Recovery of saccharides from lignocellulosic hydrolysates using membranes: A mini review on significant parameters

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Abstract. The use of lignocellulosic biomass has received a lot of attention due to concerns for environmental sustainability and an increasing global waste problem. In order to solve these problems, lignocellulosic biomass can be converted to fuels and chemicals. Since lignocellulose biomass is a renewable feedstock, the conversion process solves the waste problem and produce chemicals simultaneously. However, one of the major challenge in the development of biorefineries is the separation and purification of the biomass hydrolysates. Effective recovery of saccharides and the removal of impurities such as acetic acid and furfural are required as these compounds can inhibit the fermentation process. In this paper, a critical review of membrane technology related to the recovery of saccharides from lignocellulosic hydrolysates is presented. Effects of membrane materials, operating conditions and feed characteristics on the selectivity and productivity of the membrane processes are discussed. The challenges and future outlook of membrane assisted saccharide recovery are also presented.

1. Introduction
The limited supplies of fossil fuels and global waste problem have led the fuel and chemicals production research to focus on the utilization of renewable and green feedstock mainly from biomass sources. Globally, the research on lignocellulosic waste biomass has gained significant importance due to its abundance, high yield production per area of land, local availability, low cost to convert biomass to energy, and environmentally benign production [1]. This type of biomass refers to plant dry matter that composed of 2 major components consist of carbohydrates polymers such as cellulose and hemicellulose and aromatic polymers called lignin [2]. These carbohydrates structures can be further converted into wide range of bio-based products, which usually adopted in bioethanol production [3]. Among typical lignocellulosic biomass sources includes rice straw, wheat straw, sugarcane bagasse, woody raw materials, forest waste, timothy grass and other agricultural residues [4].

The carbohydrates content in lignocellulosic biomass can be converted into useful fermentable sugars such as glucose, pentose and hexose through feedstock pre-treatment or hydrolysisation process [5]. Then, the sugars are fermented to produce ethanol. During this process, different method including physical, chemical and biological processes is employed to enhance the lignocellulose digestibility thus improve the yield of cellulose hydrolysis [5]. Nevertheless, the pre-treatment process is often accompanied by the formation of several inhibitory by-products such as furfural and organic acids like acetic acid [4]. High content of acetic acid and other inhibitors in the hydrolysate may greatly affect the production of ethanol as it interferes the microbial activity during fermentation. In fact, many studies of bioethanol
production have faced few problems such as low concentration of fermentable sugars thus produce low concentration of ethanol and subsequently caused high operational cost and energy consumption during the following purification steps [6]. Thus, several post-treatment of the hydrolysate is needed to separate and purify the sugar streams from the unwanted inhibitors.

Separation and detoxification techniques such as chromatographic, solvent extraction, evaporation, activated charcoal adsorption, and ion exchange have reported to have few drawbacks in concentrating sugar solutions. It includes long processing time, high processing costs, generating more waste materials and high chances of losing sugars components [6]. Alternatively, membrane technology, one of the conventional method has received considerable attention in bio refinery research to separate products from process stream especially for the lignocellulosic hydrolysate recovery [7]. Membranes used in bioseparation are porous and semipermeable in general. The different characteristics of pressure-driven membranes made it useful in a wide range of industrial sectors such as waste water treatment, biotechnology, pharmaceutical, and food engineering [7]. For example, membrane technology has been utilized for application such as desalination, organic and inorganics removal and bacterial removal [8].

Nanofiltration (NF), one of the effective membrane separation technology that can be employed to separate and purify the sugars stream and acetic acid mixture. It is categorized as pressure-driven membrane having properties between reverse osmosis (RO) and ultrafiltration (UF). To compare, this type of membrane offers some advantages over the other two such as high flux, easy maintenance, low energy consumption, low operation cost, low operation pressure and high retention for small molecules such as sugars, amino acids, peptides and multivalent anion salts [9]. In addition, the performance of the nanofiltration membrane is mainly reflected upon the permeate flux and solute rejection. These variables can be computed using the following Equation (1) for permeate flux and Equation (2) for rejection:

\[ J = \frac{r^2 \cdot \Delta_{PTM}}{8 \cdot \eta \cdot \Delta x} \]  

(1)

where \( J \) represents flux, \( r \) is average pore size of the membrane, \( \Delta_{PTM} \) is transmembrane pressure, \( \eta \) is the viscosity and \( \Delta x \) is the thickness of the active filtration layer [10].

\[ R_s = 1 - \frac{C_{S,P}}{C_{S,R}} \]  

(2)

where \( R_s \) represent rejection while \( C_{S,P} \) and \( C_{S,R} \) are the concentration in the permeate and concentration in the retentate respectively [10]. These two parameters are highly affected by many factors such as membrane materials, transport mechanism, processing conditions including temperature, pH, pressure and solute concentration. In the next section, the application of nanofiltration membrane technology for the recovery of saccharides from lignocellulosic hydrolysates (Figure 1) and the factors affecting its performance are discussed.

![Figure 1. Separation of saccharide from acetic acid using Nanofiltration membrane.](image-url)
2. Effect of membrane materials and transport mechanism

Feasibility of membrane to be used for bioseparation is greatly depends on the properties of the materials used as membrane. The selection of proper and suitable materials is vital to enhance the membrane performance and avoid membrane fouling problem. The commonly used membrane in different chemical process is constructed of organic matter such as polymer as well as inorganic and hybrid membrane [11]. However, the polymeric membrane is more preferred over the other materials due to its possibility to modulate the intrinsic properties [6]. The most common polymer that usually adopted as the membrane materials includes cellulose acetate (CA), nylon (NY), polyimide, polysulfone (PS), and polyethersulfone (PES). Meanwhile, the general membrane module employed for this process consists of hollow fibre, spiral wound and flat sheet/plate-and-frame membrane [11]. Different membrane materials would impart different performance as it have distinct molecular weight cut-off (MWCO) and contact angle.

Apart from that, the transport of organic solutes such as saccharides across nanofiltration membrane is predominantly determined by the size exclusion mechanism, followed by Donnan effect and solute-membrane interactions [12]. Generally, the size exclusion mechanism is influenced by the solute’s relative size and the molecular weight cut-off (MWCO) of the membrane. Membrane’s MWCO is defined as the lowest average molecular weight of solute (in daltons) that is 90% rejected by the membrane [13]. The donnan effect or charge exclusion depends on the electrostatic interactions between solutes and the charges membrane surface which mainly affect the separation of charged species. Liu et al. [14] describes the solute-membrane interaction mechanism to be based on the adsorption of the solutes onto the membrane that in turn influence the solute retention. Nevertheless, the mechanism to separate saccharide molecules from the inhibitors is also affected by the change in the surrounding condition including temperature, pressure, pH and the feed concentration.

3. Effect of temperature

Temperature also plays a vital role in recovering saccharide using NF membrane. This critical operating condition has been highly associated with the diffusivity and viscosity behavior of the feed as well as membrane pore size that affect the concentration polarization, sugar rejection, and permeate flux [15]. The temperature effect on the feasibility of nanofiltration for saccharide recovery was studied and compared in several literatures. Wang et al. [16] observed that the permeate fluxes for all membranes tested increased linearly with the elevated temperature. Meanwhile, the retention of saccharide molecules was gradually decreased from 82.9% to 77.5% as the temperature increased from 25 to 45 C. Likewise, Li et al. [17] also found that the rise in feed temperature reduced the rejection of individual sugars and enhance the diffusion rate of each sugar. The decrease in solute retention ascribes a faster transport of the neutral solutes across membrane compared to water.

Based on these studies, general trend of increasing flux and reduction in solute rejection was observed as the temperature increased. The main reason was attributed to the solvent viscosity reduction and the increment of solute diffusivity thus, improved the mass transfer of solutes through the NF membrane [16]. Besides, Jyoti et al. [18] pointed out that the increase in temperature caused the thermal motion of the permeate molecules to increase thus promoting its diffusion as it overcome the pore wall frictional forces. In addition, the thermal motion of polymer chain also increased as function of temperature leading to a larger available free volume of the polymer matrix for diffusion. Apart from viscosity, the temperature effect is correlated with pore size increment which could enhance the mass transfer of solutes across membrane. High temperature elevates the effective pore diameter as the adsorbed water layer in the hydrophilic pore surface becomes thinner [19]. It was in agreement with study by Dang et al. [20] that reported the increased in temperature caused the effective pore radius of a NF270 membrane to rise from 0.39 to 0.44 nm. Likewise, Pruksasri et al. [21] stated a linear relationship between pore size of NP030 membrane and the temperature tested for the nanofiltration of galacto-oligosaccharides.
4. Effect of pH

pH is another well-known parameter that have great influence on NF productivity. It is important to understand the effect of pH on nanofiltration in order to manipulate and optimize the separation process. The rejection profile for polymeric membranes such as cellulose acetate, polyamide, polyimide, polysulfone and polyethersulfone is highly dependent on the change in pH due to the presence of positively and negatively charged group including carboxyl, amino and sulphonated group within the polymeric membrane structure [22]. As this functional groups are prone to be hydrated and ionized in aqueous solution, the change in pH of the surrounding may lead to change in conformation and ionization of the polymeric chains [23]. Also, it makes each membrane to possess different pH operational interval that can give remarkable impact on the membrane properties and the subsequent filtration performance.

The change in membrane properties is associated with the membrane surface charge, hydrophilicity, pore radius and membrane thickness. The membrane surface charge is measured using zeta potential which provides information about the reactivity of the surface in function of pH and the isoelectric point that have significant influence on the rejection of the nanofiltration membranes [24]. Besides, manipulation of feed pH could cause a conformational changes on the membrane surface layer as result of the protonation and deprotonation of the acid group on the polymer chains. The properties of the membrane also can be altered through different interactions between feed solutions and the polymeric membrane materials [25]. Moreover, pH effect is also associated with the hydrophilic and hydrophobic characters of the membrane indicated by contact angle value which control the surface wettability by liquids. Smaller contact angle specifies a hydrophilic membrane contributing to a high water permeability across the membrane and vice versa [26].

Furthermore, effect of pH on the membrane properties is mainly reflected in the filtration performance including the membrane flux and solute rejection. Wang et al. [16] detected a significant decreased in fluxes of xylose-glucose-furfural-HMF model solution using Alfa-Laval-NF membrane as pH increased. Meanwhile, Cohen et al. [27] observed a reduction of glucose and galactose retention as the feed pH changed from pH 4.5 to pH 8.5. Likewise, Ahsan et al. [28] found that the sugar concentration was significantly decreased as the tested pH increased. This phenomenon was probably caused by the alteration of the polymeric membrane surface properties, especially its surface charge at different pH values. According to Zhou et al. [29], the maximum fluxes can be observed at the pH neared the isoelectric point of membranes which resulted into 3 remarkable effects: 1) conformational changes in the cross-linked structure of the polymeric membrane causing the membrane pore size to increase, 2) an increased in water permeability due to the electroviscous effect and 3) an increased in net driving force for separation due to the decreased osmotic pressure.

5. Effect of pressure

As the underlying principle of nanofiltration is based on a pressure-driven process, operating pressure could be an important parameter affecting the membrane performances. Similar to other critical operating conditions, the efficiency of the nanofiltration process is predominantly indicated by the permeate flux and the solute rejection. Based on the Equation (1), the permeate flux is always proportional to the applied pressure until the maximum flux is achieved. Besides, the increase in pressure cause the decrease in pore radius, \( r \) and membrane layer thickness, \( \Delta x \). While a reduced pore radius decreases the flux, and the reduced membrane thickness increases it, so these effects are neglected at this point as it cancel out each other. Thus, the permeate flux is found to be proportional only to the pressure factor [10].

This theoretical hypothesis has been reported by previous works on recovery of saccharides by nanofiltration membrane. For example, Giacobbo et al. [30] observed a linear correlation between permeate flux and transmembrane pressure for all polymeric membrane tested due to reduction in membrane layer thickness. In another recent study, Wang et al. [16] also reported that the permeate flux for nanofiltration of xylose and glucose from furfural and HMF increased as the operating pressure changed from 20 bar to 45 bar. Apart from that, the variation in flux profile as function of pressure is
influenced by membrane fouling and concentration polarization. These phenomena occur as result of adsorption, attachment, or accumulation of solutes particles onto the membrane surface and pores causing the flux decline over time [31]. The effect was ascribed by Machado et al. [32] where further increased in transmembrane pressure for NP030 and NP270 membrane caused permeate flux decay, around 30 % due to the concentration in retentate.

Furthermore, the increase in pressure also resulted in a higher solutes rejection due to the reduced pore size and solute compaction on membrane [10]. It was reported in Pruksasri et al. [21] study at which an increasing rejection values of glucose, galactose and oligosaccharide were recorded as the pressure amplified. Likewise, Schmidt et al. [10] found that the rejection of lactose was largest in the pressure range between 1 and 3 MPa, while the rejection of fructose was noticeably increased at pressure higher than 3 MPa. This finding showed that lactose rejection was more affected at low pressure compared to fructose which may be due to the distinctions in molecular weight of solutes. As explained by Córdova et al. [19], the pore size reduction at high pressure has more significant effect for neutral solutes with low molecular weight leading to an increase in the convection flux. Besides, Wang et al. [16] reported that the high solute rejection is due to the increase in water permeability through the diffusion mechanism. At high pressure, adsorption of water into membrane is higher compared to the solutes resulting in a stronger interaction between water and the hydrophilic layer of the membrane through hydrogen bonding. Simultaneously, the membrane exerts a stronger size exclusion of solute as water is more permeable than sugar molecules. Hence, there will be lower solute concentration in the permeate flux but higher in the retention.

6. Effect of concentration
In general, sugar concentration determines the extent of concentration polarization generated on the membrane surface which in turn affect the permeate flux and solute rejection [33]. The effect was experimentally described by Li et al. [17] that observed a reduction in the permeate flux for the separation of soybean oligosaccharide as feed concentration increased. It was consistent with a recent study by Schmidt et al. [10], where the increase in saccharide concentration in the feed stream from 7 to 10 % caused a rapid decrease of the permeate flux. It was because high feed concentration is attributed to the increase of concentration polarization layer and solution viscosity thus decreasing the feed diffusivity across membrane [33].

Similar impact was observed for the solute rejection as function of feed concentration. Shi et al. [33] pointed out that the rejection of isomaltooligosaccharide components decreased when the total concentration increase. Meanwhile, Córdova et al. [19] found that the increase in total sugar concentration in the feed stream led to significant depletion of monosaccharides compared to other sugars. It was due to the fact that the increase in concentration polarization layer caused back diffusion of the simple sugar to be hindered thus reducing its rejection coefficient. Moreno-Vilet et al. [34] stated that this effect is seen to be more significant as the molecular weight of the sugars decreased and the MWCO of the membranes increased. It was confirmed in Schmidt et al. [10] where the change in rejection of monosaccharide, fructose was more affected by the increasing saccharide concentration compared to lactose as fructose possess lower solute radius and molecular weight than lactose. Nevertheless, a proper feed concentration is important in ensuring a good membrane performance since the excessive concentration may exert higher operation cost as regard to the membrane cleaning and replacement.

7. Conclusion
Nanofiltration technology is a promising approach to detoxify and purify the lignocellulosic hydrolyste from unwanted inhibitors. The nanofiltration membrane efficiency is governed by several parameters including membrane materials, transport mechanism, and the operating conditions such as temperature, pressure, pH, and feed concentration. These parameters have been reported to impart significant effects on the overall membrane performance that reflected by the permeate flux and solute rejection. The membrane performance can be improved using the computational approach such as molecular docking.
to visualize effective interaction between membrane and the feed components. However, membrane fouling issue still impede the overall nanofiltration system performance. Thus, in-depth insight of fouling mechanism should be taken into account in order to fabricate a better membrane. Consequently, the future works on the optimization strategy concerning the factors influencing the membrane productivity could be developed with regard to improve and control the membrane fouling problem.

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