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Alkaline and ultrasound assisted alkaline pretreatment for intensification of delignification process from sustainable raw-material

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ABSTRACT

Alkaline and ultrasound-assisted alkaline pretreatment under mild operating conditions have been investigated for intensification of delignification. The effect of NaOH concentration, biomass loading, temperature, ultrasonic power and duty cycle on the delignification has been studied. Most favorable conditions for only alkaline pretreatment were alkali concentration of 1.75 N, solid loading of 0.8% (w/v), temperature of 353 K and pretreatment time of 6 h and under these conditions, 40.2% delignification was obtained. In case of ultrasound-assisted alkaline approach, most favorable conditions obtained were alkali concentration of 1 N, paper loading of 0.5% (w/v), sonication power of 100 W, duty cycle of 80% and pretreatment time of 70 min and the delignification obtained in ultrasound-assisted alkaline approach under these conditions was 80%. The material samples were characterized by FTIR, SEM, XRD and TGA technique. The lignin was recovered from solution by precipitation method and was characterized by FTIR, GPC and TGA technique.

1. Introduction

The instability of oil prices and the imminent depletion in the traditional fossil fuels, have enforced a number of countries to invest a great deal into research and development with an objective of finding an alternative energy source. Plant biomass has come forward as one of the important source of alternative energy, as plant biomass can be utilized in both physico-chemical and biological conversion into several valuable products [1]. There is also a considerable interest in developing renewable energy resources to replace crude oil. Production of ethanol can be carried out using inexpensive and plentiful lignocellulosic biomass such as agricultural and forestry residues, wastepaper, a considerable portion of municipal solid waste, and woody and herbaceous energy crops. However, even though lignocellulosic material provides an economical resource, the method of conversion to ethanol is very complicated [2]. As lignocellulosic biomass is complex and strongly resistant to enzymatic hydrolysis due to its recalcitrance, pretreatment is needed in order to increase the hydrolysis rates. Various pretreatment methods have been reported for the delignification of biomass including steam explosion, acid, and alkaline treatment [3]. Alkaline pretreatment is one of the most commonly applied processes among the different proposed pretreatment methods for delignification of biomass. The intention of pretreatment is to generate reactive cellulose materials from the lignocellulosic matrix and open or moderately break up the recalcitrant structure. Subsequently, biomass can be more readily hydrolyzed by cellulase enzyme, and converted into monosaccharides, primarily glucose. Pretreatment is one of the most costly steps in biochemical conversion of lignocellulosic biomass, accounting for up to 40% of the total processing cost [4]. Furthermore, it strongly affects the downstream processing and associated costs of operation including enzymatic hydrolysis.

Pretreatment of lignocellulosic biomass with alkali such as NaOH can eradicate or modify the lignin content by rupturing the ester bonds that form cross links involving xylan and lignin, thus increasing the porosity of the lignocelluloses [5]. Alkaline pretreatments show less sugar degradation and furan derivatives formation. The alkaline pretreatment is very complex involving numerous reactive and non reactive phenomenons such as dissolution of non degraded polysaccharides, peeling off reaction (formation of alkali stable end groups), decomposition of the dissolved polysaccharides and hydrolysis of glycosidic bonds. Accordingly, the efficiency of NaOH pretreatment depends considerably on the operating parameters such as temperature, concentration of NaOH, treatment time in addition to the inbuilt characteristics of the biomass used [6].

The alkaline pretreatment process can be improved further by the application of ultrasound [7]. The present study conjugates alkaline pretreatment with ultrasound irradiation. The ultrasonic treatment of aqueous media produces cavitation, which generates conditions of high temperature, pressure and extreme shear forces. The decomposition of water molecules into free radicals by

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cavitation aids in cleaving the linkages in lignin and xylan networks [8]. Ultrasound irradiation causes homolysis of lignin–carbohydrate bonds releasing lignin [9]. The application of ultrasound for delignification of lignocellulosic matrix is still in emerging stage. Ultrasound assisted fractionation of the lignocellulosic biomass improves the effectiveness of the classical treatments such as alkaline treatment, giving proportionately higher yield and selectivity of the obtained products [10]. Ultrasound treatment shortens the processing time as well as reduces the requirement of alkali [11]. The main limitations of the alkaline pretreatment of lignocellulosic biomass include relatively longer pretreatment time and consumption of more alkali. Waste paper is an abundant and low cost substrate for production of glucose by enzymatic hydrolysis. On an average, waste paper constitutes half a municipal solid waste, and newspaper alone 14% of the waste [12]. The extensive use of papers has produced a huge amount of waste paper, however, it is difficult to recycle this sustainable resource because of the high processing cost. Presently, majority of waste paper is land filled or incinerated; but, both of these methods are of increasing environmental concern. Though European recycling ratio of paper is comparatively high i.e. 66%, still it has not reached an adequate level yet. Additionally, when paper materials are recycled, they are typically turned into lower grade paper products. By further recycling of paper, fiber length in the paper becomes shorter and this shortening of paper fibers decreases the quality of paper. This means that a major fraction of paper would always be sent to disposal. This fraction contains a considerable and underutilized source of sugar [13]. Thus, newspaper as a substrate has been selected as representative source of waste lignocellulose. Until now no work has been carried out to intensify the alkaline pretreatment of sustainable lignocellulosic biomass such as newspaper. In the present work, ultrasound-assisted alkaline approach has been studied for the delignification of waste newspaper as a sustainable raw material.

Breakthroughs in pretreatment are still required for both scientific as well as economic reasons. More exhaustive analysis of factors influencing delignification is required to establish design related information. The aim of the present study was to investigate most favourable biomass loading, NaOH concentration and sonication time, sonication power, duty cycle so as to maximize the ultrasound-assisted alkaline pretreatment with the intention to improve the delignification. The overall purpose of this research was to develop an efficient ultrasound-assisted alkaline pretreatment method for the final possible bioconversion of lignocellulosics into bioethanol.

2. Materials and methods

2.1. Materials

Newspaper as a substrate was selected as a lignocellulosic biomass for the pretreatment and was collected from a local supplier. Its composition based on the dry substrate was: 41.02% cellulose, 24.85% hemicellulose, 23.07% lignin, 5.99% ash and 3.89% moisture. The composition was determined by using standard method described by NREL. The collected newspaper was air dried for 2 h at 105 °C and mechanically grinded using electric mixer grinder in distilled water. The newspaper used for the experiments was in the form of slurry. Standard of lignin was obtained as a gift sample from Waltar Enterprises, Mumbai. Acetyl bromide was procured from Spectrochem Pvt. Ltd., Mumbai. All other reagents and chemicals were procured from S.D. Fine chemicals Pvt. Ltd., Mumbai.

2.2. Alkaline pretreatment

A fully baffled 2000 cm^3 jacketed glass reactor was used for the delignification reaction. The temperature of reaction was controlled by circulating water. A uniform suspension of newspaper (0.8% w/v) in distilled water was transferred to the reactor followed by addition of alkali (NaOH) solution. Immediately after the addition of the alkali solution, a sample was withdrawn and agitation was started. Samples were frequently withdrawn at regular time intervals and immediately centrifuged at 10,000*g* for 20 min to remove the residual particles. The clear supernatant obtained was used for measuring the lignin concentration.

2.3. Ultrasound-assisted alkaline pretreatment

A three neck fully baffled, jacketed glass reactor equipped with mechanical stirrer was used for the reaction. Ultrasonic device was a probe sonicator obtained from Dakshin Ultrasonics, Mumbai. The ultrasonic irradiation at a frequency of 20 kHz was transferred through a titanium cylindrical horn, introduced into the reactor through the side neck and submerged 1.0 cm into the reaction mixture. The horn had a diameter of 1.1 cm. The experimental setup is shown in Fig. 1. The procedure followed for the delignification studies was similar to that mentioned in alkaline pretreatment.

Integral method of analysis was followed in the present work to calculate the rate constants and it has been observed that first order kinetics explains the delignification kinetics very well. All the experiments were repeated two times to check the reproducibility and average values have been reported in the figures. Error bars have also been shown to illustrate the variation.

2.4. Recovery of lignin

For the recovery of lignin, sample was irradiated with ultrasound for delignification using horn at power of 100 W, duty cycle of 80% and using 1 N NaOH solution at room temperature. The hemicelluloses were isolated from the sample by precipitation of the acidified hydrolysate (pH 5.5 adjusted with 10% HCl) with 3 volumes of 95% ethanol. The pellet rich in hemicelluloses was filtered, washed with 70% ethanol and air dried. After evaporation of ethanol, the alkali soluble lignin was obtained by precipitation at pH 1.5 adjusted by 10% HCl. The isolated lignin was washed with acidic water (pH 2.0) and air dried. The residue rich in cellulose was washed with water and then dried at 105 °C for 6 h [14].

2.5. Analysis

The lignin concentration in solution after reaction was analyzed by UV Spectrophotometer. Samples were solubilized in a solution

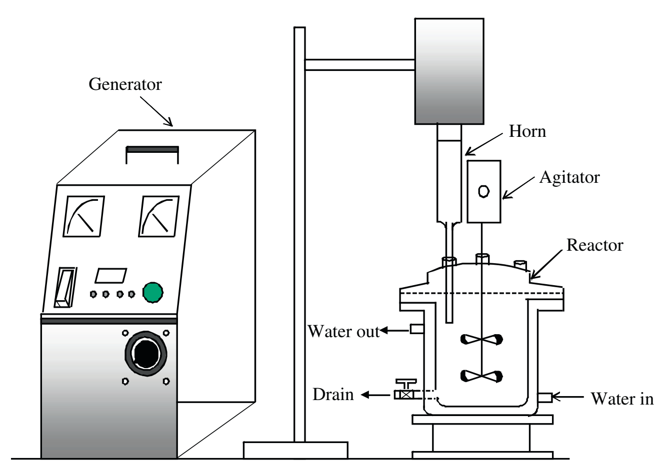

Fig. 1. Experimental setup for ultrasound-assisted alkaline pretreatment.