

Investigation of Methyl Acetate Production by Reactive Extraction

Christian Rohde, Rolf Marr
Department of Chemical Engineering and Environmental Technology
University of Technology Graz
Inffeldgasse 25, A-8010 Graz, Austria
christian.rohde@TUGraz.at

Matthäus Siebenhofer
VTU-Engineering GmbH
Parkring 18, A-8074 Grambach/Graz, Austria

Key words: Reactive Extraction, Esterification, Methyl Acetate

Prepared for Presentation at the 2004 Annual Meeting, Austin, TX, Nov. 7-12

Copyright © C. Rohde, R. Marr, University of Technology Graz;
M. Siebenhofer, VTU-Engineering GmbH
November 2004, Unpublished

AIChE shall not be responsible for statements or opinions contained in papers or printed in its publications.

Abstract

Methyl acetate is produced through catalytic esterification of acetic acid with methanol. Catalytic acceleration is induced by sulfuric acid or ion exchange resins respectively. Acceptable product yield is obtained by reactive distillation. Separation and isolation of methyl acetate has to overcome two azeotropes (methyl acetate – water and methyl acetate - methanol).

Scope of this project has been the investigation of methyl acetate formation by reactive extraction and distillative separation of methyl acetate from the solvent.

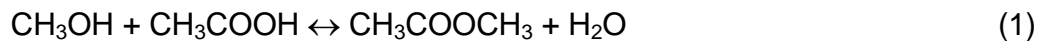
From reactive extraction an increased yield of product is expected due to immediate separation of the ester from the reaction mixture. Investigation focused on the solvent n-nonane which suffices the needs of appropriate solubility for methyl acetate and excellent vapor/liquid equilibrium data ($T_{bp, MeOAc} = 330$ K, $T_{bp, n-nonane} = 425$ K). On account of the selectivity of n-nonane for methyl acetate the formation of azeotropes during distillative separation can be avoided.

Experimental investigation of reactive extraction confirmed both an improved yield of methyl acetate as well as high product quality of 99.3% purity.

1 Introduction

In the last decade increasing interest was paid to hybrid processes both in industry and research, especially to reactive distillation and reactive extraction i.e. reported by Agreda et al. (1990). Simultaneous chemical reaction and separation of products of hybrid processes is advantageous over the process performance of separate unit operations. As a result of simultaneous operation capital cost and cost of operation are considerably lowered. Application is possible when one of the reaction products has a lower boiling point than the residual substances of a mixture or a higher solubility in the extracting agent. In fact a high selectivity of the solvent for a specific reaction product is needed to decrease its concentration in the reaction mixture, therefore increasing the rate of reaction. As a consequence conversion and rate of reaction are increased.

Esterification of acetic acid with methanol with the homogenous catalyst sulfuric acid suffices the above mentioned boundaries. Therefore this reversible reaction has intensively been studied and reported in literature (equation 1) by Bonnaille et al. (2001):



The multicomponent system has an azeotrope of methyl acetate with water (5 weight% water, boiling point = 329.25 K) and an azeotrope of methyl acetate with methanol (18 weight% methanol, boiling point = 327.05 K) (e.g. Xu and Chuang (1997)). Since the boiling point of methyl acetate (330.15 K) is very close to the boiling points of the azeotropes a complex plant design and rigorous process control is required to overcome the two constant boiling mixtures. Target of the present project was to work out an alternative process to reactive distillation design. Reactive extraction was applied to simplify the separation task.

The esterification reaction (equation 1) was chosen as a test system to verify reactive extraction. The program was split into two steps. In the first step methyl acetate was extracted selectively by n-nonane and, in a second step the extract was regenerated in a lab scale distillation column.

2 Experimental Procedure

2.1 Reactive Extraction

Experiments were carried out in a reactor (Heraeus company, type UV-RS-2) in lab scale (equipment: reaction vessel with a volume of 850 ml, diameter 0.1 m, magnetic agitator) equipped with a temperature sensor and a pH-value sensor and two sampling sockets. The reaction vessel was fed with equivalent amounts (2.5 mole) of methanol and acetic acid plus 500 ml of solvent and then mixed at constant temperature. Within each experiment several samples were withdrawn from the reaction vessel mixture for chemical analysis. During sampling the magnetic agitator was switched off and as soon as the two phases were separated a sample was withdrawn from each phase.

Each experiment was started by injecting a specific amount of sulfuric acid into the reaction mixture. Over a period of 180 minutes samples of the reaction mixture and the solvent

phase were collected. During operation the temperature of the reaction mixture was held constant at 299 ± 2 K. The samples were analyzed with a gas chromatograph, Hewlett-Packard 5960, equipped with a J&W Scientific DBVRX column. The temperature was held constant at 353 K for 5 min, ramped to 383 at a rate of 5 K/min and then ramped to 523K at a rate of 40 K/min. This temperature was held constant for 10 min. The temperature of the injection port was adjusted at 523 K and the temperature of the FID was kept at 573 K.

2.2 Solvent Regeneration

The extract phase was separated by distillation in a batch distillation column in lab scale (reboiler volume: 500 ml, height of column: 320 mm, column diameter: 30 mm). The column was equipped with a temperature sensor at the bottom and the top. A heating jacket of 150 Watt electrical power provided the reboiler with heat. By means of a data logger (Fluke company, type Hydra series II) the temperatures were displayed online on a screen. Distillation was stopped when the temperature on the top of the column started to rise above the boiling point temperature of methyl acetate. The chemical composition of the bottom product and the top product was analyzed by gas chromatography according to the above described guideline.

3 Results and Discussion

Every reactive extraction experiment was carried out in two steps by admixing pure solvent to the reaction mixture twice. In the consecutive distillation process the solute methyl acetate was separated from the solvent.

3.1 Reactive Extraction

Sulfuric acid was used as a catalyst. An amount of 8 g/l sulfuric acid was fed to the mixture of acetic acid, methanol and n-nonane (Figure 1).

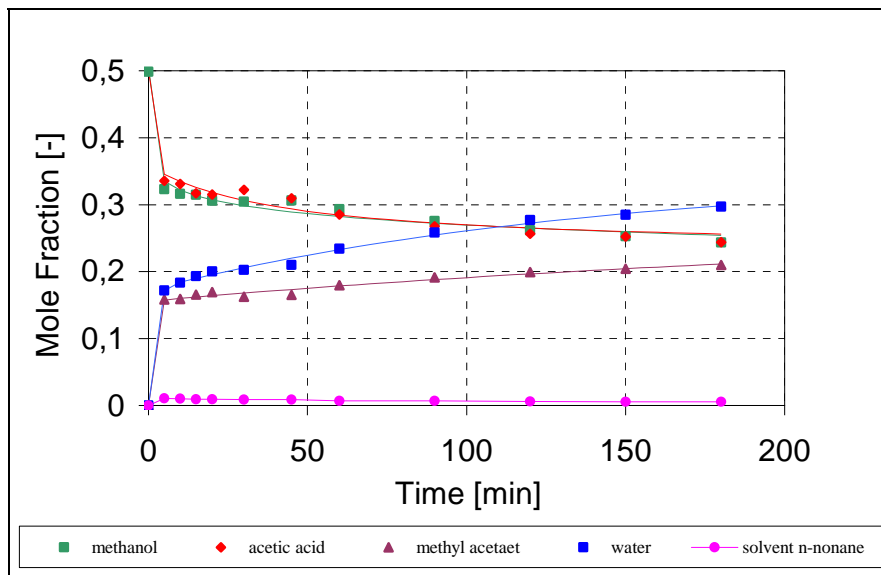


Figure 1: Concentration of the components in the reaction mixture for equimolar start of acetic acid and methanol; concentrations sulfuric acid concentration: 8 g/l, solvent: 500 ml n-nonane.

Figure 1 shows the equimolar decrease of the reactants. Since methyl acetate is partly extracted with n-nonane the amount of water and methyl acetate differ. Due to its low solubility the amount of n-nonane in the reaction mixture is negligible. Figure 2 indicates that n-nonane is a suitable solvent for extracting methyl acetate with sufficient selectivity.

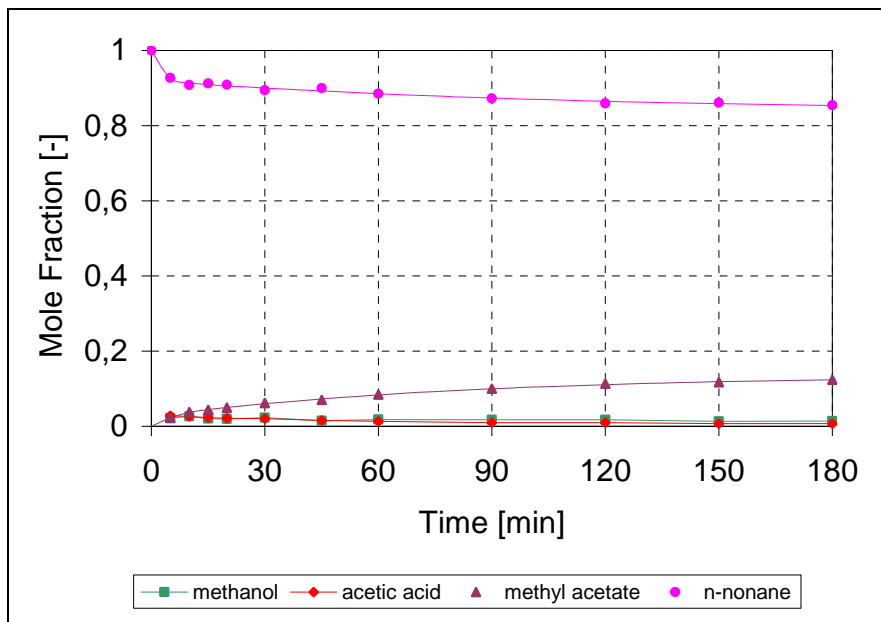


Figure 2: Concentration of the components in the solvent phase.

The load capacity of the solvent n-nonane for methyl acetate in equilibrium with the reaction mixture is limited although methyl acetate is completely miscible with n-alkanes as reported by Casas et al. (2004). Due to the excellent solubility of methyl acetate in the reaction mixture the distribution coefficient for methyl acetate of $K = 0.61$ at a temperature of 299 K was determined experimentally.

In a second extraction step the solvent phase was replaced. Compared with Figure 1 Figure 3 confirms the increase in rate of conversion.

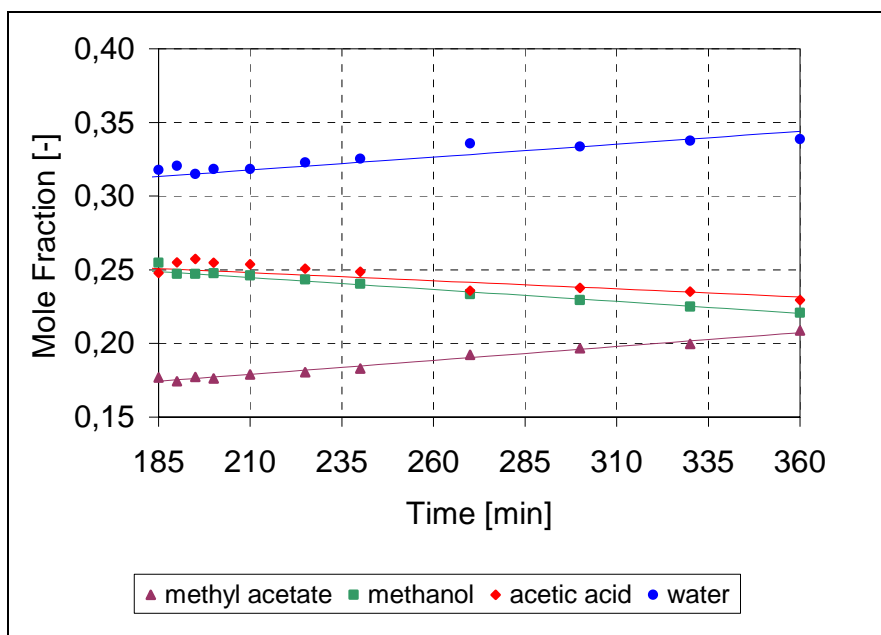


Figure 3: Composition of the reaction mixture during the second extraction step; sulfuric acid concentration: 8 g/l, solvent: n-nonane.

Conversion of methanol and acetic acid was 0.55 after the first step and 0.70 after the second step of extraction.

3.2 Solvent regeneration

The solvent mixture was separated by batch distillation in lab scale. According to the solvent composition formation of azeotropes was not observed. The temperature of the reboiler was kept constant at the boiling point of methyl acetate. Methyl acetate quality yielded in 99.3 weight%.

4 Summary

Target of the present project was to verify whether the performance of methyl acetate production from acetic acid and methanol can be improved by combining esterification with liquid/liquid extraction. The results of investigation can be summarized as follows:

- Methyl acetate is extracted from the reaction mixture with n-nonane with high selectivity.
- Rate of conversion of the esterification reaction is improved by reactive extraction.
- The solute methyl acetate can be separated from the solvent n-nonane by distillation.
- Methyl acetate quality of is 99.3 weight% can be obtained.
- Distillative separation of methyl acetate from n-nonane is neither affected by the methanol/methyl acetate azeotrope nor by the methanol/water azeotrope.
- Recycling of the solvent n-nonane after distillation is possible without further upgrading.

5 Abbreviations and Symbols Used

AcOH	acetic acid
MeOAc	methyl acetate
MeOH	methanol
T _{bp}	boiling point [K]

6 References

Agreda, V. H., Partin, L. R. and Heise, W. H., High-Purity Methyl Acetate via Reactive Distillation, Chem. Eng. Prog., Feb. 1990, pp. 40-46, 1990.

Bonnaillie, L., Meyer, X. M. and Wilhelm, A. M., Teaching reactive distillation: Experimental results and dynamic simulation of a pedagogical batch pilot-plant, 3rd European Congress of Chemical Engineering, ECCE, Nuremberg, 2001.

Casas, L. M., Orge, B., Diaz, C. and Tojo, J., Liquid-liquid equilibria for mixtures of {methyl acetate + methanol + n-alkane (C₁₀-C₁₂)} at several temperatures and 1 atm, J. Chem. Thermodynamics 36, 237-243, 2004.

Xu, Z. P. and Chuang, K. T., Correlation of Vapor-Liquid Equilibrium Data for Methyl Acetate-Methanol-Water-Acetic Acid Mixtures, Ind. Eng. Chem. Res., 36, 2866-2870, 1997.