

Investigation of reversible chemical reactions in compressed CO₂ on the basis of production of methyl acetate

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Abstract

Esterification of acetic acid with methanol with and without heterogeneous catalyst was carried out in compressed carbon dioxide. In the first part of this project the autocatalytic effect of the compressed CO₂ on this equilibrium reaction was investigated. The use of high-pressure carbon dioxide, an environmentally benign solvent, will shift the yield towards the desired product methyl acetate. The influence of temperature, pressure and water content of the feed composition on the reaction yield was studied. Temperature of operation was varied between 298.15 K to 328.15 K. The pressure of operation was up to 10 MPa. Yield of esterification without catalyst was 6%. Catalytic esterification was investigated with Amberlite IR-120, a strongly acidic ion exchanger. The yield of reaction differed significantly from esterification without catalyst.

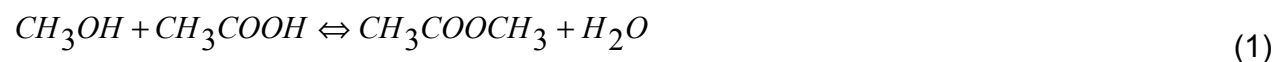
1 Introduction

Due to environmental benefits and favorable operating conditions supercritical fluids (SCFs) such as supercritical carbon dioxide have gained considerable attention in several applications. Supercritical fluids can either act as active component of a reaction or act as solvent for reactants, catalysts and products. The chemical as well as physical properties of supercritical fluids open a wide range of application. Supercritical fluids may contribute to the selectivity of a reaction by maintaining high conversion. They can dissolve reactants and catalysts of different physical state to provide homogenous operating conditions during chemical reaction, while separation of products from reactants, catalysts and unwanted by-products may evolve from altering the pressure and/or temperature of operation.

The supercritical fluid which gained the most attention throughout the chemical and materials research community is carbon dioxide (CO₂). Carbon dioxide is often promoted as a 'green' solvent with great physical properties. It is non-flammable, non-toxic, fairly inert, economical and environmentally benign. The advantages of the solvent CO₂ in chemical synthesis are based on the unique combination of physical properties of carbon dioxide in the liquid state and in the supercritical state. The adjustable solvating power of scCO₂ is an outstanding advantage in chemical synthesis. The physical properties of scCO₂ are highly dependent on pressure and temperature. This specification of scCO₂ enables fine-tuning of the reaction environment and as a result optimization of the rate and selectivity of reaction. By adjusting temperature and pressure and as a consequence the solvation power of the scCO₂ many applications in separation and purification processes can be solved [Jessop and Leitner, 1999].

Extended limitation of conventional solvents will have a profound effect on the extend to which CO₂ is used as a solvent/carrier for conducting chemical synthesis reactions in the future [Beckman, 2004]. Reversible chemical reactions are a preferred field of application for the solvent scCO₂. The solubility of the participating reaction components can be altered by pressure tuning. As a consequence the product yield of equilibrium reactions can be improved.

Esterification reactions are conventionally carried out with homogeneous catalysts such as sulphuric acid. Esterification of carboxylic acids with alcohols is a representative example of a reversible reaction that has been widely studied. Up to now few studies have been done on specific chemical equilibrium reactions in compressed carbon dioxide such as esterification reactions [Hou et al., 2001], [Vieville et al., 1999]. In particular the catalyzed/non-catalyzed esterification of acetic acid with methanol in scCO₂-medium has not been discussed in literature yet. The effect of the solvent scCO₂ on the yield of methyl acetate has therefore been investigated. In exploring alternative operating conditions for esterification reactions which show potentially higher conversions than state of the art liquid phase reactions this project focuses on methyl acetate production in compressed carbon dioxide (equation 1).



Elevated temperature and a suitable catalyst are normally required to limit the time needed for conversion of esterification reactions. In this study the effect of scCO₂ on esterification of acetic acid with methanol in the presence of different catalysts and without catalysts has been investigated.

2 Experimental Methods and Analyses

2.1 Chemicals

The quality grade of scCO₂ plays an important role in esterification of acetic acid with methanol. Low level impurities can have noticeable effects on the volumetric and phase behavior of scCO₂. Carbon Dioxide with purity of >99.94 volume% was purchased from Linde (Graz). Acetic acid and methanol, both of p.a. quality, and the solvent tetrahydrofuran (THF) of p.a. quality were supplied by Fluka (Buchs). Amberlite IR-120, a strongly acidic cation exchanger, used for the investigation of esterification with heterogeneous catalysts was provided by Fluka (Buchs). The chemicals were used without any further purification.

2.2 Apparatus and procedure

Investigation of the esterification reaction of acetic acid with methanol was performed in a static apparatus (figure 1), which was described previously by Gamse [Gamse, 2003].

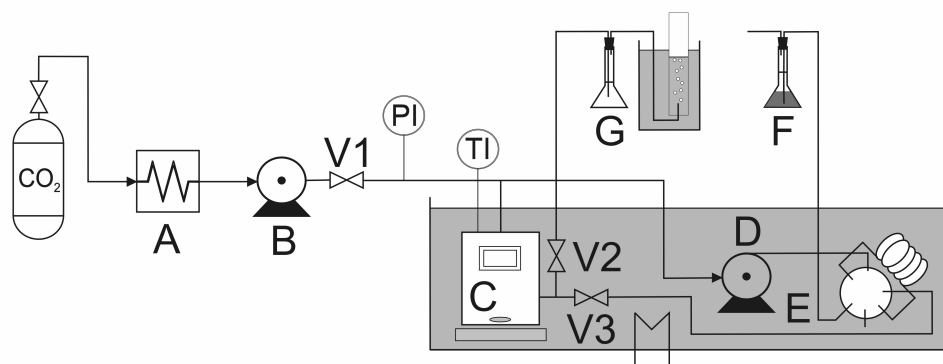


Figure 1: Schematic diagram of the experimental set up: (A) cryostat, (B) membrane pump, (C) high-pressure cell, (D) gear pump, (E) HPLC sample valve, (F) gas phase sample flask, (G) liquid phase sample flask, V1 inlet valve, V2 outlet valve, V3 valve for cycle.

The cell is designed for an operating pressure of 40 MPa at maximum temperature of 373.15 K. Volume of the cell is 140 mL. Two inspection glasses are installed at front and back side of the cell over the whole height enabling permanent visual control of experiments. The CO₂-rich phase is withdrawn on top of the cell by a gear pump. It passes a 6-port-HPLC-valve with a sample loop of 200 μ L and it is fed at the bottom of the cell. The

apparatus is placed in a temperature controlled water bath to prevent separation of substances due to temperature gradients. Pressure and temperature are measured with an accuracy of ± 0.1 K and ± 0.01 MPa respectively.

To verify the accuracy of the experimental set up and the reproducibility of data, phase equilibrium data of the test system carbon dioxide – methanol at 303.15 K were investigated prior to performing esterification of acetic acid. Comparison of the experimentally determined equilibrium data with literature data at 303.15 K showed sufficient accordance for both the liquid and the gaseous phase.

In each series of experiments a sample of 15 to 30 mL was placed in the cylindrical equilibrium cell. The samples consisted of an equimolar ratio of acetic acid and methanol. Amberlite IR-120 as heterogeneous catalyst, and in selected experiments water was added to the reaction mixture at the beginning of each experiment. After adjusting the desired operating conditions (temperatures of 298.15 K to 328.15 K and pressures up to 10 MPa) for each experiment, the liquid/supercritical carbon dioxide was pumped through the cell with a gear pump. Mixing of the liquid solution by strong turbulences was induced by circulating the gaseous phase and by stirring. During residence time of the gaseous phase in the cell, equilibrium concentration was established in the gas phase as well as in the condensed phase. The equilibrated gaseous phase was withdrawn from the cell through the HPLC sample valve and was expanded into a solvent flask (tetrahydrofuran). About 2-3 mL of THF was prepared in a calibrated 5 mL flask, which was placed in ice water in order to collect all of the sample. After expansion the sample loop (200 μ L) was washed with THF and purged with compressed air. The final sample volume was 5 mL. The so prepared sample was analyzed by gas chromatography.

The composition of the liquid phase was determined by expanding a sample of liquid phase from the bottom of the equilibrium cell into a glass vial which was weighted before and after sampling. The CO₂ stripped from the sealed top of the glass vial was collected in a volume-calibrated glass cylinder which was filled with acidified water of pH-value 0.5. At pH 2 the loss of CO₂ by dissolving in water is negligible. From the volume of CO₂ gas collected in the glass cylinder and the weight of substance in the glass vial the amount of CO₂ in the liquid phase was calculated. The density of pure carbon dioxide was derived from Bender equation [Bender, 1970]. THF was used as solvent for preparing the liquid sample for gas chromatographic analysis. Gas-side sampling was adjusted during the experiments according to the same procedure like liquid-side sampling (figure 1, G).

2.3 Gas chromatographic analysis

All samples were analyzed with a gas chromatograph, type Hewlett Packard 6890N with flame ionisation detector (GC-FID) and a capillary column (DBVRX, 30 m x 0.32 mm x 1.8 μ m). The temperature of the capillary column was kept constant at 353.15 K for 1 minute, followed by ramp of 3 K min⁻¹ to a temperature of 403.15 K, and a second ramp of 10 K min⁻¹ to a final temperature of 443.15 K and held constant for 2 minutes. For calibration the substances were dissolved in tetrahydrofuran.

3 Results and Discussion

Esterification of acetic acid with methanol was investigated in two different modes of operation. A first series of experiments was performed in compressed carbon dioxide without catalyst to examine the enhancement effect of carbon dioxide on this esterification reaction.

The effect of the heterogeneous catalyst Amberlite IR-120 on the esterification reaction was investigated in a second series of experiments. Reaction yield of the target product methyl acetate was compared with the results obtained in the first series of experiments.

Esterification conversion of the reactants is limited by the equilibrium. Typically the equilibrium constants of esterification reactions have values between 1-10. A value of 5.2 for the equilibrium constant K for esterification of acetic acid with methanol under ambient conditions is reported in literature [Agreda et al., 1990]. Esterification reactions are very slow reactions. Without catalyst esterification typically requires several days to attain equilibrium [Rönnback et al., 1997]. According to van't Hoff equation (equation 2) the equilibrium constant is temperature dependent.

$$\ln K(T) = \ln K(T^\circ) - \frac{\Delta h_r}{R} \cdot \left(\frac{1}{T} - \frac{1}{T^\circ} \right) \quad (2)$$

Because of the small temperature range investigated, the enthalpy of reaction was assumed to be constant. For our means, the esterification yield of methyl acetate is defined as the ratio of the formed methyl acetate to the reaction equilibrium yield of methyl acetate (according to equations 1 and 2).

3.1 Esterification without catalyst

In the first series of experiments, influence of compressed carbon dioxide on esterification of acetic acid with methanol was investigated. Esterification was investigated at a temperature of 298.15 K, 308.15 K and 328.15 K. Pressure was varied up to 10 MPa. The results are shown in figures 2 through 4. Figure 2 displays influence of temperature on the yield of esterification. In figure 3 the pressure dependence of the reaction at three different temperature levels is presented. The influence of feed water on the yield of methyl acetate is shown in figure 4.

3.1.1 Influence of temperature

Temperature dependence of the esterification of acetic acid with methanol was investigated in four experimental series. Three series were performed at 6.1 MPa with different feed water concentration; a fourth experimental series was operated at 9.1 MPa and a feed water concentration of 0.05 mole%.

In all series of experiments conversion increases with temperature. Without feed water the yield of esterification (at an operating pressure of 6.1 MPa) increases from 0.1 % at 298.15 K, 1.9 % at 308.15 K to 2.8 % at 328.15 K.

The results are in accordance with the expected temperature dependence of the solvent power of carbon dioxide. The solvent power of carbon dioxide strictly depends on the density which is controlled by both the temperature and the pressure of operation. Particularly in the vicinity of the critical point the influence of the pressure is important.

Density of carbon dioxide increases with increasing pressure and decreasing temperature. At low pressure the solvent power of CO₂ decreases with increasing temperature, while at elevated pressure the opposite effect is observed (Cross-Over-Point) [Brunner, 1994]. An increase in temperature results in a decrease in density and an increase of the vapor pressure. In the low pressure range the decrease in solvent density predominates. At elevated pressure the exponential increase of the vapor pressure with temperature is the predominating effect. As a consequence the solvent power of carbon dioxide increases with temperature. This phenomenon is responsible for the raise of the esterification yield shown in figure 2. At a temperature of 328.15 K the equilibrium solubility of pure methyl acetate in CO₂ is favored over acetic acid, methanol and water [Schwinghammer et al., 2004].

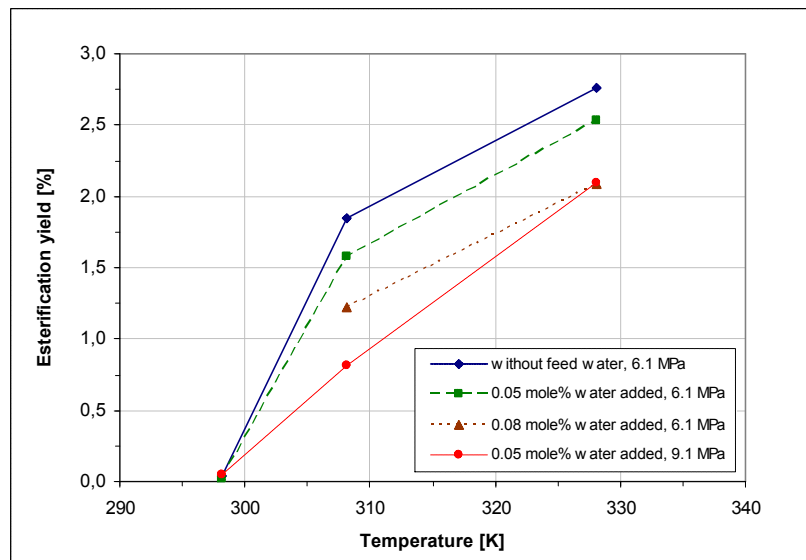


Figure 2: Temperature dependence of the esterification yield at a pressure of 6.1 and 9.1 MPa and for different feed concentrations of water.

3.1.2 Influence of pressure

To investigate the influence of pressure on esterification three different experimental series were conducted. The water content of each feed solution was held constant at 0.05 mole%. The influence of pressure was investigated at three different temperature levels (298.15, 308.15 and 328.15 K). Figure 3 shows the experimental results for a residence time of 19 hours.

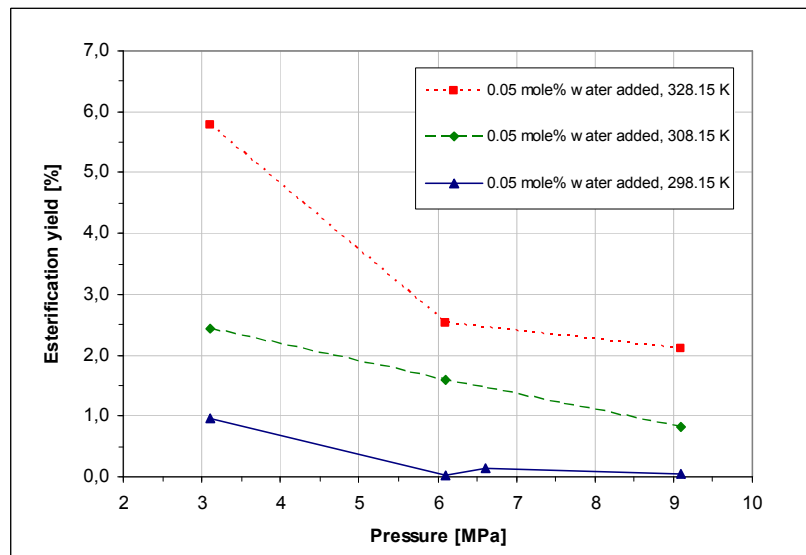


Figure 3: The influence of pressure on esterification of acetic acid with methanol for constant feed water content of 0.05 mole% at 298.15, 308.15 and 328.15 K.

As shown in figure 3 the effect of pressure on the esterification yield is obvious. In the investigated pressure range an increase in pressure results in a decrease of the esterification yield. This phenomenon is more distinct at higher temperature, but was also observed at a temperature of 298.15 K. Since in accordance with equation 1 the total number of moles does not change during esterification the observed pressure sensitivity was not expected. The molar fraction of methyl acetate in the solvent phase corresponds with Dalton's law.

At a temperature of 328.15 K and a feed water content of 0.04 mole% for instance, a decrease of the operating pressure from 6.1 to 3.1 MPa results in an increase the methyl acetate load of the carbon dioxide phase from 0.003 to 0.011 g methyl acetate per g CO₂. The same tendency is observed at a temperature of 308.15 K and 298.15 K. Specific solvent-solute interaction may also explain the increased esterification yield at lower pressure. There is evidence in literature that the local density of a solvent in the vicinity of the solute is greater than the bulk density [Ellington et al., 1994].

3.1.3 Influence of the feed water content

According to equation 1, water is expected to have a negative effect on the yield of esterification. Nevertheless the effect of feed water on the rate of reaction due to proton formation from carbon dioxide was investigated. The amount of water in the feed solution was varied up to 0.08 mol%. The results are shown in figure 4.

In the investigated temperature range an increase of water in the feed mixture will decrease the yield of esterification. Enhancement of the rate of esterification by adding water to the feed mixture was not observed. For a system temperature of 328.15 K for instance, the esterification yield dropped from 2.8% without feed water down to 2.6% with 0.05 mole% water added and further down to 2.1% with 0.08 mole% water added to the feed solution.

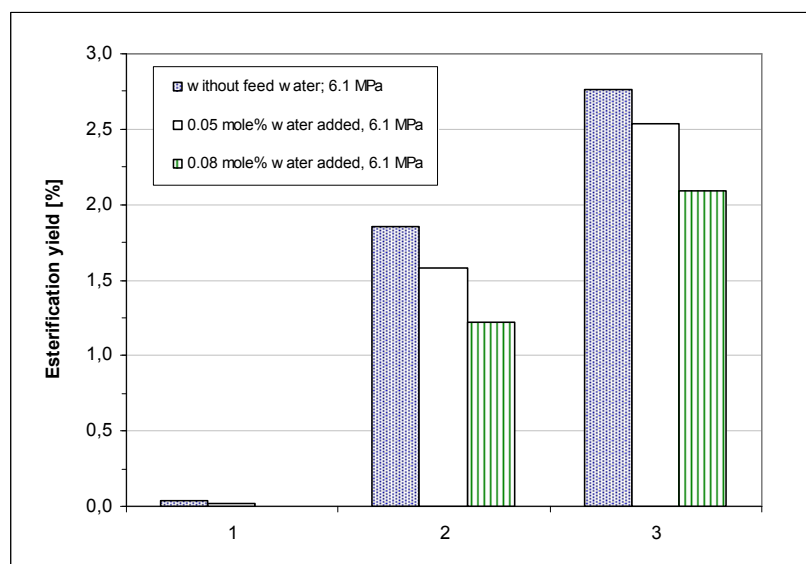


Figure 4: Effect of feed-water on the rate of esterification. Pressure: 6.1 MPa; temperature: 298.15 K(series 1), 308.15 K(series 2) and 328.15 K(series 3).

3.2 Effect of heterogeneous catalysts

In the second part of this project the effect of heterogeneous catalysts on esterification of acetic acid with methanol was investigated. The catalyst Amberlite IR-120, a strongly acidic cation exchanger in H⁺-form, was used in these series of experiments.

Esterification was again investigated at three different temperature levels of 298.15, 308.15 and 328.15 K. System pressure was varied up to 9.1 MPa. The heterogeneous catalyst was placed in the high pressure cell in a stainless steel cage prior to metering of the liquid feed mixture. Figure 5 displays the temperature influence on the esterification yield. In figure 6 the methyl acetate load of the carbon dioxide phase is compared with esterification without heterogeneous catalyst.

3.2.1 Temperature dependence of catalyzed and non-catalyzed esterification

The temperature dependence of catalytic esterification of acetic acid with methanol was investigated in two different series. The operation pressure for both series was held constant at either 3.1 or 6.1 MPa respectively. In figure 5 the comparison of the yield for catalytic and non catalytic esterification is shown.

With the heterogeneous catalyst Amberlite IR-120 a significant improvement in esterification yield was observed. At a temperature of 308.15 K and a pressure of 6.1 MPa the yield increased from 1.9% to 15.1%. This increase in the yield was achieved by adding 4.1 g of Amberlite IR-120 to an equimolar feed mixture of 30 mL which is equivalent 2.7 wt% of catalyst related to the amount of methanol in the feed mixture. As shown in figure 5 catalytic esterification does not differ from non catalytic esterification except the yield. Feed water has a negative effect on the yield as well. An increase in temperature results also in an increase in the esterification yield.

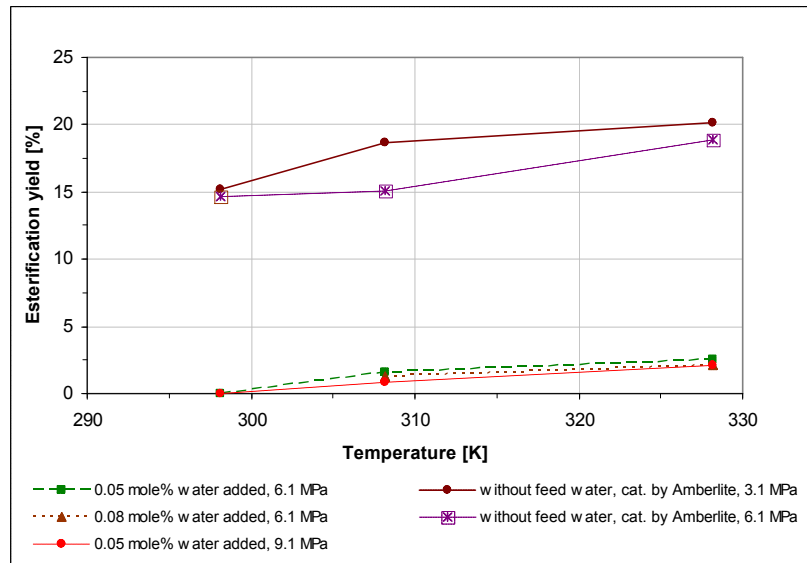


Figure 5: Comparison of the esterification yield with and without catalyst; temperature: 298.15, 308.15 and 328.15 K

3.2.2 Methyl acetate load of carbon dioxide; comparison of catalytic and non catalytic esterification

In figure 6 the temperature dependence of the methyl acetate load of the carbon dioxide vapor phase is shown. The results of catalytic esterification with Amberlite are compared with non catalytic esterification. Catalytic esterification was again based on 2.7 wt% of catalyst related to the amount of methanol in the feed. In catalytic esterification as well as non catalytic esterification an increase of the methyl acetate load of the carbon dioxide phase with increasing temperature is observed.

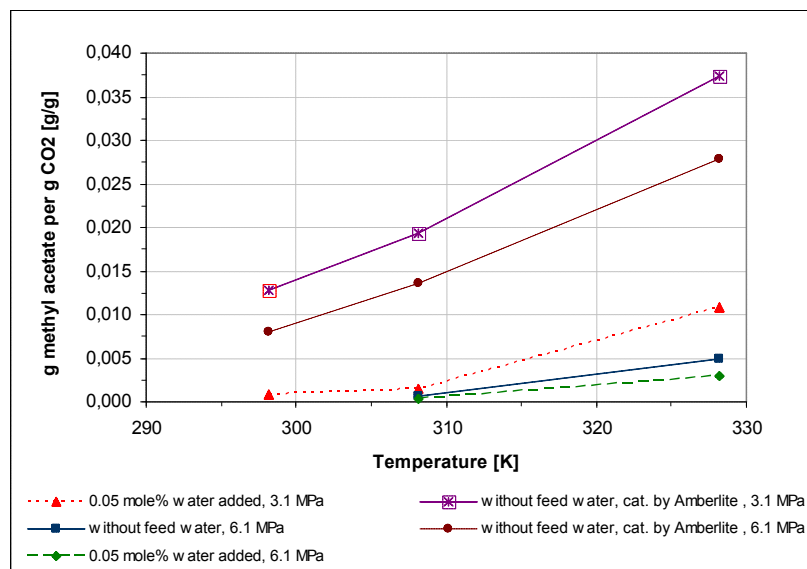


Figure 6: Methyl acetate load of the carbon dioxide phase versus temperature; parameters: operating pressure and water content of the feed

4 Summary

The effect of compressed carbon dioxide on the esterification reaction of acetic acid with methanol was investigated. The first part of the experiments focused on the influence of compressed CO₂ alone on the esterification reaction. In several experiments the influence of temperature, pressure and water content of the feed mixture was studied. Experimental results showed an increase in esterification yield with increasing temperature and a decrease in the yield with increasing pressure. As expected, feed water has a negative effect on the yield and it does not accelerate the rate of conversion due to protonation of carbon dioxide.

In the second part of the project the influence of a heterogeneous ion exchange catalyst on the esterification of acetic acid with methanol was investigated. Experiments carried out with Amberlite IR-120 as a heterogeneous catalyst showed a significant improvement of the esterification yield compared with the non catalytic reaction.

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