



EMULSION-BASED ISOLATION OF DILUTE CARBOXYLIC ACIDS

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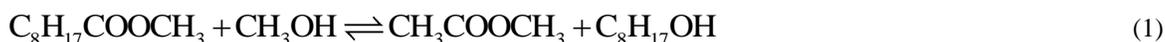
Abstract

Isolation and utilization of dilute carboxylic acids from pulping condensate is technically as well as economically a challenging task. As these valuable constituents are hitherto subject of either wastewater treatment or combustion due to a lack of suitable, efficient separation and isolation technologies, the proposed process concept by combination of liquid-liquid extraction with chemical conversion may provide a sustainable solution. Central part in this concept is the chemical conversion of carboxylic acids in a biphasic emulsified regime to tackle the specific needs of highly dilute aqueous feed. Regeneration of the product carrying solvent phase via transesterification in reactive distillation is a promising intensification step. Experimental investigation based on design of experiments provided insight into process parameter interaction and impact on process performance. The concept was tested for 1 mol/L carboxylic acid and a solvent phase consisting of 1-octanol, *n*-undecane and the catalyst 4-dodecylbenzenesulfonic acid. Additional to its catalytic Bronsted acidity, 4-dodecylbenzenesulfonic acid embodies potential surface-active properties, essential for boosting process performance. This combination of catalytic activity and surfactant properties highly enhances esterification and separation efficiency. Thus, conversion of carboxylic acids beyond 90 % is feasible, compared with 4 % in a non-catalysed reference experiment. Product isolation is easily achieved by transesterification with low molecular weight aliphatic alcohols in reactive distillation.

Keywords: reactive separation, emulsification, carboxylic acids, catalysis, reactive distillation

Introduction

Production of bulk chemicals from biobased resources is highly encouraged particularly in context with sustainability. This task is challenging biorefinery for decades, as processing of biobased raw materials has to deal with many different obstacles. Azeotrope formation, high water content and low concentration of the desired constituents are only a few of these obstacles to be faced [1]. Conventional processes are not capable of dealing with this challenge efficiently and economically. An example for such an incapability is the isolation of low molecular weight carboxylic acids from aqueous condensate streams in the pulping industry. Reactive separation technologies like reactive distillation and reactive extraction are suggested to meet the necessities of biobased feed streams [2]. Toth et al. [3] proposed the concept of combining chemical conversion with in-situ extraction of reaction products for this problem. For esterification of 1 mol/L carboxylic acid (e.g. acetic acid) with 1-octanol to octyl ester and water, the concept was proven to be applicable with the key feature of emulsification. Highly enhanced mass transfer as a consequence of emulsification is induced by the surface-active catalyst 4-dodecylbenzenesulfonic acid [4]. In order to finish the process cycle, an efficient regeneration of the solvent phase after emulsion splitting is necessary. In the present project concept, a reactive distillation step utilizing transesterification is proposed for this task. Therefore, a low molecular weight aliphatic alcohol (methanol or ethanol) is added to the laden solvent phase and used for transesterification from octyl acetate to methyl acetate or ethyl acetate. The reaction equation for transesterification with methanol is shown in equation 1.



As shown in equation 1, the transesterification leads to methyl acetate formation and 1-octanol formation. Thereby, 1-octanol, reactant for the emulsion-intensified esterification, is regenerated and the removal of the low

molecular weight ester is simply performed via distillation. The latter is achieved by reducing the boiling temperature from octyl acetate of 211 °C to 57.1 °C of methyl acetate or 77.1 °C of ethyl acetate. The process concept, including the solvent regeneration and product isolation, is shown in figure 1.

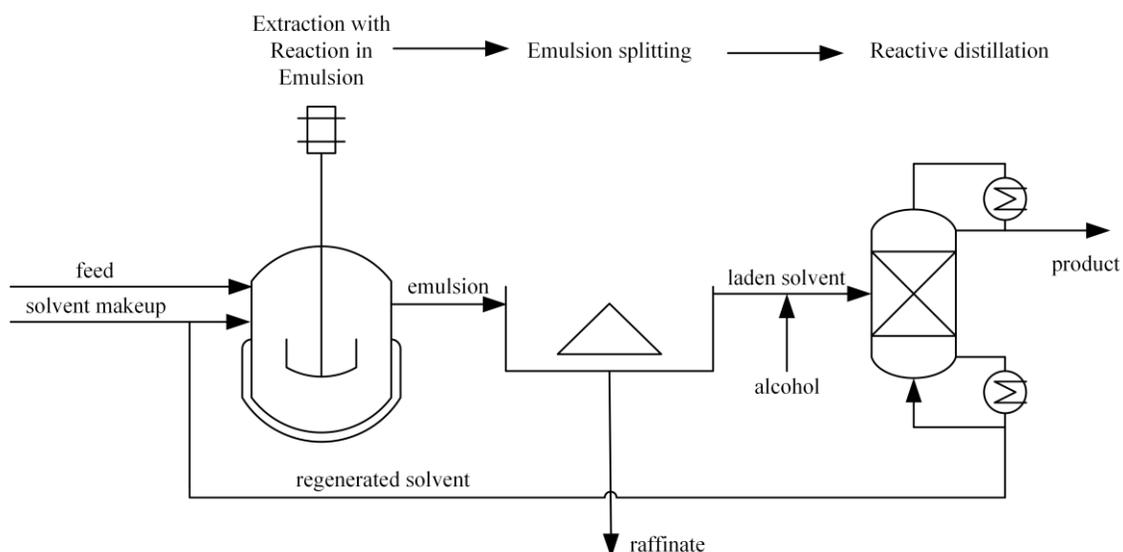


Figure 1 Proposed process concept for isolation of dilute carboxylic acids by emulsified biphasic esterification and solvent regeneration/product isolation by reactive distillation with transesterification.

Materials and methods

Materials

As feed for the esterification step 1 mol/L acetic acid was used; the solvent phase consisted of the diluent *n*-undecane, the reactant 1-octanol and the surfactant-type catalyst 4-dodecylbenzenesulfonic acid (4-DBSA). Acetic acid (SigmaAldrich) and *n*-undecane (SigmaAldrich) were used at a purity of 99.9 %. 1-octanol (SigmaAldrich) was used at 98 % and 4-DBSA (Sigma Aldrich) at 95 % purity. All chemicals were used without further preparation. The feed used for transesterification consisted of *n*-undecane, 1-octanol, octyl acetate and the catalyst 4-dodecylbenzenesulfonic acid, without residual acetic acid. The reactants methanol (ChemLab) and ethanol (ChemLab) were used at 99.9 % purity.

Methods

Esterification in the emulsified regime was investigated in a jacket batch reactor with a volume of 1000 ml. The batch reactor was stirred with a triple Rushton-Turbine impeller and heated with a thermostat with water as heat transfer medium. A custom-made PTFE-lid, comprising vents for temperature measurement, sampling and the stirrer shaft sealed the batch reactor. Reaction time was fixed to 3h. Emulsions were split with a Heraeus Labofuge 400. Samples were taken from both phases after emulsion splitting.

Transesterification kinetics for octyl acetate transesterification to methyl acetate or ethyl acetate were performed in a three-neck flask (500 ml) with a total condenser atop. The remaining necks were used for temperature measurement and sample taking. The transesterification progress was monitored via sampling every 15 min during a reaction time of 5 h.

Solvent regeneration via transesterification was performed in a batch reactive distillation setup. The setup consisted of a 500 ml three-neck flask (reboiler) with a 30 cm Vigreux column with a condenser and a reflux splitter. Temperature was measured in the reboiler and on the top of the column. The external reflux was set to infinity until the siphon of the condenser was filled with product, and then adjusted to a reflux ratio of 10 (after 2 h). The initial

temperature of 120 °C was increased by a rate of 10 °C per 30 min. Product was withdrawn, weighed and analyzed every 30 min for an overall experimental time of 7 h.

Analytcs

All samples were analyzed via gas chromatography in a Shimadzu GC2010 plus. A Zebtron ZBWaxPlus column (60 m x 0.32 mm x 0.5 µm) was used. Analytes were detected with a flame ionization detector (FID) and a thermal conductivity detector (TCD) in parallel operation. Samples were cooled to 5 °C and injected undiluted at a volume of 0.3 µl at 270 °C. The temperature program started at 40 °C with a hold time of 5 min followed by a ramp with a slope of 20 °C/min to 150 °C, and a final hold of 3.3 min at 150°C. All analytes were determined via FID, except for water.

Results and discussion

Results

Acetic acid esterification in the emulsified, biphasic regime was evaluated based on a design of experiments approach. This approach yielded a model for prediction of conversion and separation efficiency. In single-step esterification at 60 °C a conversion of over 70% is achieved, which can be further increased by using the aqueous phase again in a second step with fresh solvent. As catalyst loads above 0.06 eq/mol based on initial acetic acid cause high emulsion stability, increasing the reaction temperature was preferred for further performance optimization. A reaction temperature of 95 °C cuts reaction time compared to 60 °C experiments by 50%, yielding 75 % conversion. Elevating the reaction temperature in combination with a multi-stage process definitely offers complete isolation of acetic acid from the aqueous feed on industrial scale.

Based on the composition of the solvent phase after emulsion splitting, a feed for the solvent regeneration step was used to evaluate reaction kinetics of transesterification. To focus on transesterification rather than on simultaneous esterification of residual acetic acid and transesterification of octyl acetate, an acetic acid free feed was chosen. The concentration profile of the kinetics experiments is displayed in figure 2.

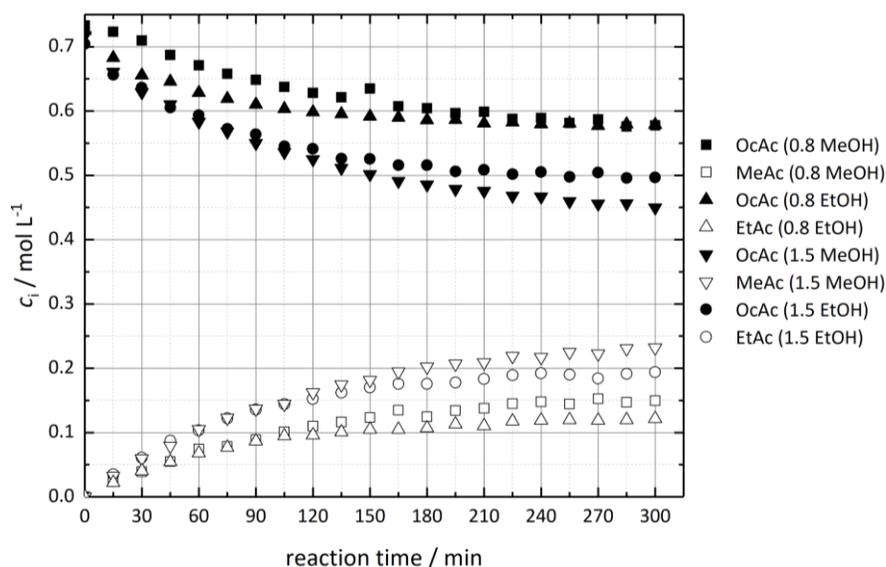


Figure 2 Concentration of octyl acetate (OcAc), methyl acetate (MeAc) and ethyl acetate (EtAc) during transesterification with methanol (MeOH) and ethanol (EtOH) at stoichiometric ratios of 0.8 and 1.5 based on octyl acetate; reaction temperature for MeOH 50 °C and for EtOH 70 °C.

The diagram in figure 2 compares the octyl acetate drop over time for transesterification with methanol at 50 °C and ethanol at 70 °C. Reaction temperatures were chosen in dependency of the boiling points of the lower esters to

avoid loss due to evaporation at ambient pressure. As displayed by the profile of octyl acetate for transesterification with a stoichiometric ratio of alcohol of 0.8, the reaction with either of the two short chain alcohols performs well within the investigated reaction time, yielding a conversion of 20.5 %. Excess usage of low molecular weight alcohol (stoichiometric ratio 1.5) increases conversion to 38 % for methanol and 30 % for ethanol.

Due to the higher temperature difference between methyl acetate and methanol, this combination was preferred over ethanol/ethyl acetate for batch reactive distillation experiments. With a 1.5-fold excess of methanol a conversion of octyl acetate of 60 % was achieved. The results confirm applicability of transesterification reactive distillation for regenerating the solvent phase.

Conclusion

The concept of emulsified, biphasic esterification combined with solvent regeneration by reactive distillation was confirmed to be suitable and practicable for isolation of acetic acid from dilute aqueous feed. Utilizing 1-octanol for esterification in the extraction/reaction step to form octyl acetate as an intermediate enables separation rates of over 80 %. Transesterification of octyl acetate to methyl acetate in reactive distillation is feasible for removal of the product and for regenerating the solvent phase, since 1-octanol is also regenerated during transesterification.

References

- [1] Painer, D., Lux, S., Graftschafter, A., Toth, A., & Siebenhofer, M. (2017). Isolation of Carboxylic Acids from Biobased Feedstock. *Chemie Ingenieur Technik*, 89(1-2), 161–171. <https://doi.org/10.1002/cite.201600090>
- [2] Talnikar, V. D., & Mahajan, Y. S. (2014). Recovery of acids from dilute streams : A review of process technologies. *Korean Journal of Chemical Engineering*, 31(10), 1720–1731. <https://doi.org/10.1007/s11814-014-0202-4>
- [3] Toth A., Lux S. & Siebenhofer M. (2017, October). *Intensified process concept for isolation of carboxylic acids from aqueous effluents*. Paper presented at the 7th International Thai Institute of Chemical Engineering, Bangkok, Thailand.
- [4] Hagen, J., & Henke, D.-I. D. (2009). Katalysatorscreening bei der Umesterung von Fetten und Ölen mit Ethanol. *Chemie Ingenieur Technik*, 81(9), 1429–1438. <https://doi.org/10.1002/cite.200800186>