

## Fuels, Refractory and Furnaces

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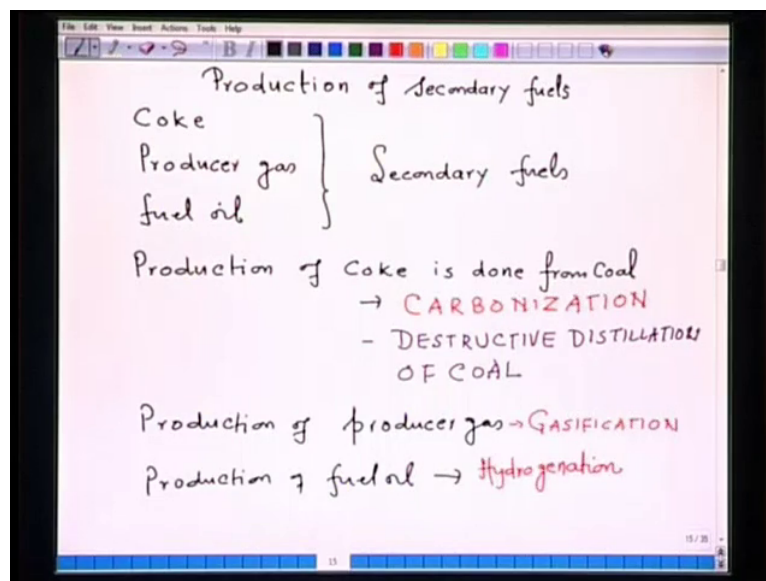
Indian Institute of Technology, Kanpur

Lecture No. # 04

### Production of Secondary Fuels: Carbonization

So, today we will talk of production of secondary fuels. Now for some applications the primary fuels cannot be used. For example, in the hot metal production through blast furnace, the fossil fuel cannot be used. So for that purpose secondary fuel production is important. So the important secondary fuels which are produced from fossil fuel.

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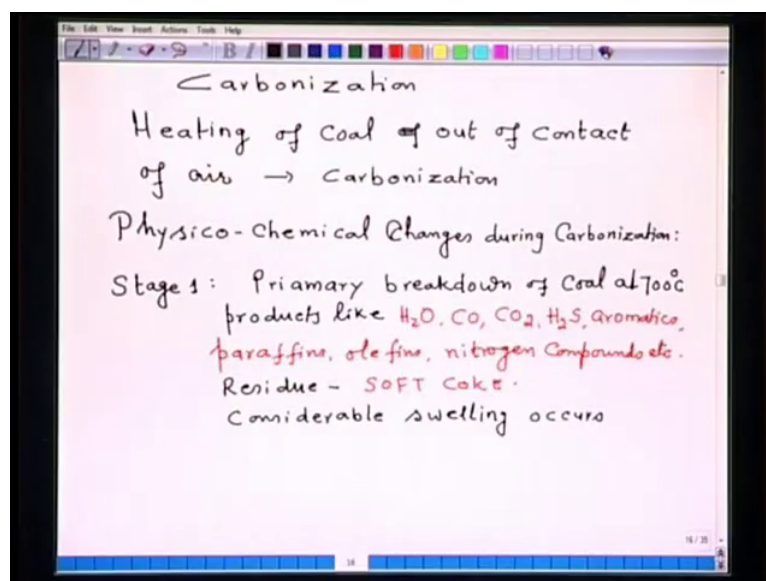


One is the coke, another is a producer gas, and third is a fuel oil. Now all these three are called secondary fuels. Secondary fuels, because they, as such do not occur in the nature; they are derived or they are produced from fossil fuel that is why we call them as secondary fuel. Now the production of coke, production of coke is done from certain quality of the coal that has the normally, they are the vitamins variety of coal. And this process is called carbonization or this process is also called destructive distillation of coal.

For the production of producer gas **production of producer gas** is again done from coal and this process is called gasification. So, in gasification the solid fuel is converted into gaseous fuel for some applications. The production of fuel oil for certain cases done from coal and this process is called hydrogenation.

So, from these three processes carbonization, gasification and hydrogenation, the primary fuel can be converted into the secondary fuel and the objective of production of secondary fuel is to meet the requirement of certain processes. Now let us take first of all carbonization.

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As I already said that carbonization is to produce coke from coal. Now, why this is required? All of you are aware that in the production of hot metal by blast furnace; coal cannot be used.

Blast furnace is a counter current heat and mass exchange reactor. In this reactor, the **burden** which consist of iron ore, coke and limestone, it travels downward and the upward gases flow like CO, CO<sub>2</sub>, hydrogen and nitrogen.

So, in this counter current movement of burden and gases, the permeability of the bed is very important or we can also say the permeability is created by the burden throughout the downward movement of the burden is very very important issue. If the permeability is not maintained, then the upward flowing of gases will not be able to flow smoothly and a choking will occur and this is not required. On account of this, if fossil fuel like coal is used, then first of all coal is very brittle; second, coal contains volatile metals.

So, if you use coal in the blast furnace, expulsion of volatile metal will cause breacking of the coal. The brittleness of the coal will also cause the destruction of coal during its downward movement and as such the permeability in the burden cannot maintain. Therefore, it can be very safely said that the blast furnace, it cannot work without availability of coke.

That is true, if the hot metal production from blast furnace is to be there, then production of coke is to be there. The production of coke is very very important particularly from steal making point of view. Around eighty to ninety percent of the coke which is produced is used in the blast furnace. So, let us see this process how it is produced from coal. In fact, as I said that the process of carbonization consist of heating of coal, heating of coal out of contact of air, out of contact of air and this is called carbonization.

Now, this can be done at low temperature as well as high temperature; low temperature of the order of six hundred to seven hundred degree Celsius and high temperature of the order of thousand to thousand two hundred degree Celsius. For the uses of coke of blast furnace quality, high temperature carbonization is done, because what is required to expel as much amount of volatile metal from coal as possible that coke will be of good quality.

So, as such the high temperature carbonization is of **consult** to high quality coke which is required for the blast furnace application or you can also call a destructive distillation. Now, what does it mean?

So, you imagine, if you heat a coal out of contact of air, if you heat coal in presence of air, then it will combust and **(( ))** form; that is not required. The whole objective of carbonization is to convert one type of solid fuel to another type of solid fuel. So, what we have to do? We have to retain the solid fuel after converting through the process of carbonization.

So, if you heat the coal out of contact of the air, then what will happen? If you imagine and if you think that coal consist of volatile metal, fix carbon, ash and moisture so, if you heat out of contact of air, then the coal will be heated up; the volatile metal will be expelled; the bonds with in the coal will be broken. Because you know, coal consists of carbon, hydrogen, oxygen, nitrogen and sulfur. The bonds will be broken since there is no contact of air so, internally what are the availability of the element are there. They will react with each other depending on their concentration.

Carbon may react with O, it will form CO; oxygen amount is very less or carbon may react with hydrogen, it may form hydrocarbons or nitrogen may react with hydrogen, it may form NH<sub>3</sub> or ammonia; so this way, this destructive distillation breaking of the bonds and formation again of the bonds that we give us the residue which we call as a coke.

So that is essentially it happens, when we heat the coal out of contact of air. The volatile metal will be expelled; moisture will be expelled. And as a result of this, we will be left with the residue which we call as a coke, which will contain carbon, S and what you are left with is hydrogen, nitrogen and oxygen.

So that is what, in short the process of carbonization is you can also call it to be destructive distillation. So, if we want to summarize this thing so, we will write that the physico-chemical changes that occurred during carbonization are as follows **Physico-chemical changes during carbonization they are as follows**: You are heating coal from twenty five degree Celsius and progressively heating to thousand or eleven hundred degree Celsius. The whole objective is to expel the volatile metal of the coal, because the volatile metal they create a lot of problem, if as such it is used for particular application.

So stage one: primary breakdown **primary breakdown** of coal at around 700 degree Celsius and this primary breakdown, it yields to products like H<sub>2</sub>O, CO, CO<sub>2</sub>, H<sub>2</sub>S, aromatics, paraffin, olefins, nitrogen compounds **nitrogen compounds** etc. Why this happens? Because, coal it consists of carbon, hydrogen, nitrogen, oxygen and sulfur.

That is what the coal consists of in terms of ultimate analysis, the organic bonds are there. So during heating, the bonds will break and wherever what element this possible depending on its affinity, it will react. And depending on the concentration, they will react; the carbon is very high concentration, low concentration of oxygen, hydrogen nitrogen and so on; that is very less.

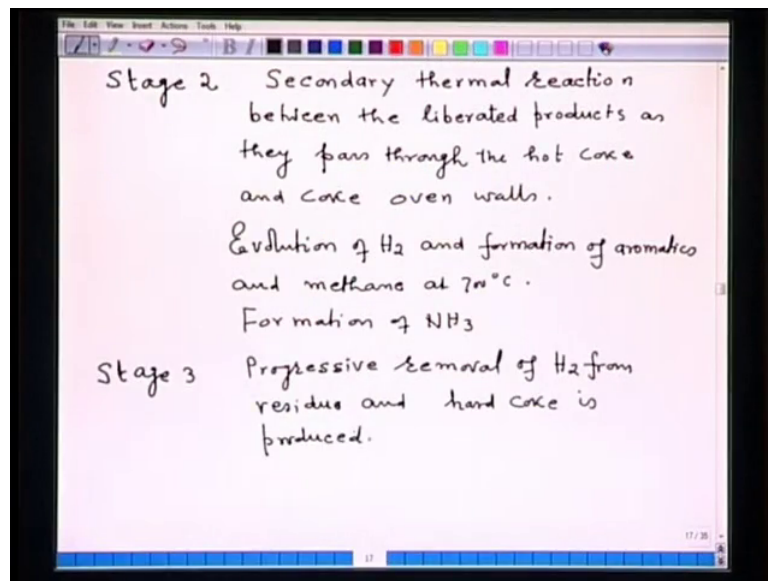
So, accordingly the reaction will be there; hydrogen will react with carbon; hydrogen may react with nitrogen; oxygen may react with the carbon and like that, because no air is over there.

So, these products will form and on account of C H, the residue left which after this the stage one is called soft coke **is called soft coke**. Now in this particular is said the coal also soils, you know because coal contains all out of organic compounds; it is a plant origin. So, there are

a constituent which have a swelling tendency so, because of soiling of the coal, these volatile metal is in the form of gases component, they will be eliminated.

So, mind you in the production of the coal, there is the considerable swelling also occurred, considerable swelling occurs. In fact, swelling is one of the properties that are desired in coal which is suitable for conversion to coke. To have the coal swells, then you should re-solidify to get you again the solid coke; otherwise it is gone.

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Stage 2: Say in the stage one, you got this soft coke but, that is not useful for the blast furnace purposes. For all other purposes, this coke can be used at seven hundred degree Celsius which is called low temperature carbonization. Now for blast furnace purposes you to heat it further.

So, in the stage 2 say secondary thermal reaction, secondary reaction between the liberated products **between the liberated products** and between the liberated products as they pass through the hot coke and coke oven walls **and coke oven walls**.

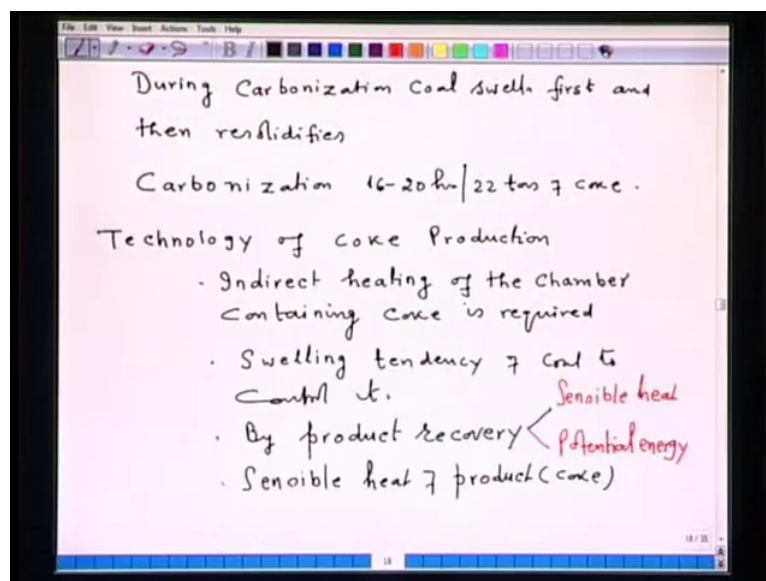
So, as the results of this evolution of hydrogen **evolution of hydrogen** and formation and formation of aromatics and methane **and methane** occurs at around 700 degree Celsius; the formation of NH<sub>3</sub> **formation of NH<sub>3</sub>** due to decomposition of nitrogen compound.

Then the stage 3, in the stage 3 because the residue which we obtained on further heating, the further removal of gases occurs, because all the volatile matter has not been expelled at around seven hundred degree Celsius; further heating eight hundred, nine hundred, thousand and eleven hundred degree Celsius, more and more volatile metal will be expelled; more and more gases will be formed and formed.

So stage 3, progressive removal **progressive removal** of hydrogen from residue **from residue** and hard coke is produced **and hard coke is produced**.

Now these three stages which have written they are in fact, when you heat from twenty five to seven hundred for example in the stage one, the further heating and whatever happens in the further heating that is the constitute. In the stage two and then further heating up to eleven hundred degree Celsius, we result in the hard coke and that is being useful.

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Now it is important to note that during carbonization **during carbonization** coal swells first and then re-solidifies **and then re-solidifies**. As it temperature rise and then it is discharge from coke oven or from the chamber and it is then cooled. The carbonization, it takes around 16 to 20 hours per 22 tons of coke. So, this is about the scientific aspects of carbonization, what we have seen over here that we want to heat coal in the absence of air.

That means we have to have a reaction chamber which is maintain at around 1200 to 1250 or 1300 degree Celsius. So, that coal can be heated up to that temperature required. We cannot heat the chamber by direct charging of the coal in combusting over there; it is not possible.

What we learn from here that the technological production of coke from coal, must meet some of the requirement. First meet, first requirement that a technology must meet is indirect heating of the chamber. So, the technology of coke production, **technology of coke production** some important problem though several thing are needed but, what I am trying to derive those technological concern that are required after going through the physico - chemical changes that occur during heating coal out of contact of air.

So, the first that we note that the coal should be heated indirectly; that means the chambers which are going to construct, it cannot be heated directly; there should be to the first requirement is that indirect heating is required. Indirect heating of the chamber containing coke containing coke is required. That is a first and foremost important requirement of any technology.

Second important thing that we can derive from, what you are learned in the physico - chemical stages is how to accommodate the swelling which will occur during conversion of coal to coke in the reaction chamber. Because when you are charging the coal at time  $t$  is equal to zero and during its conversion takes hours together. Imagine the coal which is in contact with the wall, it will swell very high; very large swell will occur. It may stick to the wall and the end of the carbonization process here to discharge the coal out of the reaction chamber.

So, another important issue that comes in my mind is the swelling tendency of coal **swelling tendency of coal** to control it. So, when is to be careful here while selecting the coal which is used for conversion of the coke though swelling is required. But if a particular swells very high, then one has to blend it with a coal which is of low swelling tendency. So, that an optimum swelling during the coking process is maintained.

Among other technological relevance's these are for example discharge and charging mechanism. Because the chamber is closed from all the sides so, you have to provide the doors for the charging as well as for discharging. Then as you also note from the physico - chemical stage, the large amount of gases product are formed and if you term coke as a

product, then all other product we call them byproduct. So, another important issue that we also see is the byproduct recovery **byproduct recovery**.

Now as you see from the physico - chemical stage, the byproduct could be of several type, could be of several component, may consist of hydrogen; it may consist of methane; it may consist of carbon monoxide, carbon dioxide and on the top of the it there are all discharged at around twelve hundred degree Celsius. So, this byproducts it not only contains sensible heat but, it also contains potential energy. So, in important aspect of technology of coke production is the byproduct recovery and byproduct recovery in the sense of say recovery of sensible heat and the potential energy.

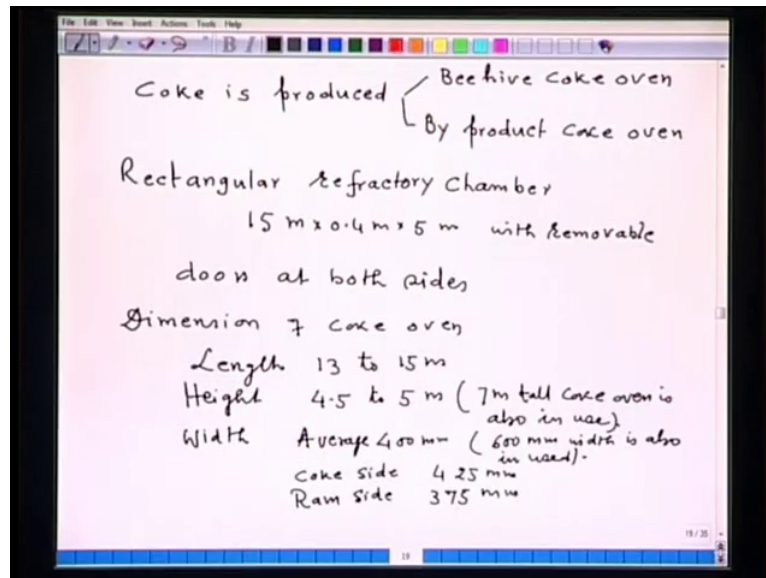
Because the byproducts contains hydrogen which has a very highly potential energy, methane which also has a high amount of potential energy and of course, carbon monoxide, ammonia they all have this so called potential energy. So, the entire technology if we think from conversion of coal to coke, it should not only be limited to the conversion of coal to coke. But, it should be limited or it should consider what is to be done to the products which are discharge from the reaction chamber. Because of the product contains very high amount of sensible heat, as well as potential energy.

Also one is... so, think the product coke when it is discharge from the chamber; it will also be discharge at twelve hundred degree Celsius and, because you are not producing a ton of coke per day; you are producing hundreds of tons of coke per day. So, if the discharge temperature of coke is twelve hundred, you can calculate the amount of sensible heat that the coke will have, it will have huge amount of sensible heat.

So, what is to be done or what the technology considering to doing with the sensible heat of the product and the byproduct and the potential energy of the byproduct so, in fact the sensible heat of the product is also important; sensible heat of product. Now with the product I mean coke, rest all of these are by product. So, while designing the technology, what do you have to consider? You to design a reaction chamber; we have to we have to design also the byproduct recovery; we have to also see, what we are going to do with this heat which is produced during conversion of coal to coke.



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So, how it can be done? Traditionally, coke is produced in Beehive coke oven where the byproduct recovery was not considered to be important. So soon these, this Beehive coke oven been replaced by that so, called byproduct coke oven **byproduct coke oven**. Now these by product coke oven is name suggest, it is a coke oven which is also which also takes care of the byproduct.

Now a heating chamber though I use earlier heating chamber, this you can also call coke oven, because here coke is produced so you call coke oven. In fact, it is a reaction chamber which is heated to a very high temperature that is why you call as a coke oven. So, this coke oven in fact it is a rectangular refractory chamber, **it is a rectangular refractory chamber**; the dimensions of the order of 15 meter, 0.4 meter into 5 meter. It has with removable doors **with removable doors** at both sides, why? To enable the hot coke to be pushed by a ram; now typically say the dimension of coke oven, typical dimension of a coke oven, it is a length it is of the order of 13 to 15 meter, height 4.5 to 5 meter. In fact, a 7 meter tall coke oven is also in use, is also in use.

Then width on average, it is a 400 millimeter although 600 millimeter width is also in use; then its width on coke side around 425 millimeter and on ram side, it is 375 millimeter.

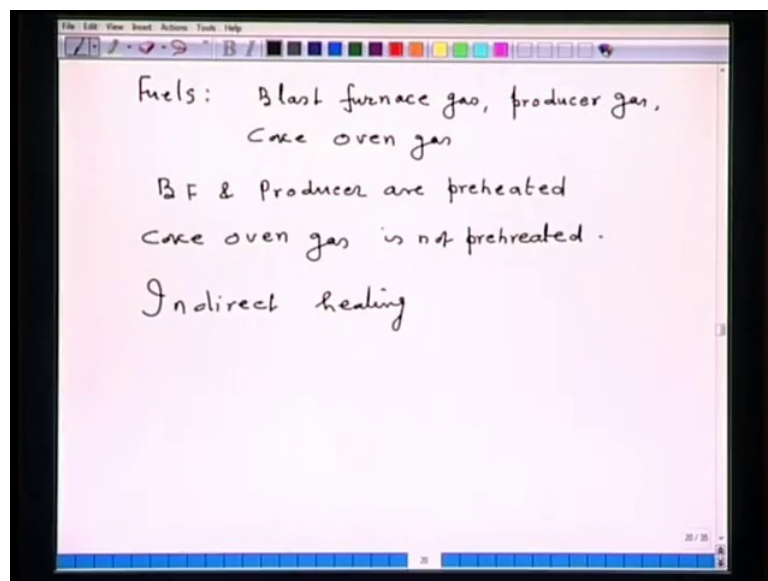
Now can you think of how this coke oven will be heated up? You cannot heat by creating heat inside the reaction of the reaction chamber, because there air will be there and coal will

burned and nothing will happen. How it can be burned or how a high temperature can be created? It has to be created indirectly so, for that purpose out in throughout the outside valve of the coke oven, the flues are cut. Flues, in fact they are the flow passage for the flow of the hot gases.

Now could you get you clue, how coke oven gas heated up. So, towards the outside valve, the flues are cut and into the fuels the hot gases flow. And in order to create the hot gases due to burn air and some fuel at some location, and that location has to be connected to the coke oven chamber; the hot product gases will flow into the flue, the hot product gases may have the temperature of fourteen, fifteen or even sixteen hundred degree Celsius, flues will be heated up. And from the heat of the few oxides, the heat will flow inside and through this mechanism the coke oven, the inside coke oven chamber gets heated up.

So, that is where the refractive wall of the coke oven chamber and its thermal conductivity is also an important issue.

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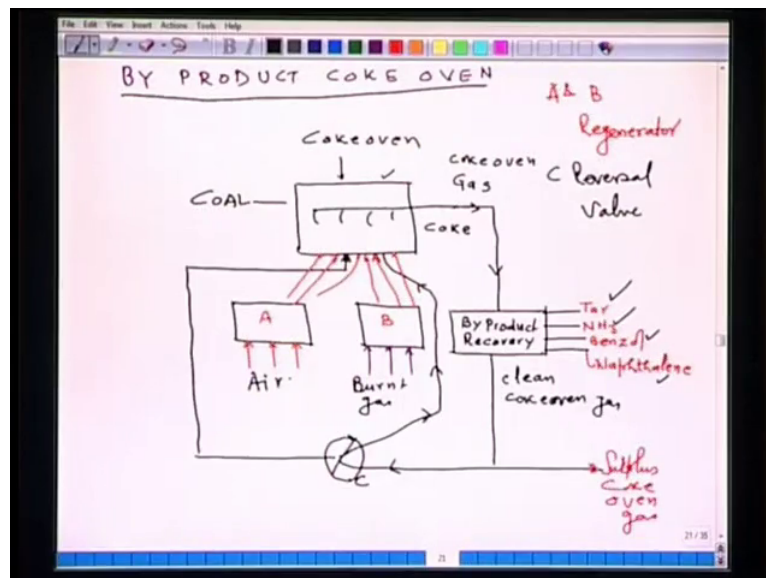
The fuels which are used, fuels which are used for the heating purpose: the blast furnace gas, producer gas and coke oven gas. Now into this combination the blast furnace gas and producer gas are preheated to a certain temperature, where as coke oven gas **where as coke oven gas** is not preheated **is not preheated**. Do you know, why? Coke oven gas that means the gas which is coming from the coke oven; it has very high as I already said it has very high

amount of potential energy. It cannot be preheated, because if you preheat, then there is methane it will decompose; it will form carbon and hydrogen and carbon will choke the flow passage.

So, that is where the coke oven gas is not preheated. As I said, the indirect heating is done; write down indirect heating is done and a thermal conductivity sketch is also very important. Now our silica bricks are being used.

So, now if you want to sketch the process of conversion of coal to coke considering the chamber, heating part and byproduct recovery; then let us this particular sketch is looks as follows.

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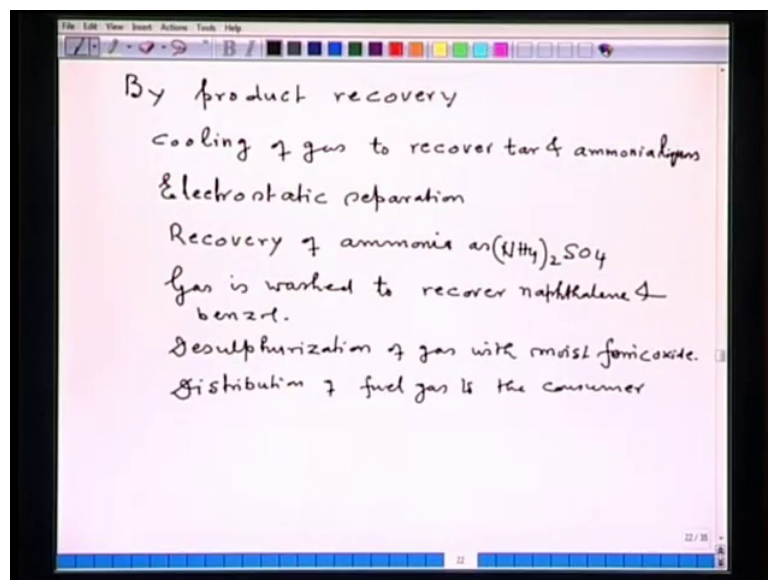


A huge plant, though I did not show the plant it is very huge **very huge** of the byproduct recovery is bigger than the coke oven plant. Because so many byproducts are recovered and mind you, the entire economy of production of coke from coal, a very large contribution is also from the byproduct recovery. So, you see several byproducts are produced and some of the byproduct: tar, tar has a very high calorific value; it can directly use in the blast furnace or somewhere else. Then large amount ammonia is produced from ammonia, ammonium sulfate can be obtained. Then benzyl, naphthalene they are being obtained. Now certain then this clean, we are gaining the clean coke oven gas **clean coke oven gas** is transferred to the coke oven plant for heating purposes.

Now if surplus coke oven gas, it is being discharged and use for somewhere else. Now in addition to this, you see A and B they are the regenerators. Now the function of regenerators is to preheat the air and the fuel gas other than coke oven gas. So, those two regenerators are used so, they are used in cycle. So, there is a C is a reversal valve so, if a regenerators heats the air and another one heats the burnt gas or fuel gas. So, here this is the air and this is the burnt gas.

So, alternatively one heats air and other brunt gas and other brunt gas and other is the air so, there you are use alternatively and the products of combustion. Therefore, to the flue which you cut into the coke oven chamber so, that is how a byproduct coke oven plants it looks.

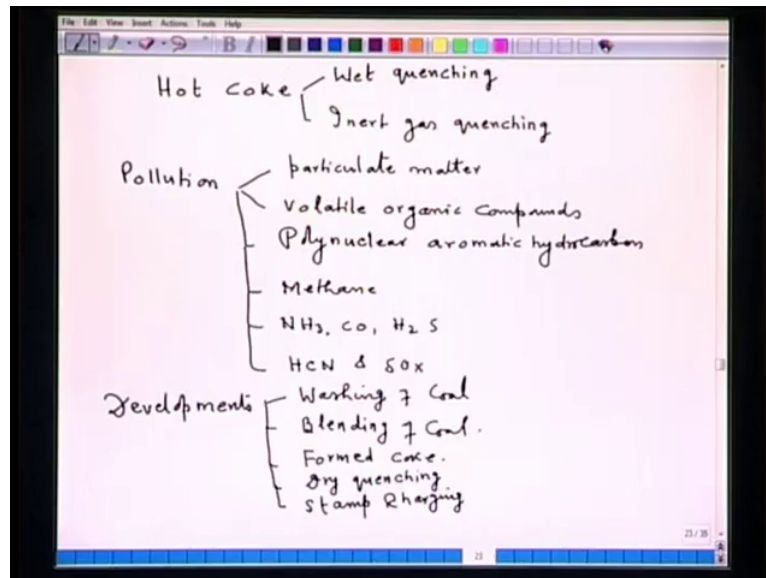
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Now the byproduct recovery **byproduct recovery** say cooling of the gas, gas is cooled; cooling of gas to recover tar and ammonia liquors **and ammonia liquors**; then electrostatic separation **electrostatic separation** of tar in order to remove the coal or dust particle. Then recovery of ammonia as ammonium sulfate **as ammonium sulfate** which is sold to the market. Then gas is washed **gas is washed** to recover naphthalene and benzyl; then desulfurization of gas, desulfurization of gas with moist ferric oxide and then ultimately it goes for distribution of this fuel gas to the consumers.

So, you see a byproduct plant or the byproduct recovery plant is also considerable in size and we try to recover as much possible from the coke oven gas.

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Now say this hot coke which is produced, it also has as I said a large amount of sensible heat. So wet quenching, can you imagine? Large amount of water is used for quenching and large amount of pollution is also been created; water is being spoiled and so on. So for now, this wet quenching is gradually replaced by the so called inert gas quenching **inert gas quenching**.

So, these are the two methods that are used to quench the coke from twelve hundred to twenty five for storage purposes. Now as you know, this coke making is associated with highly pollution. I can say the coke making is highly polluted. One, so several pollutions which are there, oval type a pollution say the process emits for example, particulate matter; particulate matter which is highly detrimental to the health. Then they also emit volatile organic compounds **volatile organic compounds**. Then they also emit poly nuclear aromatic hydrocarbon; well, methane then ammonia, carbon monoxide, H<sub>2</sub>S, HCN and SOX.

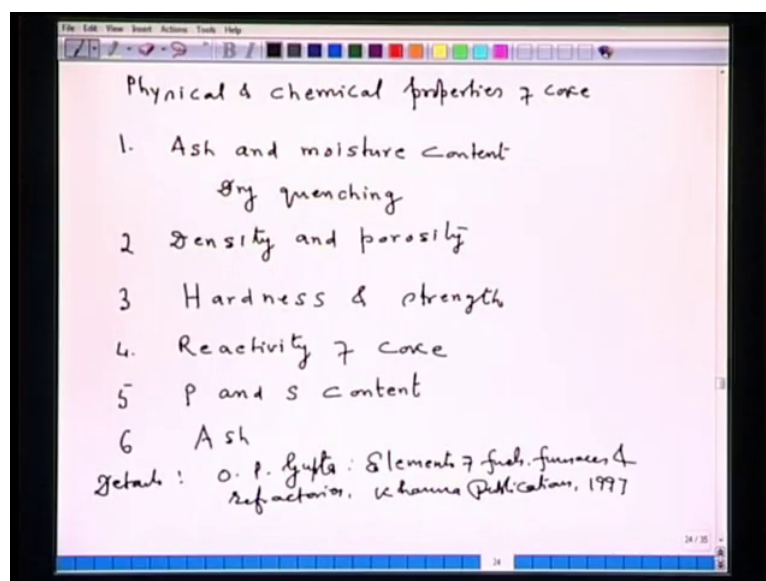
Several modifications took place over the years in order to reduce the pollution so, some of the developments say, one development is say washing of coal to reduce the S content of the coal.

Then blending of coal **blending of coal** that means coal of different qualities can be blended and this is also being one of the developments. Then third is the use of formed coke, **use of formed coke**. Now in the formed coke is made from low range highly volatile non coking

coal; it is carbonize up to five hundred degree Celsius that low quality coal. Char is obtained and that is mix with the high quality coal and then it is use for production of the coke.

Another important development is really took place is a dry quenching. Now this is a very important development as a dry quenching and the gases, hot gases which are produced are taken into the boiler or to use to reuse the energy which is obtained by cooling of the coke. Then another development is the so called stamp charging. Now in the stamp charging, mechanically pressed coal is used for conversion to coke.

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Now let me tell you here certain important physical, chemical properties of coke **important physical and chemical properties of coke**.

Now mind you, the coke or the high quality of the coke is used in the blast furnace; blast furnace is the main and principle user of the coke which is produced at high temperature. And for that purpose, the coke which is produced it must satisfy the following properties; first, ash and moisture content **ash and moisture content**. Whatever amount of ash in the coal, it will be transferred to the ash. And that we used for the example of the blast furnace ash has to be removed and ash is removed in the form of liquid that is slug. So, higher is amount of the ash, higher will be the amount of slag and accordingly the productivity. And the functioning of the blast furnace will be influence so, for that purpose that is very important.

Now also here, the wet quenching is not desirable, because during wet quenching coke absorbs moisture. So, if one percent H<sub>2</sub>O in the coke that will increase fuel consumption by around one point two percent so, here the dry quenching is desired; dry quenching is desirable. Because dry quenching, there is no moisture will be there in the coke and such it is a good.

Second important property that it has the density and porosity **density and porosity**. Now in blast furnace, high strength coke is desirable. If the coke has high strength, then naturally its density also will be high. So, complete devolatilization of coal leads to density of coke approaching that of graphite; that is if you devolatilized completely, then its density will approach to graphite. Now since coal contains hydrogen and mineral matter so, density of coke cannot reach to that of graphite.

So what is required for a coke which can be used in the blast furnace it should have high strength. Though high strength you are sacrificing with the reactivity but, the strength of the coke is more important as compared to its reactivity. Because as I said in the beginning, coke is the only component of the burden, they team parts permeability during the downward movement of burden in the blast furnace. Because coke is also only component of the burden which remains **which remains** unchanged till it comes down to the **(( ))** level.

An iron ore and limestone they react and they change and accordingly the permeability is mainly influenced by the coke, because coke react only at the **(( ))** level and from there, the appearance of the coke vanishes.

So that is why the strength of the coke is more important as compared to reactivity. Third, hardness and strength **hardness and strength**; this is required say resistance to impact package. Resistance of coke to impact package, because the coke is falling from a zero height in the blast furnace from the top before it comes at the **(( ))** level, it has already travelled around fifteen to twenty meter of height.

So, it is falling under the gravity, it has to sustain the upward flow movement of the gases so, it has to have a high strength **it has to have high strength** so, that it does not break during the impact. So, for that purpose setter index or setter text is being done in order to have whether it is suitable for blast furnace seed or not. Then fourth important thing is the reactivity of coke **reactivity of coke**. Now for the reactivity coke should do porous. So, that the oxidizing

component of air, it can diffuse and the carbon can react; but well porosity, more porosity is good from reactivity point of view but, from the strength point of view it is not good.

So an optimum has to be reached, because most important part of the coke is the strength; that is the most important part. If it breaks during its downward movement, kneeling to affect the permeability and whole smooth functioning of the blast furnace will be influence. So, the strength is more important of course, reactivity is also important, but while when is two compromise over here.

Fifth important thing is phosphorus and sulfur content. Whatever element those are there in the coal after react the same will be transferred in the coal. So, the coal contains S, entire amount of S will also be transferred into the coal, because S is not removed at all. So, whatever element which are there in S or say it may have sulfur also, sulfur containing then all the sulfur and phosphorus will also be transferred in to the coke. And such, the processing of the hot metal in the blast furnace will be influence so, control sulfur and phosphorus is also not only desirable but, is very important.

And sixth important point is a ash. As I have already said about the ash content as content should be as minimum as possible, because increase in the ash content will increase volume of the slag and accordingly product will be affected.

So, if you want to know coke further details, you can lived on the book of O. P. Gupta- Elements of fuel furnaces and refractories **of fuels furnaces and refractories**, Khanna publications the editions which have seem is 1997. So, in the next lecture, we will be doing material balance of coke oven.