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Mechanistic investigations in sono-hybrid techniques for rice straw pretreatment

Kelothu Suresh [a], Amrita Ranjan [b], Shuchi Singh [b], Vijayanand S. Moholkar [a,b,*]

[a] Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati 781 039, Assam, India
[b] Center for Energy, Indian Institute of Technology Guwahati, Guwahati 781 039, Assam, India

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ABSTRACT

This paper reports comparative study of two chemical techniques (viz. dilute acid/alkali treatment) and two physical techniques (viz. hot water bath and autoclaving) coupled with sonication, termed as sono-hybrid techniques, for hydrolysis of rice straw. The efficacy of each sono-hybrid technique was assessed on the basis of total sugar and reducing sugar release. The system of biomass pretreatment is revealed to be mass transfer controlled. Higher sugar release is obtained during dilute acid treatment than dilute alkali treatment. Autoclaving alone was found to increase sugar release marginally as compared to hot water bath. Sonication of the biomass solution after autoclaving and stirring resulted in significant rise of sugar release, which is attributed to strong convection generated during sonication that assists effective transport of sugar molecules. Discrimination between individual contributions of ultrasound and cavitation to mass transfer enhancement reveals that contribution of ultrasound (through micro-streaming) is higher. Micro-turbulence as well as acoustic waves generated by cavitation did not contribute much to enhancing of mass transfer in the system.

1. Introduction

Primary energy needs of a developing country like India are in terms of electricity and transportation fuel like diesel and gasoline. With fast depletion of fossil fuels reserves and growing concerns of global warming due to greenhouse gas emissions, quest for an alternate, renewable and carbon neutral biofuels has been a foremost research activity worldwide for past couple of decades. Alcoholic biofuels such as ethanol and butanol have emerged as potential renewable liquid biofuels [1,2]. Conventionally, the feedstock for fermentation for these alcohols has been either molasses or corn. However, due to food-value of these feedstocks, for large-scale production of alcoholic biofuels, these have been proven uneconomical. The alternate cheap feedstocks mainly include agro-residues, which is essentially lignocellulosic biomass. The major candidates in this category are wheat and rice straws. Both of these straws have high cellulose (~45% w/w) and hemicellulose (~25% w/w) content [1,3], which can be converted to fermentable sugars after physical and chemical pretreatment followed by enzymatic saccharification. In Indian context, rice is the major crop. The annual production of rice in India for past one decade is over 90 MMTPA, which generates residue of ~125 MMTPA in the form of rice straw. The usual physical techniques of pretreatment are grinding, milling, water bath treatment and steam explosion or autoclaving. The chemical techniques include dilute acid or alkali treatment. The physical and chemical treatments are mainly aimed at breaking the dense layers of lignin surrounding cellulose and hemicellulose, which hinders their accessibility. However, some hydrolysis also occurs during these physical and chemical treatments resulting in release of sugars. The process of hydrolysis has mass transfer limitation due to two-phase nature of the system (solid biomass and liquid hydrolyzing medium). In addition, other process parameters such as concentration of acid/alkali, concentration of straw, temperature, pressure of the system and time of treatment, also influence the overall process kinetics and yield.

Ultrasound and its secondary effect, cavitation, is a well-known technique for enhancement of mass transfer limited systems [4]. Ultrasound has been applied in the past for pre-treatment as well as hydrolysis of different kinds of biomass and cellulose. Some representative papers in this are by Bhattacharya et al. [5], Baxi and Pandit [6], Velmurugan and Muthukumar [7], Yachmenev et al. [8], Imam and Capareda [9] and Li et al. [10]. A detailed review of the literature in this area is recently given by Iskalieva et al. [11]. Although previous literature reports beneficial effect of ultrasound on pretreatment and hydrolysis, the exact mechanism of ultrasound-induced enhancement is not established yet. Ultra-

Abbreviations: ATCLV, autoclaving; STR, stirring; US, ultrasonication; US-EP, ultrasonication at elevated pressure; WB, water bath; TS, total sugar; RDS, reducing sugar; GLS, glucose; RS, rice straw; RSH, rice straw hydrolyzate; MMTPA, million metric tones per annum.

* Corresponding author at: Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati 781 039, Assam, India. Tel.: +91 361 258 2251; fax: +91 361 258 2291.

E-mail addresses: vmoholkar@iitg.ernet.in, vmoholkar@iitg.ac.in (V.S. Moholkar).

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sound and cavitation have both physical and chemical effects on the system. The whole process of rice straw pretreatment has two components, viz. physical component of opening up of the biomass structure, and the chemical component of hydrolysis to release sugars. The relative influence of ultrasound on each of these components, in comparison to the conventional technique, and the exact mechanism of this influence is an important issue that needs systematic investigation. In this paper, we have attempted the same task with rice straw as the biomass. We have assessed two physical techniques, viz. hot water bath and autoclaving or steam explosion, and two chemical techniques, viz. dilute acid/dilute alkali pretreatment, coupled with sonication. We term these techniques as sono-hybrid techniques. We have adopted an approach of analyzing experimental results vis-à-vis simulations of cavitation bubble dynamics. The experimental techniques are designed to discriminate the individual effects of ultrasound and cavitation [12,13]. The total sugar release, reducing sugar release and glucose content of reducing sugar have been used as yard sticks in the analysis. The total sugar released during acid or alkali hydrolysis consists of sugar present in any form, i.e., either intact monomers (pentose sugars like xylose and arabinose, hexose sugars like glucose and mannose), oligomers (cellobiose) or dehydrated forms like furfurals and hydroxy methyl furfurals (which form at much lower pH from xylose and glucose, respectively): The reducing sugar fraction of the total sugar essentially are the monomeric sugars mentioned above. These sugars are capable of reducing the oxidizing agents such as Tollen's reagent (AgO), Fehling solution (CuO) or ferricyanide in alkaline solution.

We would like to categorically state that we have not included ultrasound-assisted enzymatic hydrolysis of biomass (after pretreatment) in this paper. This issue will be addressed in a subsequent paper.

2. Materials and methods

2.1. Materials

Rice straw was obtained from local farm fields (irrigated location; Guwahati, Assam, India). Sodium hydroxide pellets and hydrogen chloride (35.5% w/v) were procured from Merck, Germany. Anthrone, glucose and dinitrosalicylic acid were procured from Himedia, India. Strips of rice straw were cut into small pieces of length 4–5 cm. These were washed with water and then dried at 80 °C in a hot air oven. Size of dried RS was further reduced to 5–10 mm using a mixer grinder (refer to Fig. A.1 of Supplementary material). The hydrolysis of rice straw was carried out using combinations of 2 chemical methods, viz. acid treatment and alkali treatment coupled with 2 physical techniques, viz. hot water bath and autoclaving. This was assisted by mechanical stirring and sonication at atmospheric as well as elevated static pressure. The rationale underlying elevated static pressure will be explained in next section.

2.2. Sonication setup

An ultrasound bath (Transsonic T-460 type, Germany, 2 L) operating at frequency of 35 kHz and power of 35 W was used for sonication. The bath as filled with water as the medium for ultrasound propagation. Temperature of the water in the bath was maintained at ~45 ± 3 °C during sonication period. Solution of grinded rice straw in distilled water in required concentration was taken in an Erlenmeyer flask (500 mL). This flask was placed at the center of the sonication bath for all the experiments. The intensity field in the ultrasound bath significant spatial variation. To avoid the changing intensity of ultrasound field, the position of the flask in the bath was carefully maintain constant during all experiments. The pressure amplitude of the ultrasound waves generated in the bath was determined as 1.5 bar (150 kPa) using calorimetric techniques. The bath had also a facility of automatic amplitude compensation that ensures constant power delivery to the system under treatment irrespective of the changes occurring in the medium. Pictures of the sonication setup are given in Supplementary material (Fig. A.2).

2.3. High pressure sonication

The technique of application of high static pressure to the medium is a tool to discriminate between effects of ultrasound and cavitation. We have used this technique for several applications in our earlier studies [12–16]. For this category of experiments, the procedure was exactly same as the previous experiments, except that the static pressure inside the Erlenmeyer flask was raised to 2.5 bar. This was done using a simple technique of closing the mouth of the flask by rubber cork with a metal tube pierced in the center. The outer end of this metal tube was connected to a nitrogen cylinder through double stage pressure regulator. A picture of the experimental set-up is given in Supplementary material (Fig. A.3).

2.4. Experiments with mechanical stirring

Experiments in this category were carried out using a 2 L glass reactor coupled to a mechanical stirrer (Make: Remi Motors Ltd.). The rate of stirring was maintained at 200 rpm for all experiments, and temperature of the rice straw solution was maintained at 60 °C using hot plate (Model: Spinot, Make: Tarsons).

2.5. Rice straw hydrolysis in neutral environment

There were total 7 experiments in this category as listed in Table 1.

2.5.1. Hot water bath

Mixture of rice straw in distilled water (100 mL) was prepared in concentration of 5% w/v in a 500 mL Erlenmeyer flask. The flask was heated to a temperature of 60 °C for 24 h. 3 mL of sample were collected at every 6 h for estimation of sugar content. Finally, RS suspension was filtered using a clean cotton cloth. Same process is repeated at different temperature of 80 and 100 °C.

2.5.2. Autoclaving (or steam explosion)

Mixture of rice straw in distilled water (100 mL) was taken at concentration of 5% w/v in a 500 mL Erlenmeyer flask. This flask was autoclaved at temperature of 121 °C for 15 min at 15 lb pressure using an autoclave (Make: Tuttnaeur, Model 3870 ELV). After autoclaving, bottle was allowed to cool and filtered using a clean muslin cloth. 3 mL of sample was collected for the analysis of sug-

Table 1
Hydrolysis with physical sono-hybrid techniques (under neutral pH).

Mode of treatment	5% w/v RS	
	TS (g/L)	RDS (g/L)
1. WB 100 °C (24 h)	4.36	2.88
2. ATCLV (15 min)	2.52	1.72
3. ATCLV (30 min)	2.6	1.72
4. ATCLV (45 min)	2.6	1.76
5. ATCLV (15 min) + US (6 h)	3.08	2.04
6. ATCLV (30 min) + US (6 h)	4.52	3.0
7. ATCLV (45 min) + US (6 h)	6.4	4.24