

Industrial Processes and Scale-up 2014/2015

Simulation of Batch and PFR starting from the kinetics, INTRODUCTION

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In order to correctly simulate either a **continuous (PFR) or discontinuous reactor (BATCH)** in terms of composition, temperature and pressure it is compulsory to have:

- A suitable kinetic model, elaborated from the experimental data;
- Equilibrium data;
- A suitable thermodynamic model, able to represent the non-ideality of mixtures. It is helpful to remember how the activity coefficients play a role “less important” compared to the fluid phase but still relevant particularly in high non-ideal mixtures (double phase systems)

As reference we will use a paper by **Prof. Jurgen Gmehling** by University of Oldenburg (Germany), published on Industrial Engineering Chemistry Research.

Ind. Eng. Chem. Res. **2000**, *39*, 2601–2611

2601

Reaction Kinetics and Chemical Equilibrium of Homogeneously and Heterogeneously Catalyzed Acetic Acid Esterification with Methanol and Methyl Acetate Hydrolysis

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INTRODUCTION

The synthesis of methyl acetate by esterification of acetic acid with methanol and the reverse reaction (hydrolysis) are of a great interest as model reaction in the reactive distillation field.

The system methyl acetate-water shows a non-miscibility zone, but becomes totally miscible by adding methanol and/or acetic acid. We can therefore assume the liquid phase as

For a correct modeling interpretation it is a must to know the reaction kinetics and the equilibrium. Also, if we consider the reactive distillation, the VLE should be known.

The reaction is catalyzed by acids, **either in homogeneous or in heterogeneous phase**. This last system offers some advantages in terms of low corrosion and ease of separation. In this work Amberlyst 15 resins was used as catalyst.

To have a reliable model it is necessary to make kinetic runs with different amount of catalyst, initial compositions, T and P.

Experimental

Chemical equilibrium: the runs were made putting the reagents (2.5 g total) and the catalyst (about 10 g) in a vial (5 mL volume). The vials were put in a thermostatic bath for 3 weeks.

Reaction kinetics: the experiments were conducted in a 500 mL reactor, thermostated and stirred between 100 and 800 rpm. A condenser was added in order to avoid losing volatiles. The other parts of the reactor were heated in order to avoid vapor condensation. The samplings were of about 1 mL each.

Experimental: methanol(or water in the case of the hydrolysis) was heated to the reaction temperature. Acetic acid (or methyl acetate) was heated in the reactor. When both the reactant reached the desired temperature, they were mixed with the catalyst. This action corresponded to time 0. In every run, at regular time intervals, from 15 to 45 samples were gathered from the reactor and analyzed (colorimetric titration)

From the acetic acid quantification, and known both the initial amount of reactants and the stoichiometry, it was possible to calculate all the species concentrations. Parallel and undesired reactions were excluded by GC analysis.

Experiments performed:

- 45 uncatalyzed reactions
- 50 catalyzed reactions
- Different initial reactant concentrations
- Temperatures between 30 and 70°C
- Different catalyst amount

Diffusion

In order to exclude all the diffusional phenomena it was used a stirring rate enough to maintain all the catalyst particles suspended in the mixture.

It was also verified that above 170 rpm the results obtained were not dependent by the stirring rate. It was chosen to operate at 250 rpm

Similarly, using catalysts with different particle size, the internal diffusion was excluded.

Activity coefficients

The activity coefficients were calculated using the **UNIQUAC equation**. The temperature dependance of the interaction parameters was considered by a ploynomial:

$$\Delta u_{ij}(T) = a_{ij} + b_{ij}T + c_{ij}T^2$$

The pure parameters, r and q, were taken from litarature while the binary interaction parameter were regressed from experimental data. The results are reported in the table below:

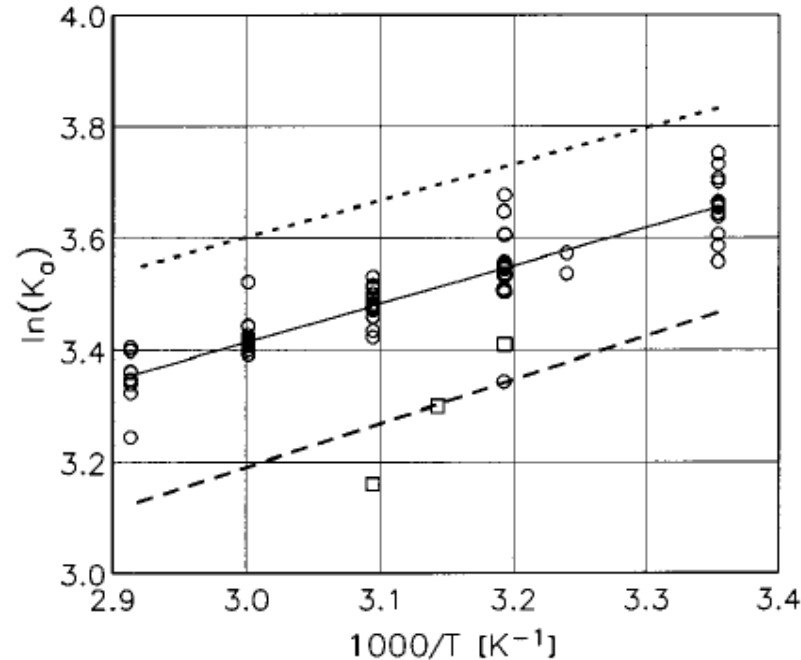
Table 3. UNIQUAC Parameters Used for the Calculation of Activity Coefficients (Eq 1)

<i>i</i>	<i>j</i>	<i>a_{ij}</i> (K)	<i>b_{ij}</i>	<i>c_{ij}</i> (K ⁻¹)
acetic acid	methanol	390.26	0.970 39	−3.0613 × 10 ^{−3}
methanol	acetic acid	65.245	−2.034 6	3.1570 × 10 ^{−3}
acetic acid	methyl acetate	−62.186	−0.436 37	2.7235 × 10 ^{−4}
methyl acetate	acetic acid	81.848	1.116 2	−1.3309 × 10 ^{−3}
acetic acid	water	422.38	−0.051 007	−2.4019 × 10 ^{−4}
water	acetic acid	−98.120	−0.29355	−7.6741 × 10 ^{−5}
methanol	methyl acetate	62.972	−0.710 11	1.1670 × 10 ^{−3}
methyl acetate	methanol	326.20	0.724 76	−2.3547 × 10 ^{−3}
methanol	water	−575.68	3.145 3	−6.0713 × 10 ^{−3}
water	methanol	219.04	−2.058 5	7.0149 × 10 ^{−3}
methyl acetate	water	593.70	0.010 143	−2.1609 × 10 ^{−3}
water	methyl acetate	−265.83	0.962 95	2.0113 × 10 ^{−4}

Composizioni all'equilibrio chimico

The chemical equilibrium is expressed using the constant **K_a**, defined as follows:

$$K_a = \prod a_i^{v_i} = \prod x_i^{v_i} \times \prod \gamma_i^{v_i}$$



From the slope and the point in which the line reach the vertical axis it is possible to calculate the standard reaction enthalpy by using the equation reported below

$$\ln K_a(T^0) = -\Delta g_r^\circ / RT^0$$

$$\ln K_a(T) = \ln K_a(T^0) - \frac{\Delta h_r^\circ}{R} \left(\frac{1}{T} - \frac{1}{T^0} \right)$$

Quest'integrazione è corretta se si assume l'entalpia costante.

Kinetic model developing

As first step, we want to model the **UNCATALYZED REACTION**.

FITTING PROCEDURE

The kinetic equations (differential equations) **are numerically** integrated using the fourth order Runge-Kutta method. The calculated acetic acid mass fraction are compared to the experimental ones, obtaining the relative and the quadratic deviation:

$$F_{\text{rel}} = \frac{\sum_{\text{all samples}} \left| \frac{w_{\text{HOAc,calc}} - w_{\text{HOAc,exp}}}{w_{\text{HOAc,exp}}} \right|}{n_{\text{samples}}} \times 100\%$$

$$F_{\text{abs}^2} = \frac{\sum_{\text{all samples}} (w_{\text{HOAc,calc}} - w_{\text{HOAc,exp}})^2}{n_{\text{samples}}}$$

By varying the parameters the values that minimize the deviations are the solutions. It is a **INTEGRATION-OPTIMIZATION PROCESS**.

Homogeneous reaction

In the case of non-catalyzed reaction, the reaction is **auto-catalyzed by acetic acid**. In this table the experiments made are reported, varying temperature between 40 and 70 °C.

Table 6. Summary of the Experiments without Catalyst Added

run number	temperature (K)	duration (days)	initial mole numbers			
			HOAc	MeOH	MeOAc	H ₂ O
1	313.15	34	1.1840	1.1645	0	0
2	313.15	11	1.2934	0.6701	0	0
3	323.15	8	1.2150	1.2085	0	0
4	323.15	8	1.4496	1.3914	0	0
5	323.15	11	0.3814	0	1.7003	1.7597
6	323.15	13	0.8944	0.2488	0.4011	0.5311
7	323.15	25	0.7933	0	0.5474	1.3108
8	328.15	20	2.7327	2.7278	0	0
9	333.15	3	1.4035	1.4033	0	0
10	333.15	6	1.2533	2.3720	0	0
11	333.15	3	1.2102	0.5637	0.0710	0.1948
12	333.15	15	0.8330	0	0.5641	1.2869
13	321.65	6	1.4373	0.1573	1.1350	1.3968
14	321.65	1	1.4167	0.1317	1.1644	1.4417

Homogeneous reaction

The model proposed for this reaction is reported here:

$$r = \frac{1}{\nu_i} \frac{dx_i}{dt} = a_{\text{HOAc}}^{\alpha} (k_1 a_{\text{HOAc}} a_{\text{MeOH}} - k_{-1} a_{\text{MeOAc}} a_{\text{H}_2\text{O}})$$

x_i is the molar fraction of component i , ν_i is the stoichiometric coefficient

a_i is the activity of the component i , k_1 and k_{-1} the kinetic constants of esterification and hydrolysis reactions respectively

$$k_i = k_i^0 \exp\left(\frac{-E_{A,i}}{RT}\right)$$

The dependence of the kinetic constant is expressed by the **Arrhenius law**.

$$r = \frac{1}{\nu_I} \frac{dx_I}{dt} = a_{\text{HOAc}}^\alpha (k_1 a_{\text{HOAc}} a_{\text{MeOH}} - k_{-1} a_{\text{MeOAc}} a_{\text{H}_2\text{O}})$$

$$k_I = k_I^0 \exp\left(\frac{-E_{A,I}}{RT}\right)$$

FOUR PARAMETERS must be regressed: two preexponential factors and two activation energies

The term before the brackets accounts for the activity coefficients of proton in the mixture. Depending on the mechanism considered, α can be 0.5 or 1. 0.5 corresponds to a catalytic action of acetic acid in its dissociated form while 1 corresponds to the acetic acid non-dissociated. For this reason α is optimized together with the other 4 parameters.

The regression was performed either considering the system ideal (activity coefficients equal to 1) or by calculating the activity coefficients using the UNIQUAC .

The routines were started with different initial values in order to be sure that the values obtained were of the absolute minimum, i.e. the real results.

The optimized parameters are reported in the following slide.

Table 7. Parameters and Residual Errors of the Different Kinetic Models Used To Fit the Experimental Data without Catalyst Added

exponent α	activities	mean relative error (%)	k_1^0 (s ⁻¹)	$E_{A,1}$ (kJ·mol ⁻¹)	k_{-1}^0 (s ⁻¹)	$E_{A,-1}$ (kJ·mol ⁻¹)
0.5	ideal	4.9	6.57×10^4	60.4	1.02×10^7	79.1
0.5	UNIQUAC	4.0	1.30×10^5	61.6	1.00×10^7	82.2
1	ideal	3.1	2.54×10^6	62.5	1.00×10^7	77.3
1	UNIQUAC	2.2	5.11×10^5	63.5	9.83×10^6	80.2
1.406	ideal	2.2	2.42×10^6	67.3	9.27×10^6	75.8
1.056	UNIQUAC	2.2	6.06×10^5	63.8	9.84×10^6	80.0

- 1) Better results are obtained using an alfa value of 1, both considering an ideal and a non-ideal mixture behaviour.
- 2) Considering the liquid mixture as non-ideal, low relative errors are obtained.
- 3) If we use UNIQUAC the regressed value for alfa is very close to 1. this shows that the auto-catalytic system is well represented by a model that considers the non-ideality of the liquid phase and the catalysis by acetic acid.

From the mathematical model we thus obtain informations about the REAL chemical physics reaction characteristics.

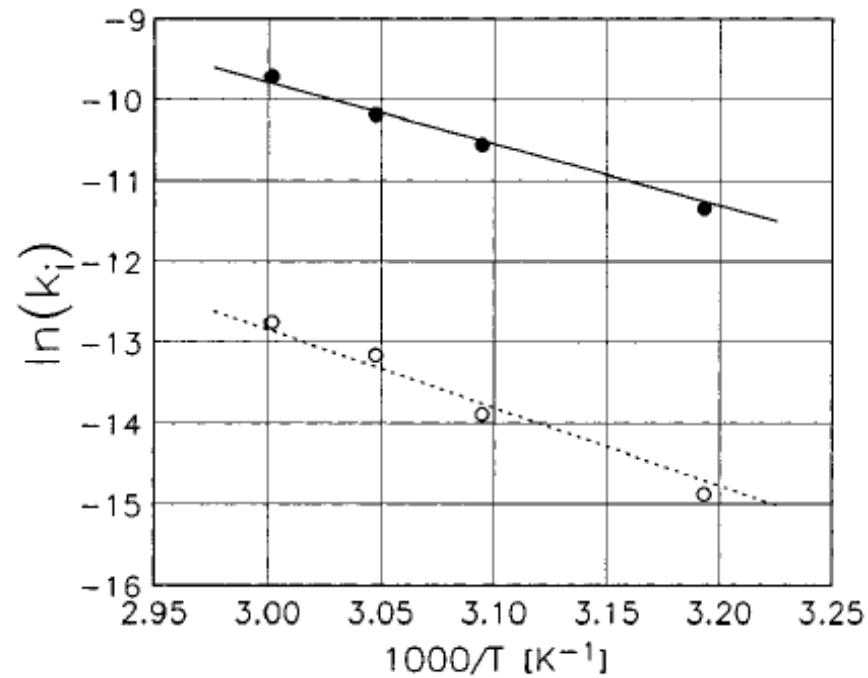


Figure 2. Arrhenius diagram of the rate constants for the esterification reaction k_1 (●) and the hydrolysis reaction (○) of the homogeneous reaction catalyzed by acetic acid (eq 6, $\alpha = 1$, activity coefficients calculated by UNIQUAC). The lines represent the result of the overall fit (compare Table 7).

k temperature dependance (**Arrhenius**)

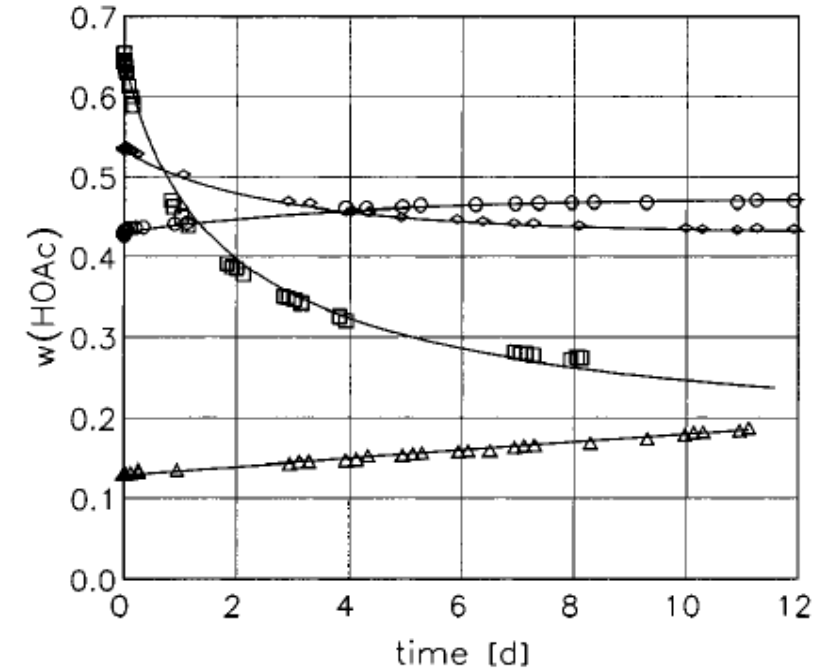


Figure 3. Experimental values for the acetic acid concentration (weight fraction) of four runs without catalyst added (□, run 3; △, run 5; ◇, run 6; ○, run 7; compare Table 6) and calculated course (eq 6, $\alpha = 1$, activity coefficients calculated by UNIQUAC).

T=50°C. **Experimental and calculated curves.** The model predicts in an accurate way both hydrolysis and esterification.

Heterogeneously catalyzed reaction

Table 8. Summary of the Experiments with Amberlyst 15 as Catalyst

run number	temperature (K)	mass of dry catalyst (g)	duration (h)	initial mole numbers (mol)			
				HOAc	MeOH	MeOAc	H ₂ O
1	304.25	18.27	23.4	1.557	1.557	0	1.014
2	303.45	31.54	23.3	1.993	2.012	0	0
3	313.63	8.84	2.0	1.621	1.618	0	0.542
4	313.14	3.81	23.4	1.646	1.608	0	0.234
5	313.00	5.76	31.6	3.589	1.591	0	0.354
6	323.00	7.17	5.6	1.997	1.999	0	0.427
7	323.15	7.71	6.4	2.031	1.982	0	0
8	323.00	7.31	4.8	1.996	2.090	0	0.441
9	323.00	6.70	5.0	2.006	2.017	0	0.363
10	323.00	23.80	5.1	2.003	2.049	0	1.485
11	323.08	8.18	17.7	1.656	1.626	0	0.502
12	323.06	8.55	18.8	1.642	1.621	0	0.524
13	323.06	17.10	21.1	1.632	1.627	0	1.049
14	323.00	3.54	23.0	2.050	1.019	0	0.217
15	323.00	8.67	3.2	1.539	2.921	0	0.531
16	323.15	7.15	5.9	0.428	3.588	0	0.440
17	333.14	4.25	23.2	1.669	1.642	0	0.261
18	333.12	8.19	20.3	1.670	1.646	0	0.502
19	333.13	17.71	20.1	1.661	1.604	0	1.087
20	333.20	23.38	4.9	1.562	1.549	0	1.230
21	304.25	18.66	23.4	0	0.367	1.614	1.546
22	313.30	17.61	19.7	0	0	1.621	2.801
23	313.00	5.70	95.1	0	0	2.539	4.156
24	323.08	17.13	18.5	0	0	1.648	2.698
25	323.15	29.52	3.7	0	0.432	1.812	1.897
26	333.03	17.78	20.9	0	0	1.623	2.785
27	323.15	12.97	6.5	2.001	2.009	0	0
28	323.15	27.61	6.5	2.012	2.008	0	0
29	323.15	36.95	6.5	2.003	1.992	0	0
30	323.15	46.35	6.5	2.015	1.998	0	0
31	323.15	55.37	3.7	2.004	2.015	0	0
32	323.15	5.02	6.5	0.246	4.761	0	0
33	323.15	7.20	6.2	0.431	3.579	0	0
34	323.15	6.14	7.1	1.008	4.073	0	0
35	323.15	5.61	5.4	2.721	0.730	0	0
36	323.15	11.19	6.2	3.590	0.387	0	0
37	323.15	5.89	1.8	3.088	0.142	0	0
38	323.15	4.32	70.6	0	0	0.595	5.400
39	323.15	4.35	24.6	0	0	1.005	3.991
40	323.15	6.65	5.4	0	0	1.997	0.499
41	323.15	5.27	4.5	0	0	1.795	0.198
42	313.15	20.73	24.5	0	0	0.898	9.362
43	323.15	20.54	5.4	0.897	0.901	0	8.454
44	323.15	59.68	1.3	0	0	0.613	5.417
45	333.15	20.49	5.4	0	0	0.904	9.366
46	343.15	21.18	3.5	0.894	0.901	0	8.517
47	313.49	17.60	21.1	1.483	0	0.640	1.477
48	313.45	17.58	19.0	1.012	0	0.956	2.328
49	333.05	17.66	15.8	0.654	1.580	0.800	1.281
50	333.09	17.58	19.0	0.459	0.149	0.934	3.866

30 < T < 60°C for:

esterification: runs 1-20

hydrolysis: runs 21-26

Also, at fixed temperature (50°C), were varied:

Catalyst amount: runs 27-31

Initial reactant amount in the esterification: Runs 32-37

Initial reactant amount in the hydrolysis: Runs 38-41

Finally in runs 47-50 an excess of water was used at **T=70°C** in order to avoid the mixture to reach the boiling point and with initial compositions similar to the one of the chemical equilibrium.

Heterogeneously catalyzed reaction

Two different models were considered. A pseudo-homogeneous one and an adsorption based one.

PSEUDOHOMOGENEOUS: it considers the catalyst as mixed in the liquid phase. This means not consider the adsorption and the diffusion phenomena. This is used because the catalyst swells in contact with the reagents, and this makes the pores enough narrow to assume the diffusion negligible.

ADSORPTION: it is based on the consideration that the system is heterogeneously catalyzed and thus that only the molecules adsorbed on the catalyst surface can react. It is not the bulk reactant concentration that act on the reaction rate but the fraction adsorbed on the catalyst (Langmuir isotherm).

PSEUDO-HOMOGENEOUS MODEL

$$r = \frac{1}{\nu_i} \frac{dn_i}{dt} = m_{cat}(k_1 a_{HOAc} a_{MeOH} - k_{-1} a_{MeOAc} a_{H_2O})$$

Catalyst could be seen as a proton source

Table 11. Parameters and Residual Errors of the Different Kinetic Models Used To Fit the Experimental Data with Amberlyst 15 as the Catalyst

model	mean relative error (%)	k_1^0 (mol·g ⁻¹ ·s ⁻¹)	$E_{A,1}$ (kJ·mol ⁻¹)	$k-10$ (mol·g ⁻¹ ·s ⁻¹)	$E_{A,-1}$ (kJ·mol ⁻¹)
pseudohomogeneous, ideal liquid phase	14.6	1.648×10^4	47.98	1.161×10^5	58.60
pseudohomogeneous, activities by UNIQUAC	13.9	2.961×10^4	49.19	1.348×10^6	69.23
Song's model with original parameters, activities by UNIQUAC	10.4	3.985×10^6	52.28	use K_a given by Song et al.	
Song's model, parameters fitted, activities by UNIQUAC	6.7	5.312×10^7	58.25	use K_a from this work	
eq 16	5.4	8.497×10^6	60.47	6.127×10^5	63.73

Ppseudohomogeneous model cannot give good results.
Also the results obtained using a different model, whose parameters were regressed from different experimental data (SONG), are compared.

Adsorption model

It is a modification of the **Langmuir-Hinshelwood-Hougen-Watson** (LHHW) model. The swelling effect however needs to be considered, and in the following table the experimental results are reported, together with the mass adsorbed by the catalyst for every component

Table 9. Experimental Swelling Ratios Obtained for the Pure Components and Adsorbed Volumes, Masses, and Moles per Gram of Dry Amberlyst 15 at 298 K

component	swelling ratio	adsorbed volume (cm ³ ·g ⁻¹)	adsorbed mass (g·g ⁻¹)	adsorbed amount (mmol·g ⁻¹)
acetic acid	1.43	0.307	0.319	5.31
methanol	1.55	0.393	0.309	9.60
methyl acetate	1.40	0.286	0.265	3.58
water	1.67	0.479	0.478	26.5

However, it is not correct to say that a constant mass of reagent is adsorbed. It is more likely to think about a cumulative constant mass adsorbed.

Sviluppo del modello di adsorbimento

From the global mass balance of every binary mixture we can obtain:

m_{cat} = massa catalizzatore; m° = peso totale solvente

w_1° = frazione in peso della massa liquida all'equilibrio

w_1^L = frazione in peso della specie 1

m_1^S e m_2^S = masse adsorbite delle specie 1 e 2

$$\frac{m^{\circ}(w_1^{\circ} - w_1^L)}{m_{cat}} = \frac{m_1^S w_2^L - m_2^S w_1^L}{m_{cat}}$$

The langmuir model expresses the covered area as reported below (being m_s the total mass adsorbed)

$$\frac{m_1^S}{m^S} = \frac{K_1 a_1}{1 + \sum_j K_j a_j}$$

By combining the two
equation we obtain

$$\frac{m^{\circ}(w_1^{\circ} - w_1^L)}{m_{cat}} = \frac{m^S}{m_{cat}} \frac{K_1 a_1 w_2^L - K_2 a_2 w_1^L}{1 + K_1 a_1 + K_2 a_2}$$

$$\frac{m^0(w_1^0 - w_1^L)}{m_{\text{cat}}} = \frac{m^S}{m_{\text{cat}}} \frac{K_1 a_1 w_2^L - K_2 a_2 w_1^L}{1 + K_1 a_1 + K_2 a_2}$$

This equation can be used for the **regression of the adsorption constants K**.

Table 10. Results of the Regression for the Nonreactive Binary Adsorption Data at 298 K

Equilibrium Adsorbed Mass

$$m^S/m_{\text{cat}} = 0.95$$

Adsorption Equilibrium Constants

$$K_{\text{HOAc}} = 3.15$$

$$K_{\text{MeOH}} = 5.64$$

$$K_{\text{MeOAc}} = 4.15$$

$$K_{\text{H}_2\text{O}} = 5.24$$

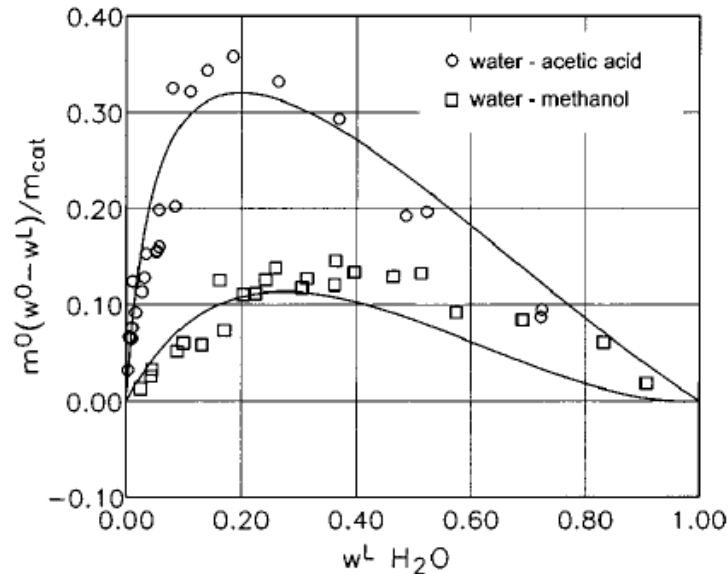


Figure 4. Relative adsorption of water from water–acetic acid (○) and water–methanol (□) mixtures on Amberlyst 15 and calculated dependence assuming constant adsorbed mass.

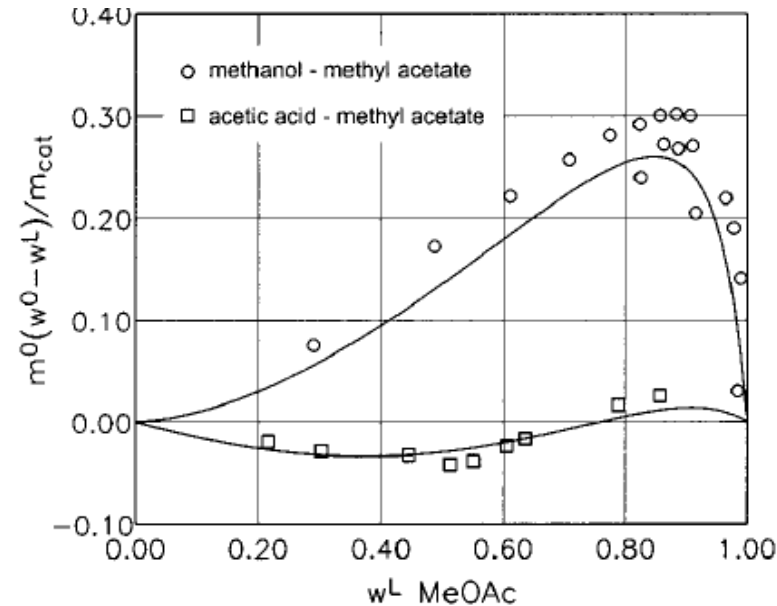


Figure 5. Relative adsorption of methanol from a mixture of methanol and methyl acetate (○) and relative adsorption of acetic acid from a mixture of acetic acid and methyl acetate (□) on Amberlyst 15 and calculated dependence assuming constant adsorbed mass.

At this point the numerical value of the equilibrium constants are determined. This means that they shouldn't be included as adjustable parameters in the regression. This lowers the number of parameters and increases the physical meaning of the others!!

Combining the Langmuir adsorption model

$$\frac{m_i^S}{m^S} = \frac{K_i a_i}{1 + \sum_j K_j a_j}$$

To the kinetic model below

$$r = \frac{1}{\nu_i} \frac{dn_i}{dt} = m_{\text{cat}} (k_1 x_{\text{HOAc}}^S x_{\text{MeOH}}^S - k_{-1} x_{\text{MeOAc}}^S x_{\text{H}_2\text{O}}^S)$$

where

$$x_i^S = \frac{m_i^S / M_i}{\sum_j (m_j^S / M_j)}$$

Represents the adsorbed molar fraction of the reactants

We obtain

$$r = \frac{1}{\nu_I} \frac{dn_I}{dt} = m_{cat} \left(\frac{k_1 a'_{HOAc} a'_{MeOH} - k_{-1} a'_{MeOAc} a'_{H_2O}}{(a'_{HOAc} + a'_{MeOH} + a'_{MeOAc} + a'_{H_2O})^2} \right)$$

with

$$a'_I = \frac{K_I a_I}{M_I}$$

With M_i the molecular weight of i

k_1 e k_{-1} sono
costanti
CINETICHE,
analogamente a
quanto visto per la
reazione non
catalitica e il mod
pseudo-omogeno

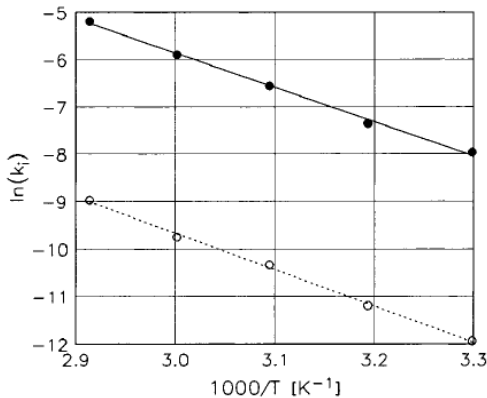


Figure 6. Arrhenius diagram of the rate constants for the esterification reaction k_1 (●) and the hydrolysis reaction (○) of the heterogeneously catalyzed reaction (eq 16, activity coefficients calculated by UNIQUAC). The lines represent the results of the overall fit (compare Table 11).

Table 11. Parameters and Residual Errors of the Different Kinetic Models Used To Fit the Experimental Data with Amberlyst 15 as the Catalyst

model	mean relative error (%)	k_1^0 (mol·g ⁻¹ ·s ⁻¹)	$E_{A,1}$ (kJ·mol ⁻¹)	$k-10$ (mol·g ⁻¹ ·s ⁻¹)	$E_{A,-1}$ (kJ·mol ⁻¹)
eq 16	5.4	8.497×10^6	60.47	6.127×10^5	63.73

Dependence of k_1 to the mass of catalyst

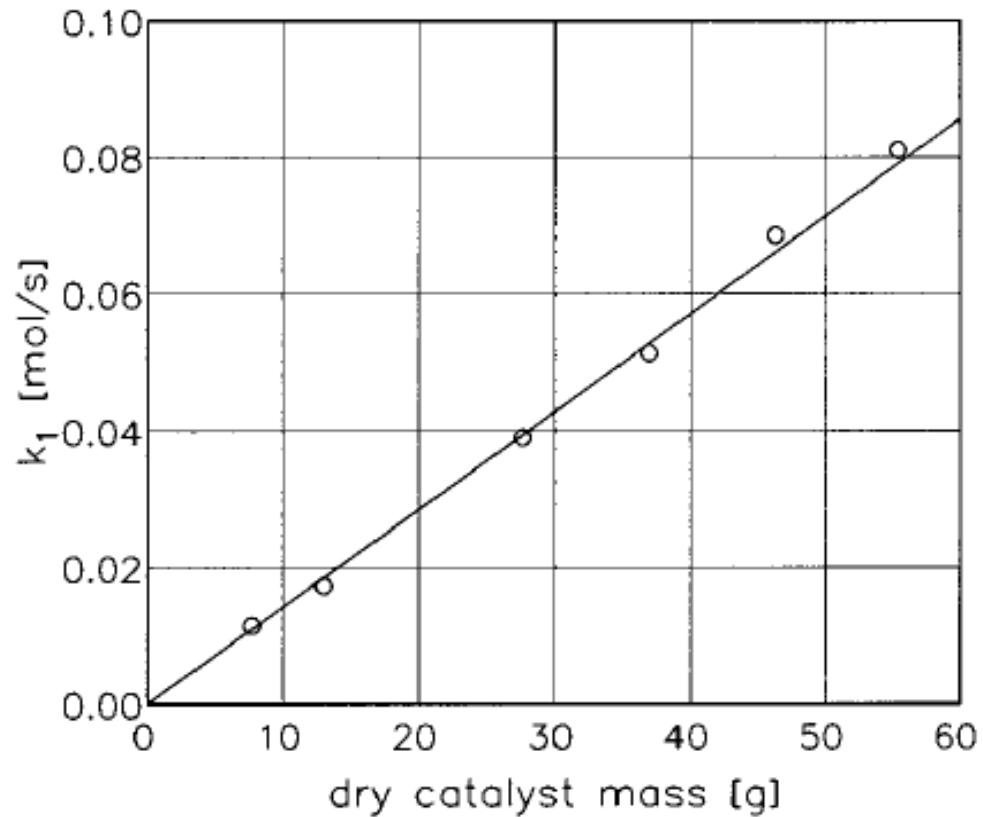


Figure 7. Rate constant of the esterification reaction k_1 (●) at 323 K versus catalyst mass for experiments 7 and 27–31. Only k_1 has been fitted for each run using the known chemical equilibrium constant from Figure 1. The line represents the result of the overall fit (compare Table 11).

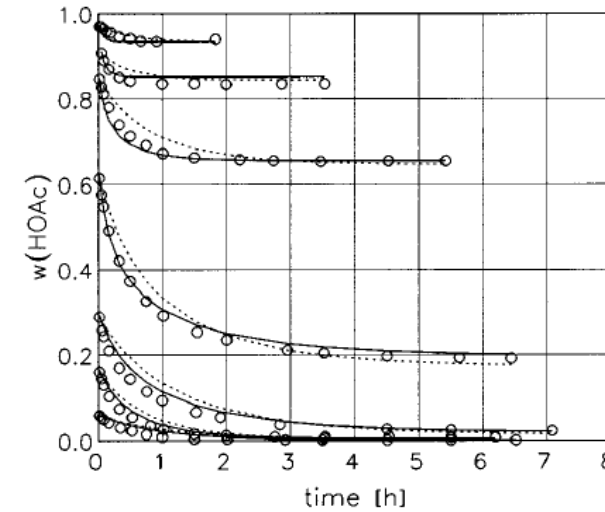


Figure 8. Experimental values (○) for the acetic acid concentration and predicted course by the pseudohomogeneous model (eq 10, dashed lines, activity coefficients by UNIQUAC) and eq 16 (solid lines). Seven runs (experiments 7 and 32–37) of the heterogeneously catalyzed esterification with varying initial reactant ratios are shown.

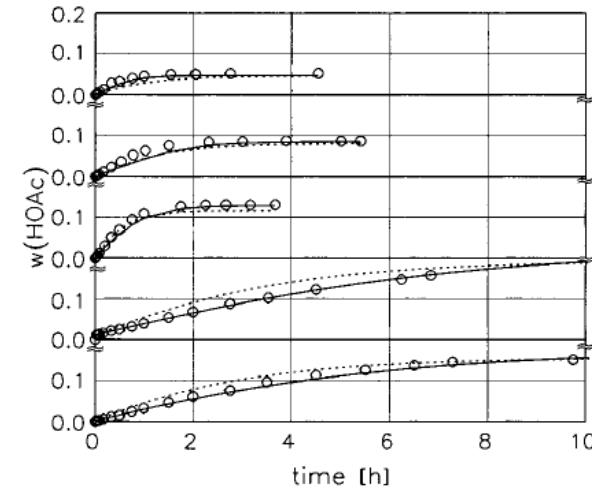


Figure 9. Experimental values (○) for the acetic acid concentration and predicted course by the pseudohomogeneous model (eq 10, dashed lines, activity coefficients by UNIQUAC) and eq 16 (solid lines). Five runs (experiments 25 and 38–41) of the heterogeneously catalyzed hydrolysis reaction with varying initial reactant ratios are shown.

Magnification
in the
next slide

— Adsorption
 - - - Pseudohomogeneous

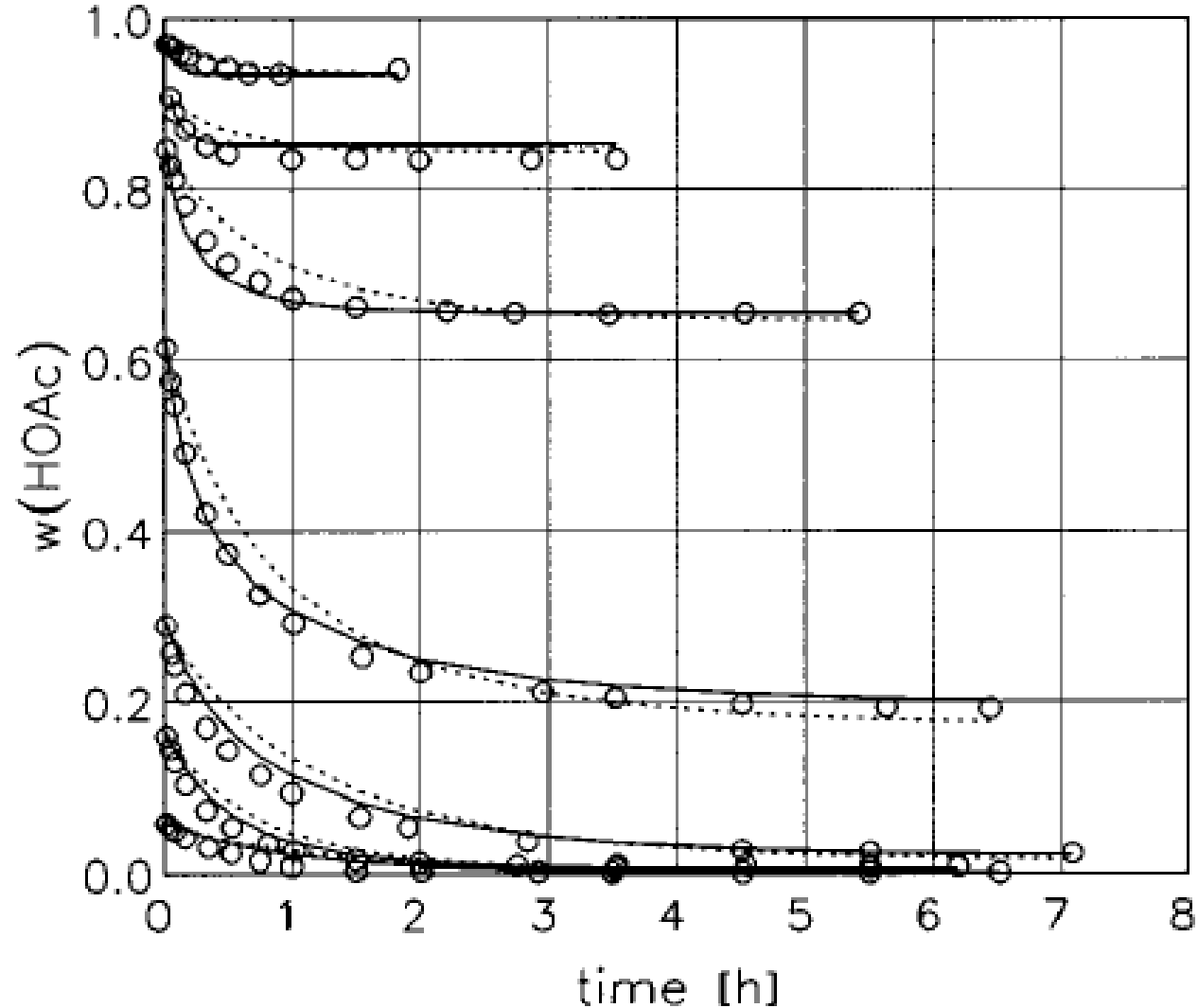


Figure 8. Experimental values (O) for the acetic acid concentration and predicted course by the pseudohomogeneous model (eq 10, dashed lines, activity coefficients by UNIQUAC) and eq 16 (solid lines). Seven runs (experiments 7 and 32–37) of the heterogeneously catalyzed esterification with varying initial reactant ratios are shown.

Both the direct and the reverse reaction are well calculated using the parameters regressed from the experimental data. Adsorption constants were obtained independently.

We report the comment of [Jurgen Gmehling](#): it is referred to the adsorption and the pseudo-homogeneous models:



Both models use the same number of adjustable parameters for the fit, that is, k_1^0 , k_{-1}^0 , $E_{A,1}$, and $E_{A,-1}$ because the adsorption constants K_i have been fitted independently to binary adsorption data. An attempt of fitting the four kinetic parameters and the four adsorption constants to kinetic data only resulted in very small residual errors, but also in a very poor extrapolability of the model to experimental data not included in the fitting procedure.