Falling Film Evaporator: Drying of Ionic Liquids with Low Thermal Stress

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The removal of water from an aqueous ionic liquid (IL) water solution is a new application for falling film evaporators (FFE). As FFE are able to operate at conditions with small thermal gradient and small residence time in the heated zone, the resulting thermal stress to the IL is considerably low compared to other separation methods, e.g. rotary evaporators.

The investigations in a steam heated single tube falling film evaporator were conducted concerning two IL water mixtures. One IL was ammonium based and the other imidazolium based. For these two IL experiments were conducted to obtain the equilibrium water content with variation of temperature and pressure.

The resulting water contents decreased with elevating the heating temperature and lowering pressure at product side. Minimal water contents of under 0.01 g_w/g_{liquid} were achieved at an film exit temperature of 140 °C and an evaporation pressure of 50 mbar abs.

1. Introduction

Falling film evaporators (FFE) are commonly used in the food and process industry for separation of purification of liquid products, e.g. milk and juices, as reported by Winchester (2000) and Karimi (2007). IL are known to suffer from thermal stress. Therefore treating IL in a FFE was seen very promising for a gentle removal of impurities. Another advantage of a FFE lies in the possibility to define the water content by setting pressure and temperature according the equilibrium state. This is beneficial in all cases where IL are used as process fluid and are in need of constant water removal as part of the recycling process. As the physical properties, e.g. viscosity, are strongly influenced by the water content, a defined water content, tolerable for the process, could reduce the viscosity and increase the pumpability and mixing properties. A recycling method without thermal degradation is one of the key requirements to IL to successfully substitute established process fluids. Recycling is imperative to achieve economic as well as ecological competitiveness of IL vs. established process fluids. The more recycling steps are needed for an IL to compete with actual process fluids, the more gentle the recycling method needs to be in order to maintain the IL's functionality. The lifetime of a IL in an industrial process is a quite new area of research as Fernández (2011) reported, and further research is needed to review and assess suitable methods of regeneration for IL.

2. Experimental setup

Two different IL were investigated in this study: dimethyl-dihydroxy-ethylammonium methylsulfonate and 1-ethyl-3-methylimidazolium ethylsulfate. Both IL are commercially available. The two groups of ammonium and imidazolium based fluids form major groups amongst the ionic liquids. By variation of

the side chains and anions the properties of IL can be influenced significantly as Wasserscheid and Welton (2003) reported.

The apparatus used was a steam heated single tube metal falling film evaporator. The tube dimensions were d_o x s x l = 32 x 2 x 2,770 mm. The experiments were conducted in batch mode and as a continuous dewatering process. The apparatus is depicted in Figure 1 for the continuous mode. The feed and bottom draw, marked out as boxes, were not used for batch experiments.
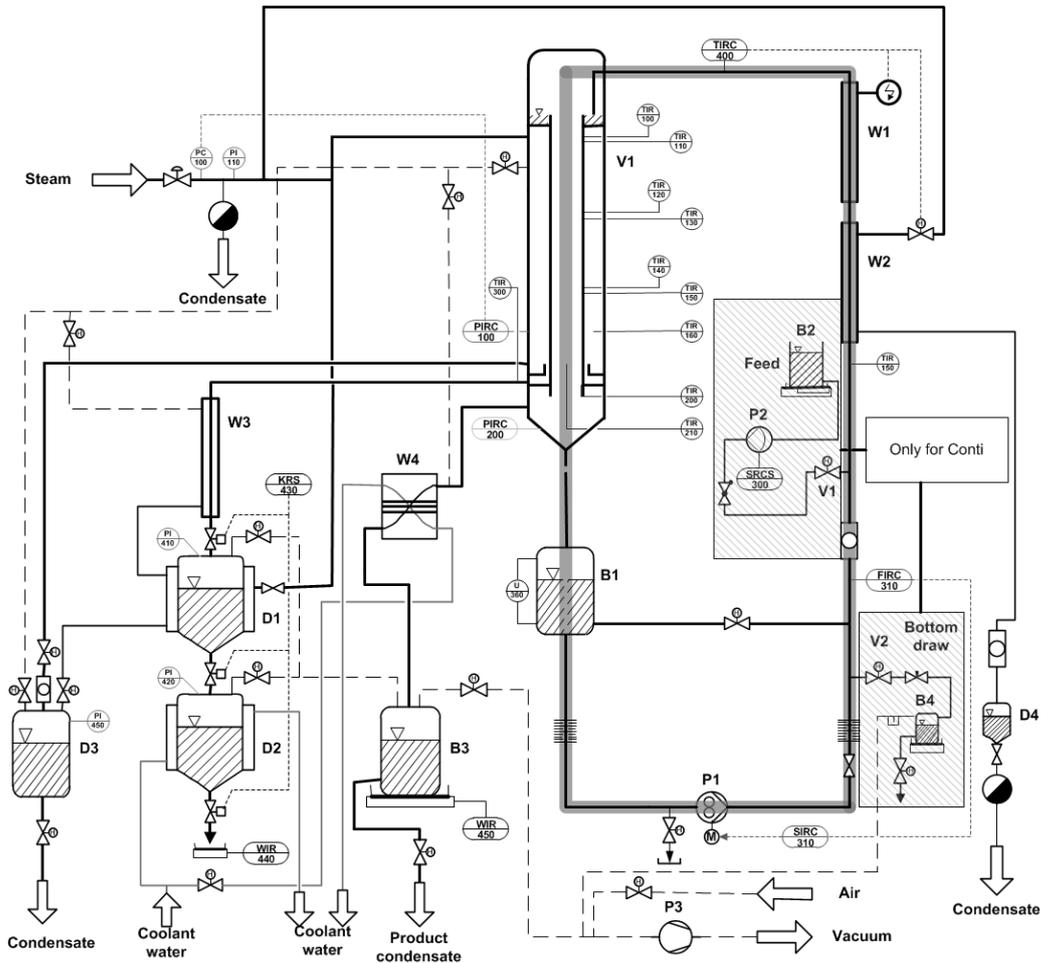

Figure 1: Flow chart of the falling film evaporator

The pump around flow, marked as the thick grey line, was initiated via pump P1, drawn from the holding tank B1 and fed in the evaporator tube V1. The liquid part exiting the tube fell back into B1, the evaporated part passed the condenser W4 and is measured in the holding tank B3 using the scale WIR 450. The water content of the mixture was measured offline using Karl Fischer (KF) titration (Mettler Toledo, C30x).

During all experiments a constant pump around flow of 150 L h^{-1} was used to ensure a sufficient wetting and prevent dry spots in the tube. This pump around flow equals a wetting rate of appr. 1.7 $m^3/m^{-1} h^{-1}$ at the tube inlet.

For the batch experiments an IL water solution is filled into the apparatus and pumped around in the FFE. The total pressure at product side was varied between 50 and 150 mbar. The local equilibrium is reached when no more water is evaporated, i.e. no increase of the mass of condensate is detected on

the scale WIR 450 (Figure 1). Starting at 90 °C the equilibrium for every step of 5 K was determined by measuring the mass of evaporated water and relating it to the starting and final water content of the mixture. The starting water content was calculated based on a mass balance of the prepared feed mixture and confirmed by KF titration. The final water content after the series of temperature steps was also determined via KF titration. All intermediate values of water content were calculated through linear interpolation based on a material balance using the distillate mass as obtained from WIR 450, see Figure 1. The distillate is assumed to be pure water with no IL evaporating.

All continuous experiments were undertaken at 50 mbar, with a nearly constant water content of the feed stream of appr. 0.06 g_w/g_{liquid} and with a constant pump around flow of 150 L h^{-1}. The holdup in the apparatus was heated up and the pressure was set to 50 mbar. After the batch equilibrium was reached, a sample was taken to measure the water content. Thereafter, the feed and bottom draw streams were started to initiate the continuous dewatering experiment. At the end of the continuous dewatering, another sample was taken for water content analysis. Afterwards, the hold-up was dewatered until the batch equilibrium was reached again. The feed mass flow was varied during the experiments and accordingly, the bottom draw was set to ensure a constant liquid level in vessel B1.

3. Results

The investigations on IL-water-mixtures were started with the batch experiments. The variation of the pressure showed the expected dependence. With lower pressure on the product side, the equilibrium water content in the mixture decreases, as more water is likely to evaporate due to the lowered evaporation temperature. Remarkably, for the highest investigated temperatures, only minimal differences in the equilibrium water content for all pressure levels were found. The water content seems to be linear connected to the temperature, as can be seen for the ammonium based IL for all pressure levels in Figure 2 and the imidazolium IL in Figure 3. For the latter IL only two pressure levels were investigated, as the time to reach the batch equilibrium was usually about ninety min, whereas for the former IL the equilibrium was reached in about 45 min.
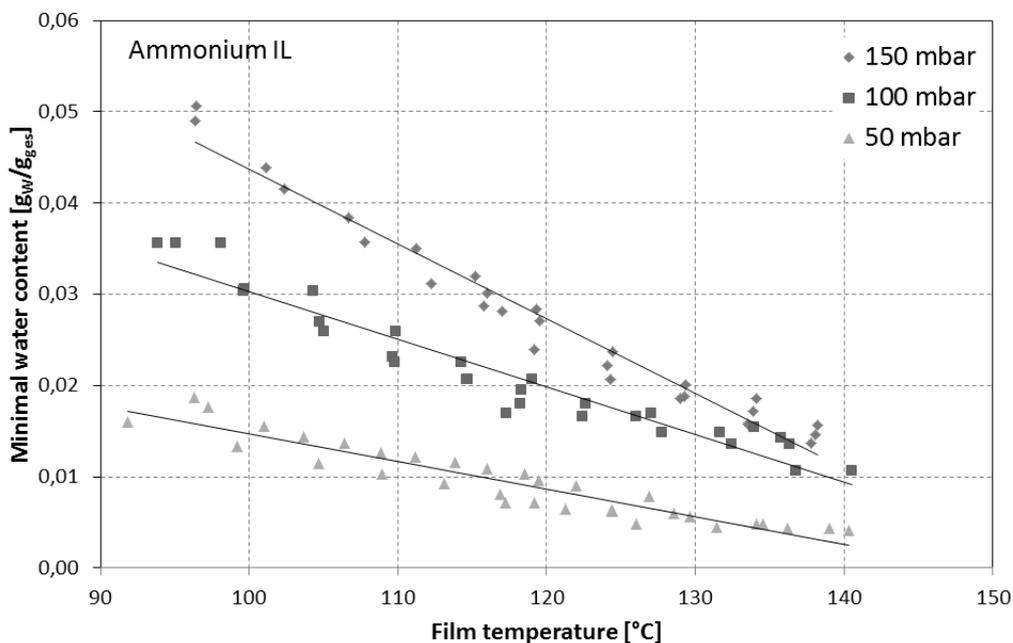

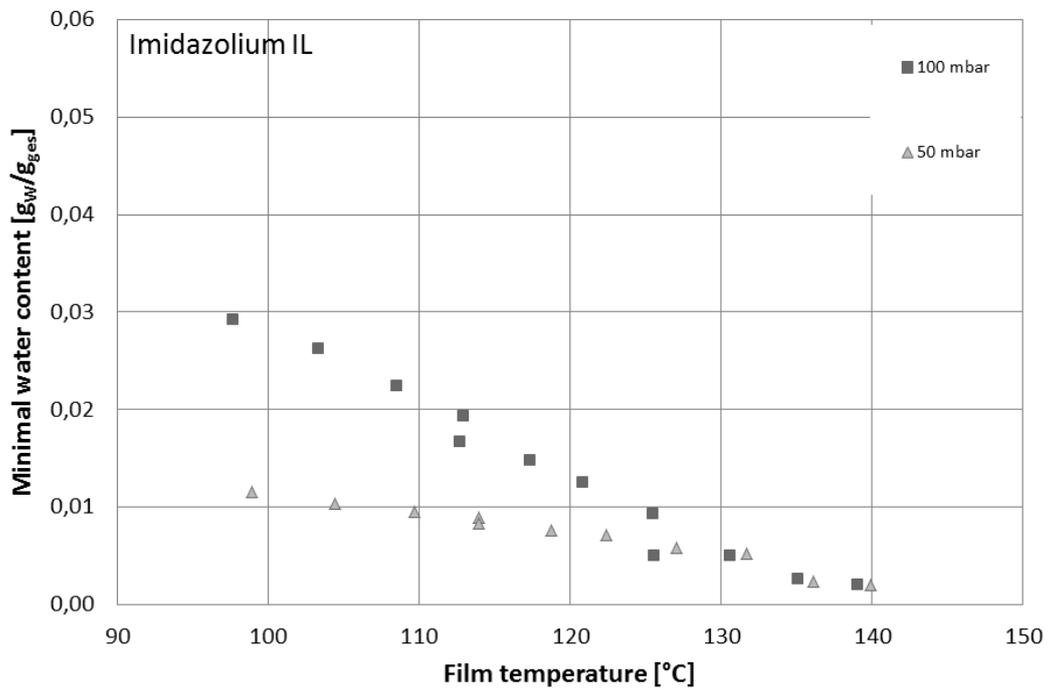Figure 2: Minimal water contents for ammonium based IL in batch dewatering. (Wellner 2011)

Figure 3: Minimal water contents for imidazolium based IL in batch dewatering.

These minimal water contents are the lowest possible water contents that can be achieved with the respective conditions and were therefore regarded as thermodynamic equilibrium values. With this data, it is possible to derive working conditions for a dewatering apparatus that will produce a mixture with specified water content, by setting pressure and temperature according to the desired water content.

Technical evaporation processes for larger production capacities are typically operated continuously. The achieved water content under continuous operating conditions is limited by thermodynamic equilibrium in combination with heat transfer and evaporation kinetics. Therefore continuous dewatering experiments were conducted. For all experiments constant pressure p = 50 mbar abs and temperature T = 120 °C as film exit temperature were set at the evaporation side.
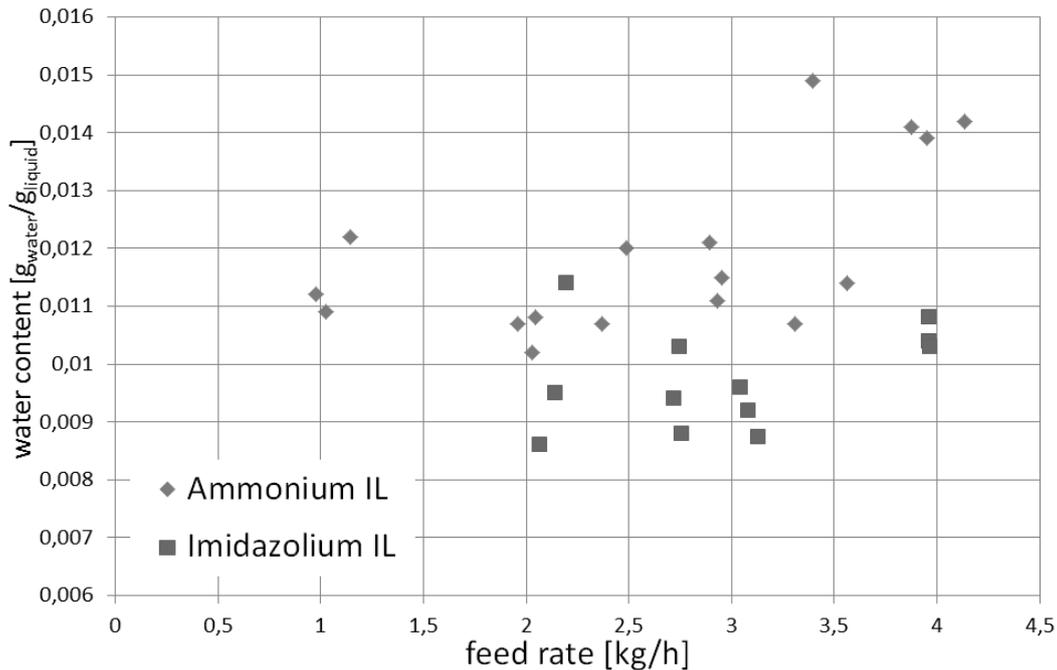
Figure 4: Water contents for continuous dewatering with variation of the feed stream.

The feed stream was varied from 1 kg h^{-1} to 4 kg h^{-1} and the bottom draw adjusted accordingly. The resulting water contents, depicted in Figure 4, show a general difference comparing batch to continuous operation: The resulting water content even for low feed streams was higher, ~ 0.012 g_w/g_{liquid}, compared to the batch results of 0.01 g_w/g_{liquid}. The difference can be explained by the finite heat transfer and evaporation kinetics of the equipment under the given component system and operating conditions. The variation of the feed rate with a constant pump around flow resulted in a variation of the residence time and the water load on the evaporator. With an increased feed stream, the mass flow of vapour is increased until the maximum evaporation rate for this apparatus is reached. At this point, no higher vapour mass flow is possible for these conditions of pressure and temperature. As another detectable result, the water content of the bottom draw stream will increase, as not all the water injected via the feed stream can be removed through evaporation. In the batch experiments the mixture was held at a specific temperature until no change in the condensate mass was detected, whereas in the continuous mode, the residence time was limited. Further the residence time becomes a function of the feed and bottom rate, resp.. As an increase in the water content can only be seen for the ammonium IL for feed rates above 3.5 kg h^{-1}, the residence time cannot be the only factor, as every increase of the feed rate lowers the residence time in the apparatus. A kinetic equilibrium is established matching heat and mass transfer kinetics of the evaporator with the average product residence time in the equipment. For the latter, the residence time based on the liquid holdup and the bottom draw is the relevant quantity:

$$\tau = \frac{V_{liquid}}{\dot{V}_{bottom}}$$ (1)

As seen in the batch experiments, it took up to ninety minutes to reach batch equilibrium. In the continuous operation mode, with low feed rates, the major part of the water can be evaporated, but the residence time is too small for the batch equilibrium to be formed. Going to higher feed rates, the maximum evaporator capacity is reached at the given conditions. This effect can be observed for feed

rates above 3.5 kg h^{-1}. From this data heat transfer performance of the falling film evaporator can be quantified and will be reported at a later stage. After completion of the continuous run for the highest feed rate, feed and bottom draw were stopped and the operation was switched to batch mode. In all cases the same residual water content was reached as in the initial pure batch mode.

Comparing the two IL, it can be seen that the imidazolium based IL can be dewatered to lower contents in the continuous mode. Furthermore, no increase in the water content can be seen for higher feed rates. Both these facts were unexpected, as the batch dewatering took considerably longer to reach the equilibrium. The reasons for this behavior are still under research, one possible explanation could be the difference in viscosity. The viscosity for the imidazolium IL was found to be 40 mPa s, whereas the viscosity of the other IL was 8 mPa s. Therefore a faster evaporation could be expected from the less viscous fluid as the turbulence is higher. As this could not be seen in the batch experiments, other additional factors need to be involved and further research is needed here, to gain fundamental data.

It could be shown, that the dewatering of an ionic liquid water solution in a falling film evaporator is possible without thermal degradation. The achieved water contents were in the range of 0.01 g_w/g_{liquid} for the applied temperatures and pressure levels. The apparatus can be used both batch wise or in a continuous mode to remove water from a solution.

Acknowlegdements

Symbols used

τ	Residence Time [h^{-1}]
V_{liquid}	Holdup Volume [kg]
$\dot{V}_{bottom}$	Feed rate [kg/h]

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