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Separation of Furfural and Acetic Acid with Liquid-Liquid-Extraction and Distillation in Biorefinery Systems: Simulations and Laboratory Experiments

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In this contribution a test distillation and a column model are presented for a quaternary system containing methyl isobutyl ketone, water, acetic acid and furfural. This chemical system is relevant for liquid-liquid extraction and distillation of extract and raffinate of wood hydrolysate, a potential source for valuable biorefinery products. The model is based on previous vapour-liquid and liquid-liquid experiments carried out in our laboratory. The laboratory distillation column was specifically designed for two liquid phase distillate and reflux stream. Temperatures, heating power, mass fractions and mass flows were measured during the experiments. The number of ideal stages in the column were determined with a separate two-component run. The simulated outlet compositions of all three products (bottoms, organic distillate and aqueous distillate) agree very well the experiments, and based on simulation model the heat loss was approximated. This work gives further confidence when large-scale separation sequences relevant to biorefinery operations are designed.

1. Introduction

The prehydrolysate is an aqueous mixture having a small quantity of furfural in a large quantity of water. The separation of valuable furfural product is challenging and energy intensive. One alternative to direct distillation is separation of furfural and acetic acid from prehydrolysate mixture with liquid-liquid extraction, and subsequent distillation from the extraction solvent. The extraction solvent should have a high capacity to reduce the solvent to feed ratio. This saves energy when furfural and acetic acid are distilled from the extract. On the other hand, solvent should have minimal solubility in raffinate to reduce solvent loss and energy requirement of purification of rejected water. Therefore processing of extract and raffinate require not only favourable liquid-liquid equilibrium (LLE) behaviour, but also favourable vapour-liquid equilibrium (VLE). The real prehydrolysate stream contains more components than water, acetic acid and furfural but from the modelling point of view, these components can be considered as the main components.

We have systematically studied several solvents for liquid-liquid extraction by measuring liquid-liquid equilibrium (LLE) at several isotherms. Although liquid-liquid extraction is operated close to room temperature, LLE studies at wider temperature ranges (between room temperature and atmospheric bubble point temperature) support both the extraction and distillation design by widening temperature and composition validity ranges. The decantation of distillate in the separation system requires LLE-information.

In this study, methyl isobutyl ketone is used as the extraction solvent. The LLE of ternary MIBK, furfural and water was measured by (Männistö et al, 2016) within the temperature interval from 298 K to 401 K. MIBK, acetic acid and water and other binary subsystem data were obtained from literature. The UNIQUAC model (Abrams et al, 1975) was used as an activity coefficient model and Hayden O'Connell (Hayden et al, 1975) with chemical theory was used as a model for fugacity coefficients in the vapour phase due to dimerization of acetic acid.

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2. Experimental

2.1 Materials

Experiments were carried out with a mixture of 4-methylpentan-2-one (MIBK, CAS: 108-10-1), acetic acid (CAS: 64-19-7) and furfural (CAS: 98-01-1) purchased from Sigma Aldrich. Sigma Aldrich has specified purities for the components as 99.5% wt. %, 99.8 wt. %, 99 wt. %, respectively. Furfural was vacuum distilled prior to use. The purity in GC was MIBK 99.6 area-% FID, acetic acid 99.6 area-% FID, 96.9 area-% TCD, furfural 99.7 area-% FID. The acetic acid was moist but as we were studying extraction of aqueous streams, effect of moisture in acid was within uncertainty of gas chromatograph (GC) analysis. The de-ionized water was purified in-house using a Millipore Milli-Q system. The analytical acetone was purchased from Merck and dried over molecular sieves to remove traces of water. Acetone was used only as an internal standard in gas chromatograph analysis of samples. Isopropanol (CAS: 67-63-0) by VWR Chemicals, 99.9 area-% FID, was used for determination of ideal stages only.

2.2 Equipment

Distillation was carried out in a column consisting 1200 mm packing height in rectifying section and 600 mm packing height in stripping section. The inner diameter of the column was 25 mm. The both sections were made by Normag and were insulated with silvered vacuum jacket with bellows. Both were filled with stainless steel wire mesh Berl saddles of 5 mm. The feed section had one conical joint for 3 mm diameter Pt100-thermometer and conical joint for the preheated feed. The feed was preheated with an in-house designed preheater (Mardani et al, 2016) having a heating cartridge bored into the block. The heating cartridge was adjusted to set temperature with an electrical PI-controller. The feed line from preheater to distillation column was 1/8 inch PTFE tubing and carefully insulated with nylon tubing to avoid any heat loss. The feed was pumped to preheater and distillation column with solenoid-driven diaphragm metering pump by ProMinent®. The feed tank was located on the Kern® precision balance 572.

The reboiler was designed in-house having two 500 W electrically heated quartz rods placed symmetrically along the column vertical axis. Hold-up of reboiler was 290 cm^3 when non-boiled. The bottoms product streamed out via overflow pipe that kept the volume of boiling two phase mixture constant. The bottoms product flow out to the container that was placed on the Kern 572 balance. The hold-up of reboiler when boiling was less than the 290 cm^3 and it was also dependent on boiling rate. The boiling rate was limited in this system to power 500 W to prevent the overheating of the quartz rods.

The condenser was designed in-house following a typical set-up of vapour dividing head condensers. The vapour dividing type distillation head is important in separating heterogenous azeotropic mixtures: If liquid dividing head were used, the ratio of the two liquid phases formed in condensation would be challenging to maintain in distillate. The socket member of spherical joint was at the bottom of glass rod laying on the ball member. Once lifted by electrical magnet, the socket member opened the route for vapour to flow to the side condenser. The ratio of time laying down to time when lifted was the reflux rate. The side condenser and the main condenser were cooled with Haake® water circulation bath.

After the side condenser the distillate flowed in the chemical resistant Tygon® tubing closer to floor level where a decanter was placed. The decanter was designed in-house to minimize the hold-up but still having enough residence time to settle the phases properly. The hold-up of decanter was 10 cm^3. The split distillate was divided to two containers, both of the containers placed on the Kern 572 balances.

The Pt100 thermometers measured temperature of the reboiler, the feed section above the preheated feed, and the distillate below the vapour dividing head. The thermometers were wired to Nokeval RMD680 series 16 channel universal input transmitter and the temperature were read into PC-computer with VisualBasic 6.0 program. The Pt100 thermometers were checked against the calibrated precision thermometer ALS F200 calibrated at the VTT MIKES Metrology. The balance readings were also recorded to PC-computer.

2.3 Procedure

The number of ideal stages were determined with a binary mixture of isopropanol and water. After starting the data acquisition system for column temperature, the gravimetrically prepared mixture was pumped into distillation column. The condenser water cooler circulation bath was set to 10 °C and the electrically heated quartz rods were powered to total 200 W. Once the boiling started, the total power was raised to 300 W. The power was kept constant through the experiment. At this stage, total reflux was used. The temperature was monitored and once the composition profile was settled the first samples of bottoms and distillate was taken. The next two samples were taken at 30 minute intervals. The samples were analysed with a gas chromatograph. After the experiments the power was turned off, the column cooled down, reboiler emptied and the column was flushed with acetone. The column was dried with gentle air flow for over 5 hours to remove any traces of water, isopropanol or acetone.

The distillation experiment of synthetic raffinate was started with making a gravimetric mixture of MIBK, water, acetic acid and furfural and it was carefully mixed and settled. The mixture was observed visually to make sure that it stayed in one liquid phase as controlled feeding of two liquid phases especially in a relatively small column is challenging.
The feed preheater was started slowly to avoid overshoot of temperature. It is recommended to have an electrical heating cartridge with integrated thermocouple, rather than separate thermocouple because overshoot of temperature is larger in separate thermocouple due to dynamics of heat conduction of the metal body of preheater. The overshoot may affect the heat sensitive components of the feed and cause some deposits into the tiny channels of the preheater. The preheater was adjusted below the boiling point of the feed, approximately to 90 °C. The superheating of the feed would adversely affect the temperature measurement in the middle section.
The mixture was pumped to the reboiler to the level the overflow pipe determines. The heating was slowly started with 300 W heating power. When the first boiling bubbles appeared the power was increased to 400 W. The level of reboiler decreases because vapour condenses onto the surface of the packing but the opposite effect is observed in the boiling two phase mixture as it that expands. However, approximately 30 cm^3 feed must be pumped into the column, otherwise the liquid level in the condenser would decrease too much. If the liquid level is too low, the heating surface of the quartz rod is in danger of overheating due to improper wetting, which may become a safety issue. It typically took 15 minutes since the start of boiling in reboiler to reach the condensing state inside the main condenser.
The feed was continuously heated via a preheater prior to entering the distillation column. The temperature profile stabilized in 10 minutes but in this work the difference between temperature of the reboiler and the top of packing of rectifying section was very small. The samples were withdrawn from the reboiler using a 1/16" capillary sampler that was flushed several times with the sample. The distillate samples were taken from the outlet of side condenser with a sampling vial. This eliminated the residence time the hosing from side condenser to decanter caused.

2.4 Analysis of samples

The samples were analysed with an an Agilent Technologies 6890N gas chromatograph (GC) equipped with both a thermal conductivity detector (TCD) and a flame ionizing detector (FID). They were connected in series from TCD to FID. A 28m capillary DBWax-ETR column from inlet to TCD to separate the sample components. The response factors are determined earlier with the technique explained in detail in (Männistö, 2016).

3. Modelling

Aspen Plus v8.8 process simulator with the "UNIQ-HOC" thermodynamic model was used to model one distillation column studied in this work. The parameters of Hayden-O'Connell model with chemical theory parameters are show in Table 1 and the parameters of UNIQUAC model in Table 2.

Table 1: Parameters of Hayden-O'Connell with chemical theory model.

	water	acetic acid	furfural	water
water	1.7	2.5	0.8	1
acetic acid	2.5	4.5	1.6	1.8
furfural	0.8	1.6	0.58	1
MIBK	1.0	1.8	1	0.9

Table 2: Parameters of UNIQUAC activity coefficient model.

component i	water	furfural	furfural	furfural	MIBK	MIBK
component j	acetic acid	water	MIBK	acetic acid	acetic acid	furfural
unit	K	K	K	K	K	K
Aij	0.0462	-4.0277	-1.6872	-1.5780	1.0391	0.0481
Aji	5.3635	0.0267	1.5640	1.2100	-2.3781	-0.1215
Bij	235.4490	68.5197	372.4532	689.7579	-14.0740	28.8931
Bji	-2413.0124	108.2790	-882.0836	-644.5795	-16.5162	-84.0912
Dij	0	0.0106152	0.00055	0	0	0
Dji	0	-0.00243286	-0.00041	0	0	0

The model of distillation column was “RadFrac”, where equilibrium stages were used, the condenser was set to total and valid phases were vapour-liquid-liquid for all stages. The simulation specifications were reflux rate and bottoms rate. The reflux was consistent specification based on electrical timer of reflux rate controller but the specification of reboiler duty with reflux rate was not the allowed combination in the simulator. In the experiments the reboiler duty was specified, not the bottoms flow rate. Column top was specified to atmospheric pressure that existed during the experiment.

4. Results and discussion

The number of ideal stages were determined with isopropanol (0.86 mole fraction) and water (0.14 mole fraction) mixture at atmospheric pressure at total relux. The distillate was isopropanol (0.705 mole fraction) giving 7 ideal stages in y-x-diagram. The number of ideal stages was less than expected, obviously channeling in the top section took place. The feed was made gravimetrically for the distillation experiment and it was in mass fraction MIBK 0.012, water 0.938, acetic acid 0.047 and furfural 0.001. The gravimetrical mass fractions were consistent with GC mass fractions within the uncertainty of GC analysis. The feed was 0.151 g/s; 0.108 g/s and 0.106 g/s during samples S7, S8 and S9, respectively. Samples S7, S8 and S9 are indicated at Figure 1 and 2. It is approximately the raffinate composition of our extraction studies that were submitted for review. The reflux ratio was 11 to promote the efficient removal of furfural from the bottoms product and heating power was 500 W. Condenser was set to 10 °C. The mass flows are presented in Figure 1 showing that after start-up the feed reached the stationary value at 4000 seconds where the sample S7 was taken. The sampling can be seen in distillate mass flow as peaks. The feed flow was decreased after the S7 where at 8000 and 9000 seconds the samples were taken. Flow of organic distillate was observed but was not measurable.

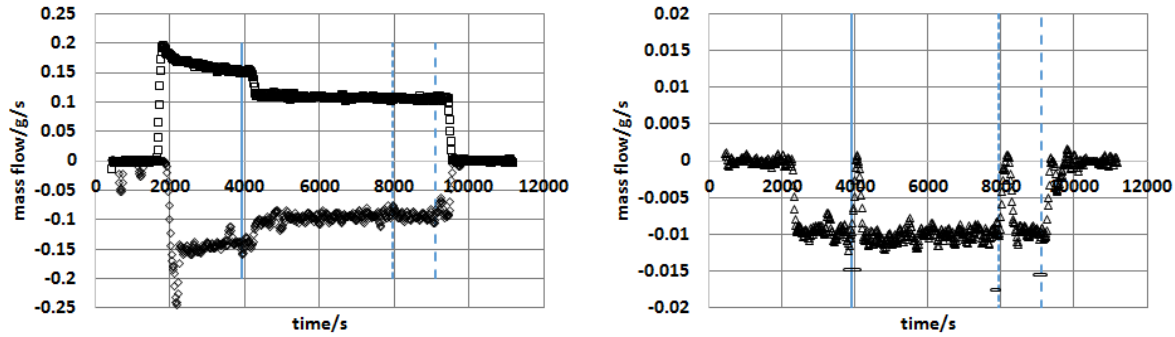

Figure 1 a, b: Mass flow of feed, □, and bottoms product, ◇, (left) and aqueous distillate, △, (right). Solid vertical line sample S7, dash line sample S8 and long dash line S9.

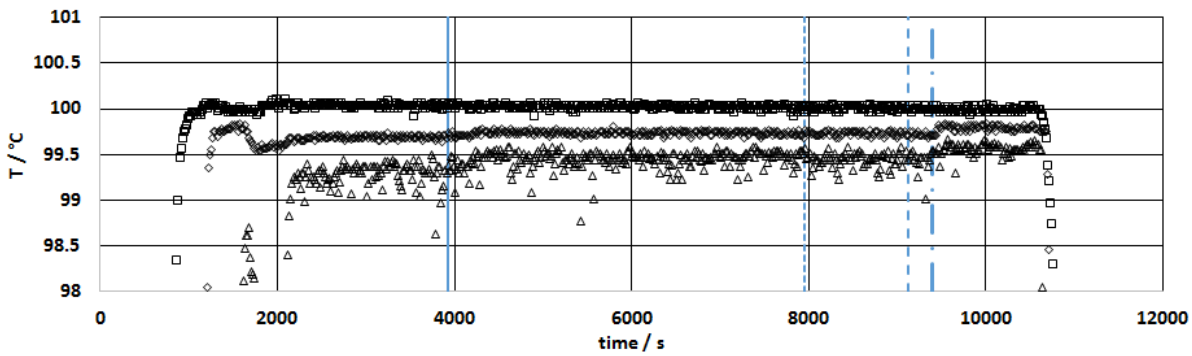

Figure 2: Temperature profile of distillation. Reboiler, □, feed section, ◇, top of packing, △, solid vertical line is sample S7, dash line sample S8, long dash line S9, long dash dot line is start of total reflux.

The temperature profile of distillation is presented in Figure 2. Temperature of reboiler was constant but at 4000 second decreased feed flow caused minimal but observable increase in temperature of distillate. The last two samples indicated that the sampling was not affecting column stability. After the last sample, the column was at total reflux mode for a short time, to demonstrate a weak change between the profile of steady-state and total reflux. Because the minimum sample volume in GC was 0.2 cm^3 the sample volume 4 cm^3 of distillate was needed due to large ratio of aqueous phase to organic phase. The steady-state was not disturbed by sampling but at total reflux the sample volume would have disturbed the column profile. The experimental and simulated temperatures were collected in Table 3. The condensation temperature was not measurable but simulated to provide information on the subcooling.

Table 3. Comparison of measured and simulated temperatures. Pressure in hPa and temperatures °C. Uncertainty in measured pressure 1 hPa, temperature of bottoms 0.1 °C and distillate 0.2 °C.

sample ID	pressure	T,bot,meas	T,bot,sim	T,top,sim	T,top,meas	T,cond,sim
S7	1007.2	100.0	100.0	99.3	99.1	88.1
S8	1006.2	100.0	100.1	99.5	99.4	88.1
S9	1006.2	100.0	100.1	99.5	99.4	88.1

The mass fraction of acetic acid in the reboiler is given in Table 4. The composition is very stable due to large hold up of the reboiler. MIBK and furfural were below the detection limit of GC in bottoms product.

Table 4. Mass fraction of components in the reboiler. Average uncertainty of measured mass fraction is 0.002.

	MIBK	water	acetic acid	furfural
S7	0.0000	0.9495	0.0505	0.0000
sim7	*0.0000*	*0.9468*	*0.0531*	*0.0001*
S8	0.0000	0.9476	0.0524	0.0000
sim8	*0.0000*	*0.9430*	*0.0570*	*0.0000*
S9	0.0000	0.9474	0.0526	0.0000
sim9	*0.0000*	*0.9440*	*0.0560*	*0.0000*

The mass fraction of components in the distillate fractions are shown in Figure 3 where MIBK in organic phase and water in aqueous phase are outside the zoom of vertical axis.

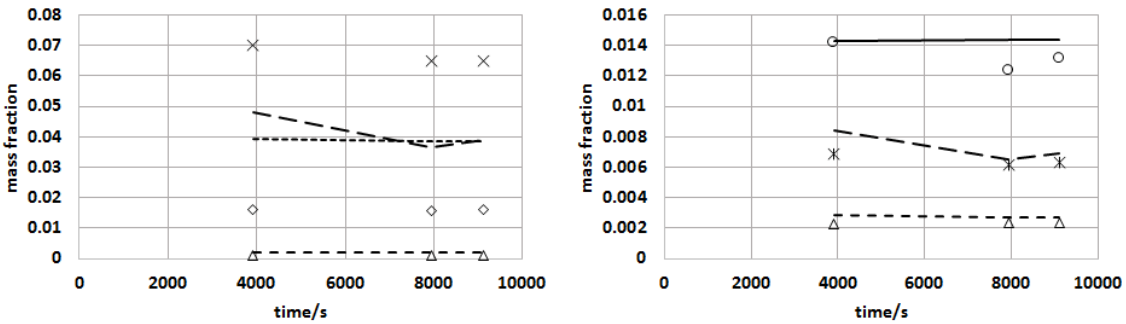

Figure 3 a, b: Mass fraction of minor components in organic (left) and aqueous (right) phase of distillate. MIBK , ○ and solid line; water, ◇ and square dot; acetic acid, △ and dash; furfural, × and long dash. Average uncertainty of measured mass fraction is 0.002.

Acetic acid was close to the detection limit of GC in organic phase. The simulation matched the experiments very well, but moderate deviation in MIBK and furfural in organic phase exists. However, amount of organic was small compared to aqueous phase. The experimental and simulated power of reboiler as well as measured and simulated mass flows are compared in Table 5.

The simulated power was less than the experimental and experimental mass flow of distillate was less than simulated mass flow. The simulation was assuming negligible heat loss thus requiring less power for reboiler. This indicates the heat loss of the real column, approximately 15 % of heating power was lost. The main heat losses are at the reboiler and feed section where the glass surface is exposed to ambient air. The conical and

spherical joints were insulated with aluminium foil. The column sections were insulated efficiently with vacuum jacket. In addition to insulation the high heating power is favourable to have larger flow of vapour and liquid inside the packing to promote mass transfer. Special attention to proper distribution of liquid to the center of packing and prevention of channelling is needed. In our set-up and simulation the reflux consisted of both the organic and the aqueous phase. The effect of aqueous phase reflux would have been interesting to study but it would have needed the modification of the existing set-up.

Table 5. Comparison of experimental and simulated reboiler power and mass flow of distillate. Uncertainty of measured power 25 W and mass flow 0.0015 g/s

sample ID	P, exp	P, sim	m,exp,aq	m,sim,aq	m,exp,org	m,sim,org
S7	500	425	0.0100	0.0149	not det	0.0021
S8	500	493	0.0100	0.0175	not det	0.0015
S9	500	438	0.0090	0.0155	not det	0.0015

5. Conclusions

This work presents a distillation test run with two liquid phases as distillate, and one liquid phase as bottoms product. The mixture was a heterogeneous minimum boiling system of MIBK, water, acetic acid and furfural. The GC analysis indicated that water and acetic acid were in the bottom product and all MIBK and furfural and some water were the distillate. As the feed is raffinate from an extraction, the distillate tends to form two liquid phases after condensing. It was necessary to use a vapour dividing head to split the vapour stream from the column into distillate and reflux parts before condensing.

The phase equilibrium model, developed earlier and including both vapour-liquid and liquid-liquid data, was used in Aspen Plus v8.8 simulation software. A very good match between experimental and measured composition and temperature was obtained. The experiments validate the phase equilibrium and simulation model. Based on the simulation the heat losses in this set-up was approximately 15 % of the reboilers power.

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