

**Biomass Conversion and Biorefinery**  
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**Lecture 12**  
**Hybrid Methods**

Good morning students. Today is lecture 3 under module 4. In this module as you know that we are discussing about the Biomass pre-treatment. Today we will discuss about the hybrid methods of pre-treatment and what is the importance of pre-treatment in a biorefinery concept.

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**Hybrid Methods of Pretreatment**

- Based on the drawbacks of single pretreatment methods, researchers have been trying to combine these methods to overcome the problems and increase efficiency.
- Since many years ago, many studies have been carried out by a combination of various pretreatment methods.
- Combinations of one or more pretreatment methods to improve the pretreatment process may be a possibility to find process designs that will be suitable for enhanced fractionation of the raw material.
- This could be, for instance, to yield process streams, which are optimized for hemicelluloses, while other streams are optimized for other compounds.



So, based on the drawbacks of single pre-treatment methods researchers have been trying to combine these methods to overcome the problems and increase efficiency. If you recall one of my class, I emphasized that why do we basically need a hybrid system; because you know any process has its own limitations in terms of the efficiency, yield or such parameters, restricted to maybe 70 to 80% depending upon the type of technology or process it is.

So, in any single step process it is very difficult to achieve a very higher yield and that is the reason why there are many operations or processes that can be combined together with the sole aim to increase the yield. So that is how actually the hybrid methods came into picture. Since many years ago many studies have been carried out by a combination of various pre-treatment methods.

Combinations of one or more pre-treatment methods to improve the pre-treatment process may be a possibility to find process designs that will be suitable for enhanced fractionation of the raw material. This could be for instance, to yield process streams which are optimised for hemicellulose while others streams are optimised for other compounds.

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- However, implementation of several, different pretreatment methods comes with an additional cost, if the methods are dissimilar.
- Therefore, it would not be advisable to apply widely different pretreatment methods.
- Nevertheless, pretreatment is commonly preceded by a size-reduction step, which can be regarded as mechanical pretreatment, if the size reduction is thorough.
- The reverse operational procedure is also a possibility.
- *Microwave* and *Ultrasounds technique* in combination with other pretreatment techniques such as pretreatment using *Deep Eutectic solvents, acids* and *alkali* has been widely used as a part of the hybrid process of pretreatment.



The implementation of several different pre-treatment methods comes with an additional cost if the methods are dissimilar. So cost is a very important aspect when you talk about commercialization. So that also need to be taken care of. So, it would not be advisable to apply widely different pre-treatment methods. Nevertheless, pre-treatment is commonly preceded by size reduction step which can be regarded as a mechanical pre-treatment. If the size reduction is Thorough.

The reverse operational procedure is also a possibility. Now Microwave and Ultrasound technique in combination with other pre-treatment techniques such as pre-treatment using the deep eutectic solvents, acids, alkalis (these are all that we have discussed in our last class) have been widely used as a part of the hybrid process of pre-treatment. Please understand that this is whatever written here, the hybrid is not only restricted to this. There are many numbers of studies. We will just discuss few of them to get an idea about actually a how and why this hybrid processes have been adopted.

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## Hybrid Pretreatment Methods

### ☐ Microwave Assisted Methods

- Microwave technology can be combined with other pretreatment technologies to increase the efficiency of the process.
- Microwave technology has been successfully applied with :
  - a) *Deep Eutectic Solvents (DES) Pretreatment*
  - b) *Alkali Pretreatment*
  - c) *Acid Pretreatment*



So, we will see the microwave-assisted method, which is one of the most common and a low-cost method and faster process also we will discuss that. So microwave technology can be combined with other pre-treatment technologies to increase the efficiency of the process. So, Microwave Technology has been successfully applied along with deep eutectic solvents pre-treatment, DES, Alkali pre-treatment and acid pre-treatment usually dilute acid pre-treatment. **(Refer Slide Time: 03:31)**

## Microwave Technology combined with DES Pretreatment

### Application in switch grass, corn stover, and miscanthus feedstocks



Figure 1: Switch grass  
Source: Dennis Primmington, Farm Energy, 2019



Figure 2: Corn stover  
Source: Jessica Ester, p109.org, 2012

- Microwave technology combined with the use of DES pretreatment was applied to ultrafast fractionation of **switch grass, corn stover, and miscanthus** feedstocks.
- The combination of microwave irradiation and ChCl and lactic acid over only 45 seconds resulted in highly effective lignin and hemicellulose removal and left the cellulose intact.
- This kind of pretreatment allowed the removal of more hemicellulose than lignin.
- Additionally, microwaves significantly improved the efficiency of the pretreatment by DESs.

Chen et al., *Biomass Technology* 250 (2018) 512-517



Let us have a look at this hybrid technology application in the switchgrass, corn stover and miscanthus feedstocks. Microwave technology combined with the use of DES pre-treatment was applied to ultrafast fractionation of switchgrass, corn stover and miscanthus feedstocks. The combination of Microwave irradiation and ChCl and lactic acid over only 45 seconds resulted in a highly effective lignin and hemicellulose removal and left the cellulose intact.

Please understand it is very faster process 45 seconds only. Now this kind of pre-treatment allowed the removal of more hemicellulose than lignin. Additionally, microwave significantly improve the efficiency of the pre-treatment by DES. So overall we can say that it is an excellent hybrid system.

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Figure 3: Miscanthus  
Source: Amann et al.

- The electromagnetic field of microwaves led to breakdown of the biomass structure, mainly due to molecular collision caused by dielectric polarization.
- In addition, microwave radiation increased the molecular polarity of DES, which enhanced the efficiency of the pretreatment.
- Pretreated biomass showed a two- to five-fold increase in digestibility during enzymatic hydrolysis in comparison to untreated feedstock.

Chen et al., *Bioresour Technol* 259 (2018) 512–517



So, the electromagnetic field of microwaves led to the breakdown of the biomass structure mainly due to molecular collision caused by dielectric polarization. In addition, microwave radiation increases the molecular polarity of DES which enhance the efficiency of the pre-treatment. Pre-treated biomass showed a 2 to 5, fold increase in digestibility during enzymatic hydrolysis in comparison to the untreated feedstock.

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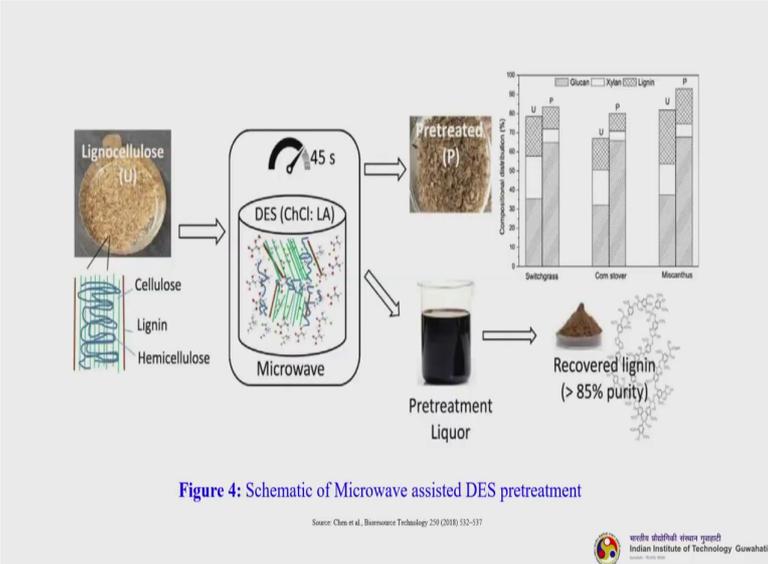


Figure 4: Schematic of Microwave assisted DES pretreatment

Source: Chen et al., *Bioresour Technol* 259 (2018) 512–517



Now, please have a look at this particular schematic of the microwave assisted DES pre-treatment. So, this is the lignocellulosic Biomass whatever it can be miscanthus, corn stover whatever we have discussed, switch grass. So, then it has been put it under a microwave reactor. Along with that DES in different concentrations of course because you need to optimise it, the process parameters.

So, you can see within 45 seconds they have degraded and result into 2 two different fractions. So, one fraction is basically pre-treatment liquor which is thick, viscous and brown in colour this colour. And then another one is the solid residue. That solid residue basically contain glucose and Xylan; basically you can say that it contains your carbohydrates. And this part which is dark in colour it contains lignin mostly.

But depending upon the efficiency of the process. It will always happen that some of the carbohydrates remains here and some of the Lignin also remains there.

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**Microwave Technology combined with Acid Pretreatment**

➤ **Application in Jabon tree**



- Microwaves with the presence of the acid intensified the decomposition of biomass during the Jabon tree pretreatment, which allowed obtaining a higher yield of sugars.
- Despite the increased efficiency in removal of lignin with the time of irradiation, the formation of side products occurred, which affected further processing.

**Figure 5:** Jabon tree  
Source: Greenagat

Ferreira et al., Waste and Biomass Valorization (2019) 10:1503–1517

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So, microwave technology combined with acid pre-treatment. So, one application is in with Jabon tree Biomass. So, Microwave with the presence of the acid, intensified the decomposition of biomass during the Jabon tree pre-treatment which allowed obtaining higher yield of sugars. Despite the increased efficiency in removal of Lignin with the time of irradiation the formation of side products occurs, which affected further processing.

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## Microwave Technology combined with Alkali Pretreatment

### ➤ Application in brewers' spent grains (BSG)



Figure 6: BSG  
Source: [20]16, Wikimedia Commons

- Microwave-assisted alkali was found as the most effective pretreatment among studied techniques (SE, AFEX, dilute acid, organosolv) used for reducing sugar production by enzymatic hydrolysis of brewers' spent grains (BSG).
- After treatment with a combination of microwaves and alkali, the surface of BSG increased due to disruption of the structure of the investigated material which resulted in larger sugar yield in comparison to the use of other pretreatment methods.

R. Parvatham et al. *Bioresour Technol* 248 (2018) 272–279

Then a microwave combined with alkali pre-treatment. Application in brewers' spent grains (BSG). So, microwave assisted alkali was found as the most effective pre-treatment among others studied techniques such as your steam explosion, Ammonia fibre explosion, then dilute acid, organosolv used for reducing sugar production by enzymatic hydrolysis of brewers spent grains that is called BSG.

After treatment with the combination of Microwave and alkali the surface of the BSG increase due to disruption of the structure of the investigated material which resulted in larger sugar yield in comparison to the use of the other pre-treatment methods.

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### ❖ Process

- A domestic microwave with a maximum output power of 800 W was employed for this purpose.
- 1% (w/v) biomass was loaded to 0.5% NaOH (w/v) solution in a stoppered flask and subjected to microwave radiation at varying power settings of 400 W, 560 W and 800 W for different residence time varying from 30 s, 60 s and 120 s.
- After pretreatment, the biomass was thoroughly washed with distilled water till pH 6.0 and dried in air.
- The dried solid residue was used for enzymatic hydrolysis and compositional analysis.

R. Parvatham et al. *Bioresour Technol* 248 (2018) 272–279

So, the process is described here in brief. So, a domestic Microwave with the maximum output power of 800 watts was employed for this purpose. 1% weight by volume biomass

was loaded to 0.5% Sodium Hydroxide weight by volume in a stoppered flask and subjected to microwave irradiation at varying power settings of 400 watts, 560 watts and 800 watts for different residence times varying from 30 second, 60 seconds and 120 seconds.

Please understand again I am telling you that the microwave techniques at superfast techniques. It is very faster than any other pre-treatment processes, even if you are combining two processes or talking about a single process also. After pre-treatment the Biomass thoroughly washed with distilled water till pH 6 and dried in air. The dried solid Residue was used for enzymatic hydrolysis and composition analysis because the that dried solid residue contains most of the carbohydrates.

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- Comprehensive studies on the effect of microwave alkali pretreatment on the crystallinity index, specific surface area, and morphology of BSG were also performed by *Kan et al. (2018)*.
- It was shown that the pretreatment of BSG caused removal of lignin from the feedstock structure and significant growth of the specific surface area from 9 m<sup>2</sup>/g for raw to 162 m<sup>2</sup>/g for the treated sample.
- The treatment of the investigated samples with alkali in the presence of microwaves assures effective removal of hemicellulose and lignin from the lignocellulosic material.
- However, the presence of a large amount of NaOH resulted in degradation of the crystalline part of cellulose, while the high microwave power and extended treatment time led to degradation of the organic fraction of cellulose, which reduced the efficiency of further processing.

Kan et al., Energy Conversion and Management 159 (2018) 115–126



Comprehensive studies on the effect of microwave alkali pre-treatment on the crystallinity index, specific surface area and morphology of BSG were also performed by Kan et al. This particular publication has been referred here. So, it is an interesting work. So those who wish to read more can please refer to this particular citation, which is given below. So, it was shown that the pre-treatment of BSG caused removal of Lignin from the feedstock structure and significant growth of the specific surface area from 9 m<sup>2</sup>/g for raw Biomass to 162 m<sup>2</sup>/g for treated samples. A huge surface area increase.

The treatment of the investigated samples with alkali in the presence of microwave assures effective removal of hemicellulose and Lignin from the lignocellulosic materials. However, the presence of a large amount of sodium hydroxide resulted in degradation of the crystalline and part of cellulose, while the high microwave power and extended treatment time led to

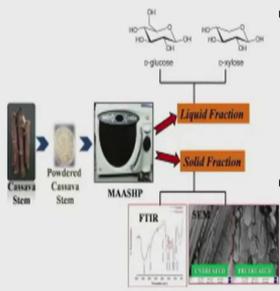
degradation of the organic fraction of cellulose which reduced the efficiency of further processing.

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➤ **Application in cassava stem**



Figure 7: Cassava stem  
Source: Panniquart



- Similar observations were noted for combined microwave and alkali pretreatment of cassava stem for sugar production which depended on reaction time, base concentration, solid to liquid ratio, and microwave frequency.
- Microwave frequency was found to be the most significant factor affecting sugar yield, and the importance of other parameters decreased in the following order: *reaction time, solid to liquid ratio, and base content.*
- Microwave with alkali treatment increased the crystallinity index of cassava stem, removing all its amorphous parts.

A. Kamalin et al., *Journal of Molecular Liquids* 254 (2018) 35-43



So, we will see the systems this hybrid process application in Cassava stem hydrolysis. So, similar observations were noted for combined microwave alkali pre-treatment of cassava stem for sugar production which depended on reaction time, base concentration, solid to liquid ratio and microwave frequency. So, microwave frequency was found to be the most significant factor affecting the sugar yield.

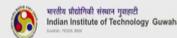
And the importance of other parameters decreases in the following order, reaction time, solid to liquid ratio, base content. So, the authors have varied basically the 4 different types of parameter. The first one is of course the microwave frequency which was found to be the most important parameter that is affecting the sugar yield followed by the others like reaction time, solid to liquid ratio and the base content. So, Microwave with alkali treatment increases the crystallinity index of cassava stem removing all its amorphous parts.

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#### Comparison of acid and alkali assisted microwave pretreatment in Cassava bioconversion

- The methods of microwave pretreatment with alkali and microwave with acid were compared for efficiency in cassava bioconversion.
- In both methods, the microwave power and process time were indicated as the main factors providing high efficiency of the initial treatment.
- It was exhibited that the yield of sugars during enzymatic cassava hydrolysis was 52% higher after microwave-assisted sodium hydroxide treatment in comparison to the microwave assisted sulfuric acid treatment.
- Differences in the performance of two types of pretreatment result from the presence of inhibitors of enzymatic hydrolysis, which are generated during the microwave acidic method. In general, the acid solubilizes hemicellulose, while the base solubilizes lignin, and the application of microwaves only intensifies chemical processing.

Sulka et al., Environ. Prog. Sustain. Energy 37 (1), 577-583



And now we can discuss the comparison of acid and alkali assisted microwave pre-treatment in cassava bioconversion. So, you have seen the individual processes clubbed with Microwave. Now, we will discuss about the comparison. So, the methods of microwave pre-treatment with alkali and Microwave with acid were compared for efficiency in cassava bioconversion. In both methods the microwave power and the process time were indicated as the main factors providing high efficiency of the initial treatment.

It was exhibited that the yield of Sugars during enzymatic cassava hydrolysis was 52% higher after microwave-assisted Sodium Hydroxide treatment in comparison to the microwave assisted sulphuric acid treatment. Differences in the performance of two types of pre-treatment results from the presence of inhibitors of enzymatic hydrolysis, which are generated during the microwave acidic method.

In general, the acid solubilizes the hemicellulose whereas the base solubilizes lignin. So, this the mechanism. And the application of microwave is only intensifying the chemical processing.

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## Hybrid Pretreatment Methods

### □ Ultrasound Assisted Methods

- Ultrasound technology can be combined with other pretreatment technologies to increase the efficiency of the process.
- Ultrasound technology has been successfully applied with :
  - a) *Ionic Liquids (ILs) Pretreatment*
  - b) *Alkali Pretreatment*
  - c) *Enzymatic Pretreatment*



Now we will discuss about the ultrasound assisted methods. So, ultrasound technology can be combined with other pre-treatment technologies to increase the efficiency of the process. Now Ultrasound Technology has been successfully applied with ionic liquids pre-treatment, alkali pre-treatment and enzymatic pre-treatment. For your information I am telling you can read little more about ultrasonication processes. In a nutshell I am telling you that this is also one of the very good technology or the process which is also a faster process compared to other such pre-treatment processes. And it is also low cost.

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### Ultrasound Technology combined with ILs Pretreatment

#### ➤ Application in sugarcane bagasse and wheat straw



Figure 8: Sugarcane bagasse

Source: Anna Foodbank, Wikimedia Commons



Figure 9 : Wheat straw

Source: Amazon.com

Yu et al., Ultrasonics - Sonochemistry 41 (2018) 418–418

- Ultrasound combined with the ILs effectively improved the process of saccharification of sugarcane bagasse and wheat straw.
- ILs, by forming hydrogen bonds with cellulose, disrupted its crystalline structure, while ultrasound treatment through the mechanical effect opened the biomass structure and intensified the chemical interaction of ILs.
- The combined method significantly *improved the efficiency of enzymatic reduction of sugars* compared to biomass treated only with ILs.



We will see the ultrasound Technology combined with IL's treatment in its application in the sugarcane bagasse and wheat straw. So, ultrasound combined with the ionic liquids effectively improve the process of saccharification of sugarcane bagasse as well as wheat straw. Ionic liquids by forming hydrogen bonds with cellulose disrupted its crystalline

structure while ultrasound treatment through the mechanical effect opened the biomass structure and intensified the chemical interaction of the ionic liquids.

The combined method significantly improves the efficiency of enzymatic reduction of Sugars compared to Biomass treated only with ionic liquid.

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❖ *Process*

- One gram of biomass (bagasse or wheat straw) was dispersed in 20 g of ionic liquid ([Bmim] Cl or [Bmim]OAc) in a double-jacketed beaker.
- Sonication was performed by a single-frequency countercurrent flow ultrasound reactor.
- The sonication system was operated at five frequencies, viz, 20, 28, 35, 40 and 50 kHz.
- Five probes with diameters of 1.34, 3.61, 3.05, 2.03 and 1.05 cm were used for the frequencies of 20, 28, 35, 40 and 50 kHz, respectively.
- After completion of the reaction, two volumes of deionized water were added to the reaction mixture. The mixture was stirred at 600 rpm by using a magnetic stirrer and filtered under suction to remove as much liquid as possible.
- The filtered biomass was soaked in ethanol, filtered again, washed three times with deionized water, dried to a constant weight and kept for further analysis.



So, we will see in brief the process how it was carried out. So, 1 gram of biomass anything either bagasse or wheat straw was dispersed in 20 grams of ionic liquids (so, in this case the [Bmim] Cl or [Bmim] OAc) in a double jacketed beaker. Sonication was performed by a single frequency counter current flow ultrasound reactor. The sonication system was operated at 5 frequencies 20, 28, 35, 40 and 50 kilo hertz.

Five different probes with diameters of 1.34, 3.61, 3.05, 2.03 and 1.05 (cm) were used for the frequencies of 20, 28, 35, 40 and 50 kilo hertz respectively. After completion of the reaction 2 volumes of deionized water were added to the reaction mixture. The mixture was stirred at 600 RPM by using a magnetic stirrer and filter under suction to remove as much liquid as possible. The filtered biomass was soaked in ethanol, filtered again, washed 3 times with deionized water, dried to a constant weight and kept further analysis.

So, this is a nut shell I just told you about the process how ultrasound-assisted ionic liquid pre-treatment method was carried out. So, one beautiful thing about the entire hybrid system is that as you know that there are so many different types of ionic liquids available or one can

tailor make ionic liquid in the lab. So, as I told you in the last class you need to take a cation and you need to take anion and fuse them together to obtain a ionic liquid.

So, if you can study the chemistry little more - chemistry of the Biomass, its structure and all, so then we can understand that what type of ionic liquid will be better suited for that particular biomass. So, with that type of study we can include those for doing the experimentation with ultrasound-assisted ionic liquid pre-treatment.

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**Ultrasound Technology combined with enzymatic hydrolysis**

➤ **Application in peanut shells, coconut shells, and pistachio shells**

- The mechanical effect of ultrasound treatment on the biomass structure can intensify the sodium hydroxide performance during the combined pretreatment of peanut shells, coconut shells, and pistachio shells before enzymatic hydrolysis to sugars.
- Ultrasound enhanced the rate of delignification by morphological changes caused by intense turbulence and shear effects.
- In addition, ultrasound created free radicals in water taking part in the cleavage of lignin and xylan structure.
- The use of this combined process, besides *intensified delignification*, *reduced the time of the process* and *the amount of alkali*, leading to a higher sugars yield.

P.B. Sahadeo et al. Ultrasonics Sonochemistry 40 (2018) 140–150

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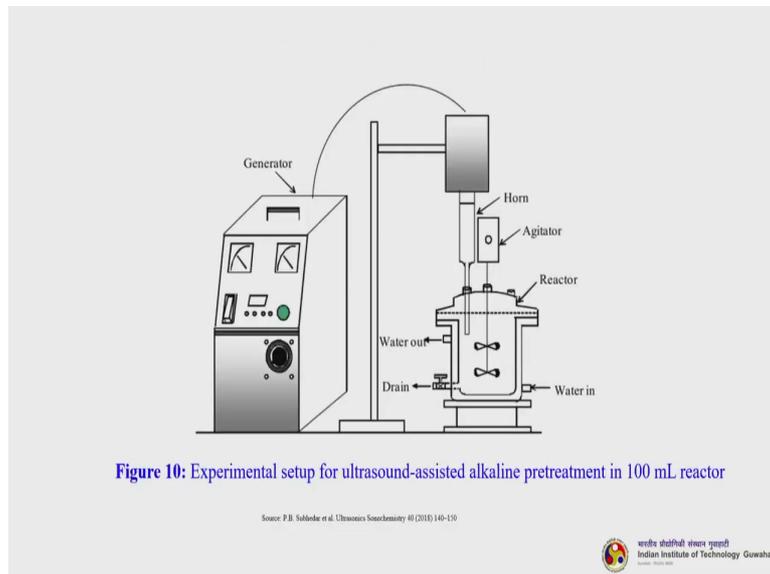
Now, the next one is ultrasound Technology combined with enzymatic hydrolysis. So we will discuss its application in peanuts shells, coconut shells and pistachio shells. The mechanical effect of ultrasound treatment on the Biomass structure and intensify the Sodium Hydroxide performance during the combined pre-treatment of peanut shells, coconut shells and pistachio shells before enzymatic hydrolysis to sugars.

Ultrasound enhance the rate of the delignification by morphological changes caused by intense turbulence and shear effects. In addition, ultrasound created free radicals in water taking part in the cleavage of Lignin and Xylan structure. The use of this combined process besides intensified delignification reduce the time of the process and the amount of alkali leading to the higher sugar yield.

As such this was proved to be a very good hybrid process. It has resulted in a more delignification. It has reduced the time of the entire process and the amount of alkali that is

being used earlier, or if you compared to the single alkali pre-treatment process so thereby resulting in a higher sugar yield.

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This is the experimental setup for ultrasound assisted alkaline pre-treatment in 100 ml batch reactor. This is a reactor simple reactor chemical reactor. So, this is the ultrasound generator, and this is the ultrasound gun or probe whatever you can say. This is the reactor and this is a jacketed reactor - you need to cool it in case the heat is evolving, and it is a stirred reactor. Stirring will further enhance the mass transfer or the rate of reaction. And it is a simple system and can be done in lab easily.

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➤ **Comparison of IL and alkali assisted ultrasound pretreatment in eucalyptus**

**Figure 11:** Eucalyptus  
Source: Ethel Azevedo, Wikimedia commons

- Wang et al. (2018) compared the effect of the ultrasound-assisted IL and alkaline pretreatment methods on the structure and chemical composition of eucalyptus and the yield of its enzymatic saccharification.
- It was shown that *ultrasound in combination with IL was more efficient in the delignification process*, while *ultrasound in combination with alkaline was more efficient in removal of hemicellulose* from the eucalyptus structure.
- In addition, ultrasound combined with ILs removed the amorphous fraction during pretreatment more effectively than alkali combined with ultrasound. As a consequence, higher yield of sugars could be obtained in the first case.

Wang et al. *Bioresource Technology*, 254, 2018, 145-150

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Now we will discuss about the comparison of the ionic liquid and alkali assisted ultrasound pre-treatment for eucalyptus. Wang et al compared the effect of the ultrasound-assisted ionic

liquid and alkaline pre-treatment methods on the structure and chemical composition of eucalyptus and the yield of its enzymatic saccharification. It was found that ultrasound in combination with ionic liquid was much more efficient in the delignification process while ultrasound in combination with alkaline was a more efficient in removal of the hemicellulose from the eucalyptus structure.

So, in addition ultrasound combined with ionic liquids remove the amorphous fraction during the pre-treatment more effectively than alkali combined with ultrasound. As a consequence, higher yield of Sugars could be obtained in the first case that means ultrasound followed by ionic liquids.

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**Table 1: Selected Examples of the Studies Concerning Application of Combined Methods**

Type of Biomass	Treatment	Chemical	Pretreatment Conditions	Efficiency the Process
Switchgrass Corn stover Miscanthus	• Microwave (800 W) + deep eutectic	Choline chloride (ChCl): lactic acid 1:2	Temperature: 25°C–152°C Time of residence: 45 s	• 2–5-fold increase in enzymatic hydrolysis, 74% glucose yield
Jabon kraft pulp	• Microwave (1000 W) + acid	1% H <sub>2</sub> SO <sub>4</sub>	Temperature: 180°C, 190°C, and 200°C Time of residence: 5, 7, 10 min	• Optimal temperature 190°C • Reducing sugar yield increases of around 40 g/100 g dry pulp
Brewer's spent grain	• Microwaves (400–800 W) alkali	0.5% NaOH	Time of residence: 30, 60, 120 s	• In enzymatic hydrolysis of reducing sugars –228.25 mg of reducing sugar/g of BSG compared to native BSG (79.67 mg/g of BSG)
Brewer's spent grain	• Microwaves (40–500 W) alkali	1% NaOH	Temperature: 31°C–259°C Time of residence: 2–6 min	• Under optimized conditions, removal of 46% of lignin and 38% of hemicellulose contributing to a 52% increase in biomethane production was observed
Cassava stem	• Microwaves (360–720 Hz) alkali	2%–4% NaOH	Time of residence: 60–120 s	• Optimal conditions: 116 s, 3.21% NaOH, 719 Hz • After pretreatment, the cellulose content of cassava stem was increased from 33.27% to 52.34%, while the hemicellulose and lignin contents were decreased from 32.30% to 27.15% and 27.15%, 14.59%, respectively • Reducing sugars 43.60 µg/mL in liquid fractions

Source: Marcar et al., The evolution of Biofuels, 2019

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So, we will see some of these results which are reported in Literature and I have tabulated here. The reference is given here from where this table have been taken. These are some selected examples where studies concerning the applications of the combined methods or hybrid method. So, all type of biomass, the different treatment method, the chemicals that are being used, then the predetermined conditions very important - this last class also I discussed, again I am telling so this is actually very important. You need to optimise the process parameters. You need to vary the range of reaction time or residence time, the temperature - if at all it is there, the amount of chemicals you're using, the amount of energy, the type of solvents, all these things are there and the efficiency of the processor. Let us see one thing we have not discussed about this one Jabon tree craft pulp.

So, it is a microwave of almost 1000 watts plus acid, in which they have used only 1% sulphuric acid and the conditions are - temperature 180 degrees centigrade, 190 and 200 degrees, that is what they have varied, three different sets of temperature and three different sets of residence time 5 minutes, 7 minutes and 10 minutes. So, the result is very interesting. So optimal temperature they found it is 190 degrees centigrade and reducing sugar yield increases of around 40 grams per 100 gram of dry pulp, which is a good yield.

Please understand the yield of sugar is directly related to type of biomass because first of all every Biomass are distinct in their composition. So, if the carbohydrate fraction is more, then we are going to get more sugar. And if the lignin is more, compared to carbohydrates, the reducing sugar yield will be of course less. Let us move ahead.

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Cassava pulp	<ul style="list-style-type: none"> <li>• Microwaves (120–160 W) acid</li> <li>• Microwaves (120–160 W) alkali</li> </ul>	1%–4% NaOH 1%–4% H <sub>2</sub> SO <sub>4</sub>	Time of residence: 40 min	<ul style="list-style-type: none"> <li>• Optimal conditions: 18 min; 2.27% NaOH; 125 W</li> <li>• Reducing sugars 0.472 g/g dry biomass</li> <li>• Optimal conditions: 25 min; 1.95% H<sub>2</sub>SO<sub>4</sub>; 135 W</li> <li>• Reducing sugars 0.306 g/g dry biomass</li> </ul>
Sugarcane bagasse, wheat straw	<ul style="list-style-type: none"> <li>• Ultrasound (20–50 kHz) ILs</li> </ul>	1. 1-Butyl-3-methylimidazolium chloride, 2. 1-Butyl-3-methylimidazolium acetate	Temperature: 80°C Time of residence: 30 min	<ul style="list-style-type: none"> <li>• Reducing sugars 0.306 g/g dry biomass</li> <li>• 1. Optimal conditions: 30 min, 80°C, 20 kHz, glucose yield 40% and 53% for bagasse and wheat straw respectively</li> <li>• 2. Optimal conditions: 30 min, 80°C, 40 kHz, glucose yield 33% and 48% for bagasse and wheat straw respectively</li> </ul>
Peanut shells, coconut coir, and pistachio shells	<ul style="list-style-type: none"> <li>• Ultrasounds 100 W alkali</li> </ul>	4% NaOH	Time of residence: 70 min	<ul style="list-style-type: none"> <li>• Delignification efficiency increased after combined treatment in comparison to alkaline one (alkaline treatment of peanut shells, coconut coir, and pistachio shells allowed for 41.8%, 45.9%, and 38% delignification while the combined method gave 71.1%, 89.5%, and 78.9% efficiency, respectively)</li> </ul>
Eucalyptus sawdust	<ul style="list-style-type: none"> <li>• Ultrasound (280, 360 W) IL</li> <li>• Ultrasound (280, 360 W) alkaline</li> </ul>	1. 12.5% or 20% Tetrabutyl ammonium hydroxide (TBAOH) 2. 0.5–0.8 mol NaOH	Temperature: 60°C Time of residence: 30, 60 min	<ul style="list-style-type: none"> <li>• Optimal conditions: 12% TBAOH; 360 W; 60°C; 60 min</li> <li>• Reducing sugar yield of 426.6 mg/g for IL-ultrasound (increased by 317% and 62% in comparison to untreated and ultrasound alkaline method, respectively)</li> </ul>
Corn stover	<ul style="list-style-type: none"> <li>• Alkaline twin-screw extrusion (ASTE)</li> </ul>	NaOH	Temperature: 99°C Time of residence: 1 h	<ul style="list-style-type: none"> <li>• The enzymatic hydrolysis efficiencies of glucan and total sugar yield of ATSE-treated samples were 87.47% and 78.75% compared to 61% and around 55% after alkaline pretreatment</li> </ul>

There are many I have listed here. So, if you see this sugarcane bagasse, wheat straw which was ultrasound with ionic liquids. So, they have used 20 - 50 kilo hertz, in that range they have varied. 1-Butyl-3-methylimidazolium chloride (Bmim Cl basically) and they have used also Bmim Acetate (OAc) and the temperature is 80 degrees centigrade, time of residence is 30 minutes. So that is again in this case that are optimised.

So, they have put that optimal condition 30 minutes, 80 degrees centigrade, 20 kilohertz and with the glucose yield of 40% and 53% for bagasse and wheat straw respectively, which is again very good in terms of glucose yield. So similarly, there are so many things as listed here. So, what I request is that you can please go through all these things.

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Type of Biomass	Treatment	Chemical	Pretreatment Conditions	Efficiency the Process
Corn stover	• Alkaline oxidative (AlkOx)	10 M NaOH/H <sub>2</sub> O <sub>2</sub>	Temperature: 60°C Time of residence: 5 h	• Combined method dissolves 93.4% and 83.5%, of lignin and hemicellulose, respectively
Sugarcane bagasse	• Ultrasound-AlkOx	0.1–0.3 M NaOH/H <sub>2</sub> O <sub>2</sub>	Temperature: 60°C Pressure: 3 bar Time of residence: 10 min	• For optimal conditions: 0.3 M NaOH, 10 min 62% lignin removal and 95% of digestibility of cellulosic fraction were achieved
Debarked white birch chips	• Steam alkali (TCP)	NaOH	Temperature: 140°C	• 10% and 5% lignin and hemicellulose removal. The sugar yield of the raw biomass was 4.42% and increased to 28.44% for TCP pretreatment
Sugarcane bagasse	• Steam and hydrogen peroxide	0.2 and 1% H <sub>2</sub> O <sub>2</sub>	Temperature: 210°C Time of residence: 15 min	• Average yield increase: 12% for glucose and as high as 34% for xylose; cellobiose yield was decreased by about 30%

We are still continuing; these are some of the more different types of hybrid treatments given here. So, corn stover Biomass alkaline oxidative treatment (AlkOx it is called). So the chemical used is 10 molar sodium hydroxide, along with the hydrogen peroxide. Temperature is 60 degrees centigrade, time of residence is 5 hours; so it takes long time. So, it was found that combined method dissolves 93.4% and 83.5% of Lignin and hemicellulose respectively, which is a very good result.

Now then ultrasound followed by AlkOx (sugarcane bagasse), then steam alkali pre-treatment (debarked white birch chips), then steam and hydrogen peroxide combined (sugarcane bagasse). Now we have discussed certain hybrid pre-treatment technology in today's class. There are many, everything it is not possible to discuss in a single class and is also out of the scope of this particular course. So the idea is to make you understand that how the hybrid processes works and it is always not true that you can just combined two any different processes and a look for that.

You can do some experiment to find out which is good or which is bad but there should be some theoretical understanding that which particular two different pre-treatment methods should be combined and why and how they will be combined. So, I hope you get an understanding about the different hybrid processes.

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## Other Combined Pretreatment Methods

### □ Alkaline treatment combined with mechanical extrusion

- As mentioned earlier, the alkaline pretreatment method is one of the most commonly used methods for pretreatment of lignocellulosic materials.
- However, alkaline treatment combined with mechanical extrusion enhanced noticeably the removal of lignin and hemicellulose from the corn stover structure.
- The use of a combined mechanical-alkaline method increased the yield of sugars by about 25% in comparison to the yield obtained after alkaline treatment solely.
- Both methods ensured destruction of the corn stover structure.
- The combination of mechanical and alkaline treatment allows for not only disruption of the recalcitrance of the biomass structure, but can also be useful in further processing.

Lu et al., Fuel 221 (2018) 21–27



So, we will just discuss briefly about other combined treatment methods. So, alkaline pretreatment combined with mechanical extrusion. So, as mentioned earlier the alkaline pretreatment method is one of the most commonly used methods for pre-treatment of lignocellulosic materials. However, alkaline treatment combined with mechanical extrusion enhance noticeably the removal of Lignin and hemicellulose from the corn stover structure. The use of a combined mechanical alkaline method increases the yield of Sugars by about 25% in comparison to the yield obtained after alkaline treatments only.

Both methods ensure destruction of the corn stover structure. The combination of mechanical and alkaline treatment allows for not only disruption of the recalcitrance of the Biomass structure, but can also be useful in further processing.

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### □ Alkaline pretreatment in the presence of hydrogen peroxide (AHP)

- AHP is an oxidative pretreatment process. It acts in the delignification of the lignocellulosic biomass which allows a greater efficiency to be achieved in the recovery of sugars in the liquid phase of enzymatic hydrolysis since the presence of lignin makes it difficult for the enzymes to attack the substrate.
- Hydrogen peroxide is unstable in alkaline conditions and decomposes, which generates hydroxyl radicals and superoxides. It can result in an increase in the efficiency of delignification of biomass.
- The effectiveness of the alkaline pretreatment with hydrogen peroxide depends on the reaction conditions, such as the amount of biomass to be treated, time, temperature, and concentration of peroxide and base.
- This type of pretreatment has low-energy consumption and does not generate inhibitors like hydroxymethylfurfural and furfural.

Datta et al., Biomass Conv. Bioref. (2015) 9:225–234



Alkaline pre-treatment in the presence of hydrogen peroxide. It is called AHP. So AHP is an oxidative pre-treatment process. It acts in the delignification of the lignocellulosic Biomass which allows a greater efficiency to be achieved in the recovery of Sugars in the liquid phase of enzymatic hydrolysis since the presence of Lignin makes it difficult for the enzymes to attack the substrate.

The hydrogen peroxide is very unstable in alkaline conditions and decomposes very fast. So that generate hydroxyl radicals and superoxide it can result in an increase in the efficiency of delignification of biomass. The effectiveness of the alkaline pre-treatment with hydrogen peroxide depends on the reaction conditions such as the amount of biomass to be treated, time, temperature and concentration of peroxide and base.

This type of pre-treatment has low energy consumption and does not generate inhibitors like hydroxymethylfurfural and furfurals. So, this is one of the best take-home-message from this particular AHP study, that, they do not generate the inhibitors; because this inhibitors HMF and furfurals and then some other intermediates they have a very bad effect on the further fermentation process.

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➤ **Application in Corn straw and Gooseweed**

- The use of a combined sodium hydroxide and hydrogen peroxide pretreatment of corn straw resulted in the removal of 93% lignin and 83% hemicellulose from the structure of the raw material.
- Effective treatment of the main components of lignocellulose during the enzymatic hydrolysis allowed the achievement of 61% conversion of cellulose to glucose and 69% conversion of hemicellulose to xylose.
- On the other hand, alkali and hydrogen peroxide did not make any difference to sugar yield obtained in gooseweed pretreatment before bioethanol production (Vu et al., 2018).
- Combined sodium hydroxide and hydrogen peroxide treatment released an equal amount of sugars in comparison to the use of the alkaline pretreatment method, therefore the researchers indicated that it is more economically justified to use only an alkaline pretreatment (Vu et al., 2018).

Vu et al., DOI: <http://dx.doi.org/10.1155/ELSR.2017.131019>

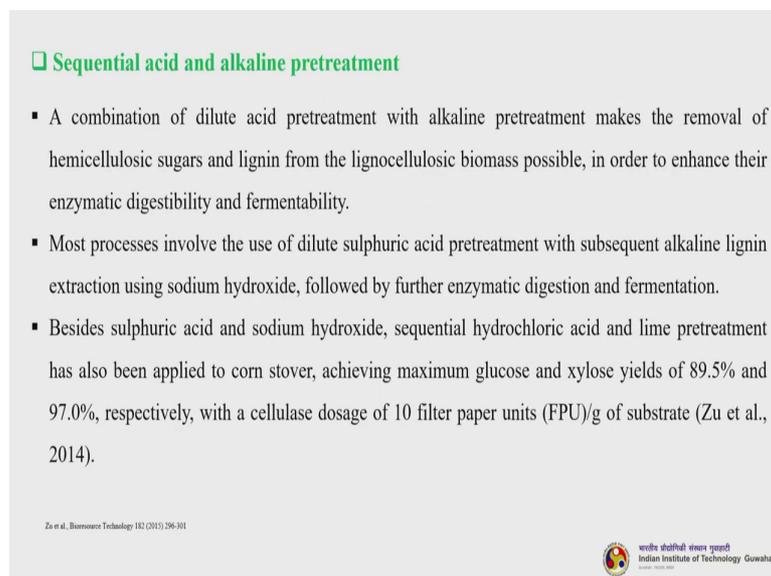
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Indian Institute of Technology Guwahati  
2017-2018

So, we will see its application in corn straw and gooseweed. The use of a combined sodium hydroxide and hydrogen peroxide pre-treatment (the AHP pre-treatment) of corn straw result in the removal of 93% of Lignin and 83% of hemicellulose from the structure of the raw material. Effective treatment of the main components of lignocellulose during the enzymatic

hydrolysis allowed the achievement of 61% conversion of cellulose to glucose and 69% conversion of hemicellulose to xylose.

And on the other hand, alkali and hydrogen peroxide did not make any difference to sugar yield obtained in Gooseweed pre-treatment before bioethanol production. Combined sodium hydroxide and hydrogen peroxide treatment released an equal amount of sugar in comparison to the use of the alkaline pre-treatment method. Therefore, the researchers have indicated that it is more economically justified to use only an alkaline pre-treatment method.

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**Sequential acid and alkaline pretreatment**

- A combination of dilute acid pretreatment with alkaline pretreatment makes the removal of hemicellulosic sugars and lignin from the lignocellulosic biomass possible, in order to enhance their enzymatic digestibility and fermentability.
- Most processes involve the use of dilute sulphuric acid pretreatment with subsequent alkaline lignin extraction using sodium hydroxide, followed by further enzymatic digestion and fermentation.
- Besides sulphuric acid and sodium hydroxide, sequential hydrochloric acid and lime pretreatment has also been applied to corn stover, achieving maximum glucose and xylose yields of 89.5% and 97.0%, respectively, with a cellulase dosage of 10 filter paper units (FPU)/g of substrate (Zu et al., 2014).

Zu et al., Bioresource Technology 182 (2015) 296-301

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So, the next combined method is sequential acid and alkaline pre-treatment. This is a very interesting study reported in Bioresource technology, the reference is given if you are interested to learn more in detail, please refer and read. So, a combination of dilute acid pre-treatment with alkaline pre-treatment makes the removal of hemicellulosic Sugars and Lignin from the lignocellulosic Biomass possible in order to enhance their enzymatic digestibility and fermentability.

Most processes involve the use of dilute sulphuric acid pre-treatment with subsequent alkaline Lignin extraction using Sodium Hydroxide followed by further enzymatic digestion and fermentation. Besides sulphuric acid and sodium hydroxide, sequential hydrochloric acid and lime pre-treatment has also been applied to corn stover achieving maximum glucose and xylose yields of 89.5% and 97% respectively with the cellulase doses of 10 filter paper units per gram of substrate.

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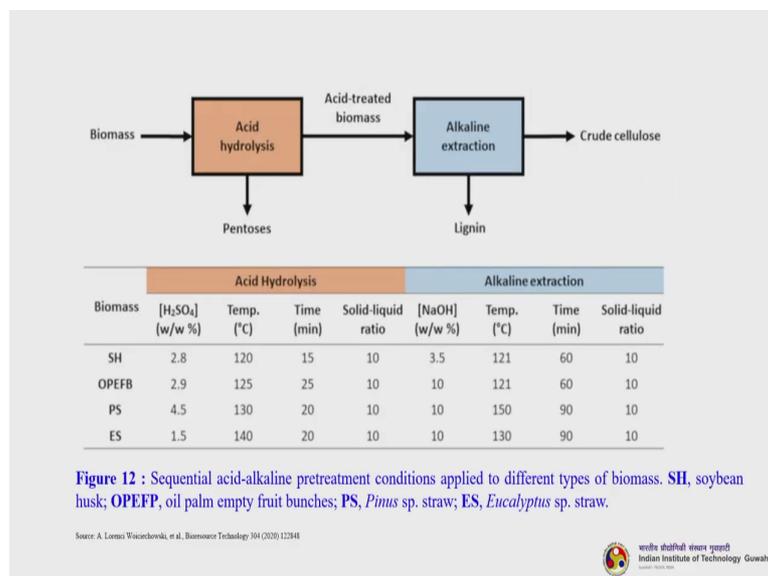
- The solid material resulting from sequential pretreatment shows a higher crystallinity index (CI), as the amorphous contributions from hemicellulose and lignin were removed.
- In addition, depending on the severity of the alkaline pretreatment, cellulose crystallinity is decreased due to polymorphic transformation of cellulose from type I to type II.
- This phenomenon results in higher enzymatic digestibility of the cellulose-rich material.

A. Lemos Wacziargowski, et al., *Bioresour Technol* 304 (2020) 122848



So, the solid material that is resulting out of the sequential pre-treatment shows a higher crystallinity index, as the amorphous contributions from hemicellulose and Lignin were removed. In addition, depending on the severity of the alkaline treatment cellulose crystallinity is decreased due to the polymorphic transformation of cellulose from type 1 to type 2. This phenomenon results in higher enzymatic digestibility of cellulose rich material.

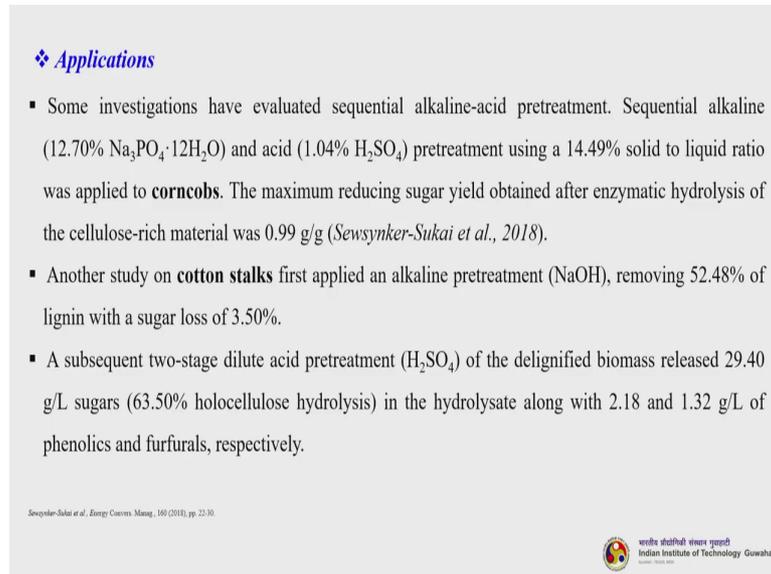
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So, these are the process conditions and the schematic. So Biomass is (subjected to) a process standard acid hydrolysis. So, you get pentoses or the C5 sugars. Then the acid treated biomass is being sent to a alkaline extraction system where you get actually Lignin as the bottom or the product which are there in the liquid fraction and you get the crude cellulose in the solid fraction. So, this is the different process condition.

So here the authors actually have studied four different types of biomass. First one is soybean husk, second one is oil palm empty fruit bunches, third is Pinus species straw and the fourth one is Eucalyptus straw. Now a different process conditions both for Acid hydrolysis and alkaline conditions are given here. So, you can have a look later on.

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❖ **Applications**

- Some investigations have evaluated sequential alkaline-acid pretreatment. Sequential alkaline (12.70%  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ) and acid (1.04%  $\text{H}_2\text{SO}_4$ ) pretreatment using a 14.49% solid to liquid ratio was applied to **corncoobs**. The maximum reducing sugar yield obtained after enzymatic hydrolysis of the cellulose-rich material was 0.99 g/g (Sewsynker-Sukai *et al.*, 2018).
- Another study on **cotton stalks** first applied an alkaline pretreatment (NaOH), removing 52.48% of lignin with a sugar loss of 3.50%.
- A subsequent two-stage dilute acid pretreatment ( $\text{H}_2\text{SO}_4$ ) of the delignified biomass released 29.40 g/L sugars (63.50% holocellulose hydrolysis) in the hydrolysate along with 2.18 and 1.32 g/L of phenolics and furfurals, respectively.

Sewsynker-Sukai *et al.*, *Energy Convers. Manag.*, 160 (2018), pp. 22-30.

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So, the applications of this particular technology and its result we will discuss. Some investigation evaluated sequential alkaline acid pre-treatment. The sequential alkaline and acid pre-treatment using a 14.49% solid to liquid this yield was applied to corncoobs. The maximum reducing sugar yield obtained after enzymatic hydrolysis of the cellulose rich material was 0.99 gram per gram.

In another study on cotton stalks first applied on alkaline pre-treatment removing 52.48% of the lignin with sugar loss of 3.5 %. A subsequent 2 stage dilute acid treatment using sulphuric acid of the delignified Biomass release 29.4 grams per litre of sugar, 63.5% Hollocellulose hydrolysis in the hydrolysate along with 2.18 and 1.32 grams per litre of phenolics and furfurals respectively.

Again, you see that there are some inhabitation and that is being resulted which is actually not warranted. We are always supposed to develop pre-treatment processes in such a way that one of the aims is to get rid of these inhibitors.

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- Finally, detoxification of the hydrolysate by over liming and adsorption with activated charcoal reduced the furfurals and phenolics by 59.12% and 78.44% , respectively (*Keshav et al., 2016*).
- However, in sequential alkaline-acid processes, considerable amount of hemicellulose is removed together with lignin, resulting in a loss of fermentable sugars as the lignin present in the black liquor inhibits microbial metabolism and xylose consumption (*Lee et al., 2015*).

Keshav et al. Ind. Crops Prod., 91 (2016), pp. 323-331

Lee et al. Biomass. Technol., 182 (2015), pp. 296-301

So finally, detoxification of the hydrolysate by over liming and adsorption with activated charcoal reduce the furfurals and phenolics. To remove the formation or to reduce the formation of this inhibitory compounds like these furfurals, activated charcoal adsorption was used and it resulted in a good removal of this furfurals and phenolics. However, in sequential alkaline acid process, considerable amount of hemicellulose is removed together with lignin, resulting in a loss of fermentable sugars as the Lignin present in the Black Liquor inhibits microbial metabolism and Xylose consumption.

So, 2 different references have been listed here. So those who are interested to read more these are classic studies and very good results, so please refer to them.

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**Table 2: Comparison of acid, alkali and hybrid acid-alkali pretreatment**

Process	Advantages	Disadvantages
Mild acid biomass pretreatment	<ul style="list-style-type: none"> <li>• High recovery yields of each biomass fraction.</li> <li>• Possibility to use all biomass fractions.</li> <li>• Low energy demands.</li> <li>• Low chemical costs.</li> <li>• Low concentration of toxic compounds in the residues.</li> </ul>	<ul style="list-style-type: none"> <li>• Long processing time.</li> <li>• Two processing steps required to recover the three main biomass constituents.</li> <li>• Greater equipment requirement.</li> <li>• More research demands to enhance the whole process.</li> <li>• More research demands to enhance the utilisation of biomass constituents.</li> </ul>
Alkaline industrial pulping process	<ul style="list-style-type: none"> <li>• Short processing time.</li> <li>• Simple processing steps.</li> <li>• Efficiency in obtaining cellulose pulp.</li> <li>• Defined processing technology.</li> </ul>	<ul style="list-style-type: none"> <li>• Highly concentrated processing media.</li> <li>• Low yields of cellulose.</li> <li>• High volumes of liquid residue.</li> <li>• Generation of polluting residues.</li> <li>• High production of toxic compounds.</li> <li>• Additional processing steps.</li> <li>• More research demands to enhance the whole process.</li> <li>• More research demands to enhance the utilisation of biomass constituents.</li> </ul>
Sequential acid and alkaline biomass pretreatment	<ul style="list-style-type: none"> <li>• Recovery of hemicellulose sugars, lignin and cellulose.</li> <li>• Enhanced enzymatic digestibility and fermentability.</li> </ul>	<ul style="list-style-type: none"> <li>• Long processing time.</li> <li>• Two processing steps required to recover the three main biomass constituents.</li> <li>• Greater equipment requirement.</li> <li>• More research demands to enhance the whole process.</li> <li>• More research demands to enhance the utilisation of biomass constituents.</li> </ul>

Source: A. Lomas Waisochewski, et al., Biomass Technology 334 (2020) 112948

So, finally we will see the comparison of an acid, alkali and hybrid acid alkali what we have discussed in a nutshell. So, you can see this mild acid biomass pre-treatment, Alkaline industrial pulping process, and Sequential acid and alkaline based pre-treatment. So, these are the advantages given here and these are certain disadvantages. So, in the case of mild acid biomass pre-treatment the advantages are high recovery yields of each Biomass production, possibility to use all Biomass fractions, low energy demand, low chemical cost, low concentration of toxic compounds. And there are certain disadvantages long processing time, two processing steps required to recover the three main biomass constituents, and greater equipment requirement to handle the corrosive environment, and more research demands to enhance the whole process, more research also demanded to enhance the utilisation of the Biomass constituents.

Then let us talk about the alkaline industrial pulping process. So short processing time, simple processing steps, efficiency in obtaining cellulose pulp and defined processing technology are some of the advantages. Now if you talk about the disadvantages, then it is highly concentrated processing media, low yields of cellulose, high volumes of liquid residue, generation of polluting residues and high production of toxic compounds.

Now let us understand the sequential acid and alkaline biomass pre-treatment. So, recovery of hemicellulose, Sugars, Lignin and cellulose with greater efficiency is one of the advantages. Then enhanced enzymatic digestibility, and fermentability. But there are few disadvantages also which are additional processing steps, more research demands to enhance the entire process and more research also demands to enhance the utilisation of biomass constituents.

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### Role of Pretreatment in the Biorefinery Concept

- A **biorefinery** can be defined as the renewable equivalent of a petroleum refinery, the main difference being the raw material.
- In the biorefinery, biomass can be converted into a wide range of chemicals and energy carriers, and it can also contribute to the development of circular economy.
- This concept is based on the model that lignocellulosic materials, which were used to generate bio-based products can be recovered (to a certain degree), and be recovered and recycled.
- The *International Energy Agency Bioenergy Task 42* defines biorefining as “the sustainable processing of biomass into a spectrum of marketable bio-based products (chemicals, materials) and bioenergy (biofuels, power, heat)”.



Now will discuss about the role of pre-treatment in the biorefinery concept. We have already discussed in a nutshell, that how the pre-treatment and why the pre-treatment is required, we will discuss in a biorefinery concept. A biorefinery can be defined as the renewable equivalent of a petroleum refinery. The main differences being raw material. In the biorefinery biomass can be converted into a wide range of chemicals and energy carriers. And it can also contribute to the development of a circular economy. The concept is based on the model that lignocellulosic materials which were used to generate bio-based products can be recovered to a certain degree and be recovered and recycled. The International Energy Agency, Bioenergy Task42 defines biorefining as the sustainable processing of biomass into a spectrum of marketable bio-based products, Chemicals, material etc and bioenergy. So, it can be biofuels, power and heat.

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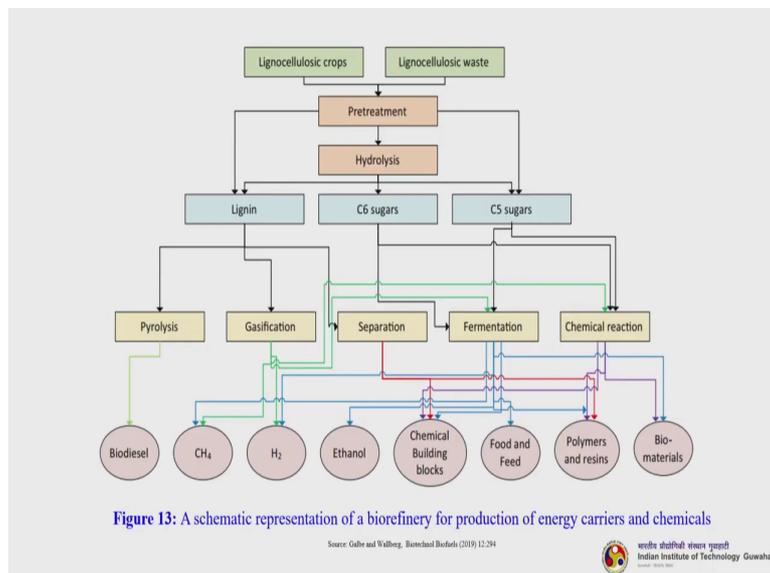


Figure 13: A schematic representation of a biorefinery for production of energy carriers and chemicals

Source: Galbe and Wallberg, *Biomass Biofuels* (2010) 12:294



So, if you see in a nutshell that this is a schematic representation of a biorefinery for production of energy carriers and chemicals. So, you see that lignocellulosic crops or lignocellulosic waste, it can be Municipal solid waste also are pre-treated, followed by hydrolysis. So, we get 3 different fractions. So, the first fraction is rich in Lignin content, the second is rich in C6 sugars, third is rich in C5 sugars.

So, they can be further processed and fed to different reactors, or let us say further processed either thermochemically or biochemically or physico-chemically to get different products such as biodiesel, Methane and hydrogen, ethanol certain chemical building blocks, food and feed, Polymers and resins and other biomaterials.

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- Some important considerations have been suggested for the biorefinery concept to become a path forward towards a less fossil-dependent society.
- The development of biorefineries is a vital key for integration of food, feed, chemicals, fuels and energy production in the future.
- Combinations of physical and biotechnological processes for production of proteins, but also for platform chemicals such as lactic acid will be of importance in the future.
- Biomass can mitigate, to some extent, the high atmospheric levels of carbon dioxide by replacing fossil fuels; in addition, in many countries around the world, the concept may be important to secure domestic energy carriers and the supply of chemicals.
- Most **lignocellulosic feedstock** is generally much more **complex and recalcitrant** than the currently used starchy materials in, e.g. the ethanol industry, which poses a **challenge**.



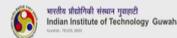
So, some important considerations have been suggested for the biorefinery concept to become a path forward towards a less Fossil dependent society. The development of biorefineries is a vital key for integration of food, feed, Chemicals, fuels and energy production in the future. Combinations of physical and biotechnological processes for the production of proteins but also for platform chemicals such as lactic acid will be of importance in the future.

That is most important thing. We have been discussing this during our many lectures that a biorefinery will become sustainable if at all we will recycle and reuse the waste that is getting generated. Second, most of the by-products when they are converted into some valuable products must be marketable. And there should be acceptability by the people also. There are so many things we have discussed during biorefinery.

So, Biomass can mitigate to some extent the high atmospheric levels of carbon dioxide by replacing fossil fuels. So, this precisely is telling that Biomass sources are carbon dioxide sequesters. So, they help in carbon dioxide sequestration. In addition, in many countries around the world the concept may be important to secure domestic energy carriers and the supply of chemicals. Most lignocellulosic feedstock is generally much more Complex and recalcitrant than the currently used starchy materials, for example, the ethanol industry, which poses a great challenge.

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- One of the major challenges that the biorefinery concept faces to become successful is to **find suitable raw materials**. It is likely that *second-grade or waste materials* will be the main raw material supply in a biorefinery.
- This includes straw, bagasse, tree roots, branches, forest thinnings, etc. However, a large part of the published research that deals with woody materials are often based on wood chips of high quality.
- This is in direct competition with, e.g. the interests of pulp producers. On the other hand, the residues from agricultural operations are in many cases available for conversion to other valuable products.
- Thus, it calls for *very robust and versatile production methods* to be able to handle raw materials of different origin. It is not likely that a biorefinery will be capable of processing all sorts of lignocellulosic materials.



One of the major challenges that the biorefinery concept faces to become successful is to find suitable raw material. It is likely that second grade or waste material will be the main raw material supply in a biorefinery. When we discussed about the Biomasses for biorefinery we have discussed about the waste material and different lignocellulosic materials. So this includes straw, bagasse, tree root, branches, forest thinning etc. to name few, there are many more.

However, large part of the published research that deals with Woody materials are often based on wood chips of high quality. Now this wood chips even including the wood sawdust also having a huge commercial value. So, when you talk about using them for converting in Biorefinery perspective to other valuable products. So, there is a challenge to it. So, this is in direct competition with, e.g., the interests of the pulp producers. This is what I was just mentioning because the pulp producers need more than in a biorefinery.

Because it has a direct commercial value, well-established marketable end product. So, on the other hand the residue from agricultural operations are in so many cases available for conversion to other valuable products and are not at all in high demand. So thus, it calls for very robust and versatile production methods to be able to handle raw materials of different origin. It is not likely that a biorefinery will be capable of processing all sorts of lignocellulosic materials.

Now till today. We understand that a single biorefinery, unless and until fitted properly with robust and versatile production method and technologies, it cannot process multiple feedstocks. And unless and until multiple feedstocks are processed a biorefinery cannot be sustainable.

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- The purpose of the biomass pretreatment step has somewhat shifted during the last decade(s); previously, the main interest was to use lignocellulosic materials for *mainly bioethanol production*.
- The interest in the other main compounds, lignin and hemicelluloses, was limited.
- Today, it is of great importance to find ways to maximise the overall yield of the valuable compounds that make up lignocellulosic materials.
- Pretreatment methods that enable efficient recovery of carbohydrates as well as lignin are desired; however, this all depends on the situation and the final product.
- The energy requirements in the production process must be met under any circumstance, either by internal or external integration of high energy streams, such as in a mill producing pulp, where the excess lignin is the main process-energy supplier.



So, the purpose of the Biomass pre-treatment step somewhat shifted during the last decades. Previously the main interest was to use lignocellulosic materials mainly for bioethanol production. If you go back to some 10-15 years back researches, you will see that whatever pre-treatment methods were being studied and reported all are aimed to get C5 and C6 Sugars. Mostly C6 sugars convert them to glucose, then convert them to and then process them in a ethanol platform to get bioethanol or sometimes may be biobutanol.

Now since few years there is a change in this attitude that researchers have looked for pre-treating the Biomass for other thermochemical conversion processes, whether it is a pyrolysis or whether it is gasification. So today it is of great importance to find ways to maximize the

overall yield of the valuable compounds that make up lignocellulosic materials. Pre-treatment methods that enable efficient recovery of Carbohydrates as well as lignin are desired.

However, this all depends on the situation and the final product. The energy requirement in the production processes must be met under any circumstances either by internal or external integration of high energy streams, such as in a mill producing pulp where the excess Lignin is the main process energy supply.

So pre-treatment is a step that is included as one of the first steps in the process to elevate access to the raw material. It is difficult to define the best pre-treatment for all situations and raw materials. However, it is vital that some important features of the pre-treatment methods are fulfilled, such as high recovery of the individual Polymers and other compounds in the lignocellulosic materials. In addition, the formation of toxic or inhibiting compounds must be low (as low as possible) to decrease the risk of negative effects in the enzymatic hydrolysis and fermentation steps if they are part of the process.

It is not true that always they will be a part of the process. If you are talking about thermochemical conversion after the first treatment, then you do not have to worry about this particular formation of toxic inhibiting compound. It is well known that too severe condition during pre-treatment because greater degradation of hemicellulosic sugars which can cause formation of highly toxic compounds such as furfural, HMF and other organic acids.

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- Preferably, the *energy requirement must be as low as possible*.
- It is also an advantage if energy integration between the pretreatment step and other parts of the production facility can be implemented, such as utilization of low-grade steam for distillation purposes.
- It has also been established that the *economic success of a biorefinery is heavily dependent on the solid content of the pretreated materials*.
- If too dilute solutions are produced, the energy costs for purification may be prohibitively high, which can cause an otherwise well-functioning pretreatment method to be discarded.

The energy requirement is another most important aspect of the entire pre-treatment process. It must be as low as possible. So, it is also an advantage if energy integration between the pre-treatment step and other parts of the production facility can be implemented, such as utilisation of a low-grade steam for distillation purposes. It has also been established that economic success of a biorefinery is heavily dependent on the solid content of the pre-treated materials.

So, if too dilute solutions are produced, the energy cost for purification may be prohibitively very high which can cause an otherwise well-functioning treatment method to be discarded. So, it is very important that if your pre-treatment processes have resulted in a too much of dilute solution, then that dilute solutions will be full of aqueous part or water rich part. You need to purify your sugar.

So that is the downstream processing part, that part will take on almost 40% of the entire product cost (40 to 45%). So, you need to decrease that. So that is why if the solid content is more in the resultant product then it is always good.

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- Effective pretreatment of available lignocellulosic biomass contributes to the generation of **sustainable biorefineries** and the decrease in environmental impacts caused by organic waste disposal.
- The polysaccharide fractions of lignocellulosic biomass including cellulose and hemicellulose can be broken down into sugar monomers.
- They are then converted into biofuels, biogas, and biochemicals through biotechnologies such as anaerobic digestion and fermentation.
- The efficiency and cost-effectiveness of the bioconversion process depend on the transformation of polysaccharides to monomer sugars.
- Commercial applications of lignocellulosic biomass are hindered by the resistance of polysaccharides to hydrolysis and the presence of recalcitrant lignin.

So effective pre-treatment of available lignocellulosic Biomass contribute to the generation of sustainable biorefineries and the decrease in Environmental impacts caused by organic waste disposal. The polysaccharide fractions of lignocellulosic biomass, including cellulose and hemicellulose can be broken down into sugar monomers. They are then converted into biofuels, biogas and biochemicals through bio technologies such as an anaerobic digestion and fermentation.

Efficiency and cost effectiveness of the bio conversion process depend on the transformation of polysaccharides to monomers sugars. Commercial applications of lignocellulosic biomass are hindered by the resistance of polysaccharides into hydrolysis, and the presence of recalcitrant Lignin.

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- A range of pretreatment methods has been developed and employed to increase conversion efficiency.
- The pretreatment of lignocellulosic biomass aims to *decrystallise cellulose structure through lignin removal, increase cellulose and hemicellulose solubility, increase accessible surface area to enzymes, and chemicals, and minimize the loss of sugars.*
- The anticipated end products also determine the choice of pretreatment method as each method induces different effects on different types of lignocellulosic biomass.
- Various by-products generated through these processes can be recovered and utilized for other biochemical productions.
- The success in identifying and applying effective pretreatment to lignocellulosic biomass can increase the socio-economic impacts and resolve global problems involving *sustainable energy and development.*



So, a range of pre-treatment methods have been developed and employed to increase conversion efficiency. The pre-treatment of lignocellulosic biomass aims to decrystallise cellulose structure through lignin removal, increase the cellulose and hemicellulose solubility, increases accessible surface area to enzymes and Chemicals and minimises the loss of sugars. So, the anticipated end products also determine the choice of pre-treatment method as each method induces different effects on different types of lignocellulosic biomass.

Various by-products generated through this processes can be recovered and utilised for other by biochemical productions. The success in identifying and applying effective pre-treatment to lignocellulosic Biomass can increase the socio-economic impacts and resolve the global problems involving sustainable energy and development.

So, with this I conclude today's lecture. So, we have completed this module 4 in which we have discussed about the pre-treatment methods. The next module this module 5 we will be dealing with physical and thermal conversion processes and the class 1 and lecture 1 of module 5 will discuss about the types, the fundamental principles, equipment and applications of thermochemical conversion processes. So, thank you very much if you have

any query, please register your query in the Swayam portal or drop a mail to me at [kmohanty@iitg.ac.in](mailto:kmohanty@iitg.ac.in), thank you.