



Lignocellulosic Biomass Pretreatment for Biorefinery: A Review

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ABSTRACT

Lignocellulosic biomass consists of cellulose, hemicellulose, and lignin, which have the potential to produce the so-called green chemicals. Many processes are available at different scales (e.g. labs, pilots, demos, commercials), utilizing lignocellulosic biomass as the raw material. Due to its complicated chemical structures, lignocellulosic biomass must be pretreated before it can be processed further. Simultaneous separation of cellulose, hemicellulose, and lignin from the biomass is an important step to maximize the full potential of the biomass. In this review, several well-known biomass pretreatment technologies are evaluated. These are low pH process (e.g. dilute acid, steam explosion, hot water liquid, and concentrated acid), high pH (e.g. NaOH, lime, NH₃), organosolv, ozonolysis, CO₂ explosion, and ionic liquids. The objective of this review is to understand how effective the pretreatment process for separating cellulose, hemicellulose, and lignin. Based on this review, organosolv is the only pretreatment process that is capable of separating cellulose, C5 sugars (from hemicellulose), and lignin, simultaneously. This process is currently at pilot scales of 30 – 100 ton per day of biomass feedstock.

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1. INTRODUCTION

Lignocellulosic biomass is considered as future sustainable feedstock for chemicals (Permatasari *et al.*, 2016). It consists of three major components, namely cellulose, hemicellulose, and lignin (Nandiyanto *et al.*, 2016; Nandiyanto *et al.*, 2017). Due to their

complicated structures, the biomass must be pretreated before undergo further processing. There are already several biomass pretreatment technologies. Some of them can be categorized into mechanical and thermochemical processes (Cherubini, 2010). Mechanical process aims only to reduce the size of biomass for subsequent processes.

Thermochemical processes (e.g. pyrolysis, gasification, etc.) produce different products, such as bio-oil or syngas for other applications. These pretreatment technologies, however, do not separate lignocellulosic biomass into its major components. This separation is an important step to maximize the utilization of lignocellulosic biomass into valuable chemicals. Hence, these pretreatment technologies are not considered in this work.

The main goal of biomass pretreatment in biofuel plants is to prepare the cellulose fraction of the biomass for subsequent enzymatic hydrolysis and yeast fermentation processes (Farobie & Hasanah, 2016; Bilad, 2016). The hemicellulose fraction is also sometimes used depending on the technology provider of those subsequent processes (Nandiyanto *et al.*, 2017). Hence, it is basically

to make access, provide large surface area, and prepare cellulose and hemicellulose for the enzymes and the yeasts.

In short, this goal is achieved technically by: (i) Increasing surface area (porosity) of the biomass; (ii) Removing inhibitor of yeast growth, e.g. furan derivatives from C5 sugars, which come from the hemicellulose. This is done via controlled hydrolysis of hemicellulose not to produce furan derivatives (via change of operating conditions or reactor design) and removal the hemicellulose from the biomass; (iii) Breaking bonds between lignin and cellulose-hemicellulose via disruption of the lignin structure and dissolution of the lignin itself; (iv) Reduction of crystallinity of the cellulose because this crystallinity feature repels water. Schematically, the pretreatment in this regard is shown in **Figure 1**.

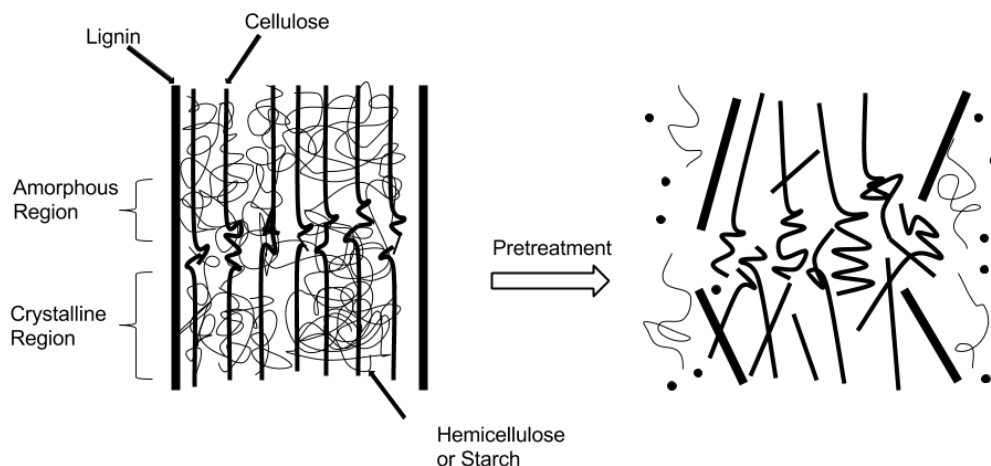


Figure 1. Schematic goals of pretreatment of lignocellulosic materials (poet.com, retrieved on June 2015)

2. Technologies used commercially

Some commercially used pretreatment technologies are:

(i) Steam explosion technology combined with dilute acid (Advanced Steam-Ex™ process) of ANDRITZ, which is used in the bioethanol plant of POET-DSM. The technology is shown in **Figure 2**. In the project Liberty (POET-DSM), sugars from both cellulose and

hemicellulose are fermented to bioethanol (<http://poet.com/pr/poet-dsm-makes-major-technology-process-purchase-for-cellulosic-bio-ethanol>). Retrieved on June 2015). The remaining lignin is sent to an anaerobic digestion treatment to produce biogas. The biogas is used to create power to run the bioethanol plant (<http://demoplants.bioenergy2020.eu/projects/info/225>, retrieved on July 2015). The schematic of the plant is shown in **Figure 3**.

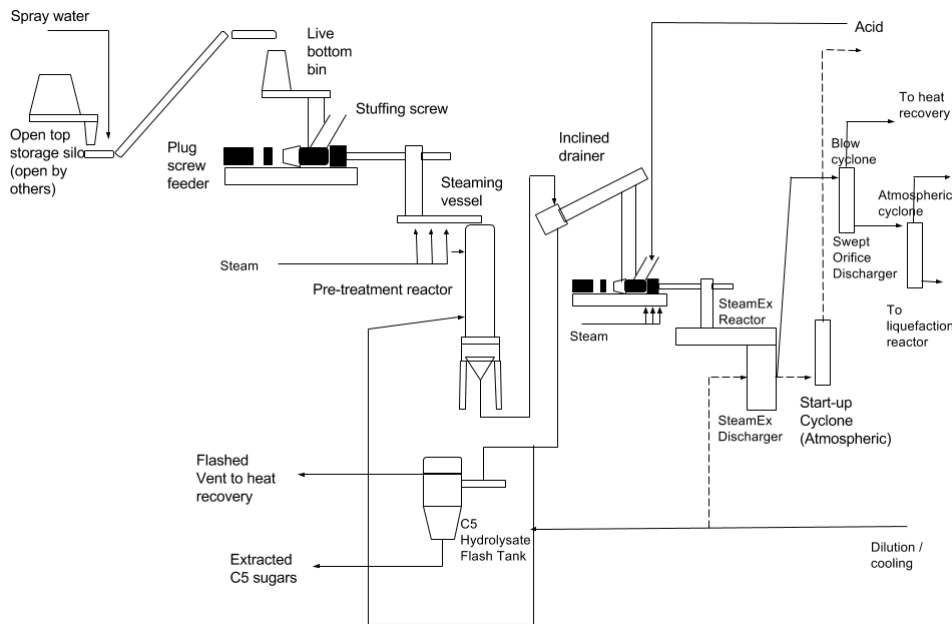


Figure 2. Advanced Steam-ExTM process of ANDRITZ used in the bioethanol plant in Project Liberty POET-DSM (energybiosciencesinstitute.org, retrieved on June 2015).

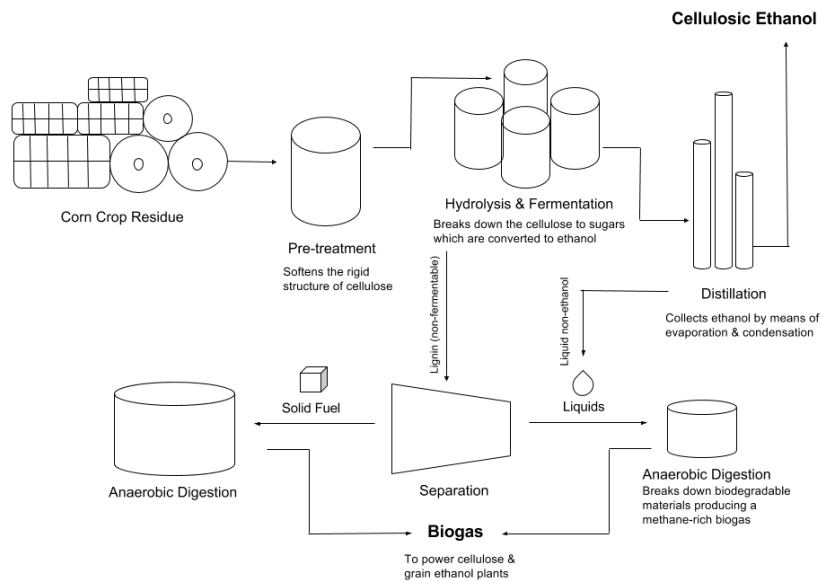


Figure 3. Schematic drawing of POET-DSM project Liberty.

(ii) Steam explosion technology combined with dilute acid developed by ENEA (Italian National Agency for New Technologies, Energy and Sustainable Economic Development) is also used in the bioethanol plant of Beta Renewables, the Crescentino plant (<http://www.chemicals-technology.com/projects/mg-ethanol/> and http://www.enea.it/en/events/amazon_30jun14/Biomassasasou

[rceofEnergy Biofuels Chemicals](http://www.enea.it/en/events/amazon_30jun14/Biomassasasou), retrieved on June 2015). Figure 4 shows the steam explosion pretreatment developed by ENEA. In this particular Crescentino plant, sugars from both cellulose and hemicellulose are fermented to bioethanol, while lignin is used as an energy source to create power (<http://www.betarenewables.com/proesa/biorefinery>, retrieved on July 2015).

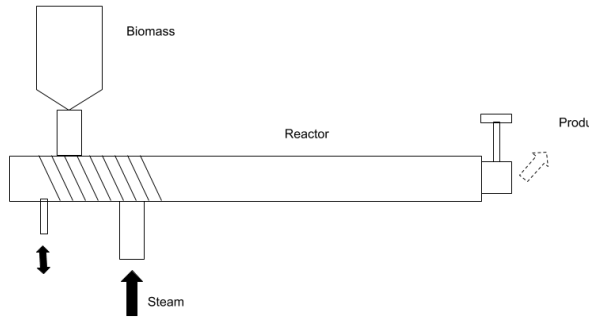


Figure 4. Steam explosion pretreatment by ENEA (www.iea.com, retrieved on June 2015)

(iii) Steam pretreatment combined with dilute ammonia developed by joint technology of DuPont and NREL is probably being used in the on-going construction of a bioethanol plant of DuPont (<http://biofuels.dupont.com/cellulosic-ethanol/nevada-site-ce-facility/>, retrieved on June 2015).

3. Biomass pretreatment in pulp & paper industries

3.1. Goal of the pretreatment

The main goal of the pretreatment in the pulp and paper industries is to preserve cellulose while removing both hemicellulose and lignin. In the Kraft process, this is done by treating the biomass chips with white liquor (a mixture of NaOH and Na₂S). The hemicellulose and lignin are dissolved in the solution giving a black liquor mixture. This black liquor is evaporated and then sent to a recovery boiler to produce green liquor. The green liquor is then treated chemically with lime to produce again the white liquor (http://ipst.gatech.edu/faculty/ra-gauskas_art/technical_reviews/Kraft%20Pulping%20and%20Recovery%20Process%20basics.pdf, retrieved on June 2015). This Kraft process is shown in **Figure 5**. The remaining cellulose is washed and bleached and it is then called pulp. It can be seen in **Figure 6**. This cellulose pulp is then sent to paper manufacturing plants.

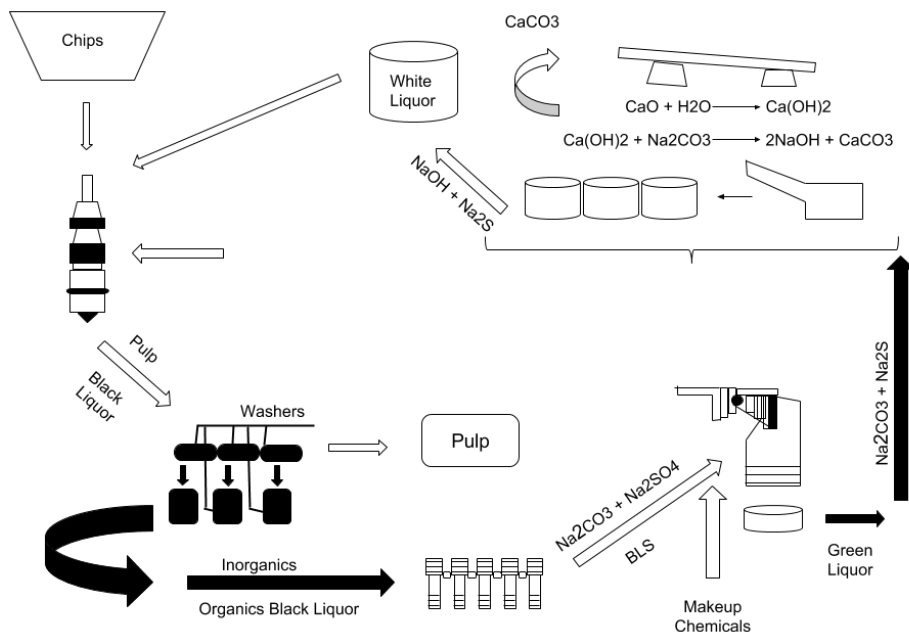


Figure 5. Kraft process (www.domtar.com, retrieved on July 2015).



Figure 6. Cellulose pulp. Figure was adopted from youtube.

3.2. Technologies used commercially

Pulp and paper making industries have existed for years and there are many technology suppliers such as ANDRITZ or Metso. An improved digester (Compact Cooking G2) from Metso is shown in Figure 7.

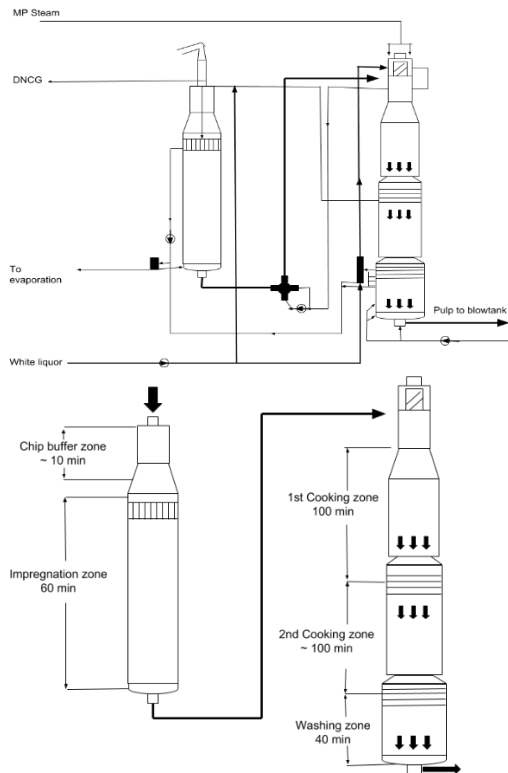


Figure 7. An improved digester (Compact Cooking G2) from Metso (Harmsen et al., 2010)

From the black liquor, lignin has been commercially extracted with a process called LignoBoost. The technology is owned by Valmet (http://www.valmet.com/en/products/chemical_recovery_boilers.nsf/Web-WID/WTB-090518-22575-328A1?OpenDocument&mid=BAD0112EAFD7623BC2257C2B003A12E1, retrieved on July 2015). It has been applied in Domtar pulp mill's site in Plymouth, North Carolina (domtar.com, retrieved on July 2015). LignoBoost is schematically shown in Figure 8.

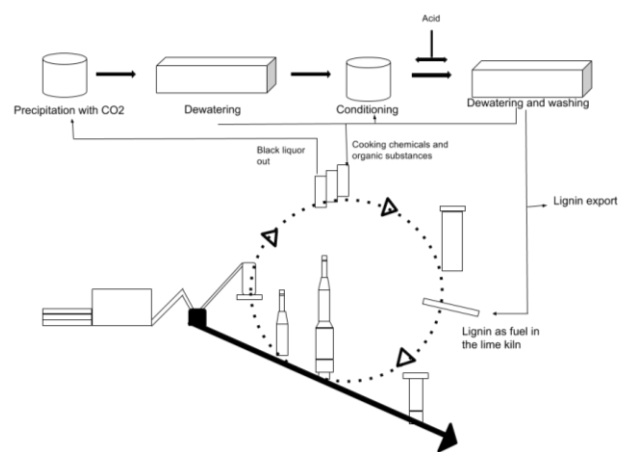


Figure 8 LignoBoost process to extract lignin out of black liquor (domtar.com, retrieved on July 2015)

4. CONCLUSION

This paper reviews pretreatment technologies for separating cellulose, hemicellulose, and lignin from the biomass. Several well-known biomass pretreatment technologies are evaluated. Many processes are available at different scales (e.g. labs, pilots, demos, commercials), utilizing lignocellulosic biomass as the raw material. These are low pH process (e.g. dilute acid, steam explosion, hot water liquid, and concentrated acid), high pH (e.g. NaOH, lime, NH₃), organosolv, ozonolysis, CO₂ explosion, and ionic liquids. The objective of this review is to understand

how effective the pretreatment process for separating cellulose, hemicellulose, and lignin.

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6. AUTHORS' NOTE

The author(s) declare(s) that there is no conflict of interest regarding the publication of this article. Authors confirmed that the data and the paper are free of plagiarism.

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