

Effect of Organic Solvents in Separation Section of Levulinic Acid Production: Synthesis of Distillation Sequences

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This work highlights the system specific characteristics encountered when considering a distillation-based separation strategy for levulinic acid (LA) and the by-product formic acid (FA) in the presence of water and water-miscible sulfolane or γ -valerolactone (GVL) solvents. Simulation using Aspen Plus® was applied to identify the presence of distillation boundary surfaces and tangent pinches resulting from the non-ideal behaviour of the mixtures in question. In the applied feed composition regions, the separation performance of the GVL solvent system in particular is limited by these restricting conditions. Minimum energy requirements for the separation of valuable components are presented as the conceptual design performance indicators, allowing the benchmarking of separation strategies. Sidedraw column configurations offer advantages in enriching the dilute valuable compounds from the feed and performing difficult separations at lower solvent quantities. This is especially advantageous for the sulfolane system where both LA and FA are intermediate-boiling.

1. Introduction

Levulinic acid (LA) was identified as one of the most promising platform chemicals attainable from biorefinery carbohydrates as early as in 2004 by the US DoE (Werpy & Petersen, 2004) and has been included in more recent reviews (Bozell & Petersen, 2009). Levulinic acid can be produced from cellulose by acid-catalysed hydrolysis to glucose, as in Eq(1), further dehydrating to 5-hydroxymethylfurfural (5-HMF), as in Eq(2), which undergoes a subsequent rehydration to LA according to Eq(3). Besides LA, the rehydration reaction yields formic acid (FA) as a by-product, commonly assumed to be formed in stoichiometric amounts, although recently Flannelly et al. (2016) pointed out a slightly higher formation of FA over LA from hexose carbohydrates. It is worth noting that the water balance around the overall reaction of one cellulose glucose unit converting to LA is zero. In addition to the products mentioned above the overall reaction scheme is characterized by the inevitable formation of both water soluble and insoluble humin by-products (Hoang et al., 2015).



Many publications focused on LA reaction schemes consider monomeric sugars as feedstock, namely glucose and fructose, as reviewed by Antonetti et al. (2016). Cellulose, however, can be directly subjected to acid-catalysed processing in different solvent systems presenting roughly similar LA yields as compared to monomeric sugar feedstocks (Mukherjee et al., 2015).

When cellulose is used as a feedstock, γ -valerolactone (GVL) solvent increases the reaction rates and allows lower concentrations of mineral acid catalysts to be used. High concentrations of GVL solvent also advantageously solubilise both the cellulose and formed humin by-product under reaction conditions, alleviating fouling in the reactor and making heterogeneous catalytic approaches more accessible in downstream processing (Alonso et al., 2013). Wettstein et al. (2012) also suggested that the need for the

separation of LA could be eliminated by direct catalytic hydrogenation of LA to GVL in the presence of GVL as a solvent. Sulfolane, an organosulphur solvent miscible both in water and hydrocarbons and widely applied in the separation of aromatics from hydrocarbon mixtures, was recently identified as showing comparable performance to GVL as a solvent in the acid-catalysed thermochemical conversion of cellulose to LA. A sulfolane-water solvent, preferentially in a mass ratio of 90/10, results in high LA yields, increases reaction rates and effectively restricts the formation of solid residues. (Wang et al., 2017)

Although favourable reaction conditions for LA production using different solvent systems have been extensively studied, less emphasis has been given to the separation of valuable components from reactor effluents. Suggested methods are mostly applied for aqueous reactor effluents and include, for example, solvent extraction (Nhien et al., 2016) and reactive extraction (Brouwer et al., 2017).

Distillation is the most widely used separation method for chemical mixtures in industry and distillation based separation system is commonly synthesised first for process performance evaluations. If the vapour-liquid equilibrium (VLE) does not create restrictions to the system, cascading a sufficient number of separation stages in ordinary distillation permits the attainment of unlimited product purities. Other benefits include reliable design methods and simple scale up to high throughputs. Even though distillation is highly energy intensive, its strengths are the motivation to subject it to preliminary evaluations of chemical recovery in LA production.

2. Methodology

The simulations were performed with an Aspen Plus® (V10) commercial process simulator. The thermodynamic properties of the system were determined according to the NRTL-HOC property method. Built-in model binary parameters were used for FA-water and sulfolane-water component pairs. Binary parameters for GVL-water and LA-water were adopted from Zaitseva et al. (2016) and Resk et al. (2014), respectively. The remaining binary pair parameters were estimated based on the UNIFAC functional group contribution method.

The feasibility of different separations was assessed based on minimum energy requirements for a given separation in individual columns. This was achieved using a reasonably high number of equilibrium stages (in this case, 80) in RADFRAC, the rigorous MESH equation-based distillation model in Aspen Plus.

The base case feed composition (in a 90/10 solvent-to-water ratio) for distillation section in this study was determined assuming 4 wt % cellulose feed consistency and around 50 mol % LA yield in the reactor section. The same LA and FA mass concentrations were assumed in 50/50 solvent-to-water ratio evaluations. The presence of a possible acid catalyst and humin material in the reactor effluents was not taken into account in this study. Mass basis is applied in reporting flow rates and concentrations throughout the article. Energy consumptions are reported per metric tons of LA recovered.

While sulfolane has a boiling point of 287 °C in atmospheric conditions, its decomposition into acidic compounds is accelerated at temperatures above 220 °C (Clark, 2000). The column pressures in sulfolane systems were thus fixed to 0.2 bar, where pure sulfolane boils at 220 °C. This also permits the use of high pressure steam as heating medium in the reboiler. Since GVL has a lower boiling point and is known to be thermally stable, the pressure in GVL systems was fixed to a more moderate 0.4 bar, allowing medium and high pressure steam utilities to be applied. Uniform column pressures were used in conceptual design simulations. Column feeds are at their bubble point temperatures in the column pressures.

3. Results and discussion

Water is always the lightest component (the unstable node) in the quaternary system regardless of whether GVL or sulfolane is present as a solvent and must be evaporated and recovered as a distillate. The effect of water was thus assessed by targeting high purity water as a distillate from the feed composition (the direct split scenario) in 90/10 and 50/50 solvent-to-water mass ratios while keeping the feed FA and LA concentrations constant. Another inevitable separation is the recovery of LA from the solvent where the main differences are due to the boiling points of the two solvents. The normal boiling point of LA is 245-246 °C, which renders it the heaviest component in the GVL-containing system (207-208 °C) while being more volatile than the sulfolane solvent (287 °C). LA-solvent separation was assessed in a binary distillation scheme where the solvent and LA quantities present in the quaternary feed mixture (F_1) to column C1 form the binary feed mixture (F_3) in column C3.

3.1 Sulfolane system

The direct split of water from the sulfolane system is relatively straightforward in the feed compositions in question (Figure 1a). A binary y-x plot indicates an easy separation between water and the high-boiling

sulfolane, and high purity water is separated with low reflux requirements. In Figure 1a, the residue curve map can be interpreted as the base of a regular tetrahedron, representing a quaternary water-LA-FA-solvent mixture with pure LA in the fourth vertex. Since LA concentrations in the direct split scenario are limited to less than 1.1 wt %, the distillation boundary line in the ternary diagram gives a good estimation for deducing the limiting effect of the actual four component distillation boundary surface near the pure solvent vertex of the composition region. The distillation boundary surface terminates in the lower edge of the triangle before the pure sulfolane vertex and thus exhibits no separation limiting effect on the removal of water from the bottom of column C1, as shown in Figure 1a.

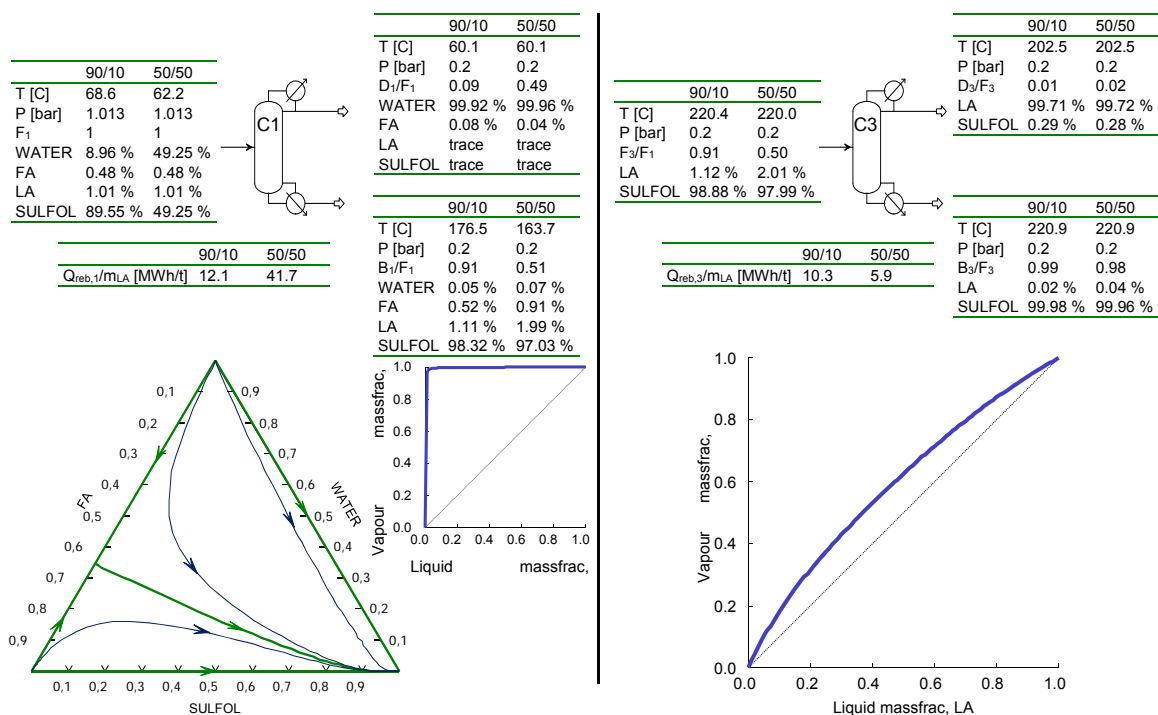


Figure 1: Sulfolane solvent system (0.2 bar) in a) direct water split in 90/10 and 50/50 solvent-to-water ratios and b) with a subsequent solvent-LA separation

When considering the effect of different feed solvent-to-water ratios, it is evident that the evaporation of large amounts of water with high heat of vaporization leads to high energy consumption in the reboiler. The energy consumption of a direct water split in the 90/10 solvent-to-water ratio is 71 % lower compared to the 50/50 system (Figure 1).

The subsequent separation of LA from sulfolane solvent is demonstrated in Figure 1b in a binary scenario. The y-x plot indicates that the separation of LA from sulfolane is a difficult one, requiring high reflux and a large number of stages. A higher solvent-to-water ratio leads to separation of LA from a higher solvent quantity. The energy requirements in the 90/10 solvent system are 76 % larger than in the 50/50 system.

3.2 GVL system

When considering the direct split of water from the feed mixture, the GVL system shows some complexing features. While the GVL-water binary system is known to be zeotropic (Horváth et al., 2008), it exhibits a tangent pinch near the pure water composition region (Figure 2a y-x plot and also apparent in the measured data of Zaitseva et al., 2016), which has an effect on the distillate purity of multicomponent separation. Targeting high purity product compositions is impractical in a tangent pinched system because of excessive reflux requirements. The assessment in the GVL direct split scenario was thus made by using the same energy input as in the sulfolane system, which does not show a tangent pinch nor is limited by the distillation boundary in the feed composition range (Figure 1a). The GVL system was then evaluated on the basis of achievable separation with this particular energy requirement. The results are shown in Figure 2a.

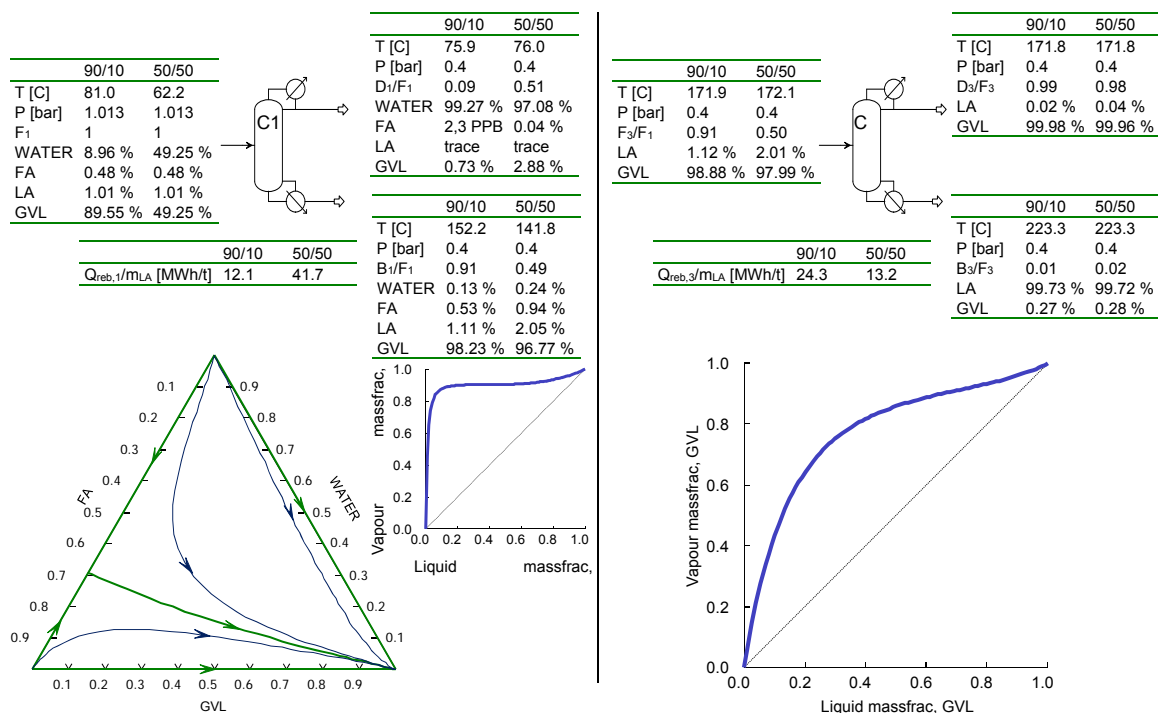


Figure 2: GVL solvent system (0.4 bar) in a) direct water split in 90/10 and 50/50 solvent-to-water ratios and b) with a subsequent solvent-LA separation

The equivalent energy input in the GVL system results in relatively high water purities even in the presence of a tangent pinch. Still, with large capacities, this purity limitation originating from the VLE of the system would lead to intolerable solvent losses and wastewater treatment requirements, especially if the feed water content is increased (50/50 solvent to water ratio in Figure 2a). Applying more reflux and thus more energy input against the tangent pinched distillate composition increases the purity, with approximately 26 % more energy input required to reach 99.99 wt % water purity in the 90/10 solvent-to-water ratio, as compared to results in Figure 2a. In addition, complete water removal from the bottoms is hindered by the fact that the distillation boundary surface extends from the water-FA binary maximum boiling azeotrope to the pure GVL vertex.

The separation of a higher-boiling LA from the GVL solvent leads to the recovery of LA as a bottoms product (Figure 2b). This leads to the evaporation of large solvent quantities to obtain pure LA. Moreover, according to the estimated VLE, this separation is also characterized by a tangent pinch ($y-x$ plot in Figure 2b), which in this case makes it difficult to completely recover LA to the bottoms product. The energy requirement with the 90/10 solvent-to-water ratio is 24.3 MWh/t of recovered LA and 13.2 MWh/t of LA with the 50/50 ratio (Figure 2b), which is 135 % and 125 % higher respectively than in the sulfolane case (Figure 1b) with the same LA purity and recovery specifications. In respect of an actual separation train based on GVL, it is likely that the bottoms-recovered concentrated LA product would require an additional purification step to attain market quality LA.

3.3 Sidedraw distillation sequences with 90/10 solvent-to-water ratio

As the higher 90/10 solvent-to-water ratio and sulfolane as a solvent clearly stood out from the simple distillation evaluation, the system in question was chosen as a basis for further assessment. Since both valuable components in the system, FA and LA, are intermediate-boiling in the sulfolane solvent system, a distillation sequence utilizing a liquid sidedraw below the main feed was set for further evaluation. The sequence is presented in Figure 3.

High purity water is evaporated from the C1 distillate. The intermediate-boiling FA and LA concentrate in the sidedraw. A rather low sidedraw-to-feed ratio (here 0.182) can be specified which effectively achieves a high recovery of both LA and FA to the sidedraw while also keeping the water concentration in the sidedraw very low. This facilitates the recovery of concentrated formic acid (over 99 wt %) from C2 distillate with very low energy requirements. Recovery of heat-sensitive FA from the sidedraw also prevents its exposure to high temperatures in the reboiler.

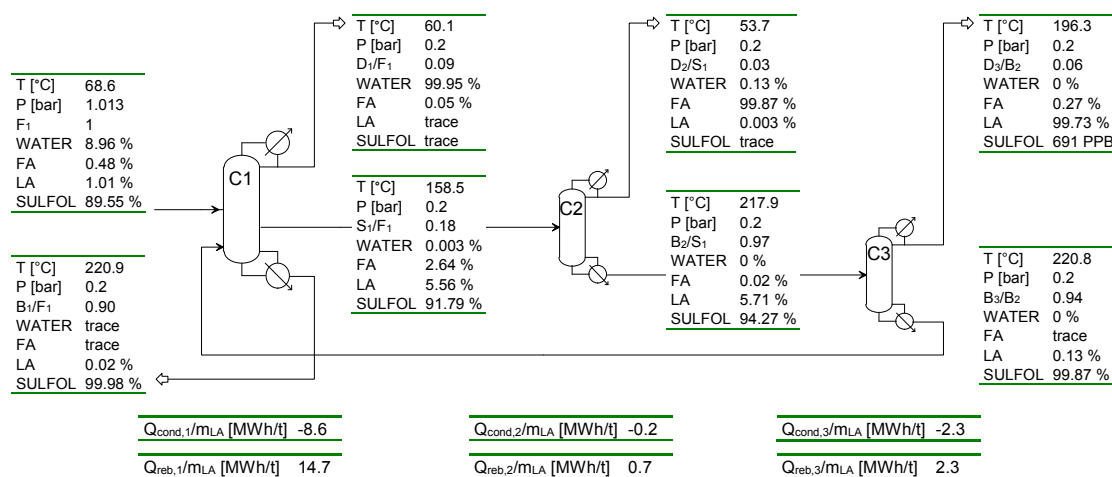


Figure 3. Sulfolane sequence utilizing liquid sidedraw in column C2

Directing LA to the C1 sidedraw alleviates its difficult separation from the bulk solvent as the total mass flowrate in the C3 feed is 80 % smaller and the feed LA concentration is 5.7 wt-% as compared to 1,1 wt % in simple distillation (Figure 1b, C3 feed). Furthermore, the contamination of both product streams with the solvent can be avoided, as the main impurity in the FA product (Figure 3, C2 distillate) is water while the residual FA ends up in the LA product (Figure 3, C3 distillate). Column C3 bottom stream containing sulfolane and residual LA is recycled to the lower part of column C1. The minimum energy requirement of the whole sequence is 17.7 MWh/t of recovered LA, which is 21 % lower than the combined energy requirement of 22.4 MWh/t if the direct water split and LA recovery from sulfolane are considered together (Figure 1a and Figure 1b).

Pure sulfolane is a low volatile solvent but its vapour pressure climbs with even small concentrations of water present in the mixture (Lee & Coombs, 1987). The feed temperature to column C1, determined as the bubble point temperature at a column pressure of 0.2 bar, is rather low (Figure 3). It follows that a large amount of the heat supplied in the reboiler goes to the sensible heat requirements of the solvent quantity to reach the high boiling point temperature of pure sulfolane in the reboiler. This is evident in the difference between condenser and reboiler duties (Figure 3). In a broader scenario, these high temperature bottom streams of sulfolane columns can be integrated into the reactor section of the LA manufacturing process or other surrounding processes in a lignocellulosic biorefinery for heat recovery.

A GVL-containing system was also considered with a sidedraw approach. Complete recovery of FA to the liquid sidedraw under the main feed of column C1 can also be accomplished when GVL is the solvent. However, the fact that the distillation boundary surface extends to the pure GVL vertex in the composition region (Figure 2a) now limits the amount of water removal that can be achieved in the sidedraw. Water in the sidedraw ends up in the formic acid product in the C2 distillate, limiting its concentration to a more dilute range. As LA is heavier than GVL, the introduction of a sidedraw cannot alleviate the separation of dilute LA as a large quantity of solvent must be evaporated at some point to recover the valuable compound.

4. Final remarks

As high solvent-to-water ratios have been shown to be beneficial in the reactor section of LA production, lowering the water content also yields obvious benefits in terms of energy consumption in the separation section, as less water with a high heat of vaporization needs to be evaporated.

Both sulfolane and GVL solvents enable the isolation of by-product FA in concentrated form although with GVL more water is present because the distillation boundary limits the product composition. This is a valuable advantage since in a solely water based system the recovery and concentration of dilute FA by distillation would be highly impractical because the maximum-boiling azeotrope restricts the composition and requires large quantities of water to be evaporated.

The most notable benefits of applying a high-boiling solvent such as sulfolane are that dilute intermediate-boiling valuable components can be directed to a sidedraw in higher concentrations and then recovered in high purities as distillates. The VLE poses additional limitations to GVL solvent systems as tangent pinches complicate high purity water removal and the efficient recovery of LA from the large quantities of solvent.

Experimental vapour-liquid equilibrium measurements are necessary to validate the behaviour of components in both solvent systems as the VLE-model binary pair parameters between FA-solvent and LA-solvent have been estimated by UNIFAC in this assessment.

Acknowledgments

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