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Modeling and optimization of bi-directional delignification of rice straw for production of bio-fuel feedstock using central composite design approach

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ABSTRACT

The present study investigates the extraction of lignin from rice straw by bi-directional delignification methodology through minimal energy input towards feedstock preparation for bio-fuel production. In the first stage, the rice straw was treated with sodium chlorite of pH 5.5 followed by sodium hydroxide while in the second stage with sodium hydroxide alone under controlled parameters like, concentration, time and temperature at constant liquor-to-solid ratio. The process was mathematically modeled using central composite design approach and optimized by quadratic regression model with ANOVA (analysis of variance) for showing the relative significance of the factors. The percentages of delignification in two different optimized routes were estimated to be 77.84 and 44.09 respectively. The loss of feedstock in terms of glucose concentration was measured to be 4.23 and 2.51% in the preceding two-stages. Hence, this dual route method well-supported by the impressive experimental results could be promising technique of delignification of rice straw for bio-fuel generation.

1. Introduction

In the recent years, increasing of conventional fuel price and the gradual decline of storage and growing demand of energy have forced the researchers to pay attention for the development of an economically effective and environmentally benign technique for the utilization of lignocellulosic biomass for generation of cellulosic bio-fuel [1,2]. Energy can be produced from a variety of lignocellulosic biomass including forestry residues, agricultural residues and municipal wastes. Among different sources of these kinds of biomass, agricultural residues have gained considerable momentum of interest because of its large quantity production on a regular basis in a short period [3]. Technological breakthroughs have been made on both food-based first generation and non-food based second generation bio-fuels. Different process configurations have been studied using tight coupling of first and second generation ethanol production from sugarcane [4]. To avoid food shortage for humanity, the non-food based bio-fuel research has received a major society support where non-food crops are the feedstock for the production of bio-fuel. Hence, the attention must be concentrated towards the development of suitable technique for efficient utilization of non-food based lignocellulosic biomass in generating bio-energy.

Rice straw, the most common agricultural residue, is produced worldwide every year (Africa: 20.9 million tons, Asia: 667.6 million tons, Europe: 3.9 million tons, America: 37.2 million tons and Oceania: 1.7 million tons) and is vastly under-utilized [5]. Rice straw has been traditionally used as animal feed and feedstock for paper industry. In order to develop a new route of its uses and to increase its value, the conversion of rice straw into ethanol [6] and butanol [7], i.e. as a source of bio-energy and other chemicals have been studying extensively. Now a days, the annual production of rice straw in the world is 731 million tons while Asia region alone produces over 90% of the total rice output in which China and India share 28.7% and 19.5%, respectively [8]. Out of this, consumption for domestic use and other uses (including animal fodder) is 27 and 47 million tons, respectively. Despite these uses, a large amount of rice straw (63 million tons) remains unused, and can form potential feedstock for bio-fuels production [9]. The major components in rice straw are cellulose (32–47%), hemicellulose (19–27%) and lignin (5–24%) [10].

In order to produce bio-alcohol from rice straw biomass, delignification is one of the major unit processes. Delignification is the pretreatment method involving the removal of lignin and

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disruption of the crystalline structures of cellulose. To produce good quality and higher yield of alcohol from rice straw, delignification plays a dominant role including all processes resulting in partial or total removal of lignin from lignocellulosic biomass by the action of appropriate chemical reagents or physical means while retaining the most fermentable sugars [2,11,12]. Among the chemical treatments, oxidative treatments are principally affecting the degradation of lignin, whereas hydrolytic agents cleave the lignin-carbohydrate linkages. Coupling of the hydrolysis and the oxidative treatment gives better delignification efficiency [13]. In very recent year, superiority of different pretreatment types for lignocellulosic materials using alkaline solution has been made based on the enzymatic digestibility [14]. Therefore, choosing the right pathway of delignification for efficient and cost effective utilization of cellulosic biomass towards bio-fuel production is the present day challenge.

Over the past decades, many intensive studies have been conducted to develop efficient delignification of rice straw. The most common methods are sodium chlorite process [15–17], alkali treatment [3,11,18], alkaline peroxide treatment [18,19], aqueous ammonia treatment [2,11] and organosolv process [1,5,18]. These methods requires longer times, higher temperature and pressure and recycling of organic solvents. The major process parameters affecting the delignification process are chemical concentration, reaction temperature and time and the optimization of these process variables is very much essential from efficient delignification point of view. In conventional approach of optimization of process parameters, changing of one variable at a time is done while keeping all others at constant value. The limitations associated with this classical approach are time consuming, requires lot of experiments and could not depict the interactive effects of process variables at a single time. These shortcomings can be eliminated by using statistical optimization method such as RSM (Response Surface Methodology). Very few works have been reported to find out the optimum condition of delignification of rice straw employing RSM.

The present investigation aims to delignify the rice straw in two different directions. In the first route, the rice straw is delignified with acidic sodium chlorite prior to sodium hydroxide while only sodium hydroxide was chosen as the delignifying agent in the next route. The effectiveness of the first stage delignification process has been studied for the comparative assessment with the second stage. Response surface methodology based on CCD (Central Composite Design) was used for optimization of process variables in both the delignification stages and to determine the optimum delignification condition. No investigation was performed so far to explore the delignification process of rice straw in successive two-stage using low quantity of chemical reagents viz., sodium chlorite, sodium hydroxide and low energy input employing statistical experimental design.

2. Materials and methods

2.1. Raw material

Rice straw for the delignification process was collected from local area, Burdwan, West Bengal. After removing the leaves surrounding the stem, it was chopped into 2–5 mm in size for all experimentations. Sodium chlorite (Loba Chemie, India), sodium hydroxide pellets (Merck), glacial acetic acid (Merck), lignin-alkali (Sigma–Aldrich), silver sulfate (Merck), hydrochloric acid (35% pure, Merck), sulfuric acid (98% pure, Merck), D-glucose anhydrous (Sigma–Aldrich), acetonitrile (HPLC (high-performance liquid chromatography) grade, Merck) were used. Ultra-pure water (Millipore) was used in preparing solutions for experiments.

2.2. Physico-chemical characterization

2.2.1. Proximate analysis

Proximate analysis determines the moisture, volatile matter, ash and fixed carbon content (wt%) in the rice straw either dry or wet basis. Proximate analysis of rice straw was conducted using standard biomass analytical procedures of the National Renewable Energy Laboratory (NREL) [20].

2.2.2. Silica content

Ash produced from rice straw contents around 75% by weight silica with trace amounts of Al_2O_3, TiO_2, Fe_2O_3, CaO, MgO, Na_2O, K_2O, SO_3 and P_2O_5. Its content in the rice straw was determined according to the methods described by Refs. [1,18].

2.2.3. Lignin content and solid fractions

Lignin content in original rice straw and solid fractions obtained during each stage of delignification process, as shown in Fig. 1, were measured according to NREL (National Renewable Energy Laboratory) LAPs (standard Laboratory Analytical Procedures). Lignin fraction in biomass is a sum of AISL (acid insoluble lignin) and ASL (acid soluble lignin). Both, AISL and ASL concentrations were determined according to LAP-003 [21] and LAP-004 [22], respectively.

2.3. Experimental design for delignification

A mathematical and statistical approach of RSM (response surface methodology) was applied to solve multivariate equation from quantitative experimental values for delignification of rice straw. It determines optimum process parameters in a sequential testing procedure with the advantage of reduced experimental trials, less time consumption, presence of interactions between different variables and efficiency to predict the global optimum [23]. Many design matrices in RSM have been reported such as, CCD (Central

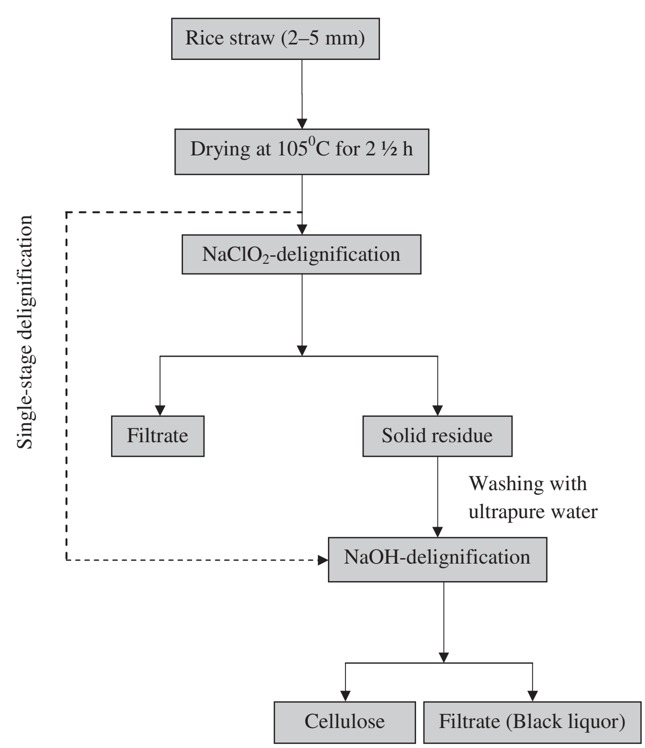

Fig. 1. Scheme for bi-directional delignification of rice straw.