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Membranes as a tool to support biorefineries: Applications in enzymatic hydrolysis, fermentation and dehydration for bioethanol production

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A R T I C L E I N F O

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A B S T R A C T

The consumption of fossil fuels in excess leads to chronic effect of greenhouse gas (GHG) emissions on the environment. These adverse environmental impacts of GHG have invoked reasonable awareness on renewable energy resources. Bioethanol from lignocellulosic agricultural residue (profusely available renewable raw materials in the tropical areas) exhibits promising alternative to the petroleum based fossil fuel which reduces the net emission of GHGs. But due to certain technological barriers the large scale production of lignocellulosic bioethanol has not been successfully commercialized. To achieve the goal, economically viable bioethanol production technology, which includes pretreatment, enzymatic hydrolysis, fermentation, and dehydration, needs to be developed. Ionic liquid aided pretreatment can recover more than 80% cellulose and 42% lignin from lignocelluloses, which generally contains 30–46% cellulose and 18–25% lignin. Processing of the recovered cellulose towards bioethanol production requires enzymatic hydrolysis, which gives almost 76% reducing sugar yield. Use of ultrafiltration and nanofiltration in hydrolysis concentrates 27% reducing sugar as well as recovers more than 73% enzyme with 50% catalytic activity. Ultrafiltration rejects 100% yeast as well as reveals 15 g/l/h ethanol productivity, which can be subjected to membrane based dehydration by way of pervaporation to produce 99.8 wt% ethanol. The scope of this review focuses on eco-friendly and sustainable method for bioethanol production. A holistic and dedicated approach of this review helps to solve the various technological concerns and realize large scale commercialization of lignocellulosic ethanol.

1. Introduction

International Energy Outlook (IEO) 2013 predicts an increase of 56% in World energy consumption over 30 years (from 2010 to 2040). Herein 79.7% of the consumed energy is supplied by non renewable fossil energy source (coal, natural gas, crude oil/petroleum etc.) and nuclear source, 15.3% is supplied by hydro-power and rest 5% by other renewable energy source. High cost, limited reservoir, depleting supply, and random consumption hinder the dependency on petroleum as transport fuel [1]. Over consumption of fossil fuel is a major threat to environment as it leads to acid rain, climate change, global warming, and harmful effect on human health and aquatic life. Global scenario shows extensive use of conventional diesel engines throughout the world due to flexibility, reliability, high burning efficiency, and low cost

Abbreviations: GHG, Green house gas; IEO, International Energy Outlook; NO_x, Nitrous oxide; SCR, selective catalytic reduction; CO, Carbon monoxide; HC, Hydrocarbon; RFA, Renewable Fuel Association; CO_2, Carbon dioxide; NaOH, Sodium hydroxide; [bmim]Cl, 1-butyl-3 methylimidazolium chloride; [bmim][CH_3SO_3], 1-butyl-3 methylimidazolium methylsulfonate; [EMIM]oAc, 1-ethyl-3-methylimidazolium acetate; [EMIM]Ace, 1-ethyl-3-methylimidazolium acesulfamate; [BMIM]Ace, 1-butyl-3 methylimidazolium acesulfamate; AEL, alkaline ethanol lignin; H_2SO_4, Sulphuric acid; IL, Ionic liquid; EFB, empty fruit bunch; FTIR, Fourier Transform Infrared Spectrophotometer; TGA, Thermogravimetric Analysis; NMR, Nuclear magnetic resonance; GPC, Gel permeation chromatography; DFRC, Derivatization followed by reductive cleavage; DMSO, Dimethyl sulfoxide; MWL, Milled wood lignin; ILL, Ionic liquid lignin; APAWAO, Alkaline Peroxide Wet Air Oxidation; PEG, Polyethylene glycol; DWC, Dividing-wall columns; CA, cellulose acetate; NY, Nylon; PS, Polysulfone; PES, Polyethersulfone; UF, Ultrafiltration; NF, Nanofiltration; RO, Reverse osmosis; MWCO, Molecular weight cut off; MD, Membrane distillation; PTFE, Polytetrafluoroethylene; PP, Polypropylene; PVDF, Polyvinydilene fluoride; DCMD, Direct Contact Membrane Distillation; EtOH, Ethanol; VMD, Vacuum membrane distillation; PDMS, Polydimethylsiloxane; PDMS-PS IPN, polydimethylsiloxane-polystyrene interpenetrating polymer network; PS, Polystyrene; PDMS-PS, Polydimethylsiloxane-polystyrene; PVA, Poly(vinyl alcohol); MMMMs, Multilayer mixed matrix membranes; PVA, Poly(vinyl alcohol); SA, Sodium alginate; PTMSP, 1-(trimethylsilyl)-1-propyne; PDMS, Poly[dimethylsulfoxane]; $NH_{42}SO_4$, Ammonium sulfate; PTMSP, Poly(1-trimethylsilyl-1-propyne)

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[2] but the most detrimental pollutants (particulate matter like carbon, trace element, inorganic ion etc. and nitrous oxide (NO_x)) are emitted from diesel engines [3]. Application of two-cell selective catalytic reduction (SCR) system in diesel engine can reduce pollutant emission to a certain extent, as the first catalyst cell minimizes NO_x emission whereas the second cell adsorbs ammonia generated from the previous cell [4]. But the major limitation of SCR system is the chance of contamination and blocking of the catalyst's pore by fine particles, silicon compounds etc. Contrastingly, the use of natural gas in a single cylinder diesel engine by dual fuel mode of application decreases carbon dioxide, particulate matter, and NO_x but a drastic increase in carbon monoxide (CO) and hydrocarbon (HC) emission occurs as compared to the emission observed in the case of traditional diesel engine [5]. These major drawbacks have invoked reasonable awareness regarding investigation of alternative renewable energy sources, which are environmentally benign, economically and technically feasible, biodegradable, and non-toxic [6]. Water, biomass, wind, geothermal heat can serve as renewable energy source and can potentially substitute fossil fuel [7,8]. The developed nations are focussing on the application of biomass based fuel, given that biofuel is a cost wise competitor of fossil fuel, as it satisfies all the necessities of clean technology, including renewability, sustainability, common availability, reduction in green house gas emission, and biodegradability [9]. Biofuel can be classified into two groups. Primary biofuel is referred to as natural and untreated biomass, such as wood chips and fuel wood. These are directly combusted to supply energy for cooking, heating and electricity production. Secondary biofuel is produced by processing or modifying primary biofuel. These are generally solid, liquid or gases. Secondary liquid biofuel can be further divided into three generation fuel depending upon the raw material used [10]. First generation liquid requires simple production process and uses sugar [11] or grain [12] as possible raw material while second generation fuel is produced from agricultural lignocellulosic biomass by biological or thermochemical process and third generation biofuel is derived from microbes and microalgae [10,13]. Main aim of biofuel research is to produce energy products like bioethanol, biomethanol, biodiesel, biogas, biohydrogen etc. using biological source [14].

Bioethanol and bioethanol/gasoline are most commonly used transport fuel worldwide and can be viewed as viable alternatives to petroleum fuel [15]. As burning of ethanol causes emission of carbon dioxide, it can be mixed with gasoline to oxygenate the fuel mixture to reduce carbon dioxide emission. Bioethanol is mainly produced from biomass by hydrolysis of cellulose and fermentation of sugar, which comes from energy crops including maize and wheat crops, sawdust, cord grasses, sorghum plants, corn, sugarcane etc. The main advantage of bioethanol over conventional fuel is its biodegradability, less toxicity, reduction of green house gas emission and use of renewable and ubiquitous biomass as primary substrate. Bioethanol-based economy is more environmentally beneficial than gasoline-based or conventional petroleum-based economy and endorsement of the use of Bioethanol can also inspire rural economy to cultivate the required crops. Fig. 1 Shows the graph of year wise worldwide average bioethanol production. Brazil and United States account 87.1% of World bioethanol production in 2011 as estimated by Renewable Fuel Association (RFA). US produce fuel ethanol from corn stover [16] where Brazil use sugarcane bagasse and straw as the possible raw material for ethanol production. Sugarcane is the most plentiful agricultural crop cultivated in this country [17]. Brazil has been producing sugarcane ethanol since early 20th century [18] and the popularity of sugarcane ethanol increased in 2003 with the use of flex fuel vehicle. Currently, 5% ethanol blending policy with gasoline has been followed in India. Later, it will move towards 20% blending by 2020. But, the currently available feedstock in the form of sugarcane molasses is inadequate to meet the necessity and also raises the food vs fuel debate [19]. Thus bioethanol produced from agricultural residue especially lignocelluloses came into scenario to overcome this debate. Huge demand of lignocelluloses residue to support industrial production of bioethanol can be enhanced by increasing the cultivation of potential agricultural crops which can be successfully achieved by implementing modern agriculture and irrigation system. Applying proper agricultural water management, the ratio of irrigation to cultivated area can be improved day by day in Indian Ocean Islands [20] which can influence the agriculture strategy of India. Among available different irrigation systems surface irrigation has been used in most of the agricultural areas all over the world. Due to the complexity of the technique three different models have been investigated to simulate surface irrigation. Among these zero inertia and full hydrodynamic models are more powerful as compared to kinematic wave model [21]. Trickle and sprinkle irrigation system also improves overall cultivation process but for applying these techniques pressure loss must be appropriately adjusted to avoid the failure of the system, which can be done by using tapered pipes [22]. Due to requirement of large amount of water in irrigation process, world population suffers from water crisis. Therefore use of non-conventional water resources, mostly treated wastewater, will be effective in this aspect in developing countries like India and Brazil [23]. Water lifting technology, which is attained by pump system, also plays a vital role in irrigation practice. Though the use of modern pump improves water supply for expanding irrigating agriculture, but this require high energy which is supplied conventional electric power [24]. This may leads to energy crisis which can be overcome by the use of biomass based energy. Hence lignocelluloses based bioenergy, more specifically bioethanol may contribute for the generation of its own source. Production of bioethanol from lignocellulosic biomass grabs attention because of renewable and ever-present nature of biomass, its non-competitiveness with food crops and reduction of threat to global warming.

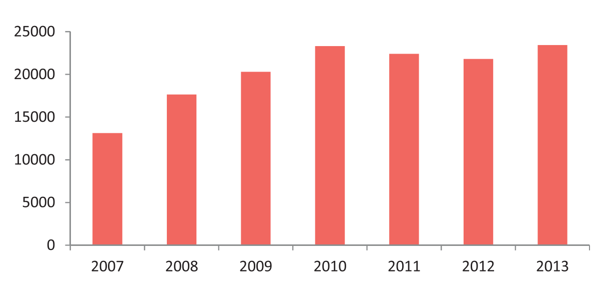

Fig. 1. Year wise worldwide bioethanol production as reported in Outlook 2008–2013 reports.

Lignocelluloses are generally composed of lignin, cellulose, hemicelluloses, organic extractives and some inorganic components which turn into ash after combustion [25]. Cellulose and hemicelluloses are strongly linked to lignin through covalent linkage and hydrogen bonding [26]. Cellulose consists of hexose sugar monomer and hemicellulose consists of different pentose sugar monomers which are fermented by microorganism to produce ethanol. Thus cellulose is the main component which is converted to bioethanol. The main sources of lignocellulosic biomass are forest woody feedstock (including different plant woody material like pine, fir, hemlock spruce etc.), forestry and industrial residue, agricultural wastes i.e different crops residue such as corn stalks, rice straws, sugarcane bagasse etc [27,28]. Fig. 2 shows a chart of potential lignocellulosic residue generated per year in million metric tons in India. The potentiality of all the resource in bioethanol production has been studied. Maximum cellulosic ethanol concentration of 3.20 ± 0.36 g/l was achieved when rice husk was used as raw material which contained 35–50% cellulose [29]. Rice straw (contains 32.70% cellulose), a potential lignocellulosic substrate, has been well studied for bioethanol synthesis. Surfactant assisted combined ultrasonic pretreatment and enzymatic hydrolysis of rice straw produced maximum 0.374 g/g reducing sugar which was subjected to fermentation and 1.48% ethanol yield was achieved with