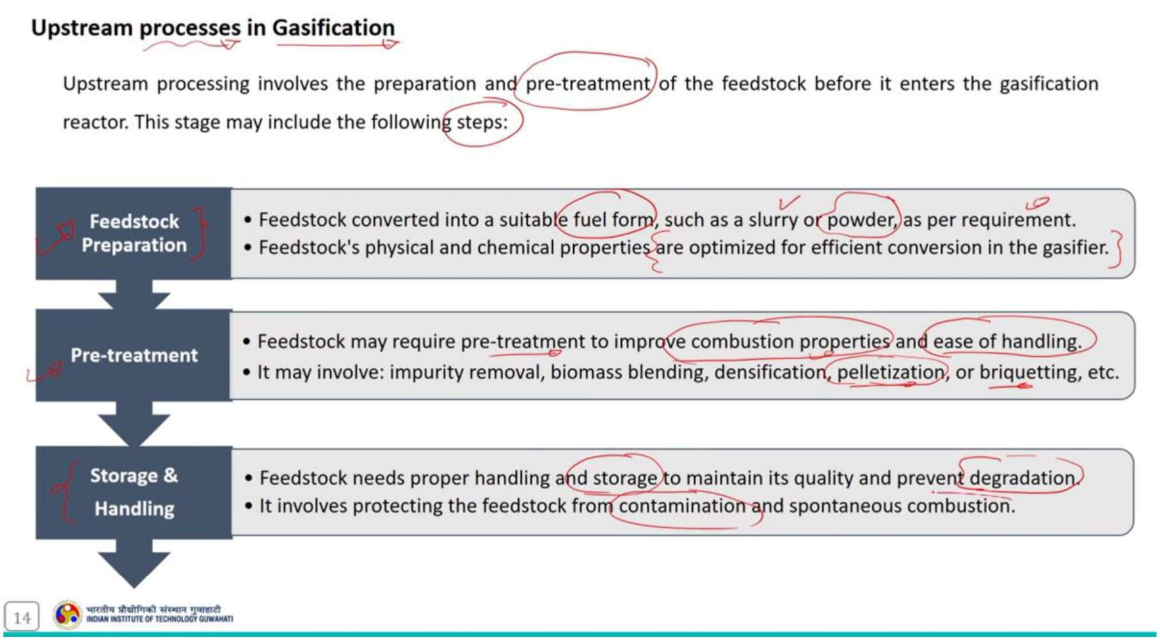

So, now let us discuss about the upstream processes which are essential in the gasification process. And this upstream process here, it involves the preparation and the pretreatment of the feedstock before it enters the gasification reactor and this may include the following steps. The feedstock preparation. If the source material is not available in the proper form then the feedstock needs to be converted into a suitable form such as either slurry or we need to convert it into a powder material as per the process requirement. Its physical and chemical properties need to be optimized for efficient conversion in the gasifier. So, small kind of a treatment or the preparation may require from the feedstock side. Apart from that the second step is a pre-treatment. Certain feedstock it may require pre-treatment to improve the combustion properties and even the ease of handling. And it may include the impurity removal, biomass blending, densification, pelletization and the briquetting. So, by which we can convert the powder material also into a pellet form as well as the briquet form and which eventually helps in the combustion process. Because as we discussed earlier, gasification is also partial oxidation process or the partial combustion process. So, if the feedstock is available in the proper form then it also helps in partially combusting the material, so that it can provide the necessary energy which is required during the gasification process. Storage and handling. The prepared feedstock needs to be handled properly and stored to maintain its quality and prevent from the degradation. And it also involves the protection of the feedstock from contamination and the spontaneous combustion.

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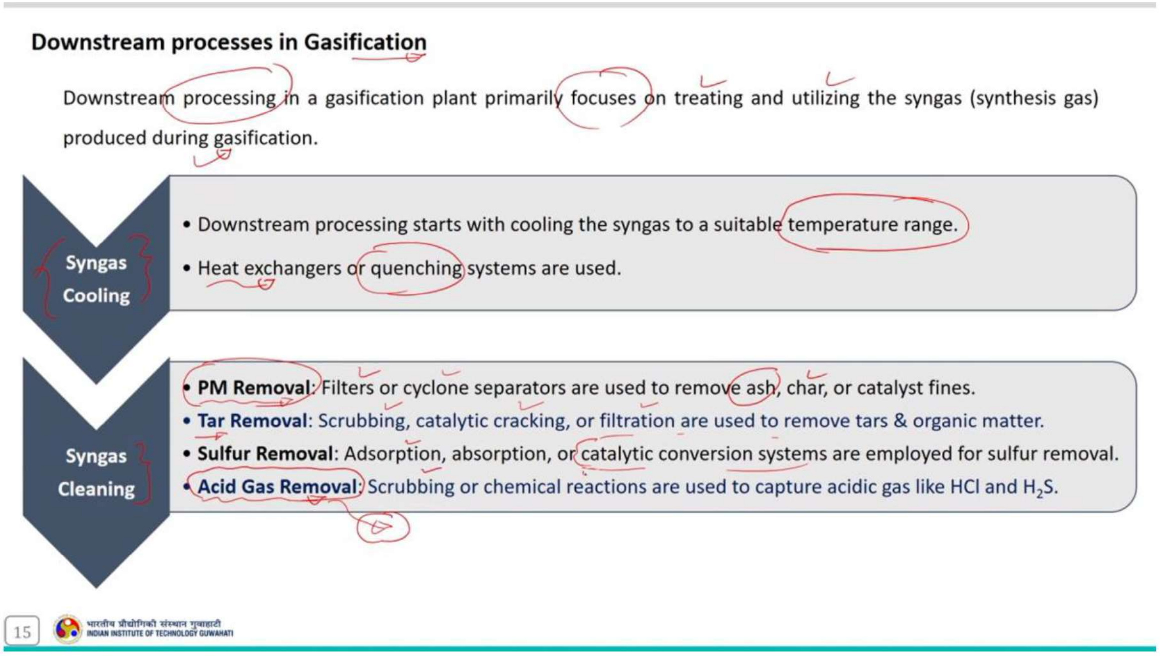

Similarly, the downstream processes in the gasification process is also essential. Because the downstream processing in gasification plant primarily focuses on treating and utilizing the syngas produced during the gasification process for further use. So, first important operation in the downstream processing is the cooling of the syngas to suitable temperature range and for which heat exchanger or quenching systems are used to reduce the temperature of the syngas and bring down to a suitable temperature range. Similarly, the cleaning of the syngas because syngas may contain certain amount of particulate matter, tar, even Sulphur and some acid gas as well. So, this need to be clean before being utilized for the further conversion purpose. So, particulate matter removal filters or cyclone separators can be used to remove the ash, char and the catalyst fines from the syngas. Similarly scrubbing, catalytic cracking or the filtration are used to remove tar and other organic matter from the syngas. For the removal of the sulphur, adsorption, absorption or the catalytic conversion systems can be used so that we can remove effectively the sulphur from the syngas. Acid gas removal is also essential, so that the produced syngas can be used effectively for further applications. And if some application involves the catalytic reaction, then the presence of the traces of gases may impact the performance of the catalyst even. So, this can be removed using the scrubbing and the chemical reaction to capture the acidic gases like HCl and H_2S.

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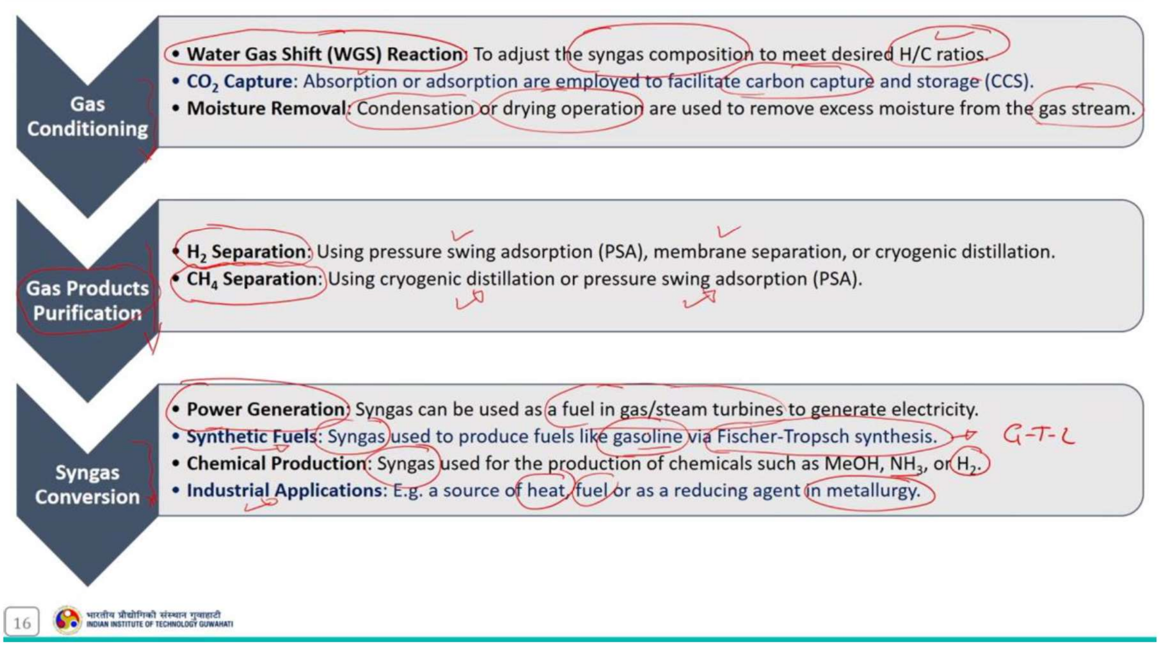

Similarly, the conditioning of the gas is also important. In this case it helps to adjust the syngas composition to meet the desired H by C ratio. And that can be done using the water gas shift reaction so that we can maintain the desired H by C ratio which is required in the syngas composition. The CO_2 capture, as we discussed earlier, these are unit like absorption or adsorption, can be employed to facilitate the carbon capture as well as the storage. Moisture removal, this can be done using the condensation or the drying operation, to remove the excess moisture from the flue gas stream. Followed by the gas conditioning, the purification of the gas can also be done using a proper operation that is in the form of pressure swing adsorption, membrane separation or cryogenic distillation to separate out the hydrogen gas from rest of the gaseous mixture. Or even methane can be separated out from the rest of the gaseous mixture using cryogenic distillation and pressure swing adsorption technique. And produced purified syngas can be used for the power generation, as mentioned here, because syngas can be used as a fuel in the gas and the steam turbine to generate the electricity. Apart from that the syngas can also be used to produce the synthetic fuel like gasoline via Fischer-Tropsch synthesis process. And this is one of the very widely known technique to convert gas into the liquid that is called as a GTL technique- gas to liquid technique. By Fischer-Tropsch synthesis process we can convert the syngas to liquid product like gasoline diesel or jet fuel. Similarly, the syngas can also be used for the production of the chemicals such as methanol, ammonia or hydrogen as we just discussed before. Either we can separate out the hydrogen during this gas purification technique or it can be syngas can further be converted into the hydrogen using a suitable chemical reaction. Industrial application, it can be used as a source of heat, fuel or as a reducing agent. in the metallurgical industries. So, the syngas has wide range of applications. It can directly be used as a fuel in gas or steam turbine to generate electricity or it can be processed further to produce synthetic fuel or also it can be used to produce value added chemicals. This covers our discussion on the conventional gasification processes.

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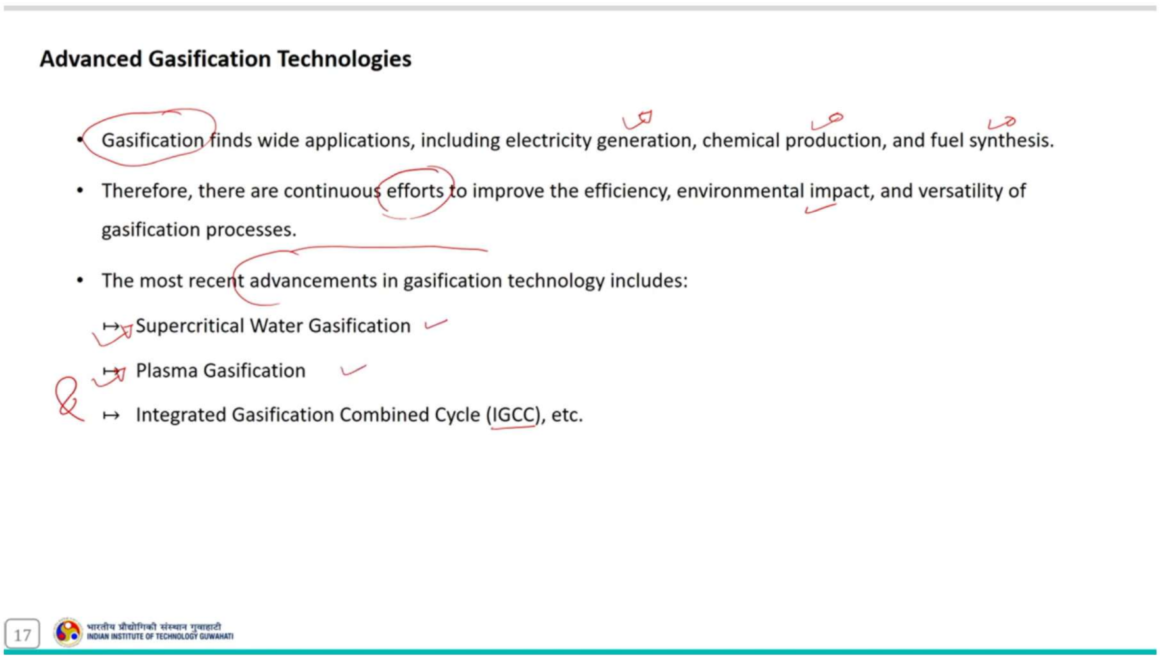

Apart from the conventional gasification processes, advanced gasification technologies are also available for the conversion of solid feedstock into useful and convenient product gas that can be burnt to release energy or can be converted into useful product. And this advanced gasification technology includes sub and supercritical water gasification, plasma gasification and integrated gasification combined cycle which is also called as IGCC. So, let us discuss about this advanced gasification technology one by one. As we discussed earlier, the gasification it finds wide applications including in the field of electricity generation, chemical production and fuel synthesis. So, because of that there are continuous efforts to improve the efficiency, environmental impact and versatility of gasification processes. The most recent advancement in gasification technology, it includes supercritical water gasification. And sometime this operation is also carried out under the subcritical water range, plasma gasification and integrated gasification combined cycle that is also termed as IGCC. So, in this module our focus is on supercritical water gasification and plasma gasification techniques.

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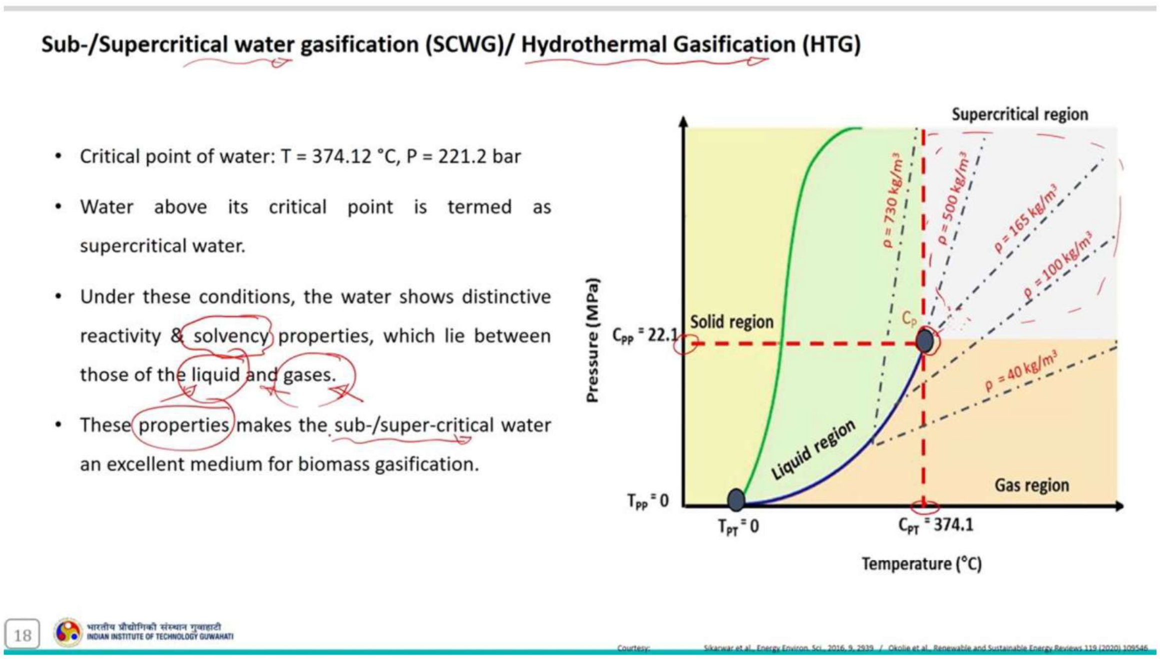

Sub and supercritical water gasification are also termed as hydrothermal gasification technique. And if you look at this particular point here on the graph, it is a critical point of water, and this indicate here the critical temperature, and this is a critical pressure. And above its critical point the water is termed as a supercritical water. So, this particular zone here which indicates the supercritical water region, and under this condition the water shows distinctive reactivity and the solvency properties and which lie between those of the liquid and gases. So, this solvency property here is of such nature that it lies between that of the liquid and gases. So, it can also impart the some of the properties of liquid and it can also impart some of the properties of the gases. And these properties make the sub and the supercritical water an excellent medium for the biomass gasification.

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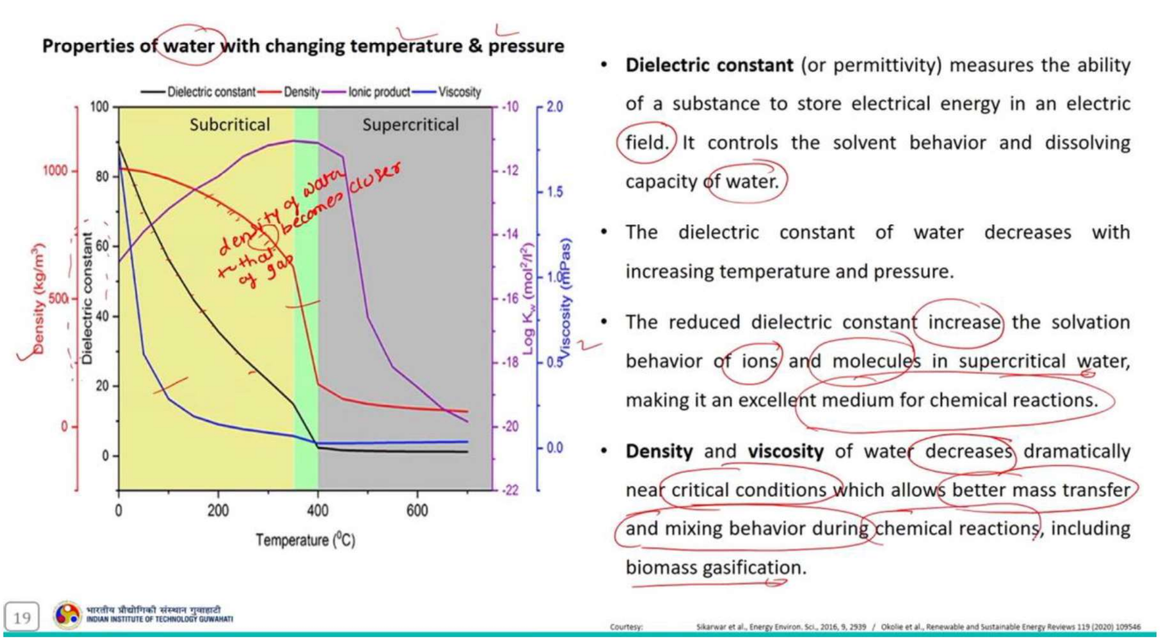

So, if you look at this particular graph here, it shows the properties of water with changing temperature and the pressure. The dielectric constant which measures the ability of a substance to store the electrical energy in an electric field it controls the solvent behavior and dissolving capacity of the water. The dielectric constant of the water it decreases this black line it shows the dielectric constant of the water and it decreases with increasing temperature and the pressure. And the reduced dielectric constant increases the solvation behavior of ions and molecules in the supercritical water thus making it an excellent medium for the thermochemical reaction and that is also for the biomass gasification. Now, if you talk about the density and the viscosity, the density as well as the viscosity decreases dramatically near the critical condition. And which allows better mass transfer and the mixing behavior during the chemical reaction including the biomass gasification. Because in case of density here if you see this graph of the density, the density of this supercritical water it varies non-linearly. This behavior is non-linear in nature with temperature and the pressure and at supercritical condition the density of water becomes closer to that of gas. Density of water becomes closer to that of gas which still allows for substantial solvation capacity. And this unique density behavior it plays a crucial role in the solubility and the transport of reactant making supercritical water an excellent candidate for other chemical reaction as well as for the biomass gasification.

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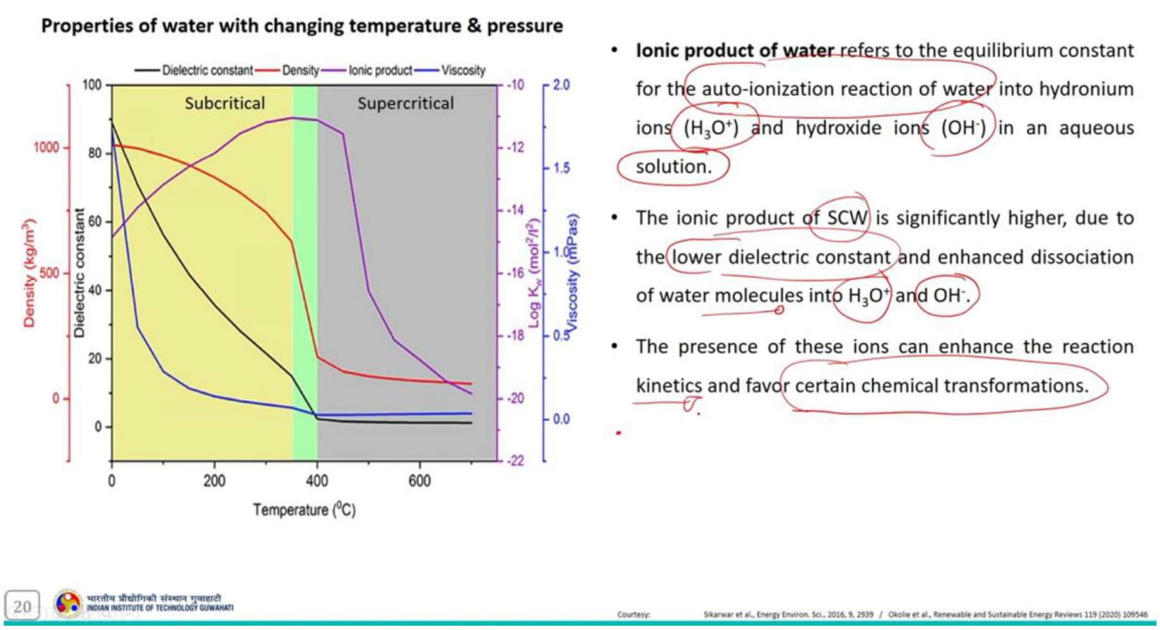

The ionic product of the water here, it refers to the equilibrium constant for the atom ionization reaction of water into the hydronium ion and the hydroxide ion in the aqueous solution. The ionic product of this supercritical water is significantly higher and that is due to the lower dielectric constant and the enhanced dissociation of the water molecule into hydronium ion and the hydroxide ions. And presence of this ions can enhance the reaction kinetics and also favors certain chemical transformation. And because of that this sub and the supercritical water gasification technique is widely being used to convert the solid as well as the wet feedstock material into gaseous product and even with high quality of the product.

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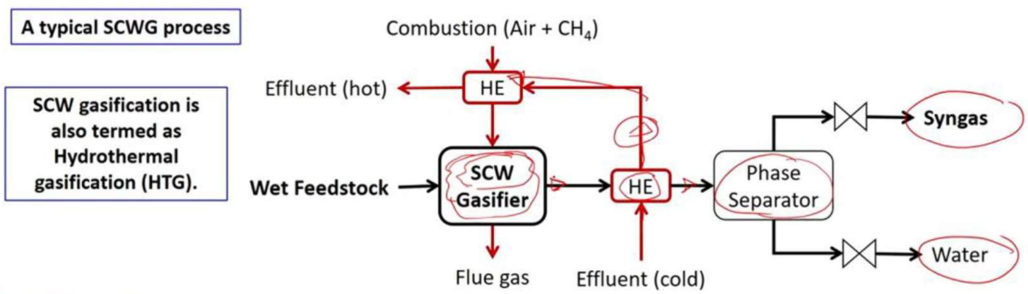
- SCWG can been applied to **wet biomass feedstock** without the need for pre-drying, including diverse feeds such as lignocellulosic biomass, algae, agro-/food-wastes, sewage sludge, and industrial effluents.
- SCWG was also found suitable for **fossil fuels feedstock** including coal, bitumen, petroleum coke, asphaltene, diesel oil, and organic solvents.
- **Product gas** from SCWG mainly comprises H_2, CO_2, CH_4 and CO.
- Tar and coke formation are controlled by rapid dissolution of product gas components in SCW.



So, as I mentioned the supercritical water gasification it can be applied to the wet biomass feedstock as well. Because in that case then no need of any pre-processing of the feedstock is required. Because the wet biomass can directly be used as a feedstock material in the supercritical water gasification process because here the medium is used as a water. So, the moisture contained in the feedstock itself is sufficient enough to provide the medium which is required for the supercritical water gasification reaction. However, some additional amount of water still required to reach to the critical temperature of water in the reaction condition. It also involves diverse feed material such as lignocellulosic biomass, algae, agro and the food waste. Because it also contains higher amount of the moisture in its composition. Sewage sludge also has significant amount of the moisture and the industrial effluents. So, such wet biomass-based feedstock can be easily gasified using the supercritical water gasification system. And it also found suitable for fossil fuel feedstock including the coal, bitumen, petroleum coke, asphaltene, diesel oil and the organic solvent. The product gas of the supercritical water gasification system mainly comprises of hydrogen, carbon dioxide, methane and the carbon monoxide. However, the tar and the coke formation are controlled by rapid dissolution of the product gas component in the supercritical water and that is what is the advantage of this process here. That tar and the coke formation can be controlled using this particular technique because of the rapid dissolution of the produce gas in the supercritical water medium. And this scheme here it represents the supercritical water gasification process. So, here the wet feedstock undergoes the supercritical water gasification operation and the hot product gas produced at the end of the process is passed through this heat exchange unit where it is allowed to exchange the heat with the incoming effluent coal stream. So that the hot stream which comes out from this unit is passed on to the second heat exchanger unit where it can reach to a required temperature of the supercritical water gasification. And the product which is coming out from this exchanger unit is passed on to phase separator unit here to separate out the product gas from water. And this is how the supercritical water gasification system operate to produce good quality product.

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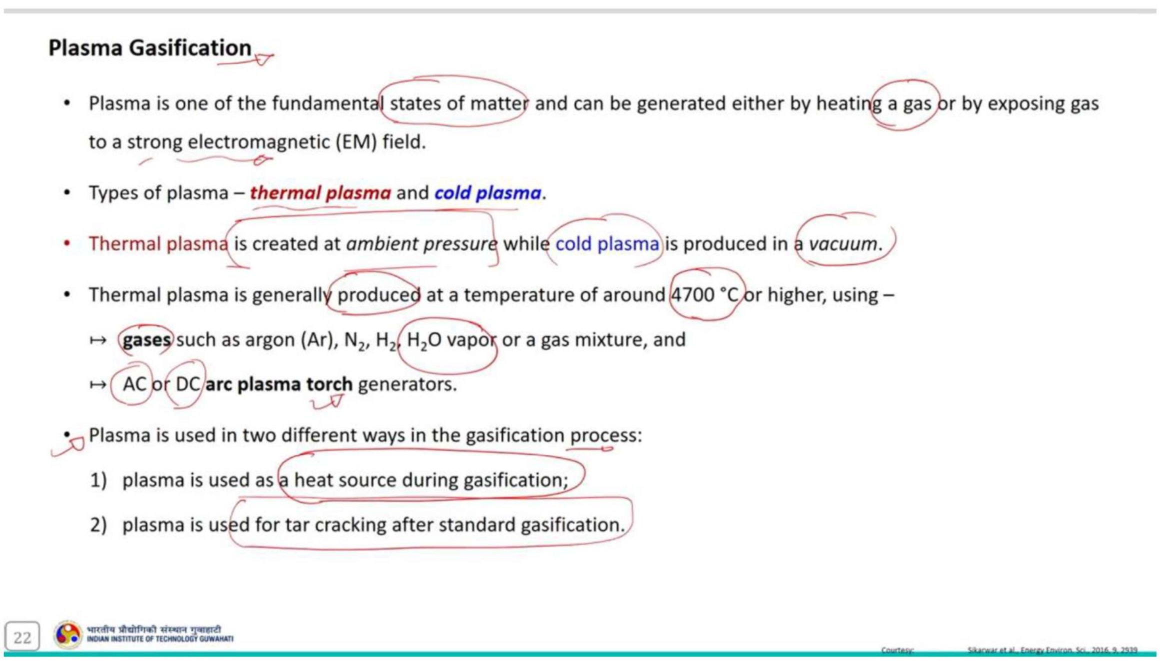

So, another important advanced technology is the plasma gasification. It is one of the fundamental states of matter and can be generated either by heating a gas or by exposing gas to a strong electromagnetic field. The types of plasma it includes the thermal plasma and the cold plasma. The thermal plasma is created at an ambient pressure but while cold plasma is produced under vacuum, and this is the difference between the cold plasma and the thermal plasma. And this thermal plasma is generally produced at temperature of around 4700 degrees Celsius or even higher using gases such as argon, nitrogen, hydrogen, water vapor or a gas mixture or it can be produced using AC or DC arc plasma torch generators. This plasma is used in two different ways in the gasification process. First it is used as a heat source during the gasification operation or even it is used for tar cracking after the standard gasification process.

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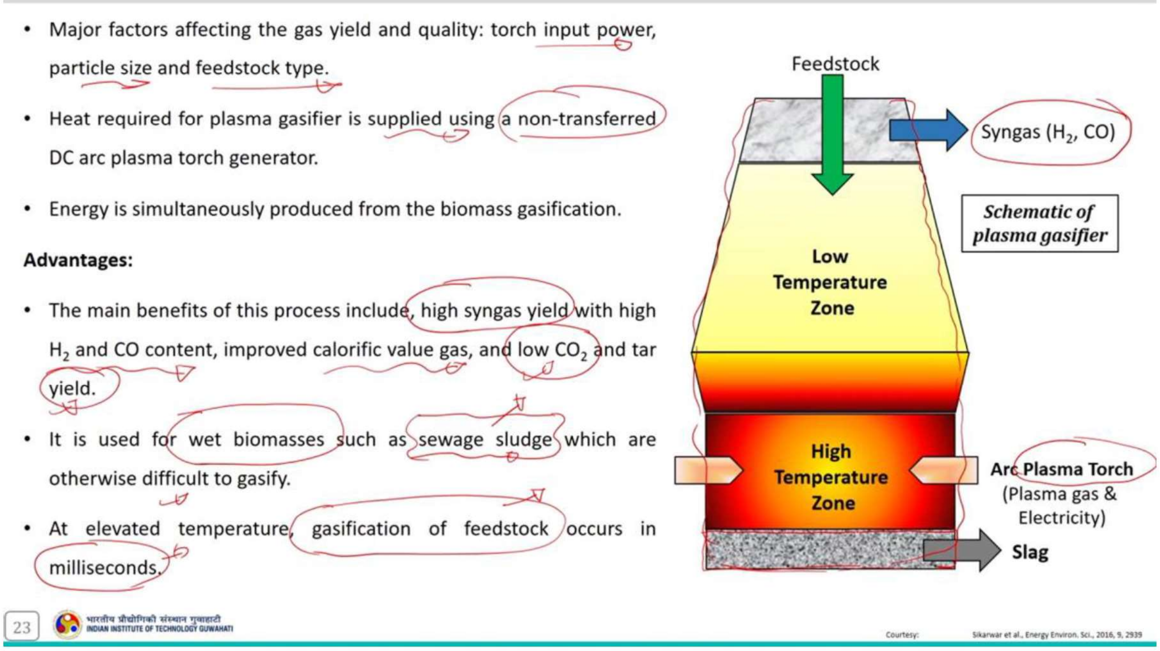

So, this schematic here it represents the plasma gasification system. So, the major factor which affect the gas yield and quality of the gas during the plasma gasification process are torch input power, particle size and the feedstock type. And the heat which is required for the plasma gasification is supplied using a non-transferred DC arc plasma torch generator here. And energy is simultaneously produced from the biomass gasification system here because as we discussed earlier the gasification is a partial oxidation process. So, the amount of energy released during this combustion and the oxidation process is simultaneously used during this gasification operation. And the advantage of this plasma gasification process, is it gives high syngas yield with high hydrogen and CO content, improved calorific value gas and low CO_2 and the tar yield. This is one of the important benefits of the plasma gasification process where it gives low CO_2 and the tar yield. It is also used for the wet biomass material such as sewage sludge which are otherwise difficult to gasify. Because of the higher moisture content in the sewage sludge, it is difficult to gasify such feedstock to produce good quality gas. However, it can be gasified easily using the plasma gasification system. At elevated temperature the gasification of the feedstock occurs in the milliseconds. So, this is one of the major advantages of this plasma gasification process, that the gasification of the feedstock can be carried out in milliseconds. And this particular part in the plasma gasification system represents the slag which is produced during the gasification process.

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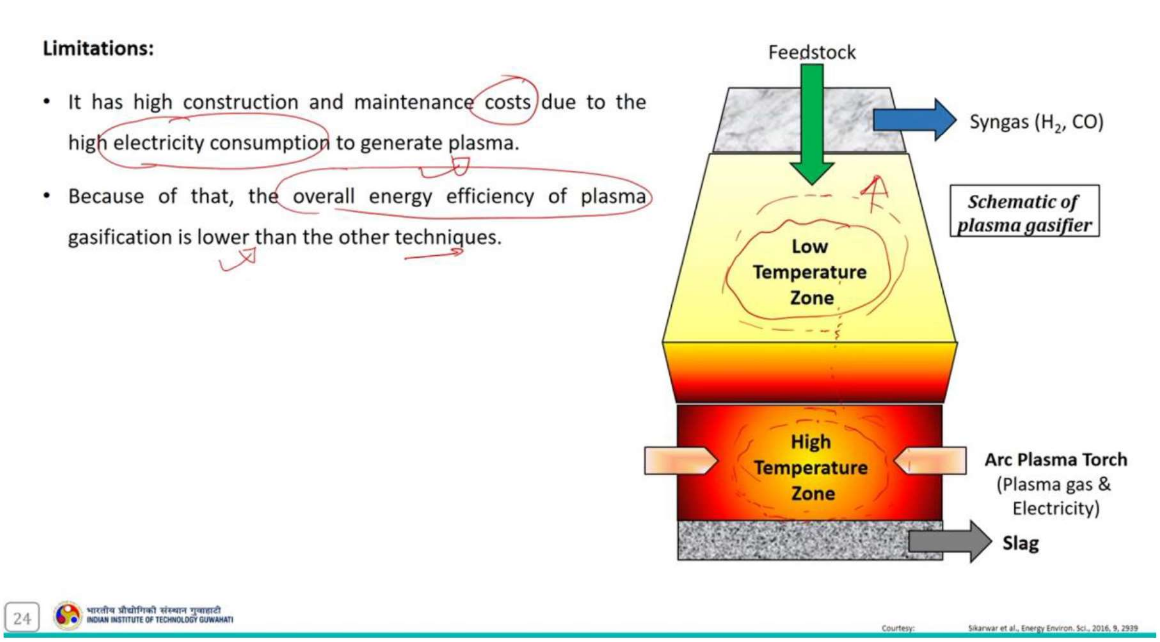

However, this plasma gasification process also has certain limitations. because it has high construction and the maintenance cost and that is mainly due to the high electricity consumption to generate the plasma. And because of that the overall energy efficiency of the plasma gasification is lower than the other techniques. So, in plasma gasification system as well this upper portion represent the low temperature zone and this bottom part here it represents the high temperature zone. Here basically the arc plasma torch generation takes place. As a result, the temperature is sufficiently high in this particular zone. And the heat released during this operation here is transferred in the upward direction to the top of the plasma gasification system. So as a result, here the temperature is relatively low than that of the temperature which is available here in the bottom portion. And this particular low temperature zone here is also essentially useful to remove the excess moisture which is present in the incoming feedstock material.

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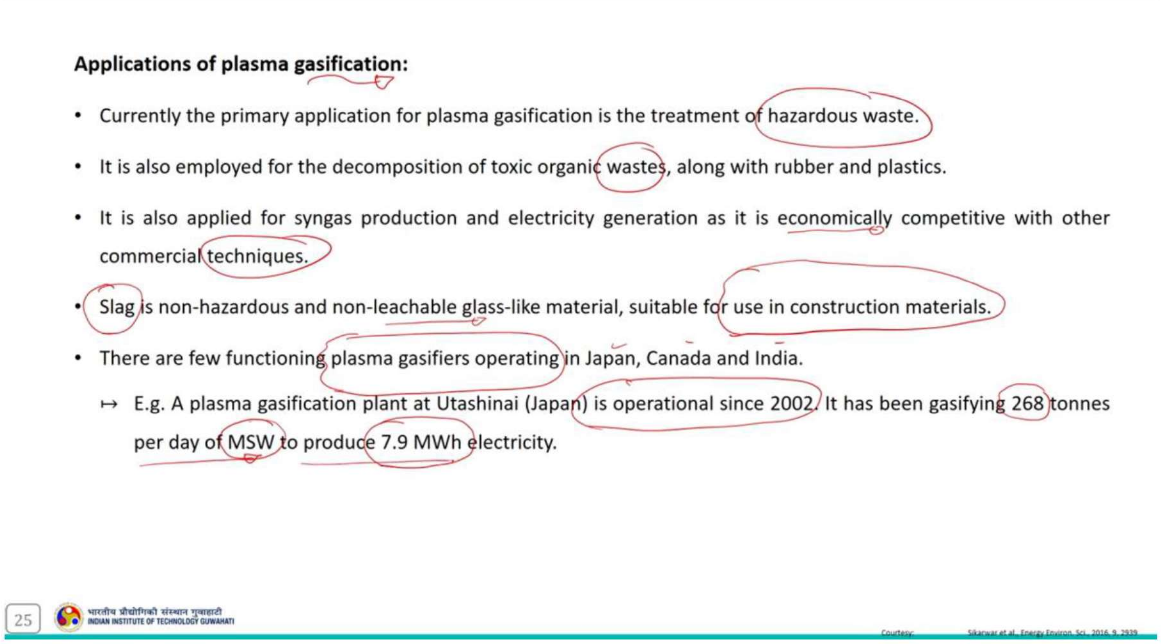

Application of the plasma gasification system- current primary application of this plasma gasification is in the treatment of the hazardous waste. It is also employed for the decomposition of the toxic organic waste along with the rubber and the plastic. And also, it is applied for the syngas production and electricity generation, as it is economically competitive with the other commercial techniques. The slag which is produced during this plasma gasification is a non-hazardous and non-leachable glass like material. And it can find its application or use in a construction industry. And there are few functioning plants which are using the plasma gasification technique and also in operation in Japan, Canada and India. One such plasma gasification plant at Japan is operational since 2002 and it has been gasifying around 268 tons of municipal solid waste per day to produce 7.9 MWh of electricity. So, this kind of plants are operational in few places for the management of waste that is in the form of hazardous waste or toxic organic waste or even the municipal solid waste is also getting converted to produce good amount of the electricity using this technique.

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Comparison of conventional gasification with advanced gasification processes

Parameter	Conventional gasification	SCW gasification	Plasma gasification
Feedstock compatibility	Dry feedstock including biomass, coal, coke, MSW, etc.	Wet & high moisture feedstock including sludge, algae, biomass, organic waste, etc.	Dry or Wet feedstock including biomass, MSW, industrial & hazardous waste, etc.
Operating conditions (T, P)	700–1500 °C, 10–40 bar	200–600 °C, 100–250 bar	~5000 °C, atmospheric P
Gasification time	Minutes to several hours	10 s – 120 min	Milliseconds
Source of heat	Partial oxidation of feedstock	External heat source (biomass or steam)	Intensely hot plasma arc (5000 °C) generated using electricity

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This table here it depicts the comparison of the conventional gasification with that of the advanced gasification techniques. So, in terms of feedstock compatibility the conventional gasification prefers dry feedstock, including the biomass coal, coke and MSW. While the supercritical water gasification technique can handle wet and high moisture feedstock including sludge, algae, biomass, organic waste, etc. Similarly, in case of plasma gasification dry or wet feedstock including the biomass, municipal solid waste, industrial and the hazardous waste are compatible in plasma gasification system. Operating condition here the temperature in case of conventional gasification it varies between 700-1500 °C and pressure is around 10-40 bar. Whereas in case of supercritical water gasification the operating conditions are like this. And in case of plasma gasification the temperature is way high that is around close to 5000 °C. However, the entire operation takes place at atmospheric pressure. Gasification time minutes to several hours whereas in case of supercritical water gasification it varies between say 10 second to maximum up to 120 minutes. While in case of plasma gasification the entire operation takes only milliseconds. Source of heat the partial oxidation of the feedstock provides the thermal energy which is required for the gasification in the conventional gasification system. However, in case of supercritical water gasification the external heat source is required. Either the heat produced using combustion of biomass or the steam. In this case intensely hot plasma arc generated using the electricity is used as a heat source where the temperature reaches up to even 5000 degree Celsius. And the heat generated from such hot plasma arc is used for the gasification operation in the plasma gasification process.

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Parameter	Conventional gasification	SCW gasification	Plasma gasification
Syngas composition	CO, H_2, CO_2, CH_4, and other trace gases	Relatively high H_2O vapors and less CH_4.	Higher H_2 content and lower impurities.
Process efficiency	• High process efficiency; • High energy input for Pre-drying of biomass	• Higher conversion; • Nutrient recovery in biochar	Complete destruction of feedstock into cleaner syngas and inert slag.
Energy efficiency	~ 60–80%	Up to 80%	~ 50–60%
Operating & Maintenance cost	Low	Medium	High
Environmental Impact	• Produce more tar and PM; • Produce GHG emissions; • Require additional gas cleaning step	• Lower emissions; • Nutrient recovery in byproducts	• Hazardous waste mgt; • Minimized emissions; • Metal recovery

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So, composition of the syngas using conventional gasification process is shown here. However, in case of supercritical water gasification, relatively high amount of H_2O vapors is observed along with less methane contained in its composition. However, in case of plasma gasification, higher hydrogen content and lower impurities are observed in the syngas. Process efficiency - high process efficiency observed in a conventional gasification process. High energy input for pre-drying of biomass. Here also the energy conversion is relatively high, the nutrient recovery in biochar. Complete destruction of feedstock into cleaner syngas and the inert slag. So, the slag produced in plasma gasification is inert in nature and hence as just discussed few slides back it can find its application in the construction material. Energy efficiency here it is around 60 to 80 percent, however, in case of supercritical water gasification it is up to 80 percent and in case of plasma gasification, it is slightly low that is around 50-60%. Because most of the energy goes in generating a high temperature which is required for the plasma gasification process that is close to around 5000 degrees Celsius. Operating and the maintenance cost it is low here this is medium in case of supercritical water gasification technique. However, we already discussed this particular point, the operating and the maintenance cost is relatively high in case of plasma gasification technique. Environmental impact - it produces tar and the particulate matter in the conventional gasification process also produces greenhouse gas emissions and require additional gas cleaning setup. However, in case of supercritical water gasification lower emissions, the nutrient recovery in byproduct is also applicable here. Plasma gasification it helps in the hazardous waste management as we discussed here it can also use to decompose the hazardous waste as well as the toxic solid waste. It also minimizes the emission and the material recovery.

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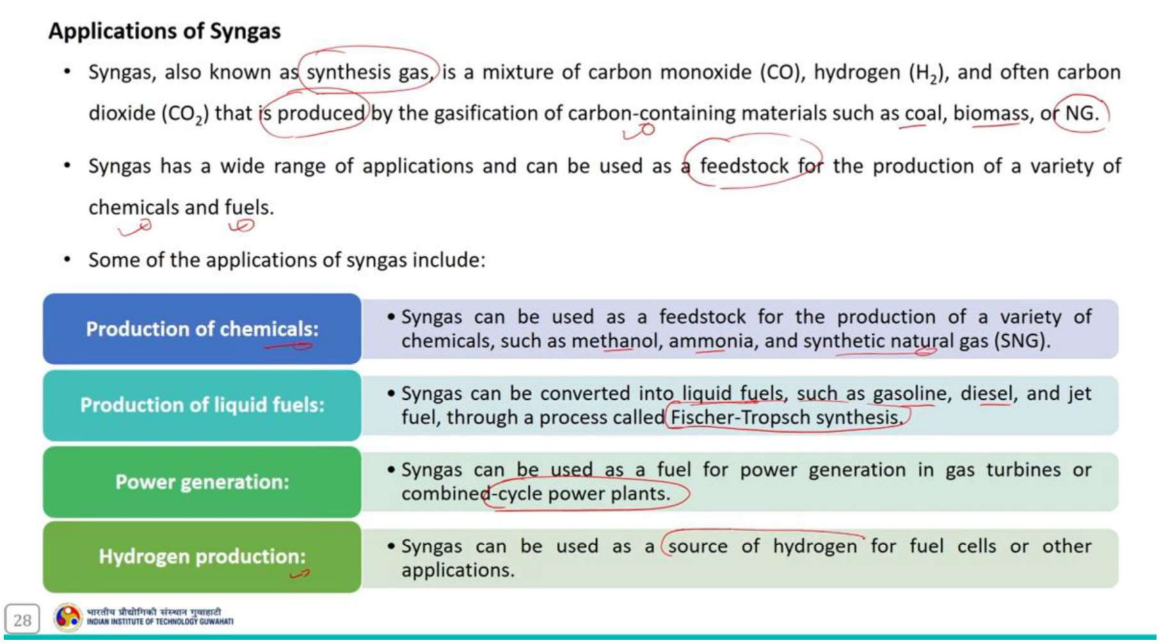

The syngas produced from the gasification process finds wide application in the field of fuel as well as in the production of value-added chemicals. For example, here if you see syngas is also known as a synthesis gas and it is a mixture of carbon monoxide, hydrogen and often carbon dioxide and that is produced by gasification of the carbon containing material such as coal, biomass or natural gas even. In this syngas it has a wide range of application as I just mentioned it can be used as feedstock for production of variety of chemicals and fuels. And some application of this syngas includes in the field of production of the chemicals. Syngas can be used as a feedstock for the production of the variety of the chemicals including methanol, ammonia, synthetic natural gas. Also, it can be used for the production of the liquid fuel. Because syngas can be converted into the liquid fuel such as gasoline, diesel and jet fuel through process called Fischer-Tropsch synthesis. And these points we already discussed about the conversion of syngas into the liquid product. Also, it finds application in the power generation because syngas can be used as a fuel for power generation in the gas turbines or combine cycle power plants. Syngas can be used as a source of hydrogen for fuel-cells or other application.

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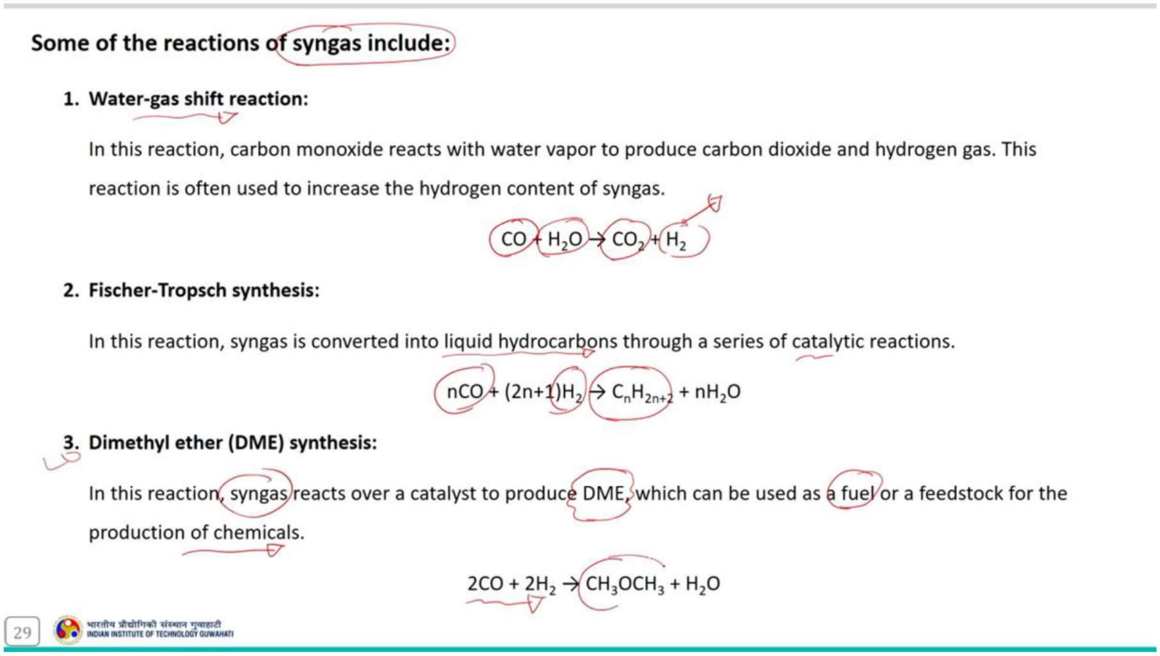

And some of the important reactions of the syngas are shown here that is water gas shift reaction. In this reaction the carbon monoxide and the water vapor react to produce carbon dioxide and hydrogen gas. And this reaction is often used to increase the hydrogen content of syngas. The Fischer-Tropsch synthesis process so in this reaction syngas majorly the carbon monoxide and the hydrogen converted into the liquid hydrocarbon through a series of catalytic reaction. And that is what is the importance of the Fischer-Tropsch synthesis process, by which the syngas can be converted into liquid hydrocarbon product that is also the range of liquid hydrocarbon product. The dimethyl ether synthesis this is also one of the important reactions which can be carried out using the syngas. So, in this reaction the syngas reacts over a catalyst to produce dimethyl ether that is also commonly termed as DME which can be used as a fuel/feedstock for the production of the chemicals. So, this represents the reaction of syngas using a suitable catalyst to produce DME.

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4. Hydroformylation reaction:

In this reaction, syngas reacts with an olefin to produce an aldehyde. This reaction is used in the production of a variety of chemicals, including plasticizers and detergents.

$$CO + H_2 + CH_2{=}CH_2 \rightarrow CH_3CH_2CHO$$

5. Oxidative coupling reaction:

In this reaction, syngas is converted into higher hydrocarbons through a series of catalytic reactions. This reaction is used in the production of a variety of chemicals and fuels.

$$2CO + 2H_2 \rightarrow C_2H_4 + H_2O$$

The reactions of syngas are highly versatile and can be used to produce a wide range of chemicals and fuels. The choice of reaction depends on the specific application and the desired product.

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Apart from that the hydroformylation reaction, in this case the syngas reacts with an olefin to produce the aldehyde and this reaction is also used in the production of a variety of chemicals including the plasticizer and the detergents. And the oxidative coupling reaction, in this case the syngas is converted into the hydrocarbon through a series of reaction and this reaction is used in the production of variety of the chemicals and as well as the fuel. The reaction of this syngas is versatile and can be used to produce wide range of the chemicals and the fuels and the choice of the reaction it mainly depends on the specific application. And the desired product which need to be produced using syngas conversion reaction.

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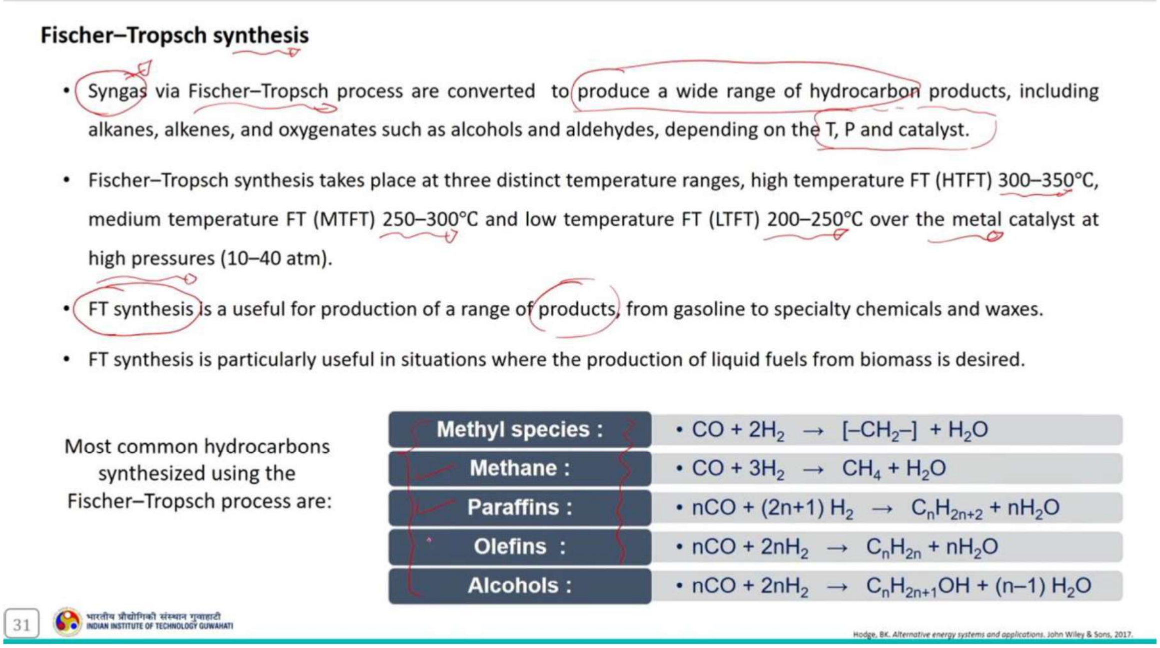

Fischer-Tropsch synthesis is a very widely used reaction for the conversion of syngas to produce wide range of hydrocarbon product including the alkanes, alkenes, oxygenates such as alcohol and the aldehydes. And the conversion as well as the production of this different hydrocarbon here it depends on certain parameter that is temperature, pressure and the catalyst used during this conversion processes. This FT synthesis process it takes place at three distinct temperature ranges that is high temperature range which varies between 300 to 350-degree Celsius, medium temperature range it varies between 250 to 300 degree Celsius and the low temperature range it is between 200 to 250 degree Celsius. And based on this temperature range the choice of the product can be produced by converting syngas with the help of FT synthesis process. over the metal catalyst at high pressure that is between 10-40 atmospheric pressure. This FT synthesis process is useful for the production of range of products from gasoline to specialty chemicals and waxes. And this particular synthesis process is useful in the situation where the production of the liquid fuel from the biomass is desired. And some most common hydrocarbons synthesized using FT process are shown here in this particular slide that is synthesis of methane, paraffins, olefins and alcohols.

This covers our discussion on the different thermochemical conversion processes. So, the next lecture that is third lecture of the module 4 we will practice few examples on heat and mass balance in the pyrolysis process, heat and mass balance in the gasification process, followed by that we will try to solve one example on equivalence ratio. As well as we will try to solve one example on FT synthesis process with the help of one-specific reaction, we will try to find out the product, which can be obtained from the FT process.

Thank you.