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Research paper

Microbubble-enhanced dielectric barrier discharge pretreatment of microcrystalline cellulose

Alexander Wright[a], Adam Marsh[a], Federica Ricciotti[a,b], Alex Shaw[c], Felipe Iza[c], Richard Holdich[a], Hemaka Bandulasena[a,*]

[a] Department of Chemical Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, United Kingdom
[b] Department of Civil, Chemical, Environmental and Materials Engineering, University of Bologna, 40136, Italy
[c] Wolfson School of Mechanical, Electrical and Manufacturing Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, United Kingdom

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ABSTRACT

Cellulose recalcitrance is one of the major barriers in converting renewable biomass to biofuels or useful chemicals. A pretreatment reactor that forms a dielectric barrier discharge plasma at the gas-liquid interface of the microbubbles has been developed and tested to pretreat α-cellulose. Modulation of the plasma discharge provided control over the mixture of species generated, and the reactive oxygen species (mainly ozone) were found to be more effective in breaking-up the cellulose structure compared to that of the reactive nitrogen species. The effectiveness of pretreatment under different conditions was determined by measuring both the solubility of treated samples in sodium hydroxide and conversion of cellulose to glucose via enzymatic hydrolysis. Solutions pretreated under pH 3 buffer solutions achieved the best result raising the solubility from 17% to 70% and improving the glucose conversion from 24% to 51%. Under the best conditions, plasma-microbubble treatment caused pronounced crevices on the cellulose surface enhancing access to the reactive species for further breakdown of the structure and to enzymes for saccharification.

1. Introduction

Depletion of fossil fuels and emission of greenhouse gases have led to an increase in demand for sustainable biofuels derived from renewable sources [1,2]. Biofuels can be broadly categorised as first generation (mainly sugars and starch), second generation (lignocellulosic biomass) and third generation (algae). Biofuels derived from lignocellulosic materials have gained significant attention recently due to criticism over first generation biofuels for using resources allocated for food production, needing government subsidies to be competitive and high net greenhouse gas emissions. In lignocellulosic biomass, approximately two-thirds of the total dry weight consist of cellulose and hemicellulose, connected either by covalent or hydrogen bonds and shielded by lignin. Bioethanol or biogas is mainly derived from cellulose and hemicellulose [3,4], while lignin can be combusted to generate heat and electricity. Pure cellulose can be isolated from feedstocks such as lignocellulosic biomass, cotton and bacterial cellulose using highly commercialised pretreatment methods that often include multiple stages of treatments [5]. α-cellulose isolated from such treatment methods contains both amorphous and crystalline parts, and through further treatment, the amorphous sections can be broken-down to form microcrystalline cellulose (MCC). However, extensive treatments significantly increases the cost MCC production; hence their use is often limited to pharmaceutical, cosmetic and food industries [5].

Cellulose is often hydrolysed by enzymes or acids to form glucose, which can then be fermented by yeast to produce bioethanol and other chemical by-products [1]. Alternatively, cellulose can also be converted into biogas by anaerobic digestion. In either case, the conversion rate is often limited by crystallinity of cellulose making the polymer hard to degrade as well as being insoluble in most solvents [6,7]. There is significant interest in increasing the solubility of cellulose for improving hydrolysis or facilitating accessibility by anaerobic bacteria [7]. Steam explosion [8] and chemical treatment [9,10] are commercially developed pretreatment methods to achieve this task, but combination of several methods have proven to be more effective [11,12]. However, a large proportion of the costs associated with biofuel production from lignocellulosic biomass is spent on pretreatment; therefore, cheap and more effective methods are sought to make the process viable.

Recently, atmospheric pressure plasmas (APPs) have received increased attention due to its ability to produce a wide range of highly reactive species that can potentially break-up the highly crystalline

* Corresponding author.
E-mail address: H.C.H.Bandulasena@lboro.ac.uk (H. Bandulasena).

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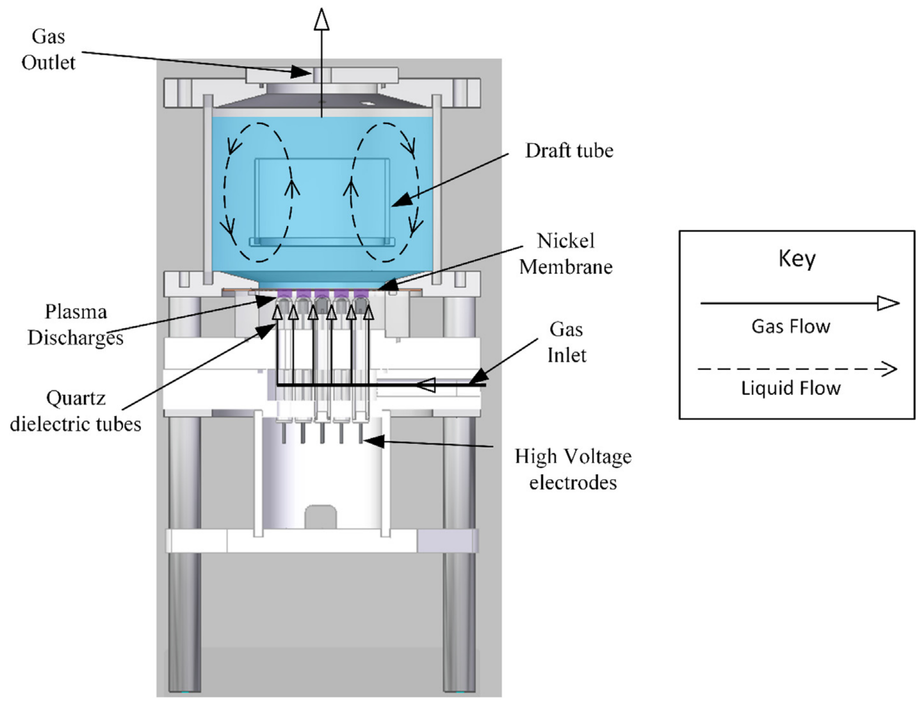

Fig. 1. A schematic diagram of the plasma-microbubble reactor.

cellulose structure. When air is used as the feed gas, APPs produce reactive oxygen species (ROS) such as ozone, hydrogen peroxide and hydroxy radicals and reactive nitrogen species (RNS) such as nitric acids and peroxynitrites [13]. The concentration of each reactive species in the cocktail of gaseous output depends on the conditions used to produce the plasma such as electrical characteristics of the power supply and composition of the feed gas. The use of APPs to reduce crystallinity of cellulose has been reported by Jun et al., where an argon feed jet was used to treat cotton fibre with an α-cellulose content of 96.8% [14]. Both, increased treatment time and power applied to the plasma improved the solubility of cellulose. A decrease in hydrogen bonds was observed within the cellulose structure as solubility increased. It should be noted that, whilst high solubility is achievable through the use of APPs, ozone can also damage the cellulose structure which selectively attacks C═C through ozonolysis [15].

Plasma jets can produce high concentrations of reactive species within a small area of interest, but their scalability is limited due to small volumes of liquid treated by each jet. There is significant interest in treating large volumes at industrial scale using APPs; hence scalable designs and technologies are needed. Huang et al., designed a pretreatment reactor that produces a Dielectric Barrier Discharge (DBD) plasma above the liquid surface to treat MCC solutions [16]. It was found that the carrier gas had no significant effect on the pretreatment, and the radical species generated by the plasma such as hydroxyl radicals, hydrogen peroxide and hydrated electrons were mainly responsible for the depolymerisation effectiveness. A 50-min pretreatment of MCC in this reactor reduced the crystallinity index (CI) from 82.8% to 58.9%, demonstrating the suitability of plasma treatment for reducing intramolecular and intermolecular bonds. Even though this study demonstrated that radicals and ROS were the key species for reducing crystallinity of MCC, the effect of RNS should not be neglected. In a separate study, NO_2 has been shown to effectively oxidise cellulose to glucose, reducing the need for a further processing either by enzymes or acid hydrolysis [17].

The conversion of MCC into glucose without either acid or enzymatic hydrolysis has also been facilitated by plasma. Prasertsung at al. used two opposing submerged electrodes to hydrolyse cellulose into reducing sugars directly [18]. The iron particles sputtered into the solution from the iron electrodes reacted with hydrogen peroxide to form high concentrations of hydroxy radicals through Fenton reactions. Hydroxy radicals are known to breakdown complex molecules effectively; however they often react indiscriminately and can break down sugars [19]. Whilst this approach sounds promising in reducing the costs associated with enzymatic hydrolysis or acid treatments in producing sugars, the issue of scalability and additional cost of removing nanoparticles from the liquid remains. Therefore, this study will focus on facilitating the hydrolysis process of α-cellulose with reactive species generated from a DBD plasma and identifying the limiting factors that may be present.

Energy efficient fluidic oscillation-mediated microbubbles have been demonstrated to improve mass transfer rates significantly due to their high surface to volume ratio, and this technology has been applied to various processes needing efficient gas-liquid mass transfer such as waste water treatment, aqua culture and bioreactors [20,21]. In addition to improved mass transfer, microbubbles provide efficient mixing of the reactor contents, removing the need for mechanical mixing; hence reducing the energy requirement for pretreatment [22]. This plasma-microbubble reactor treatment has been demonstrated as an effective approach in pretreating lignocellulosic biomass for bioethanol production [23].

The main purpose of this study is to determine the effectiveness of plasma-microbubble pretreatment for improving solubility and digestibility of cellulose. Pure α-cellulose was chosen as the feedstock over raw biomass to isolate the effect of reactive species produced by the APP on cellulose fraction of the biomass. Optimum operating conditions for the reactor have been determined, and a pretreatment procedure has been developed to maximize the effect. This paper is organised as follows. In Section 2, plasma-microbubble reactor used in this study and various characterisation tests are described under Materials and Methods. In Section 3, results on the reactor performance and effectiveness of the pretreatment method used is discussed. In section 4, conclusions are drawn.