

SYNTHESIS AND ISOLATION OF METHYL ACETATE THROUGH HETEROGENEOUS CATALYSIS WITH LIQUID/LIQUID-EXTRACTION

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Summary

Methyl acetate is synthesized through esterification of acetic acid with methanol. In the production of methyl acetate the formation of the two low boiling azeotropic mixtures methyl acetate/methanol and methyl acetate/water results in separation difficult product isolation. In this research project alternative reaction paths as well as the combination of synthesis with extractive isolation of methyl acetate from the multi component mixture methanol/acetic acid/methyl acetate/water were investigated in order to avoid or bypass these low boiling azeotropes. The esterification reaction was heterogeneously catalyzed with strongly acidic cation-exchange resins.

Keywords

Process intensification

Introduction

In chemical industry the formation of azeotropic mixtures results in extended separation demand. Stringent efforts for product isolation are required. The production of methyl acetate through esterification of acetic acid with methanol is a representative example for processes with high separation demand due to azeotrope formation. Methyl acetate forms binary low boiling azeotropic mixtures with methanol (19 weight per cent methanol at 54 °C) and water (3.5 weight per cent water at 56.5 °C). This property is a major obstacle for simple product isolation and plant design.

The industrial production of methyl acetate is based on a well established reactive distillation process, the so called Eastman Kodak process.¹

In this project an alternative approach for production and isolation of methyl acetate is investigated. Methods of chemical reaction engineering are systematically investigated in order to avoid the formation of the methyl acetate/methanol azeotropic mixture. Moreover the esterification reaction is combined with extractive isolation of methyl acetate from the multi component mixture methanol/acetic acid/methyl acetate/water. This efforts help overcome the methyl acetate/water azeotrope.

Project

For heterogeneous catalysis of the esterification reaction cation-exchange resins in the H⁺-form were used. The resins were strongly acidic macroporous resins with

sulfonic acid substituents as functional groups. The reaction was carried out in a temperature controlled batch reactor and in an isothermal plug flow reactor. Temperature was varied between 20 °C and 50 °C. Acetic acid was used in excess in order to minimize the amount of methanol in the reaction mixture.

Extractive isolation of methyl acetate was directly combined in the batch reactor and applied in series when performing synthesis of methyl acetate in the plug flow reactor. In both applications hydrocarbons (C₈ to C₁₀) were used as solvent. The experimental setup for the combination of chemical reaction with liquid/liquid-extraction for batch synthesis is shown in Figure 1.

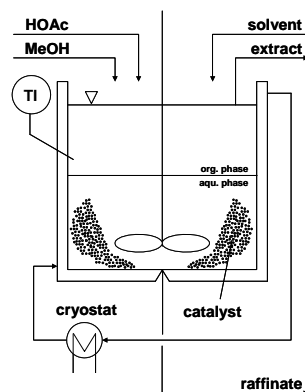


Figure 1.
Experimental setup for the combination of chemical reaction with liquid/liquid-extraction for batch synthesis of methyl acetate.

For investigation of reaction kinetics the product mixture was analyzed by gas chromatography. The water content

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in the reaction mixture was quantified with Karl Fischer titration. Residence time distribution in the plug flow reactor was quantified through refractive index measurements.

Results

Homogeneous acid catalyzed esterification of acetic acid with methanol follows second order kinetics.² The limiting conversion of the reactants is determined by the equilibrium.³ According to Le Chatelier's principle the equilibrium can be shifted towards the products if the concentration of one reactant is increased. This effect can be used in order to overcome the methyl acetate/methanol azeotropic mixture. The stoichiometric ratio of acetic acid to methanol in the feed was varied and the influence on the product composition was investigated. The results are shown in Figure 2. By increasing the stoichiometric ratio of acetic acid to methanol in the feed complete conversion of methanol can be achieved. Thereby the formation of the low boiling azeotropic mixture methyl acetate/methanol is avoided.

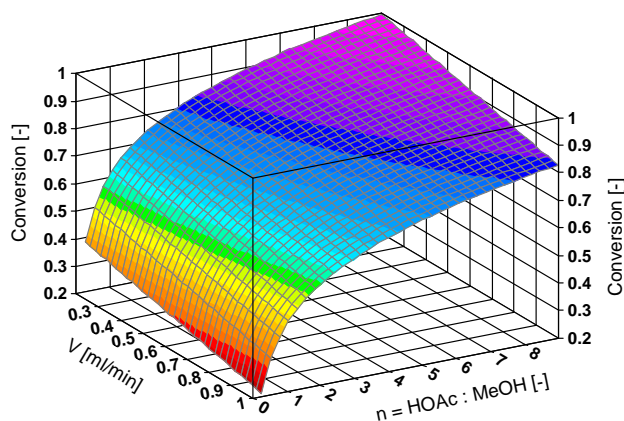


Figure 2. Effect of the variation of the stoichiometric ratio of acetic acid to methanol in the feed on the product composition; $T = 323\text{ K}$.

Strongly acidic cation-exchange resins are able to heterogeneously catalyze the esterification reaction. As for homogeneous catalysis with H_2SO_4 the byproduct water significantly inhibits catalysis.² In principle the swelling of the resins enables the removal of the byproduct water from the reaction mixture which has a positive effect on the yield of methyl acetate. Water can be removed from the catalyst by evaporation under mild conditions. Swelling of the resin in different media was investigated. Furthermore the effect of the water retained in the resin on the yield of methyl acetate was studied.

However, this method is not appropriate for continuous synthesis of methyl acetate. In continuous production the low boiling azeotropic mixture methyl acetate/water can be overcome through selective extraction of methyl acetate from the multi component reaction mixture. For extractive separation of methyl acetate from the reaction mixture the

solvent and the catalyst must not undergo any disadvantageous mutual interaction. *n*-Decane for example can be used as an appropriate solvent for batch combination of chemical reaction and extraction as well as for continuous operation.⁴

Cation-exchange resins can be used several times without loss of activity.⁵ Extensive studies of long term stability were executed in a plug flow reactor.

Discussion

A novel approach for methyl acetate synthesis through heterogeneous catalysis of acetic acid with methanol was investigated. With acetic acid in stoichiometric excess to methanol in the feed the low boiling azeotropic mixture of methyl acetate and methanol can be avoided. Methyl acetate is isolated from the reaction mixture through liquid/liquid-extraction. Representatively the solvent *n*-decane was investigated. With this step formation of the low boiling azeotropic mixture of methyl acetate and water can be avoided. Selective separation of methyl acetate through subsequent distillation as well as recovery of acetic acid from the raffinate phase are simple unit operations.

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