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REACTIVE DISTILLATION FOR SOLVENT REGENERATION; HOMOGENEOUS VS. HETEROGENEOUS CATALYSIS

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Abstract

Biobased processes may be faced with dilute multicomponent mixtures. During wood valorization for example by-products like carboxylic acids and hydroxycarboxylic acids are produced besides lignin. For complete usage of biomass these by-products need to be isolated. However, the isolation step is challenging. State of the art process concepts involve reactive extraction for acid isolation from the effluent and several distillation steps for solvent regeneration and product isolation. To simplify the downstream processing, reactive distillation was investigated for solvent regeneration as well as product isolation. Methanol as esterifying agent produces low boiling methyl esters which can easily be separated in the distillation step. Therefore, the reaction equilibrium composition is shifted to the product side and complete solvent regeneration is feasible. To provide high regeneration efficiency for great extraction performance, homogeneous and heterogeneous catalysis was investigated. Heterogeneous catalysts can be fixed in the distillation column. Separation of the catalyst from broths is simple. Deactivation of the catalyst by components in the effluent has to be considered. For homogeneous catalysis a concept was developed and tested to keep the catalyst in the solvent phase during extraction via adduct formation with the reactive extractant. The catalyst must suffice the needs of extraction as well as chemical conversion. During distillation the catalyst is released from the extractant adduct due to elevated temperature. Therefore also in homogeneous catalysis no additional catalyst separation step is necessary.
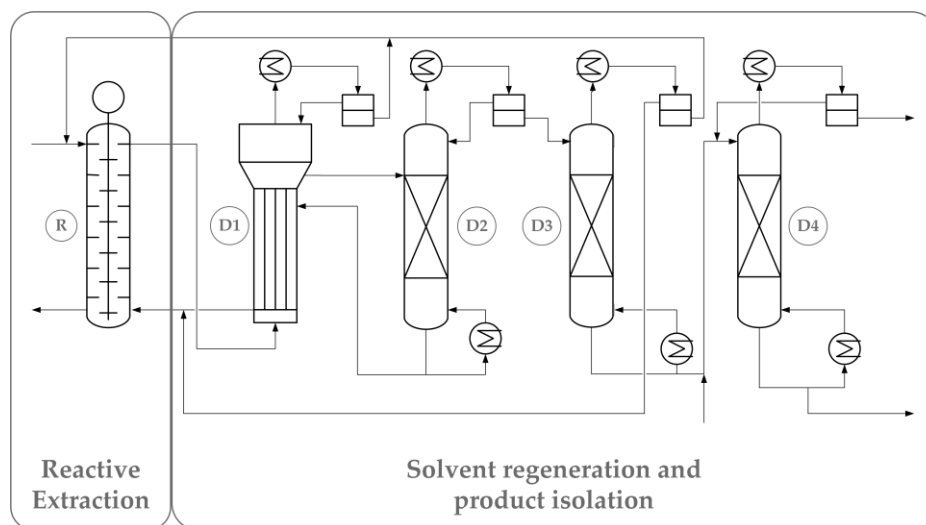
Keywords: Solvent regeneration, Reactive distillation, By-product recovery, Biobased processes, Process intensification

Introduction

To reduce the CO_2 content in the air, a shift from fossil fuel based to biobased resources is necessary. But to deal with the multitude of biobased feed, complete utilization of biobased feedstock material needs to be enforced and implemented. In wood valorization for example mainly the fibers are used as product and all by-products such as lignin, carboxylic acids and hydroxycarboxylic acids are still used for thermal energy production. Before incineration the water content must be removed from black liquor via evaporation. Together with the water also volatile carboxylic acids such as acetic acid and formic acid are removed from black liquor. Without further treatment this wastewater would harm the environment. The growing mind for environmental protection led to strict pollution control laws and pushed the need of wastewater treatment. In 1981 a process for pulping wastewater treatment with isolation of by-products like acetic acid, formic acid and furfural was patented [1]. As can be depicted from figure 1, reactive extraction (R) for removal of the impurities from the wastewater is an ease. However solvent regeneration and final product isolation performed via several vacuum distillation and entrainer distillation steps (D1-D4) is the challenging and energy intensive task.

The aim of this research project is to intensify the treatment of wastewater from black liquor thickening, to reduce the energy demand and investment costs by implementing reactive separation techniques. For solvent regeneration, reactive distillation was investigated to circumvent azeotrope formation for simplified downstream processing. Admixture of methanol to the laden solvent in the distillation column leads to formation of low boiling methyl esters which can be easily separated from the solvent via distillation. Due to the slow rate of esterification reactions, appropriate catalysts were screened to achieve high solvent regeneration efficiency within short residence time. Heterogeneous catalysts have the big advantage of simple separation from the reaction broth, nevertheless

several steps such as mass transfer, diffusion to the active centers, adsorption and desorption contribute to the overall reaction rate. Catalyst deactivation by impurities cannot be avoided, especially in wastewater treatment. For comparison, homogeneous catalysis has the only drawback of catalyst separation which makes an additional separation step necessary. The heterogeneous catalyst Amberlite®IR-120 and the homogeneous catalyst 4-dodecylbenzenesulfonic acid (DBSA) were tested and compared in batch reactive distillation experiments. To avoid catalyst separation of the homogeneous catalyst from the solvent after distillation, its impact on the extraction step was investigated. The solvent mixture was made up of the diluent *n*-undecane and the Lewis basic extractant Cyanex®923 plus the catalyst. The reactive extractant Cyanex®923 prefers stronger acids over weaker acids, it therefore primarily forms adducts with the strong acidic catalyst DBSA. The interaction of the catalyst with the extractant keeps it in the solvent phase during extraction, but for catalysis this interaction is disadvantageous. However, in reactive distillation the catalyst is released from the reactive extractant due to elevated temperature and can catalyze the esterification reaction.

Reference: Adapted from Kanzler et al. (1981) [1]

Figure 1 Pulping wastewater treatment for recovery of acetic acid via reactive extraction followed by solvent regeneration and product isolation via azeotropic distillation

Materials and methods

Materials

Acetic acid (99-100 %), formic acid (98-100 %) and methanol (99,8 %) were purchased from ChemLab. The reactive extractant Cyanex®923 (93 %) was obtained from Cytec. From Sigma-Aldrich the catalysts 4-dodecylbenzenesulfonic acid (≥95 %) and Amberlite®IR-120 (H^+ form) and the diluent *n*-undecane (99 %) were obtained. All chemicals were used without further purification.

Methods

The experimental setup of the batch reactive distillation shown in figure 2 consisted of a 500 cm^3 three necked flask as reboiler, an insulated 30 cm Vigreux column, a condenser and a reflux splitter. The reboiler was heated and steadily stirred by a Heidolph heating plate with magnetic stirrer. The condenser was cooled to 5 °C with a Lauda cryostate and the reflux splitter was controlled by a Lab.-Kybernet controller from Brand. The distillate was collected in a product funnel.
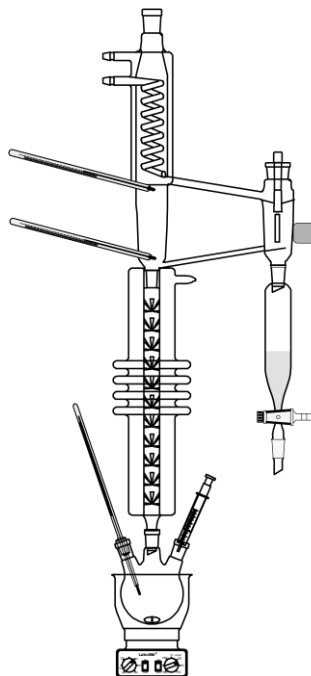
Figure 2 Scheme of experimental setup for batch reactive distillation

The solvent phase (70 w% Cyanex®923 in *n*-undecane) was mixed with the catalyst, formic acid and acetic acid in the reboiler, which was then fixed to the Vigreux column. Before heating was started methanol was added and well stirred. The heating plate temperature at the beginning was 120 °C. For 30 min the distillation was performed at total reflux to provide sufficient time for reaction, afterwards the reflux splitter was adjusted to a ratio of 10:1. Every 30 min the product funnel was discharged, the product mass was measured and the distillate composition was analyzed via gas chromatography (GC, Shimadzu GC 2010 Plus). As the low boiling components were removed continuously from the reboiler, the boiling point of the reaction broth increased. Therefore, the heating plate temperature was increased by 10 °C hourly. The experiment was finished after 6.5 h due to the decline of the distillate amount and acid concentration in the reaction broth. At the end a sample from the reboiler was withdrawn and analyzed by GC.

The yield was calculated with the molar amount of esters collected in the distillate divided by the initial molar amount of the associated acid, as shown in equation 1.

$$Yield_{Ester}[\%] = \frac{n_{Ester,Distillate}}{n_{Acid,0}} \times 100 \tag{1}$$

Results and discussion

Batch reactive distillation results

For comparison between heterogeneous and homogeneous catalysis in batch reactive distillation the experiments were performed with the same H^+-ion concentration of the catalysts, shown in figure 3. After 30 min of heating and reaction period, the reflux ratio was adjusted from total reflux to a ratio of 10:1. Both catalysts showed similar behavior: First methyl formate is produced and separated in the distillate product until complete conversion of formic acid is achieved. Acetic acid esterification is slower compared to formic acid esterification and reached yield of methyl acetate in the distillate of 92 % after 6.5 h. During reactive distillation, the methyl acetate yield catalyzed with Amberlite®IR-120 is slightly higher than the results of DBSA catalyzed experiments. This may be due to partly blocked DBSA by the reactive extractant Cyanex®923. For Amberlite®IR-120 not all active centers can be blocked by Cyanex®923 due to steric hindrance, therefore there are enough catalytic active centers available for

catalysis. With ongoing experiment, the temperature in the reboiler increases, which leads to a higher adduct cleavage of DBSA and Cyanex®923. Therefore, the methyl acetate yield of the DBSA catalyzed experiment increases faster compared to Amberlite®IR-120 catalyzed results. After 6.5 h both experiments reached the same ester yields therefore both catalysts are applicable for solvent regeneration.
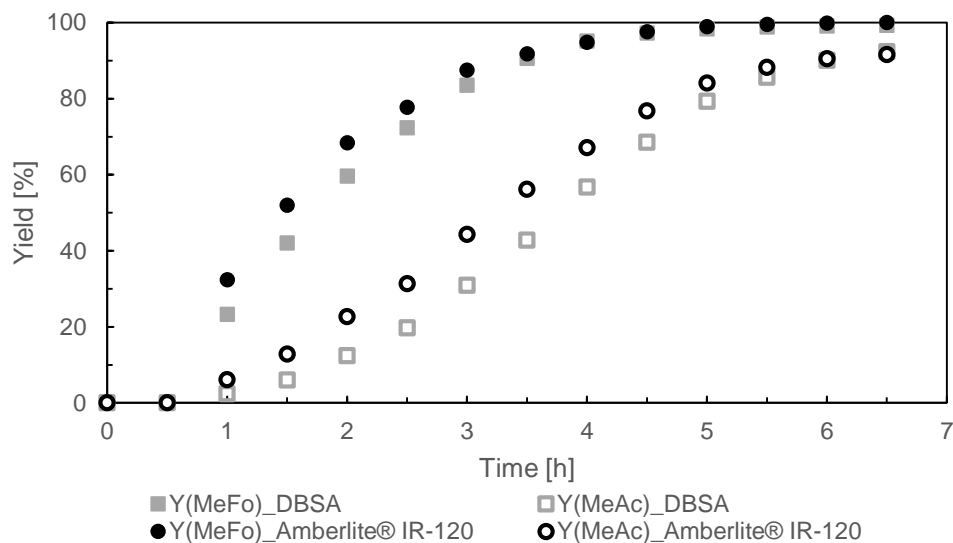

Reference: DBSA catalyzed data from Painer et al. (2018) [2]

Figure 3 Yield of methyl formate (MeFo) and methyl acetate (MeAc) in the distillate from batch reactive distillation experiments for solvent regeneration; Solvent: 70 w% Cyanex®923 in *n*-undecane; Solvent load: 87 g kg^{-1} formic acid, 154 g kg^{-1} acetic acid; Molar ratio of methanol:both acids=2:1; Catalysts: 5 w% 4-dodecylbenzenesulfonic acid (DBSA, 32 mEq), 3.6 w% Amberlite®IR-120 (32 mEq)

Homogeneous catalyst cycle

With regard to possible temperature limitation and deactivation of heterogeneous catalysts by wastewater impurities, a process route for homogeneously catalyzed reactive distillation without catalyst separation was developed. Due to the preferred adduct formation of the reactive extractant Cyanex®923 with strong acids the catalyst can be kept in the solvent phase during extraction. Indeed, a part of the reactive extractant is blocked by the catalyst but without loss of the catalyst during extraction. The influence of DBSA laden solvent was checked with liquid-liquid equilibrium experiments of simultaneous extraction of formic acid and acetic acid. Figure 4 compares simultaneous extraction of both acids with 70 w% Cyanex®923 in *n*-undecane with a solvent phase of 70 w% Cyanex®923 in *n*-undecane containing 5 w% DBSA. A decrease in extraction efficiency is mainly seen in formic acid extraction as formic acid is no longer the strongest acid in the mixture. Especially at low concentration of the acids in the aqueous phase there is still a good liquid-liquid equilibrium for extraction which enables the homogeneous catalyst cycle. [2]
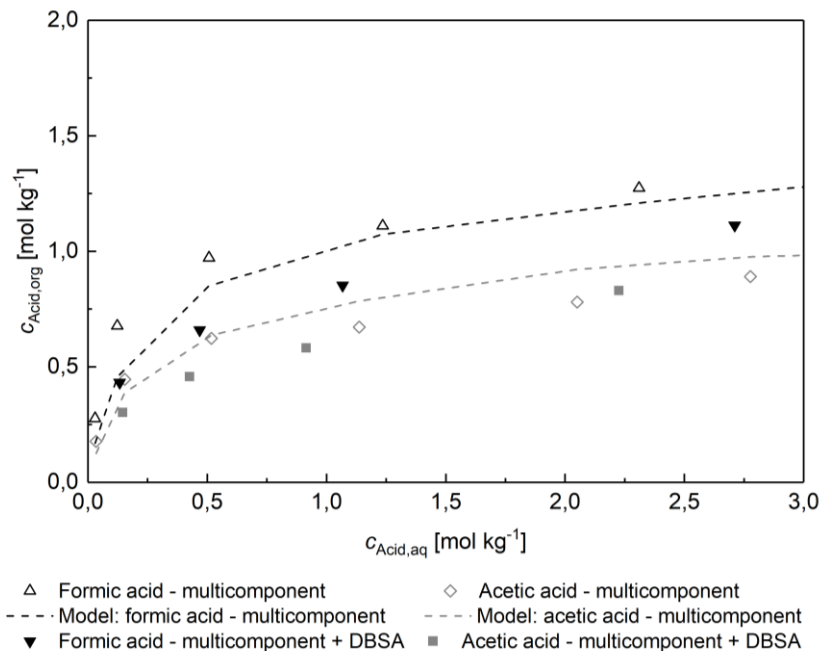
Reference: Painer et al. (2018) [2]

Figure 4 Impact of 5 w% 4-dodecylbenzenesulfonic acid (DBSA) on the liquid-liquid equilibria of formic acid and acetic acid; solvent: 70 w% Cyanex®923 in *n*-undecane

Conclusion

Reactive distillation, homogeneously or heterogeneously catalyzed, for solvent regeneration from wastewater treatment was proven applicable. Both catalysts enabled complete conversion and removal of formic acid, and 92 % yield of methyl acetate was obtained. To check recycling of the homogeneous catalyst in the solvent phase, the impact of DBSA laden solvent on simultaneous formic acid and acetic acid extraction was investigated. The results confirmed that reactive distillation with homogeneous catalyst slightly affects extraction performance. However the overall process concept is applicable.

References

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