L04

BIOMASS PRETREATMENT: SEPARATION OF CELLULOSE, HEMICELLULOSE AND LIGNIN. EXISTING TECHNOLOGIES AND PERSPECTIVES

Raspolli Galletti Anna Maria, Antonetti Claudia
UNIVERISTY OF PISA, DEPARTMENT OF CHEMISTRY AND INDUSTRIAL CHEMISTRY

Via Risorgimento 35, 56126, Pisa, Italy
roxy@dcci.unipi.it

Birth date: November 19, 1958
Title: Associate Professor of Industrial Chemistry, University of Pisa
Education:
1982: Doctor Degree in Industrial Chemistry, University of Pisa, Italy
1986: PhD Degree in "Chemical Sciences"
Scientific activity: The scientific activity has always been devoted to the applied catalysis, and in particular to these topics of industrial interest:

- Catalytic conversion of renewable products in fine chemicals
- Synthesis and catalytic activity of nanostructured metal catalysts
- Polymerization/oligomerization catalysts: synthesis and catalytic activity

She has scientific collaborations with many Italian and European Universities and contributed actively in the organization of seven national and six international Symposia. She is and has been team leader of many Research Programs in collaboration with relevant national and international Companies and member of the Steering Committee of the Interdivisional Catalysis Group of Italian Chemical Society. From 2007 is member of the Administration Board of the University of Pisa.
Author of 120 publications in ISI Internationals Journals, 5 chapters in books and 20 patents.

Abstract
Biomass pretreatment is an important tool for effective cellulose conversion processes and it is the subject of this chapter. Pretreatment is required to alter the structure of biomass in order to make cellulose more accessible to the enzymes that convert the carbohydrate polymers into fermentable sugars. The optimum conditions strictly depend on the characteristics of each raw material as well as on the final purpose of the process itself.

Introduction
Biomass pretreatments involve many different approaches for the separation of the three main components and their successive exploitation [1]. The historical pretreatment, acid hydrolysis, unfortunately showed some relevant drawbacks; as a consequence, recently, different approaches have been investigated which can be classified into the main different categories: physical, physicochemical, chemical and biological pretreatments [2].

Results and discussion

In this chapter, several pretreatments have been analysed and compared each other. The most important pretreatments are of chemical type: acid and alkaline ones.

Acid pretreatment can be performed with diluted or concentrated acids, but these last are more hazardous, highly corrosive for reactors and equipments and must be recovered after the pretreatment. Moreover, if the pretreatment is preceding to enzymatic hydrolysis, drastic acid conditions favour the formation of degradation and inhibiting compounds and cause the fast condensation and precipitation of solubilized lignin [3]. For these reasons, only diluted acid pretreatment appears attractive for large scale applications. An efficient mild acid pretreatment completely solubilizes the hemicellulosic component of the biomass and only a little part of cellulose (at low acid concentration), thus making undissolved cellulose more accessible to enzymes. The most commonly employed acid is sulphuric one, generally in concentration below 4 wt %, applied to a wide range of lignocellulosic biomass [4].Taking into account that acid hydrolysis involves expensive materials for plants, high pressures, neutralization and conditioning of the residual biomass before of an eventual successive enzymatic step, it is compulsive to carefully evaluate the proper dilute acid treatment. The most recent studies have been devoted to the optimization of the hydrolysis under very mild acid conditions combined with MW irradiation in order to reach high yields into sugars [5].

Alkaline pretreatment employes alkaline solutions, such as sodium hydroxide, calcium hydroxide or ammonia for the treatment of biomass, among which sodium hydroxide being more deeply studied, in order to remove lignin and part of hemicellulose and to efficiently increase the accessibility of cellulose. This approach is basically a delignification process, where a significant amount of hemicellulose is also solubilized. The use of an alkali causes the degradation of ester and glycosidic side chains, resulting in structural alteration of lignin, cellulose swelling, partial decrystallization of cellulose and partial solvatation of hemicellulose [6]. Alkaline treatment is usually more effective on biomasses with low lignin content than on those with high lignin content. This pretreatment can be carried out at lower temperatures and pressures than other pretreatment technologies, even up to room conditions, but, especially if performed at room temperature, long times and high concentrations of base are required. The most considerable drawback of alkaline pretreatments is the conversion of alkali into irrecoverable salts and/or the incorporation of salts into the biomass during the pretreatment reactions, making the treatment of a large amount of salts a challenging issue for alkaline approach.

Among physicochemical processes (pyrolysis, steam exploiosion, torrefaction, ammonia fiber explosion, CO_2 explosion) steam explosion is the most commonly used pretreatment of biomass and uses both physical and chemical methods to break the structure of the lignocellulosic material with an hydrothermal treatment [7]. The biomass is treated with high pressure steam at high temperature for a short time, then it is rapidly depressurized and the fibrils structure is destroyed by this explosive decompression, improving significantly the substrate digestibility and bioconversion as well as its reactivity toward other catalytic reactions. Another revealing treatment is torrefaction consisting of biomass heating to a moderate temperature working under inert or nitrogen atmosphere [8]. The increase of torrefaction temperature decreases solid biochar yield with a contemporary increase of the yield in volatile matters including liquid and noncondensable gases. Unfortunately, this termochemical approach has not developed enough yet to be feasible on large scale.

A very recent approach to the pretreatment of biomass involves the use of ionic liquids (ILs) as solvents [9].Their very high solvating properties have been used for dissolving cellulose, lignin and also raw biomass. Before ILs application on large industrial scale, their recovery and recycle should be improved because their price is generally high. In addition, it is evident that their recycle can not be performed indefinitely due to impurities accumulation.

Conclusions

The separation of the three main components of lignocellulosic biomass is severely limited by many factors, such as lignin content, cellulose crystallinity, water content and available surface area which also influence the future exploitation of the pretreated materials. The choice of the best pretreatment strictly depends on the downstream use of the pretreated fraction itself. In order to overcome the disadvantages of every method, the most recent papers suggest the usefulness of combined approaches, which can lead to the optimal fractionation of the different components. An efficient integrated process should allow the exploitation of all the three main components of biomass, including the up to now underutilized lignin. In the context of a combined process, torrefaction and MW irradiation appear particularly promising if joined with chemical pretreatments.

References

1. D.J. Hayes, *Catal. Today* **2009**, 145, *138*.
2. L. De Costa Sousa, S.P.S. Chundawat, , V. Balan, V., B.E. Dale, *Curr. Opin. Biotechnol.* **2009**, 20, *339*.
3. C. Liu, C.E Wyman, *Ind. Eng. Chem. Res*. **2003**, 42, *5409*.
4. J.W. Lee, T. W. Jeffries, *Bioresour. Technol*. **2011**, 102, *5884*.
5. A.M. Raspolli Galletti, E. Ribechini, M. Martinelli, E. Bonari, N. Nassi, L. Angelini, *It. Pat. Appl. FI* **2009** A000210 (29/9/2009).
6. D.L. Sills, J.M. Gossett, *Bioresour. Technol.* **2011**, 102, 2, *1389*.
7. P. Kumar, D.M. Barrett, M.J. Delwiche, P. Stroeve, *Ind. Eng. Chem. Res.* **2009**, 48, *3713*.
8. M.J. Prins, K.J. Ptasinski, F.J.J.G. Janssen *Energy* **2006**, 31, *3458*.
9. M. Mora–Pale, L. Meli, T.V. Doherty, R.J. Linhardt, J.S. Dordick, *Bioresour. Bioeng.* **2011**, 108, *1229*.

Acknowledgements

The authors would like to thank University of Pisa for providing financial support through a Claudia Antonetti research fellowship.