

# Development of a Hydrogel Column for Water Removal from Fuels

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The maximum water content in biodiesel is an important specification of quality, since the presence of free water (when the water concentration exceeds the saturation value) leads to microbiological development, degrading the fuel and generating sludge. Also, if a biodiesel with inappropriate water content is employed, problems such as corrosion and performance impairment can happen. Some sources of the water present in biodiesel are the washing process, during the fuel production, and the absorption of water during storage. Therefore, alternative ways to remove water from biodiesel have been studied, leading to new technologies for this purpose. It was demonstrated, in previous works, that dried hydrogels immersed in fuels can remove water even in small concentration. In this study, hydrogels of poly(acrylamide-co-sodium acrylate) were synthesized using different monomers quantities, following a central composite rotational design, aiming the improvement of the swelling characteristics. The highest value of swelling degree was 162, obtained at 20 °C, almost 11 times higher than the value obtained for polyacrylamide hydrogels. Then, based on this formulation, hydrogel discs were employed on a sieve plate column, for the removal of free water from biodiesel on continuous flow. The bed configuration featured on this study was efficient for removing all the free water from the feed being suitable for further applications in water removal from fuels without the bed clogging effect.

## 1. Introduction

Fuel contamination by water is a frequent problem, potentially occurring along its productive chain, transport or storage. The presence of high water contents leads to quality problems, such as the development of microorganisms, the occurrence of sludge, corrosion, and increase of turbidity, affecting the fuel performance (Sørensen et al., 2011). The techniques currently employed for the removal of water, like vacuum flash, are costly or difficult to implement outside of an industrial environment. Therefore, researches have been investigating alternative ways to remove water from diesel and biodiesel, developing new technologies for this purpose, being the use of hydrogels one of these. In recent works, dried polyacrylamide (PAAm), poly(acrylamide-co-acrylic acid) and poly(acrylamide-co-sodium acrylate) hydrogels were applied successfully for the removal of free and solubilized water from these fuels (Fregolente et al., 2015, Fregolente et al., 2018, Paula et al., 2019, Santos et al., 2019, Gonçalves et al., 2020).

Polymer hydrogels are three-dimensional networks of polymer chains with high water affinity and retention capacity. These networks are constituted of chains linked by physical interactions and crosslinks (Aouada, 2009), and the polymers constituting the hydrogel affects its properties. Hydrogels have a wide range of application fields, such as pharmaceutical, medical, environmental and agricultural (Peppas et al., 2006, González-Delgado et al., 2016, Meri et al., 2017, Das et al., 2020). While it is known that hydrogel particles present high degree of water retention when inside aqueous medium, it was noted that dried PAAm hydrogel particles immersed in organic medium adsorbed water even in small concentration, showing practically no physical or chemical interactions with the organic phase (Fregolente et al., 2015; Nur et al., 2009).

In previous research, Fregolente et al. (2018) investigated important properties of poly(acrylamide-co-sodium acrylate) (pAAm-co-SA) hydrogels such as swelling and diffusion parameters. It was noted on preliminary

experiments that pAAm-co-SA hydrogels have higher swelling degree and are better for removing water from fuels than pAAm hydrogels. Other characteristics of hydrogels, such as thermal stability, were studied by Gonçalves et al. (2020), in whose work the effects of different hydrogel formulations were related to the water removal capacities from fuels. The hydrogel constitution highly affects the water transfer from the fuel into the hydrogel. Some traits that can result on this mass transfer are the electrostatic interaction caused by ionic charges on the hydrogel surface (HUA, QIAN, 2001) - for instance on a poly(sodium acrylate) hydrogel – and the existence of functional groups, like amide or carboxylic acid (ÇAYKARA; INAM, 2004).

An important characteristic of the hydrogels is the swelling degree, a mass ratio of water adsorbed and dry hydrogel, related to the hydrogel interaction with the medium. Diffusive and elastic forces are involved in the mass transfer, respectively promoting and resisting it. Chain expansion can occur after the first adsorption process and further diffusion process, resulting on a volumetric increase. The swelling equilibrium state occurs when these forces are equal (Aouada, 2009), and can be affected by pH, temperature and salt concentration.

In this paper, a statistical study considering a star configuration experimental design was applied, with the purpose of evaluating the effect of pAAm-co-SA hydrogels' formulations on their capacity of retaining water. Afterwards, hydrogels discs made of pAAm-co-SA and poly(acrylamide-co-acrylic acid) (pAAm-co-AA) were produced and applied in structured beds to continuously remove water from biodiesel. Here this configuration is named Hydrogel Discs on Sieve Trays (HDST). While previous studies on hydrogels are focused on the removal of solubilized water from fuels, this bed configuration, that uses hydrogels in the form of discs, can be applied as a single bed to remove free water from fuel, without bed clogging due to hydrogel volumetric increase. Another possible application for this bed configuration is the use as a guard bed, protecting posterior beds designed for removal of solubilized water. To the best of our knowledge, there are no published papers studying this bed configuration to remove water from fuels or other organic media.

## 2. Materials and methods

### 2.1 Materials

The synthesis of the hydrogels used acrylamide (AAm) ultrapure (Amresco), sodium acrylate (SA) 97 % (Aldrich), acrylic acid (AA) 99.5 % (Acros Organics), N,N'-methylenebisacrylamide (mBAAm) ultrapure (USB), potassium persulfate 99 % (Fisher Scientific) and N,N,N,N'-tetramethylethylenediamine (TEMED) 99 % (Sigma-Aldrich). Biodiesel was purchased from the local market, and its composition is shown on Table 1.

Table 1: Fatty acid profile of the employed biodiesel

Fatty acid	Mass (%)
C16:0	13.79 ± 0.05
C18:1trans	3.27 ± 0.13
C18:1cis	19.43 ± 0.07
C18:3γ	55.44 ± 0.10
C18:3α	6.87 ± 0.04
C20:0	0.36 ± 0.00
C20:1cis	0.26 ± 0.00
C22:0	0.47 ± 0.00
C24:0	0.11 ± 0.10
Saturated fatty acid	14.73
Monounsaturated fatty acid	22.96
Polyunsaturated fatty acid	62.31

### 2.2 Hydrogel synthesis

The pAAm-co-SA hydrogels were synthesized at room temperature and the pAAm-co-AA one was synthesized at 50°C. The monomers were mixed with mBAAm in distilled water, on the proportion of 0.015 mol of mBAAm/total mol of monomers, and 1 ml of TEMED at 0.57 mol/l was added to the mix, resulting on 48 ml of solution. The solution was deoxygenated by bubbling N<sub>2</sub> for 10 minutes, and 2 ml of water with 0.020 g of potassium persulfate was added to it. The bubbling continued until the hydrogel formation. After the synthesis, the hydrogels were left to rest for 24 hours, cut in discs and oven-dried at 70 °C until achieving constant mass. A composition with 2.000 g of AAm and 0.500 g of SA was chosen as starting point. From this, a central composite rotatable experimental design (star design) was done, containing four factorial points, four axial points and one central point, in which replicas were performed. These hydrogels were used on the swelling experiment, being chosen based on the work of Gonçalves et al. (2020), that studied the hydrogel swelling at a different temperature. The values of each variable level are shown on Table 2.

Table 2: Variables Levels for Hydrogel Compositions of Acrylamide (AAm) and Sodium Acrylate (SA)

	$-\sqrt{2}$ ( $-\alpha$ )	-1	0	+1	$+\sqrt{2}$ ( $+\alpha$ )
AAm (g)	1.626	1.750	2.000	2.250	2.354
SA (g)	0.217	0.300	0.500	0.700	0.783

### 2.3 Maximum swelling degree

For the swelling study, initial quantities of each dry hydrogel presented on Table 2 were weighed, immersed on distilled water inside of beakers, and kept inside a bath at 20 °C. The hydrogels were then weighed until reaching their maximum swelling degree. The swelling degree ( $W$ ) is defined by Equation 1:

$$W = \frac{m_i - m_0}{m_0} \quad (1)$$

Being  $m_0$  the initial polymer dry mass, and  $m_i$  its mass measured after being immersed in distilled water during “i” time units. The maximum swelling degree ( $W_{max}$ ) corresponds to the equilibrium state. This analysis led to the knowledge of the pAAm-co-SA hydrogels maximum water retention capacity.

### 2.4 Water content determination

The water contents of the biodiesel samples were determined using the Karl Fischer technique, following the ASTM E203 (2016) standard, using a Metrohm 841 Titrando equipment. The Karl Fischer method is based on the oxidation of  $SO_2$  by  $I_2$  when water is present, being the sample solubilized on a methanol with imidazole solution (BRUTTEL and SCHILINK, 2006).

### 2.5 Water removal from biodiesel using HDST

The HDST is the design developed in this work, which contains compartments in the form of sieve plates of 4.0 cm of diameter, with holes diameters of 2 mm. It was made of polyamide 12 using additive manufacture. Each compartment contains a perforated hydrogel disk of 26 mm diameter with 5 holes of 2 mm diameter. The perforations were made to allow the passage of biodiesel, even if the hydrogel swelled (avoiding the occurrence of clogging). While the biodiesel percolates the HDST, the water present on it is retained by the hydrogel, resulting on the reduction of the biodiesel water content. The bed scheme is illustrated in Figure 1.

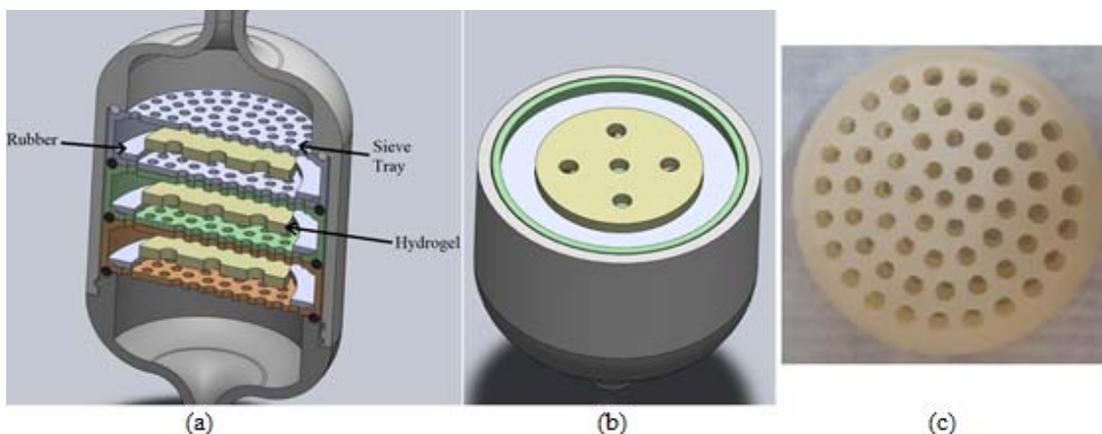


Figure 1: Bed Scheme for Removal of Water from Biodiesel. Internal (a) and External (b) views, (c) Sieve Tray

In the first set of experiments, named EXP1, runs at room temperature were carried out in two steps. In the first step, hydrogels discs of pAAm-co-SA were applied. Biodiesel containing 3% of water was fed at a flow rate of 1 ml/min to the bed shown in Figure 1, as a downward stream. After passing through the bed, samples of the effluent were collected every 30 minutes for 330 minutes to determine their water content.

Then, in a second step of experiments (EXP2), two different runs were carried out, one using hydrogel discs of pAAm-co-SA and the other, for comparison purposes, using hydrogel discs of pAAm-co-AA, varying the inlet water content (biodiesel saturated with water, 5% and 10%) and biodiesel flow rates (1 ml/min, 3 ml/min and 5 ml/min), now as an upward stream. For this second step, biodiesel samples were collected in the outlet after one hour for all the flow rates. Then the water content was determined. For these experiments, the hydrogel's water affinity was prioritized, thus the pAAm-co-SA hydrogels were synthesized using 1.000 g of AAm and 1.500 g of SA, and the pAAm-co-AA was synthesized with 1.000 g of AAm and 1.500 g (1,429 ml) of AA.

### 3. Results and discussions

#### 3.1 Maximum swelling degree

Table 3 shows  $W_{max}$  of the hydrogels, being the center point experiment (composition 0) done in triplicate. From this table, lower acrylamide amounts during synthesis frequently led to hydrogels with greater  $W_{max}$  values, what was expected, since it results in materials with greater sodium acrylate percentages in their formulations and poly(sodium acrylate) hydrogels have higher  $W_{max}$  than polyacrylamide ones. This effect of the SA/AAM proportion was also seen by Magalhães (2009). However, comparing the 0-2 and 5-7 hydrogel pairs, greater values of  $W_{max}$  are obtained with less SA amounts during synthesis, indicating that the total amount of monomers during synthesis could also affect  $W_{max}$ . This demonstrates how the interaction between these two monomers, as well as the definition of the hydrogel formulation with the best set of characteristics, can be complex. The effect of AAm and SA contents on the hydrogel composition were obtained using the Statistica™ software, considering pure error and 95 % of confidence level (Table 4).

Table 3: Maximum swelling degree ( $W_{max}$ ) for the various hydrogel compositions

Compositions	AAm (g)	SA(g)	mBAAm (g)	$W_{max}$
				136
0	2.000 (0)	0.500 (0)	0.0773	136
				141
1	2.000 (0)	0.217 ( $-\sqrt{2}$ )	0.0703	114
2	2.000 (0)	0.783 ( $+\sqrt{2}$ )	0.0842	125
3	1.646 ( $-\sqrt{2}$ )	0.500 (0)	0.0658	150
4	2.354 ( $+\sqrt{2}$ )	0.500 (0)	0.0888	136
5	1.750 (-1)	0.300 (-1)	0.0642	162
6	2.250 (+1)	0.300 (-1)	0.0805	130
7	1.750 (-1)	0.700 (+1)	0.0741	129
8	2.250 (+1)	0.700 (+1)	0.0903	131

Table 4: Effect of Monomers Content on pAAm-co-SA Hydrogels  $W_{max}$  (Q – quadratic, L – linear)

Factor	Effect	Std. Err. Pure Err.	t(2)	P	-95% Cnf. Limt	+95% Cnf. Limt
Mean/interc.	137.7	1.7	82.60000	0.0001	130.5	144.8
(1) AAm (L)	-12.4	2.0	-6.09911	0.0258	-21.2	-3.7
AAm (Q)	8.7	2.4	-3.58432	0.0698	-1.7	-19.2
(2) SA (L)	-4.1	2.0	-2.01393	0.1816	-12.9	4.7
SA (Q)	-14.8	2.4	-6.08820	0.0259	-25.2	-4.3
1L by 2L	17.0	2.9	5.88897	0.0276	4.6	29.4

Table 4 indicates that smaller monomers quantities would result on higher values of  $W_{max}$ , since the linear effects are negative. Also, the quadratic effect of AAm and linear effect of SA were not significant ( $p > 0.05$  and their confidence intervals contain zero). The negative value for the quadratic effect of SA indicates that variations in the formulation, in relation to the central point, results in lower values for  $W_{max}$ .

Considering only the significant effects, and with proper adjustment of the factors for the model, Equation 2 can be obtained, for the codified variables.

$$W_{max} = 141.8 - 6.2 \cdot AAm - 8.7 \cdot SA^2 + 8.5 \cdot AAm \cdot SA \quad (2)$$

It is expected that hydrogels with higher  $W_{max}$  will need to be regenerated less frequently for their reuse, when employed on industrial processes, what can reduce the need for operational pauses, in comparison with hydrogels with smaller  $W_{max}$ . The quality of the model was evaluated by ANOVA, based on the F-test. Calculated F-value (regression/residual) is 4.56, greater than the critical F value at 95% confidence ( $F_{3/7} = 4.34$ ), indicating that the regression is statistically significant. There is no evidence of lack of fit for the model, as the calculated F-value (lack of fit/pure error) is 12.66, smaller than the critical F-value ( $F_{5/2} = 19.30$ ).

#### 3.2 Water removal from biodiesel using the HDST

The result of the first set of experiments (EXP1), is shown in Figure 2. The new design of column was used to treat biodiesel with 3 % (30000 ppm) of water as the inlet stream. The pAAm-co-SA hydrogel was employed inside the HDST, and the point at 150 min was not included because it was considered an outlier.

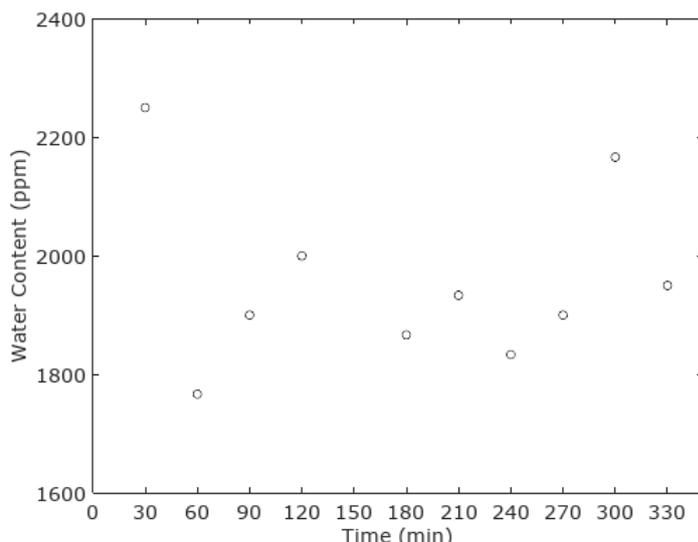


Figure 2: Outlet Water Content in Biodiesel for EXP1

During the experiment, a considerable reduction of water content was reached (up to 94.1 %), and it can be noted that from the first experimental point (after 30 minutes of operation of the bed), only small oscillations happened. These results demonstrate that HDST suitable as a guard bed, and the biodiesel can afterwards be treated by another bed containing hydrogel, to achieve commercial standards, without the risk of bed clogging. Based on works about biodiesel equilibrium humidity (Fregolente et al, 2012, Roosta, 2018), it can be said that practically all the free water was removed. Also, no aqueous phase was visible on the outlet stream.

Results of the second set of experiment (EXP2), considering different levels of flowrate are shown in Table 5. It can be noted that the effect of the inlet flowrate on the water concentration in the outlet stream can be disregarded for practical purposes. The biodiesel initially with 5 % (50000 ppm) and 10 % (100000 ppm) of water resulted on similar final water contents, and the saturated biodiesel had an initial water content of  $2042 \pm 37$  ppm. The values presented on Table 5 are the outlet water content.

Table 5: Outlet water content in biodiesel from experiments using a pAAm-co-SA hydrogel

Inlet flow (ml/min)	Inlet – Saturated Biodiesel (ppm)	Inlet – Biodiesel with 5% of water(ppm)	Inlet- Biodiesel with 10% of water (ppm)
1	1510 ± 33	1597 ± 28	1889 ± 15
3	1518 ± 11	2134 ± 17	2111 ± 28
5	1397 ± 48	2371 ± 4	2219 ± 16

Nevertheless, there is an overall increase of the water content in the outlet biodiesel stream as the initial water content is incremented. However, for the saturated biodiesel, at 5 ml/min the water content is smaller than at flow rate of 3 ml/min. It is believed that at the start of the experiment, when the hydrogel was drier, the water access into the interior of the material was hampered, what made the diffusion slower, becoming faster as the experiment went on. A similar event occurred with the pAAm-co-AA hydrogel (Table 6).

Table 6: Outlet water content in biodiesel from experiments using a pAAm-co-AA hydrogel

Inlet flow (ml/min)	Inlet – Saturated Biodiesel (ppm)	Inlet – Biodiesel with 5% of water(ppm)	Inlet- Biodiesel with 10% of water (ppm)
1	1985± 31	1833 ± 11	2046 ± 6
3	1873± 23	2016 ± 36	2118 ± 24
5	1512± 3	2361 ± 9	2069 ± 13

Comparing the runs with pAAm-co-SA and pAAm-co-AA hydrogel discs, it was expected that for all the runs applying pAAm-co-SA, the water removal would be higher due to the strong SA hydrophilicity. However, it did not occur at two of the operating conditions (10 % of water and 5 ml/min; 5 % of water and 3 ml/min). While it is expected that when there is enough residence time it would not happen, it is suspected to occur due to variations on the ease the water has to access the interior of the hydrogel as it swells. In all experiments, no aqueous phase was visually present in the outlet samples.

#### 4. Conclusions

From the swelling experiments, a model for the  $W_{\max}$  of the pAAm-co-SA hydrogel was obtained, and an interaction between the monomers' quantities during synthesis was observed, demonstrating the complexity of the formulation. The highest observed value for  $W_{\max}$  was 162. The HDST was efficient in removing water from biodiesel, even considering high inlet water concentrations. Water contents between 1397 ppm and 2371 ppm were observed in the HDST outlet stream, what makes possible to affirm that practically all the free water was removed. The great reduction on the water content gives the system a potential use as a guard bed.

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