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# Modified Anopore$^{TM}$ hybrid membranes for the microfiltration of cellulose acid hydrolysis mixtures

Yong-Hong Zhao, Daniel F. Shantz*

*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843-3122, United States*

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ABSTRACT

Three classes of nonfouling substances, poly[poly(ethylene glycol) methyl ether methacrylate] (POEM), poly(sulfobetaine methacrylate) (PSBMA), and perfluoroalkyl tagged poly(ethylene glycol) surfactants (fPEG) were covalently tethered onto the surface of Anopore$^{TM}$ membranes (nominal pore size 0.2 μm) to form a series of organic–inorganic hybrid membranes. These membranes were then used for the microfiltration of cellulose acid hydrolysis mixtures. Flux recoveries of over 80% after three filtration cycles were observed for the hybrid membranes. Thus the fluxes of the three synthesized hybrid membranes could be largely recovered by washing with methanol and water after the microfiltration of cellulose hydrolysis mixtures. In contrast the bare membranes showed much lower flux recoveries. It was also shown that the grafted polymer layer improves the stability of the membranes in acidic environment. The synthesized membranes were also characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS), which were used to understand the morphology and chemical compositions of the membrane surfaces, and the results of these methods correlate with the microfiltration data presented. Mathematical modeling of the microfiltration data indicates that the pore constriction model best describes the fouling behavior of the bare Anopore$^{TM}$ membrane, while the cake filtration model fits the data most satisfactorily for the three groups of hybrid membranes. The current work presents an alternative approach to membrane design for biomass related separations.

## 1. Introduction

The confluence of global warming and decreasing reserves of petroleum has brought increasing impetus for alternative (i.e. non-petroleum) chemical feedstocks and renewable fuels [1]. While many solutions are being explored, fuels and chemicals from renewable biomass sources have emerged as one solution with both short- and long-term potential [2,3]. Nature produces the vast amount of 170 billion metric tons of biomass per year by photosynthesis, 75% of which can be assigned to the class of carbohydrates [4]. Biomass carbohydrates are the most abundant renewable resources available, and they are currently viewed as a possible fuel and chemical feedstock of the future [5–7].

Lignocellulosic materials, comprised of cellulose, hemicellulose and lignin, represent the largest fraction of biomass carbohydrates [8]. A variety of chemistries and processes can be applied to convert lignocellulosic biomass to valuable fuels and chemicals [9]. For instance, thermal reactions are exploited in the pyrolysis of lignocellulose to charcoal, oil and/or gases and its gasification to synthesis gases and/or hydrogen. Alternatively, lignocellulose can also be hydrolyzed to liberate the lignin and depolymerize the polysaccharides. Compared with pyrolysis and gasification, the reaction conditions of chemical hydrolysis are more moderate [10]. Chemical hydrolysis typically uses acids or bases to induce the solubilization of the saccharides [3]. Acid-catalyzed hydrolysis schemes are used most frequently, and by changing reaction conditions (e.g., acid type, acid concentration, temperature and treatment time, etc.), the acid hydrolysis reaction can be tuned to produce sugar mixtures, which are the main sources for the production of transportation biofuels such as ethanol through biological conversion [11,12]. Hydrolysis reactions can also be geared towards the direct production of some important chemicals, such as furfural, 5-hydroxymethyl furfural, levulinic acid, etc. These chemicals can be further converted to a variety of chemical intermediates [13].

Although extensive efforts have been made to develop effective methods to convert lignocellulosic biomass to valuable products or intermediates, the separation of low molecular components (e.g., sugars) from residual solids formed via the hydrolysis remains a great challenge [1]. Since the decomposition of lignocellulosic biomass typically leads to a complex mixture of highly oxygenated compounds that are quite hydrophilic and not thermally stable [9], the processing of these compounds should occur under much

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* Corresponding author. Tel.: +1 979 845 3492; fax: +1 979 845 6446.
*E-mail address:* shantz@mail.che.tamu.edu (D.F. Shantz).

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different conditions than that of current refineries. Separation schemes such as distillation are energy intensive, and will be more so for these compounds given the likely need for reduced pressures due to thermal stability considerations. Extraction has also been employed, but the large quantities of organic solvents needed partially negate the green benefits of alternative fuels [14]. Alternatively, membrane-based separation technologies could offer a solution for biomass related separation or purification, because of their high energy efficiency, ease of implementation, and cost effectiveness [15]. Compared with their polymeric counterparts, inorganic membranes, especially ceramic membranes, should be more suitable for biomass separations, owing to their advantages in industrial operations in terms of high temperature durability, sufficient mechanical strength, chemical inertness, and the absence of swelling in the presence of organic solvents [16]. Recently, increasing attention has been paid to the application of ceramic membranes in biomass related separations. Javaid et al. [17] used tubular ceramic membranes to remove char particles about 1 μm in size from fast pyrolysis bio-oil. Gomes et al. [18] separated glycerol from biodiesel using tubular-type $\alpha$-$Al_2O_3/TiO_2$ membranes. Kuhn et al. [19] used MFI zeolite membranes in bioethanol enrichment from an aqueous solution under pervaporation conditions.

However, membrane fouling is still a significant factor that must be considered in all applications of membrane filtration [20,21]. One route to improving fouling resistance is to incorporate nonfouling substances to the membrane surfaces [21]. Among the most promising nonfouling materials, poly(ethylene glycol) (PEG) has shown extraordinary resistance to non-specific protein adsorption as demonstrated by a number of publications [22–25]. Although the exact mechanism of PEG-mediated protein resistance is still a matter of debate, a general understanding is that the key factors that determine the non-fouling property of PEG include the steric repulsion, large excluded volume, and unique coordination with surrounding water molecules in aqueous solutions [26,27]. Zwitterionic polymers, in which cation and anion groups are located on the same monomer residue and maintain overall charge neutrality, have been reported as a new generation of nonfouling material [28–30]. The nonfouling behavior of zwitterionic polymers is due to their ability to form a hydration layer at the surface via electrostatic interactions [31]. More recently, amphiphilic polymers containing ethoxylated fluoroalkyl groups have emerged as a promising material for marine antifouling/fouling-release applications [32–36]. Ober and coworkers synthesized a series of block copolymers possessing perfluoroalkyl tagged oligoethylene glycol moieties as side chains and used them to prepare novel anti-biofouling polymeric coatings [37,38]. The antifouling and fouling release properties of these coatings are attributed to the very low interfacial energy with water because of the ethylene glycol (EG) groups, and the non-adhesive nature due to the perfluoroalkyl groups [32,37].

In this work, a series of organic–inorganic hybrid membranes were synthesized by grafting the above-mentioned three nonfouling substances to the surfaces of Anopore$^{TM}$ ceramic membranes. These hybrid membranes were then used for the separation of low molecular components from cellulose hydrolysis mixtures. The fouling tendency and mechanism were systematically investigated for the pristine Anopore$^{TM}$ membranes and the modified hybrid membranes. It was anticipated that, by integrating the mechanical strength and chemical inertness of a ceramic with the nonfouling property of an organic polymer, these hybrid membranes should offer the ability to partition the oxygenated compounds in cellulose hydrolysis mixtures through the membrane while reducing the ability of large particulates and aggregates to irreversibly adsorb. This is in fact observed for all the three nonfouling substances modified Anopore$^{TM}$ membranes and the results point to the potential of designing high performance hybrid membranes that could have potentially superior properties to either purely ceramic or purely polymeric membranes for biomass related separations.

## 2. Experimental

### 2.1. Materials

Anopore$^{TM}$ alumina membranes (Whatman, 25 mm diameter membranes, 200 nm diameter cylindrical macropores) were used as received without any cleaning. Microcrystalline cellulose with an average particle size of 90 μm was purchased from Acros organics and used as received. Tetraethylorthosilicate (TEOS, 99%) was purchased from Fluka. 3-Aminopropyltriethoxysilane (APTES, 99%), poly(ethylene glycol) methyl ether methacrylate (POEM, average $M_n \sim 300$), 2-(*N*-3-sulfopropyl-*N*,*N*-dimethyl ammonium) ethyl methacrylate (SBMA, 97%), 2,2′-bipyridyl (Bpy, 99%), 2-bromoisobutyryl bromide (BIBB, 98%), CuBr (98%), $CuBr_2$ (99%), 4,4′-oxydiphthalic anhydride (ODPA, 97%), *p*-toluenesulfonic acid monohydrate (TSA, 98.5%), magnesium sulfate ($MgSO_4$, 99%), hydrochloric acid (HCl, 37%) and sodium hydroxide (NaOH, 98%) were purchased from Aldrich and used as received. Triethylamine (TEA, 99%) from Aldrich was purified by distillation and stored over 4 Å molecular sieves. Ethanol, methanol, toluene and tetrahydrofuran (THF) (all ACS reagent grade) were purchased from VWR. Toluene and THF were dried using a MBRAUN MB-SPS solvent drying system; all other solvents were used as received. Perfluorinated surfactants (fPEG) were purchased from Dupont (trade name Zonyl® FSN-100, $M_n \sim 950$) and were dried in a solution of anhydrous THF and $MgSO_4$ and purified using a syringe filter (Whatman, 0.2 μm) before use. Deionized (DI) water (18 MΩ) purified with a Milli-Q system (Millipore) was used in all syntheses and measurements.

### 2.2. Surface modification of Anopore$^{TM}$ membranes

The synthetic protocols used in this work to modify the Anopore$^{TM}$ membranes are depicted in Scheme 1. All the membranes were first coated with a silica layer and then functionalized with APTES. The reason for the coating of a silica layer is because it is difficult to achieve a high graft density of APTES directly on alumina surfaces [39]. The silica coating solution was prepared by mixing 100 mg of TEOS with 50 ml of ethanol (10 mM) that contains 1.3 ml of HCl (0.032 N). The silica layer was deposited by immersing a membrane in the solution at room temperature for 2 h, removed from the solution and dried at 95 °C for 15 min. After cooling the membrane to room temperature, amine functionalization was performed by immersing the membrane into a solution of 220 mg of APTES in 100 ml toluene (10 mM) at room temperature for 24 h. The membrane was removed from the solution and repeatedly rinsed with toluene, THF and water to remove excess APTES. The APTES grafted membranes, denoted as M-APTES, were dried at 40 °C under vacuum for 24 h, and then stored in a desiccator for further modification.

### 2.2.1. Surface-initiated atom transfer radical polymerization (ATRP) of POEM and SBMA

Routes 1 and 2 in Scheme 1 show the process for the surface-initiated ATRP of POEM and SBMA from the M-APTES membrane surface. First, under nitrogen protection, M-APTES membranes were reacted with 2-bromoisobutyryl bromide at room temperature in the presence of TEA, using anhydrous THF as solvent. The membranes (denoted as M-Br) were then washed sequentially with methanol–DI water–methanol. Then, CuBr (1 mmol), $CuBr_2$ (0.25 mmol) and three M-Br membranes were placed into a 100 ml Pyrex® bottle under nitrogen protection. The monomers (POEM or SBMA, 7.5 mmol) and Bpy (2 mmol) were dissolved in