METALLURGICAL AND ELECTRONIC WASTE RECYCLING

Dr. Arunabh Meshram

Department of Materials Science and Engineering

Indian Institute of Technology Kanpur

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Lecture-34

Greetings, I welcome you all to the new lecture of this course where in now we will be discussing on the pyrometallurgical processes of WPCB recycling. Now, we had very recently discussed the importance of pretreatment. and how ECs are to be removed from the WPCBs and we have also discussed the delamination. It becomes very important that after delamination we must have a very well-defined route for recycling the PCBs. One of the ways that by default we can just think of is basically we go into the pyrometallurgical process. Suppose, that we have a large stock of WPCBs that we can easily recycle. That stock can be directly charged in a suitable furnace and we can go ahead for the pyrolysis or let us say metal recovery. One of the ways that one should be thinking of for metal recovery is that we can do it in the conventional way or we can have some other modifications during the process so that we are able to tap out maximum from the pyrometallurgical operations that we do. There are lot many variations to pyrometallurgical operations. Some of the furnaces can be rotated, some of the environments that are present inside the furnaces can be controlled. Inert atmosphere or not inert atmosphere, what is the process parameter for a given furnace that governs what is going to be the end result of the pyrolysis operation.

We can have extensive discussions on lot many operations that have been explored and are being implemented at different levels. But presently we are going to concentrate on some of the processes that generate in general good output. It is fair enough to assume that in case we are going to for conventional processes we can end up with metal master alloys. That may be a good product, but at then after that we will have to go think about the refining of the master line for the separation of metals if we want to go into that route. And there is the generation of slag, then the slag recycling and the process dust that is generated, effluent dust that has to be processed separately. Metal extraction is a challenge and the generation of slag is also a problem which means one has to invest on these fronts as well. We are going to discuss pyrometallurgical processes that are oriented towards maximum metal recovery along with other materials as well.

We know that we have been discussing extensively on WPCB. The composition is already known to us. It is like 30 to 40% metal is present. We have nearly 30% of polymers and we can have 30 to 40% of oxides, refractories basically. These are oxides and we also know that nearly from a general perspective we know that 3 to 7% of total e-waste is WPCB which means it is a very big contribution given the gigantic quantity of e-waste that we are producing per year and considering the case of India we have this means this is the quantity 4,137,000 metric tons.

This is 1000 metric tons and this value is very large and this is just a very recent data it is in 2022 and we are talking about India. This is the e-waste generation in our country. We know that WPCBs have lead, chromium, mercury, cadmium, of course, these are present in smaller quantities but nonetheless these are present and these are hazardous. Therefore, recycling becomes so important directly charging it in a furnace may not be a very attractive option because of the generation of gases. We are looking at just in the previous classes we had discussed that the epoxy resins are present, flame retardants are present, these are materials that lead to the generation of hazardous gases. If these gases are coming in contact with humans, then it can lead to lots of repercussions and health hazards.

One has to really think how we are going to go about the whole pyrolysis operation. What are the important pretreatments? Important pretreatments specifically for pyrometallurgical operations. In such a case, we can go for crushing or shredding. Why are we doing this? Because we want to reduce the particle size. Then we can have screens. Again, why we wish to have separation of particles on basis of size and shapes, then we have magnetic properties we are using what we are using magnetic separators or drum separators and then we have electrostatic separators electrostatic properties, so we know that we are going to have eddy current separators.

Similarly, following that we have density separations so we can have fluidized bed or cyclones, hydrocyclones and finally we can have surface properties. We go for froth floatation. When we have such long chain of important pre-treatments, it's not necessary, it just adds to the quality of feed. One can totally bypass these types of operations and one can just directly charge the PCB assembly even without delamination to into a furnace. That will do what? That will just lead to the melting of all of the components.

We have let us say appropriate temperatures, we have good slagging materials, slagging materials means we have good fluxes just melt the whole PCB itself.

We will generate lots of gases, the slag composition is going to be very complex because we are going to have lot many polymers and different materials coming into picture. And the product that we will get may not be of our desired composition. Removal of components and pretreatment helps us to make the metal fraction more concentrated, more oriented. The raw feed is of our own choice. We are able to design our raw feed for higher metal recovery. This means material control; material properties help in designing feed of the process and this leads to what improved metal recovery.

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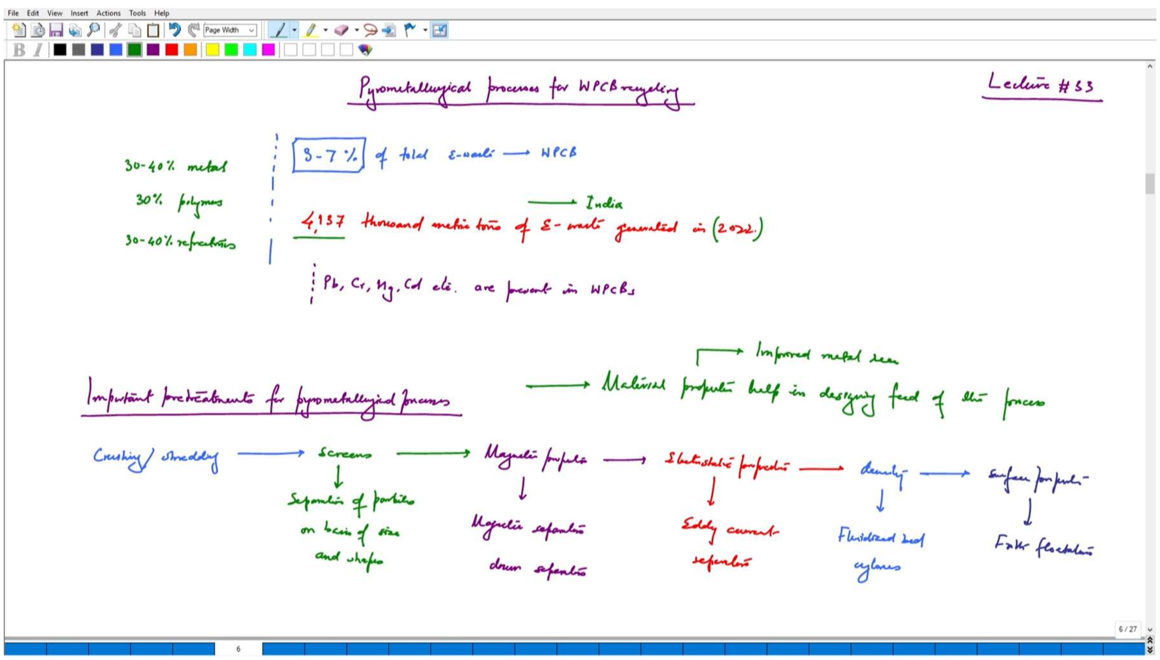

What exactly are the types of pyrolysis? What are the types of pyrolysis operations? Pyrolysis operations mean what are the operations in pyrometallurgy that have controlled atmosphere for good material recovery because we don't want the hazardous gas to generate. Thermogravimetric analyzer, fixed bed reactor, right now we are just describing different types of facilities that can help in the pyrolysis. We see that thermogravimetric analyzer has poor mixing. You can have good control over temperature, but you will get poor mixing of products. Fluidized bed reactor is basically continuous operation, low operation cost and poor temperature control. We have batch reactor it gives us high efficiency, but it has high labor cost because one has to remove the material and recharge the furnace. Then there is the problem of variation. Variation of batch-to-batch output. This is very crucial. Because we do not know what we are charging and it becomes very difficult to really be very sure about what is the overall concentration that we will be getting from up single batch to the next batch. This is a very big of a challenge. In microwave we know that electricity requirement is important parameter. Because it is not just heating it is also providing the microwave input. We have good control, easy control and good heat transfer, but the mass control is difficult to handle. Difficult mass control in the process.

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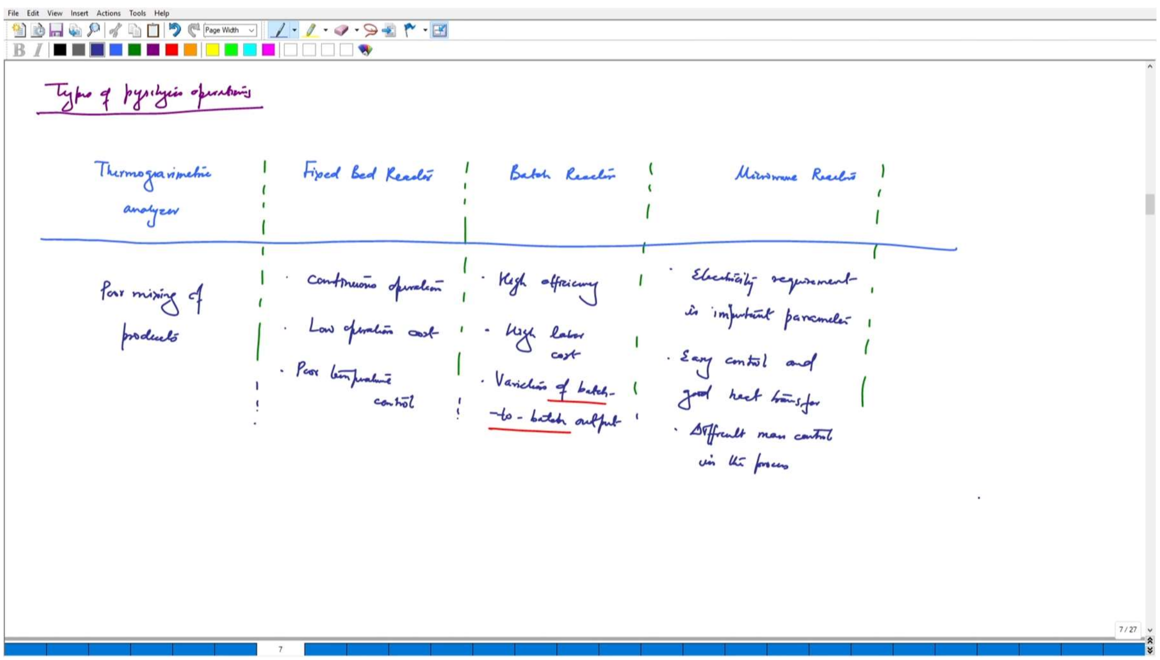

We have different types of pyrolysis operations and we see that for every reactor that we have let's say fixed bed or a batch reactor or we can have other heating mechanisms also and we can have microwave or we just go for a very controlled small experimental setup. Each reactor itself has its own advantages and disadvantages. What is it that we wish to optimize? It is dependent upon the reactor itself. Both batch reactor and continuous reactors can have their own nuances, one can have different types of advantages and disadvantages associated to them.

We will go ahead and see what are the important parameters, Pyrolysis Process Parameters and we know that typically speaking we have 300 to 800 °C. This temperature range can go to, as we had discussed in the previous class, it could go to up to around 1300 °C, but generally speaking it is it can be up to 300 to 800 °C and this is the temperature range. And what exactly are we looking inside? We have important chemical reactions. What are the chemical reactions that happen? We have dehydration, debromination, and dehydrogenation. Dehydration and dehydrogenation both are present in the pyrolysis of WPCBs.

What really happens is basically smaller molecules are produced, and it leads to generation of heterogeneous mixture. One just might wonder what type of mixture are we talking of. The composition of this mixture we really can't predict it depends upon what we have fed in what quantity and what was the initial composition of whatever we have fed and then we let's say operated at given operation parameters and then we get to see the output, this heterogeneous mixture is what we get after the pyrolysis. Gaseous products, the oil, pyrolysis oil, and char we separate that out and the there is its heterogeneous mixture which contains metal and other fractions. We cannot really pinpoint key this is going to be the composition it again depends upon the feed and how we processed it. The heterogeneous mixture which is basically having the metal is produced with the gases and char. We are also considering oil inside. Gases, pyrolysis oil, and char. What are the parameters? This is general outline.

This is the outline of operation. But what are the parameters? When we look at parameters we have temperature. Then we have power and heating rate. And then we have particle size. When we talk about temperature, generally speaking high temperature, we know the temperature range itself. High temperature generally means good reaction rate and decomposition of WPCBs. By decomposition of WPCB means we are going to get heterogeneous mixture, char, pyrolysis oil and gases. The changes in temperature does not affect the mass of residue the heterogeneous mixture itself much. It does not affect the mass of the residue much, but it provides we should say promotes not just provides, it provides an opportunity, promotes the conversion of volatile materials to volatiles or volatile materials to gases. Higher temperature can lead to this. It really does not affect the mass. When we talk about power, we can have microwave, if we are using microwave. Microwave power can lead to, if we are increasing this, we are leading to higher reaction rate, higher heating rate and higher heating rate means, everything is actually interconnected, higher heating rate means early decomposition, it starts early it ends early and higher decomposition rate, so not just early it becomes quicker. We have the particle size. Now, this is something that we can debate powdered particles. If somebody has used powdered PCB, it leads to higher gas generation.

Whereas, if the particle size is larger, which means coarser particles. Larger means coarser particles. We can have higher pyrolysis oil generation which means that it is not complete which indirectly it means that we have to go for incomplete pyrolysis. If we are using powder particles, we have gas generation. We have larger particles; we can have oil generation. What exactly is it that we wish to perform is totally dependent on what is the product that we wish to make. Do we want gas or do we want pyrolysis oil? What is it that we wish to generate? In what quantities that will decide whether we want powdered particles or somewhat larger PCB particles.

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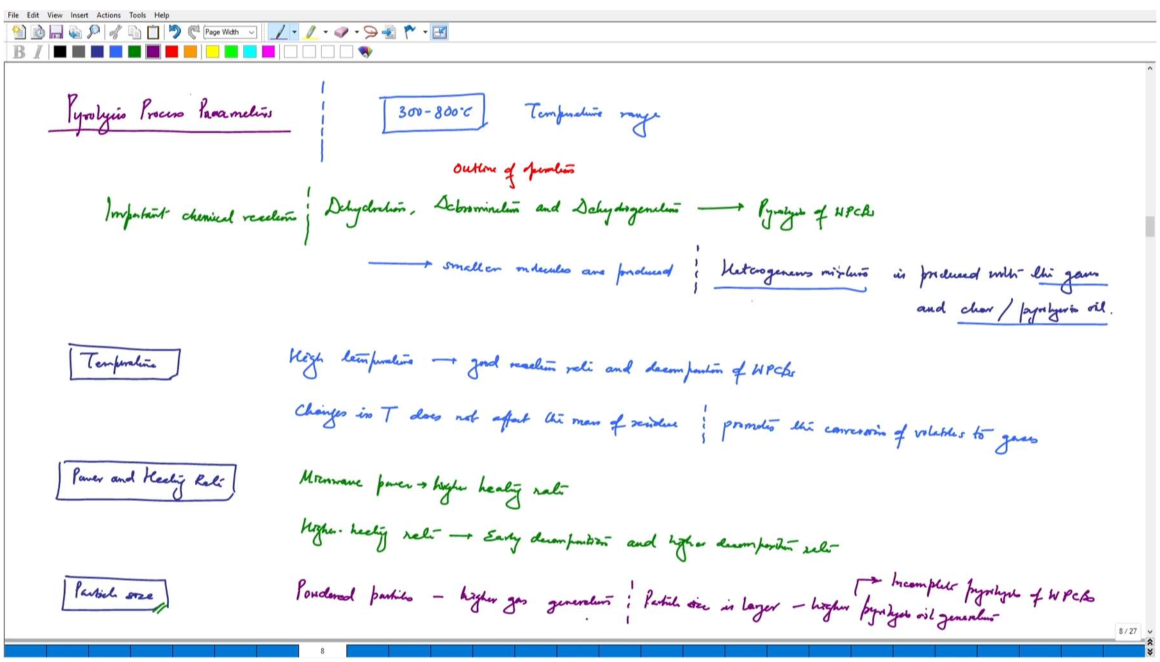

There are some advanced processes also which we will be discussing. We have catalytic pyrolysis wherein we are going to use catalysts; we have co-pyrolysis wherein we can have different materials coming into picture along with the PCB itself, and then we have molten salt pyrolysis where in we are going to use molten salt. When we look out for catalytic pyrolysis we have use of zeolites and metals and metal compounds, metals and metal oxides. It is zeolites and metals and metal oxides. What are the common examples?

We can have MgO, CaO and then ZSM-5. ZSM-5 is a zeolite and then we can also have copper and iron. These are the catalysts that have been used for the pyrolysis and then what are the properties that we get? We have generation of lower pyrolysis oil, we have reduction of pyrolysis time and activation energy, so it becomes easier.

We have bromides converted to bromine and/or hydrogen bromide so when we think of co-pyrolysis, It's a bit different. When we are using two or more materials for pyrolysis, it's called co-pyrolysis. We can use Chinese fir sawdust or rice husk or red mud and people have been exploring lot many different materials so not just these and if we are doing this with the WPCB, we are going to get some different output, we have high-quality, high-value pyrolysis oil which can be used as a fuel so and but the bromine goes in char. Bromine fraction in char. Char that is produced has the total bromine. When we look at salts, so generally speaking salt bath can have, of course, this is just a typical example that we are looking at Li_2CO_3, Na_2CO_3 and K_2CO_3 so it could be having all of equimolar concentration so 33% each if this bath is used then we are we can also have an advantage of let's say bromine conversion 99% bromine in salt bath and it leads to alkaline bromine, alkaline metal bromides and we have recovery of 95% copper. Metal recovery is also described.

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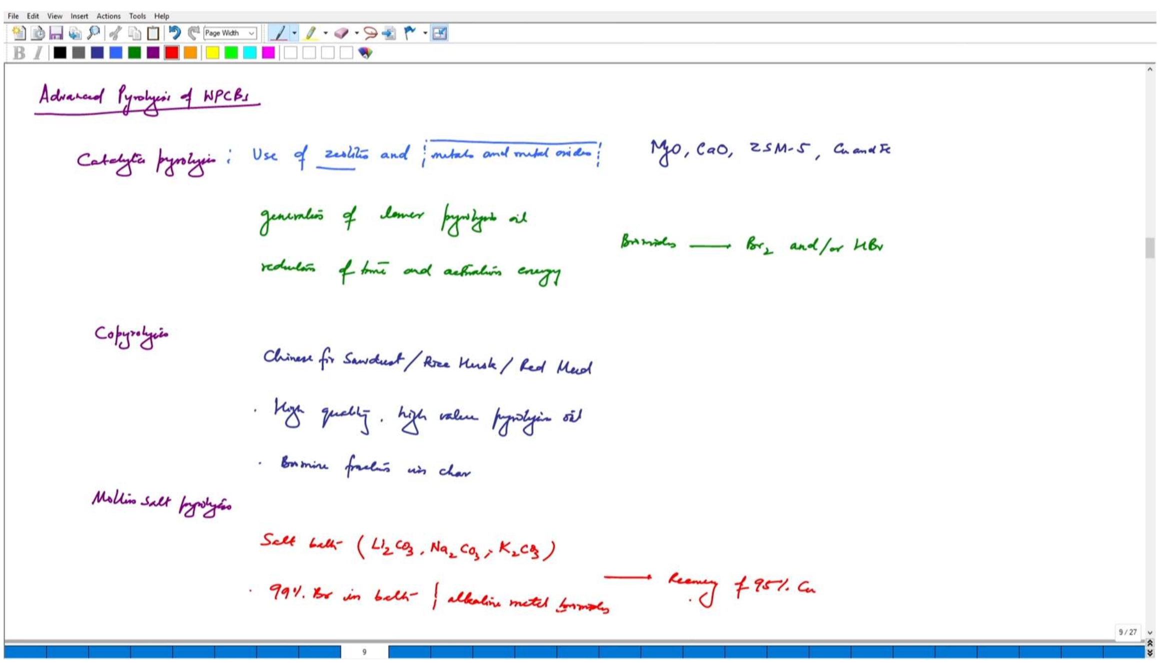

When we look at the overall in general PCB recycling, we must look at energy and material flows. These are very important and it helps us in understanding how material is extracted when we go into pyrometallurgical route of recycling. A generalized diagram we are trying to draw here. Let us have WPCBs and we had our operations, so we did pyrolysis and we also had energy conversion what we get is thin gases, liquid products and then we have solid residues. But these gases can be treated as fuels, so we have fuel and this is basically energy One path is basically wherein we are just going from pyrolysis to gases and then to gases to energy uses. If we are really not interested in that then we can go for material path. When we look at material path, we have liquid products and liquid products basically means chemical materials. One has to purify it and get different types of output from it and we also have solid residue.

We will now discuss what we are looking at when we think of material output. Separately we have solids and then we have liquids. We are still discussing material flow. We have metal fractions and we have non-metal fractions and in liquids we have the liquid generated products we have the chemical materials; we need to go for de-bromination and the purification and we get the final chemical products and it follows a very good stream line that we are able to recover lots of products. In the case of solids when we look at metal fraction and non-metal fractions, we have non metal fractions is basically synthetic products and metal fractions are basically one has to purify and get the overall output final recovery. When we think of pyrolysis liquids liquid oil, we get that this product is not very good fuel for incinerations and it means that one has to have lot many further facilities because the presence of particulate matter in this output makes it difficult to use in a general as a general fuel. When we think of pyrolysis oil, we can get key components like phenol and isopropyl phenol, but the key challenge is generation of pollutants which makes this whole process a bit of a typical health hazard kind of situation.

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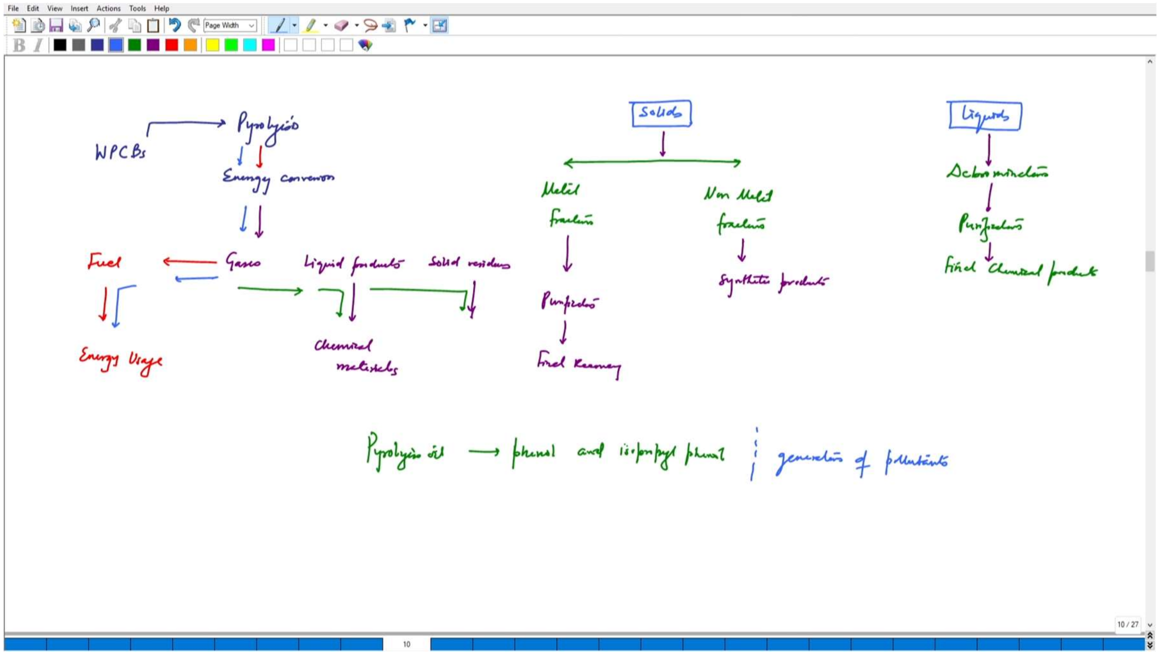

One has to think around these pyrolysis products if they wish to reutilize them as fuels. We have seen that in this class that lot many processes are available in pyrometallurgy that give us wide range of alternatives products and of course, one has to think about refining the final metal products to get the desired composition and one has to go into other routes in combination with pyrometallurgy to get the final output. We will discuss in the upcoming classes. Thank you.