

WEEK 4: BIOENERGY

INTRODUCTION

Lignocellulosic Biomass and Pre-treatment

Lignocellulosic biomass (LCB) such as energy crops like switchgrass, wood wastes, paper wastes and agricultural residues can be converted to fermentable sugars for ethanol production and this product is called cellulosic ethanol. Unlike food based sources, conversion of LCB to fermentable sugars and then to ethanol is not an easy job.

LCB is mainly the plant material that contains cellulose, hemicellulose and lignin. LCB is categorized in four main groups.

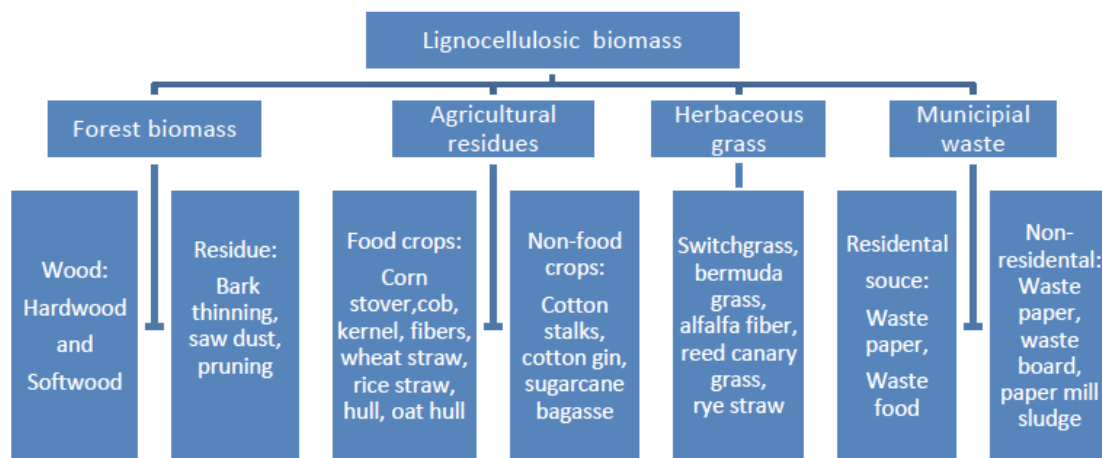


Figure 1. Classification of lignocellulosic biomass (adapted from Hu et al., 2008).

Cellulose, hemicellulose, and lignin contents of common agricultural residues and wastes. According to the table below, LCB consists of these components at different proportions.

Table 1. Cellulose, hemicellulose, and lignin contents of common agricultural residues and wastes (Sun and Cheng, 2002 and Haykir et al., 2013).

Lignocellulosic biomass	Cellulose (%)	Hemicellulose(%)	Lignin (%)
Hardwood stems	40-55	24-40	18-25
Softwood stems	45-50	25-35	25-35
Cotton stalks	41	16	28
Nut shells	25-30	25-30	30-40
Corn cobs	45	35	15
Grasses	25-40	35-50	10-30
Paper	85-99	0	0-15
Wheat straw	30	50	15
Sorted refuse	60	20	20
Leaves	15-20	80-85	0
Cotton seed hairs	80-95	5-20	0
Newspaper	40-55	25-40	18-30
Waste paper from chemical pulps	60-70	10-20	5-10
Primary waste water solids	8-15	-	24-29
Swine waste	6	28	-
Coastal Bermuda grass	25	35.7	6.4
Switchgrass	45	31.4	12

An attractive starting point that offers promising platforms for the production of biofuels and biochemicals. According to the US Department of Energy, more than 1 billion tons of dry biomass can replace 30% of US annual petroleum consumption without any modification in the agriculture. Utilization of lignocellulosic biomass brings in the following main advantages:

- 1) Lignocellulosic biomass consumes CO₂ that is released by the combustion of fuels ----- net CO₂ emissions reduction.
- 2) Lignocellulosic biomass is an abundant, cheap and naturally occurring raw material
- 3) Many forms of renewable energy are suited only to electricity production and are, therefore, difficult to utilize to fuel vehicles. Biomass is uniquely suited among renewable energy sources for conversion to transportation fuel.
- 4) Biomass is unique as the energy it contains is stored as chemical bonds, and indeed biomass is the only renewable source of carbon atoms.

According to the chart below, production of biofuels for transportation constitutes only roughly 1%. Among all renewable sources, traditional methods for biomass utilization has a share of almost 50%. Even though this amount was considered as a significant fraction, traditional biomass corresponds to the biomass burned for energy generation as we, human beings, have been doing for ages.

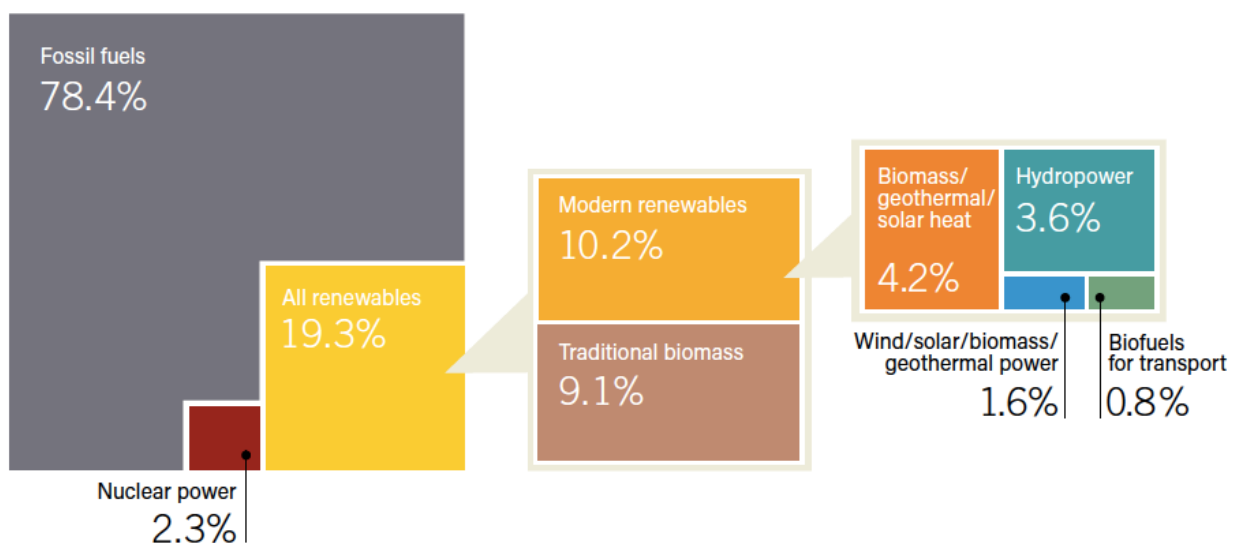


Figure 2. Estimated Renewable Energy Share of Total Energy Consumption in 2015 (REN21).

Can edible biomass be used for biofuels production? Starch and sugar can directly be utilized for biofuels production. However, poverty, finite area for plantation and increase in food prices are the major global restrictions for the valorization of edible biomass and strengthen the interest in cellulosic ethanol production.

The Chemical Structure of Lignocellulosic Biomass

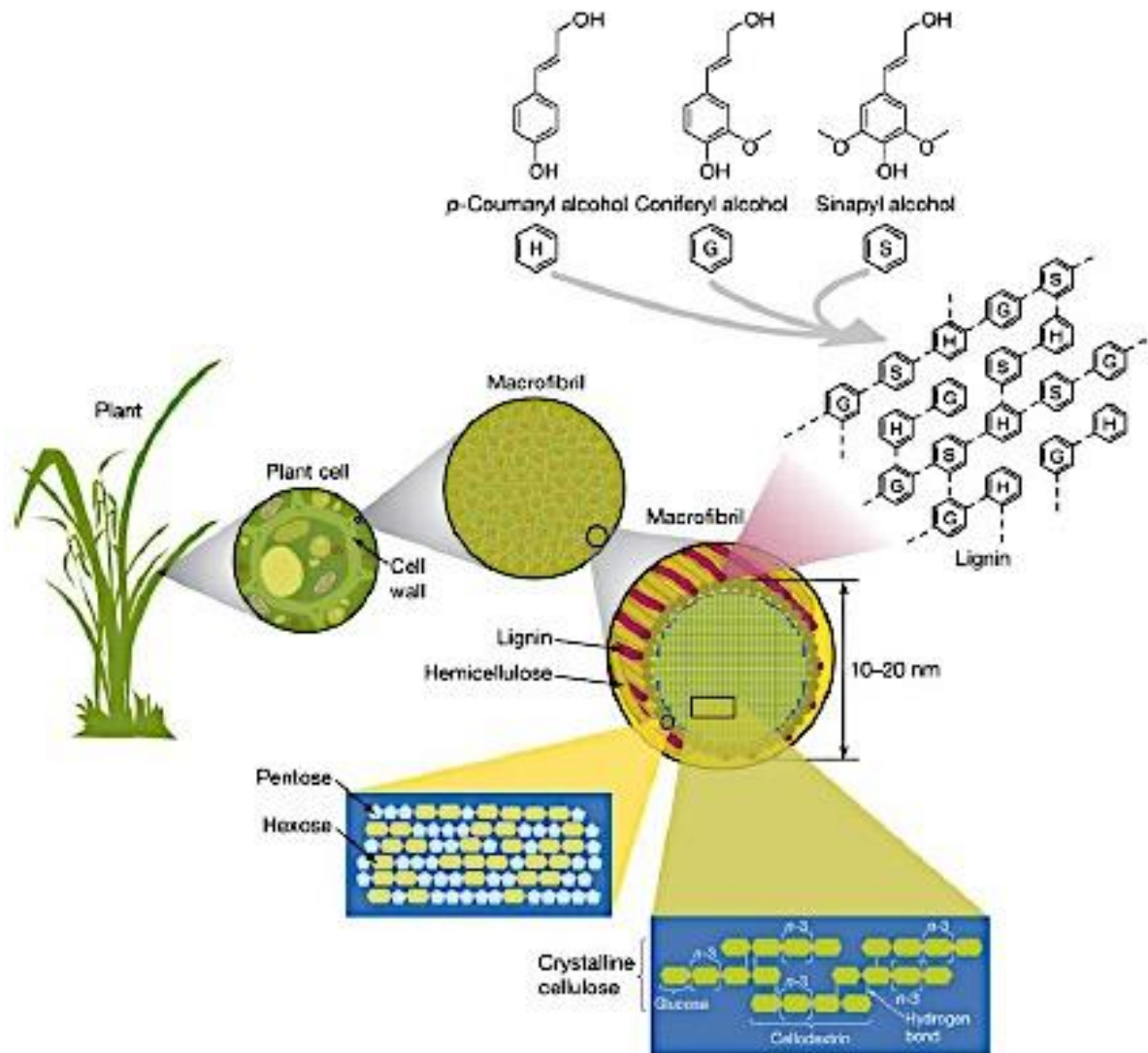


Figure 3. The Chemical Structure of Lignocellulosic Biomass (Rubin, 2008).

Cellulose

Cellulose is literally the most abundant organic polymer on earth and also is the major raw material in cellulosic ethanol production. Cellulose is composed of glucose monomers which are linked to each other by the β -1,4 glycosidic bonds.

The interchain (between the chains) and intrachain hydrogen bonds (within the chains) between glucose subunits form an organized network. This hydrogen bonded

network includes mainly the *crystalline regions* which hardly get deconstructed by enzymatic attack and some amorphous regions that are more susceptible to the enzymatic attack.

Due to its adverse effect on enzymatic accessibility of cellulose, crystalline structure of cellulose has been monitored via numerous types of characterization techniques such as *XRD (X-ray diffraction)*.

Each glucose is linked by glycosidic bonds.

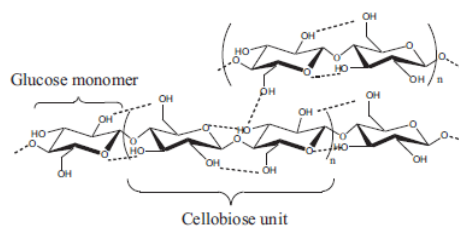


Figure 4. Cellulose structure (Cabiac et al., 2011).

Not every region of cellulose is crystalline. Cellulose has amorphous regions (less organized) which are accessible to enzymatic attack as shown below.

Conversion of cellulose to glucose takes place by the enzymes meaning that production of glucose from cellulose is an enzymatic reaction. Acids can also catalyze the conversion of cellulose to glucose but not as selectively as the enzyme do. Besides acids operating under severe conditions (high temperature) can lead to the formation of inhibitors production.

Conversion of cellulose to glucose by means of enzymatic reactions involves utilization of the cellulolytic enzymes. Enzymatic hydrolysis of cellulose is fundamentally a heterogeneous reaction in which insoluble cellulose is cleaved through the β -1,4 glycosidic linkages via cellulases.

Owing to its biocompatible structure, cellulose has been shown to form composites with synthetic polymers and biopolymers in addition to its well-recognized use in ethanol production.

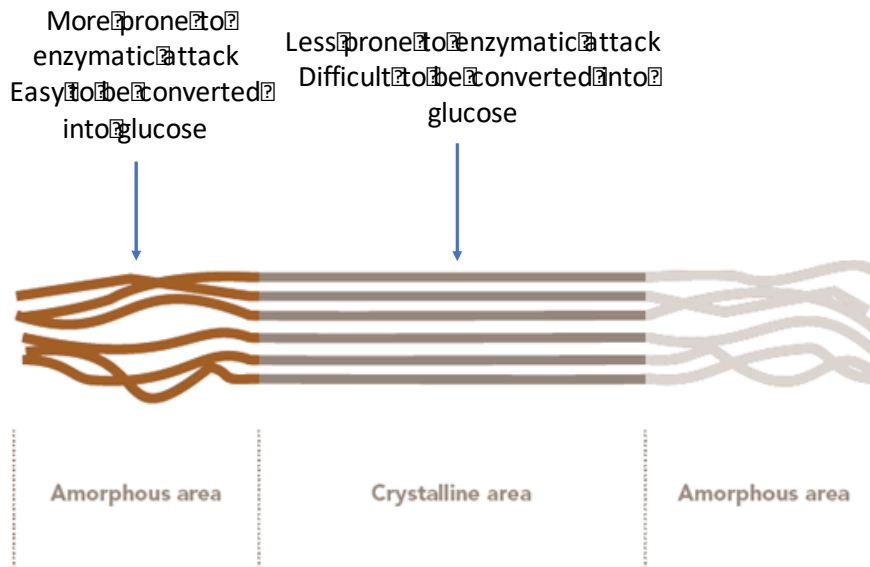


Figure 5. Crystalline and amorphous regions of cellulose (Cotton Inc., 2013).

Hemicellulose

Hemicellulose is identical to cellulose with respect to being a sugar based polymer but it is made up of shorter and branched chains of various subunits compared to the long strands of glucose subunits forming the organized structure of cellulose. Another significant structural difference between cellulose and hemicellulose is that hemicellulose is entirely an amorphous polymer. While possessing six-carbon sugars including, glucose, mannose, galactose and it also consists five-carbon sugars, including xylose and arabinose.

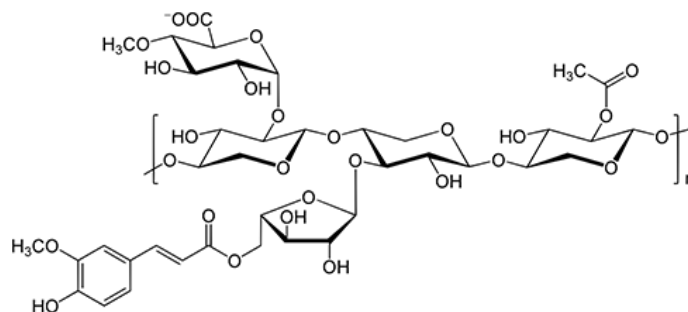


Figure 6. Hemicellulose structure (E-Education)

Lignin

Lignin provides water-proofing and reinforcement to the structure. Built from up to three monomers: coniferyl, sinapyl and para-coumaryl alcohol. Lignin is the most abundant aromatic polymer on earth. It is an amorphous polymer.

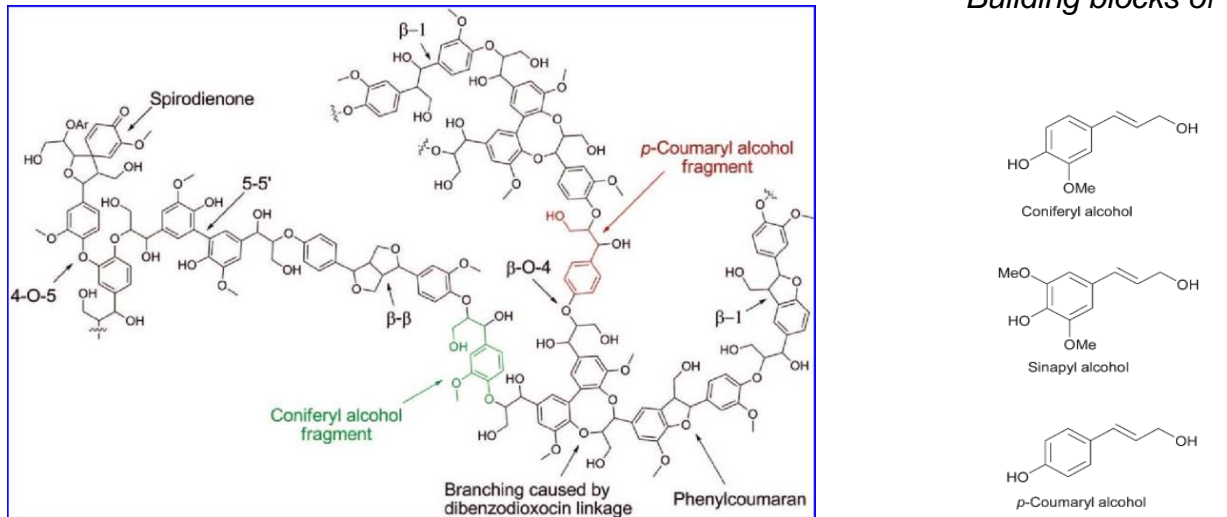


Figure 7. Lignin structure and lignin subunits (Zakzeski et al., 2010 and Brandt et al., 2013)

98% of lignin is either combusted or converted to kraft lignin (a product of Kraft pulping) and liginosulfonates (a product of sulfite pulping). The existing markets for liginosulfonates are dispersant, binder and adhesive applications. On the other hand, vanillin production from liginosulfonates is an exception. Borregaard, a Norwegian firm, is the only company in the world producing wood based vanillin and has been carrying on this process for over 50 years (Borregaard, Vanillin).

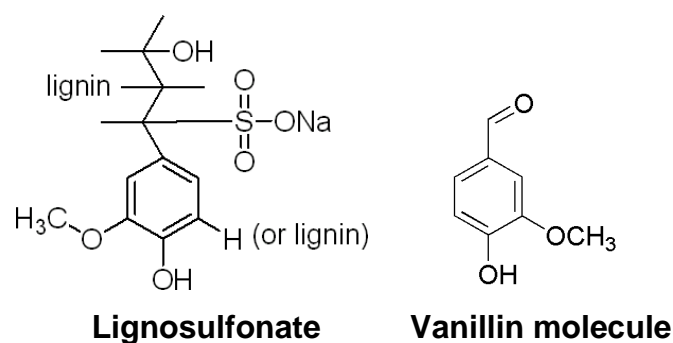


Figure 8. Structures of liginosulfonate and vanillin

“Kraft pulping” was introduced into the literature in the last 19th century for papermaking. This patented process, in which wood is subjected to pretreatment by sodium hydroxide and sodium sulfide at temperatures 423-473 K, is the current commercial source of lignin.

Pretreatment of lignocellulosic biomass

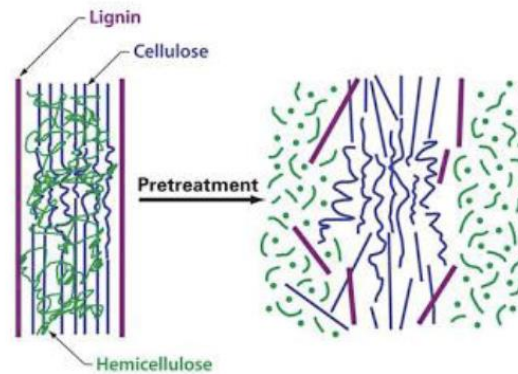


Figure 9. Schematic representation of biomass pretreatment (Mosier et al., 2005)

In order to make use of each biomass component as much as possible, pretreatment of biomass is essential. Pretreatment is the initial step of the process for the conversion of biomass into biofuels and biochemicals. The major objectives of biomass pretreatment are:

- Cellulose decrystallization or disruption of cellulose crystalline structure
- Lignin removal
- Increase of biomass' surface area

The digestibility of cellulose can be enhanced if one or two of these objectives are accomplished. In other words, the major factors that limit the digestibility of the biomass (biomass conversion into sugars) are:

- Presence of lignin in the native form of biomass has been reported to result with nonspecific adsorption of cellulases on lignin. Lignin not only hinders the enzymatic reaction through non-productive binding of the enzymes onto it, it also physically prevents the enzymes to get in touch with cellulose due to its sheathing effect.

- Crystalline structure of cellulose - Cellulose is composed of glucose subunits that are linked to each other in a well-organized fashion via strong hydrogen bonds. This ordered network, which appears as an obstacle for enzymatic hydrolysis of cellulose, need to be disrupted somehow.

Pretreatment techniques

According to the table below, pretreatment methods differ based on their impact on the structure of lignocellulosic biomass. While grinding of biomass (physical pretreatment method) is effective on cellulose decrystallization, alkaline pretreatment is very effective on the disruption of lignin and its removal from the structure.

Table 2. Impacts of pretreatment methods on the lignocellulose structure (adapted from Mosier et al., 2005 and Alvira et al., 2010).

	Increases accessible surface area	Decrystallizes cellulose	Removes hemicellulose	Removes lignin	Alters lignin structure	Generation of inhibitory compounds
Biological				•••	•••	
Physical	•••	•••				
Steam	•••		•••	••	•••	•••
Liquid hot	•••		•••	•	••	•
Acid	•••		•••	••	•••	•••
AFEX	•••	•••	••	•••	•••	•
Supercritical	•••		•••			
Alkaline		•		••	••	

Biological pretreatment

Biological pretreatment of lignocellulosic biomass is an environmentally benign approach that employs fungi species with the aim of reducing lignin content of the biomass. The white-rot fungi, *Phanerochaete chrysosporium*, which secretes lignin degrading enzymes, peroxidases and laccases, has been widely recognized. *P.*

chryso sporium has been capable of degrading high amounts of lignin to produce ethanol from various lignocellulosic feedstocks. Though introduced advantages over the conventional chemical pretreatment for being a low cost method and not presenting detrimental effects on environment, the duration of pretreatment, which is almost 14 days, is much longer compared to the other types of pretreatments.

Physical pretreatment

Among the physical pretreatment methods, mechanical comminution consist milling, grinding and chipping of the lignocellulosic feedstocks. These mechanical methods differ from each other according to the final particle size of the biomass. While chipping reduces the particle size of the biomass to 10-30 mm, milling and grinding result with particles having a much smaller particle size which range between 0.2-2 mm.

Chemical pretreatment methods – Some of the conventional methods are summarized below.

Steam explosion

Biomass is exposed to high pressurized steam at almost 0.69-4.85 MPa and 160-290°C for a few minutes and the reaction is terminated via venting the steam suddenly and lowering the pressure to atmospheric pressure. This sudden explosive decompression that biomass is exposed in the final step of the process brings substantial impacts on the structural features of the biomass. It not only opens up the structure but also removes considerable amounts of hemicellulose.

Dilute acid pretreatment

Conducted through interaction of the biomass with dilute acids at a temperature ranging between 120–200°C for a period ranging from minutes to seconds. Besides its considerable effect on hemicellulose, elevated temperatures are shown to result with cellulose hydrolysis. Despite being favorable for fermentable sugar formation, dilute acid pretreatment has less impact on lignin such that it only resulted with redistribution

of lignin. Sulfuric acid, hydrochloric acid and nitric acid are used.

Alkaline pretreatment

Alkaline pretreatment results in lignin removal which enhances the enzymatic accessibility of cellulose. Various alkaline agents such as sodium hydroxide, calcium hydroxide (lime) and hydrogen peroxide have been employed. While being very effective in lignin removal, alkaline pretreatment is also able to make modifications in hemicellulose by removing the acetyl groups. Alkaline agents also found to present swelling effects on the biomass which accordingly result with an increase in the surface area of the biomass.

Ionic liquid pretreatment

Ionic liquid (IL) pretreatment has attracted researchers as a promising pretreatment method from the time when Swatloski and his co-workers (2002) have found out that cellulose could be dissolved in ionic liquids under certain heating conditions.

Ionic liquids are room temperature salts that consist solely of anions and cations. No solvent addition is required for the ions to get apart from each other however such a solvent addition is necessary for sodium chloride as seen in the figure which puts an emphasis on the distinction between an ionic liquid and ionic solution. Ionic liquids usually have low melting points, below 100°C and low vapor pressures at ambient conditions. Owing to their non-volatile characteristics, they are regarded as environmentally benign solvents compared to organic solvents and highly promising for sustainable processes. They are described as “tunable solvents” due to the convenience of making modifications in their anion or cation types according to specific targets components.

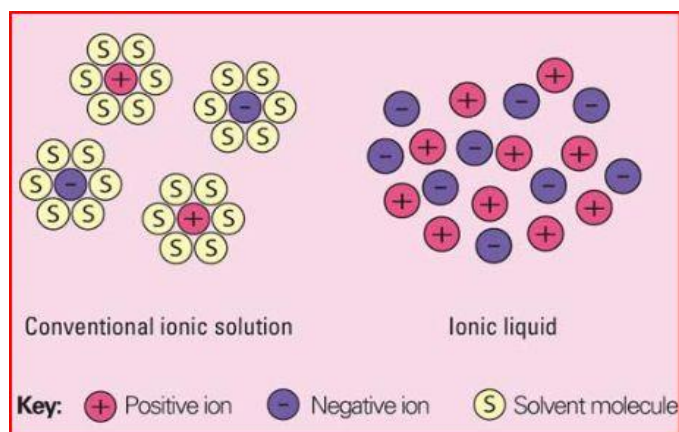


Figure 10. Basic difference between ionic liquids and conventional ionic solutions (BP, 2009).

Ionic liquid pretreatment introduces several advantages over conventional techniques such as being recyclable and having low vapor pressure. Having high viscosity and high cost have been considered as disadvantages. Below, EMIMAc (1-ethyl-3-methylimidazolium acetate) is shown. EMIMAc is one the most strongest and thus, promising ionic liquid towards lignocellulosic biomass.

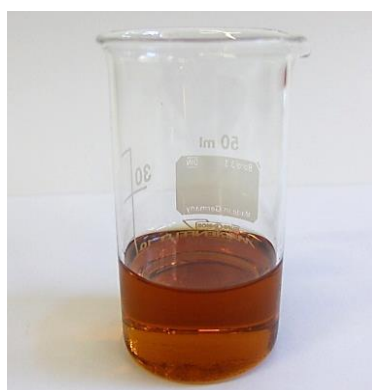


Figure 11. EMIMAc (1-ethyl-3-methylimidazolium acetate) at room temperature

Below pictures show biomass pretreatment with ionic liquids by simply demonstrating the interaction between cellulose and EMIMAc. For convenience, hydrogen bonds within two cellulose chains are demonstrated. Cellulose before pretreatment has a crystalline structure and composed of powderlike, fine particles. During pretreatment, EMIMAc attacks on the OH group of the cellulose. That is how ionic liquids disrupt the crystalline network (hydrogen network) of lignocellulosic biomass. To terminate the reaction, water added as an antisolvent to the medium. This time, bond formation is observed between EMIMAc and water. Thereby, cellulose is precipitated. Precipitated

cellulose has got a decrystalline structure (amorphous).

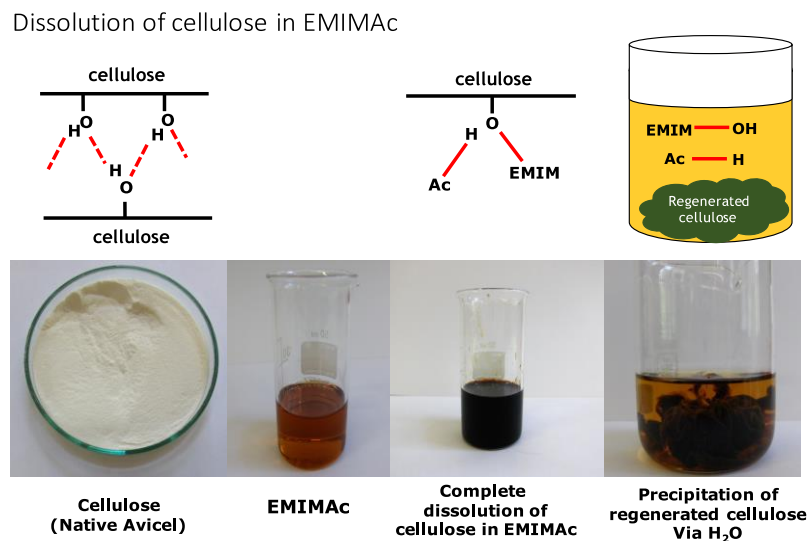


Figure 12. Dissolution of cellulose in EMIMAc

References:

- 1- Hu, G., Heitmann, J.A., & Rojas, O. J. (2008). Feedstocks Pretreatment Strategies for Producing Ethanol From Wood, Bark and Forest Residues. *BioResources* 3 (1), 270-294.
- 2- Haykir, N. I., Bahcegul, E., Bicak, N., & Bakir, U. (2013). Pretreatment of cotton stalk with ionic liquids including 2-hydroxy ethyl ammonium formate to enhance biomass digestibility. *Industrial Crops and Products*, 41(1), 430-436.
- 3- Sun, Y., & Cheng, J. (2002). Hydrolysis of lignocellulosic materials for ethanol production: A review. *Bioresource Technology*, 83(1), 1-11.
- 4- http://www.ren21.net/wp-content/uploads/2017/06/17-8399_GSR_2017_Full_Report_0621_Opt.pdf.
- 5- Rubin, E. M. (2008). Genomics of cellulosic biofuels. *Nature*, 454(7206), 841-845.
- 6- Cabiac, A., Guillon, E., Chambon, F., Pinel, C., Rataboul, F., & Essayem, N. (2011). Cellulose reactivity and glycosidic bond cleavage in aqueous phase by catalytic and non catalytic transformations. *Applied Catalysis A: General*, 402(1-2), 1-10.

- 7- <http://www.cottoninc.com/product/NonWovens/Nonwoven-Technical-Guide/Cotton-Morphology-And-Chemistry/>
- 8- <https://www.e-education.psu.edu/egee439/node/664>
- 9- Zakzeski, Joseph, Pieter C. A. Bruijninx, Anna L. Jongerius, and Bert M. Weckhuysen. 2010. "The Catalytic Valorization of Lignin for the Production of Renewable Chemicals." *Chemical Reviews* 110 (6):3552-3599. doi: 10.1021/cr900354u.
- 10-Brandt, A., Grasvik, J., Hallett, J. P. and Welton, T. (2013) 'Deconstruction of lignocellulosic biomass with ionic liquids', *Green Chemistry*, 15(3), pp. 550-583.
- 11-Alvira, P., Tomás-Pejó, E., Ballesteros, M., & Negro, M. J. (2010). Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. *Bioresource Technology*, 101(13), 4851-4861.
- 12-Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y. Y., Holtzapple, M., & Ladisch, M. (2005). Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology*, 96(6), 673-686.