Pervaporation assisted esterification in a membrane reactor

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Abstract: The esterification of n-propanol and caproic acid, as model compounds were performed with/without pervaporation for comparison. By means of simultaneously removing the water from the solution via pervaporation, the overall reaction favors the product side, thus further to enhance the conversion of caproic acid based on Le Chatelier principle. Compared with no pervaporation, the results showed that the conversion was enhanced 3% at 70°C, using 5 wt% Amberlyst 15 catalyst and n-propanol to caproic acid = 1.39 by pervaporation in 12 hours. Instead of Amberlyst 15, the conversion was enhanced 6% when 0.05 wt% sulfuric acid catalyst was used with pervaporation in 9 hours.

Keywords: Pervaporation, Esterification, Membrane Reactor.

1. Introduction (11-point boldface)

Nowadays, our life is intimately linked with fossil fuels. With more and more concerns about oil shortage and environmental issues, seeking for alternative energy turns out to be crucial. Biodiesel is a kind of general biofuel, and it is clean, renewable and has combustion properties like fossil diesel. In order to overcome the saponification and hydrolysis problems of producing biodiesel by using alkaline catalysts which is usually caused by free fatty acid (FFA) contained in raw oil. A two-step method, pre-esterification followed by transesterification can be performed. In this study, we focused on the first step, pre-esterification. We designed a reactor consisting of a pervaporation module to remove water to enhance the conversion of esterification. The esterification of n-propanol and caproic acid, as model compounds, were performed with/without pervaporation for comparison.

2. Experimental

Reaction conditions were performed in liquid phase under various parameters including initial molar ratio of n-propanol to caproic acid (M), reaction temperature, ratio of effective membrane area to the reaction solution volume (S/V). The reaction solution was heated to the desired temperature until steady state was reached. Once the set-point temperature was reached, this was taken as zero time of the reaction and then pour the preheated reaction solution into the reaction-pervaporation composite apparatus. The aliquots of sample were withdrawn at fixed intervals and analyzed. The permeate products separated by the membrane were condensed by using the chillers which contain liquid nitrogen. The condensed permeate products were collected, weighed and analyzed.

3. Results and discussion

Figure 1 shows the conversions with/without pervaporation from 60-80℃. At 60℃, the conversion of reaction with pervaporation is lower than without pervaporation, the reason is that the water removal rate is not fast enough. But the conversion of reaction with pervaporation is catch up at 12 hr, which indicates that combining pervaporation still has its effect. Compared to no pervaporation, at 70℃and 80℃, the conversion of reaction with pervaporation can be enhanced about 3% after 3 hr and at the beginning respectively. Figure 2 compares with different initial alcohol/acid molar ratio with pervaporation. We can find that when M= 0.74 increases to M= 1.39, the conversions increase as our expectation based on Le Chatelier principle, but the conversion of M= 2.08 is the lowest. And the reason be due to the lower acid concentration for higher initial alcohol/acid molar ratio. In the theory, compared to no pervaporation, increasing the S/V ratio can also increase the conversion enhancement due to faster water removing rate. However, we cannot see this situation in figure 3 for S/V= 0.2804 cm^{-1}. Although the conversion is lowest for S/V= 0.2804 cm^{-1} with pervaporation. But it grows dramatically after 3 hr and catch up the performance of no pervaporation at 12 hr.

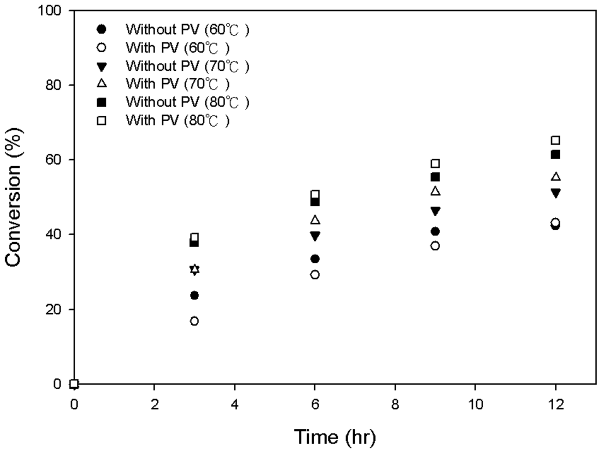

Figure 1. Effect of temperature on conversion (M= 0.74, 5 wt% catalyst, S/V= 0.1470 cm^{-1})

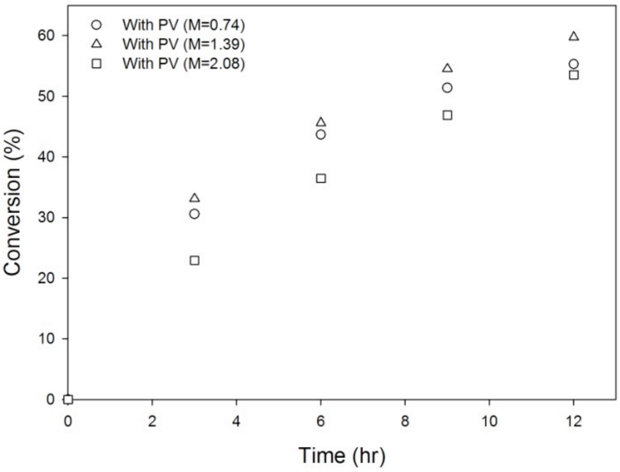

Figure 2. Effect of initial alcohol/acid molar ratio (M) on 70℃, 5 wt% cat.

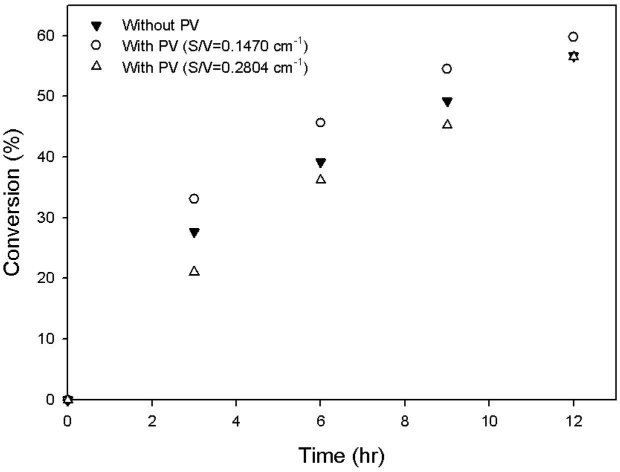

Figure 3. Effect of the ratio of membrane area to reaction solution volume on conversion (M= 1.39, 70℃, 5 wt% catalyst)

4. Conclusions

The esterification of n-propanol and caproic acid, as model compounds, were performed with/without pervaporation for comparison. Compared with no pervaporation, unlike M= 0.74 and M= 1.39, the conversion of M= 2.08 cannot enhanced due to lower reaction rate and higher alcohol permeation. For increasing S/V ratio to S/V=0.2804 cm^{-1}, little amount of water flux was collected in the beginning so that the conversion was lowest. But after 3 hr reaction, the conversion of the S/V=0.2804 cm^{-1} enhanced rapidly due to higher water removal rate and catch the performance of without pervaporation up at the end of reaction. In addition, the reactor consisting of a pervaporation module we designed could also see the conversion enhancement as homogeneous catalyst used.

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