



Pre-treatment Methods of Rice Residual Waste for Ethanol Production

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ABSTRACT

Rice residual waste, such as rice straw and rice husk is one of the most abundantly found renewable agricultural wastes. It is one of the richest sources of the lignocellulose which usually comes under the common practice of burning after harvesting of rice as this waste is of no other use. But it can be utilized for the production of bioethanol. The major challenge for the bioethanol production from the rice residual waste is the pretreatment of this lignocellulosic waste for the removal of lignin content which limits the accessibility of cellulose to the enzymes. This review article focuses on various pretreatment strategies which are most effective for rice residual waste to get the high yield of bioethanol.

Keywords: Bioethanol; Pretreatment; Rice husk; Rice straw; Lignocellulose

INTRODUCTION

The fast depletion of fossil fuels, increasing costs of fuels, raised level of global warming and other environmental concerns lead to the research for production of some alternative fuels to meet the current demand [8]. Ethanol is one such fuel, demand of which is increasing in many industries for different industrial processes [1]. Ethanol is considered as one of the excellent fuel for the combustion engines due to its less evaporation as compared to the gasoline [31].

First generation biofuel can be produced from sugar and starchy feedstock such as sugarcane, potato, sugarbeet, maize millet etc. But due to feed and fodder concerns, the interest has shifted towards second generation biofuels [28]. Second generation biofuels can be produced from lignocellulosic wastes. LCM are less expensive compared to the agricultural feedstock [9]. Lignocellulose generally composed of cellulose, hemicellulose and lignin [12, 35]. It is the largest source of monomeric sugars such as pentose and hexose which results into high yield of ethanol [5]. Different types of lignocellulosic waste are available in abundance in the surroundings. Rice waste is one of the most common lignocellulosic waste available in the environment. Rice is considered as the third most important crop grown in the world after wheat and corn [6] which produces residues such as rice straw and rice husk. Rice straw is the one of the most abundantly available lignocellulosic waste which results into the production of 205 billion liters of bioethanol annually [5]. Composition of rice husk is that it contains 75-90% of organic matter such as lignin, cellulose and hemicellulose [21]. Rice straw usually consisted of 41.2% cellulose, 31.7% hemicellulose and 21.8% lignin [24]. Rice husk constitutes around one fifth of the annual gross production of the rice that is 545 million metric tons of the world [5]. Rice husk consists of 29.3% hemicellulose and 34.4% cellulose [21]. Rice residual waste is used commonly in practice of burning as these are of no use and burning of these wastes produce various harmful gases and are the main cause of serious health issues [3].

Need for pretreatment

In second generation biofuel production, pretreatment of LCM is one of the important concern unlike in the first generation biofuel production [35]. As lignin forms an effective enclosure covering cellulose and hemicellulose,

hence limits the enzymatic degradation [2]. Pretreatment of lignocellulosic waste is required as it degrades the outer coverings of the cellulose and the cellulose can be exposed to enzymes for better production of ethanol [16]. Pretreatment of lignocellulosic waste results into change in the chemical composition at microscopic level, hence monomeric sugars become available for enzymatic degradation and further high yield of ethanol can be obtained [7]. There are various pretreatment methods used for the efficient and effective yield of ethanol such as physical methods, chemical methods, biological methods, combined pretreatment methods etc.

Different types of pretreatment methods for rice residual waste

Physical Pretreatment methods: Physical pretreatments are effective as they increase the surface area and pore size of the substrate or the raw sample and decrease or loosen the crystalline structure. It does not require any kind of chemicals or solutions.

Mechanical methods

Milling, chipping or grinding are the different methods to reduce the size and crystallinity [6]. Milling and grinding are also having subtypes. Wet disk milling is more efficient compared to the ball milling in the physical pretreatment of rice straw [11].

Electron beam irradiation

The irradiation method is usually performed after milling or grinding for effective pretreatment. The electron beam irradiation pretreatment of rice straw has been reported in which accelerated electrons were produced by electron accelerator to irradiate the milled rice straw [14]. In the process of irradiation the polar bonds disrupt which results into various physical, chemical and biological changes [34].

Microwave oven pretreatment

Microwave oven pretreatment alone has not found as an effective pretreatment for rice straw as it showed the same results as the raw rice straw sample [41] but has found effective when performed by adding glycerin medium and water [18]. Microwave pretreatment resulted into 43-55% of reducing sugars after lignin reduction of rice straw [18].

Physicochemical pretreatment methods

These pretreatments include physical as well as chemical exposure to work effectively. Parameters like temperature, pressure etc. have the basic role in these pretreatment methods.

Steam explosion method

In this method high pressure steam with high temperature is used for few minutes and instant decompression is used to stop the reaction [30] and this results into the separation of fibers due to the expansion of steam with the substrate [5]. Rice husk was treated for the duration of 45-60 minutes, under very high pressure and then pressure was slowly released which resulted into effective enzymatic treatment of filamentous fungi [27].

Ammonia fiber explosion method (AFEX)

Ammonia is effective in breaking the carbohydrate complex as well as ether and ester bonds [6, 17] in lignocellulosic material. AFEX uses anhydrous ammonia with high temperature and high pressure steam explosion. AFEX has found to be one of the effective pretreatments for the rice straw as it resulted into availability of 3% reducing sugar [40].

Chemical pretreatment methods

Different types of chemicals are required to degrade the lignin and hemicellulose so that exposure of enzymes to cellulose could be done in most effective way. Different acids, bases, solutions or other types of chemicals can be used.

Acid pretreatment

Rice husk treated with 0.2 N sulphuric acid kept on the hot plate at the temperature of about 65 °C- 70 °C has found effective pretreatment for production of reducing sugars [20]. Acid along with high temperature conditions results into the release of monomeric sugars by its degradation to furfural and 5-hydroxymethylfurfural [10, 25]. In another research the rice straw was treated with 10% w/v sulphuric acid for 15 minutes and then used for further enzymatic treatment [24]. When different concentrations of H₂SO₄ and HCl were used at varying temperatures conditions and

for different time durations, it was found that rice husk provided highest sugar yield when treated with 5% H₂SO₄ at 30 °C for 20 minutes [28].

Alkaline pretreatment

Diluted calcium hydroxide saturated solution was used to pretreat rice husk at 60 °C for 24 hours [27]. NaOH can partially remove lignin as well as hemicellulose by breaking the ester bonds [39]. Rice husk when treated with NaOH and Na-chlorite at the varying concentrations from 1-5%, the effective results were obtained at 5% NaOH and 5% Na-chlorite [35]. Rice straw was boiled in the presence of 0.5 M NaOH for 1 hour and the treated with different enzymes [7]. 3% w/v NaOH was used to pretreat the rice husk at 121 °C for 30 minutes gave the best results [26].

Sulfite formaldehyde pretreatment

This pretreatment required highly equipped methods for high delignification and increased release of sugars. Rice straw was most effectively treated when 12% sodium sulfite was used at 160 °C for 1 hour and highest sugar yield of 88.8% were obtained. Sodium sulfite and formaldehyde were used in equal amounts i.e. 1:1 [15].

Ammonia pretreatment

Ammonia treatment effectively removes the lignin content of the lignocellulosic material [17, 19]. Rice straw was soaked in the aqueous ammonia solution and then slurry was separated by filtration [19]. It has been found that when ammonia concentration is increased from 15-30% at the constant temperature of 60 °C for 24 hours, it increases the effect of enzymatic hydrolysis [17, 19].

Oxidizing agent pretreatment

Oxidizing compounds such as hydrogen peroxide or peracetic acid are used in addition to water. Hydrogen peroxide is effective in delignification and provides better enzymatic accessibility by solubilizing the lignin content [6, 22]. It has been reported that enzymatic efficacy of rice straw was increased to four times after the hydrogen peroxide pretreatment [37].

Organosolv pretreatment

It includes the organic solvents such as ethanol, ethylene glycol, glycerol, phenols, ketones etc. The rice straw was treated with diethyl glycol and ethylene glycol at atmospheric pressure [13].

Combined pretreatments

When one pretreatment is used in the combination of other pretreatment, it shows better results compared to the separate pretreatment processes. Rice husk when pretreated with alkali in combination with microwave irradiation, it required less temperature compared to the normal [32]. Rice straw pretreated with combination of dilute sulphuric acid and aqueous ammonia, 83% of ethanol yield was obtained at the optimum conditions of 42.75 °C for the time period of 48 hours [16]. The combination of 1% dilute H₂SO₄ with 1.25% of NaOH in this particular sequence resulted into higher sugar yield with the less utilization of these reagents [38].

Enzymatic hydrolysis

Enzymatic hydrolysis is required to degrade the cellulose and produce more reducing sugars. Cellulase enzyme system consists of endoglucanases and cellulohydrolase [7]. Different fungus species produce different types of enzymes to degrade hemicellulose and cellulose. It has been reported that *Trichoderma sp.* resulted into higher xylanase activity when grown in solid substrate compared to the submerged cultivation of rice husk [4]. The xylanase activity was found maximum at temperature of 50 °C and pH 5 [4]. It has found that *Trichoderma sp.* has the high cellulolytic enzyme activity that converts rice husk constituents to simple sugars [23, 27]. *A.niger* celluloses has also found to be effective for the degradation of rice husk at lower costs [27, 33]. Co-culturing of *A.fumigatus* and *T. reesei* was done for the higher yield of reducing sugars i.e. 24.9 g/l [24].

CONCLUSION

Pretreatment is one of the most important process in the production of second generation fuels. It is required to remove the lignin and hemicellulose to get the higher yield of ethanol. Most of the cost in the production of bioethanol is comprised by the pretreatment methods, so there is the need to find out the optimized pretreatment strategies which would be cost effective and may result into highest productivity. Different types of substrates

require different pretreatment methods according to the percentage of lignin and hemicellulose in their composition. For rice residual waste, combined pretreatments are found to be highly effective as it requires less chemicals, hence reduces the cost and provide efficient results.

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