

ESTERIFICATION OF ACETIC ACID WITH
METHANOL: A KINETIC STUDY ON
AMBERLYST 15

Renier Schwarzer

Esterification of acetic acid with methanol: A Kinetic Study on Amberlyst 15

by

Renier Schwarzer

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of the requirements for the subject CVD 800

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Synopsis

Reaction rate data at 50°C was generated in a batch reactor over a wide range of initial concentrations in the reaction mixture. In each case the reaction was allowed to reach equilibrium. Equilibrium conversion data clearly indicated that it is important to consider the non-ideality of the system. The NRTL activity model proved to be the most suitable model to calculate the activity based equilibrium constant, as the percentage standard deviation of the equilibrium constant calculated in this manner was only 7.6 % for all the different experiments as opposed to 17.8 % when the equilibrium constant was based on concentration. The NRTL parameters used were obtained from Gmehling & Onken (1977) who determined the parameters from vapour liquid equilibrium. The Langmuir-Hinshelwood kinetics proposed by Song et al. (1998) and Pöpken et al. (2000) provided an excellent representation of the reaction rate over a wide concentration range with an AARE of 6% and 5 % respectively. It was shown that when the NRTL activities were used in the rate expression that a power law model provided a similarly accurate prediction of the reaction rate (AARE = 4.1 %). When the Eley-Rideal reaction expression (in terms of the adsorption of methanol and water) was used, a slight improvement was achieved (AARE = 2.4%). As both the Langmuir-Hinshelwood and Eley-Rideal models require separate experiments for the measurement of adsorption constants, it seems that the activity based power law model should be the kinetic expression of choice. It can be concluded that a two parameter activity based rate expression predicts the reaction rate with similar accuracy as the multi-parameter adsorption models. This indicates that it is not necessary to know the concentration on the resin surface (adsorption models) or in

the resin gel (absorption models) when describing the reaction rate as long as the bulk liquid phase activities can be adequately described.

Keywords : Equilibrium constant, sorption selectivity, cation exchange resin, Methyl acetate and kinetic modelling.

CONTENTS

1	Introduction	1
2	Background	3
2.1	Cation exchange resins	3
2.2	Reaction Rate Models on Cation Exchange Resins	5
2.2.1	Pseudo Homogeneous	5
2.2.2	Activity Based Reaction Models	6
2.2.3	Adsorption Based Reaction Models	13
2.2.4	Absorption Based Modelling	19
2.3	Reaction Equilibrium Constant	22
2.3.1	Reaction equilibrium constant from Gibbs Energy of Formation	22
2.3.2	Equilibrium Constants from the Literature	23
2.4	Water Inhibition on Cation Exchange Resins	25
3	Experimental	29
3.1	Experimental Setup	29
3.2	Materials	29
3.3	Analysis	31
3.4	Experimental Procedure	32
4	The Reaction Rate Prediction with Existing Models	36
4.1	Modelling the Reaction Rate	36
4.2	Performance of Rate models	37
4.2.1	Pseudo Homogeneous Reaction rate	37
4.2.2	Langmuir-Hinshelwood Reaction rate	37
4.3	Summary	39

5	Reaction Rate Prediction	44
5.1	Equilibrium Constant	44
5.1.1	Concentration Based Reaction Equilibrium Constant	44
5.2	Activity Based Reaction Equilibrium Constant	46
5.3	Reaction Rate Modelling	48
5.3.1	Pseudo Homogeneous Reaction Rate	48
5.3.2	Langmuir-Hinshelwood Reaction Kinetics	49
5.3.3	Eley-Rideal Reaction Kinetics	50
6	Conclusions	55
A	Appendix	60
A.1	Calculation of the volume adsorbed onto a catalyst bead	60
A.2	Experimental	61
A.2.1	Sample make up for the determination of the analytical repeatability.	61
A.3	Experimental data	62
A.4	Method Followed for the Prediction of Rate data	67

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CONTENTS

1	Introduction	1
2	Background	3
2.1	Cation exchange resins	3
2.2	Reaction Rate Models on Cation Exchange Resins	5
2.2.1	Pseudo Homogeneous	5
2.2.2	Activity Based Reaction Models	6
2.2.3	Adsorption Based Reaction Models	13
2.2.4	Absorption Based Modelling	19
2.3	Reaction Equilibrium Constant	22
2.3.1	Reaction equilibrium constant from Gibbs Energy of Formation	22
2.3.2	Equilibrium Constants from the Literature	22
2.4	Water Inhibition on Cation Exchange Resins	25
3	Experimental	28
3.1	Experimental Setup	28
3.2	Materials	28
3.3	Analysis	30
3.4	Experimental Procedure	31
4	The Reaction Rate Prediction with Existing Models	35
4.1	Modelling the Reaction Rate	35
4.2	Performance of Rate models	36
4.2.1	Pseudo Homogeneous Reaction rate	36
4.2.2	Langmuir-Hinshelwood Reaction rate	36
4.3	Summary	40



5	Reaction Rate Prediction	43
5.1	Equilibrium Constant	43
5.1.1	Concentration Based Reaction Equilibrium Constant	43
5.2	Activity Based Reaction Equilibrium Constant	45
5.3	Reaction Rate Modelling	47
5.3.1	Pseudo Homogeneous Reaction Rate	47
5.3.2	Langmuir-Hinshelwood Reaction Kinetics	48
5.3.3	Eley-Rideal Reaction Kinetics	49
6	Conclusions	54
A	Appendix	59
A.1	Calculation of the volume adsorbed onto a catalyst bead	59
A.2	Experimental	60
A.2.1	Sample make up for the determination of the analytical repeatability.	60
A.3	Experimental data	61
A.4	Method Followed for the Prediction of Rate data	66

NOMENCLATURE

α	Constant in Freundlich isotherm	
α_{ij}	NRTL parameter	
β_i	UNIFAC parameter	
η_i	Inhibition factor	
γ_i	Activity coefficient for component i in the liquid phase	
λ	Reaction extent	mol
Λ_{ij}	Wilson interaction parameter	
τ_{ij}	NRTL and UNIFAC parameter	
θ_i	UNIFAC and UNIQUAC parameter	
θ_j	Surface coverage of component j	
v_i	Stoichiometric coefficient of component i	
A	Methanol	
a_i	Liquid phase activity of component i	
a_i^p	Activity of component i in polymer phase	
A_{ij}	Wilson and NRTL parameter	cal.mol ⁻¹
a_{mk}	Interaction parameter	K
B	Acetic Acid	

C	Methyl Acetate	
C_i	Concentration of component i	$\text{mol}.\ell^{-1}$
C_t	Total concentration in the reaction mixture	$\text{mol}.\ell^{-1}$
D	Water	
e_{ij}	UNIFAC parameter	
g^C	Combinatorial UNIFAC term	
G_i^E	Gibbs excess energy of component i	$\text{kJ}.\text{kmol}^{-1}$
g^R	Residual UNIFAC term	
G_F^o	Standard state Gibbs energy of formation	$\text{kJ}.\text{kmol}^{-1}$
G_{ij}	NRTL parameter	
H_F^o	Standard state enthalpy of formation	$\text{kJ}.\text{kmol}^{-1}$
J_i	UNIFAC and UNIQUAC parameter	
k_1	Rate constant	$\ell.\text{g}^{-1}.\text{min}^{-1}$
k'_1	Rate constant	$\ell^2.\text{g}^{-1}.\text{min}^{-1} \text{ mol}^{-1}$
K_a	Activity based reaction equilibrium constant	
K_C	Reaction equilibrium constant based on concentration	
K_i	Equilibrium adsorption constant for component i	
k'_{-1}	Reverse reaction rate constant	$\ell^2.\text{g}^{-1}.\text{min}^{-1}.\text{mol}^{-1}$
K_γ	Activity coefficient equilibrium constant	
K_{eq}	Equilibrium constant based on theoretical data	
l	Used as a subscript to define the liquid phase	
L_i	UNIFAC and UNIQUAC parameter	
m^i	Total mass adsorbed	g
m^o	Total solvent weight	g
m_i^S	Mass adsorbed of component i	g

m_{cat}	Mass dry catalyst	g
MM_i	Molar mass of component i	
n_i	Moles of component i	mol
n_o	Initial amount of moles	mol
N_t	Total amount of moles in the reaction mixture	mol
P	System pressure	kPa
P_i^{sat}	Saturation pressure for component i	kPa
q	Swelling ratio	
Q_i	UNIFAC and UNIQUAC subgroup parameter	
q_i	UNIFAC and UNIQUAC parameter	
R	Ideal gas constant	$\text{kJ.kmol}^{-1}.\text{K}^{-1}$
r_A	Reaction rate	$\text{mol.g}^{-1}.\text{min}^{-1}$
R_i	UNIFAC and UNIQUAC subgroup parameter	
r_i	UNIFAC and UNIQUAC parameter	
S	Used as a superscript to define the resin phase	
s_i	UNIFAC and UNIQUAC parameter	
T	Temperature	K
T	Used as superscript to encapsulate the total reaction area, resin and liquid phase	
T°	Standard state temperature	K
V	Reaction volume	ℓ
V_i	Molecular volume of component i	mol.m^{-3}
v_i	Volume of component i in sample	$\mu\ell$
v_k^i	Amount of subgroups, k , in molecule, i . UNIFAC and UNIQUAC parameter	
V_p°	Volume of the dry polymer phase	m^3
W_i	Weight of reagent i	μg

w_i	Weight of fraction of component i	
x_i	Mole fraction of component i in the liquid phase	
y_i	Mole fraction of component i in the vapour phase	
E	Apparent activation energy of reaction	kJ.kmol^{-1}
W	moles H^+ ions/moles of mixture	$\text{H}^+.\text{mol}^{-1}$

CHAPTER 1

Introduction

The esterification of acetic acid, equation 1.1, is a classical reaction system where the conversion achieved is bound by equilibrium.



With the volatility difference between the products, reactive distillation is an ideal process for the synthesis of methyl acetate (Xu & Chuang, 1996). When modelling this process the reaction rate and reaction equilibrium should be well defined, subsequently these aspects have received considerable attention in the literature. The reaction has been studied using both homogeneous – (Rönneback et al., 1997) and cation exchange resin catalysts (Lode et al., 2004; Song et al., 1998; Pöpken et al., 2000; Xu & Chuang, 1996; Mäki-Arvela et al., 1999; Yu et al., 2004).

Cation exchange resins bring interesting facets to heterogeneous catalysis. The ability of exchange resins to preferentially sorb components out of the liquid mixture increases the catalyst's usability as a selective catalyst (Chakrabarti & Sharma, 1993). Cation exchange resin is particularly susceptible to the sorption of polar components, and water in particular. The selective sorption of water decreases the amount of active sites available for the reaction to propagate, thereby inhibiting the reaction rate (Vaidya et al., 2003; Limbeck et al., 2001; Toit & Nicol, 2004).

The selective sorption of cation exchange resins, results that the concentration of the reaction mixture on the surface of the resin might be significantly different to that of the bulk liquid mixture. This results that a variety of methods have been used to model the reaction rate on a cation exchange resin: 1) pseudo homogeneous reaction kinetics (Xu & Chuang, 1996) 2) modelling the adsorption of the all the species onto the resin surface (Langmuir-Hinshelwood reaction kinetics) (Song et al., 1998; Pöpken et al., 2000); 3) selective adsorption of components from the reaction mixture (Eley-Rideal reaction

kinetics) (Lilja et al., 2002; Altiokka & Citak, 2003) and lastly 4) description of the resin phase concentration by absorption models (Lode et al., 2004; Mazzotti et al., 1997; Sainio et al., 2004).

The purpose of this investigation was first of all to generate experimental data for the reaction rate of this system over a wide concentration range using Amberlyst 15 Wet, a macroreticular ion exchange resin. Secondly, the aim was to compare the ability of different models from literature to describe the reaction data generated and to develop a more suitable rate model if possible. As there is discrepancy regarding the description of the equilibrium constant in literature, all experimental runs were allowed to reach equilibrium in order to test the different models.

The reaction was carried out in a batch reactor at 50°C. Only the forward reaction, the synthesis of methyl acetate, was considered.

CHAPTER 2

Background

2.1 Cation exchange resins

The industrial shift towards processes which are more environmentally friendly, initiated the move from homogeneous catalysis to heterogeneous catalysis. When considering acid catalysts, the advantages of heterogeneous catalysts are more profound than their homogeneous counterparts (Harmer & Sun, 2001):

- Reduced equipment corrosion,
- separation cost reduction,
- reduce the possibility for the contamination of recycle and product streams,
- could result in more process options available for the engineer,
- the reaction selectivity could also be better than that achieved for a homogeneous catalyst.

Cation exchange resins are one such heterogeneous catalyst. A cation exchange resin can be described as an insoluble polymer matrix that can exchange ions with the adjacent mixture. The resin can be formed by the copolymerisation of styrene with divinylbenzene, which acts as crosslinking agent (figure 2.1). The amount of crosslinking has a pronounced effect on the resin's ability to swell when immersed in solution (Laatikainen et al., 2002).

For the reaction to proceed on the catalyst surface, active sites need to be placed on the resin matrix. For cation exchange resins, acid sites are deposited on the polymer matrix by the treatment of the polymer matrix with a strong acid. For the formation of sulphonated cation exchange resins the polymer matrix is treated with concentrated sulfuric acid (figure 2.2). The acid loading of the resin is a measure of the catalytic

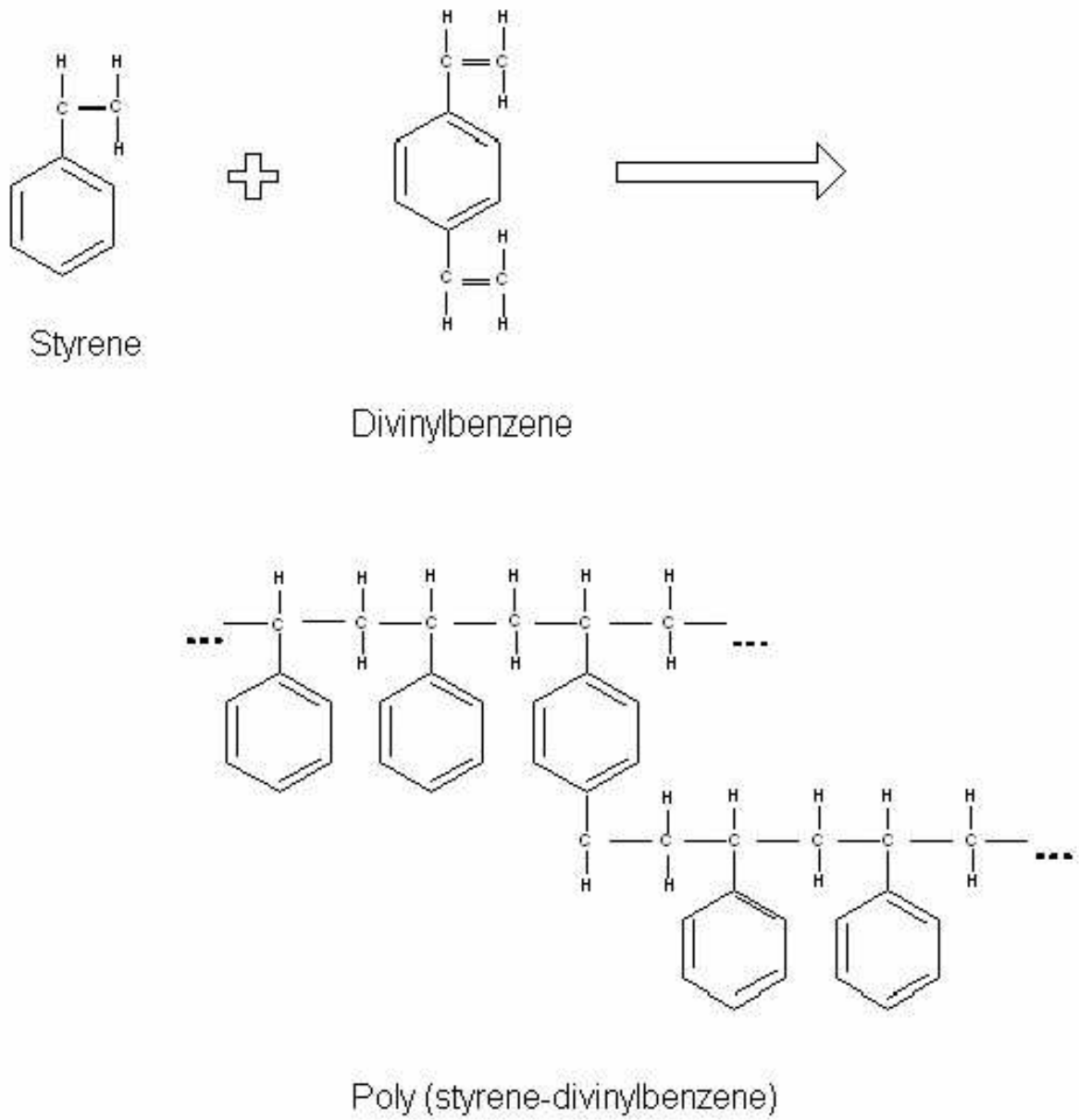


Figure 2.1: The copolymerisation of styrene and divinylbenzene (Helfferich, 1962)

activity of the polymer matrix, and plays an important part in catalysis (Chakrabarti & Sharma, 1993).

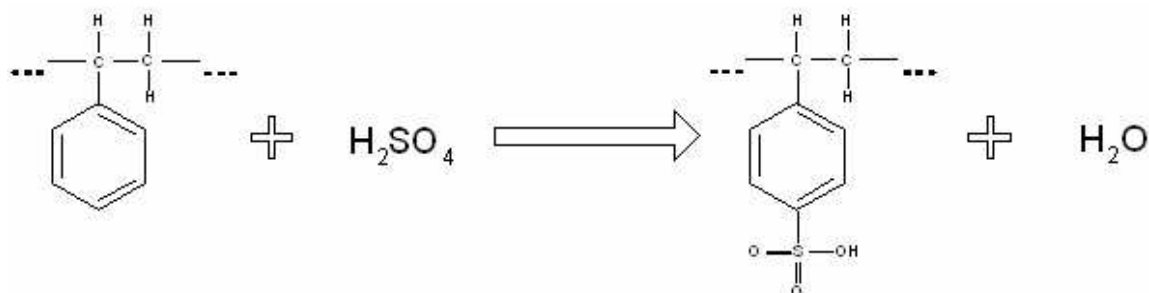


Figure 2.2: The sulphonation of the polymer matrix

Cation exchange resins can be divided into two groups:

- Gellular resins, a homogeneous polymer gel matrix.
- Macroreticular resins, consists of small polymeric beads interspersed with macro-pores.

When gellular resins are totally dried the polymeric resin matrix will collapse, the matrix will then be as close as allowed by atomic forces. In this state the resin will not be catalytically active, unless the reagents added to the mixture will result in the swelling of the polymer matrix. The main difference between a macro porous resin and a gellular resin is that the gel structure is interspersed with macro pores that allow for easy access to the active sites inside the resin. This allows that the macroreticular resins do not require swelling to be induced for the resin to become catalytically active.

The resin that was used in this investigation, Amberlyst 15, is such a macro-porous ion exchange resin. In the absence of polar compounds the reaction would be limited to the macro-pores. However, polar compounds will result the micro beads to swell, enabling access for the reagents deeper into the gel structure where more acid sites are situated. The esterification of methanol is such a polar system.

The influence that the swelling of the resin has on the resin phase and the subsequent sorption of fluid is discussed more elaborately in section 2.2.4.

2.2 Reaction Rate Models on Cation Exchange Resins

2.2.1 Pseudo Homogeneous

For a reaction to occur in the presence of a heterogeneous catalyst, the reactants first needs to travel from the bulk fluid, to the surface of the catalyst; from here the reactants

still needs to diffuse into the pores of the catalyst and lastly adsorb onto the catalyst surface Fogler (1999: p. 592).

When pseudo homogeneous reaction kinetics are used to describe the reaction, the adsorption of the reactants onto the catalyst surface is assumed to be negligible (Helfferich, 1962).

The chemical reaction equation will then just be written as:

$$r_A = -k'_1 \left(C_A C_B - \frac{1}{K_C} C_C C_D \right) \quad (2.1)$$

where,

$$K_C = \frac{k'_1}{k'_{-1}} = \frac{C_C C_D}{C_A C_B} \quad (2.2)$$

where, r_A is the reaction rate in terms of the amount of dry catalyst (m_{cat}), k'_1 is the forward reaction rate and K_C is the equilibrium constant based on concentration of the reagents in the liquid mixture. A , B , C and D represents methanol, acetic acid, methyl acetate and water respectively. With the determination of the equilibrium constant based on the liquid phase concentration it is implied that the liquid mixture is ideal, and that the volume of the liquid mixture stays constant.

When considering most reactions catalysed by a heterogeneous catalyst the reaction on the catalyst surface is more complex than a normal elementary reaction equation and the mechanisms are not so easily reducible to achieve a pseudo homogeneous rate equation. This is even more true for a resin catalyst, where the additional gel phase comes into play.

2.2.2 Activity Based Reaction Models

When modelling the reaction for a liquid system where the mixture is non ideal, correction must be made to the concentration to indicate the departure from the ideal case. The non-ideality spawns from differences in interaction between the molecules, as well as size and shape differences in the molecules participating in the liquid mixture. Usually a phase model such as the UNIFAC (universal functional activity coefficient), UNIQUAC (universal quasi-chemical equation) and NRTL (non random two liquid) phase equilibrium models are used to predict this non-ideality factor, the activity coefficient (γ).

The activity coefficient is determined from the excess Gibbs energy (G_i^E), this excess originates from the difference between the Gibbs energy of mixing for the real liquid mixture subtracted by the Gibbs energy of mixing of an ideal mixture at the same temperature, pressure and mole fraction (Winnick, 1997).

The non-ideality of the mixture then needs to be approximated in the rate equation,

more so to model the non-ideality on the reaction equilibrium (section 2.3.1) than to predict the reaction rate. Generally the rate equation is then written in terms of the activity of each component (a_i) participating in the reaction mixture (equation 2.4).

$$a_i = \gamma_i x_i \quad (2.3)$$

$$r_A = k_1 \left(a_A a_B - \frac{1}{K_a} a_C a_D \right) \quad (2.4)$$

with

$$K_a = \prod (x_i \gamma_i)^{\nu_i} \quad (2.5)$$

where K_a is the activity based reaction equilibrium constant. The relationship between the rate of reaction given in equation 2.2 (k'_1) and 2.4 (k_1) can be determined by the substitution of activity coefficient into the concentration reported in equation 2.2. Firstly the concentration needs to be written in terms of activity:

$$C_i = \frac{n_i}{V} = \frac{x_i N_t}{V} = \frac{a_i N_t}{\gamma_i V} \quad (2.6)$$

substituted in equation 2.2 gives,

$$r_A = -k'_1 \left(\frac{a_A a_B}{\gamma_A \gamma_B} \left(\frac{N_t}{V} \right)^2 - \frac{a_C a_D}{\gamma_C \gamma_D} \frac{1}{K_C} \left(\frac{N_t}{V} \right)^2 \right) \quad (2.7)$$

with

$$K_\gamma = \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \quad (2.8)$$

and

$$C_t = \frac{N_t}{V} \quad (2.9)$$

gives,

$$r_A = -\frac{k'_1 C_t^2}{\gamma_A \gamma_B} \left(a_A a_B - \frac{a_C a_D}{K_\gamma K_C} \right) \quad (2.10)$$

thus, by dividing equation 2.4 with equation 2.10:

$$k_1 = \frac{k'_1 C_t^2}{\gamma_A \gamma_B} \quad (2.11)$$

where N_t is the total amount of molecules in the reaction mixture, C_t is the total mixture concentration and V is the reaction volume.

The only problem that still remains is the prediction of the activity coefficients needed to establish the activities used to model the rate equation for the non-ideal case. As stated before the activity coefficient is a function of the excess Gibbs energy, this can be written as given in equation 2.12.

$$\ln\gamma_i = \left[\frac{\partial (G^E/RT)}{\partial n_i} \right]_{P,T,n_j} \quad (2.12)$$

The miscibility of methyl acetate and water is such that a clear division in the mixture is apparent but with the addition of acetic acid and methanol this phase division disappears. This indicates that liquid-liquid equilibrium should be used for the description of the liquid phase non-ideality.

However, lack of experimental liquid-liquid equilibrium (LLE) data resulted that the vapour-liquid equilibrium (VLE) data were used to predict the non-ideality of the system. The activity coefficient is usually determined from the VLE for the binary pairs. The activity coefficient can be experimentally determined from VLE data by using equation 2.13.

$$\gamma_i = \frac{y_i P}{x_i P_i^{sat}} \quad (2.13)$$

where, P is the system pressure, P_i^{sat} is the saturation pressure of component i and y_i is the vapour fraction of component i .

The UNIFAC (Ahtiokka & Citak, 2003), UNIQUAC (Pöpken et al., 2000) and Wilson (Song et al., 1998) local composition models were used in this investigation due to the fact that authors in the literature used these specific models to account for the non-ideality in the liquid phase. The NRTL local composition model was also used due to the ability of the model to describe the non-ideality of a solution for a large concentration range (Smith et al., 2001).

UNIFAC Group contribution method

A novel method to predict the activity of a liquid mixture is by building each component from the individual components that the molecule is composed of and then using this to predict the activity coefficient based on the bulk mixture composition.

The UNIFAC group contribution method is based on this principle, it relies on an extensive database that has been updated throughout the years. To determine the activity of a mixture the excess Gibbs energy is divided into two parts, the combinatorial (C) and residual (R) part (equation 2.14). The combinatorial term is based on molecular parameters that are developed from the individual groups and do not take any interaction

terms into account. The residual term describes the interaction between different groups in the mixture (Winnick, 1997: p. 410).

$$g \equiv g^C + g^R \quad (2.14)$$

Since the activity coefficient is dependent on the ΔG_{excess} , the activity coefficient is then similarly given by equation 2.15. The activity coefficient is then basically a function of each of the subgroups properties (R_k and Q_k) but also the interaction between each of these subgroups (a_{mk}). The complete UNIFAC function is given in equation 2.15 to equation 2.27 (Smith et al., 2001: p. 763).

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (2.15)$$

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i \left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i} \right) \quad (2.16)$$

$$\ln \gamma_i^R = q_i \left[1 - \sum_k \left(\theta_k \frac{\beta_{ik}}{s_k} - e_{ki} \frac{\beta_{ik}}{s_k} \right) \right] \quad (2.17)$$

$$(2.18)$$

with,

$$J_i = \frac{r_i}{\sum_j r_j x_j} \quad (2.19)$$

$$L_i = \frac{q_i}{\sum_j q_j x_j} \quad (2.20)$$

$$r_i = \sum_k v_k^{(i)} R_k \quad (2.21)$$

$$q_i = \sum_k v_k^{(i)} Q_k \quad (2.22)$$

$$e_{ki} = \frac{v_k^{(i)} Q_k}{q_i} \quad (2.23)$$

$$\beta_{ik} = \sum_m e_{mi} \tau_{mk} \quad (2.24)$$

$$\theta = \frac{\sum_i x_i q_i e_{ki}}{\sum_j x_j q_j} \quad (2.25)$$

$$s_k = \sum_m \theta_m \tau_{mk} \quad (2.26)$$

$$\tau_{mk} = \exp \frac{-a_{mk}}{T} \quad (2.27)$$

The term v_k^i is used to identify the amount of subgroups (k) in the molecule (i). The relevant UNIFAC vapour liquid equilibrium (VLE) subgroup parameters for the chemical system in this investigation are given in table 2.1, and the interaction parameters, a_{mk} , is given in table 2.2. These parameters were obtained from Fredenslund et al. (1977).

Table 2.1: UNIFAC-VLE Subgroup parameters

Main Group	Subgroup	R_k	Q_k
CH_3	CH_3	0.9011	0848
CH_3OH	CH_3OH	1.4311	1.432
H_2O	H_2O	0.92	1.4
CH_2CO	CH_3CO	1.6724	1.488
CH_2O	CH_3O	1.1450	1.088
$COOH$	$COOH$	1.3013	1.224

Table 2.2: UNIFAC-VLE Interaction parameter (Fredenslund et al., 1977)

	CH_3	CH_3OH	H_2O	CH_2O	CH_2CO	$COOH$
CH_3	0.00	697.2	1318	476.4	251.5	663.5
CH_3OH	16.51	0.00	-181.0	23.39	-180.6	-289.5
H_2O	580.6	289.6	0.00	-280.8	-400.6	-225.4
CH_2CO	26.76	108.7	605.6	0.00	5.202	669.4
CH_2O	83.36	339.7	634.2	52.38	0.00	664.6
$COOH$	315.3	1020	-292.0	-297.8	-338.5	0.00

UNIQUAC Group contribution method

The UNIQUAC model is very similar in structure to that of the UNIFAC model. The combinatorial term is the same as given in equation 2.16, the residual term however differs (equation 2.28) Smith et al. (2001: p. 764).

$$\ln \gamma_i^R = q_i \left(1 - \ln s_i - \sum_j \theta_j \frac{\tau_{ij}}{s_j} \right) \quad (2.28)$$

with

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (2.29)$$

When Pöpken et al. (2000) worked with the UNIQUAC activity model, a polynomial temperature dependence was introduced for the interaction parameter (τ_{ij}) by equation 2.30. The coefficients used by Pöpken et al. (2000) is given in table 2.3. This temperature dependence was also used in this investigation.

$$a_{mk} = a_{ij} + b_{ij}T + c_{ij}T^2 \quad (2.30)$$

It should just then be noted that the interaction parameter a_{mk} specified by Pöpken et al. (2000) has units of K^{-1} . The parameter was fitted to VLE data, the activity at infinite dilution and heat of mixing data.

Table 2.3: UNIQUAC temperature polynomial parameters for τ_{ij} (Pöpken et al., 2000)

i	j	$a_{ij}(K)$	b_{ij}	$c_{ij}(K^{-1} \times 10^3)$
Acetic acid	Methanol	390.3	0.97	-3.06
Methanol	Acetic acid	65.2	-2.03	3.16
Acetic acid	Methyl acetate	-62.2	-0.44	0.27
Methyl acetate	Acetic acid	81.8	1.12	-1.33
Acetic acid	Water	422.4	-0.05	-0.24
Water	Acetic acid	-98.1	-0.29	-0.076
Methanol	Methyl acetate	63.0	-0.71	1.17
Methyl acetate	Methanol	326.2	0.72	-2.35
Methanol	Water	-575.7	3.15	-6.07
Water	Methanol	219.0	-2.06	7.01
Methyl acetate	Water	593.7	0.01	-2.16
Water	Methyl acetate	-265.8	0.96	0.20

NRTL Local Composition Method

The NRTL method was developed for long range interactions between molecules. The primary purpose of this model was to estimate thermodynamic properties, from diluted aqueous electrolyte solutions to pure molecular systems (Carslaw et al., 1997).

For a multicomponent system the NRTL equation is given by:

$$\ln \gamma_i = \sum_{j=1}^n \frac{\sum_{j=1}^n \tau_{ji} G_{ji} x_j}{\sum_{j=1}^n G_{ji} x_j} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{k=1}^n x_k \tau_{kj} G_{kj}}{\sum_{k=1}^n x_k G_{kj}} \right) \quad (2.31)$$

with

$$\tau_{ij} = \frac{A_{ij}}{RT} \quad (2.32)$$

with $\ln G_{ij} = -\alpha_{ij}\tau_{ij}$ ($G_{ii} = G_{jj} = 1$), $\alpha_{ij} = \alpha_{ji}$ and $\tau_{ii} = 0$. This equation has three parameters, τ_{ij} , τ_{ji} and α_{ij} , that can be determined from experimental data. The NRTL parameters were obtained from the fitting achieved by Gmehling & Onken (1977) on the binary vapour equilibrium data. Table 2.4 gives the parameters needed for the solution of the system under investigation. It should just be noted that for the parameters given that $R = 1.987 \frac{\text{cal}}{\text{mol.K}}$.

Table 2.4: NRTL interaction parameters (Gmehling & Onken, 1977)

		A_{ij} (cal/mol)	A_{ji} (cal/mol)	α_{ij}
Methanol	Acetic acid	16.65	-217.13	0.305
Methanol	Methyl acetate	443.88	290.35	0.297
Methanol	Water	-243.55	872.813	0.299
Acetic acid	Methyl acetate	-635.89	1218.87	0.360
Acetic acid	Water	-495.74	1295.60	0.297
Methyl acetate	Water	641.15	1492.48	0.2848

Wilson Local Composition Method

The Wilson multicomponent local composition model (equation 2.33) was used by Song et al. (1998) to describe the non-ideality of the liquid phase.

$$\ln \gamma_i = 1 - \ln \left(\sum_{j=1} x_j \Lambda_{ij} \right) - \sum_{k=1} \left(\frac{x_k \Lambda_{ki}}{\sum_{j=1} x_j \Lambda_{kj}} \right) \quad (2.33)$$

$$\Lambda_{ij} = \frac{V_j}{V_i} e^{-\frac{A_{ij}}{RT}} \quad (2.34)$$

where V_i is the molecular volume, and A_{ij} is the Wilson parameter given in table 2.5 (Song et al., 1998).

Although the Wilson model would not be able to describe a system where a phase separation is evident, as is the case for methyl acetate and water, the model was still included due to the use of the model by Song et al. (1998) to account for the liquid phase non-ideality.

Table 2.5: Wilson parameters, A_{ij} (cal/mol)

	CH_3OH	CH_3COOH	CH_3COOCH_3	H_2O
CH_3OOH	0	-547.52	813.18	107.38
CH_3COH	2535.2	0	1123.144	107.38
CH_3COOCH_3	-31.19	-696.5	0	645.72
H_2O	469.55	658.03	-21.23	0

2.2.3 Adsorption Based Reaction Models

Due to selectivity differences between the resin and the different components in the reaction mixture, the concentration distribution on the surface of the catalyst might be significantly different to that encountered in the liquid mixture. For an accurate description of the reaction rate this concentration needs to be known.

Adsorption type isotherms are used to relate the concentration on the resin surface to the bulk concentration. When the adsorbents are dilute in the fluid phase a linear isotherm can be used to approximate the concentration of the reactants on the resin phase (Yu et al., 2004). This approach however will only work at dilute concentrations, for higher concentrations a Langmuir adsorption isotherm is popular (Song et al., 1998; Pöpken et al., 2000).

In this report emphasis is put on using Langmuir adsorption isotherms to describe the amount of adsorbed reactants on the resin.

Langmuir-Hinshelwood and Eley-Rideal kinetics

The Langmuir-Hinshelwood model for reaction is based on the principle that the reactants are initially chemisorbed before the reaction can proceed (Thomas & Thomas, 1997: p. 460). Afterwards the reagents can rearrange and react before desorption. An example of what could possibly occur is given in equation 2.35 to 2.39.



The reaction rate can then simply be given as a function of the fraction of each species adsorbed onto the catalyst (equation 2.40).

$$r_a = k_1 \left(\theta_A \theta_B - \frac{1}{K_{eq}} \theta_C \theta_D \right) \quad (2.40)$$

where θ_i is the fractional coverage of component i . It can be assumed that the rate of adsorption is usually faster than the rest of the steps. From the kinetic theory of adsorption the Langmuir adsorption isotherm can be derived by equating the rate of adsorption and desorption and by applying the following simplifying assumptions (Ruthven, 1984: p. 49):

- The molecules are adsorbed to a fixed number of sites.
- Only one adsorbate is allowed for each adsorption site.
- All the adsorption sites are energetically equivalent.
- There is no interaction between adsorbed molecules.

The Langmuir adsorption isotherm for component A is then given by equation 2.41.

$$\theta_A = \frac{K_A C_A}{(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D)} \quad (2.41)$$

If the adsorption of all the components is described in this manner and then substituted into the rate expression, equation 2.40, the resulting equation describing the reaction rate is given by equation 2.42.

$$r_a = \frac{k_1 \left(K_A C_A K_B C_B - \frac{1}{K_{eq}} K_C C_C K_D C_D \right)}{(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D)^2} \quad (2.42)$$

where K_i is the equilibrium adsorption constant for each component. The derivation for Eley-Rideal reaction kinetics is much the same. The only difference is that it is assumed that only part of the molecules participating in the reaction adsorbs onto the catalyst. This will result in a rate equation as given by equation 2.43.

$$r_a = k_1 \left(\theta_A C_B - \frac{1}{K_{eq}} C_C \theta_D \right) \quad (2.43)$$

The fractional coverage of each reactant adsorbing onto the resin is again approximated using the Langmuir adsorption isotherm. The fractional coverage of component A, is then given by:

$$\theta_A = \frac{K_A C_A}{1 + K_A C_A + K_D C_D} \quad (2.44)$$

Substituting both the fractional coverage into the reaction equation will then give:

$$r_a = \frac{k_1 \left(K_A C_A C_B - \frac{1}{K_{eq}} C_C K_D C_D \right)}{(1 + K_A C_A + K_D C_D)} \quad (2.45)$$

It should be noted that the adsorption model used are more relevant to gas phase reactions. This is due to the fact that the isotherms used to predict the concentration on the surface of the catalyst is more applicable to low sorbate concentrations. For liquid adsorption, this however is not the case. The concentration on the surface tends to reach saturation, which results that deviations occur (Ruthven, 1984: p. 121). This method is however used for the prediction of liquid phase adsorption, but instead of fractional coverage the isotherm is used to describe the mass or mole adsorbed. Both Pöphen et al. (2000) and Song et al. (1998) used Langmuir-Hinshelwood based reaction kinetics to model the reaction rate. The method used for the modelling of the adsorption was different for both.

Song et al. (1998) used a similar approach to that specified in the previous section. Adsorption experiments were done for the binary, non-reactive components. For the determination of the amount adsorbed, the mole balance over the liquid phase was determined with the composite isotherm given by Kipling (1965) (equation 2.46).

$$\frac{n_o \Delta x}{m_{cat}} = n_1^S x_2 - n_2^S x_1 \quad (2.46)$$

where n_o is the total amount of moles initially, Δx is the change of mole fraction in the liquid phase, n_1^S and n_2^S are the amounts of moles of component A and B that adsorbed onto a unit mass of catalyst. The superscripts S identifies the surface of the catalyst and where no superscript is presented, the liquid phase is indicated.

As expected the only unknowns in equation 2.46 are n_1^S and n_2^S . As is, the equation only explains the mole balance for the two components, some refinement is necessary to determine the equilibrium adsorption constant. As stated earlier Song et al. (1998) modelled the adsorption for the binary pairs (e.g. methanol and methyl acetate), which results that competitive sorption is applicable (equation 2.47).



where the subscript l is used to describe the liquid phase concentration. In effect this is a composite of the equilibrium constant of equation 2.35 and 2.36. This can then be used to determine the adsorption equilibrium. Song et al. (1998) accounted for non-ideal liquid phase behaviour, which resulted that the liquid phase concentration was rather described with activity. This would then give an adsorption equilibrium constant as shown in equation 2.48.

$$K_{2,1} = \frac{x_1^S a_2}{x_2^S a_1} \quad (2.48)$$

A simple mole balance would reveal that $x_2^S = 1 - x_1^S$, which can be substituted into the adsorption equilibrium to give equation 2.49.

$$x_1^S = \frac{K_{2,1} a_1}{K_{2,1} a_1 + a_2} \quad (2.49)$$

Since the total number of sites on the resin is constant, and all of the molecules occupy the same number of sites. Song et al. (1998) specified that the total amount of moles adsorbed on the surface would be independent of the surface composition (therefore $n_1^S + n_2^S = n^S$), and since $x_1^S = \frac{n_1^S}{n^S}$ equation 2.49 can be written as:

$$n_1^S = n^S \frac{K_{2,1} a_1}{K_{2,1} a_1 + a_2} \quad (2.50)$$

A similar expression can be derived for n_2^S . These two can be substituted into equation 2.46, resulting in equation 2.51.

$$\frac{n_o \Delta x}{m_{cat}} = \frac{n^S (K_{2,1} a_1 x_2 - a_2 x_1)}{K_{2,1} a_1 + a_2} \quad (2.51)$$

This expression was then applied to experimental adsorption data. Song et al. (1998) predicted the two parameters $K_{2,1}$ and n^S (this parameter was however not given) by the linear regression of the experimental adsorption data. These could then be used to determine the equilibrium adsorption of the individual reagents using the relationship between equation 2.47 and equation 2.35 - 2.36, given by equation 2.52.

$$K_2 = \frac{K_{2,1}}{K_1} \quad (2.52)$$

The adsorption experiments for four pairs of components could be run (the others reacted). Of these only three pairs are independent, the fourth can be used as a consistency check. The adsorption equilibrium constant for each component could be written in terms of a reference component, as given in equation 2.53. The value of the reference adsorption equilibrium constant, $K_{Methyl\ Acetate}$, was fitted on the kinetic data at 45°C together with the rate constant. The equilibrium adsorption constants predicted by the author is given in table 2.6.

$$\begin{aligned} K_{Methanol} &= K_{1,3} K_{Methyl\ Acetate} \\ K_{Acetic\ acid} &= K_{2,3} K_{Methyl\ Acetate} \\ K_{Water} &= K_{4,3} K_{Methyl\ Acetate} \end{aligned} \quad (2.53)$$

When modelling the adsorption of each species on the resin, Pöpken et al. (2000) did not assume that the total amount of moles adsorbed stayed constant (n_1^S), as proposed by Song et al. (1998). The amount adsorbed based on volume, mass and moles were measured for each component. From this it was rather assumed that the mass adsorbed stayed constant, since the value of the mass adsorbed for each component deviated the least.

This resulted that Pöpken et al. (2000) used a mass balance over the liquid phase, to give an expression similar to the one used by Song et al. (1998), to describe the adsorption of the binary pairs (equation 2.54).

$$\frac{m^o (w_1^o - w_1)}{m_{cat}} = \frac{m_1^S w_2 - m_2^S w_1}{m_{cat}} \quad (2.54)$$

where w_i is the weight fraction of component i , m^o is the total solvent weight and m_i is the mass adsorbed for each component. Pöpken et al. (2000) then assumed that the Langmuir adsorption is based on mass fraction adsorbed, which would then give equation 2.55. Which is very similar to equation 2.41, except that it is based on weight fractions.

$$\frac{m_i}{m^s} = \frac{K_i a_i}{1 + \sum_j K_j a_j} \quad (2.55)$$

m^s is the total mass adsorbed. This equation together with equation 2.54 (derived similarly to the method described in the work done by Song et al. (1998)), results in:

$$\frac{m^o (w_1^o - w_1)}{m_{cat}} = \frac{m^s}{m_{cat}} \frac{K_1 a_1 w_2 - K_2 a_2 w_1}{1 + K_1 a_1 + K_2 a_2} \quad (2.56)$$

From this the $\frac{m^s}{m_{cat}}$ and both the adsorption equilibrium constants K_1 and K_2 could be determined from binary adsorption data. The adsorption constants found by the author are given in table 2.6. The $\frac{m^s}{m_{cat}}$ was found to be 0.95.

Table 2.6: Adsorption equilibrium constants

	Song et al. (1998)	Pöpken et al. (2000)
$K_{Methanol}$	4.95	5.64
$K_{Acetic\ Acid}$	3.18	3.15
$K_{Methyl\ Acetate}$	0.82	4.15
K_{Water}	10.5	5.24

The difference between the adsorption equilibrium constants (table 2.6), is due to the difference in adsorption assumed by both these authors (constant mole and constant mass adsorbed).

Both these authors then used Langmuir-Hinshelwood reaction kinetics to describe the esterification of acetic acid. The reaction rate was described sufficiently in both cases.

Pöpken et al. (2000),

$$r = m_{cat} \left(k_1 \frac{a'_A a'_B - \frac{a'_C a'_D}{K_a}}{(a'_A + a'_B + a'_C + a'_D)^2} \right) \quad (2.57)$$

with,

$$a'_i = \frac{K_i a_i}{M M_i} \quad (2.58)$$

Song et al. (1998)

$$r = \frac{k_s \left(a_A a_B - \frac{a_C a_D}{K_a} \right)}{(1 + K_A a_A + K_B a_B + K_C a_C + K_D a_D)^2} \quad (2.59)$$

with,

$$k_s = k_{so} W e^{\frac{E}{RT}} \quad (2.60)$$

where W is the moles H⁺ ions/moles of mixture and E the apparent activation energy.

Lilja et al. (2002) used a postulate by Taft (1951) to predict the reaction mechanism on a cation exchange resin for esterification of acetic acid with ethanol. From this an Eley-Rideal adsorption model was used with only the adsorption of acetic acid and water onto the resin surface. In general it is assumed that cation exchange resins are more selective to polar compounds, which would imply that water and ethanol should rather be used for the bases of this assumption. This is confirmed by the equilibrium adsorption constants predicted by both Song et al. (1998); Pöpken et al. (2000). However, Lilja et al. (2002) did get good results with the model that he used, which is to be expected since the equilibrium adsorption constants and the equilibrium constant were fitted to describe the reaction rate.

For the esterification of acetic acid with isobutanol Altiokka & Citak (2003) also used Eley-Rideal adsorption but with the adsorption of water and isobutanol onto the cation exchange resin. The selection of the adsorbed molecules was made due to the effect of the alcohol and water on the initial reaction rate. Both the water and the isobutanol restricted the initial reaction rate. The restriction of the initial reaction rate due to the water concentration is shown in figure 2.3. The Eley-Rideal kinetic model proved sufficient to model the concentration of the liquid mixture on the surface of the catalyst, and a good fit of the rate data was achieved.

The choice of which adsorption method (Eley-Rideal or Langmuir-Hinshelwood) would

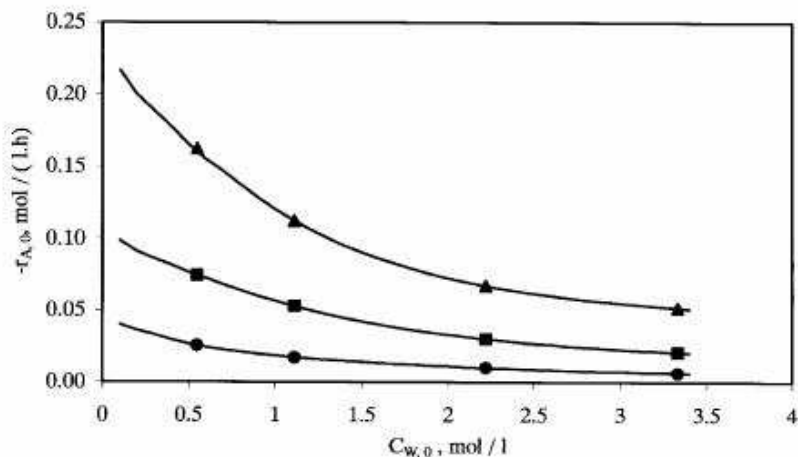


Figure 2.3: The initial reaction rate measure with different initial concentrations of water. ▲ - 348 K; ■ - 333 K; ● - 318 K (Altiokka & Citak, 2003).

be most useful for the description of the sorbed concentration, can only be based on experimental adsorption data. Both Pöpken et al. (2000); Song et al. (1998) determined that all the species adsorb onto the resin. From table 2.6, it seems that on a mass basis all the components sorb equally (Pöpken et al., 2000). On a mole basis a different story is evident, the water is adsorbed to a greater extent followed by methanol and then acetic acid. Methyl acetate sorbed hardly at all.

2.2.4 Absorption Based Modelling

With this type of model it is assumed that the reaction only occurs in the gel phase of the catalyst (Mazzotti et al., 1996; Lode et al., 2004; Mazzotti et al., 1997; Sainio et al., 2004). This approach is justified by the work done by Gusler et al. (1993) on different polymeric resins (Reillex-425, XAD-8, XAD-4, XAD-16, XAD-12). Gusler et al. (1993) determined that the amount of monolayers adsorbed differed for the sorption of different molecules. The amount of monolayers formed differed significantly, between 10^{-4} monolayers to 10^3 monolayers (figure 2.4) depending on the sorbed species. The amount of the reagent sorbed was connected to the capability of the resin to swell while adsorbing the reagent. It was noted that the amount sorbed was in excess of the pore volume, this suggested that absorption into the gel phase was more probable.

Pöpken et al. (2000) gave the sorption data for the esterification of acetic acid on Amberlyst 15. Based on this and the resin properties given by Sainio et al. (2004) it can be shown that the amount of water and methanol sorbed (in a single component system) is in excess of the pore volume (the method followed in this calculation is shown in appendix A.1). An indication that absorption might be the appropriate mechanism on a molecular level. To determine the resin phase concentration an appropriate phase model

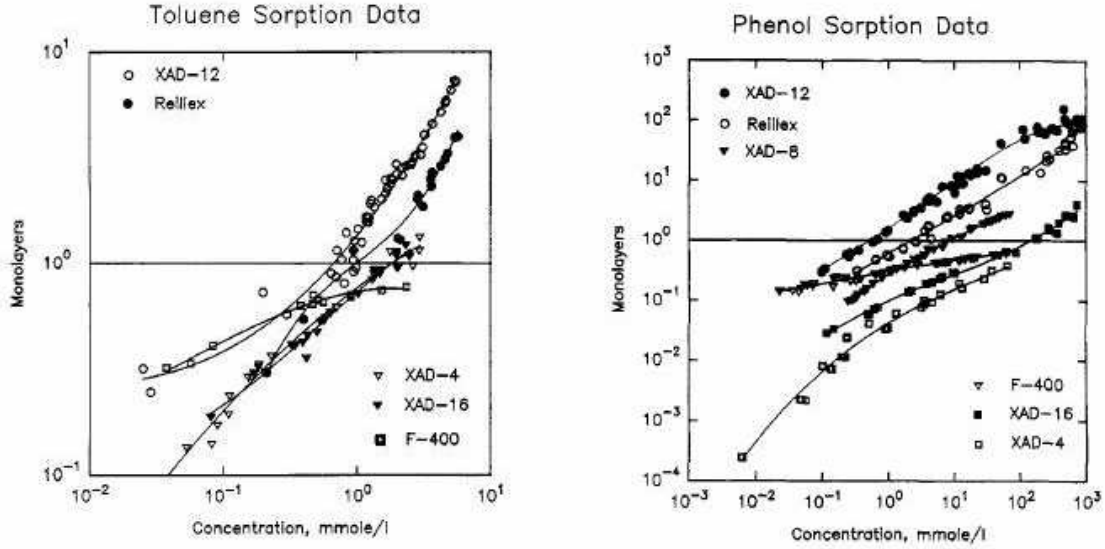


Figure 2.4: Amount of monolayers formed with the adsorption of toluene and phenol (Gusler et al., 1993).

should be used. For a mixture where a polymer exists in the solution the deviations from ideality are extreme and needs to be described with a more rigorous phase equilibrium model (Flory, 1953). The derivation of the polymer phase local composition model in principal is the same as for the liquid phase, except that the interactions of the long carbon chain with itself and other molecules need to be compensated for. However, the deviations that might occur with the mixing of a polymer with a liquid might not alone describe the deviations between the real fluid and the ideal fluid. When liquid is sorbed deeper into the polymer chain, the polymer swells which influences the configuration of the polymer phase. This will then result that the entropy of the polymer will change, and in turn this will influence the Gibbs mixing of the resin with the fluid. This then indicates that two contributions are present when modelling the change in free energy due to the mixing of the polymer phase and the fluid phase; 1) the mixing of the polymer and the fluid and 2) the swelling of the polymer phase (equation 2.61).

$$\Delta G_R = \Delta G_R^M + \Delta G_{swelling-R} \quad (2.61)$$

The change in Gibbs energy due to the mixing of the polymer and the liquid can then be described using models such as the proposed by Flory (1953). This can then be used to derive an expression for the resin phase activity.

This resin phase activity expression contains the binary interaction parameters (for each component in the sorbed phase, including the interaction between the sorbed components and the polymer phase), the elasticity parameter of the polymer phase and the volume fraction of each component on the resin phase. The volume fraction of each com-

ponent in the resin phase is determined by assuming ideal mixing, and then determining the volume fraction from the moles adsorbed of each specie per unit dry mass of resin.

The fitting of this activity model is usually done using experimental absorption data for the binary non-reactive pairs of each component of interest. The concentration of each component is determined by a mole balance over the liquid and resin phase, together with a constant phase equilibrium between the liquid and the resin phase (meaning $a_i^L = a_i^P$). For each binary pair there are three unknowns (the two binary interaction parameters) and then the elasticity parameter of the polymer phase. For the prediction of the interaction parameter for the esterification of acetic acid on methanol, Lode et al. (2004) fit the interaction parameters for the reactive pairs on reaction data as an extra parameter.

Simultaneous reaction and adsorption can now be modelled by solving the following set of equations simultaneously (equation 2.62 - 2.65).

$$\frac{dn_i^T}{dt} = qV_p^\circ k_1 c_{Aceticacid}^S c_{Ethanol}^S (1 - \Omega) \quad (2.62)$$

$$\Omega = \prod_{i=1}^N (a_i^S)^{v_i} \frac{1}{K_{eq}} \quad (2.63)$$

$$n_i^T = n_i^\circ + \lambda v_i \quad (2.64)$$

$$a_i^S = a_i^L \quad (2.65)$$

where q is the swelling ratio of the polymer phase, V_p° is the volume of the dry polymer phase, n_i^T is the total amount of moles for component i in the liquid and resin phase ($n_i^T = n_i^p + n_i^l$), n_i° is the initial amount of moles for component i , λ is the reaction extent, a_i^L and a_i^p is the liquid and resin phase activity. The reaction rate is therefore given as a function of the resin phase concentration and activity.

The resin phase activity is modelled with activity models such as the expression proposed by Flory (1953) and the liquid phase activity can be approximated using a liquid phase local composition model. For the esterification of acetic acid with methanol, Lode et al. (2004) modelled the liquid phase activity using the UNIFAC local composition model and the polymer phase model proposed by Flory (1953) for the resin phase activity.

This absorption based model is especially suited for the modelling of batch reaction systems, as the change in volume of the resin phase and subsequently the concentration of reactants in the resin phase is accounted for. Here the amount of catalyst, especially when relatively high amounts of catalyst are used, will influence the equilibrium conversion in a batch reactor as shown to be the case by Mazzotti et al. (1997) in their work on the ethanol esterification system.

For highly crosslinked resins with polar groups the absorption based modelling is not

so well understood, and inconsistent results have been reported (Mazzotti et al., 1997). Due to the complexity involved in the modelling of the phase equilibrium between the liquid and the resin phase together with a reaction on the resin phase, this method of describing the reaction rate has been ignored in this investigation.

2.3 Reaction Equilibrium Constant

For any reaction, it is imperative to know the equilibrium constant. As this will indicate the conversion that will be achieved at the reaction equilibrium. The reaction equilibrium constant is determined from the thermodynamics of the system. For a liquid phase reaction it is accepted that the equilibrium constant is only a function of temperature (Winnick, 1997). In very limited cases, where the liquid solution behaves ideally, the experimentally determined equilibrium constant can be calculated from the mixture concentration at equilibrium (K_C). However, in most cases the liquid system deviates from ideality and the equilibrium activities must be used to determine the equilibrium constant (K_a).

2.3.1 Reaction equilibrium constant from Gibbs Energy of Formation

For a chemical reaction the change in Gibbs energy can be given by equation 2.66.

$$\Delta G = \sum_i^n v_i G_i \quad (2.66)$$

where v_i is the stoichiometric coefficient for component i . The equilibrium constant for a specific reaction is then a function of this change in Gibbs Energy for the reaction, equation 2.67 Smith et al. (2001: p. 475).

$$\ln K_{eq} = \frac{-\Delta G}{RT} \quad (2.67)$$

with

$$\frac{\Delta G}{RT} = \frac{\Delta G^o}{RT^o} - \frac{\Delta H^o}{R} \left(\frac{1}{T} - \frac{1}{T^o} \right) \quad (2.68)$$

When modelling the equilibrium constant from experimental data, the constant can be determined by using equation 2.5. For an ideal liquid mixture $\gamma_i = 1$, this however is generally not the case and the non-ideality of the solution should be taken into account. The activity coefficient can be determined using a variety of local composition models, such as those proposed in section 2.2.2.

2.3.2 Equilibrium Constants from the Literature

For the modelling of the equilibrium constant various approaches have been followed in the literature, from the assumption that the liquid mixture is ideal (Rönneck et al., 1997; Xu & Chuang, 1996) to the use of different activity models to take the non-ideality of the liquid phase into account (Mäki-Arvela et al., 1999; Song et al., 1998; Pöpken et al., 2000). The deviation, dependant on which assumptions was used is quite significant (figure 2.5).

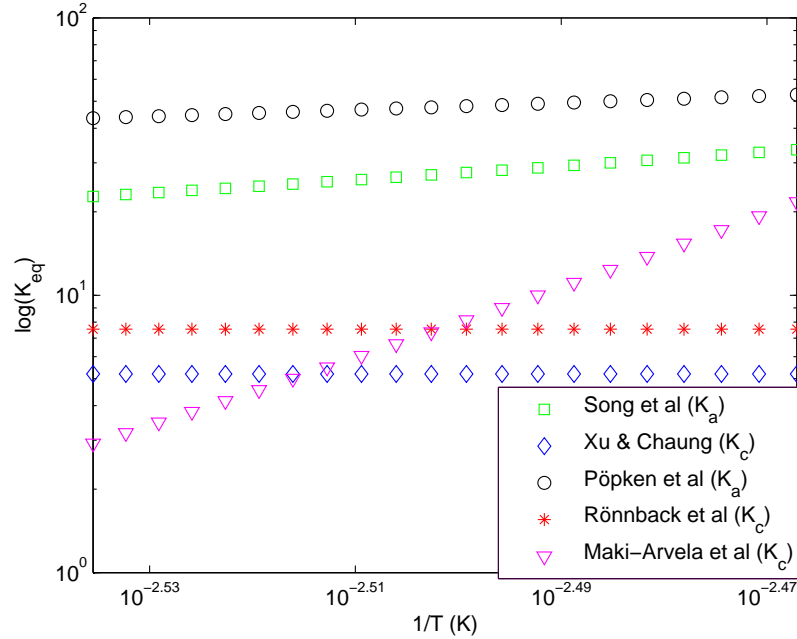


Figure 2.5: The equilibrium constant for the esterification of acetic acid as reported by various authors.

The equilibrium constant determined by Rönneck et al. (1997), 7.54, and Xu & Chuang (1996), 5.2, differed only slightly since both these authors determined the equilibrium constant based on the equilibrium concentration (K_C). Of the authors that determined the activity based equilibrium constant (K_a), Mäki-Arvela et al. (1999) determined an equilibrium constant that is essentially the same as those given when assuming an ideal liquid mixture. This suggests that the liquid mixture is nearly ideal according to the UNIFAC activity model.

A larger deviation between the K_c and K_a is noticeable in the work done by Song et al. (1998) and Pöpken et al. (2000) who used the Wilson and UNIQUAC local composition models to calculate the activity coefficients of the liquid phase. The scattered distribution that occurs with the prediction of the K_a , when using different phase equilibrium models, indicates that different models describes the non-ideality of the liquid phase differently (e.g. at 50°C $K_{a-UNIFAC} = 6.0$ and $K_{a-Wilson} = 26$). Pöpken et al. (2000) showed the deviation in his best fit equilibrium constant versus what was expected from thermodynamics and experimentally predicted by Song et al. (1998) (figure 2.6)).

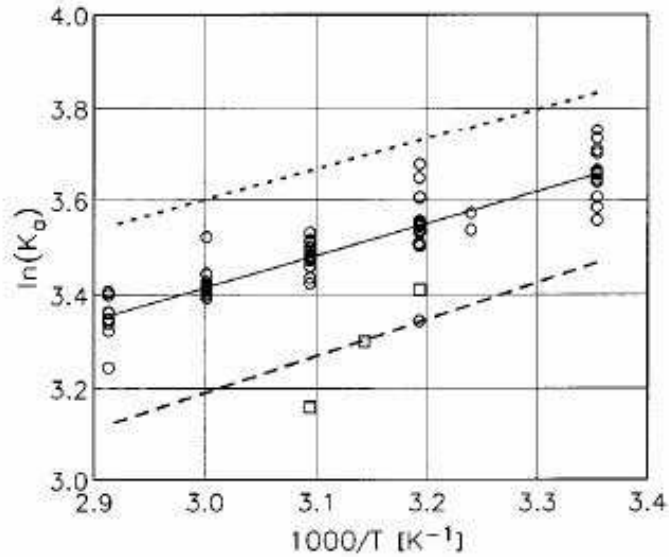


Figure 2.6: The experimentally determined equilibrium constant (K_a) given by Pöpken et al. (2000). The solid line was the best fit the author obtained for the experimental data. The short dashed line represents the thermodynamically determined equilibrium. The long dashed line the equilibrium constant as given by Song et al. (1998).

Although the theoretical equilibrium constant can be determined from the Gibbs energy of formation and enthalpy of formation at standard state using equation 2.68, all the authors in the literature used experimentally determined equilibrium constants. This is due to the fact that the Gibbs free energy of formation for each component is large and the difference in Gibbs energy, ΔG_F° , is small which results that small errors in the measured G_F° and H_F° result in large deviations in the predicted equilibrium constant. The results achieved with this method has a large uncertainty and proved unreliable (Song et al., 1998). As illustration the Gibbs energy of formation and enthalpy of formation at standard state were gathered from Aspen-Technology (2001), NIST (2005) and Pöpken et al. (2000), these are given in table 2.7. The order for the values of the different G_F° and H_F° reported was generally the same, although when using equation 2.68 and 2.67 to predict the theoretical equilibrium constant, large deviations occurred in the prediction. At 50°C the determined equilibrium constant was 752.2, 4.2×10^{-4} and 52.7 respectively. The exponent in equation 2.67 results that small errors get expanded quickly. Of the theoretical determined equilibrium constants, only the data supplied by Pöpken et al. (2000) gave a result that was close to what the equilibrium constant was determined to be. Pöpken et al. (2000) worked with a K_a of 46.7 at 50°C which is close to the predicted equilibrium constant of 52.7.

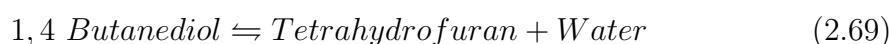
Table 2.7: The Gibbs energy of formation and enthalpy of formation at standard state needed for the determination of the change in Gibbs energy for the reaction (reported in kJ/mol , with $T^\circ = 298.15$ K). The data given in the table are with reference to the liquid phase.

Component	Aspen-Technology (2001)		NIST (2005)		Pöpken et al. (2000)	
	G_F°	H_F°	G_F°	H_F°	G_F°	H_F°
Methanol	-162.3	-238.8	-199.7	-238.4	-166.9	-239.1
Acetic acid	-374.6	-484.4	-382.9	-483.5	-389.2	-484.10
Methyl acetate	-324.2	-444.4	-325.4	-445.9	-328.4	-442.8
Water	-228.6	-285.8	-237.1	-285.8	-237.1	-285.8

2.4 Water Inhibition on Cation Exchange Resins

A cation exchange resin is known to have a particular affinity to polar components. It has been observed that water especially inhibits the rate of reaction while working with a cation exchange resin. The inhibiting effect of water on a cation exchange resin has been observed in the dehydration of 1,4-butanediol (Vaidya et al., 2003), synthesis of tetrahydrofuran (THF) (Limbeck et al., 2001) and the formation of mesityl oxide (MSO) from acetone (Toit & Nicol, 2004). The effect of the selectivity of water on the cation exchange resin, indicates that the kinetic expression may have to be modified to compensate for the water inhibition.

- While investigating the dehydration of 1,4-butanediol, Vaidya et al. (2003) concluded that the water inhibited the rate of reaction. The water was assumed to inhibit the reaction not only by the decrease of the active sites available for the reaction to proceed, but also due to the increased solvation of the ionic groups ($-SO_3H$). This implies that more than one molecule of water will be attached to the $-SO_3H$ site (multilayer adsorption). For this reaction, the initial rate of reaction against the initial water concentration is shown in figure 2.7. With increased water concentration the reaction rate decreases significantly. The effect of the water on the reaction rate was accurately described using a Langmuir-Hinshelwood rate equation. The Langmuir-Hinshelwood rate equation therefore accurately described the concentration of the reagents on the catalyst surface, thereby modelling the inhibition of water.
- Limbeck et al. (2001) concluded that small amounts of water influenced the synthesis of tetrahydrofuran (THF) on a sulphonic ion exchange resin (equation 2.69).



To determine the influence of the dilution of the reaction mixture with water, the

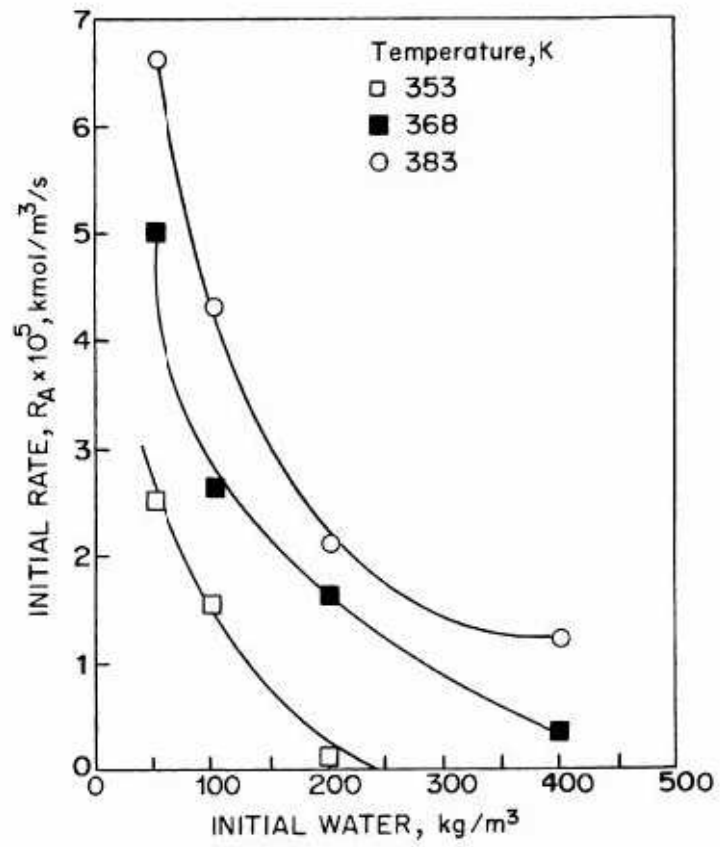


Figure 2.7: Effect of the initial water concentration on the dehydration of 1,4-butanediol (Vaidya et al., 2003).

reaction mixture was diluted with both water and THF. If an elementary rate model is accepted, the concentration of both these products should influence the reaction rate to the same extent if no external mass transfer is present. For the dilution of the reaction mixture with water the reaction rate did decrease as expected. However when THF was used to dilute the reaction mixture the reaction rate was not inhibited to the same extent (figure 2.8).

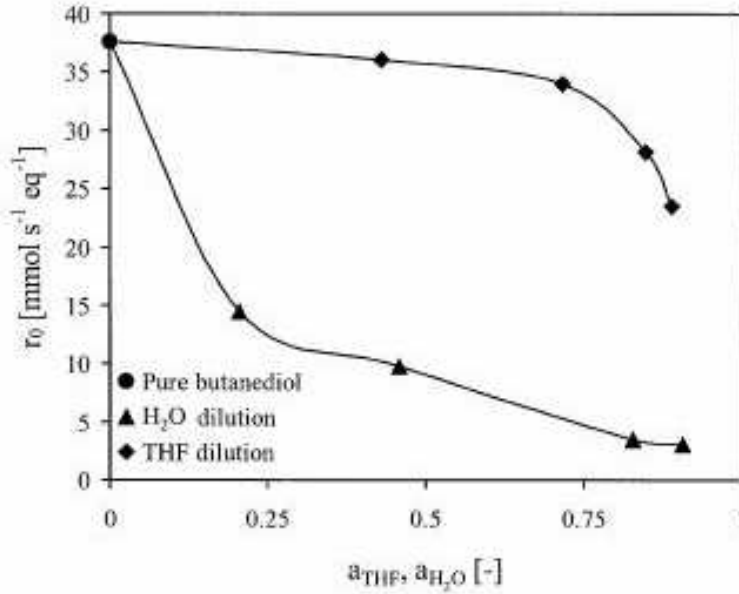


Figure 2.8: The initial rate dependency on the initial mixture composition (Limbeck et al., 2001).

For the modelling of the reaction data, Limbeck et al. (2001) suggested that a Langmuir-Hinshelwood reaction model be used, but with an additional inhibition factor (η_i) to compensate for the water effect on the system (equation 2.70-2.71).

$$r_A = \eta_i k \frac{K_A a_A}{1 + K_A a_A} \quad (2.70)$$

$$\eta_i = \frac{1}{1 + K_{\text{H}_2\text{O}} \sqrt{a_{\text{H}_2\text{O}}}} \quad (2.71)$$

This resulted in a good prediction of the inhibiting effect of water on the rate of reaction. The inhibition factor is purely empirical, and was fit on experimental data. The relevance of this effectiveness factor on other systems is questionable.

- For the conversion of acetone to mesityl oxide on a cation exchange resin, Toit & Nicol (2004) also found that water had a negative effect on the reaction rate. To compensate for the effect of water on the system, it was assumed that the active

sites associated with water would not participate in the reaction. The amount of adsorbed water was then described with a Freundlich adsorption model. This was then used to predict the ratio of catalytic sites blocked by water to the amount catalytic active sites available (equation 2.72 - 2.74).

$$\theta = \frac{[H^+]_{\text{blocked by water}}}{[H^+]_{\text{total}}} \quad (2.72)$$

$$\theta = K_a [H_2O]^{\frac{1}{\alpha}} \quad (2.73)$$

$$[H^+]_{\text{available}} = \left(1 - K_a [H_2O]^{\frac{1}{\alpha}}\right) [H^+]_{\text{total}} \quad (2.74)$$

To compensate for the inhibition of water on the reaction rate, the rate model was rewritten in terms of the amount of acid sites available for the reaction to proceed. This resulted in a good description of the experimental results for the formation of mesityl oxide from acetone using Amberlyst 16.

The modelling of the water inhibition by these authors is mostly by the description of the fractional coverage of the water on the catalyst surface. This just emphasises the importance of knowing the actual concentration on the resin surface. The method followed for the determination of the surface concentration, whether it be adsorption or absorption, would only help describe the reaction rate better if it can determine the actual surface concentration on the resin to a greater extent. An inhibiting term would then only be applicable to systems where adsorption is ignored, e.g. pseudo homogeneous reaction models, since the reaction rate model does not account for the difference in the concentration between the resin and the liquid phase.

CHAPTER 3

Experimental

3.1 Experimental Setup

For the measurement of the reaction rate a batch reactor was used. The setup consisted of a 500 ml ball flask with two access points. The temperature was measured with a thermo couple at one of the access points. A contact thermometer, Heidolph *EKT* 3001, was used to measure the mixture temperature. The resolution and accuracy of the temperature measurement was ± 1 °C, around the reaction temperature of 50°C. The reaction temperature was reached and maintained by a Selecta Agimatic-N electronic magnetic stirrer with temperature control. The second access point was used to gather the sample needed for analysis. Due to volatility of the reaction mixture a condenser was used to ensure that the reagents did not evaporate during the reaction (figure 3.1).

3.2 Materials

Analytical grade methanol (purity > 99.9 %), acetic acid (purity > 99.8 %) and distilled water was used for the rate measurements. For the analytical calibration methyl acetate (purity > 99.5 %) and 4-Methyl-2-pentanone (MiBK, purity > 99 %) was used.

The heterogeneous catalyst was the sulphonated macro-porous cation exchange resin, Amberlyst 15 wet. The properties of the catalyst was obtained from Rohm & Haas (2004), see table 3.1. The water content was also measured experimentally to be ± 50 %. This was measured by placing a known sample of Amberlyst 15 wet in a oven at 100 °C for 24 hours. The sample weight was then measured again and the percentage water fraction was calculated.

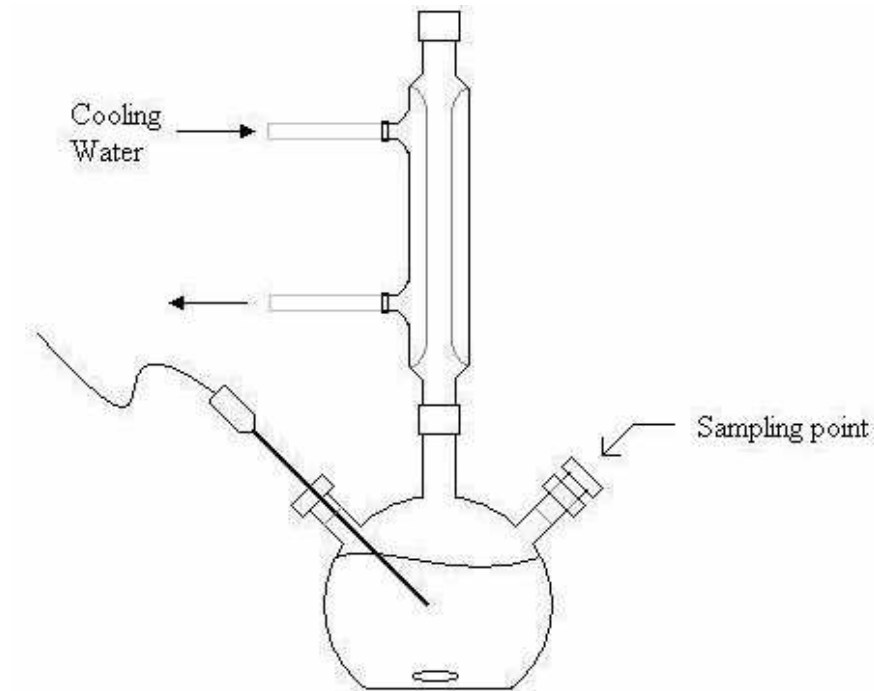


Figure 3.1: The experimental setup for the measuring of the reaction rate and the reaction equilibrium.

Table 3.1: Properties of Amberlyst 15 wet

Physical form	Opaque beads
Concentration of acid sites	$\geq 4.7 \text{ eq/kg}$
Moisture content	$\pm 50 \%$
Surface area	$53 \text{ m}^2/\text{g}$
Maximum operating temperature	$120 \text{ }^\circ\text{C}$
Macro porosity	35%
Polymer density	1410 kg/m^3
Bulk density	600 kg/m^3

3.3 Analysis

The analysis of the sample was done using a Varian Star 3400 CX gas chromatograph (GC) with a flame ionisation detector (FID). Separation was carried out on a 30 meter Chrompack CP-select 624 FS column. The temperature profile proposed by Rönneck et al. (1997) was used. The column started at 45 °C, where the temperature was held for three minutes, then heated to 200 °C at a rate of 15 °C/min where it was held for one more minute. In all analysis 4-Methyl-2-pentanone was used as internal standard.

The GC was calibrated using a known sample of methanol, acetic acid, methyl acetate and water. To ensure that the method would be applicable to a wide concentration profile, the calibration was done for varied relationships of the product to reagent concentration. The sample concentration used for the calibration curve is given in table 3.2. In both cases 20%, by mass, of MiBK was added as internal standard.

Table 3.2: Weight fraction of the two samples used for the calibration of the GC

	1 (%)	2 (%)
Methanol	11.4	17.9
Acetic Acid	55.5	28.5
Methyl Acetate	33.1	53.7

This calibration was tested with 4 samples, the make up of these four samples are given in appendix A.2.1. The actual weight fraction and analysed weight percentages of these four samples are given in table 3.3. It should also be noted that for the calculation of these weight fractions a constant sample density of 871.6 kg/m³ with an injection volume of 0.5 μ l was assumed. The weight fractions reported are only in terms of the analysed sample, therefore the weight fractions reported are only with reference to the measured concentration of methanol, methyl acetate and acetic acid in the sample.

For all the sampled analysed, a good prediction of the actual sample concentration was evident. The average error between the theoretical and analytical prediction was 1.0 % with a standard deviation of 1.1%.

Since the water concentration could not be measured with the FID, the water concentration was calculated with a mass balance over the liquid reaction mixture. The resin has a particular affinity for water and methanol (Song et al., 1998; Lode et al., 2004), resulting that the mass balance in the liquid phase could approximate the water concentration incorrectly. It was assumed that the bulk liquid to resin phase ratio in this work was such that the amount of components sorbed by the resin would have a negligible effect on the bulk liquid concentration. The effect of the resin selectivity on the prediction of the water concentration was tested by determining the error between the analytical measurement and the predicted measurement when using the conversion

Table 3.3: Theoretical and analytical prediction of the weight fraction of a known sample

	1		2	
	Theoretical (%)	Analysed (%)	Theoretical (%)	Analysed (%)
Methanol	17.9	17.9	11.4	11.1
Methyl acetate	53.7	53.8	33.1	33.3
Acetic acid	28.5	28.3	55.5	55.6
	3		4	
	Theoretical (%)	Analysed (%)	Theoretical (%)	Analysed (%)
Methanol	34.8	34.5	11.2	10.6
Methyl acetate	0.0	0.2	33.4	32.2
Acetic acid	65.2	65.3	55.4	57.2

of one of the reagents competing in the reaction. The mean absolute error between the experimental and predicted concentration, is given in table 3.4. The method used for the prediction of the sample concentration is described in appendix A.2.1.

Table 3.4: The absolute error between the analysed sample and the concentration determined from the conversion of each analysed component ($Error = \sum_i^n \frac{|C_{Analysed} - C_{Predicted}|}{C_{Analysed}} \cdot \frac{1}{n} \times 100$)

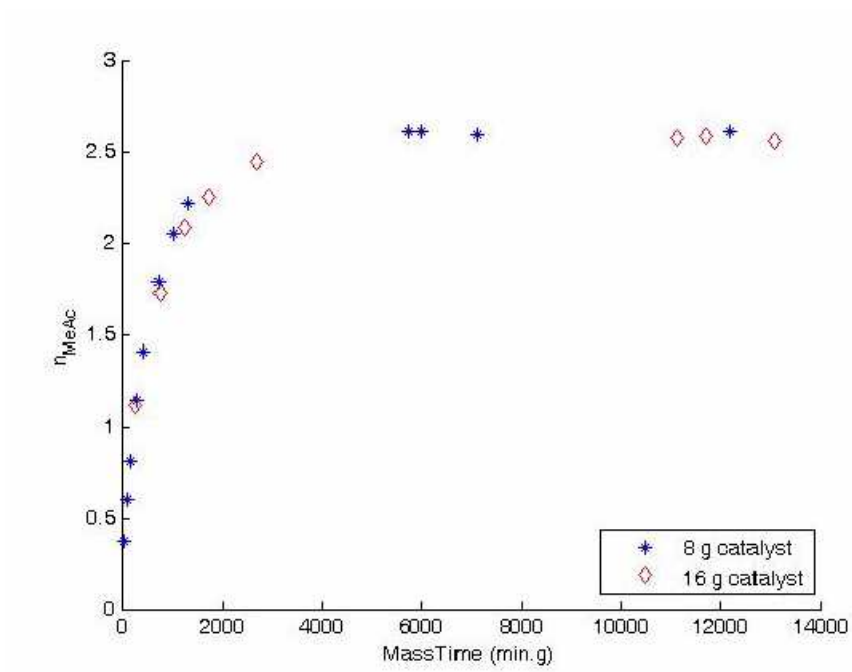
Base	Methanol	Acetic acid	Methyl acetate
Methanol	n/a	4.0 %	4.0 %
Acetic acid	4.2 %	n/a	1.7 %
Methyl acetate	1.9 %	2.9 %	n/a

When comparing the reaction rate for two reactions with the same initial reagent feed, but with 16 g and 8 g of catalyst, no comparable difference was measured in the conversion against catalyst residence time (*min.g*) (figure 3.2). This was done for both an excess of methanol and acetic acid. This is a further indication that the selectivity of the resin does not influence the liquid phase concentration.

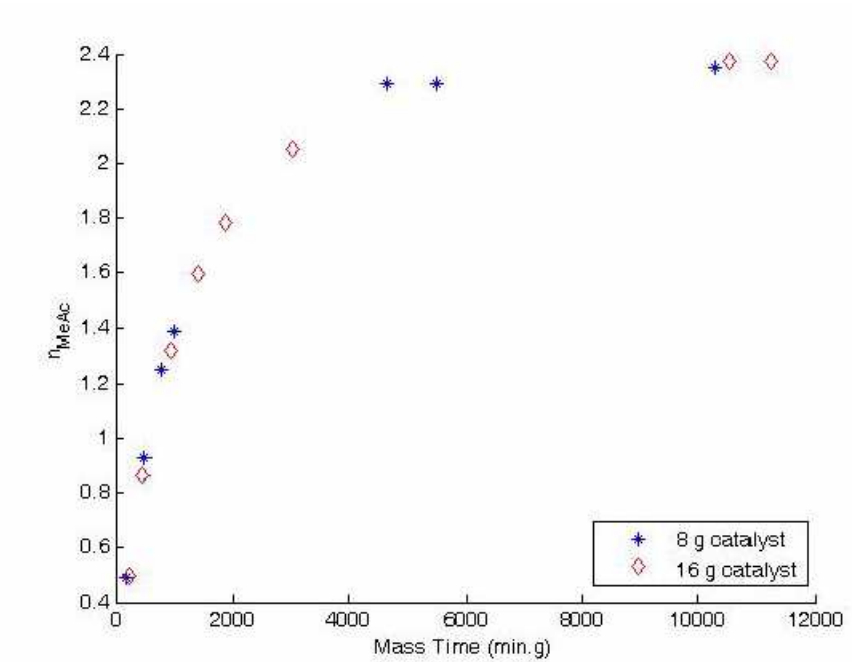
Since the methyl acetate has the lowest selectivity to the resin, the composition in the liquid phase was used to predict the conversion at each experimental point.

3.4 Experimental Procedure

The rate of reaction was measured for a variety of initial concentrations to investigate the effect of the resin selectivity on the rate of reaction. Not only was the effect of water on the system evaluated but also the effect of acetic acid and methanol.



(a) Initial makeup: 3 moles methanol, 5 moles acetic acid



(b) Initial makeup: 5 moles methanol, 3 moles acetic acid, 1 mole water

Figure 3.2: Experimentally measured moles of methyl acetate compared for two reaction with the same initial composition of reagents, but with different amounts of catalyst added.

The two reagents were heated separately to 50°C, before being added together. The catalyst was fed as soon as the reagents were mixed together. Amberlyst 15 wet was used as received from the distributor. For the duration of the experiment the reaction mixture was kept isothermal at 50°C. The different experiments that were run are shown in table 3.5. Each experiment was allowed to reach equilibrium. The reaction mixture was analysed after 24 hours, and again after 4 hours. If the analysis of the consecutive samples did not differ it was assumed that the reaction has reached equilibrium.

Table 3.5: Experiments that were run during this investigation. The experimental data for each experiment is given in appendix A.3 (table A.3). The water concentration reported in the table is the total moles of water in the solution (added initially, present in the resin and as an impurity in the chemicals). As a rule of thumb, when the moles added initially is discussed the actual total amount of water is 0.5 moles more.

	Catalyst (g)	Methanol (mol)	Acetic Acid (mol)	Water (mol)
R1	8.4	3.0	5.0	0.3
R2	16.1	3.0	5.0	0.5
R3	16.0	3.0	5.0	1.5
R4	15.9	3.0	5.0	2.5
R5	16.0	4.1	4.1	0.5
R6	16.1	4.0	4.0	1.5
R7	16.1	4.0	4.0	1.5
R8	8.0	4.0	4.0	2.3
R9	16.0	4.1	4.1	2.5
R10	8.0	5.0	3.0	0.3
R11	16.0	5.0	3.0	0.5
R12	16.0	5.0	3.0	0.5
R13	16.0	5.0	3.0	1.0
R14	8.1	5.1	3.0	1.3
R15	15.6	5.0	3.0	1.5
R16	16.0	5.0	3.0	1.5
R17	15.8	5.0	3.0	2.5
R18	16.0	5.0	3.0	2.5
R19	16.0	5.0	3.0	3.0
R20	16.0	5.0	3.0	3.0

All the different experiments resulted in an initial reaction mixture of approximately 410 mL. Samples of 2 mL each were taken to measure the reaction rate. No more than 12 samples were taken per experiment. The combined effect of the sampling and sorption of the mixture by the resin was assumed to be negligible on the total reaction volume, and a constant reaction volume was assumed in all calculations.

Exploratory work on this reaction system, at 60°C, indicated that the reaction rate did not differ when the stirring speed of the reactor was changed from 350 to 650 rpm. In this investigation all experiments were run with a stirrer speed of 700 rpm to ensure

that external mass transfer effect would not influence the reaction rate. Figure 3.2 again justifies the assumption of negligible external mass transfer. The catalyst was used as received, internal mass transfer effects were not evaluated. No abrasion of the resin beads occurred as a result of the magnetic stirrer. However, it should be noted that the fitted rate constants may only be apparent values.

The experimental repeatability achieved is graphically illustrated in figure 3.3 where the methyl acetate concentration are shown as a function of time for two repeat experiments. Based on all the data available for repeat experiments the average deviation based on methyl acetate concentration (equation 3.1) was calculated to be 3.5 %. This deviation was based on the repeatability of experiments taken from both rate and equilibrium data.

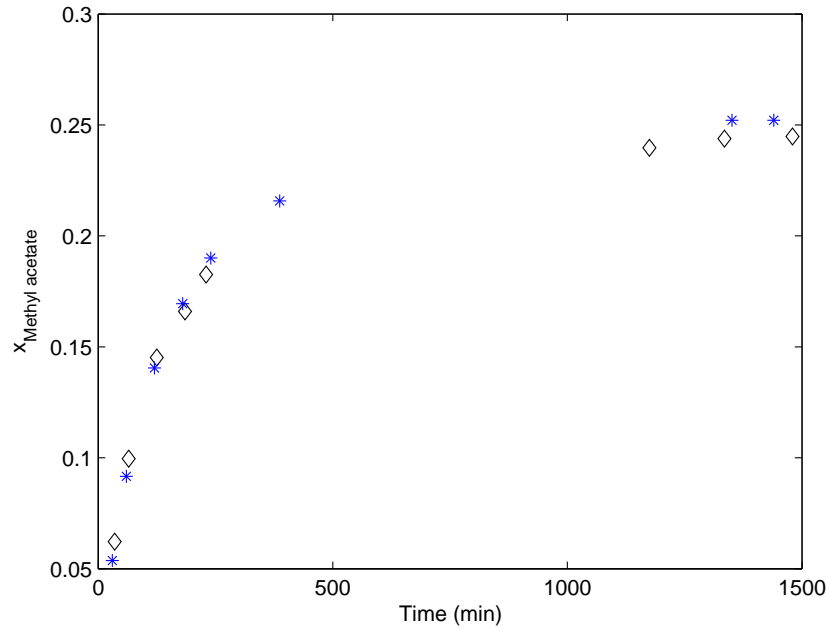


Figure 3.3: The mole fraction of the methyl acetate for both experiment R505301160 and R505301161, visually indicating the experimental repeatability.

$$R = \sum_i^n \frac{|C_i^{R1} - C_i^{R2}|}{\overline{C_i^{R1+R2}}} \cdot \frac{1}{n} \quad (3.1)$$

where n is the amount of repeat experiments, $R1$ and $R2$ represents the repeated experiments.

CHAPTER 4

The Reaction Rate Prediction with Existing Models

4.1 Modelling the Reaction Rate

For this reaction system the reaction rate has been described using simple pseudo homogeneous reaction models (Xu & Chuang, 1996; Mäki-Arvela et al., 1999), to Langmuir-Hinshelwood reaction kinetics (Song et al., 1998; Pöpken et al., 2000).

The ability of models used to describe the reaction rate in the literature were tested by using rate models from the literature where the reaction parameters and equilibrium constants were well defined. The models proposed by Xu & Chuang (1996), Song et al. (1998) and Pöpken et al. (2000) were chosen in this investigation. These authors all worked with Amberlyst 15 as catalyst, and achieved good fittings of experimental data.

The reaction model, local composition model, rate – and equilibrium constant used by these authors were used to describe the experimental reaction rate measured for this investigation. The rate - and equilibrium constant for each of these authors are given in table 4.1. The adsorption constants used by Song et al. (1998) and Pöpken et al. (2000) are given in table 2.6. The methodology followed to predict the reaction rate, is given in appendix A.4.

Table 4.1: Reaction rate and equilibrium constant used by the relevant authors.

	Rate constant	Equilibrium constant
Xu & Chuang (1996)	$1.76 \times 10^6 e^{\frac{-7035.2}{T}}$ ($\frac{1}{g.min}$)	5.2
Song et al. (1998)	$5 \times 10^{10} e^{\frac{-6287.7}{T}}$ ($\frac{1}{min}$)	$2.3 e^{\frac{782.98}{T}}$
Pöpken et al. (2000)	$5.1 \times 10^8 e^{\frac{-7273.274}{T}}$ ($\frac{mol}{g.min}$)	$13.9 e^{\frac{392.109}{T}}$

Figure 4.1 to 4.9 gives a graphical representation of the performance of each model to describe the reaction rate based on the experimental value of the methyl acetate mole fraction.

As an indication of the error between experimental and predicted values it was thought best to use the absolute average relative error (AARE), given below. The AARE was reported in terms of the methyl acetate formed during the reaction.

$$AARE = \sum_i^n \frac{|C_{Experimental} - C_{Predicted}|}{C_{Experimental}} \cdot \frac{1}{n} \times 100 \quad (4.1)$$

4.2 Performance of Rate models

4.2.1 Pseudo Homogeneous Reaction rate

Xu & Chuang (1996) used pseudo homogeneous reaction kinetics to describe the reaction rate for the esterification of acetic acid (equation 2.2). Xu & Chuang (1996) did not use an activity model to compensate for the non-ideality of the reaction mixture. Furthermore, the reaction equilibrium constant was determined to be independent of temperature, with $K_c = 5.2$.

From figure 4.1 to figure 4.3 it is noticeable that the model becomes more accurate as the water concentration is increased. This is to be expected since Xu & Chuang (1996) only worked with dilute concentrations methanol and acetic acid in water. The model is especially accurate where an excess of methanol was added to the reaction mixture. An offset between the reaction model and the experimental data is also perceivable at the experimental equilibrium. This indicates that an activity model might be necessary to compensate for the non-ideality in the reaction mixture. The AARE achieved with the rate model proposed by Xu & Chuang (1996) for all the experimental data was 13 %. It can be accepted that this model can not be extrapolated to concentration ranges other than for which it was developed.

4.2.2 Langmuir-Hinshelwood Reaction rate

When Song et al. (1998) predicted the rate of reaction, the adsorption of the reaction mixture onto the catalyst was surface was taken into account by using Langmuir-Hinshelwood reaction kinetics, equation 2.59. The non-ideality of the reaction mixture was also taken into account by using the Wilson local composition model, of which the parameters used by Song et al. (1998) is given in table 2.5.

From Figure 4.4 to 4.6 it is clear that the model gives a relatively accurate description of the reaction rate. The most obvious deviation between experimental and predicted values is where methanol is in excess in the reaction mixture and at reaction equilibrium

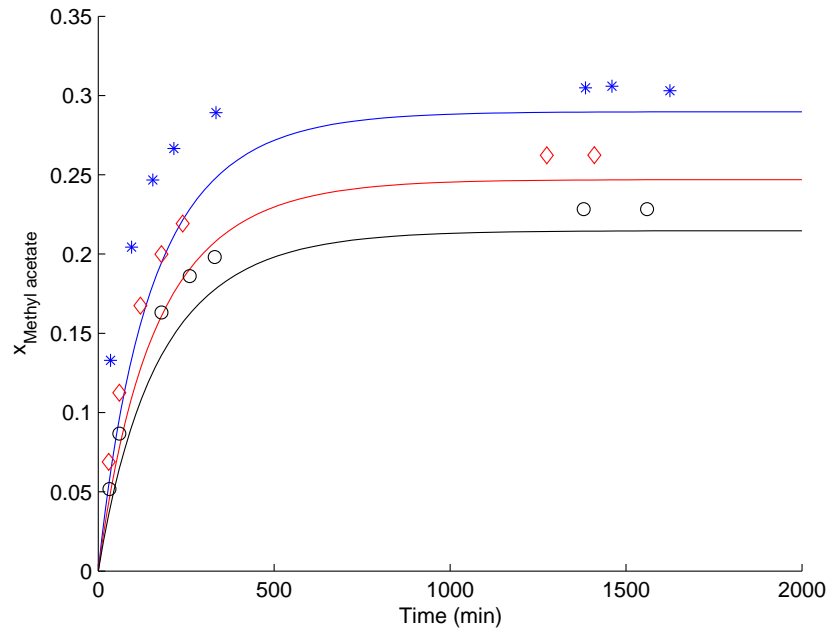


Figure 4.1: Methyl acetate mole fraction for experiments, with initial composition of 3 moles methanol and 5 moles acetic acid. Modelled with the expression proposed by Xu & Chuang (1996). * - $n_{\text{Water}}^o = 0$; \diamond - $n_{\text{Water}}^o = 1$; \circ - $n_{\text{Water}}^o = 2$

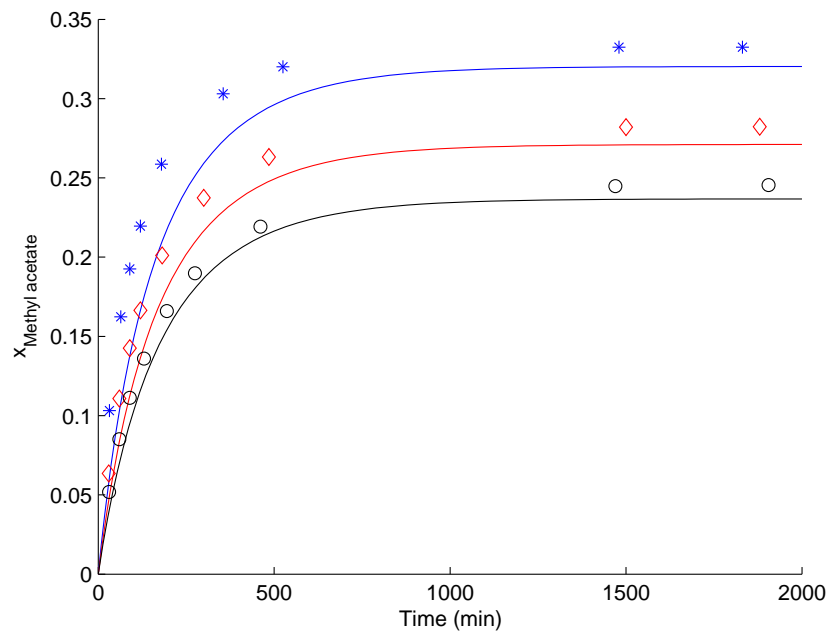


Figure 4.2: Methyl acetate mole fraction for experiments with initial composition of 4 moles methanol and 4 moles acetic acid. Modelled with the expression proposed by Xu & Chuang (1996). * - $n_{\text{Water}}^o = 0$; \diamond - $n_{\text{Water}}^o = 1$; \circ - $n_{\text{Water}}^o = 2$

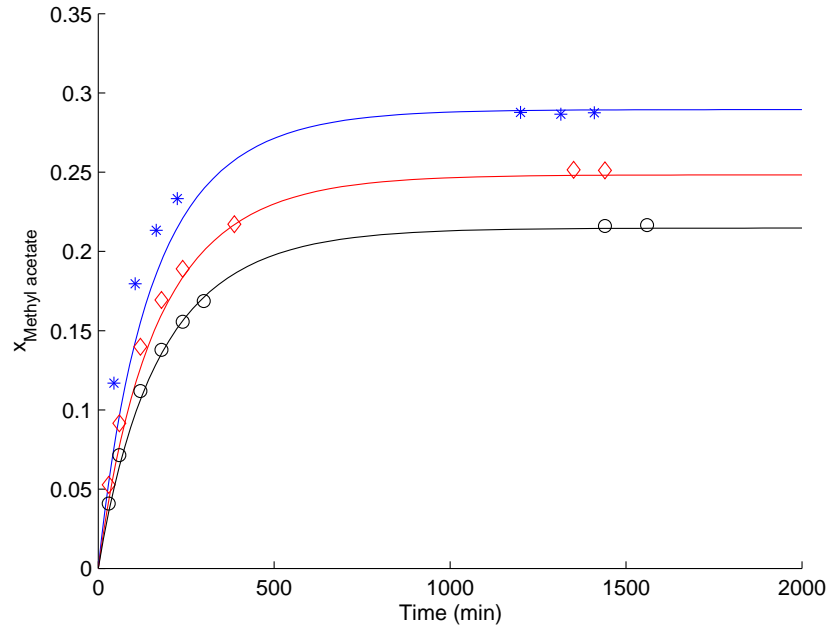


Figure 4.3: Methyl acetate mole fraction for experiments with initial composition of 5 moles methanol and 3 moles acetic acid. Modelled with the expression proposed by Xu & Chuang (1996). * - $n_{Water}^o = 0$; \diamond - $n_{Water}^o = 1$; \circ - $n_{Water}^o = 2$

where acetic acid was in excess. However, the overall AARE of 6% indicates that this model can be used over a wide concentration range.

Based on an overall AARE of 5% the model proposed by Pöpken et al. (2000) (equation 2.57) performed the best on the experimental data generated in this work (figure 4.7 to 4.9). With this model the biggest error between experimental and predicted values is for the system where an excess of acetic acid was initially used. Slight deviations are also evident as the reaction proceeds to equilibrium. Pöpken et al. (2000) used the UNIQUAC local composition model with temperature dependant parameters, given in table 2.3, to model the non-ideality of the system.

In general the description of the reaction rate was more than adequate for each of the reaction systems. An AARE of 5 % was achieved in the fitting of experimental data.

4.3 Summary

The prediction of the reaction rate with the kinetic parameters from the literature proved sufficient to describe the experimental data obtained in this investigation. The AARE achieved with the rate models of the various authors are given in table 4.2.

When using the reaction models proposed by Song et al. (1998) and Pöpken et al. (2000) a good prediction of the reaction rate and the equilibrium was achieved. Only when using the pseudo homogeneous reaction model with the parameters given by Xu &

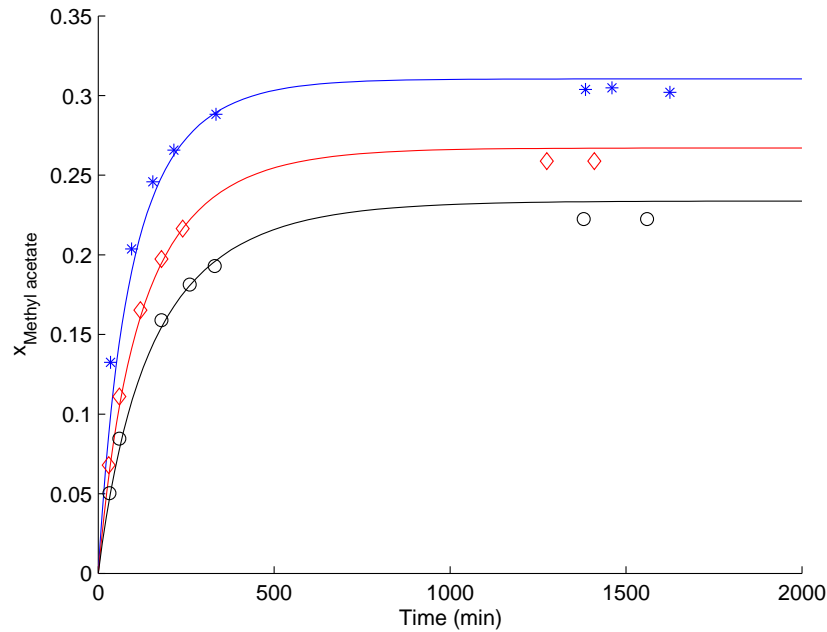


Figure 4.4: Methyl acetate mole fraction for experiments with initial composition of 3 moles methanol and 5 moles acetic acid. Modelled with the expression proposed by Song et al. (1998). * - $n_{Water}^o = 0$; \diamond - $n_{Water}^o = 1$; \circ - $n_{Water}^o = 2$

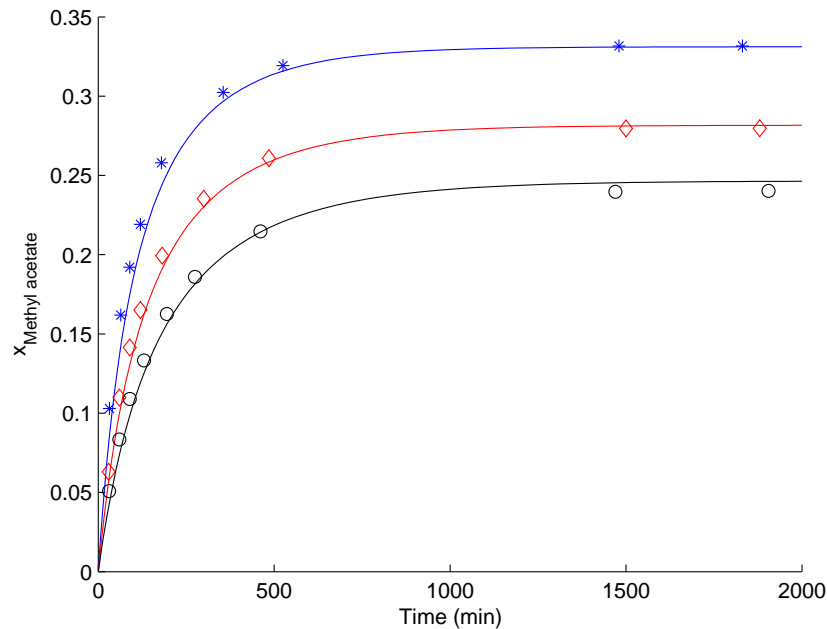


Figure 4.5: Methyl acetate mole fraction for experiments with initial composition of 4 moles methanol and 4 moles acetic acid. Modelled with the expression proposed by Song et al. (1998). * - $n_{Water}^o = 0$; \diamond - $n_{Water}^o = 1$; \circ - $n_{Water}^o = 2$

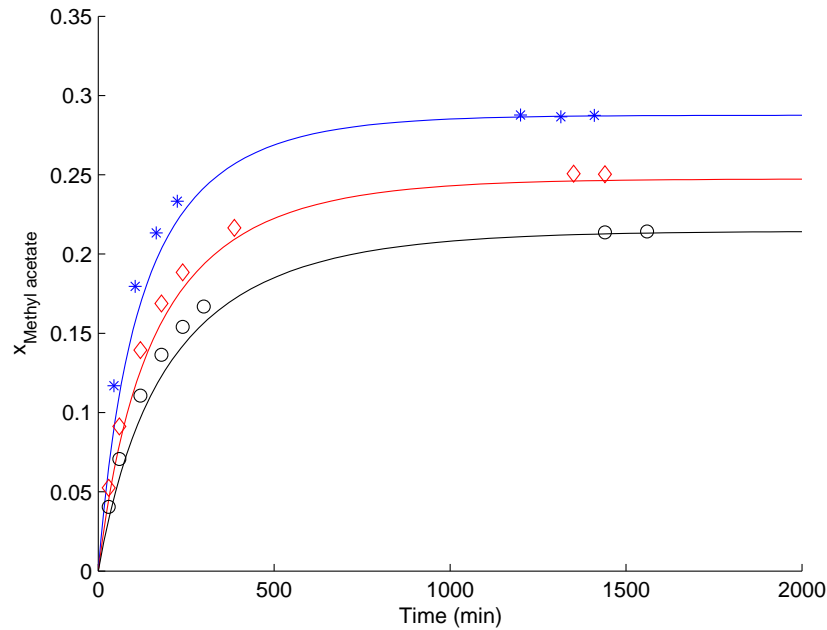


Figure 4.6: Methyl acetate mole fraction for experiments with initial composition of 5 moles methanol and 3 moles acetic acid. Modelled with the expression proposed by Song et al. (1998). * - $n_{Water}^o = 0$; \diamond - $n_{Water}^o = 1$; \circ - $n_{Water}^o = 2$

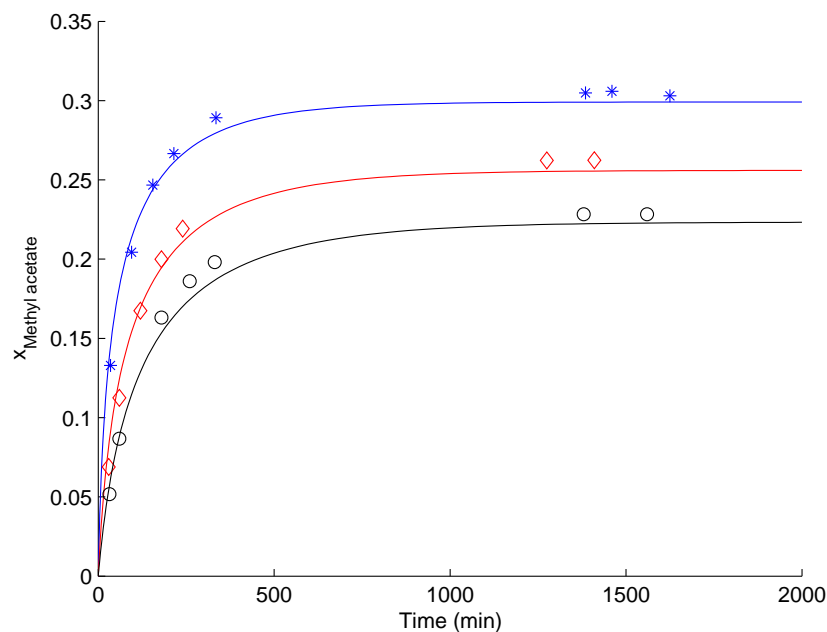


Figure 4.7: Methyl acetate mole fraction for experiments with initial composition of 3 moles methanol and 5 moles acetic acid. Modelled with the expression proposed by Pöpken et al. (2000). * - $n_{Water}^o = 0$; \diamond - $n_{Water}^o = 1$; \circ - $n_{Water}^o = 2$

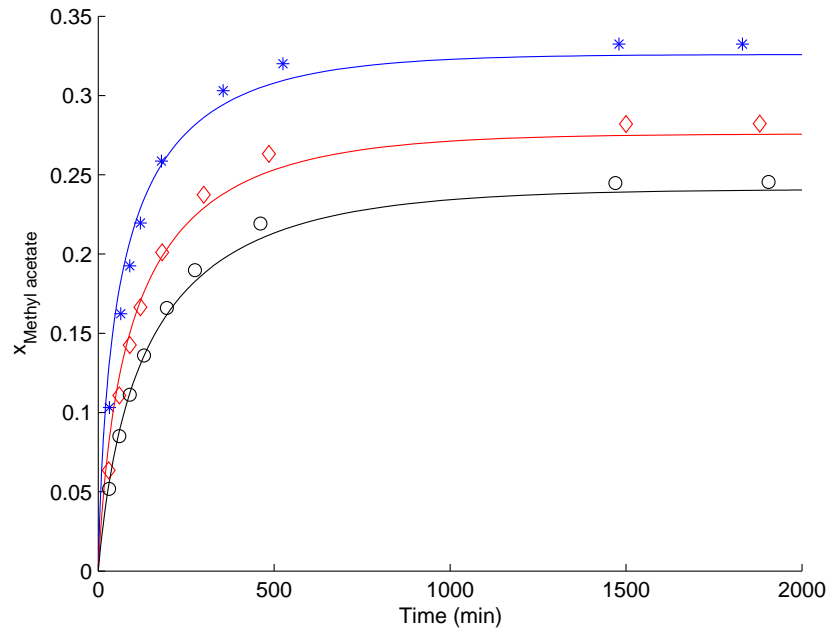


Figure 4.8: Methyl acetate mole fraction for experiments with initial composition of 4 moles methanol and 4 moles acetic acid. Modelled with the expression proposed by Pöpken et al. (2000). * - $n_{\text{Water}}^o = 0$; \diamond - $n_{\text{Water}}^o = 1$; \circ - $n_{\text{Water}}^o = 2$

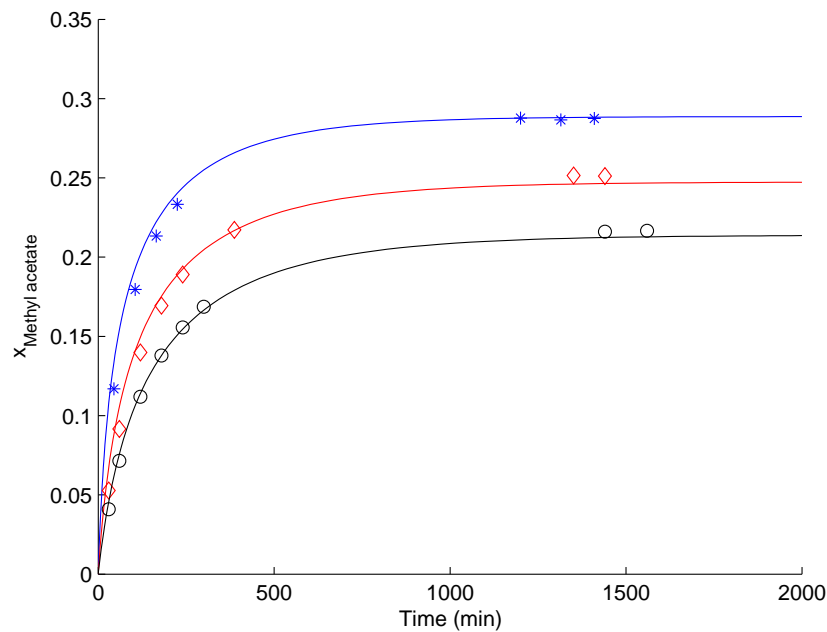


Figure 4.9: Methyl acetate mole fraction for experiments with initial composition of 5 moles methanol and 3 moles acetic acid. Modelled with the expression proposed by Pöpken et al. (2000). * - $n_{\text{Water}}^o = 0$; \diamond - $n_{\text{Water}}^o = 1$; \circ - $n_{\text{Water}}^o = 2$

Table 4.2: The difference between the experimental data and the prediction using the kinetic models proposed in the literature.

	AARE
Xu & Chuang (1996)	13 %
Song et al. (1998)	6 %
Pöpken et al. (2000)	5 %

Chuang (1996), did the prediction of the reaction prove inadequate. This poor prediction by Xu & Chuang (1996) could be due to either of two reasons *1)* the fact that the reaction was modelled with reference to the liquid mixture concentration and not the resin phase concentration or *2)* the fact that Xu & Chuang (1996) only worked with dilute mixtures of methanol and acetic acid.

For the prediction of the reaction equilibrium, the equilibrium constant postulated by Xu & Chuang (1996) could also not accurately describe experimentally measured reaction equilibrium. Only in the case where methanol was in excess could the equilibrium constant, proposed by Xu & Chuang (1996), predict the experimental equilibrium sufficiently. This indicates that the non-ideality of the reaction mixture should be taken into account for the modelling of the reaction equilibrium constant.

CHAPTER 5

Reaction Rate Prediction

5.1 Equilibrium Constant

5.1.1 Concentration Based Reaction Equilibrium Constant

When a liquid mixture behaves ideally the equilibrium constant can be approximated using the concentration of the liquid phase (K_C). However, the reaction mixture in this investigation tends to deviate from ideality and a phase separation will be evident between water and methyl acetate.

While working with a homogeneous catalyst (hydrogen iodide), Rönback et al. (1997) stated that due to the changes in K_γ as the reaction proceeds it is necessary to predict the equilibrium constant using activities instead of concentrations. The use of an activity based reaction model did however not result in a drastic improvement of the description of the reaction rate. It was therefore concluded to be unnecessary to use an activity based reaction model to describe the reaction rate. Mäki-Arvela et al. (1999) reported that the use of an activity model did not improve the description of the reaction rate. Both Rönback et al. (1997) and Mäki-Arvela et al. (1999) used the UNIFAC local composition model to describe the non-idealities in the liquid phase. Xu & Chuang (1996) also assumed that the equilibrium constant would only be dependant on concentration. When using the equilibrium constant (K_C) given by Xu & Chuang (1996), a deviation was perceptible between the experimentally measured equilibrium and the equilibrium constant used in the model proposed by Xu & Chuang (1996) (figure 4.1- 4.2). As the acetic acid became more dilute with water and methanol the prediction of the experimental reaction equilibrium approached the equilibrium proposed by Xu & Chuang (1996). This indicated that it might be necessary to predict the reaction equilibrium based on activity and not on concentration.

If the reaction equilibrium constant, calculated from concentration (equation 2.2) for all the reactions that were run are plotted against the moles of water added initial, a significant scatter is evident (figure 5.1).

For deviation between experimental data, it was thought best to report the error based on the percentage standard deviation (equation 5.1).

$$Error = \left(\frac{1}{n} \sum_i^n (x_i - \bar{x})^2 \right)^{\frac{1}{2}} \frac{100}{\bar{x}} \quad (5.1)$$

with

$$\bar{x} = \frac{1}{n} \sum_i^n x_i \quad (5.2)$$

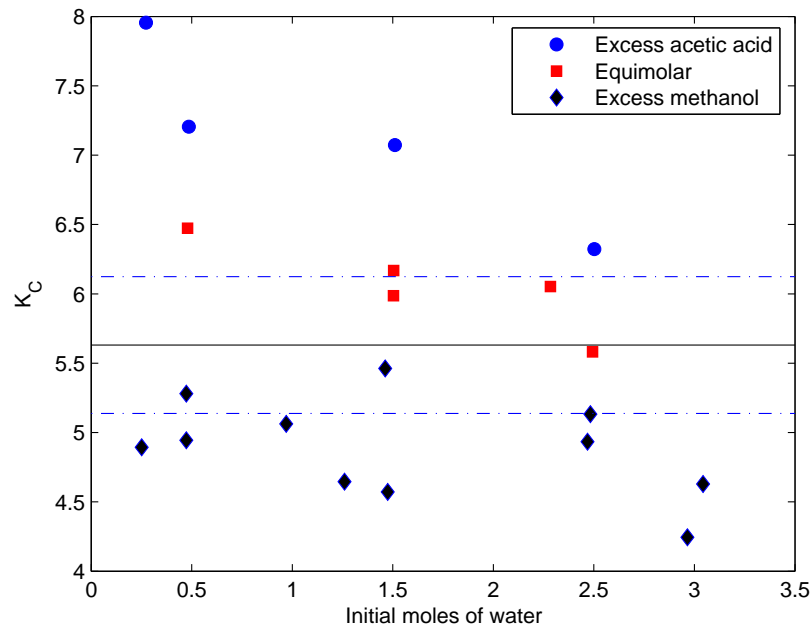


Figure 5.1: Experimental Equilibrium constant for the esterification of acetic acid. Solid line represents the $K_C - Mean = 5.6$, with the dashed line representing the experimental repeatability of the equilibrium constant $E = 9\%$ determined with equation 5.4. ● - excess acetic acid; ■ - equimolar feed; ◆ - excess methanol.

This scatter in the equilibrium constant might however be due to experimental error. For the determination of the experimental deviation in the equilibrium constant, the error was determined for all the repeat experiments, sixteen in all. The propagation of the error due to multiplication and division was taken into account by using equation 5.4 for the error determination.

$$E = \frac{x_C x_D}{x_A x_B} \quad (5.3)$$

$$\frac{\Delta E}{E} = \left(\left| \frac{\Delta \bar{x}_A}{\bar{x}_A} \right| + \left| \frac{\Delta \bar{x}_B}{\bar{x}_B} \right| + \left| \frac{\Delta \bar{x}_C}{\bar{x}_C} \right| + \left| \frac{\Delta \bar{x}_D}{\bar{x}_D} \right| \right) \quad (5.4)$$

where x_i , is the concentration of each component, and \bar{x}_i is the average concentration measured. From this the error in the experimental repeatability was found to be 9 %, this is less than the percentage standard deviation in the experimentally measured reaction equilibrium constant of 17.8 %. This would indicate that the difference in the measured equilibrium constant is not due to experimental error but rather to another influence on the system.

It has been shown that Amberlyst 15 is more selective to polar compounds such as the water and methanol, and less selective to the relatively non-polar methyl acetate (Song et al., 1998; Lode et al., 2004). The concentration of reactants and products in the reacting resin phase would therefore be different than the concentration in the bulk liquid phase - implying that K_{cResin} would not be equal to K_{cBulk} . However, phase equilibrium between the resin and the bulk phase dictates that $a_i^{Resin} = a_i^{Bulk}$. This would mean that $K_{aResin} = K_{aBulk}$ and therefore that $(K_\gamma K_c)_{resin} = (K_\gamma K_c)_{bulk}$. Except for the non-ideality of the liquid phase, this is a further motivation for the use of activities to describe the equilibrium constant.

5.2 Activity Based Reaction Equilibrium Constant

The activity based equilibrium constant (based on the experimental equilibrium concentrations measured in this work) was determined using equation 2.5 for each of the following local composition models:

- UNIFAC (parameters in table 2.1-2.2)
- Wilson (with parameters from Song et al. (1998), table 2.5)
- UNIQUAC (with parameters from Pöpkén et al. (2000), table 2.3)
- NRTL (parameters from Gmehling & Onken (1977), table 2.4)

The average value obtained for K_a together with the standard deviation in each case are given in table 5.1.

Of these the data for the UNIFAC local composition model are the easiest to obtain (table 2.1 - 2.2). This is generally why the UNIFAC local composition method is such a popular choice. When K_a was determined for each of the experiments in this investigation, the mean reaction equilibrium constant was determined to be 5.9. Which is quite

Table 5.1: The deviation in the experimentally measured reaction equilibrium, when assuming ideality (K_C) and when using activity models to compensate for the non-ideality (K_a). The mean equilibrium constant is also reported for each method.

	% Standard deviation	K_{Mean}
K_C	17.8	5.6
UNIFAC	25.4	5.9
Wilson	11.7	23.9
UNIQUAC	9.1	26.8
NRTL	7.6	29.6

similar to the K_{C-mean} of 5.6. This would indicate that the UNIFAC local composition model approximates the K_γ as ideal ($K_\gamma \approx 1$). This would most probably be why an improvement of the equilibrium prediction was not evident when using the UNIFAC local composition method and when assuming an ideal liquid mixture for the experimental data of Mäki-Arvela et al. (1999).

The variation of the K_a when using the UNIFAC local composition model is however larger than when assuming an ideal reaction mixture. This indicates that the prediction of the reaction equilibrium constant does not improve when the UNIFAC local composition model is used.

For the work of Lode et al. (2004) on this reaction system, a complex absorption based model was used to approximate the concentration on the resin phase. The liquid phase activity was however approximated with the UNIFAC local composition model. The large deviation that occurred when predicting the reaction equilibrium constant when using the UNIFAC local composition model, would suggest that the UNIFAC model can not accurately describe the non-ideality of the liquid phase. This would indicate that the resin phase activity coefficient parameters predicted by Lode et al. (2004) is based on a liquid phase local composition model that can not predict the non-ideality of the liquid phase. The liquid phase non-ideality should rather be described with another local composition method.

When using the Wilson local composition model the scatter in the calculated equilibrium constant lessened (percentage standard deviation was 11.7 %) around a mean of 23.9. This is quite close to the predicted reaction equilibrium of Song et al. (1998) at 50°C of 26.1. Confirming the experimentally measured reaction equilibrium constant.

For the UNIQUAC local composition model the percentage standard deviation in the reaction equilibrium constant was 9.1 % with a K_{a-Mean} of 26.8. This is quite different from the equilibrium constant proposed by Pöpken et al. (2000) of 46.7 at 50°C. This deviation was also apparent from the comparison of the experimental equilibrium constant given by Pöpken et al. (2000) and Song et al. (1998), figure 2.6. The equilibrium experimental data from this investigation supports the measured equilibrium proposed

by Song et al. (1998), and will therefore be taken as the correct equilibrium constant.

The NRTL local composition model gave the best results of the proposed liquid phase activity coefficient models. The percentage standard deviation of the reaction equilibrium constant was 7.6 %, around a mean of 29.6. This indicates that the NRTL local composition model is the most suited to predict the non-ideality in the reaction mixture.

5.3 Reaction Rate Modelling

As the NRTL model was the most successful to describe the reaction constant K_a , it was decided to use this model to calculate the activities in the remainder of this chapter. In addition the average activity based equilibrium constant calculated from all the experiments ($K_a = 29.6$) was used in all the rate expressions discussed in this section. An activity based power law-, Langmuir Hinshelwood and Eley-Rideal expression were used to model the reaction rate. In each case the only parameter that had to be solved was the rate constant, k_1 . This was done by minimising the AARE for all of the reaction rate data available. Adsorption constants given by Song et al. (1998) were used on the adsorption based rate expression.

For each of the methods used to describe the reaction rate (pseudo homogeneous, Langmuir-Hinshelwood and Eley-Rideal reaction kinetics), the AARE and the rate constant achieved with each model is given in table 5.2.

Table 5.2: The error between experimental results and the predicted rate of reaction when using different methods to model the reaction rate, together with the relevant rate constant is given for each instance.

Kinetic model	AARE	k_1 ($\frac{mol}{g.min}$)
Pseudo-Homogeneous	4.1 %	2.0×10^{-2}
Langmuir-Hinshelwood kinetics	3.9 %	1.24
Eley-Rideal kinetics	2.3 %	0.134

The reaction equations discussed in chapter 2 are repeated in the sections bellow to facilitate readability.

5.3.1 Pseudo Homogeneous Reaction Rate

The ability of an activity based power law expression (equation 2.4) to model the reaction rate are illustrated in figure 5.2 to 5.4.

$$r_A = -k_1 \left(a_A a_B - \frac{1}{K_a} a_C a_D \right)$$

The suitability of this model is evident both from this graphical representation and the overall AARE between predicted and experimental values for the methyl acetate mole fraction of 4.1%. The accuracy of this model is therefore comparable to the more complex models proposed by Pöpken et al. (2000) and Song et al. (1998).

The main advantage of this model lies in its simplicity. It is not necessary to determine adsorption parameters separately and except for the equilibrium constant only one parameter needs to be solved if a suitable model (with known parameters) is available to calculate the activities. The reaction rate constant was determined to be, 2.0×10^{-2} mol/(g.min).

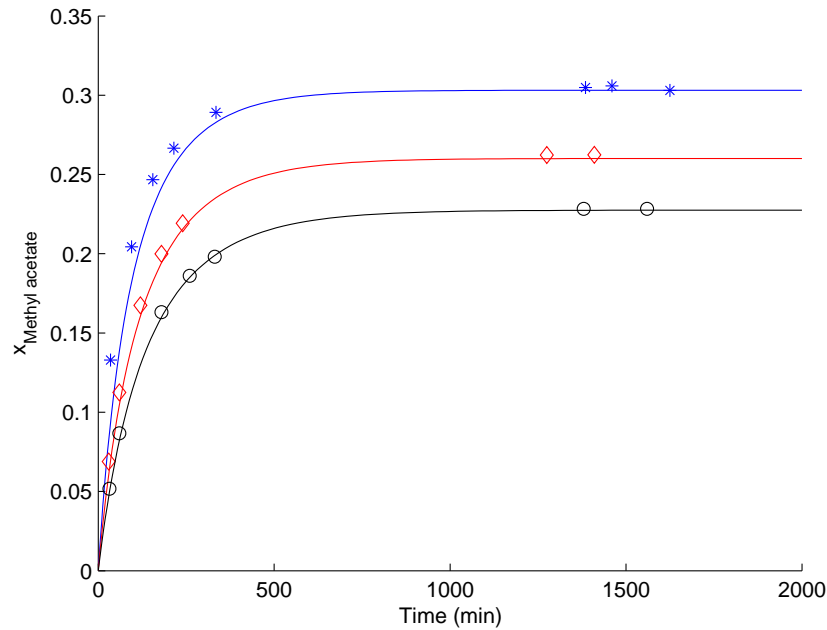


Figure 5.2: Methyl acetate mole fraction for experiments with initial composition of 3 moles methanol and 5 moles acetic acid. $x_{Methylacetate}$ represents the mole fraction of methyl acetate formed. Fitted with a pseudo homogeneous rate equation using the NRTL local composition model. * - $n_{Water}^o = 0$; \diamond - $n_{Water}^o = 1$; \circ - $n_{Water}^o = 2$

5.3.2 Langmuir-Hinshelwood Reaction Kinetics

To see if the fact that the NRTL model is used to describe the reaction kinetics improves the performance of the Langmuir Hinshelwood models:

$$r_A = \frac{-k_1 \left(a_A a_B - \frac{a_C a_D}{K_a} \right)}{\left(1 + K_A a_A + K_B a_B + K_C a_C + K_D a_D \right)^2}$$

A new rate constant was determined for the model proposed by Song et al. (1998) (similarly to equation 2.59), with the K_a value of 29.6. From figure 5.5 - 5.7 and the AARE of 3.9% it can be concluded that only a small improvement is achieved. The rate

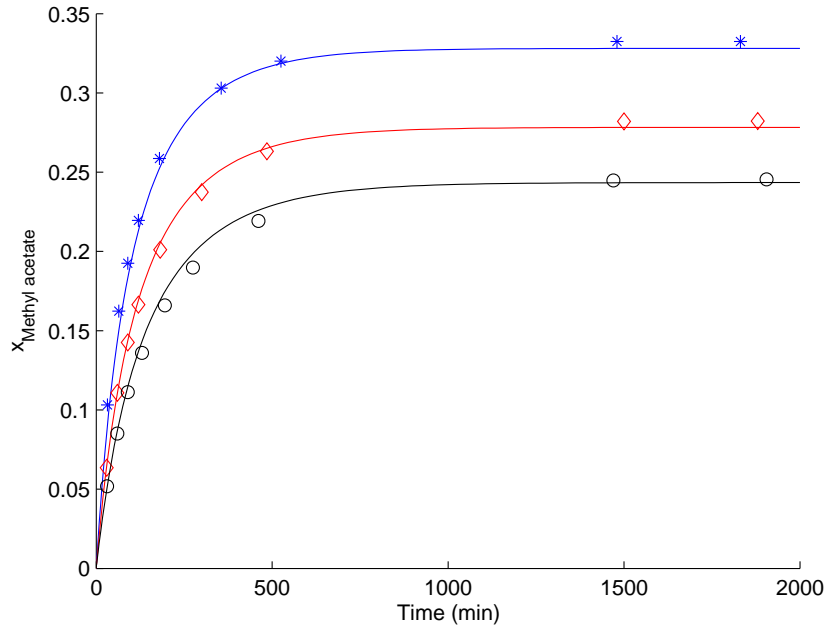


Figure 5.3: Methyl acetate mole fraction for experiments with initial composition of 4 moles methanol and 4 moles acetic acid. Fitted with a pseudo homogeneous rate equation using the NRTL local composition model. * - $n_{Water}^o = 0$; \diamond - $n_{Water}^o = 1$; \circ - $n_{Water}^o = 2$

constant determined here is also in good agreement with the one proposed by Song et al. (1998). What is of more significance is the fact that this model does not really improve on the ability of the activity based power law model to describe the reaction rate. The rate constant determined for the fitting of the Langmuir-Hinshelwood reaction kinetics was $1.24 \text{ mol}/(\text{g}\cdot\text{min})$.

5.3.3 Eley-Rideal Reaction Kinetics

It was previously noted that the cation exchange resin, Amberlyst 15, is more selective to water and methanol than to the rest of the reaction mixture (Lode et al., 2004; Pöpken et al., 2000). This indicates that Eley-Rideal kinetics, with methanol and water adsorbed, can be used to describe the reaction rate (equation 5.5).

$$r_A = \frac{-k_1 \left(a_A a_B - \frac{1}{K_a} a_C a_D \right)}{\left(1 + K_A a_A + K_D a_D \right)} \quad (5.5)$$

The description of the reaction rate using Eley-Rideal kinetics was quite good with an AARE of 2.3 %, the fit achieved is given in figure 5.8 - 5.10. This is an improvement on both the Langmuir-Hinshelwood and pseudo homogeneous reaction model. However, the improvement relative to the pseudo homogeneous model is not significant enough to warrant the inclusion of the two additional parameters (the adsorption equilibrium

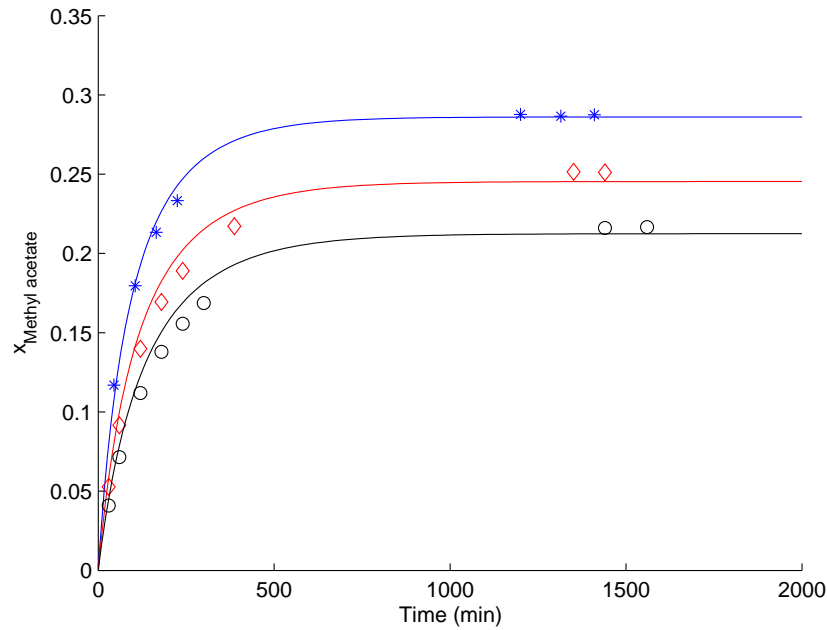


Figure 5.4: Methyl acetate mole fraction for experiments with initial composition of 5 moles methanol and 3 moles acetic acid. Fitted with a pseudo homogeneous rate equation using the NRTL local composition model. * - $n_{\text{Water}}^o = 0$; ◇ - $n_{\text{Water}}^o = 1$; ○ - $n_{\text{Water}}^o = 2$

constants of water and methanol).

The fact that the pseudo homogeneous reaction model described the experimental reaction rate to a similar accuracy as the adsorption based model, implies that it is not necessary to know the concentration of the reaction mixture on the surface of the resin. A two parameter pseudo homogeneous reaction model results in a more than adequate prediction of the reaction rate as long as the activities of the reaction mixture is thoroughly known.

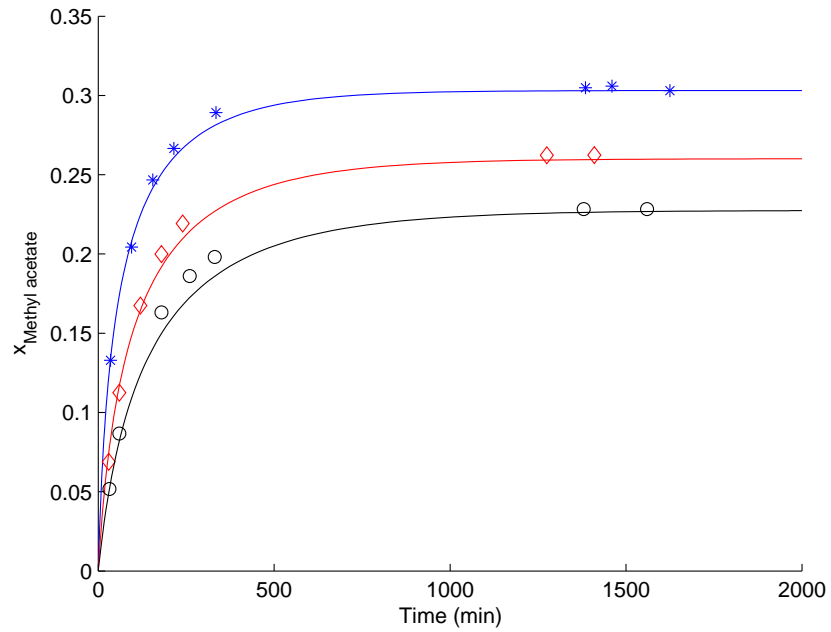


Figure 5.5: Methyl acetate mole fraction for experiments with initial composition of 3 moles methanol and 5 moles acetic acid. Fitted with Langmuir-Hinshelwood reaction kinetics using the NRTL local composition model. * - $n_{Water}^o = 0$; \diamond - $n_{Water}^o = 1$; \circ - $n_{Water}^o = 2$

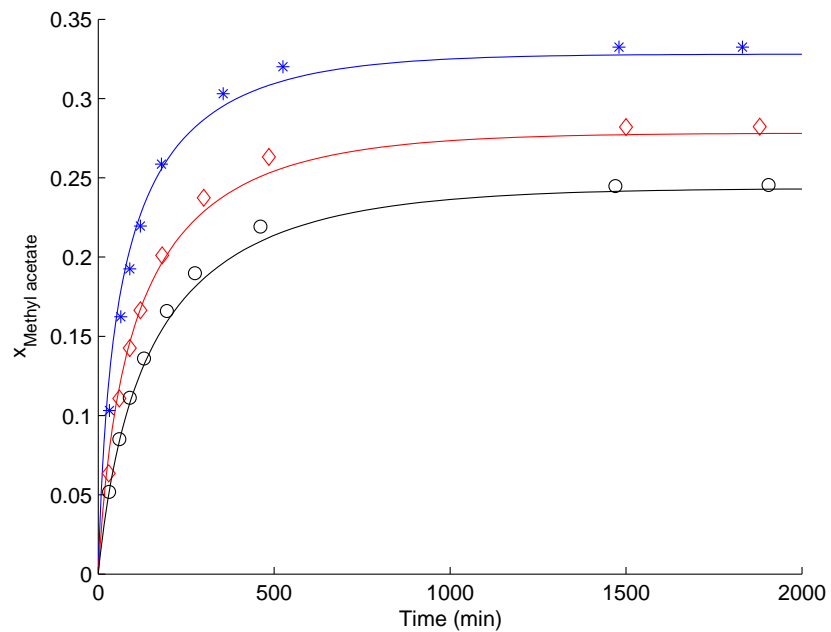


Figure 5.6: Methyl acetate mole fraction for experiments with initial composition of 4 moles methanol and 4 moles acetic acid. Fitted with Langmuir-Hinshelwood reaction kinetics using the NRTL local composition model. * - $n_{Water}^o = 0$; \diamond - $n_{Water}^o = 1$; \circ - $n_{Water}^o = 2$

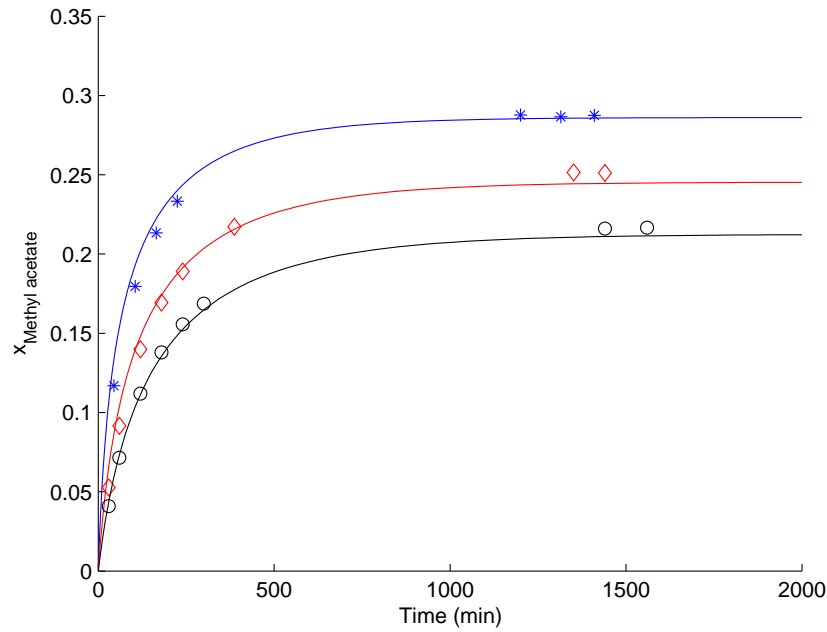


Figure 5.7: Methyl acetate mole fraction for experiments with initial composition of 5 moles methanol and 3 moles acetic acid. Fitted with Langmuir-Hinshelwood reaction kinetics using the NRTL local composition model. * - $n_{Water}^o = 0$; \diamond - $n_{Water}^o = 1$; \circ - $n_{Water}^o = 2$

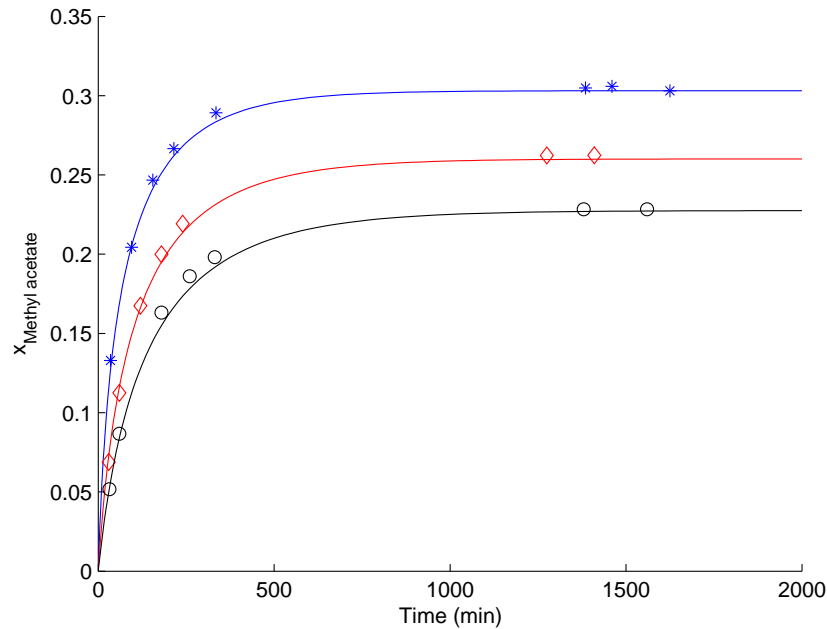


Figure 5.8: Methyl acetate mole fraction for experiments with initial composition of 3 moles methanol and 5 moles acetic acid. Fitted with Eley-Rideal reaction kinetics using the NRTL local composition model. * - $n_{Water}^o = 0$; \diamond - $n_{Water}^o = 1$; \circ - $n_{Water}^o = 2$

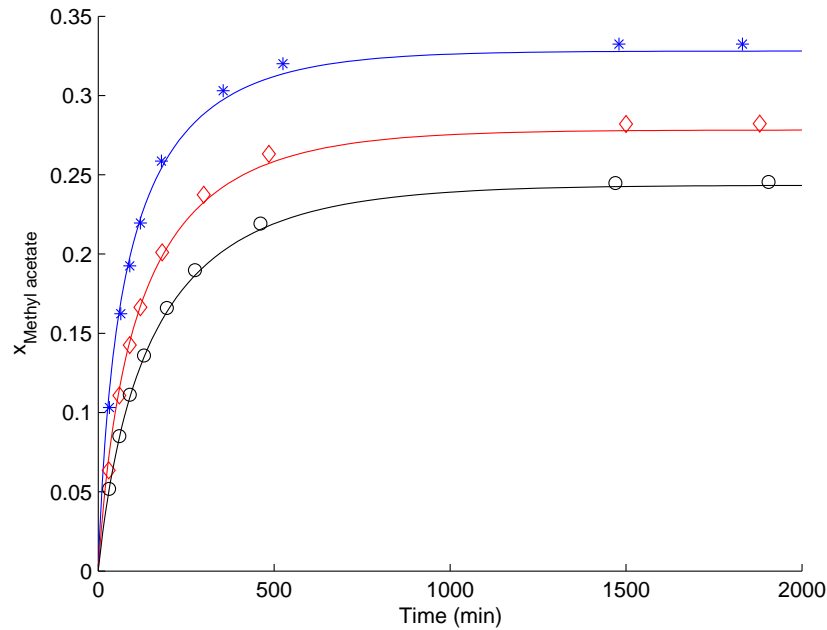


Figure 5.9: Methyl acetate mole fraction for experiments with initial composition of 4 moles methanol and 4 moles acetic acid. Fitted with Eley-Rideal reaction kinetics using the NRTL local composition model. * - $n_{\text{Water}}^o = 0$; \diamond - $n_{\text{Water}}^o = 1$; \circ - $n_{\text{Water}}^o = 2$

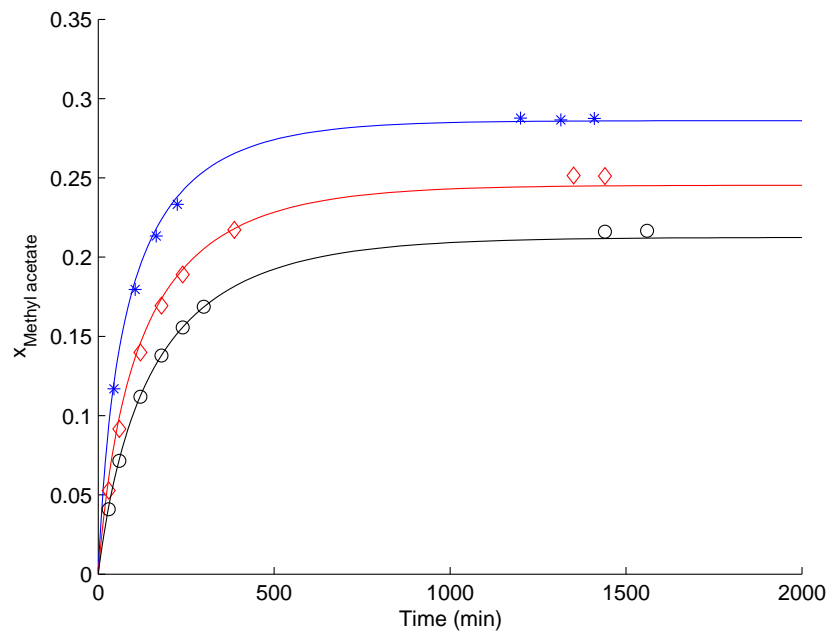


Figure 5.10: Methyl acetate mole fraction for experiments with initial composition of 5 moles methanol and 3 moles acetic acid. Fitted with Eley-Rideal reaction kinetics using the NRTL local composition model. * - $n_{\text{Water}}^o = 0$; \diamond - $n_{\text{Water}}^o = 1$; \circ - $n_{\text{Water}}^o = 2$

CHAPTER 6

Conclusions

Reaction rate and equilibrium data for the esterification of acetic acid with Amberlyst 15 as catalyst was generated in a batch reactor, varying the initial concentrations of water, methanol and acetic acid. Both the Langmuir-Hinshelwood adsorption based kinetic expressions proposed by Pöpken et al. (2000) and Song et al. (1998) adequately predicted the reaction rate and equilibrium achieved for the data generated. An overall AARE of 6 % and 5 % respectively was obtained using their rate models and kinetic parameters. Both these models use activities in the rate expression to compensate for the liquid phase non-ideality. Song et al. (1998) used the Wilson local composition model to calculate activity coefficients while Pöpken et al. (2000) used a temperature dependant UNIQUAC model. The concentration based pseudo-homogenous reaction model proposed by Xu & Chuang (1996) did not prove to be suitable over a wide concentration range, (AARE = 13 %). This model was developed for dilute concentrations of methanol and acetic acid in water and it was proven in this investigation that the prediction of the reaction rate improved with increased dilution of acetic acid.

Deviations in the attained equilibrium concentration was perceptible when using the equilibrium constant proposed by Xu & Chuang (1996), who worked with a concentration based equilibrium constant. This deviation was much less when using the equilibrium constant, and subsequent local composition model, proposed by Song et al. (1998) and Pöpken et al. (2000). From the deviation in the experimentally measured reaction equilibrium constant (K_C), a large deviation in the equilibrium constant was apparent (percentage standard deviation of 17.8 %). From this deviation it was concluded that the non-ideality of the reaction mixture should be taken into account when modelling the reaction equilibrium constant.

The ability of the UNIFAC, Wilson, UNIQUAC and NRTL activity coefficient models to describe the reaction equilibrium constant was compared. The NRTL local composition

model, with parameters obtained from literature Gmehling & Onken (1977) based on VLE data, performed the best and resulted in a standard deviation of 7.6 %, which is within the limits of the experimental repeatability, around a mean K_a of 29.6 at 50°C. The Wilson local composition model (with parameters given by Song et al. (1998)) and the UNIQUAC model (with parameters from Pöpken et al. (2000), also gave an adequate description of the equilibrium constant, with an AARE of 11.7 % and 9.1 % respectively. Only the UNIFAC local composition model failed to describe the equilibrium constant.

The reaction rate was modelled with different activity based reaction equations using the NRTL local composition model (rate constants given in table 5.1). The reaction rate could be described with similar accuracy (AARE of 4.1 %) to that achieved by Pöpken et al. (2000) and Song et al. (1998) while assuming pseudo homogeneous reaction kinetics. Although the pseudo homogeneous reaction model does not precisely portray the reaction on the surface of the resin, the simplicity and ease of use gives the pseudo homogeneous reaction model an edge since no adsorption data is necessary for the modelling of the reaction rate. A slight improvement on this was achieved when assuming Eley-Rideal reaction kinetics, AARE of 2.3 %. However, the resulting improvement relative to the pseudo homogeneous reaction prediction does not warrant the inclusion of the two additional equilibrium adsorption parameters.

It can be concluded that a two parameter activity based rate expression predicts the reaction rate with similar accuracy as the multi-parameter adsorption models. This indicates that it is not necessary to know the concentration on the resin surface (adsorption models) or in the resin gel (absorption models) when describing the reaction rate as long as the bulk liquid phase activities can be adequately described.

BIBLIOGRAPHY

- Altiokka, M. R. and Citak, A. (2003) “Kinetics of esterification of acetic acid with isobutanol in the presence of amberlite catalyst”, *Applied Catalysis A: General*, *239*, 141–148.
- Aspen-Technology “Aspen plus 11.1”, Software (2001).
- Carslaw, K. S.; Peter, T. and Clegg, S. (1997) “Modelling the composition of liquid stratospheric aerosols”, *Reviews of Geophysics*, *35*, 125–154.
- Chakrabarti, A. and Sharma, M. M. (1993) “Cationic ion exchange resins and catalyst”, *Reactive Polymers*, *20*, 1–45.
- Flory, P. J. (1953) *Principles of Polymer Chemistry*, Cornell University Press, London.
- Fogler, H. S. (1999) *Elements of Chemical Reaction Engineering*, Prentice Hall, New Jersey 3 edition.
- Forsythe, G.; Malcolm, M. and Moler, C. (1977) *Computer Methods for Mathematical Computations*, Prentice-Hall, New Jersey.
- Fredenslund, A.; Gmehling, J. and Rasmussen, P. (1977) *Vapor-Liquid equilibrium using UNIFAC a group-contribution method*, Elsevier Scientific Pub. Co New York, New York.
- Gmehling, J. and Onken, U. (1977) *Vapour liquid equilibrium data collection*, , I of *Chemistry data series* Dechema, Frankfurt.
- Gusler, G. M.; Browne, T. E. and Cohen, Y. (1993) “Sorption of organics from aqueous solution onto polymeric resins”, *Ind. Eng. Chem. Res.*, *32*, 2727–2735.
- Harmer, M. A. and Sun, Q. (2001) “Solid acid catalyst using ion-exchange resins”, *Applied Catalysis A: General*, *221*, 45–62.

- Helfferich, F. (1962) *Ion Exchange*, McGraw-Hill Book Company Inc., New York.
- Kahaner, D.; Moler, C. and Nash, S. (1989) *Numerical Methods and Software*, Prentice-Hall, New Jersey.
- Kipling, J. J. (1965) *Adsorption from solutions of non-Electrolytes*, Academic Press, New York.
- Laatikainen, M.; Markkanen, I.; Tiihonen, J. and Paatero, E. (2002) “Liquid-liquid equilibria in ternary systems of linear and cross-linked water-soluble polymers”, *Fluid phase equilibria*, 201, 381–399.
- Lilja, J.; Murzin, D. Y.; Salmi, T.; Aumo, J.; Mäki-Arvela, P. and Sundell, M. (2002) “Esterification of different acids over heterogeneous and homogeneous catalyst and correlation with the taft equation”, *Journal of Molecular Catalysis*, 182-183, 555–563.
- Limbeck, U.; Altwicker, C.; Kunz, U. and Hoffmann, U. (2001) “Rate expression for THF synthesis on acidic ion exchange resin”, *Chemical Engineering Science*, 56, 2171–2178.
- Lode, F.; Freitas, S.; Mazzotti, M. and Morbidelli, M. (2004) “Sorbptive and catalytic properties of partially sulfonated resins”, *Ind. Eng. Chem. Res.*, 43, 2658–2668.
- Mäki-Arvela, P.; Salmi, T.; Sundell, M.; Ekman, K.; Peltonen, R. and Lehtonen, J. (1999) “Comparison of polyvinylbenzene and polyolefin supported sulphonic acid catalysts in the esterification of acetic acid”, *Applied Catalysis A: General*, 184, 25–32.
- Mazzotti, M.; Kruglov, A.; Neri, B.; Gelosa, D. and Morbidelli, M. (1996) “A continuous chromatographic reactor: Smbr”, *Chemical Engineering Science*, 51 (10), 1827–1836.
- Mazzotti, M.; Neri, B.; Gelosa, D.; Kruglov, A. and Morbidelli, M. (1997) “Kinetics of liquid-phase esterification catalyzed by acidic resins”, *Ind. Eng. Chem. Res.*, 36, 3–10.
- NIST “Nist chemistry webbook”, <http://webbook.nist.gov/chemistry/> (2005).
- Pöpken, T.; Götze, L. and Gmehling, J. (2000) “Reaction kinetics and chemical equilibrium of homogeneously and heterogeneously catalyzed acetic acid esterification with methanol and methyl acetate hydrolysis”, *Ind. Eng. Chem. Res.*, 39, 2601–2611.
- Rohm and Haas “http://www.rohmhaas.com/ionexchange/ip/15wet_typical.html”, website (2004).
- Rönback, R.; Salmi, T.; Vuori, A.; Haario, H.; Lehtonen, J.; Sundqvist, A. and Tirronen, E. (1997) “Development of a kinetic model for the esterification of acetic acid with methanol in the presence of a homogeneous acid catalyst”, *Chemical Engineering Science*, 52, 3369–3381.

- Ruthven, D. M. (1984) *Principles of Adsorption and Adsorption Processes*, John Wiley and Sons, New York.
- Sainio, T.; Laatikainen, M. and Paatero, E. (2004) “Phase equilibria in solvent mixture-ion exchange resin catalyst systems”, *Fluid Phase Equilibria*, *218*, 269–283.
- Smith, J. M.; Ness, H. C. V. and Abbott, M. M. (2001) *Introduction to Chemical Engineering Thermodynamics*, Chemical Engineering Series McGraw Hill, New York 6 edition.
- Song, W.; Venimadhavan, G.; Manning, J. M.; Malone, M. F. and Doherty, M. F. (1998) “Measurement of residue curve maps and heterogeneous kinetics in methyl acetate synthesis”, *Ind. Eng. Chem. Res.*, *37*, 1917–1928.
- Taft, R. W. (1951) “Polar and steric substituent constants for aliphatic and o-benzoate groups from rates of esterification and hydrolysis of esters”, *Journal of the American Chemical Society*, *74*, 3120–3128.
- Thomas, J. M. and Thomas, W. J. (1997) *Heterogeneous catalysis*, VCH Publishers Inc, New York.
- Toit, E. D. and Nicol, W. (2004) “The rate inhibiting effect of water as a product on reactions catalysed by cation exchange resins: formation of mesityl oxide from acetone as case study”, *Applied Catalysis A: General*, *277*, 219–225.
- Vaidya, S. H.; Bhandari, V. M. and Chaudhari, R. V. (2003) “Reaction kinetics studies on catalytic dehydration of 1,4-butanediol using cation exchange resin”, *Applied Catalysis A: General*, *242*, 321–328.
- Winnick, J. (1997) *Chemical Engineering Thermodynamics*, John Wiley, United States of America.
- Xu, Z. P. and Chuang, K. T. (1996) “Kinetics of acetic acid esterification over ion exchange catalysts”, *The Canadian Journal of Chemical Engineering*, *74*, 493–500.
- Yu, W.; Hidajat, K. and Ray, A. K. (2004) “Determination of adsorption and kinetic parameters for methyl acetate esterification and hydrolysis reaction catalyzed by amberlyst 15”, *Applied Catalysis A: General*, *260*, 1–15.

APPENDIX A

Appendix

A.1 Calculation of the volume adsorbed onto a catalyst bead

Table A.1: Adsorption equilibrium constants

	Value	Unit
Macro porosity	0.35	%
Average bead diameter	0.775	mm
Adsorbed amount		
Acetic acid	0.307	cm ³ /g
Methanol	0.393	cm ³ /g
Methyl acetate	0.286	cm ³ /g
Water	0.479	cm ³ /g
Polymer density	1410	kg/m ³
Volume of one bead	2.4E-10	m ³
Pore Volume	8.5E-11	m ³
Polymer volume	1.6E-10	m ³
g Polymer	2.2E-04	g
Amount adsorbed in pores		
Acetic acid	6.9E-11	m ³
Methanol	8.8E-11	m ³
Methyl acetate	6.4E-11	m ³
Water	1.1E-10	m ³

A.2 Experimental

A.2.1 Sample make up for the determination of the analytical repeatability.

Table A.2: Weight of each species added to the sample (g)

	1	2	3	4
Methanol	0.20	0.10	0.40	0.10
Acetic acid	0.32	0.50	0.75	0.50
Methyl acetate	0.61	0.30	0.00	0.30
Water	0.13	0.24	0.00	0.24
MiBK	0.31	0.30	0.30	0.30

Sample concentration calculation

The report generated by the GC gave a μg quantity of each of the components in the sample mixture e.g. methanol = 53.11 μg , methyl acetate = 75.69 μg and acetic acid 207.40 μg .

This gave an indication of the sample composition after a known amount of time has passed. To determine the concentration of the analysed sample, the volume of the sample should be known. The water concentration however is unknown, and the volume of sample injected is also not known.

The volume ($v_{sample} = \sum_i^n v_i$) of the sample injected can be determined by calculating the volume of each component ($\frac{x \mu\text{g}}{\rho_x}$). All that needs to be known is the volume of water. Using the initial amount of water added, both fed to the reactor and present in the catalyst, together with the assumption that the amount of methyl acetate in the liquid phase is an indication of the reaction conversion, the volume water in the sample can be calculated (equation A.1).

$$v_{water*} = \left(\frac{n_D^o \cdot MM_D}{\sum_i^n n_i^o MM_i + \frac{\sum_i^n (n_i^o MM_i) \times 0.2}{0.8}} \right) \frac{871.61}{2000 \cdot \rho_D} + \frac{W_C MM_D}{MM_C \cdot \rho_D} \quad (\text{A.1})$$

where v_{water*} (in $\text{m}\ell$) indicates the volume of water based on the analysed sample concentration, W_C weight of methyl acetate in the sample (75.69 μg), MM_i the molar mass of component i , and n_i^o is the initial moles of component i and ρ_i the densities of each specie. This calculation of the initial water concentration is exactly the same as for the method followed for the calibration of the GC. This can then be used to determine the concentration of the reaction mixture based on the analysis ($C_i = \frac{W_i}{MM_i \sum_i^n v_i}$).

Since only the conversion of one compound should be known to determine the reaction mixture concentration, one component can be selected and the concentration of the rest can be determined from the initial reactor feed (e.g. taking the formation of methyl acetate, equation A.2). This can then be used to indicate which species will give the most accurate description of the liquid mixture.

$$X = \frac{C_C}{\frac{n_C}{V}} \quad (\text{A.2})$$

where V_{R^o} is the initial reactor volume. This conversion can then be used to predict the concentration of the other two components (in this case acetic acid and methanol) and compared to the analysed concentration. The error was then calculated using all of the analytical data, when choosing acetic acid, methanol and methyl acetate as basis for the calculation (the results are shown in table 3.4).

A.3 Experimental data

The experimental data obtained in this investigation is given in table A.3 all data are given in concentration (mol/ ℓ).

Table A.3: All experimental data gathered in this investigation.

Time (min)	Methanol	Acetic acid	Methyl acetate	Water
The experimental data for reaction: R1				
15	6.4	11.4	0.9	1.6
30	5.9	10.8	1.5	2.1
45	5.3	10.3	2.0	2.7
75	4.5	9.5	2.8	3.5
105	3.9	8.8	3.4	4.1
170	3.0	7.9	4.4	5.0
240	2.3	7.3	5.0	5.7
310	1.9	6.9	5.4	6.1
1370	0.9	5.9	6.4	7.1
1430	0.9	5.9	6.4	7.1
1695	1.0	5.9	6.4	7.0
2910	0.9	5.9	6.4	7.1

Continued on Next Page ...

Time (min)	Methanol	Acetic acid	Methyl acetate	Water
The experimental data for reaction: R2				
35	4.6	9.5	2.8	4.0
95	3.1	8.0	4.3	5.4
155	2.2	7.1	5.1	6.3
215	1.8	6.7	5.6	6.7
335	1.4	6.2	6.0	7.2
1385	1.0	5.9	6.3	7.5
1460	1.0	5.9	6.4	7.6
1625	1.1	5.9	6.3	7.5
The experimental data for reaction: R3				
30	5.5	10.2	1.5	5.1
60	4.6	9.2	2.5	6.1
120	3.3	8.0	3.7	7.3
180	2.6	7.2	4.5	8.0
240	2.2	6.8	4.9	8.4
1275	1.2	5.9	5.9	9.4
1410	1.2	5.9	5.9	9.4
The experimental data for reaction: R4				
32	5.6	10.0	1.2	6.8
60	4.7	9.2	2.1	7.7
180	2.9	7.4	3.9	9.5
260	2.4	6.8	4.4	10.0
331	2.1	6.6	4.7	10.3
1380	1.4	5.8	5.4	11.0
1560	1.4	5.8	5.4	11.0
The experimental data for reaction: R5				
32	8.0	8.0	2.2	3.4
64	6.7	6.7	3.5	4.7
90	6.0	6.1	4.2	5.4
120	5.4	5.5	4.8	5.9
180	4.6	4.7	5.6	6.8
355	3.6	3.7	6.6	7.8
525	3.3	3.3	6.9	8.1
1480	3.0	3.1	7.2	8.4

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Time (min)	Methanol	Acetic acid	Methyl acetate	Water
1831	3.0	3.1	7.2	8.4
The experimental data for reaction: R6				
30	8.3	8.3	1.5	5.2
60	7.2	7.2	2.6	6.3
90	6.5	6.4	3.3	7.0
120	5.9	5.9	3.9	7.5
182	5.1	5.1	4.7	8.3
300	4.3	4.2	5.5	9.2
485	3.7	3.6	6.1	9.8
1500	3.2	3.2	6.5	10.2
1880	3.2	3.2	6.6	10.2
The experimental data for reaction: R7				
2880	3.3	3.2	6.5	10.2
The experimental data for reaction: R8				
15	8.9	8.9	0.5	5.8
30	8.6	8.6	0.8	6.1
45	8.3	8.3	1.1	6.4
65	7.9	7.9	1.5	6.8
120	7.1	7.1	2.2	7.6
150	6.8	6.8	2.6	7.9
180	6.5	6.5	2.9	8.2
2040	3.3	3.3	6.1	11.4
2350	3.3	3.2	6.1	11.5
2410	3.3	3.2	6.1	11.4
The experimental data for reaction: R9				
31	8.2	8.0	1.3	7.0
60	7.4	7.2	2.1	7.8
90	6.8	6.6	2.7	8.5
130	6.1	6.0	3.3	9.1
195	5.4	5.2	4.1	9.8
275	4.8	4.7	4.7	10.4
461	4.1	3.9	5.4	11.1
1470	3.5	3.3	6.0	11.7
1905	3.5	3.3	6.0	11.7

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Time (min)	Methanol	Acetic acid	Methyl acetate	Water
The experimental data for reaction: R10				
45	11.5	6.2	1.8	2.5
105	10.3	4.9	3.1	3.8
180	9.3	4.0	4.0	4.7
250	8.8	3.4	4.6	5.3
350	8.2	2.8	5.2	5.8
1300	6.9	1.5	6.5	7.2
1455	6.8	1.5	6.5	7.2
1590	6.8	1.4	6.6	7.2
The experimental data for reaction: R11				
45	10.7	5.4	2.6	3.9
105	9.3	3.9	4.1	5.3
165	8.5	3.2	4.8	6.1
225	8.1	2.7	5.3	6.5
1200	6.9	1.5	6.5	7.8
1315	6.9	1.5	6.5	7.8
1410	6.9	1.5	6.5	7.8
The experimental data for reaction: R12				
1495	6.8	1.4	6.6	7.8
1665	6.8	1.4	6.6	7.8
The experimental data for reaction: R13				
1495	6.8	1.6	6.2	8.8
The experimental data for reaction: R14				
45	11.5	6.4	1.2	4.4
120	10.4	5.3	2.3	5.5
190	9.6	4.5	3.2	6.3
240	9.2	4.1	3.5	6.7
1155	7.0	1.8	5.8	9.0
1365	7.0	1.8	5.8	9.0
2550	6.8	1.7	6.0	9.1
The experimental data for reaction: R15				
30	11.5	6.4	1.3	5.0
60	10.5	5.4	2.2	5.9

Continued on Next Page ...

Time (min)	Methanol	Acetic acid	Methyl acetate	Water
120	9.4	4.3	3.4	7.1
180	8.7	3.6	4.1	7.8
240	8.2	3.1	4.6	8.3
387	7.5	2.4	5.2	9.0
1351	6.7	1.6	6.1	9.8
1440	6.7	1.6	6.1	9.8

The experimental data for reaction: R16

35	11.3	6.1	1.5	5.2
65	10.4	5.2	2.4	6.1
125	9.3	4.1	3.5	7.2
185	8.8	3.6	4.0	7.7
230	8.4	3.2	4.4	8.1
1175	7.0	1.8	5.8	9.6
1335	6.9	1.7	5.9	9.7
1480	6.9	1.7	5.9	9.6

The experimental data for reaction: R17

30	11.1	6.3	1.0	7.1
60	10.4	5.5	1.8	7.9
120	9.3	4.4	2.9	8.9
180	8.7	3.8	3.5	9.6
240	8.2	3.3	4.0	10.0
300	7.9	3.0	4.3	10.4
1440	6.7	1.8	5.5	11.6
1560	6.7	1.8	5.5	11.6

The experimental data for reaction: R18

1490	6.7	1.8	5.5	11.5
1670	6.7	1.8	5.5	11.5

The experimental data for reaction: R19

1490	6.8	2.0	5.1	12.2
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The experimental data for reaction: R20

2160	6.7	1.9	5.2	12.4
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A.4 Method Followed for the Prediction of Rate data

In this report the mathematical evaluation and optimisation of the data was done using MatlabTM.

For the prediction of the reaction rate the rate and equilibrium constants proposed by the individual authors were used (table 4.1). Using the applicable reaction model the differential equation (equation A.3), describing the change in moles of each component (n_i) with time, was solved using the MatlabTM function ode45 to solve the differential equation numerically. The ode45 function is based on an explicit Runge-Kutta (Forsythe et al., 1977; Kahaner et al., 1989) formula. For an activity based pseudo homogeneous reaction rate equation the method followed for the prediction of experimental data can be explained as:

- Define k_1 and K_{eq} .
- Solve differential equations of the reaction rate, equation A.3:

$$\frac{dn_i}{dt} = v_i k_1 m_{cat} \left(a_{Methanol} a_{Aceticacid} - \frac{1}{K_a} a_{Methylacetate} a_{Water} \right) \quad (\text{A.3})$$

The activity coefficient can be calculated at each interval using the local composition model used by the author, as given in section 2.2.2.

- This will then give the predicted reaction rate, which can then be plotted together with the experimentally measured rate of reaction (figure 4.1 to 4.9).

For the cases where the reaction model was fitted to experimental data, the rate constant k_1 was varied until a minimum error was achieved between the experimental and predicted data. The error was determined using equation 4.1 for all relevant experiments, the optimisation function `fminsearch` of MatlabTM was then used to find the optimum k_1 value for the description of the experimental data. The function `fminsearch` finds the minimum of a scalar function of several variables, starting at an initial estimate. The differential equation was described similarly as mentioned above.

BIBLIOGRAPHY

- Altiokka, M. R. and Citak, A. (2003) “Kinetics of esterification of acetic acid with isobutanol in the presence of amberlite catalyst”, *Applied Catalysis A: General*, *239*, 141–148.
- Aspen-Technology “Aspen plus 11.1”, Software (2001).
- Carslaw, K. S.; Peter, T. and Clegg, S. (1997) “Modelling the composition of liquid stratospheric aerosols”, *Reviews of Geophysics*, *35*, 125–154.
- Chakrabarti, A. and Sharma, M. M. (1993) “Cationic ion exchange resins and catalyst”, *Reactive Polymers*, *20*, 1–45.
- Flory, P. J. (1953) *Principles of Polymer Chemistry*, Cornell University Press, London.
- Fogler, H. S. (1999) *Elements of Chemical Reaction Engineering*, Prentice Hall, New Jersey 3 edition.
- Forsythe, G.; Malcolm, M. and Moler, C. (1977) *Computer Methods for Mathematical Computations*, Prentice-Hall, New Jersey.
- Fredenslund, A.; Gmehling, J. and Rasmussen, P. (1977) *Vapor-Liquid equilibrium using UNIFAC a group-contribution method*, Elsevier Scientific Pub. Co New York, New York.
- Gmehling, J. and Onken, U. (1977) *Vapour liquid equilibrium data collection*, , I of *Chemistry data series* Dechema, Frankfurt.
- Gusler, G. M.; Browne, T. E. and Cohen, Y. (1993) “Sorption of organics from aqueous solution onto polymeric resins”, *Ind. Eng. Chem. Res.*, *32*, 2727–2735.
- Harmer, M. A. and Sun, Q. (2001) “Solid acid catalyst using ion-exchange resins”, *Applied Catalysis A: General*, *221*, 45–62.

- Helfferich, F. (1962) *Ion Exchange*, McGraw-Hill Book Company Inc., New York.
- Kahaner, D.; Moler, C. and Nash, S. (1989) *Numerical Methods and Software*, Prentice-Hall, New Jersey.
- Kipling, J. J. (1965) *Adsorption from solutions of non-Electrolytes*, Academic Press, New York.
- Laatikainen, M.; Markkanen, I.; Tiihonen, J. and Paatero, E. (2002) “Liquid-liquid equilibria in ternary systems of linear and cross-linked water-soluble polymers”, *Fluid phase equilibria*, 201, 381–399.
- Lilja, J.; Murzin, D. Y.; Salmi, T.; Aumo, J.; Mäki-Arvela, P. and Sundell, M. (2002) “Esterification of different acids over heterogeneous and homogeneous catalyst and correlation with the taft equation”, *Journal of Molecular Catalysis*, 182-183, 555–563.
- Limbeck, U.; Altwicker, C.; Kunz, U. and Hoffmann, U. (2001) “Rate expression for THF synthesis on acidic ion exchange resin”, *Chemical Engineering Science*, 56, 2171–2178.
- Lode, F.; Freitas, S.; Mazzotti, M. and Morbidelli, M. (2004) “Sorbptive and catalytic properties of partially sulfonated resins”, *Ind. Eng. Chem. Res.*, 43, 2658–2668.
- Mäki-Arvela, P.; Salmi, T.; Sundell, M.; Ekman, K.; Peltonen, R. and Lehtonen, J. (1999) “Comparison of polyvinylbenzene and polyolefin supported sulphonic acid catalysts in the esterification of acetic acid”, *Applied Catalysis A: General*, 184, 25–32.
- Mazzotti, M.; Kruglov, A.; Neri, B.; Gelosa, D. and Morbidelli, M. (1996) “A continuous chromatographic reactor: Smbr”, *Chemical Engineering Science*, 51 (10), 1827–1836.
- Mazzotti, M.; Neri, B.; Gelosa, D.; Kruglov, A. and Morbidelli, M. (1997) “Kinetics of liquid-phase esterification catalyzed by acidic resins”, *Ind. Eng. Chem. Res.*, 36, 3–10.
- NIST “Nist chemistry webbook”, <http://webbook.nist.gov/chemistry/> (2005).
- Pöpken, T.; Götze, L. and Gmehling, J. (2000) “Reaction kinetics and chemical equilibrium of homogeneously and heterogeneously catalyzed acetic acid esterification with methanol and methyl acetate hydrolysis”, *Ind. Eng. Chem. Res.*, 39, 2601–2611.
- Rohm and Haas “http://www.rohmhaas.com/ionexchange/ip/15wet_typical.html”, website (2004).
- Rönback, R.; Salmi, T.; Vuori, A.; Haario, H.; Lehtonen, J.; Sundqvist, A. and Tirronen, E. (1997) “Development of a kinetic model for the esterification of acetic acid with methanol in the presence of a homogeneous acid catalyst”, *Chemical Engineering Science*, 52, 3369–3381.

- Ruthven, D. M. (1984) *Principles of Adsorption and Adsorption Processes*, John Wiley and Sons, New York.
- Sainio, T.; Laatikainen, M. and Paatero, E. (2004) “Phase equilibria in solvent mixture-ion exchange resin catalyst systems”, *Fluid Phase Equilibria*, 218, 269–283.
- Smith, J. M.; Ness, H. C. V. and Abbott, M. M. (2001) *Introduction to Chemical Engineering Thermodynamics*, Chemical Engineering Series McGraw Hill, New York 6 edition.
- Song, W.; Venimadhavan, G.; Manning, J. M.; Malone, M. F. and Doherty, M. F. (1998) “Measurement of residue curve maps and heterogeneous kinetics in methyl acetate synthesis”, *Ind. Eng. Chem. Res.*, 37, 1917–1928.
- Taft, R. W. (1951) “Polar and steric substituent constants for aliphatic and o-benzoate groups from rates of esterification and hydrolysis of esters”, *Journal of the American Chemical Society*, 74, 3120–3128.
- Thomas, J. M. and Thomas, W. J. (1997) *Heterogeneous catalysis*, VCH Publishers Inc, New York.
- Toit, E. D. and Nicol, W. (2004) “The rate inhibiting effect of water as a product on reactions catalysed by cation exchange resins: formation of mesityl oxide from acetone as case study”, *Applied Catalysis A: General*, 277, 219–225.
- Vaidya, S. H.; Bhandari, V. M. and Chaudhari, R. V. (2003) “Reaction kinetics studies on catalytic dehydration of 1,4-butanediol using cation exchange resin”, *Applied Catalysis A: General*, 242, 321–328.
- Winnick, J. (1997) *Chemical Engineering Thermodynamics*, John Wiley, United States of America.
- Xu, Z. P. and Chuang, K. T. (1996) “Kinetics of acetic acid esterification over ion exchange catalysts”, *The Canadian Journal of Chemical Engineering*, 74, 493–500.
- Yu, W.; Hidajat, K. and Ray, A. K. (2004) “Determination of adsorption and kinetic parameters for methyl acetate esterification and hydrolysis reaction catalyzed by amberlyst 15”, *Applied Catalysis A: General*, 260, 1–15.