Process design scheme on the feasibility of 1-decanol as a solvent in liquid-liquid extraction to recover anhydrous citric acid from water
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Abstract

In this present study, we developed a theoretical process design scheme (PDS) to check the feasibility of solvent 1-decanol to recover citric acid from water by liquid-liquid extraction followed by series of unit operations such as vacuum evaporator, crystallizer, and filter using ASPEN PLUS™. Literature suggested that the 1-decanol can serve as a solvent to recover the citric acid from water. However, the conditions maintain for the maximum production of anhydrous citric acid have been reported under the equilibrium condition. We incorporated the binary interaction parameters of the NRTL model in the simulation, as reported in the literature. The separation factor obtained from the simulation is compared and validated with the published literature data under a room temperature (25°C). We performed the mass balance and sensitivity analysis for the developed PDS. The results show that the maximum quantity of anhydrous citric acid is obtained in the extract phase when the solvent to feed ratio is more than six.

Introduction

Citric acid is a commercially important carboxylic acid widely used in various industries such as chemical, food and beverages, cosmetics, pharmaceutical, metal, textiles, paper, and tobacco industries. Of these industries, about 70% of citric acid produced is principally used in food and beverages because it is safe, gives pleasant flavour and taste, higher solubility, and offers resistance towards microbial growth that leads to a good food preservative. [1-2] In the year 2008, citric acid global production was reported as 1.4 million tons. [3] It became 2.3 million tons in 2020, and by 2026 it is expected to reach 2.9 million tons. [4] Citric acid can be produced from citrus fruits and microorganisms by chemical and biochemical (or fermentation) routes. In recent days, due increase in awareness of the eco-friendly production process, most global citric acid demand, about 99%, is satisfied through the fermentation process. [5]
Citric acid recovery from the fermentation mash involves the following steps: (i) the separation of insoluble biomass (suspended cells debris, proteins, minerals, and so on), (ii) segregation of organic compounds, (iii) recovery of citric acid from water and (ii) purification or concentration of citric acid to meet the required specification an end product. The primary unit operations used in these steps are filtration, solvent extraction, distillation, vacuum evaporation, crystallization adsorption, ion-exchange, electrodialysis, ultrafiltration, and advanced membrane separation using liquid membranes. [6-7,1] Among these unit operations, solvent extraction (liquid-liquid extraction) can be a suitable process to recover citric acid from the aqueous solutions where a large quantity of water is present in pre-treated fermentation mash. The other unit operations are recommended based on the concentration of citric acid from the aqueous solution, however for acid concentration <40 % w/w, it has been reported that the appropriate or suitable unit operation can be liquid-liquid extraction (LLE). Also, using LLE is a low cost and has relatively fewer environmental problems in the recovery of citric acid, especially from water, compared to other unit operations. [8-10]

The liquid-liquid extraction process uses the difference in the solubility of components in a liquid mixture whereby a solvent is added to the aqueous feed solution to preferentially extract the solute from the feed resulting in the extract and raffinate phase. In general, the extract phase consists of higher concentration of the extracted component. On the other hand, a relatively lower concentration of the extracted component in the raffinate phase. In some cases, based on a solvent’s properties selected for the extraction, the reverse may also be possible. Due to the solvent's presence in both the extract and raffinate phase, additional unit operations are required to recover the solvent. Other unit operations may be employed, following liquid-liquid extraction to recover solvent and further purification of extracted components.

The selection of Solvent for LLE plays a crucial role in predicting the feasibility of the process. Researchers used many solvents based on amines, ketones, esters or ethers, alkyl sulphoxides, and tributyl phosphate in the experimental analysis of Liquid-Liquid Equilibrium for the extraction of citric acid from water in the last few decades. [11-15,1] Even though the guidelines for selecting a suitable solvent for LLE are well established in the literature, detailed experimental and theoretical studies are required for commercial implementation. [16] We observed that minimal literature is published on the LLE of citric acid, followed by solvent recovery. [17-20, 9] Therefore, there is a need to develop a process design scheme (PDS) to understand suitable solvent's feasibility in extracting and purifying from water for commercial manufacture of citric acid. A process design scheme mentioned here communicates the arrangement of unit operations in a sequential manner that converts the raw material (feed) into useful product theoretically, along with mass balance and operating conditions (temperature and pressure) for each unit's operations.
In this present study, we attempt to develop a theoretical process design scheme (PDS) to check the feasibility of 1-decanol as a solvent reported [10] to recover anhydrous citric acid from water in feed at 0.111 (w/w). The separation factor in the literature mentioned above through experimental liquid-liquid equilibrium data using 1-decanol as the solvent is compared and validated in the present simulation using the Non-Random Two Liquid (NRTL) thermodynamic model. We perform a sensitivity analysis to identify the maximum recovery of citric acid by varying different solvent mass flow rates. The results obtained from the simulations are analyzed and presented.

**Problem formulation**

The process design scheme was developed and simulated using steady-state process simulator ASPEN PLUS™ V9. The properties of the feed components considered for the simulation is given in table 1.

| S. No. | Material/ Components | Chemical Formula | Density (kg/m³) |
|--------|----------------------|-----------------|-----------------|
| 1.     | Water                | H₂O             | 995             |
| 2.     | Citric acid          | C₆H₈O₇          | 1130            |
| 3.     | 1-decanol            | C₁₀H₂₂O₈         | 821             |

The water and citric acid are in the aqueous form of various compositions, and the solvent (1-decanol) added is pure. Initially, citric acid is extracted from the water by adding 1-decanol using a liquid-liquid extraction column and recovered through a series of unit operations. The unit operations chosen for the study are a liquid-liquid extractor, vacuum evaporator, crystallizer, and a rotary filter. The feed concentration is taken from the literature [10]. Even though the extraction of citric acid from water using 1-decanol is reported [10], the 1-decanol's feasibility as a solvent with series of unit operations to extract and recover the citric acid from water is not reported. Therefore, in this study, we considered a theoretical process design scheme with a series of possible unit operations to recover the citric acid from water.

**Process design scheme**

The process design scheme with a series of unit operations starting from liquid-liquid extraction to solid-liquid filtration is presented in figure 1. The feed is introduced at the top and the pure solvent at the bottom of the extraction column (EXTRTS). The extractor's product has two streams routes: (i) the extract stream (EXTRACT) route and (ii) the raffinate stream (RAFFINAT) route. The extract stream is fed into the vacuum evaporator (VACEVP1) to remove the solvent (EXTVAP), and the liquid
containing solvent and citric acid (EXTCONC) is further concentrated in the vacuum evaporator (VACEVP1) and finally growth of the crystal in crystallizer (CRYS1). The concentrated liquid (EXTAFCRY) is then filtered in a filter (FILTER1) to get crystals of citric acid (EXTCRY). A similar scheme is adopted in the raffinate stream (RAFFINAT) from the extraction column with a vacuum evaporator (VACEVP2) to separate the water (RAFFVAP) from citric acid (RAFFCONC), followed by the concentration of citric acid in crystallizer (CRYS2) and filter (FILTER2). The final anhydrous crystals of citric acid (RAFCRYS) is obtained from the raffinate stream [Figure 1].

![Diagram](image_url)

Figure 1 Process design scheme for the recovery of acetic acid from water

**Results and Discussion**

The process design scheme developed and presented in figure 1 is systematically studied through data validation, mass balance, and sensitivity analysis. We discussed the results obtained from the simulation here.

**Process Validation**

Using a process simulator like ASPEN PLUS™ the validation of results with experimental data becomes essential. As a first step, the components such as water, citric acid, and the solvent 1-decanol
are selected, and then the NRTL model was chosen. The interaction parameters for the NRTL model is taken from the literature [10] and assigned in the Aspen for three different feed concentrations. The resulting data from the simulation are compared with the separating factor reported in the literature [10] and presented in table 2.

Table 2: The comparison between simulated results and the published literature

| S. No. | The concentration of feed (w/w) | Separation factor (-) from literature | Separation Factor (-) from simulation | Percentage deviation, (%) |
|--------|---------------------------------|--------------------------------------|--------------------------------------|---------------------------|
| 1.     | 0.1110                          | 4.2501                               | 3.9894                               | 5.0132%                   |
| 2.     | 0.2005                          | 3.6429                               | 3.4961                               | 3.9532%                   |
| 3.     | 0.2720                          | 3.2125                               | 3.1276                               | 2.7163%                   |

The separation factor (dimensionless) is defined as the ratio of distribution coefficients of water and citric acid in both the extract and raffinate phases. It is noted that the percentage deviation is in the acceptable range between 2.7 and 5.01% for all the feed concentrations considered.

**Process design scheme with mass balance**

The PDS showed in figure 1 is simulated to get the anhydrous crystals. The process simulation was performed with a mass flow rate of 250 kg/h with concentrations of citric acid in water in the feed, as shown in table 1, and the optimized solvent (1-decanol) flow rate as 2000 kg/h. The mass balance and the operating conditions for each unit’s operations (temperature and pressure) used in the PDS at 25°C are summarized and given in table 3.

Table 3 Mass balance data obtained from the simulation

| Stream Name | Units | FEED | SOLVENT | EXTRACT | EXTVAP | EXTCONC | EXTACEV1 | EXTACRY | EXTFIL1 | EXTFIL2 | RAFFINAT | RAFFVAP | RAFFCONC | RAFFACEV1 | RAFFACRY | RAFFFIL1 | RAFFFIL2 | FILTER1 | FILTER2 |
|-------------|-------|------|---------|---------|--------|---------|----------|---------|---------|---------|----------|---------|----------|----------|----------|---------|---------|---------|---------|---------|
| Description |       |      |         |         |        |         |          |         |         |         |          |         |          |          |          |         |         |         |         |
| From | EXTRTR | EXTRTR | VACEV1 | VACEV1 | CRYSTL | CRYSTL | FILTER1 | FILTER1 | ENTRTR | ENTRTR | VACEV2 | VACEV2 | CRYSTL | CRYSTL | FILTER2 | FILTER2 | FILTER2 | FILTER2 |
| Temperature [°C] | 25.05 | 25.05 | 26.55 | 26.55 | 26.55 | 26.55 | 26.55 | 26.55 | 26.55 | 26.55 | 26.55 | 26.55 | 26.55 | 26.55 | 26.55 | 26.55 | 26.55 | 26.55 |
| Pressure [bar] | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 |
| Mass Flows [kg/hr] | 25.05 | 25.05 | 25.05 | 25.05 | 25.05 | 25.05 | 25.05 | 25.05 | 25.05 | 25.05 | 25.05 | 25.05 | 25.05 | 25.05 | 25.05 | 25.05 | 25.05 | 25.05 |
| Water | kg/hr | 22.22 | 22.22 | 22.22 | 22.22 | 22.22 | 22.22 | 22.22 | 22.22 | 22.22 | 22.22 | 22.22 | 22.22 | 22.22 | 22.22 | 22.22 | 22.22 | 22.22 |
| 1-Decanol | kg/hr | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Mass Fractions |       |      |         |         |        |         |          |         |         |         |          |         |          |          |          |         |         |         |         |
| WATER |       | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1-Decanol |       | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
The overall percentage recovery of anhydrous citric acid (%OPRACA) defined as the sum of the ratios of mass flow rate ($m$) of anhydrous citric acid obtained at EXTCRY and RAFCRYS to that of mass flow rate ($m$) of citric acid fed into the extraction column (EXTRTR).

\[
%\text{OPRACA} = \left[ \frac{m_{\text{citric acid at EXTCRY}}}{m_{\text{citric acid in EXTRTR}}} \right] \times 100 + \left[ \frac{m_{\text{citric acid at RAFCRYS}}}{m_{\text{citric acid at EXTRTR}}} \right] \times 100
\]

Table 3 shows that the maximum citric acid recovery % OPRACA is obtained through the extract stream route when compared to the raffinate stream route. About 90.09% of anhydrous citric acid is produced at 25°C.

**Sensitivity analysis**

Sensitivity analysis for the principal unit operations (extraction column, the vacuum evaporator units in both extract and raffinate stream routes) is performed by varying the mass flow rates, temperatures, and solvent flow rate as the product’s (anhydrous citric acid) function. The recovery of anhydrous citric acid crystals is reported as the temperature in the vacuum evaporators (VACEVP1 and VACEVP2), as shown in figure 2. The temperature range selected for the analysis is based on the boiling point of the solvent (1-decanol) in the vacuum evaporator (VACEVP1) of the extract stream from the extraction column (EXTRTR) and the boiling point of water in the vacuum evaporator (VACEVP2) of raffinate stream (RAFFINAT) from the extraction column (EXTRTR). The mass flow rate of citric acid in the extract and raffinate phase for various temperature ranges is shown in figure 2.

![Figure 2](image-url)

Figure 2 Anhydrous citric acid formation as a function of temperature in (a) VACEVP1 (b) VACEVP2 at 0.1 and 0.6 atm, respectively
Figure 3 Variation of solvent flow rate (a) formation of anhydrous citric acid at EXTCRY and RAFCRYS (b) mass flow rate of citric acid at EXTRACT and RAFFINAT.

Figure 3 shows that citric acid present in the extract and raffinate phase and the formation of anhydrous citric acid in filter1 and filter2 vary the solvent mass flow rate. The solubility of citric acid in decanol is less than water. Thus, the solvent's mass flow required more to extract citric acid in the extract phase than the feed's mass flow.

**Conclusion**

We developed a process design scheme to understand the solvent 1-decanol to recover citric acid from water by liquid-liquid extraction using ASPEN PLUS™ V9. The sensitivity analysis shows that maximum anhydrous citric acid crystals were obtained for the higher mass flow rates of solvent at room temperature (25 °C). It is noticed from the results that the 1-decanol can separate the citric acid from water. However, the crystals’ recovery from aqueous solution may be more without using the liquid-liquid extractor at 25°C. Furthermore, the formulated simulation may extend the present simulation for other suitable solvents, a wide range of operating conditions, and the techno-economic feasibility for the industrial-scale citric acid manufacturing processes. Hence, the proposed PDS may be useful for the process design engineers involved in the preliminary design and development of downstream processing of citric acid from water to produce anhydrous citric acid.
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