



Acetone pretreatment for improvement of acetone, butanol, and ethanol production from sweet sorghum bagasse



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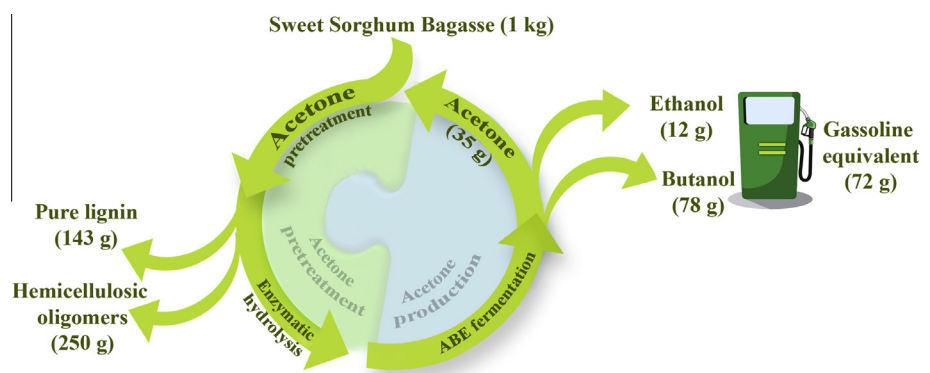
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HIGHLIGHTS

- Production of ABE was significantly improved by acetone pretreatment.
- A high hydrolysis yield of 94.2% and sugar concentration of 36.3 g/L were obtained.
- More than 140 g lignin was removed from each kg SSB into the solvent.
- The solvent used for pretreatment of SSB, acetone, was produced from SSB.
- From one kg SSB, advanced biofuel equivalent to 72 g gasoline was produced.

GRAPHICAL ABSTRACT



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ABSTRACT

Development of efficient and cost-effective pretreatment prior to hydrolysis is essential for the economical production of biobutanol from lignocelluloses. In this study, acetone pretreatment with a number of advantages over the other pretreatments was used to improve enzymatic hydrolysis and fermentation with *Clostridium acetobutylicum* for acetone–butanol–ethanol (ABE) production from sweet sorghum bagasse (SSB). Using the pretreatment at 180 °C for 60 min, the yield of enzymatic hydrolysis of SSB was improved to 94.2%, leading to a hydrolysate with 36.3 g/L total sugar, which was subsequently fermented to 11.4 g/L ABE. This process resulted in the production of 78 g butanol, 35 g acetone, 12 g ethanol, 28 g acetic acid, and 6 g butyric acid from each kg of SSB. Through the pretreatment, 143 g lignin per kg of SSB was dissolved into the solvent, with the potential to be recovered as unaltered pure lignin. Furthermore, the co-production of acetone by the ABE fermentation alleviated the concern about unavoidable solvent loss in the pretreatment, i.e., 24 g acetone/kg SSB, using an integrated process for biobutanol production from SSB. The energy equivalent obtained in the form of butanol and ethanol (72 g gasoline equivalent/kg SSB) was higher than that obtainable via ethanolic fermentation (less than 70 g/kg SSB).

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1. Introduction

Plant biomass is one of the primary foreseeable sustainable sources of food, organic materials, and liquid fuels in the future, predating the current dependency on fossil resources [1].

Considering the concerns of the food-versus-fuel conflict, lignocellulosic materials, the inedible part of plant biomass, are the main potential alternatives for replacing the current fossil resources. Lignocellulosic materials are largely unused and available in high volume at relatively low price. Therefore, using inexpensive and efficient bioconversions techniques, it is possible to produce sustainable fuel and chemicals from these resources [2].

Among the wide range of chemicals attainable from lignocellulosic materials, only a few have the potential to be used in place of the current transportation liquid fuels, responsible for about 30% of global carbon emissions. In this regard, butanol, naturally produced by the genus *Clostridium*, has attracted the greatest attention as an advanced biofuel with superior properties [3,4]. High energy density, hydrophobic characteristics, and ease of blending with gasoline in high concentration are the most significant among the unique advantages of biobutanol [5].

Butanol has been evaluated as a fuel for use in conventional engines, and positive results were achieved in power, energy consumption, and unburned hydrocarbon and carbon monoxide emissions [6]. In addition, butanol added to biodiesel fuel [7] and Jet A [8] improves the performance as well as emission characteristics of diesel engines and gas turbine, respectively. However, the relatively high cost of biomass feedstock, i.e., sugary and starchy substrates, is one of the main obstacles of the cost-effective production of biobutanol [9]. Therefore, acetone, butanol, and ethanol (ABE) fermentation of the hydrolysates obtained by enzymatic hydrolysis of pretreated lignocellulosic wastes with *Clostridia* sp. has been suggested for the economical production of biobutanol [10]. All hydrolysate sugars, including hexoses and pentoses, are fermented to ABE through the solventogenesis phase of the fermentation.

Sweet sorghum is a potential energy crop characterized by high photosynthetic efficiency and drought resistance. It is a short perennial crop growing in marginal areas that can be adapted to almost all temperate and tropical climates, even as an alternative summer crop. In addition to the starchy grain of sweet sorghum, its sugar-rich stem can be used either for food or for energy production. Extraction of juice from its stem is a proper approach for the utilization of sweet sorghum stem, providing the opportunity to use the juice in food or biofuel production industries [11]. After juice extraction, the leftover stalks, called sweet sorghum bagasse, are an inedible lignocellulosic source, suitable for biofuel, e.g., biobutanol, production [11].

However, sweet sorghum bagasse, like other lignocelluloses, is highly resistant to biological conversions. Thus, the economical production of fermentable hydrolysate from the bagasse is possible only after a suitable pretreatment [5]. It has been shown that the possibility and economy of ABE production from lignocelluloses are highly dependent on the type and conditions of pretreatment [12]. However, most pretreatments are first developed for bioethanol production, which may not provide the prerequisites of ABE fermentation. Dilute sulfuric acid pretreatment, one of the leading pretreatments for bioethanol production, is not suitable for ABE production from lignocelluloses without an additional detoxification process [13]. Inhibition of the clostridial fermentation by lignocellulosic hydrolysates is one of the main bottlenecks of biobutanol production from lignocelluloses [12,13]. It has been shown that phenolic compounds derived from lignin are responsible for the poor fermentability of most lignocellulosic hydrolysates [13]. Therefore, delignification of lignocelluloses is one of the promising methods for preparing hydrolysates fermentable by *Clostridia* for ABE production [14,15].

Extraction of lignin by an organic solvent is the main feature of the most promising delignification pretreatments, known as organosolv pretreatment [16]. Providing three main product streams of cellulosic fibers, solid lignin, and an aqueous solution of the hemicellulosic sugars, this pretreatment facilitates the inte-

grated utilization of lignocelluloses in a biorefinery application. Even though different organic solvents have been utilized for organosolv pretreatment of lignocelluloses, only a few, such as methanol [17], ethanol [18,19], acetone [20], formic acid [21], and glycerol [22], can be obtained from renewable sources, making them suitable for sustainable production of fuel and chemicals. Ethanol organosolv pretreatment has been widely studied for enzymatic hydrolysis of lignocellulosic materials [18,19]. However, the technical and economic feasibility of the pretreatment is highly dependent on the type of organic solvent [16,21]. Chen et al. [21] evaluated Formiline and Acetoline processes in comparison to ethanol for delignification of wheat straw in order to improve the enzymatic hydrolysis. From a technical point of view, the solvent should be responsible for the dissolution of lignin and hemicellulose through the pretreatment without negatively affecting the subsequent enzymatic hydrolysis and fermentation. From an economic point of view, the benefits obtained by using the pretreatment should prevail over the costs imposed by the solvent loss as well as the energy consumed for its recovery [23]. The main obstacle of using organosolv pretreatment is that the relatively high cost of solvent loss makes the pretreatment impractical, especially for biofuel production [24].

In the current study, for the first time, acetone was used as a delignifying solvent in the process of butanol production from lignocelluloses, where acetone was also produced as the main by-product providing the make-up stream. The solubility of lignin in acetone is significantly higher than other low boiling point solvents, e.g., ethanol [20]. Thus, the use of acetone improves the delignification of biomass and thereby further enhances lignin recovery, the enzymatic digestibility of the cellulose fraction, and the fermentability of the resulting hydrolysates [20,23]. Furthermore, acetone can be easily recovered after the pretreatment, compared to ethanol and similar solvents, as it is highly volatile (low boiling point of 56 °C). Moreover, it does not form azeotrope with water and can be purified to over 99% by simple distillation. However, complete recovery of the solvent is not generally possible, and a make-up stream is required to compensate for the unavoidable solvent loss. Using an integrated process, the make-up acetone can be provided from the acetone inevitably formed through ABE fermentation, to improve the overall economy of the butanol production process. To our knowledge, the current study has yielded the first publication on utilization of acetone pretreatment for ABE production from lignocelluloses.

In this study, pretreatment with acetone was evaluated for use in the process of ABE production from sweet sorghum bagasse. Acetone pretreatment at different conditions was used prior to enzymatic hydrolysis and fermentation by *C. acetobutylicum* for the improvement of ABE production. It was shown that the acetone produced by the fermentation is high enough to provide the solvent make-up stream, making acetone pretreatment an efficient and promising method for enhancement of ABE as well as pure lignin production from sweet sorghum bagasse.

2. Materials and methods

2.1. Raw materials

Sweet sorghum (Sofra, Italy) was planted at the Agricultural Research Station of the University of Isfahan and harvested in October 2014. Sweet sorghum stalk was air-dried, hammer milled, and sieved to achieve a size between 833 µm (20 mesh) and 177 µm (80 mesh). The juice was separated by batch extraction at 30 °C for 2 h with a solid:liquid ratio of 1:10 and shaken at

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