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# INVESTIGATION OF SEGMENTED FLOW PATTERN FOR BIODIESEL SYNTHESIS IN MICROREACTOR

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**Abstract.** *In order to reduce the amount of fossil fuels used for combustion processes, alternative fuel sources have to be investigated where one promising option is biodiesel. To increase the efficiency of the so far used batch reaction process, new ways of production are needed. Hence microreactors gained a lot of attention over the past few years and were investigated intensively. However, the flow pattern exhibited and its correlation to conversion efficiency was mainly neglected, even though it can play a crucial role in the conversion of triglycerides to esters. Therefore, the flow pattern was the main point of interest in this work. The aim is to figure out in what way a drop flow pattern affects the efficiency of the biodiesel synthesis. This was done by using a co-flowing device made out of glass capillaries. For experiments soybean oil was used as the continuous phase and the drops consisted of ethanol containing a base catalyst (NaOH). By means of this reactor the influence of the parameters molar ratio, residence time, temperature and catalyst concentration on biodiesel production was observed. It was found that droplet flow pattern shows under the right conditions a higher conversion efficiency than stratified flow. By using a molar ratio of 18.7:1, a catalyst concentration of 1.5wt%, an intermediate residence time of 0.84 minutes and a temperature of 43.1 °C it was possible to reach a yield of ethyl esters of 97.2%.*

**Keywords:** *Biodiesel, Drop, Microreactor, Microfluidics*

## 1. INTRODUCTION

It's a global trend nowadays that several countries are researching new energy alternative sources with the objective to reduce/eliminate the consumption of fossil fuels. According to the Bp statistical review of world energy 2018, more than 80% of the world's primary consumption came from fossil fuels in 2017. Despite the efforts directed to reduce the emissions of greenhouse gases, such as the Kyoto protocol, the development of new sources that can provide the same amount of energy without damaging the planet.

Between the research fields available today, biodiesel production is the most promising ones, due to its similar energy capacity and biodegradable and non-toxic characteristics (Tiwari *et al*, 2018). The most common procedure of producing biodiesel is by a transesterification reaction, using an animal or vegetable fat source, a short-chain alcohol and an acid or base catalyst, performed in a batch-stirred reactor (Costa Junior, 2017). But this mainly used process has several drawbacks: long residence times, high energy consumption and low efficiency (Tiwari *et al*, 2018; Costa Junior, 2017; Yeh *et al*, 2016). One of the alternatives to overcome this problem is to use microdevices to perform transesterification reaction. Microreactors dragged attention from the research field due to its intensified efficiency of heat and mass transfer and its residence time were shortened 10-100 fold, when compared with the traditional ones (Dai

*et al.*, 2014). Surface area to volume ratio can be determined by the nature of flow between the two phases. The droplet-based flow performs better than other methods of continuous-flow production (Tiwari *et al.*, 2018). Lopez-Guajardo *et al.* (2017) suggested using droplet flow pattern to achieve higher interfacial area and intensify local mixing for higher conversions.

Yeh *et al.* (2016) fabricated a cross-flowing microreactor which uses a Teflon tube as microchannel. With this configuration they were able to have methanol as the dispersed phase (droplets) and soybean oil as the continuous phase. They reported increased conversion efficiencies by increasing the molar ratio (MR), the residence time (RT), the catalyst concentration (CC) and the temperature.

Costa Junior (2017) has used soybean oil and ethanol to produce biodiesel. He used a 3D printed metal microreactor to check the influence of MR, RT, CC and temperature. His reactor consisted of a stack of 10 microreactors with heat exchangers in between. Using this device with a MR of 20, a RT of 0.582 minutes, a CC of 1.5wt% and a temperature of 64.9 °C (reactor temperature) he was able to reach 99.6% biodiesel in a channel that was 43.26 cm long. With the approach of using 10 microreactors in parallel and the aforementioned configuration he was able to produce 34 mL of biodiesel in 5 minutes and 37 seconds from the moment of reagent injection to the moment he stopped the pumps.

This present work has the objective to study and analyze a segment flow pattern transparent microdevice for the transesterification of sunflower oil and ethanol catalysed by sodium hydroxide and investigate the influence of the molar ratio, residence time, temperature and catalyst concentration in biodiesel production and in the flow pattern.

## 2. METHODOLOGY

### 2.1. Device fabrication

A cylindrical glass capillary from World Precision Instruments with an inner diameter of 0.58 mm was tapered down in a capillary puller (World Precision Instruments, PUL-1000) to an internal diameter of 380 to 400  $\mu\text{m}$  which was justified by means of a Hirox 3D microscope. This capillary was then placed inside a squared glass capillary (VitroCom) with an internal dimension of 1.05 mm. Since the external dimension of the cylindrical capillary is 1 mm it almost centered itself with a neglectable error. The length of the reactor from the cylindrical tip to the end of the squared capillary was 14 cm and therefore the total reactor volume was 0.1544  $\text{cm}^3$ .

Two holes were drilled at the middle height of a dispense tip from Nordson EFD through which the two capillaries were stick through in a way that the beginning of the squared capillary sits in the middle of the dispense tip which can be seen in Fig. 1. The dispense tip is represented in pink, the cylindrical capillary in blue and the squared one in green. The holes were closed with glue and the whole arrangement was then glued on a glass slide to immobilize it and make it stand up straight. Since alcohol is contained in the dispersed phase and glass exhibits hydrophilic characteristics, the channel walls will be wetted by the alcohol in case of contact. To make sure the glass walls repel the alcohol drops and to remain the drop pattern stable as long as possible the channel was treated with a water repellent which is usually used for car windshields. The repellent was injected into the channel and left in there for approximately 5 minutes and then blown out with compressed air.

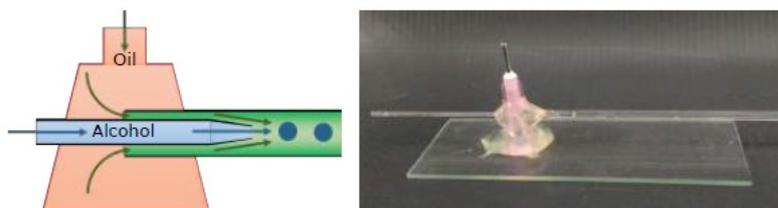


Figure 1. Schematical representation of a microreactor fabricated with glass capillaries. Dispense tip in pink, cylindrical capillary in blue and squared capillary in green.

### 2.2. Experimental apparatus

The test setup consists of two syringe pumps (New Era Pump Systems, NE-1000), glass syringes from Hamilton, one camera (Dino-Lite, AM3111), a DAQ module from Keysight and a microcomputer for acquisition and processing of data of the probe temperature and of the images. Figure 2 shows the setup ready for testing with the microreactor connected to the syringes and the temperature probe (blue wire). For tests at elevated temperatures, the same setup as mentioned before was used with the only difference that a lamp is mounted perpendicular above the reactor. To reach different temperatures, the height of the lamp was varied. As reagents for the biodiesel production, commercially available soybean oil, ethanol with a purity of 99.8% and sodium hydroxide (NaOH) as catalyst were used. At the end of the reactor the products were caught in a glass beaker which was surrounded by ice cubes to make sure the reaction stops and does not continue reacting back nor forth and falsify the yield of biodiesel by droplets.

The experimental procedure is initiated by pumping the ethanol / NaOH solution and the soybean oil to the microreactor through two independent syringe pumps with controlled flow rates. The reactants come into contact within the

micro-reactor and the mass transfer process and the transesterification reaction occur. The final product of the reaction is collected in a beaker immersed in a water bath and ice, which is used to stop the transesterification reaction. Then, the final product of the reaction is placed in a separation funnel where the two phases are separated (fatty acid ethyl esters (FAEE) and glycerol). Finally, the glycerol is discarded and the ethyl esters are washed with distilled water at a temperature of about 75 °C. The analysis of the ethyl esters were made through a high-performance liquid chromatography (HPLC) from Thermo Scientific, model Ultimate<sup>TM</sup> 3000.

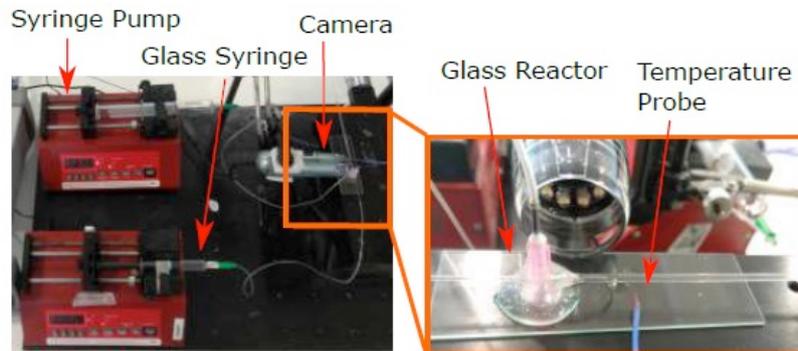


Figure 2. Experimental apparatus for biodiesel synthesis showing the glass microreactor, the syringe pumps and the camera.

### 2.3. Experimental plans

Each parameter was tested at three different levels (high, intermediate and low) and only temperature was tested at four levels. First, flow rates had to be found at which the device exhibited a nice drop pattern. This led to MR values of 8.4:1, 15:1 and 18.4:1. Following these MR were increased or decreased to reach an RT of 0.3, 1 and 1.8. The influence of CC was tested at levels of 0.5, 1 and 1.5wt% with respect to the oil mass. Ultimately the temperature was varied from 25°C to 55 °C in cases 8-8.4 and from 28.6°C to 61°C in cases 9-9.4 to analyze its influence in the droplet formation and at reaction rates. The levels chosen in this work were initially tested by Arias (2010) and later explored by Paiz (2018) and Costa Junior (2017), achieving good results in similar operational conditions. The different combinations tested and its respective results are shown in Tab. 1.

Table 1. All different configurations for biodiesel production used.

<b>Case</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8.1</b>	<b>8.2</b>	<b>8.3</b>	<b>8.4</b>
<b>Temp. (°C)</b>	24.3	24.3	25.0	24.9	25.4	25.3	25.0	25.8	33.3	43.1	55.0
<b>MR</b>	8.4:1	8.4:1	8.4:1	15:1	15:1	15:1	18.7:1	18.7:1	18.7:1	18.7:1	18.7:1
<b>RT (min)</b>	0.35	1.18	1.90	0.28	0.94	1.87	0.25	0.84	0.84	0.84	0.84
<b>CC (wt%)</b>	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
<b>% ester</b>	62.2	62.1	78.8	39.0	63.4	70.0	19.0	59.2	71.8	96.4	57.7
<b>Case</b>	<b>9.1</b>	<b>9.2</b>	<b>9.3</b>	<b>9.4</b>	<b>12</b>	<b>13</b>	<b>14</b>	<b>15</b>			
<b>Temp. (°C)</b>	28.6	36.4	44.0	61.0	26.2	25.2	24.7	24.3			
<b>MR</b>	18.7:1	18.7:1	18.7:1	18.7:1	8.4:1	8.4:1	8.4:1	8.4:1			
<b>RT (min)</b>	1.68	1.68	1.68	1.68	0.35	0.35	1.18	1.18			
<b>CC (wt%)</b>	1.5	1.5	1.5	1.5	0.5	1.0	1.0	0.5			
<b>% ester</b>	58.1	80.6	89.4	42.2	10.8	31.5	55.6	17.5			

## 3. RESULTS AND DISCUSSION

### 3.1. Visual analysis

Figure 3 shows the pattern flow between the molar ratios evaluated in this work. It can be seen that as we decrease the molar ratio, meaning less ethanol or more oil in the reactional system, the droplets decrease sizes and the distance between them increases, as observed by Yeh *et al* (2016) and Sun *et al* (2010). Another important phenomenon in common observed by Sun *et al* (2010) is the coalescence of the droplets when temperature is applied at the system. Besides the effects on the reaction itself by increasing the temperature, such as increasing the conversion of triglycerides and other products, the change in temperature affects the viscosity and density of the chemical compounds inside the reactional system. This could make the droplet pattern impossible to happen, as it can be seen in Fig. 4. Using droplet-flow pattern is a simple way to increase surface area to volume ratio which may leads to many benefits for the

process such as increasing advection between phases, enhance the heat and mass transfer at the interfaces and also affecting the reaction rates.



Figure 3. Typical droplet size and spacing in between droplets: a) Molar ratios of 18.8:1 (case 9.1). b) Molar ratio of 14.9:1 (case 5). c) Molar ratio of 8.4:1 (case 14).



Figure 4. Internal flow at different temperatures. a) Case 9.3 (44°C). b) Case 9.4 (61°C).

It is important to highlight that this microreactor represents a very complex process, whereas besides the mechanisms necessary to generate the droplet and the mixing, all chemical compounds present in the reactions can alter the pattern flow and inter-droplet separation, as can be seen in Fig 5 when we compare for the same case the droplets appearance right after they break up and close to the end of the reactor. This could also be evidenced when we increase the amount of catalyst (above 1.5% wt). Besides increase the conversion, as it will be discussed later, increasing the amount of catalyst generates a high occurrence of saponification reaction, forming a slimy mass that could cause blockage or increases pressure, as illustrated in Fig 6.

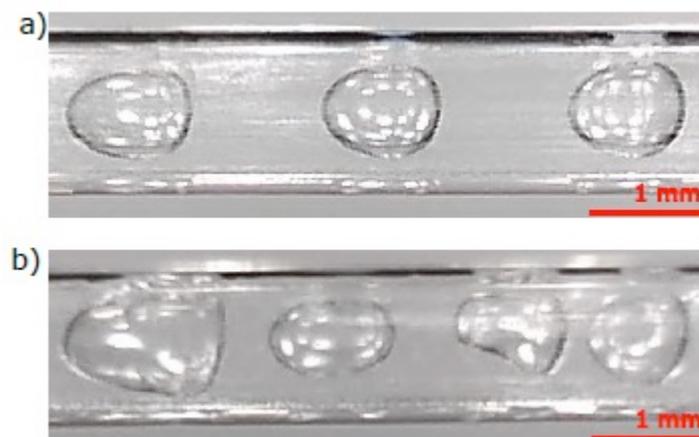


Figure 5. Evolution of droplet size and spacing over the whole channel: a) Right after the droplet breaks up. b) 2 cm before the end of the channel.

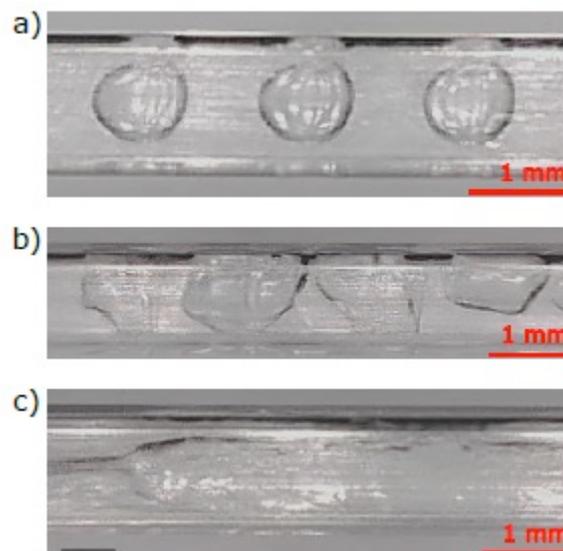


Figure 6. Evolution of a flow with a high content of catalyst: a) Right after droplet break-up. b) Droplets are more solid due to saponification. c) Stratified flow.

### 3.2. Chemical analysis

After the washing was done, all the biodiesel samples were headed to HPLC analysis aiming to get the yield of the ethyl esters, considering that the oil was made of 100% of triglyceride. Some of the cases indicated in Table 1 were repeated twice in order to obtain the experimental error of 7.03%. This value could be attributed to some issues such as difficulties in weight the same mass of catalyst every experiment and dissolve in the alcohol and changes in the laboratory temperature.

Figure 7 shows the different esters percentage for the different values of molar ratios from 8.4:1 up to 18.7:1 used in the experiments, and from these 3 curves it can be seen that as the molar ratio increase, the biodiesel production is reduced. The red line shows the test cases 1, 4 and 7 from Table 1, the green line represents cases 2, 5 and 8 and the blue line cases 3, 6 and 9. The experiments were conducted at ambient temperature and with a targeted catalyst concentration of 1.5wt%. Similar trends were also reported in the literature using a similar droplet flow microdevice, Rahimi *et al* (2014), Sun *et al* (2010) and Yeh *et al* (2015) have varied the molar ration from 6:1 to 12:1, authors have reported some growth in the conversion for MR from 6:1 to 9:1 but a decay for higher MRs due to the excess of alcohol that makes the separation between glycerin and ethyl esters harder.

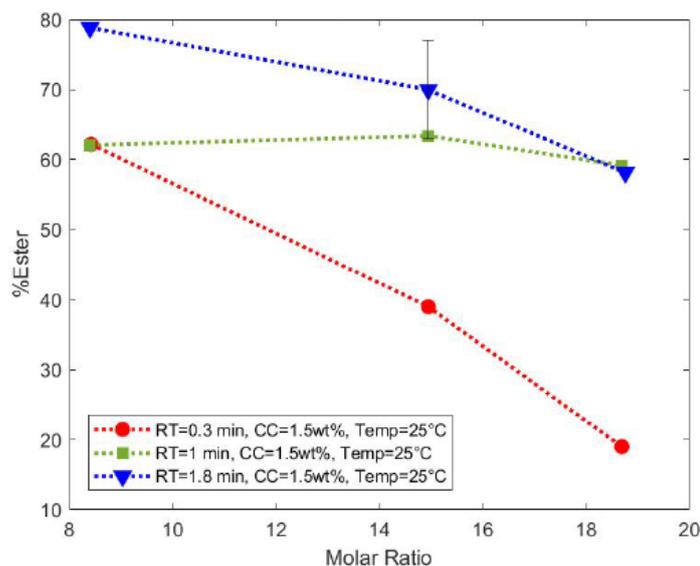


Figure 7. Ester yield for different molar ratios at approximately 25°C.

The influence of residence time on the ester's yield is shown in Fig. 8 for a fixed amount of catalyst concentration of 1.5wt%. The red line shows the test cases 1, 2 and 3 from Table 1, the green line represent cases 4, 5 and 6 and the blue line the cases 7, 8 and 9. As expected, for all cases evaluated here, as greater is the residence time, higher is the biodiesel production, once an increased residence time guarantee longer period in contact between reactants and catalyst.

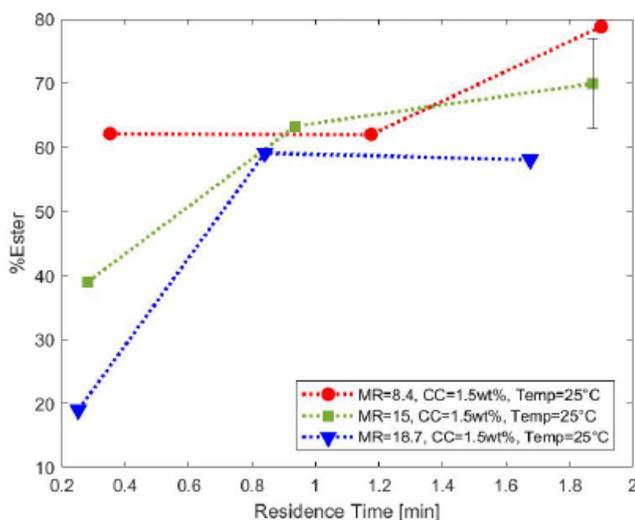


Figure 8. Ester yield for different residence times at approximately 25°C.

The influence of the catalyst concentration at ambient temperature is shown in Fig. 9. The red line shows the test cases 1, 12 and 13 from Table 1, and the green line the cases 2, 14 and 15. Although it can be seen that the ester's yield increases with the addition of more catalyst on the system, Rahimi *et al* (2014) and Yeh *et al* (2015) alerts that an excessive amount of catalyst, despite favoring the reaction, might lead to a point where it would react with the FFA forming soap and eventually blocking the microchannel or altering the droplet pattern, especially if the oil has a high amount of free fatty acid (FFA). It's also necessary to remind that catalyst are usually an expensive cost to the process, so there is a tendency to decrease its amount to as little as possible and promote the production controlling the others parameters.

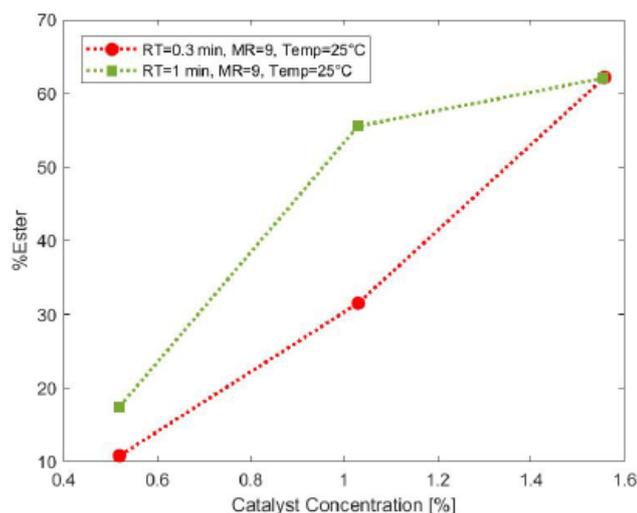


Figure 9. Ester yield for different catalyst concentrations at approximately 25°C.

The reaction temperature is also an important parameter in the transesterification process, and its influence on the biodiesel production is shown in Fig. 10. The red line shows the test cases 8.1, 8.2, 8.3 and 8.4 from Tab. 1, and the green line the cases 9.1, 9.2, 9.3 and 9.4. The increment of ester yield is steep for both analyzed RT (1 min – red line, and 1.8 min – green line) up to 45 °C when it starts to decrease. As previously commented (also through Fig 4), higher reaction temperatures increases ester's yield but as here observed also affects the reactant flow pattern, favoring the

droplets coalescence, and so decreasing the ester's yield. Indicating that might exist a relation of compromise in between the gain provided by the droplet pattern and the temperature enhancement in the ester's yield.

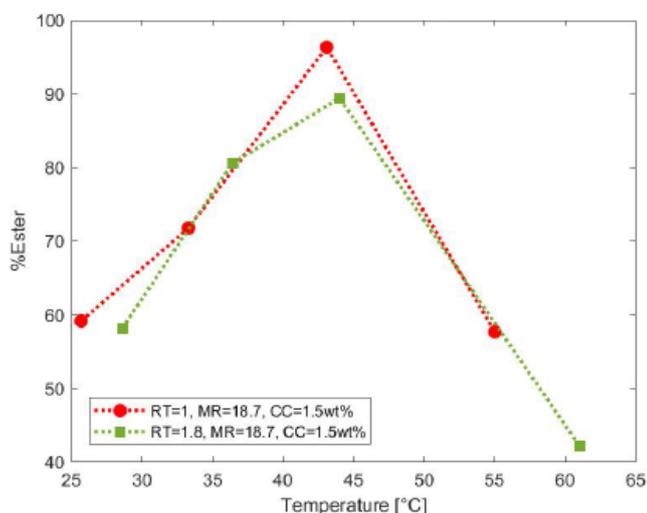


Figure 10. Ester yield for different temperatures varying the molar ratio.

Using the microdevice described in this work, it was possible to obtain 97.2% of ethyl esters using the following configurations of case 8.3: MR of 18.7:1, CC of 1.5wt%, RT of 0.84 minutes and temperature of 43°C. The full experiment took one hour and was able to produce more than 3.5 ml of biodiesel (after washing) using a single glass capillary device.

#### 4. CONCLUSION

Using a single capillary device, it was possible to reproduce the droplet pattern flow to achieve a high rate of ester yield in mild operational conditions. Although an optimization process still possible to be implemented, some parametric study was here implemented varying the catalyst concentration, the residence time and the reaction temperature and it was possible allowing a 97.2% of biodiesel conversion using a MR of 18.7:1, a CC of 1.5wt%, a RT of 0.84 minutes for a temperature of 43.1°C.

Through the system analyzed in this work it was possible to observe that ester yield is favored by an increment in the catalyst concentration, temperature and residence time. However an excessive amount of catalyst might eventually block the microchannel or alter the droplet pattern. We have also pointed out that there might exist a relation of compromise in between the gain provided by the droplet pattern and the temperature enhancement in the ester yield, since as known a higher reaction temperatures increases ester yield but might affect flow pattern, favoring the droplets coalescence, and so decreasing the ester's yield.

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