**Reactive Extraction and Solvent Regeneration for Efficient Biobased Byproduct Isolation.**

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**Highlights**

* Reactive extraction is perfectly suited for recovery of dilute carboxylic acids.
* Reactive distillation shows high potential for efficient solvent regeneration.
* High yields of methyl esters were achieved in reactive distillation with catalysis.
* Homogeneous catalyst circulation between extraction and distillation is feasible.

**1. Introduction**

In the biorefinery, downstream processing is often faced with dilute multicomponent mixtures with high tendency to azeotrope formation. In pulping for example, a wastewater is produced, which contains carboxylic acids, mainly acetic acid and formic acid. For a 200 000 t a-1 pulp production capacity Sjöström [1] calculated the formation of carboxylic acid and hydroxycarboxylic acid with 75 500 t a-1. Depending on the process, the volatile carboxylic acids are evaporated from the black liquor with the water before the black liquor is incinerated. Due to environmental reasons the carboxylic acids need to be removed from the wastewater. By isolating the pure acids wastewater treatment could contribute to process economics. State of the art process for the recovery of carboxylic acids from aqueous streams is reactive extraction with several distillation steps (e.g. entrainer distillation, vacuum distillation), necessary for solvent regeneration. The aim of this project is to simplify downstream processing for the economic recovery of carboxylic acids from pulping.

**2. Methods**

*Process concept:* Reactive extraction is well investigated and perfectly suited for acid recovery from aqueous effluents. For solvent regeneration, reactive distillation is investigated to improve separation performance in distillation. Therefore, the carboxylic acids are esterified with methanol to produce low boiling methyl esters. The esters are continuously separated in the distillate, which forces the reaction equilibrium composition in the solvent to complete conversion. The regenerated solvent with the reaction water is cycled back to the extraction step, where the reaction water is transferred to the raffinate.

*Reactive extraction:* Liquid-liquid equilibrium experiments were performed for single acid and multi acid aqueous mixtures with Cyanex®923 as reactive extractant (70 w% in *n*-undecane) at 25 °C. The influence of a strong acid (4-dodecylbenzenesulfonic acid) in the solvent phase on the equilibria was quantified.

*Reactive distillation:* Solvent regeneration was investigated in batch reactive distillation experiments with different acid concentrations and molar ratios of methanol to acid. To increase the reaction rates, strong acidic catalysts were admixed. For catalysis, Amberlite IR-120, a heterogeneous catalyst, and the homogeneous catalyst 4-dodecylbenzenesulfonic acid were studied.

**3. Results and discussion**

*Reactive extraction:* The reactive extractant Cyanex®923 showed good extraction efficiencies in single and multi-acid mixtures. In single-acid experiments, formic acid and acetic acid were extracted in a similar extent while for a multi-acid mixture, formic acid was preferably extracted to the solvent phase. This occurs due to the tendency of Cyanex®923 to adduct formation with stronger acids. This behavior was also observed when 4-dodecylbenzenesulfonic acid was admixed to the solvent phase. In this case, Cyanex®923 formed the adducts with the strongest acid, limiting the extraction efficiencies of formic acid and acetic acid. However, at low acid concentration like in wastewater from pulping, enough reactive extractant is available in the solvent phase for adduct formation with all acids. [2]

*Reactive distillation:* High solvent regeneration efficiency is essential for appropriate extraction efficiency. Uncatalyzed batch reactive distillation experiments showed already high yields of methyl formate transfer to the distillate of 95 %. Acetic acid reacted too slow for appropriate solvent regeneration. The low rate of acetic acid esterification was the main reason for admixing 4-dodecylbenzenesulfonic acid to the solvent phase for catalysis. The yield of methyl acetate increased from 19 % for uncatalyzed to 88 % for catalyzed experiments with an amount of 5 w% 4-dodecylbenzenesulfonic acid in the solvent phase. [2] The heterogeneous catalyst Amberlite IR-120 increased the reaction rate to a similar extent. The main advantage of heterogeneous catalysis is, that catalyst separation from the solvent is not necessary as it is fixed in the distillation column. However, a temperature limitation has to be considered.

In homogeneous catalysis, the drawback is the catalyst separation step. To avoid an additional process step, the influence of the catalyst in the solvent phase during extraction was investigated. As already mentioned the reactive extractant Cyanex®923 prefers adduct formation with strong acids, loss of catalyst to the aqueous phase can be neglected. The limited extraction efficiency can be circumvented by increased phase ratio of the solvent to the raffinate phase. Because of the partition characteristic of the system carboxylic acid/Cyanex 923 based solvent/water, which is a Langmuir-type liquid-liquid equilibrium, low acid concentration in the aqueous phase does not suffer from admixture of 4-dodecylbenzenesulfonic acid.

**4. Conclusions**

Reactive separation shows high potential for efficient downstream processing of aqueous multicomponent mixtures. Combination of reactive extraction and reactive distillation for solvent regeneration offers the opportunity of economic isolation of acetic acid and formic acid from waste effluents by transferring them into their methyl esters.

**References**

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2. D. Painer, S. Lux, M., C. Almer, S. Daniel, Siebenhofer, Sep. Sci. Technol. 53 (2018) 1957-1965