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Screening of Hydrogels for Water Adsorption in Biodiesel using Crosslinked Homopolymers

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One production challenge of biodiesel is to lower the water concentration after the washing process applied to remove the excess of glycerin and catalyst. To address this issue, industry usually adopts vacuum distillation which requires high capital expenditure and costly operational expenditure to achieve legal water specification. Alternatively, water content specifications can be met by using hydrogels as adsorbents. Recent works applied polyacrylamide (pAAm) hydrogel and polyisopropylacrylamide microgel to remove water from biodiesel; however, one open question is if polyacrylic acid (pAA) or sodium polyacrylate (SpA) might adsorb water from the biodiesel. Our rationale was that SpA may adsorb more water than the previous studied hydrogels since the electrostatic interaction between water and acrylate group is stronger than the hydrogen bonding between water and amide or acrylic groups. To test this hypothesis, in this work we made the homopolymeric polyacrylamide, polyacrylic acid and sodium polyacrylate hydrogels by free radical polymerization. So, to determine if these materials can remove water from biodiesel, we compared the hydrogel-treated biodiesel with a control sample without adsorbent addition. The initial water concentration was 6977 mg/kg, and our findings showed that the final water concentration in hydrogel-treated biodiesel was lower than the control sample, and the water content after 24h of contact was lower than 1100 mg/kg for the best case. Moreover, SpA presented similar performance as pAAm; however, no clear difference between pAAm and SpA was observed in this screening experiment. The results from our study point towards the idea that SpA could be used in process and product development for new green technologies as alternative to costly and unfriendly environmental vacuum distillation.

1. Introduction

With growing global concern about climate change, new energy sources are sought to reduce the use of fossil fuels. A worldwide consolidated alternative is biodiesel, which has its synthesis and purification widely studied by the scientific community. In addition to being miscible in all proportions with fossil fuel, combustion engines do not need modifications to burn the renewable energy source (Liu, 2017). For this reason, biodiesel was quickly accepted as an alternative energy source for the mechanical power generation on motor vehicles. In addition, other advantages can be listed, such as complete combustion process in motors, handling safety once biodiesel has higher flash point than diesel, reduced aromatics and sulfur content, and biodegradability (Abed et al., 2019; Leung, Wu, Leung, 2010).

Industrially, manufacturers apply wet washing (extraction) technique to purify biodiesel. In this step, the biofuel and acidified water is mixed inside a stirred tank to neutralize the basic catalyst and decompose soap (Atadashi et al., 2011). Then, the raffinate phase is removed, and a second step is to feed heated water to the tank with sufficient agitation to avoid an emulsion (Atadashi et al., 2011). The process is repeated until colorless extract phase is observed. In general, 3 to 10 L of water are required (Bateni, Saraeian, Able, 2017) for each biodiesel liter synthesized. Afterwards, the raffinate phase is saturated with water, and it is mandatory to dry the biodiesel before commercialization. One important challenge of biodiesel production process remains to meet the maximum water content specification after wet washing (extraction) stage. Water in biodiesel may cause methyl and ethyl esters hydrolysis, failure in engine pumps, and microorganisms can

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grow on water/oil interface (Atadashi et al., 2012). To overcome these problems, manufacturers of biodiesel use vacuum distillation or hot air bubbling (Veljković; Banković-Ilić; Stamenković, 2015); however, those processes demand high capital expenditure and/or costly operational expenditure, it may require high energy input, and specialized workers. Alternatively, adsorption is a cheap and easy technique which can remove water from biodiesel. In this niche, polymeric hydrogels might play an important role due to the intrinsic polymer hydrophilicity. Polymeric hydrogels are three dimensional cross-linked networks that swell in water without dissolution due to cross-linked network (Ahmed, 2015). The swelling happens in three steps: water adsorption, water diffusion/network expanding, and osmotic-elastic counterbalancing forces (Ganji; Vasheghani-Farahani; Vasheghani-Farahani, 2010). In the first step, monomers side groups attract the water by hydrogen bonding or ionic interaction, and further steps occur when huge water amount is available in the media (Ganji; Vasheghani-Farahani; Vasheghani-Farahani, 2010). Since water solubility in biodiesel at ambient temperature is around 2000 mg/kg (Fregolente; Fregolente; Maciel, 2012) or even less, the hydrogel swells only little in each batch treatment. This is a great advantage because the hydrogel could be used several times until regeneration.

In previous research works, polyisopropylacrylamide microgel (Nur et al., 2009) and polyacrylamide hydrogel (Fregolente; Maciel; Oliveira, 2015) successfully removed water from biodiesel. In both studies, side groups interacted with water due to hydrogen bonding between amide-water; therefore, the polymer entrapped the free or soluble water in biodiesel phase, and reduced water content by adsorption. Also, poly(acrylamide-co-sodium acrylate) copolymer (Fregolente et al., 2018; Gonçalves et al., 2020) adsorbed water from biodiesel and the last study suggested that hydrogels with high amount of sodium acrylate could enhance water removal; however, it is still unclear if a hydrogel containing only sodium acrylate as a monomer can remove water from biodiesel. Since carboxylate might interact stronger than amide with water, in this work we considered new homopolymeric hydrogels to dry biodiesel. To the best of our knowledge, no report has investigated sodium polyacrylate homopolymer as water adsorbent in biodiesel.

Thus, our objective was to compare homopolymers designed to dry raffinate biodiesel. We expected to enhance water removal since electrostatic interaction between carboxyl and water may be stronger than hydrogen bonding between amide and water. The answer for this question should pave the way for hydrogel adsorption technology to reduce costs, to minimize wastewater effluents and to reduce process time during biodiesel drying process.

2. Methodology

2.1 Materials

Acrylamide (AAm, Amresco), acrylic acid (AA, Acros Organics), sodium acrylate (SA, Aldrich), bis- acrylamide (MBAAm, Amresco), potassium persulfate (KPS, Fischer Scientific), and N'N'N'-tetramethylethylenediamine (TEMED, Sigma Aldrich) were used for hydrogel synthesis. The biodiesel was donated from a local supplier from Paulínia, São Paulo. Distilled water was used in all experiments.

2.2 Hydrogel synthesis

Homopolymeric hydrogels of AAm, AA and SA were made using MBAAm as the cross-link agent. To compare different materials, we set up the total monomer concentration, degree of cross-linking, the amount of initiator, and catalyst (Table 1) for each hydrogel; therefore, differences between treatments may only be a function of the homopolymer composition. Synthesis details were described elsewhere (Paula et al., 2019). Briefly, monomers, MBAAm, and KPS were solubilized in water, and the solution was slightly heated. Next, TEMED was added and the reaction proceeded quickly. Post-synthesis treatments were hydrogel dehydration in ethanol, drying in vacuum oven at 60 °C until constant mass. The dried product was grounded in impact mill, and sieved to produce particle average diameter of 2.4 mm.

Table 1: General composition of homopolymers used in assays.

Monomer (mol L^{-1})	MBAAm (mol.mol^{-1})	TEMED (% v/v)	KPS (% m/v)
0.98	0.015	2.0	0.04

2.3 Hydrogel characterization

Morphology

Investigation of hydrogel particle morphology was carried out through Scanning Electron Microscopy (SEM) with 300x magnification in a Leo 440i, LEO Electron Microscopy (England, Oxford). Before been analyzed, hydrogels were immersed in liquid nitrogen to fracture the particle and then coated in gold chamber.

Density

To measure the real density of the hydrogel particles, we performed a helium pycnometry in a AccuPyc 1330, Micromeritics (Norcoss, USA). Briefly, an amount of hydrogel was measured in a plate, which was placed inside the equipment for density measurement.

2.4 Water Adsorption in Biodiesel

To check if homopolymers could remove water from biodiesel, we conducted an experiment to compare the hydrogel-treated biodiesel with a control sample without adsorbent addition. Firstly, we prepared a blend of 1000 mL of biofuel with 300 mL of water under mixing for 30 min at ambient temperature to simulate extraction process. The mixture was left for 24 hours allowing water to decant; then, extract phase was discarded, and raffinate phase samples were taken to measure the initial water concentration. Then, 100 mL of organic phase was transferred to enclosed Erlenmeyer flasks with 0.4 g of each polymer. The flasks were placed in an orbital incubator with controlled ambient temperature (25 °C) and agitation (200 rpm) for 24 h. Thereafter, the hydrogels were collected by filtration in nylon sieve. The treated biodiesel samples were analyzed in replicates by Coulometric Karl Fischer technique according to ASTM D 6304 (ASTM, 2016) in a Metrohm 852 Titrando. In addition, a control sample without hydrogel addition was conducted in same conditions.

3. Results and Discussion

3.1 Hydrogel characterization

SEM images revealed a smooth surface morphology (Figure 1). Both pAAm and pAA hydrogels showed no pores in surface since homopolymers were dried in vacuum oven; thus, capillary force closed the relaxed state pores (Hüsing; Schubert, 1998). Interestingly, even though not so expressive, we observed some porosity in sodium polyacrylate hydrogel. Since ionic groups are extremely hydrophilic (Yang; Rana; Lan, 2015), we hypothesized the hydrogel adsorbed air's moisture, which leaded to the observed morphology due to swelling initial stage.

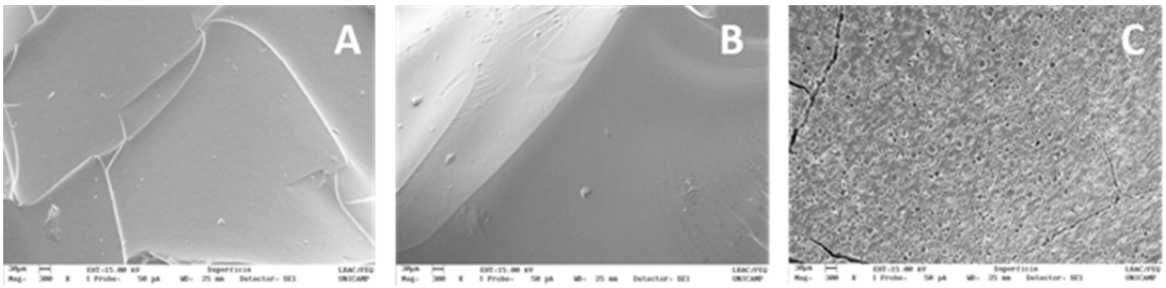

Figure 1: Scanning electron micrography images of poly(acrylamide) (A), poly(acrylic) acid (B) and sodium poly(acrylate) (C) with 300x magnification.

As expected, the measured hydrogels densities were greater than water and biodiesel (Table 2). Since water is more dense than biodiesel, the hydrogels might adsorb free water even in stationary biodiesel.

Table 2: Hydrogel skeletal density.

Hydrogel	ρ (g/mL)
Polyacrylamide	1.2888 ± 0.0003
Polyacrylic acid	1.3924 ± 0.0028
Sodium polyacrylate	1.2976 ± 0.0004

3.2 Water adsorption in biodiesel

Treatments and control sample started with a cloudy biodiesel containing 6977 mg/kg of water. When pAA hydrogel treated biodiesel (Figure 2B), no visual discrepancy between the assay and control (Figure 2D) was detected after 24 h; however, we observed a clear biodiesel when pAAm hydrogel (Figure 2A) and SpA hydrogel (Figure 2C) treated the mixture. Similar results were obtained when pAAm hydrogel (Fregolente; Maciel; Oliveira, 2015) and acrylate-containing hydrogels (Gonçalves et al., 2020) treated biodiesel. Thus, the evidence points toward the idea that pAAm and SpA hydrogels can remove water from the biodiesel. To determine differences between them, as also described in the methodology, we measured the water content by Coulometric Karl Fischer.

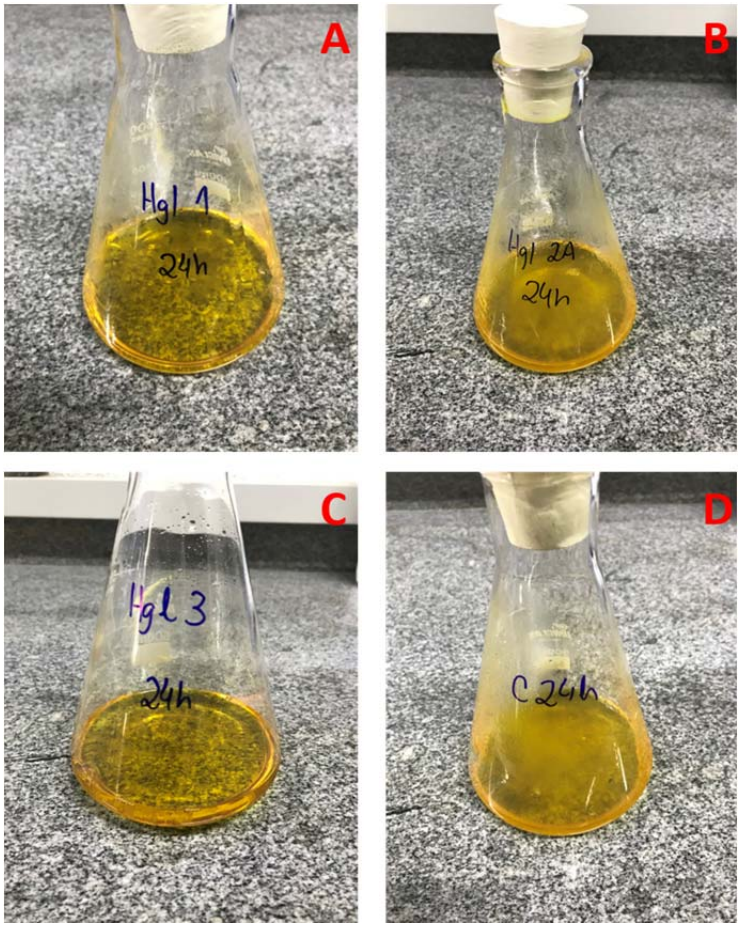

Figure 2: Biodiesel treated with polyacrylamide (A), polyacrylic acid (B), sodium polyacrylate (C) hydrogels, and a control sample without hydrogel (D).

We found pAA, pAAm, and SpA removed water from biodiesel (Figure 3). Moreover, SpA and pAAm tends to remove more water than pAA; however, we did not observe a clear distinction between SpA and pAAm hydrogel. Conversely, pAA had limited water removal (40.8 %), and further studies might investigate the observed behavior. Since the carboxyl-water interaction is stronger than water-amide hydrogen bonding, acrylate-containing hydrogels should remove more water than acrylamide-containing hydrogels. Thus, we expected to see an important contrast in final water concentration; however, both hydrogels displayed similar free water removal: while pAAm removed 82.1 %, SpA adsorbed 84.3 % of water. Nevertheless, our findings suggested that acrylate hydrogels with tailored-made properties could adsorb water during biodiesel drying process. Therefore, when SpA hydrogels treated biodiesel containing almost 7000 mg/kg of initial water, it was possible to reach 1098 mg/kg after 24 h.

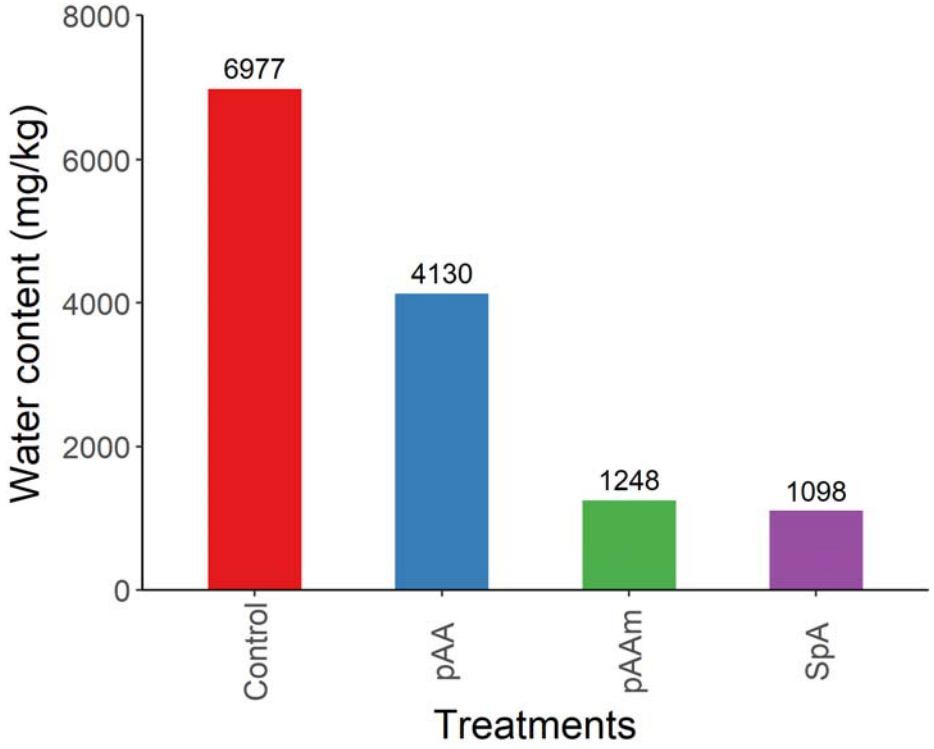

Figure 3: Hydrogel-treated biodiesel and control sample water content after 24 h of batch treatment.

4. Conclusion

Our results showed that pAA, SpA, and pAAm hydrogels with no significant pores in the homopolymeric structure were produced. These hydrogels can adsorb water from biodiesel. It was demonstrated that pAA hydrogel presented limited water removal, while pAAm hydrogel and SpA hydrogel eliminated the turbidity of the biodiesel. After 24 h of contact of 0.4 g of SpA hydrogel with 100 mL of biodiesel under agitation, the water content was decreased from 6977 mg/kg to 1098 mg/kg. Therefore, the evidence collected can pave the way to hydrogel adsorption technologies, which may contribute to reduce costs, to minimize wastewater effluents and to reduce process time during biodiesel drying process.

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