

Evaluation of Different Types of Hydrogels for Water Removal from Fuels

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This work aims to develop a separation process for water removal from liquid fuels, using fixed beds of hydrogel particles. The packing comprised of polyacrylamide (PAAm) hydrogels, containing one of two different monomers (sodium acrylate or acrylic acid). Diesel and biodiesel samples were saturated with water and fed to a hydrogel bed. Experimental runs were carried out according to two-level factorial designs, in order to evaluate the effect of temperature and hydrogel formulation on removal of water from fuels. The hydrogel which utilised the sodium acrylate monomer presented the best results for water removal. Temperature is also an important factor; it was observed that the hydrogel bed is more efficient at the lowest temperature studied (25°C). This may be related to the lower solubility of the water in the fuel, obtaining a percentage of water removal of approximately 54% for biodiesel and 50% for diesel fuel.

1. Introduction

A recurring problem in the production, distribution and storage of fuels is contamination by water, which impacts directly on their quality. Water content in fuel above a recommended level may promote growth of microorganisms in storage tanks, formation of sludge and increase turbidity. This, in turn, can cause the blocking of fuel filters, ultimately damaging the vehicle fuel injection system (Shah et al., 2010, Koßmehl and Heinrich, 1998). There are specific recommendations for microbiological contamination found in the ASTM (American Society for Testing and Materials) guide, presenting water control as a key factor for fuel quality control.

Fuels can accumulate water during their production, transportation and storage. For instance, during petroleum refining, water can be incorporated by the injection of live steam into distillation towers to reduce the partial pressure of the hydrocarbons. Also, fuels can accumulate water during transportation in polyducts, where a temperature gradient may occur, causing the release of free water. As different types of fuels flow into water is transferred from less hydrophilic products to products with greater affinity with water.

During biodiesel production, water content is significantly increased due to the washing step, which removes residual catalyst and glycerol. Some water separation processes commonly applied for meeting specifications of regulatory agencies are drying under vacuum or salt filtering. The first process is a relatively energy intensive process and the second may result in fuel contamination.

An alternative process for water separation from fuels is the use of hydrogels, highly hydrophilic crosslinked polymeric materials. They are inert substances which can remove water present in an organic medium, whilst only consuming relatively small amounts of energy. The properties of hydrogels depend on their chemical composition, crosslink density and the number of hydrophilic groups (Lee and Yuk, 2007). Hydrogels have been studied for application in various fields, such as biotechnological, medical, pharmaceutical and chemical process. In the latter most case, emphasis is placed on an environmental application. Aouada et al. (2009) studied the characteristics of poly (acrylamide) and methylcellulose (PAAm-MC) hydrogels as an adsorbent material to remove a pesticide from an aqueous solution. Kang et al. (2018) studied hydrogels prepared with

exfoliated montmorillonite nanosheets (MMTNS) and chitosan (CS) as an adsorbent for removing methylene blue (MB) from water.

Hydrogels particles swell in the presence of an adequate solvent and soak the solvent into the cross-linked matrix of the particle. Consequently, they have great potential to remove soluble and insoluble water from organic media. Currently, literature presents few studies on the use of hydrogels for the removal of water from fuels. Nur et al. (2008) studied poly-N-isopropylacrylamide hydrogels (PNIPAAm) as well as other emulsion-polymerized monomers to produce microgels. A valuable conclusion of this work was the ability of the material to reduce the water content in biodiesel from 1800 ppm to less than 500 ppm.

Fregolente et al. (2012) studied the use of polyacrylamide hydrogels (PAAm), synthesized via polymerization of free radicals, to remove water from diesel and biodiesel samples. The tests were carried out with samples with an initial water content of 2100 ppm in biodiesel and 240 ppm in diesel. Reductions of 53.3% and 65% in water content were observed, respectively.

Fan et al. (2015) evaluated the use of hydrogel coated paper filters for the separation of oil and water applied to challenging environments, such as the sea and to industry. Within these environments, tests were carried out under adverse conditions (acid medium, basic and with high salt concentration), aiming to remove water in emulsified systems.

Fregolente et al. (2018) studied kinetic parameters and hydrophilic properties of new hydrogels, synthesized with polyacrylamide and poly (acrylamide-co-sodium acrylate) (AAm-co-SA) to remove water from biodiesel. The study obtained a swelling ratio (W , mass of the swollen sample as a function of the dry sample) of 108.8 g water/g hydrogel, which is much higher than hydrogels developed in previous research ($W = 14.36$ g/g).

In this work, a new process of water separation from fuels has been developed through the use of dry polyacrylamide-based hydrogels particles in a fixed, packed bed column. These hydrogels, as observed by Fregolente et al. 2018, display a high capacity to incorporate water into their polymeric chains. Here, the water removal was assessed as a function of varying hydrogel formulation; either poly (AAm-co-SA) or poly (acrylamide-co-acrylic acid)(AAm-co-AA). The influence of temperature was also studied by conducting the experiments at 25°C and 40°C.

2. Methodology

2.1 Materials

The synthesis of the hydrogels was carried out using acrylamide (AAm) ultrapure (Amresco), sodium acrylate (SA) 97 % (Aldrich), N,N'-methylene-bis-acrylamide (mBAAm) ultrapure (USB), potassium persulfate 99 % (Fisher Scientific), acrylic acid 99% (Sigma) and N,N,N',N'-tetramethyl-ethylenediamine (TEMED) 99 % (Sigma-Aldrich). Commercial Diesel B10 (10 % of biodiesel with maximum 10 ppm of sulfur) was purchased at the local market. The soybean biodiesel was donated by a research group from the Laboratory of Separation Process Development of the State University of Campinas.

2.2 Synthesis of Hydrogels

The formulation of poly (AAm-co-SA) and poly (AAm-co-AA) hydrogels to be used in the packed beds were performed based on prior knowledge of the research group. 1.5 g of acrylamide monomer (AAm) in aqueous solution was polymerized via free radical polymerization at 25°C. The aqueous solution contained 0.015 mol of crosslinking agent N', N'-methylene-bis-acrylamide (MBAAm), and 1.25 g of sodium acrylate. 1 ml of N, N, N', N'-tetramethylethylenediamine (TEMED) was added to the reaction media as the catalyst and 0.02 g of sodium persulfate was used to initiate the polymerization reaction. After the aqueous mixture was prepared, N₂ was bubbled into the polymer solution for 20 min. The hydrogel obtained was removed, dehydrated in an oven at 70 °C and manually milled. This resulted in the particles which would be packed directly in the bed of the prototype. The synthesis of the poly (AAm-co-AA) hydrogel was carried out under the same conditions of the poly (AAm-co-SA) hydrogel, using 1.25 g of acrylic acid at 40°C.

2.3 Hydrogel Packed Bed

The tests, aiming to remove water from fuel were performed using the synthesized hydrogel particles of poly (AAm-co-SA) and poly (AAm-co-AA). Within the prototype bed, packing fill design was random. This is a practical configuration to apply to material developed in small scale or for industrial applications. A schematic representation of the prototype is shown in Figures 1A and 1B. Within Figure 1A, a reservoir to store fuel saturated with water (1), pump (2), hydrogel bed with heating jacket (3) and dry fuel tank (4) can be identified. The total bed length is 24 cm long and 3 cm in diameter, filled with 3 cm of hydrogel.

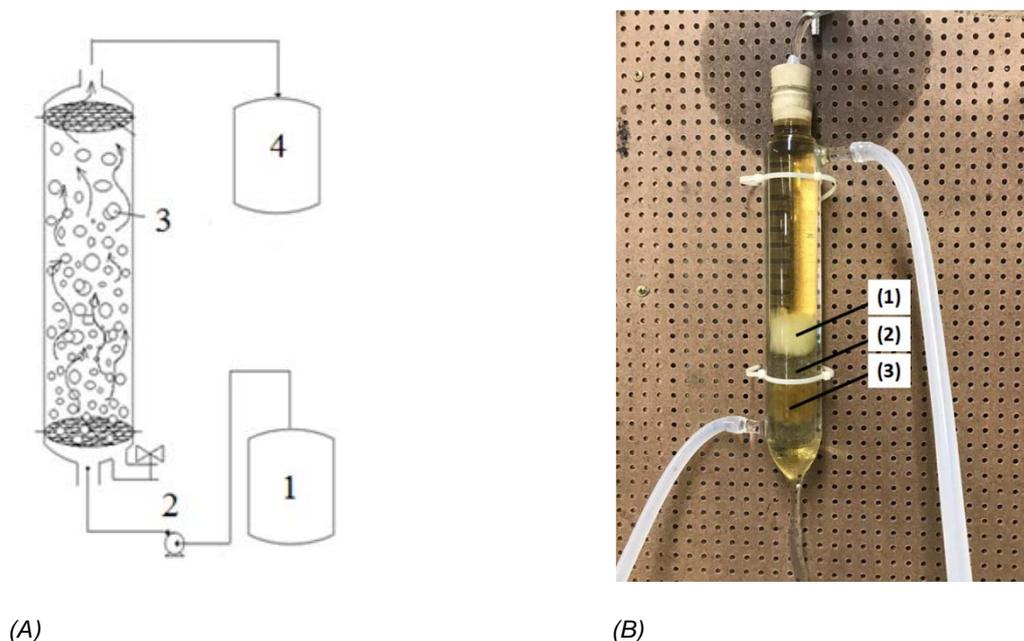


Figure 1: Packed bed prototype for the water removal from fuel. A) Schematic representation B) Actual configuration of the experiment: 1- glass wool; 2- glass spheres; 3- hydrogels.

2.4 Physical Characterization of Hydrogel Particles

The hydrogel used in the packed bed column was characterized by particle size distribution, density and sphericity. Density of hydrogels was determined in a pycnometer using kerosene (SIGMA) as a reference liquid. The hydrogel sample volume was calculated using a mass of kerosene with a known density, which is displaced by the solid when immersed in the liquid contained in the pycnometer (Gauzner et al., 1972). The particle size distribution of the hydrogel was performed by sieve analysis. This technique is used to determine the mass percentage of each specified range of particle size compared to the total mass. The sphericity of the hydrogel particles (Eq1) was calculated by the ratio of the volume of a hydrogel particle to the volume of a sphere of the same diameter.

$$\Phi = \frac{\text{Volume of the hydrogel particle}}{\text{volume of the sphere}} \quad (1)$$

The calculation of the area and volume for an empty column was performed using the geometry of the cylinder as reference. The bed porosity was calculated using Equation 2, which represents the fraction of voids within the column filled with hydrogel.

$$\varphi = \frac{\text{Volume of empty spaces}}{\text{Total volume}} = \frac{V_{\text{total}} - V_{\text{hydrogel}}}{V_{\text{total}}} \quad (2)$$

2.5 Determination of Water by the Karl Fischer Method

The water content in fuel samples was determined by potentiometric titration using the Karl Fischer method, according to ASTM 6304-7. It is suitable for determining the water content in the range of 10 to 25000 mg/kg. The equipment used was a Mettler Toledo DL31.

2.6 Experiments in a Packed Bed Column with Hydrogels

Initially, based on the method developed by Fregolente and Maciel (2012), samples of diesel and biodiesel were saturated with 30% v/v distilled water under vigorous stirring for 4 hours. They were placed in a separating funnel to separate phases. Free water was discarded and the saturated fuels were then fed into the hydrogel packed bed. The fuel flow rates were set at 1 ml/min by adjusting the speed of a peristaltic pump. Two effluent samples were collected every 30 min up to 300 min. Water content was determined by the Karl

Fischer method to monitor water removal efficiency. For diesel and biodiesel, experiments were carried out at 25°C and 40°C, as well as for both formulations of hydrogel particles; poly (AAm-co-SA) and poly (AAm-co-AA). The combinations of these operating conditions were performed according to two-level factorial design in order to evaluate their effect on water removal from fuels.

3. Results and discussions

3.1 Physical Characterization of the Hydrogel Particles

As an example, Figure 2 shows the particle size distribution of the poly (AAm-co-SA) hydrogel sample milled manually. Among the diameter ranges obtained, particles with a diameter of 4750-3350 µm were chosen for the packed bed column experiments.

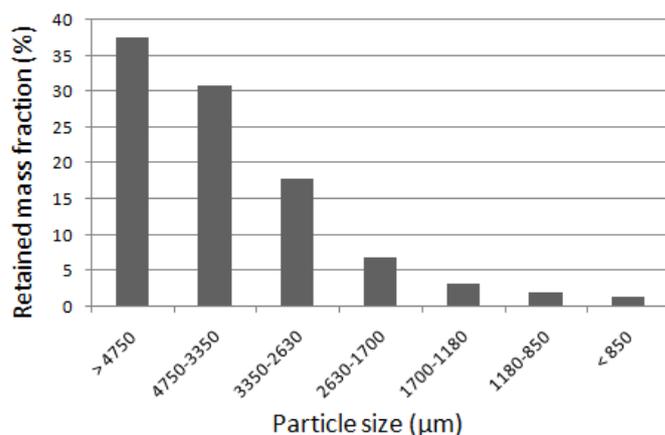


Figure 2: Particle size distribution of the poly (AAm-co-SA) hydrogel particles.

In Table 1 physical properties of particles of both poly (AAm-co-SA) and poly (AAm-co-AA) hydrogel are shown. The bed porosity for poly (AAm-co-SA) hydrogel and poly (AAm-co-AA) hydrogel were 0.443 and 0.418, respectively.

Table 1: Physical characteristics of the hydrogel particles.

Parameters	Poly (AAm-co-SA) hydrogel	Poly (AAm-co-AA) hydrogel
Density* (g /cm ³)	1.26	0.47
Volume mean diameter (mm)	4.05	4.80
Sphericity	0.649	0.664

*Reference temperature of 25°C

3.2 Removal Water content in fuels using Packed Bed prototype

The change in water content over time in the outlet stream was monitored. For all experiments, after 200 min of bed operation, water removal appeared to remain constant. This is exemplified in Figure 3 for runs carried out with biodiesel at 25°C using poly (AAm-co-SA) hydrogel and poly (AAm-co-AA) hydrogel. No breakthrough curves were observed for the 300 min time interval. This may be due to the high capacity of hydrogels to retain water. This means that hydrogels in the bed did not approach saturation; an interesting observation for practical applications. Visually, it was not possible to observe the hydrogels swelling. It is important swelling can be monitored to avoid an increased pressure drop in the bed. To assess the maximum water removal capacity of the bed, it is suggested new experiments, over longer period of times and with a higher initial water content, are undertaken. Figure 4 (A) and (B) present results of the average ratio of outlet-to-inlet water concentration (C/C_0) as a function of temperature and hydrogel type for diesel and biodiesel, respectively. It was observed that, for diesel higher water removal efficiency was observed at 25°C for both hydrogel formulations. This observation may be explained by the higher solubility of water in the fuel at higher temperatures (Fregolente and Maciel, 2012). Therefore water removal by hydrogels was made more difficult,

reducing the efficiency of the packed bed. The temperature effect on C/C_0 was not significant according to 95% confidence limits testing only for runs using biodiesel and poly (AAm-co-AA) hydrogel. However, the effect of temperature was more pronounced for runs carried out with the packed bed filled with particles of poly (AAm-co-SA) hydrogel.

The water removal efficiency of the poly (AAm-co-AA) hydrogel, with an average particle mean diameter of 4.80 mm, was compared to the efficiency of the poly (AAm-co-SA) hydrogel, with volume mean diameter of 4.05 mm. Analysing Figures 4 (A) and (B), it is clear that the formulation of poly (AAm-co-SA) presented higher water removal efficiencies for diesel. In case of biodiesel, the greater performance of poly (AAm-co-SA) was only observed at the lowest temperature level studied (25°C).

For diesel and biodiesel, the lowest levels of C/C_0 were observed under operation with poly (AAm-co-SA) hydrogel at 25°C. The values attained were 0.29 and 0.43, respectively.

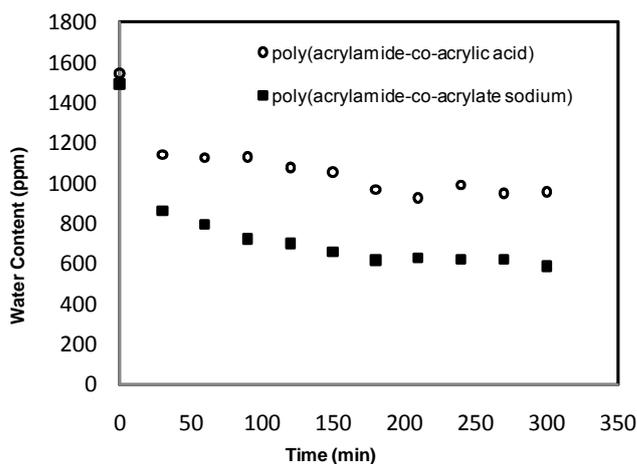


Figure 3: Water content (ppm) as a function of time (min) for biodiesel at 25°C.

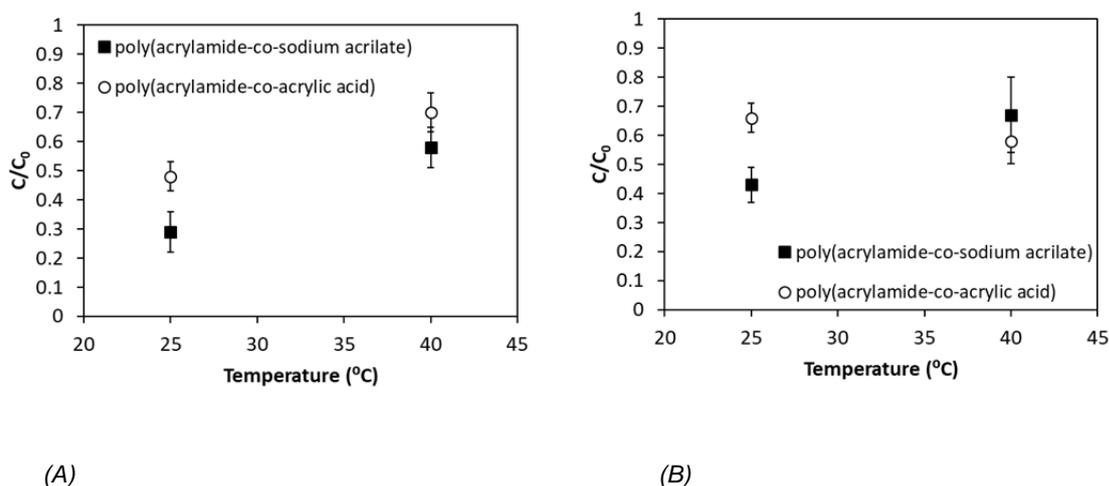


Figure 4: Average ratio of the outlet-to-inlet water concentration (C/C_0) as function of temperature and hydrogel type for diesel (A) and biodiesel (B).

4. Conclusion

It was observed that packed beds randomly filled with hydrogels is a promising technology for water removal from fuels as a continuous process. For diesel and biodiesel, the maximum water removal efficiencies were achieved using the fixed bed packing, poly (AAm-co-SA) hydrogel, at 25°C. The values of C/C_0 were 0.29 and 0.43, were attained for diesel and biodiesel respectively. The hydrogel particles did not approach saturation

during operation which is advantageous for the development of hydrogel particle technology. Not only does this mean the packing has a high capacity for water retention but also means that particle swelling was avoided, which would have increased the pressure drop of the bed. Future studies are still required to assess the maximum water removal capacity of the bed. New experiments, considering longer period of times and a higher initial water content, have been suggested. Finally, looking to the future, new studies considering hydrogel regeneration are important for consolidation of the technology.

Acknowledgments

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