

Hydrogel Raschig Rings: Synthesis, Geometric Studies and Application for Water Removal from Biodiesel

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The presence of water in fuels can lead to significant operational challenges, including microbiological growth that results in fuel degradation and sludge formation, corrosion of equipment, increased turbidity, and impaired engine performance. To address these issues, regulatory standards have been established to limit water content in fuels. In this context, copolymeric hydrogels have emerged as effective materials to remove water from fuels due to their hydrophilicity, enabling them to retain moisture both on their surface and within their structure. The technology of hydrogels as desiccant material can be applied in structured or random packed-beds. In this work, poly(acrylamide-co-sodium acrylate) hydrogels in the shape of Raschig rings were produced using an innovative production method. This geometry, characterized by hollow cylinders with similar height and outer diameter, provides a good surface area-to-volume ratio, making it suitable for chemical engineering applications. The height, inner and outer diameter distributions for the Raschig rings were analyzed before and after the swelling process. It was verified that the geometry of the hydrogels does not undergo noticeable changes after the material is swollen and dried. The Raschig rings at different swelling degrees were used as bed random packings for turbidity reduction from biodiesel in continuous biodiesel treatment process. With a residence time of approximately 10 minutes and hydrogel swelling degrees up to 0.80 g water/g hydrogel, no reduction in performance for the removal of emulsified water was noticed. Furthermore, it was demonstrated that the Raschig rings show geometrical stability after removing water from biodiesel.

1. Introduction

Fuels are prone to oxidative degradation over time, a process that can be accelerated by the depletion of additives, high temperatures and the presence of contaminants, with water being one of them. High water content not only increases fuel turbidity - a critical quality parameter - but also leads to corrosion issues, adversely affects fuel characteristics, impairs engine performance, and promotes the growth of microorganisms (Gonçalves et al., 2020). Given its impact on fuel quality and performance, monitoring water content is essential for the commercialization of fuels. In the European Union, regulations permit up to 500 ppm (mass) of water in biodiesel (EN 14214, 2019), while in the United States, a tolerance level of up to 0.05% (volume) for water and sediments is established (ASTM D6751, 2023).

To address the challenge of water removal from fuels, various technologies can be used. Physical unit operations (e.g. gravity separation, centrifuge, coalescing filters) are more suitable for high water contents and mass transfer operations (e.g. distillation, salt beds) are typically used for low water contents (Troyer, 2019). However, these conventional methods often come with drawbacks including high installation and operational costs, complexity, and limited efficiency.

In light of these limitations, this study explores an alternative approach utilizing polymeric hydrogels as a means of removing water from fuels. Polymeric hydrogels are materials with high water affinity and retention capacity, offering a solution capable of removing water in its three forms (free, emulsified and solubilized), while offering ease of operation and potential for reused (Fregolente et al., 2023). Building on recent research (Gonçalves et

al., 2023), this work investigates the use of Raschig rings made from poly(acrylamide-co-sodium acrylate) hydrogels as random packings designed for efficient water removal from biodiesel.

The application of hydrogel-filled beds for water removal from fuels holds significant practical advantages in relation to existing technologies: less energy requirement when compared to distillation, reduced production of effluents and the process can be carried out on different scales, with potential uses at industrial level. To facilitate this approach, a specialized apparatus was designed for the efficient production of hydrogel Raschig rings, for which a patent application has been filed (application number BR102023017601-1). This article presents a detailed description of the apparatus and outlines the procedure employed to achieve the desired geometry of the Raschig rings. A critical characteristic of these hydrogel Raschig rings is their ability to maintain consistent water removal performance over time during continuous use. This can be evaluated by increasing the hydrogel swelling degree (i.e. the amount of water retained by the hydrogel) to be used inside the bed for water removal from fuels.

Previous research (Gonçalves et al., 2023) demonstrated that hydrogel Raschig rings can be regenerated and reused without a performance decrease; however, assessing their effectiveness between regeneration cycles has not been previously explored. Investigating this aspect is one of the primary objectives of this article.

Another desired characteristic of hydrogels packings for use in continuous processes is geometric stability. This property can affect the hydrogel-fuel contact and the path followed by the fuel as it percolates through the bed. As hydrogels swell, they expand, and it is crucial to assess their ability to retain their original geometry after drying/regeneration, which was studied here. While high swelling degrees are not expected during the removal of soluble water, fluctuations in the water content of the feed stream or extended intervals between regenerations could lead to such scenarios, an aspect that has not been addressed in previous research. Understanding these dynamics is essential for optimizing hydrogel performance in practical applications.

2. Materials and methods

2.1 Materials

The hydrogel Raschig Rings were made using acrylamide (AAm) ultrapure (Amresco), sodium acrylate (SA) 97 % (Aldrich), potassium persulfate 99 % (Fisher Scientific), N,N,N,N'-tetramethylethylenediamine (TEMED) 99 % (Sigma-Aldrich) and N,N'-methylenebisacrylamide (mBAAm) ultrapure (USB). Biodiesel was produced using soybean oil and methanol. It was mainly constituted of esters from linoleic acid (around 68 %), palmitic acid (around 17 %), α -linolenic acid (around 8 %) and oleic acid (around 5 %).

2.2 Production of hydrogel Raschig rings

The Raschig rings made of poly(acrylamide-co-sodium acrylate) were produced as follows. The material was synthesized by free radicals polymerization, based on a previous work (Gonçalves et al., 2020). A monomer ratio of 3:2 for sodium acrylate to acrylamide was selected due to its favorable outcomes in that study. The pre-gel solution was prepared in distilled water by combining 5.21×10^{-2} g of monomers/ml, 1.5×10^{-2} mol of mBBAAm/mol of monomers and 1.19×10^{-5} mol of TEMED/ml. In another beaker, sodium persulfate was solubilized in distilled water, at the concentration of 1×10^{-2} g/ml. In a separate beaker, sodium persulfate was dissolved in distilled water at a concentration of 1×10^{-2} g/ml. A specialized apparatus was developed to achieve the desired hydrogel geometry, as illustrated in Figure 1, which represents one of the innovations of this study.

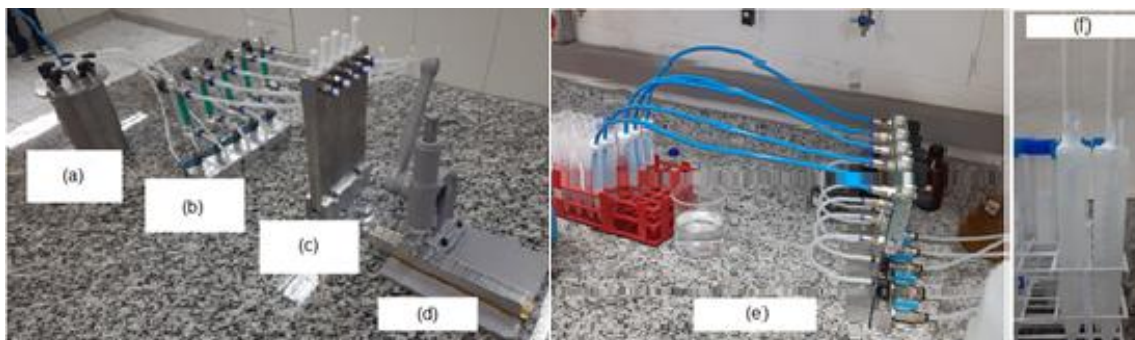


Figure 1: Apparatus for the production of hydrogels as Raschig rings: buffer tank (a), flowmeters and valves (b), mold (c), slotted guillotine (d), with the use of plastic tubes (e) and glass rods (f)

This apparatus consists of a stainless steel buffer tank designed for distributing nitrogen gas (N_2), equipped with five outlets connected to a series of flowmeters and valves. The nitrogen flow from this tank can be directed into cylinders (plastic tubes) with a diameter of 15 mm or a split mold matching these dimensions were used. Glass or Teflon rods are also part of the apparatus, as well as a slotted guillotine to cut the rings at the required height. The pre-gel solution was introduced into the tubes/mold and bubbled with nitrogen flux for 10 minutes to deoxygenate the mixture. Subsequently, the sodium persulfate solution was added at a ratio of 1 ml for every 24 ml of pre-gel solution, and concentric 10 mm-diameter rods were inserted into the tubes or mold. Afterwards, the system was left to rest for at least 12 hours, the rods were removed, and the resulting hydrogel cylinders were cut using the slotted guillotine to produce rings measuring 15 mm in height. Finally, these rings were dried in an oven at 60 °C to obtain the hydrogel Raschig rings.

2.3 Geometric stability of Hydrogel Raschig rings

To assess the geometric stability of the poly(acrylamide-co-sodium acrylate) hydrogel Raschig rings, a total of 35 rings were randomly selected for dimensional analysis. The height, inner diameter, and outer diameter of each ring were measured using a caliper. The hydrogel rings were then swollen by immersing them in distilled water for 5 seconds and the swelling degree was determined (i.e. a swelling degree of $W = 0.80$ g water/g hydrogel indicates that 0.80 g of water was absorbed for every gram of dry hydrogel).

Afterwards, the dimensions of the hydrogel rings, now swollen, were re-measured using the caliper. These rings were then dried in an oven at 60 °C until they reached a constant mass. After drying, their dimensions were measured again. This methodology allowed the evaluation of how swelling impacts the dimensions of the rings and whether the sequence of swelling followed by drying affects their original geometry.

2.4 Water removal performance over time

To emulate the water removal capacity of the hydrogel Raschig rings after some operating time on a continuous process, the dry hydrogels were swollen in distilled water until reaching swelling degree of $W = 0.12, 0.18, 0.24$ and 0.80 g water/g of hydrogel. The swollen hydrogel Raschig rings were then employed as random packing within a column designed for continuous water removal from a water-biodiesel emulsion under ascending flow conditions. The column had a diameter of 4.5 cm and was filled with 42.5 g of hydrogel when it was dry, corresponding to a height of 7.0 cm. The system was operated at a temperature of 25 °C with a flowrate of 7.5 ml/min. Outlet biodiesel samples were collected after 90 minutes of operation to assess the water content. Figure 2 illustrates the hydrogel bed (at $W = 0.80$ g water/g hydrogel) being filled with biodiesel.



Figure 2: Bed containing hydrogel Raschig rings ($W = 0.80$ g water/g hydrogel) for water removal from fuels

The water-biodiesel emulsion fed into the hydrogel bed was prepared by adding distilled water to biodiesel and mixing it using an Ultra Turrax disperser (IKA, model T65 digital) for 30 minutes at a rotation speed of 4000 rpm. The water content at the bed outlet was monitored throughout the experiments using coulometric Karl-Fischer titration on a Metrohm 852 Titrando instrument, following the ASTM D6304 standard (2020). When this emulsion was introduced into an empty bed (bed without hydrogel), it resulted in an outlet stream with 5729 ± 160 ppm of water.

3. Results and discussions

The results from the study of the hydrogel Raschig rings geometrical stability and their use (at different swelling degrees) for water removal from biodiesel are presented in this section.

3.1 Hydrogel Raschig rings geometric stability study

Tables 1, 2 and 3 show a sequence of dimension analyses after the procedure of swelling and drying hydrogels: Table 1 presents the initial size distribution of the hydrogel Raschig rings; Table 2 shows their dimensions when swollen, as well as the swelling degree; Table 3 indicates the dimensions after the rings were oven dried.

Table 1: Size distribution of the hydrogel Raschig rings

Height (mm)	Frequency	D _{int} (mm)	Frequency
2.8 - 3.0	0	2.8 - 3.0	4
3.1 - 3.3	1	3.1 - 3.3	19
3.4 - 3.6	2	3.4 - 3.6	11
3.7 - 3.9	1	3.7 - 3.9	1
4.0 - 4.2	1	Mean	3.3 ± 0.2
4.3 - 4.5	1		
4.6 - 4.8	3	D _{ext} (mm)	Frequency
4.9 - 5.1	5	4.4 - 4.6	2
5.2 - 5.4	8	4.7 - 4.9	12
5.5 - 5.7	6	5.0 - 5.2	15
5.8 - 6.0	5	5.3 - 5.5	4
6.1 - 6.3	2	5.6 - 5.8	1
6.3 - 6.6	0	5.9 - 6.1	1
Mean	5.1 ± 0.7	Mean	5.0 ± 0.2

Table 2: Hydrogel Raschig rings dimensions when swollen and swelling degree distributions

Height (mm)	Frequency	D _{int} (mm)	Frequency	W	Frequency
2.8 - 3.0	1	4.0 - 4.3	5	0.64 - 0.67	1
3.1 - 3.3	1	4.4 - 4.7	10	0.68 - 0.71	3
3.4 - 3.6	2	4.8 - 5.1	13	0.72 - 0.75	6
3.7 - 3.9	1	5.2 - 5.5	4	0.76 - 0.79	5
4.0 - 4.2	1	5.6 - 5.9	3	0.80 - 0.83	3
4.3 - 4.5	3	Mean	4.8 ± 0.5	0.84 - 0.87	8
4.6 - 4.8	7			0.88 - 0.91	0
4.9 - 5.1	6	D _{ext} (mm)	Frequency	0.92 - 0.95	2
5.2 - 5.4	8	5.2 - 5.5	4	0.96 - 0.99	5
5.5 - 5.7	4	5.6 - 5.9	8	1.00 - 1.03	1
5.8 - 6.0	0	6.0 - 6.3	12	1.04 - 1.07	0
6.1 - 6.3	0	6.4 - 6.7	10	1.08 - 1.11	1
6.3 - 6.6	1	6.8 - 7.1	1	1.12 - 1.15	0
Mean	6.2 ± 1.0	Mean	6.2 ± 0.4	Mean	0.83 ± 0.11

A comparison of the mean dimension values for the hydrogel Raschig rings before (Table 1) and after swelling (Table 3) reveals no significant difference in the number of significant digits used. A detailed evaluation of each hydrogel ring, both pre- and post-swelling, indicates minimal variations: height exhibited a change of $0.14 \pm 3.59\%$, inner diameter varied by $1.11 \pm 8.07\%$, and outer diameter showed a variation of $-0.46 \pm 4.26\%$. These results show that in practice the hydrogel maintains its shape consistently during regeneration, even when it retains more water than anticipated during normal operation (i.e., the hydrogel bed would be regenerated prior to reaching this swelling degree).

Table 3: Size distribution of regenerated hydrogel Raschig rings

Height (mm)	Frequency	D _{int} (mm)	Frequency
2.8 - 3.0	0	2.8 - 3.0	4
3.1 - 3.3	1	3.1 - 3.3	19
3.4 - 3.6	2	3.4 - 3.6	11
3.7 - 3.9	0	3.7 - 3.9	1
4.0 - 4.2	2	Mean	3.3 ± 0.2
4.3 - 4.5	1		
4.6 - 4.8	3	D _{ext} (mm)	Frequency
4.9 - 5.1	4	4.4 - 4.6	2
5.2 - 5.4	9	4.7 - 4.9	12
5.5 - 5.7	7	5.0 - 5.2	15
5.8 - 6.0	4	5.3 - 5.5	5
6.1 - 6.3	2	5.6 - 5.8	0
6.3 - 6.6	0	5.9 - 6.1	1
Mean	5.1 ± 0.7	Mean	5.0 ± 0.2

The dimensions of the swollen hydrogel (as shown in Table 2) display a broader range of values and larger standard deviations compared to those in Tables 1 and 3. This increase in variability can be attributed to the loss of stiffness in the hydrogel as it absorbs water.

In terms of percentage changes, the most significant variation was observed in the inner diameter, which increased by 49.04 ± 17.85 %. The outer diameter and height experienced changes of 20.50 ± 6.50 % and 22.56 ± 8.51 %, respectively. Additionally, the wall thickness of the hydrogels went from an average of 0.9 ± 0.2 mm in its dry state to 0.7 ± 0.2 mm when swollen.

Although the swelling degree investigated in this study did not yield statistically significant differences in wall thickness, and no clogging was observed (section 3.2), it is important to note that higher swelling degrees could potentially obstruct the pathways through which fuels travel within the bed or the interior of the rings. Furthermore, throughout all experiments, the intervals with the highest frequency of measurements were close to the mean values.

3.2 Water removal performance over time

Figure 3 illustrates the water content of biodiesel at the outlet stream of the bed after 90 minutes of operation time, utilizing hydrogels with varying swelling degrees ($W = 0.00, 0.12, 0.18, 0.24,$ and 0.8 g water/g hydrogel). It's worth noting, especially at $W = 0.12$ g water/g hydrogel, that the swelling degrees within the studied range not only did not reduce bed performance, compared to dry hydrogel, but also enhanced it for emulsion treatment. This finding aligns with previous research (Gonçalves et al., 2023), which reported similar improvements with a narrower swelling range. According to a proposed mechanism for water removal by hydrogels (Fregolente et al., 2023), water coalesces at the surface of the hydrogel, followed by intraparticle mass transfer. Thus, the hydration of polymeric chains in the hydrogel facilitates droplet coalescence, while pore expansion and chain relaxation due to swelling enhance interparticle mass transfer.

However, it is important to note that while bed performance improved at moderate swelling degrees, this enhancement declined as swelling increased further. Although no reduction in bed performance was observed within the studied range, regular regeneration of the hydrogel is recommended. Increased swelling degrees can lead to hydrogel expansion, potentially resulting in bed clogging, material embrittlement, rupture of the hydrogel Raschig rings, and an increase in pressure drop. Also, there is a discernible trend indicating that as swelling degrees increase, the capacity for water removal may decline.

The smaller standard deviation observed for $W = 0.12$ g water/g hydrogel can be attributed to the results falling within the solubilized water range, which minimizes the dispersion of water as droplets and reduces fluctuations during Karl-Fischer titration. In contrast, the other measurements correspond to emulsified or free water.

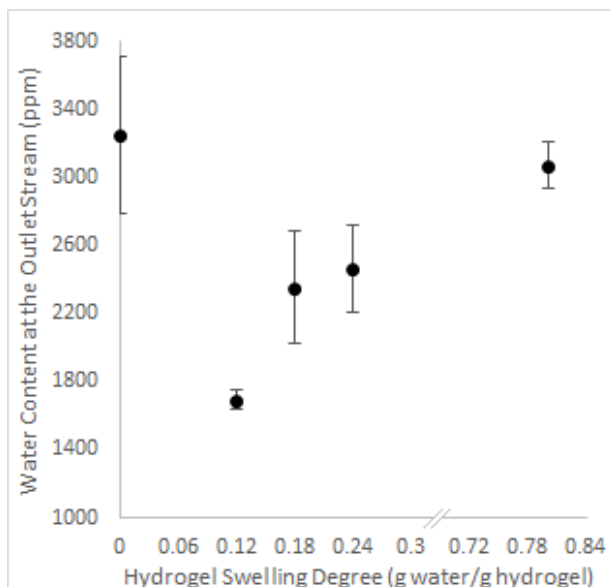


Figure 3: Outlet water content using the hydrogel bed with different swelling degrees

4. Conclusions

This work presented an innovative method for producing hydrogels in the well-defined geometry of Raschig rings. It was demonstrated that, under the studied conditions, the material retains its geometric integrity after undergoing swelling and subsequent drying. This characteristic is crucial for ensuring that the hydrogel bed maintains its design parameters and expected performance over time. Additionally, the hydrogel bed capacities of removing water from water-biodiesel emulsions were studied at different swelling degrees, simulating conditions that may occur between regeneration cycles. Notably, no reduction in performance was observed with swelling degrees of up to 0.80 g water/g hydrogel, underscoring the robustness of the equipment. Overall, this work represents significant advancements in the use of hydrogel beds for water removal from fuels, offering a simpler, cleaner and potentially more cost-effective industrial solution. These findings pave the way for further research and development in this area, with implications for improving fuel quality.

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