



Microwave-assisted ionic liquid-mediated rapid catalytic conversion of non-edible lignocellulosic Sunn hemp fibres to biofuels

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ABSTRACT

Sunn hemp fibre – a cellulose-rich crystalline non-food energy crop, containing 75.6% cellulose, 10.05% hemicellulose, 10.32% lignin, with high crystallinity (80.17%) and degree of polymerization (650) – is identified as a new non-food substrate for lignocellulosic biofuel production. Microwave irradiation is employed to rapidly rupture the cellulose's glycosidic bonds and enhance glucose yield to 78.7% at 160 °C in only 46 min. The reactants – long-chain cellulose, ionic liquid, transition metal catalyst, and water – form a polar supramolecular complex that rotates under the microwave's alternating polarity and rapidly dissipates the electromagnetic energy through molecular collisions, thus accelerating glycosidic bond breakage. In 46 min, 1 kg of Sunn hemp fibres containing 756 g of cellulose produces 595 g of glucose at 160 °C, and 203 g of hydroxymethyl furfural (furanic biofuel precursor) at 180 °C. Yeast mediated glucose fermentation produces 75.6% bioethanol yield at 30 °C, and the ionic liquid is recycled for cost-effectiveness.

1. Introduction

The global temperature rise may be held below 2 °C (Rogelj et al., 2016) if the world's CO₂ storage in the form of bioenergy increases to 21% by 2050 and 56% by 2100 (Schleussner et al., 2016), with a global target of sustainable production of 200 EJ of bioenergy/year by 2050. Therefore, it is necessary to identify widely-cultivated lignocelluloses with high cellulose content, which do not conflict with food sources.

However, the basic challenge of hydrolysing lignocelluloses to fermentable sugars and biofuel precursors stems from the fact that most plants have naturally evolved to resist bio-/chemical deconstruction of their cell walls (Armstrong et al., 2016). Photosynthesis is a process of biological self-assembly, in which the resulting carbohydrates are stored in the recalcitrant plant cell walls consisting of layered, resilient linked matrices of three polymers: lignin, hemicellulose and cellulose. Lignin, an aromatic polymer of p-coumaryl, coniferyl and sinapyl alcohols, links covalently (Harmsen et al., 2010) with hemicellulose, an amorphous polysaccharide of β-(1 → 4)-glycosidic bond-linked xylose, with galactose, glucose, manose, arabinose as side chains. They together form a hydrophobic structure (Silveira et al., 2013) that fills the microfibrils of the secondary plant cell walls and prevents enzymes and chemicals from accessing the hydrophilic (Yang et al., 2013), crystalline cellulose chains and rupturing the β-(1 → 4)-glycosidic bonds between their monomeric glucose units. Cellulose, the earth's most abundant

natural polymer, is further protected from being deconstructed to glucose by the hydrogen bonds that interlink it with the hemicellulose matrix (Dutta and Chakraborty, 2015).

In this paper, a cellulose-rich crystalline lignocellulose – Sunn hemp (*Crotalaria juncea*) fibre – is identified as a new non-edible bioenergy crop. Sunn hemp (*Crotalaria juncea*) is widely grown as a non-edible nitrogen-fixing lignocellulosic cover crop in the subtropics of Bangladesh, Brazil, India, Pakistan, Russia, Sri Lanka, USA, Uganda, etc. A shrubby, herbaceous, fast-growing, sub-tropical annual legume, it produces 2268 kg dry biomass/acre in only 9–12 weeks (Clark, 2012), with 19 MJ of energy/kg dry biomass (Cantrell et al., 2010) at a global production of 130,000 MT/year (Duke, 1983). Recently, bio-oil obtained from Sunn hemp seeds have been transformed to produce biodiesel (Sadhukhan and Sarkar, 2016). Sunn hemp fibre, with its low lignin and hemicellulose contents, high cellulose content, and high energy content of 2.5×10^9 MJ/year even at its present global cultivation rate, has the unique potential of being converted to transportation biofuels rather than being merely used as bast fibre (Yu and Chen, 2012). The main obstacle to its large-scale deployment as a future fuel in our fight against climate change is its low porosity and high crystallinity and Degree of Polymerization (DP), which render the cleaving of the glycosidic bonds between the glucose monomers rather challenging.

This challenge is addressed by innovating a smart technology that

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uses microwave irradiation (at 160–200 °C) in the presence of ionic liquid medium and alkali metal catalyst to rapidly rupture the glycosidic bonds of cellulose (Gaikwad and Chakraborty, 2014) and produce glucose, leading to faster, cheaper production of lignocellulosic biofuels from Sunn hemp fibres. The microwave radiation alternates the polarity of its electromagnetic energy much faster than the diffusion timescales of the reacting molecules. The application of a rapidly oscillating energy field (Tagliacucchi et al., 2014) reduces the optimum time for hydrolysis of Sunn hemp fibres to glucose and other biofuel precursors such as 5-hydroxymethyl furfural (HMF), levulinic acid (LA) and formic acid (FA) in only 46 min in the microwave reactor. Microbial fermentation of the glucose produces bioethanol, and the ionic liquid is recycled for cost-effective biofuel production.

The process parameters such as temperature and mixing speed are known to significantly influence the reaction rate and the product yields. The dissolution of lignocellulosic materials in ionic liquid medium above 100 °C is favored by the reduction of viscosity of the ionic liquid at such high temperatures (Yoon et al., 2012). As the reaction temperature increases from 180 °C to 200 °C, glucose and HMF yields decrease gradually, while the yield of LA increases (Peng et al., 2010). Higher mixing speed reduces the interfacial mass transfer resistance, and the glucose and HMF yields are observed to maximize at the optimal mixing speed of 700 rpm when the system transitions from the mass-transfer limited regime to the kinetically controlled regime (Gaikwad and Chakraborty, 2014). The crystalline nature of the biomass also an important determinant of the optimal process conditions. The crystallinity of the sugarcane bagasse remains unaltered after reacting at 150 °C, but decreases significantly after reacting at temperatures above 150 °C (Kimon et al., 2011). Therefore, one of the goals of this paper is to optimize the process parameters – reaction temperature, water concentration, lignocellulose, ionic liquid and catalyst loadings – that maximize the product yields and regulate the product distribution obtained from a highly crystalline lignocellulose such as Sunn hemp fibres.

2. Materials and methods

2.1 Materials

Lignocellulosic substrate Sunn hemp fibre is obtained from the Indian Council of Agricultural Research – Central Research Institute for Jute and Allied Fibres, India. Ionic liquid 1-Butyl-3-methylimidazolium chloride and CuCl₂ are purchased from HIMEDIA Labs, and S.D Fine Chemicals Limited, Mumbai, India, respectively. Alkali lignin, HMF, glucose, LA, FA and potassium phosphate tri-basic are purchased from Sigma Aldrich Co., USA. 2, 2' biconinonate, sodium carbonate, sodium bicarbonate, copper sulphate, L-serine, Hydrogen peroxide, glacial acetic acids, sodium chloride, 1-Butanol, acetone, iso-butyl-methylketone (MIBK) and phenol are purchased from Merck chemicals, India. Wild type yeast strain *Saccharomyces Cerevisiae* (MTCC 170) is purchased from Microbial Type Culture Collection and Gene Bank, India. Sodium hydroxide, Malt, yeast extract and peptone are purchased from SRL, Mumbai, India. All chemicals used in this study are of analytical grade.

2.2. Methods

2.2.1. Substrate characterization

2.2.1.1. Compositional analysis of the substrate. The cellulose, hemicelluloses, acid soluble lignin, acid insoluble lignin, ash and moisture contents in dry Sunn hemp fibre are measured by the procedure described in the literature (Toribio-Cuaya et al., 2014). 500 mg of Sunn hemp fibre is mixed with 10 ml of a 0.275 M of H₂SO₄ at 150 rpm for 24 h at 25 °C. The solution is autoclaved at 118 °C for 30 min. After cooling, the solid is recovered by filtration, and the filtrate is centrifuged at 3000 rpm for 15 min. The acid-soluble lignin

concentration is determined by UV–Vis Spectrophotometer (Agilent Technologies) at 280 nm. The oven-dried solid is mixed with 6 ml of 0.375 M sodium hydroxide and 90 µl of 12.8 M of hydrogen peroxide at 50 °C and 150 rpm for 3 h. After the reaction, the solid is filtrated, dried and weighed to measure its cellulose content. The filtered liquor is acidified with acetic acid (50% v/v) to precipitate the alkaline lignin. Then the solution is centrifuged, and the precipitate of alkaline lignin is dried and weighed. In order to measure hemicelluloses, the extractive free 500 mg of lignocellulosic material is reacted with 10 ml of a 1 M NaOH solution at a mixing speed of 100 rpm and a temperature 25 °C for 24 h. The insoluble material is filtrated and washed. The filtrate is acidified using acetic acid 50% (v/v) so that its pH decreases from 9.0 to 4.0. The resultant suspension is centrifuged at 3000 rpm. Hemicellulose A is recovered by removing the supernatant, and the solid is dried and weighed. The supernatant is added drop by drop into a methanol solution in the ratio of 1:3 (v/v) to precipitate the hemicellulose B. The mixture is centrifuged, and the hemicellulose B is recovered as a solid by removing the methanol supernatant, dried at 90 °C, and weighed. The ash content is measured by burning 1 g of lignocellulosic material in a muffle furnace at 550 °C up to 5 h. After combustion, the material is weighed, and the weight percentage of ash is calculated by dividing the ash weight by the initial dry lignocellulosic material weight. The moisture content is measured by drying 1 g of lignocellulosic material at 105 °C for 5 h, and the moisture percentage is determined by the measuring the difference in weight between the initial lignocellulosic biomass and the oven-dried lignocellulosic biomass.

2.2.1.2 Determination of Degree of Polymerization (DP). DP of the cellulose in Sunn hemp fibre is calculated as the ratio of glycosyl monomer concentration measured by phenol-sulphuric acid method divided by the reducing-end concentration determined by the modified 2, 2' biconinonate (BCA) method (Ryu and Lee, 1986; ; Zhang and Lynd, 2005).

2.2.1.3 X-ray diffraction (XRD) analysis. Powder XRD patterns of unreacted and reacted Sunn hemp fibres are obtained using a PANalytical diffractometer (model: PW-3050/60), using Cu-K α radiation at 40 kV and 30 mA with 2 θ angle scanning from 100 to 900. The relative amount of crystalline material in each sample is calculated using the peak height method, also known as the Segal method (Park et al., 2010; Thygesen et al., 2005).

2.2.1.4 Fourier Transform infrared spectroscopy (FTIR) analysis. The FTIR analysis of the lignocellulosic substrate is recorded by the Perkin Elmer Fourier Transform (Model: Spectrum 100) spectrometer between 500 and 4000 cm⁻¹. The dried samples are mixed with KBr and pelleted for FTIR analyses.

2.2.1.5. Surface morphology. Field Emission Scanning Electron Microscopy (FESEM) is performed on the Sunn hemp fibre by using JEOL (Model: JSM-7610F) FESEM analyzer with a voltage of 2 KV, after coating the samples with platinum in a vacuum sputter coater.

2.2.1.6. Surface area and pore size measurement. The surface area and the pore size of Sunn hemp substrate are determined by using Quantachrome AUTOSORB 1 instrument. The samples are degassed at 110 °C for 8 h under high vacuum. The specific surface area is calculated by Brunauer-Emmett-Teller (BET) method, while the pore surface area, pore volume and average pore diameter are determined using the Barrett-Joyner-Halenda (BJH) method.

2.2.1.7. Particle size measurement. The particle size of the Sunn hemp fibre are measured by estimating the average particle size and the particle size distribution by Dynamic Light Scattering (DLS) technique using zetasiser nanoparticle analyzer (Malvern, UK) with laser at a

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