International Journal of Universal Print
ISSN: 2454-7263 ID: ACTRA 2018 069 Published Mar. 2018
Volume No. 04, Issue No.07, Copyright © Universal Print
Web: www.universalprint.org , Email: ijup@universalprint.org
Title Key: X-ray diffractions studies during dilute …

X-RAY DIFFRACTION STUDIES DURING DILUTE ACID PRETREATMENT OF LIGNOCELLULOSIC BIOMASS.

A.D. Bhetalu [1]*, N.V.Lawale N.V.[2], S.S.Patil.[3], N.W. Ingole [4]

1. Assistant Professor, Department of Engineering Chemistry, Dr.Rajendra Gode Institute of Technology and Research, Amravati, Maharashtra, India
ashish_bhetalu@rediffmail.com
2. Assistant Professor, Moreshwar Arts, Science and Commerce College, Bhokardan, Jalna
narayanlawale78@gmail.com
3. Professor and Director, Department of Adult, Continuing Education Extension Services, Sant Gadge Baba Amravati University, Amravati
drsspatil1999@gmail.com
4. Professor, Department of Civil Engineering, Prof. Ram Meghe Institute of Technology and Research, Badnera, Amravati, Maharashtra, India
nwingole@yahoo.com

Abstract

Lignocellulosic biomass is proven raw material for production of bioethanol production. This biomass material is a complex mixture of various organic materials. The presence of carbohydrates in these biomass materials is making it an attractive alternate for conventional fuels. However, certain Pretreatment processes need to be employed in order to utilize these carbohydrates to produce bio-ethanol. This article aims towards the study of the effect of pretreatment process by using diluted acid on lignocellulosic biomass. The XRD study of samples reveals the changes in the morphology of the biomass material.

Keywords: Bioethanol; Diluted acid; Lignocelluloses; Pretreatment; X-ray diffraction

Subject Classification: Environmental Chemistry

International Journal of Universal Print
ISSN: 2454-7263 ID: ACTRA 2018 069 Published Mar. 2018
Volume No. 04, Issue No.07, Copyright © Universal Print
Web: www.universalprint.org , Email: ijup@universalprint.org
Title Key: X-ray diffractions studies during dilute …

1. Introduction

Biomass is organic plant materials which do not directly go into foods or consumer products. These plant materials contain a complex mixture of carbohydrates, fats, and proteins. The amounts of these constituents are different in each type of biomass. Mostly, carbohydrates and lignin are the abundant components of biomass. The carbohydrates present as cellulose and hemicellulose fibers, are polysaccharides which provide strength to the plant structure[1]. The lignin forms covalent bonds with theses polysaccharides; thereby cross-linking the fibers together. Cellulose contains the six-carbon sugar monomer glucose. Hemicellulose contains both five and six carbon sugar monomers that include glucose, xylose, mannose, galactose, and arabinose. Xylose is the most abundant polysaccharide in hemicellulose [2]. These Polysaccharides are used in a conversion process to make ethanol.

For the production of ethanol from biomass, first, the carbohydrates need to be hydrolyzed into their component sugars using either acid or enzymes. Then, yeast is used to convert the sugars into ethanol [3].Although the basic process is very simple but there are a variety of factors that need to be taken into consideration like choice of acid, the concentration, temperature, soaking time etc. Every variable has its unique effect on the outcome of the process.

In order to convert the lignocelluloses to ethanol, several pretreatment methods have been employed so far. Dilute acid treatment is one of the most commonly employed methods for this purpose. This process has several advantages over the other methods [4].

The aim of pretreatment process is to change the properties of lignocellulosic material for degradation. The best pretreatment method and condition depend on the type of lignocellulose. This research aims to study the effect of pretreatment process by using diluted acid to the characteristic of three biomass samples in term of surface morphology.

According to Nathan et.al [5] and Zheng et.al [7], pretreatment process by using diluted acid can dissolve almost all hemicellulose and break lignin and cellulose bonding so it can increase digestibility of enzyme/catalyst in hydrolysis process. Yang et.al use diluted sulfur acid in the chemical pretreatment process and this chemical pretreatment process can dissolve almost all hemicellulose component (80-90%), increase susceptibility of cellulose, but little break lignin component [6]. Pretreatment process by using diluted acid can dissolve almost all hemicellulose, but not for lignin component [7].

2. Materials and method

2.1 Materials

The lignocellulosic biomass material used during this study includes three plans viz. water hyacinth, Cattails and Duckweeds. Whole water hyacinth plantswere collected from the banks of river *Morna* in Akola city, Maharashtra, India. Cattails and Duckweeds were collected locally from a pond located at Kathora road, Amravati.

International Journal of Universal Print
ISSN: 2454-7263 ID: ACTRA 2018 069 Published Mar. 2018
Volume No. 04, Issue No.07, Copyright © Universal Print
Web: www.universalprint.org , Email: ijup@universalprint.org
Title Key: X-ray diffractions studies during dilute …

2.2 Method

The biomass was subjected to pretreatment with Sulphuric acid. The dilute acid pretreatment of biomass samples was carried out by treating 10 g biomass sample with dilute sulphuric acid. The hydrolyzate after treatment was separated by filtering the contents through double layered muslin cloth. The liquid part was used for subsequent fermentation and solid part was used for characterization.

2.3 Characterization

Characterization of biomass samples before and after pretreatment has been analyzed by using X-ray Diffraction (XRD) following the method of Segal et al 1959. The dry samples were filled in the cell mount and scraped with a spatula to give smooth, flat surface which was flush with the surface of cell mount. The samples were then exposed to X-rays using Rigaku MiniFlex II Desktop X Ray Diffractometer with a diffracted beam graphite monochromatic running on Cu Kα radiation. Samples of the cellulose powder are placed on a glass slide and analyses are performed from 10^0 to 70^0 of 2θ angle at a rate of 5 degrees per minute.

3. Results and discussion

For effective conversion of cellulose to ethanol, it is imperative to break through the crystalline structure of cellulose. The key aspect is the conversion of crystalline cellulose into amorphous cellulose. The peak height indicates the crystallinity of cellulose levels. The effect of various pretreatment methods on the crystalline structure of cellulose can be studied using XRD pattern. During the treatment process, the cellulose chain expands due to diffusion of chemicals into the crystalline cellulose. Furthermore, the cellulose chain will undergo re-arrangements that result in damage to the structure of crystalline cellulose. Damage in the crystalline structure to non-crystalline cellulose led to an increase in amorphous cellulose.

Lignocellulose biomass is composed by cellulose, hemicellulose and lignin connected each other because of amorphous structure and 1,4'- bonding in cellulose and also the existence of lignin between cellulose chain [5].

The X-ray diffraction spectra reveal substantial changes to cellulose crystallinity of the aquatic macrophytes under investigation. There is a strong relation between cellulose crystallinity and effectiveness of hydrolysis. The crystallographic structures of biomass samples before and after the dilute sulphuric acid hydrolysis were examined by X-ray diffractometer (XRD). The X-ray diffraction analyses were carried out on samples using a Rigaku MiniFlex II Desktop X Ray Diffractometer with a diffracted beam graphite monochromatic running on Cu Kα radiation. Samples of the cellulose powder are placed on a glass slide and analyses are performed from 10^0 to 70^0 of 2θ angle at a rate of 5 degrees per minute.

Figure 1, 2 and 3 show the XRD spectra of untreated samples and the remaining solids after acid hydrolysis of water hyacinth, cattails and duckweed samples respectively. All plant cells are surrounded by a polysaccharide-rich

International Journal of Universal Print
ISSN: 2454-7263 ID: ACTRA 2018 069 Published Mar. 2018
Volume No. 04, Issue No.07, Copyright © Universal Print
Web: www.universalprint.org , Email: ijup@universalprint.org
Title Key: X-ray diffractions studies during dilute …

wall, which provides support, strength and shape to the plant. This structural material in the cell wall is known as lignocellulose which composed mainly of cellulose (Crystalline), hemicellulose and lignin (Amorphous).

The cellulose chain adopts a linear structural arrangement and, due to its intra- and intermolecular hydrogen bonding, various ordered crystalline arrangements are observed. In general, cellulose extracted from plant materials contains both amorphous region and a crystalline region.

Spectra show the ordered arrangement of the glucan chains that regulate the physical and chemical characteristics of cellulose. These bonds not only present a regular crystalline arrangement of the glucans molecules resulting in distinct X-ray diffraction patterns but also relate to the swelling and reactivity of cellulose.[8]

The XRD spectra show that there were some changes in peak intensity. For untreated samples, the crystalline peak predominates and is well defined at common scale. This could support the hypothesis of differences between cellulose crystallinity among samples. It seems that unhydrolyzed samples have high crystalline cellulose content.

In acidic media, the amorphous hemicelluloses in lignocellulosic biomass hydrolyze quicker (than cellulose) to soluble sugars and some oligomers especially in mild conditions through the disruption of xylosidic bonds and cleavage of acetyl ester groups and the lignin seal is degraded through substitution reactions and broken links accompanied by condensation reactions that prevent dissolution. Cellulose undergoes preferential degradation of amorphous regions leading to enlarged cellulose fibrils and fibril aggregates and an increase in the crystallinity index of the pretreated material.

Based on the calculated diffraction peaks shown in Figures 1 raw water hyacinth display three main diffraction peaks at $2\theta = 23^0$ 28.6^0 and 40.9^0 whereas the preatreated water hyacinth shows peaks at $2\theta = 22.4^0$ and 26.5^0.

Pretreated cattails display main diffraction peaks at $2\theta = 23.1^0$ 28.7^0, 32^0, 40.8^0 and 45.8^0 whereas the hydrolyzed cattails shows only an amorphous peaks at $2\theta = 21.8^0$. A distinct change in the crystallinity can be clearly observed from the spectra.

Raw duckweeds display many diffraction peaks at $2\theta = 11.9^0$, 21.0^0, 23.6^0, 26.9^0, 29.3^0, 31.4^0, 33.6^0, 34.3^0 and 40.9^0 whereas the pretreated duckweed sample shows a broad amorphous peaks at $2\theta = 22.1^0$ and several peaks at $2\theta = 27.0^0$ and 29^0.

The XRD spectrum provides evidence of changes in the crystallinity of the samples under investigation i.e. water hyacinth, cattails and duckweeds. It is conceivable that the hydrolysis plays a key role in the changes in the crystalline nature of lignocellulosic materials.

International Journal of Universal Print
ISSN: 2454-7263 ID: ACTRA 2018 069 Published Mar. 2018
Volume No. 04, Issue No.07, Copyright © Universal Print
Web: www.universalprint.org , Email: ijup@universalprint.org
Title Key: X-ray diffractions studies during dilute …

Fig 1. X-ray diffraction pattern for (a) raw and (b) acid treated Water hyacinth

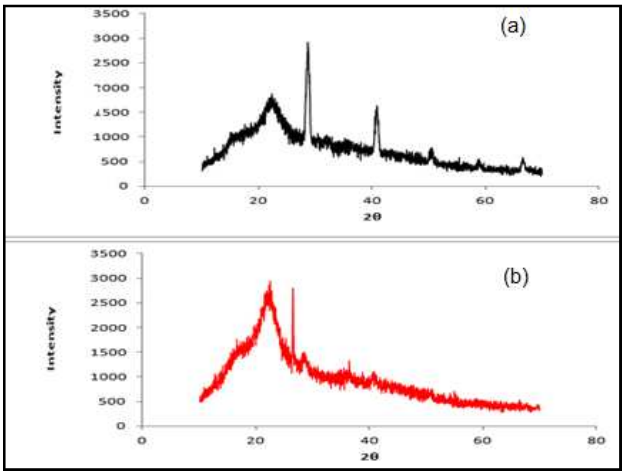


Fig 2. X-ray diffraction pattern for (a) raw and (b) acid treated cattails

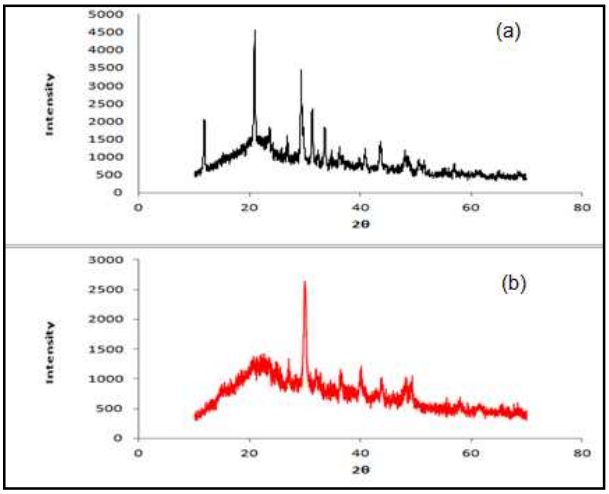
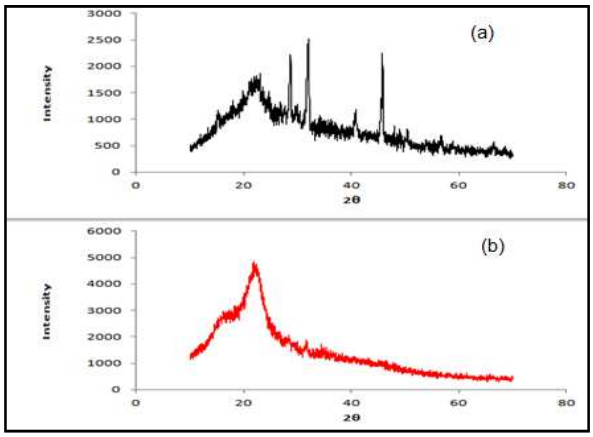


Fig 3. X-ray diffraction pattern for (a) raw and (b) acid treated duckweeds



4. Conclusion

The intention of employing the pretreatment is to change their morphology and crystallinity of the biomass material. As can be seen from the XRD spectra, it is clear the change of their morphology before and after pretreatment process. On this basis, it may be concluded that the pretreatment process could increase the amorphous part and consequently decrease the crystal part of the substrate morphology. The amorphous part will make cellulose more accessible for the yeast that converts the carbohydrate polymers into fermentable sugars.

International Journal of Universal Print
ISSN: 2454-7263 ID: ACTRA 2018 069 Published Mar. 2018
Volume No. 04, Issue No.07, Copyright © Universal Print
Web: www.universalprint.org , Email: ijup@universalprint.org
Title Key: X-ray diffractions studies during dilute …

5. References

[1] McKendry P. Energy production from biomass (part 1): overview of biomass. *Bioresource Technol* 2002:83;37-46.
[2] Sjöström E. *Wood chemistry: fundamentals and applications*. San Diego: Academic Press; 1993.
[3] Taherzadeh MJ. Karimi K. Pretreatment of Lignocellulosic Wastes to Improve Ethanol and Biogas Production: A Review.*Int J Mol Sci* 2008:9;1621-1651.
[4] Taherzadeh MJ, Karimi K. Acid-based hydrolysis processes for ethanol from lignocellulosic materials: A review. *Bio Resources* 2007:2;472-499.
[5] Nathan M. et al. Features of promising technologies for pretreatment of lignocellulosic biomass. *J Bioresource Technology* 2005:96;673–686.
[6] Yang B, Wyman CE. Pretreatment: the key to unlocking low-cost cellulosic ethanol. *Biofuels Bioprod Bioref* 2008:2;26-40.
[7] Zheng Y, Pan Z, Zhang R. Overview of biomass pretreatment for cellulosic ethanol production. *Int J Agric & Biol Eng* 2009:2(3);51-68.
[8] Franz, G., and Blaschek, W. (1990), in: *Methods in Plant Biochemistry.* P.M. Dey (ed). Academic Press Limited, San Diego, CA, pp. 291-322.