

Technical solutions used in different pretreatments of lignocellulosic biomass: a review

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Abstract. Bioethanol production from lignocellulosic biomass has attracted a lot of attention as one of the most promising alternative to liquid fossil fuels. Over the last decades a lot of research has been done to find the optimal methods & devices to produce bioethanol from all kind of lignocellulosic biomass. A traditional three-step production process is used to produce bioethanol from lignocellulosic biomass – pretreatment, enzymatic hydrolysis, & fermentation. Today, the high cost of the pretreatment prevents bioethanol from competing with petrol. In this review article, the positive & negative aspects of different pretreatment methods & patented devices are investigated & analysed. Based on the analysis several options on how to lower lignocellulosic biomass pretreatment costs & how to increase the competitiveness of bioethanol are proposed.

Key words: bioethanol, pretreatment devices, pretreatment methods, biomass.

INTRODUCTION

Presently, most of the primary energy (up to 80%) consumed worldwide is produced from fossil fuels. From this 58% is used by the transportation sector alone (Nigam et al., 2011). Demand for energy rises year by year but fossil fuels are a limited resource. This limitation has driven scientists to search for new alternatives that could replace fossil fuels as our primary energy source & to ensure some degree of energy independence from them. Biofuels are considered as the most favourable choice at the moment compared to syngas, hydrogen or solar energy due to their renewability, biodegradability & cost-effectiveness (Nigam et al., 2011; Tutt et al., 2012).

Biofuels are classified as primary & secondary biofuels. Primary biofuels are natural & non-refined biomass including firewood, wood chips & pellets used to produce heat or electricity. Secondary biofuels are further divided into three sub-groups: first-, second- & third-generation. Classification is based on the origin of the raw material & technology used for their production (Nigam et al., 2011). First generation biofuels are produced from food crops that are rich in starch or sugar (maize, wheat, sugar-cane etc.) (Agbor et al., 2011). Second-generation biofuels use lignocellulosic biomass (the whole above ground plant biomass) as feedstock (Kikas et al., 2015). Third generation biofuels use algae as feedstock but currently the research in this field is in early stages (Podkuiko et al., 2014).

The most promising natural resource at the moment for the production of liquid biofuels is lignocellulosic biomass. In contrast to the first generation biofuels, it does not

compete with food crops. Lignocellulosic biomass is the most economical renewable resource with an annual growth rate of around 200 billion tons (Tojo et al., 2014). Other positive aspects to using lignocellulosic biomass as feedstock include worldwide distribution, the abundance of lignocellulosic wastes (agricultural, municipal & forestry wastes) & low effect on global warming (Galbe & Zacchi, 2012; Raud et al., 2017).

The basic production process of bioethanol from lignocellulosic biomass consists of five main steps: gathering feedstock, pretreatment, hydrolysis, fermentation & distillation. Four of these processes (feedstock gathering, hydrolysis, fermentation & distillation) have been widely studied & optimal methods have been found. Since every lignocellulosic biomass has its own unique chemical composition (Raud et al., 2015a; Raud et al., 2015b), which also depends on the maturity of the plant, makes it harder to find one certain pretreatment method that would suit for all different lignocellulosic biomasses (Tutt et al., 2013). Therefore, low-cost & optimal solution for pretreatment of lignocellulosic biomass is yet to be found.

The aim of this article is to give an overview of different pretreatment methods from the technical point of view & to analyse their advantages & disadvantages. Overview of technical solutions is given for viable methods that already are or have potential to be commercialized.

BIOMASS PRETREATMENT

The aim of the pretreatment process is to facilitate better access of biocatalysts to cellulose that needs to be converted into fermentable sugars by changing physio-chemical characteristics of the biomass (Galbe & Zacchi, 2012; Akhtar et al., 2016). The surface area is increased by unbounding cellulose from lignin & hemicellulose, but this process is very difficult & energy-consuming due to the complex structure of the lignocellulose. The effectiveness of the pretreatment process plays an important role in the efficiency of subsequent processes - high cellulose yield = high sugar yield = high ethanol yield = higher competitiveness with fossil fuels.

Pretreatment method is considered efficient if it meets the following criteria (Galbe & Zacchi, 2012; Silveira et al., 2015):

- Provides high sugar yield,
- Forms minimum amount of inhibitory compounds,
- Consumes minimum amount of energy,
- Requires minimum amount of enzyme for hydrolysis,
- Allows the recovery of other compounds (lignin, hemicellulose, etc.) for conversion into other valuable co-products,
- Prevents sugar & lignin degradation,
- Provides maximum enzyme accessibility to cellulose,
- Costs minimum amount of money.

Several lignocellulosic biomass pretreatment methods (AFEX, steam explosion, alkaline pretreatment, etc.) have been developed & studied with common objective – to find the best possible method that guarantees maximum efficiency. Today the high cost of pretreatment process prevents the availability of second-generation bioethanol as a commercial fuel.

Although numerous review articles concerning different pretreatment methods have been published, the suitability of the proposed technical solutions for industrial scale biofuel production has not been analysed so far.

PRETREATMENT METHODS

Pretreatment methods are classified into four main groups: physical, biological, chemical & physio-chemical methods.

Physical pretreatment

Milling

The main goal of mechanical pretreatment is to reduce the biomass particle size, cellulose crystallinity & to reduce the degree of polymerization, which results in increased specific surface area (S. Sun et al., 2016). Milling also causes shearing of the biomass (Conde-Mejía et al., 2012). Due to the effects mentioned, it is easier for enzymes to react with cellulose, which results in increased glucose yield.

Milling, solely as a pretreatment method, has not reached commercialization due to its high-energy consumption, which is directly related to the particle size. In order to achieve high hydrolysis yields the biomass needs to be grinded into very fine particles, which consumes more energy than we harvest. Currently, only rough milling is used as the first stage for several other pre-treatment methods (nitrogen explosion, acid/alkaline pretreatment etc.).

Irradiation

This method uses microwaves, gamma rays or electric beams to disrupt cellular integrity. The advantages of irradiation methods include increased specific surface area & porosity of the biomass, & decreased cellulose crystallinity. It also softens & partially depolymerizes lignin (Agbor et al., 2011; Balat, 2011).

Today irradiation is not economically feasible for large scale utilization due to expensive equipment & lacking research in this specific field. It is also energy consuming & the use of gamma rays raises environmental & safety concerns (Agbor et al., 2011).

Biological pretreatment

Biological pretreatment uses fungi, selective enzymes &/or microorganisms to degrade the lignin & hemicellulose, which cover the cellulose. Positive aspects of biological pretreatment are low energy consumption, chemical-free processing & mild pretreatment conditions. Although it is an environmentally friendly method, it is not viable for commercial fuel production due to very long pretreatment time, large space requirement & need for constant monitoring of microorganisms growth (Haghighi Mood et al., 2013; Silveira et al., 2015; S. Sun et al., 2016).

Chemical pretreatment

Acid pretreatment

Acid pretreatment is the most studied & commonly used chemical pretreatment method. The method uses concentrated or diluted acids as catalysts in order to dissolve lignin & hemicellulose (Akhtar et al., 2016). Most commonly used acids are sulphuric,

hydrochloric, nitric etc. (Behera et al., 2014). The process is carried out at temperatures up to 210 °C depending on the acid concentration. At high temperatures (temperatures over 160 °C) diluted acids are used & at lower temperatures concentrated acids are used (Badiei et al., 2014).

Using concentrated acids results in high yields of fermentable sugars at low temperatures, but has several disadvantages, which limit the competitiveness of bioethanol produced in this way compared to fossil fuels we use today.

Concentrated acids are highly corrosive & therefore, the equipment is expensive. In addition, the acids are very expensive & for economical sustainability, the process requires acid recovery. Acid recovery itself is an energy consuming process, which reduces the efficiency of the overall process. Furthermore, the pretreated biomass requires neutralization prior enzymatic hydrolysis. Acids toxicity also raises environmental & health safety concerns (Rabemanolontsoa et al., 2016). While treating biomass with acids, different inhibitory by-products such as aliphatic carboxylic acids, phenolic compounds, furans, etc. are produced, which may have negative effects on the downstream processes (Chiaromonti et al., 2012; Tutt et al., 2012; Jönsson et al., 2016).

Alkali pretreatment

Alkali pretreatment uses several different reagents such as sodium-, ammonium-, potassium-, calcium hydroxides & sodium carbonate (Kim et al., 2016, Rabemanolontsoa et al., 2016). Pretreatment with alkali uses lower temperatures & pressures than pretreatment with acids (Tutt et al., 2012). It results in reduced energy input & therefore, is more cost-effective.

Main positive effects of this method are: decreased degree of polymerization & crystallinity, broken structural linkages between lignin & carbohydrates, disrupted lignin structure, increased biomass porosity. Effect of this method highly depends on the lignin content in the biomass (Y. Sun et al., 2002; Silveira et al., 2015; Kim et al., 2016).

The disadvantages of this method are: long pretreatment time (measured in hours or even in days) & formation of irrecoverable salts or incorporation into biomass, chemicals used are more expensive than the ones used in acid pretreatment (Mosier et al., 2005; Behera et al., 2014). Similarly to the case of acid pretreatment, the pretreated biomass needs to be neutralized prior to the enzymatic hydrolysis in order to lower the pH, & remove lignin & inhibitory by-products (salts, phenolic acids, furfural & aldehydes) (Menon et al., 2012). Alkali recovery system is needed in order to keep the end product price down.

Ionic liquids

Ionic liquid pretreatment uses salts as solvents. These salts have low melting point (liquid at room temperatures) & are stable up to 300 °C. Due to its non-volatility it is considered an environmentally friendly solvent (Guragain et al., 2011). Ionic liquids are also often called as designer solvents because their physical & chemical properties can be adjusted by choosing different cations, anions & substituents (Xiao et al., 2012).

This pretreatment method has several advantages. Ionic liquids dissolve cellulose, but leave lignin & hemicellulose intact & unaltered which allows their extraction for other chemical uses. Solvents adjustability gives an opportunity to dissolve different biomass types more efficiently.

The main drawbacks of using ionic liquids are solvents high costs & enzyme deactivation (Akhtar et al., 2016).

Organosolv

Method uses an organic or aqueous organic solvent mixture with inorganic acid catalysts depending on the temperature at which the process is conducted (Y. Sun et al., 2002; Behera et al., 2014). Preferred solvents have low boiling point, such as methanol or ethanol due to their low cost & ease of recovery (Zhang et al., 2016). Also, solvents with high boiling point are used, such as ethylene glycol, glycerol, etc. or other organic compounds, such as ethers, ketones or phenols (Y. Sun et al., 2002; Zhang et al., 2016). Organosolv pretreatment increases enzymatic hydrolysis efficiency by delignification & hemicellulose removal. Cellulose-rich residue is easily hydrolysed with enzymes to almost theoretical glucose yields (Binod et al., 2010).

On the positive side, this method can be used on both soft- & hardwood & relatively pure lignin can be recovered as a valuable co-product. Unfortunately, it also has several disadvantages, such as high capital investment, formation of toxic inhibitors & need for solvent recycling (Akhtar et al., 2016).

Physio-chemical pretreatment

Ammonia fibre explosion (AFEX) pretreatment

In this method lignocellulosic biomass is exposed to liquid ammonia at relatively high temperatures & pressures for a period of time. Contact with ammonia at high temperatures & pressures causes swelling & partial decrystallization of cellulose. Explosive decompression disrupts cellular integrity & therefore, enhances biomass digestibility (Tutt et al., 2014; Rawel Singh et al., 2016).

AFEX pretreatment has several advantages as it does not form toxic compounds, increases accessible surface area, & is very effective for herbaceous & low lignin content biomass (Behera et al., 2014; S. Sun et al., 2016).

Disadvantages of this method are that AFEX pretreatment does not perform very well on biomass with high lignin content, it does not remove lignin instead it alters its structure & it does not solubilize hemicellulose. One of the biggest drawbacks is that ammonia & its recycling is very expensive (Akhtar et al., 2016; Rawel Singh et al., 2016).

Steam explosion pretreatment

In steam explosion pretreatment high pressure (1–3.5 MPa) saturated steam is used to treat the lignocellulosic biomass. The biomass is heated rapidly to the desired temperature, incubated for a period of time (5–10 minutes) & followed by a rapid decompression (Renu Singh et al., 2014; Silveira et al., 2015).

Rapid decompression causes superheated water in plant cells to flash into steam & the steam volume expands explosively resulting in cell structure disruption. The cellulose bundles are defibrillated therefore, enhancing enzymatic hydrolysis efficiency. In order to remove hemicellulose high pretreatment temperatures are needed (150–250 °C) (Tutt et al., 2014).

Steam explosion is currently the most widely used pretreatment method for bioethanol production from lignocellulosic biomass, but it has several disadvantages such as formation of inhibitory compounds, incomplete disruption of lignin-

carbohydrate matrix, is not effective enough at lower temperatures (Chiaramonti et al., 2012; Tutt et al., 2014).

Nitrogen explosion pretreatment

A novel pretreatment method developed in the Estonian University of Life Sciences Institute of Technology. This method uses pressurized N₂ (pressure up to 6 MPa) & high temperature (up to 175 °C) combined with explosive decompression to open the biomass structure for more efficient enzymatic hydrolysis (Raud et al., 2014; Raud, Olt, et al., 2016; Raud, Rooni, et al., 2016; Tutt et al., 2016).

Due to high pressure, lignocellulosic biomass cells are filled with nitrogen saturated water. Rapid pressure change to normal pressure elicits a sudden change in volume of the nitrogen causing cell walls to rupture & resulting in better cellulose fibre exposure to enzymes (Raud, Olt, et al., 2016).

ANALYSIS OF PATENTED PRETREATMENT TECHNOLOGIES

There are several various patented technical solutions available for the pretreatment of lignocellulosic biomass. Large proportion of patented technical solutions is based on AFEX or steam explosion methods. Although there are lot of different technical solutions for pretreatment, they all have both, advantages & disadvantages. Most common disadvantages are the use of toxic chemicals (alkali, acids, ammonia, etc.) or need for extreme conditions (high pressure & temperature).

Steam explosion pretreatment devices

All the devices described in patents US 8,603,295 B2 (Dottori et al., 2013), US 2012/0111515 A1 (Nilsen et al., 2012), US 5,328,562 (Scott et al., 1994) use the conventional approach to pressurize the biomass in pretreatment reactors by adding sufficient amount of steam. One exception is the device described in US patent 2008/0277082 (Pschorn et al., 2008), where the final desired pressure is achieved by a high-pressure discharge compressor. The reason for using this compressor is to reduce the amount of hot steam needed for the pressurisation of the biomass. The energy needed to drive the compressor is considered lower than the energy needed to produce steam to raise pressure 0.5–1 bar.

Most of the devices use regular blow-valves to achieve the explosive decompression. Device described in US patent 2012/0111515 A1 uses 2-stage decompression in order to prevent erosion of the pressure relief tank. It is questionable if this multi-step decompression prevents erosion since the first pressure drop is preferably 2–13 bar & the second one only 0.2–1.6 bar (Nilsen et al., 2012). This two-staged decompression eliminates erosion in the final pressure relief tank, but it probably takes place in the first pressure relief tank. In addition, it is questionable if such two-stage pressure relief guarantees maximum disruption in the biomass cellular structure.

One negative aspect is that most of the devices described in the patents do not use the excess heat energy released during the rapid decompression of the steam. By using the excess heat, energy for preheating the biomass prior to entering the pretreatment reactor could significantly reduce the energy input of the process.

Disadvantage of most of the analysed devices, is that they tend to use acids or alkali in order to gain better access to cellulose fibres. Using acids or alkali significantly

increases the cost of the final product. Not only are the added alkali & acids expensive, by using chemicals the pretreated biomass needs further neutralization before the enzymatic hydrolysis can take place. In a laboratory-scale, small amounts are used, but for industrial-scale, large quantities of acids or alkali are needed. Therefore, expensive specialised tanks are needed to store the chemicals. Furthermore, extra certified & trained personnel are needed to handle it. While using chemicals in the process, there is always an environmental risk involved.

One way to reduce pretreatment costs in steam explosion devices is to use the pressure generated by steam to transfer biomass from one vessel to another instead of using screw devices (US patent 8,603,295 B2 (Dottori et al., 2013)) or high pressure compressors (pressure is generated by pistons, US patent 2008/0277082 (Pschorn et al., 2008)). Steam with elevated temperatures should be able to generate enough overpressure to move biomass through pipes & tanks, & to guarantee explosive decompression at the blow-valve.

Using different augers or compressors makes the device more complex & thus, more expensive. Using many different units increases the cost of the device as well as the frequency of the device maintenance.

AFEX pretreatment devices

All investigated AFEX pretreatment devices have one common disadvantage; the method uses highly volatile & toxic ammonia. The use of ammonia, whether in gaseous or liquid form, raises both environmental & health concerns. In addition, none of the devices described in the patents are continuous pretreatment devices, instead, they are batch systems.

Positive aspect of devices described in patents US 2013/0244284 A1 (Machida et al., 2013), is that they all recover & reuse most of the ammonia. Ammonia recovery & reuse can be considered as an advantage, but also as a disadvantage. Reusing ammonia helps to lower the price of the final product. On the other hand, it makes the device technologically even more complex.

N₂-explosion pretreatment device

Unlike the pretreatment methods described previously, nitrogen explosion pretreatment uses pressurised nitrogen gas to disrupt cellular integrity of the biomass thus, exposing cellulose to the enzymes (Raud, Olt, et al., 2016, Tutt et al., 2016).

The method uses lower pressures & temperatures compared to steam explosion devices, where effective temperatures are around 200+ °C & pressures up to 22 bars (Dottori et al., 2010). Pretreatment temperatures & pressures with nitrogen explosion range from 100 °C to 175 °C (with optimum at 150 °C) & from 10 to 60 bar (optimum at 30 bar), respectively (Raud, Rooni, et al., 2016; Tutt et al., 2016). A positive aspect of the device is also that no chemicals are used during the pretreatment process. It helps to lower pretreatment costs, since no additional treatment of the pretreated biomass is required.

The biggest flaw of the device described in patent EE05784 B1 at the moment is that it is not continuous pretreatment device & therefore, the productivity is very low. In addition, the excess heat, released during the explosion, is not utilised, which could lower the final cost of bioethanol production (Kikas et al., 2016).

Acid & alkali pretreatment device

The device described in patent EE05748B1 (Kikas et al., 2013) is a device that is usable for bioethanol production via chemical pathway.

Positive aspects of the device described in this patent are that it is an integrated system & the system allows continuous ethanol production. Also, the pretreatment system does not need any additional energy input, because it is interconnected to distillation unit, where temperature is held constantly at 130 to 150 °C.

The main problem is that the usage of chemicals makes the process very costly. When we use acids or alkali, we also need additional chemicals to adjust the pH to levels acceptable for enzymes. In addition, since the device uses an upright container for fermentation without any mixing unit probably the solids & liquid are separated & the fermentation is not efficient. The same applies to hydrolysis process. If the flow rate is very slow the solids & liquid may separate from each other & high efficiencies are not reached.

DISCUSSION

There are many methods & patented pretreatment devices for the pretreatment of the lignocellulosic biomass, yet only few of them (AFEX, steam explosion) are commercially used for bioethanol production. There are several reasons why any particular method or device is not used, but they all lead to one disadvantage, high product cost compared to fossil fuels. The cost of the final product is the main reason why only few of these methods & devices are used in commercial scale.

Most of the drawbacks are common to all of the patented devices reviewed in this article, whether it is AFEX or steam explosion device. Some of them are due to the nature of the material that is processed but also due to the chemicals that are used in the pretreatment process. Since chemicals & biomass are both corrosive, the devices must be made of stainless steel, which is expensive. In addition, since most of the devices use high pressures & temperatures the reactor vessels need to be made of hardened & tempered stainless steel that could withstand such extreme conditions.

Although the usage of chemicals (alkali, acids, etc.) improves the ethanol yields, it raises the question whether it is justified. The usage of chemicals requires:

1. Competent personnel to handle the chemicals/toxic gases;
2. Additional equipment for storage of chemicals/toxic gases;
3. Additional process prior hydrolysis (neutralization);
4. Additional equipment to recycle/neutralize chemicals/toxic gases;
5. Additional waste treatment system(s)/device(s).

All these requirements add to the production costs & therefore, raise the price of the final product & make it uncompetitive with the traditional petrol.

In order to increase lignocellulosic bioethanol competitiveness with fossil fuels the main goal is to lower the production costs. Since the pretreatment is the most expensive step in the bioethanol production, the pretreatment devices need to be improved & optimized.

There are several options to reduce the energy input. All of the methods that are used commercially today use high temperatures, & a lot of excess heat is released during the explosion, whether it is steam or ammonia fibre explosion. If the excess heat would be used to preheat the biomass prior the pretreatment, it would be possible to

considerably reduce the amount of energy needed to reach the necessary process temperatures.

A novel N₂-pretreatment device has been developed & investigated in the Estonian University of Life Sciences Institute of Technology that uses no catalysts or chemicals, which makes this pretreatment method attractive. In addition, the process uses quite modest temperatures compared to steam explosion or AFEX pretreatment. Even though the production costs can be reduced on the expense of using no chemicals & lower temperatures, it still has several drawbacks, such as lack of recycling of excess heat released during the explosive decompression & the fact that it is a batch system.

CONCLUSIONS

From the analysis of the literature & patents available, we can conclude that even though there has been a lot of research & technological development in the field of second-generation biofuel production from lignocellulosic biomass, an economical, cost-effective & feasible apparatus for the pretreatment of lignocellulosic biomass is still to be developed. Therefore, in the near future the second-generation bioethanol will still not be able to compete with the fuels derived from the fossil resources.

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