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Adsorption and reaction in the transesterification of ethyl acetate with methanol on Lewatit K1221

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ABSTRACT

The reaction kinetics of the liquid-phase transesterification of ethyl acetate with methanol to methyl acetate and ethanol have been investigated in a temperature range from 303.15 K to 333.15 K as a model reaction for the transesterification of triglycerides in the production of biodiesel. The reaction has been catalyzed by the acidic ion-exchange resin Lewatit K1221. The effect of the initial reactant molar ratio and the temperature on the reaction kinetics was investigated and kinetic models, based on pseudo-homogeneous (PH), Eley-Rideal (ER) and Langmuir–Hinshelwood (LH) mechanisms, were used to describe the reaction rate. Because of the pronounced non-ideality of the reaction mixture, the kinetics were expressed in terms of activities. Additional experiments, based on a D-optimum design of experiments, were performed to obtain more precise parameter estimates as required for final model discrimination. The kinetic model with the surface reaction of adsorbed methanol with ethyl acetate from the bulk as the rate-determining step according to an Eley–Rideal mechanism was found to best describe the observed kinetics. The corresponding rate equation agrees with a reaction mechanism in which physically adsorbed methanol reacts with protonated ethyl acetate.

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1. Introduction

Catalytic technologies have played a vital role in the economic development of the chemical industry during the 20th century, with a total estimated contribution of catalytic processes amounting to about 20% of the world's GNP. In the 21st century, there is a drive toward cleaner technologies brought about by public, legislative and corporate pressure to provide new and exciting opportunities for catalysis and catalytic processes [1].

The well-known disadvantages of homogeneous catalysis are reinforced by environmental policies and result in heterogeneous catalysis as a rapidly growing area [2,3]. Although heterogeneously catalyzed processes are widely used in large-scale petrochemical processes, the majority of fine, speciality, and pharmaceutical chemicals manufacturing processes still relies on homogeneous catalysts as, e.g., in the (trans)esterification. Many of these processes were developed about a half century ago [4,5]. While aiming at maximizing product yields, the environmental impact of inorganic waste and toxic by-products formed during the reaction was disregarded. Most of the waste is generated during the separation stage of the process by a typical water quench and neutralization, such as in acidic or alkaline catalyzed reaction technologies. Increasing waste disposal costs are adding to the environmental and societal costs of an increasingly critical public toward chemical waste.

Esters are of great significance in various industrial products including fragrances, flavors, solvents, plasticizers, medicinal and surface-active agents [6]. Esterification and transesterification plays an important industrial role with numerous applications. Large scale applications of transesterification are, e.g., the production of biodiesel, polyesters or PET in the polymer industry, while small scale fine chemical production includes synthesis of intermediates in the pharmaceutical industry, the production of food additives or surfactants and the curing of resins in the paint industry [7].

Transesterification reactions can be performed using base catalysts, such as metal hydroxides, metal alkoxides, alkaline-earth oxides or hydrotalcites or using acid catalysts, such as sulfuric, sulfonic, phosporic and hydrochloric acids. Base catalysts are typically preferred because of the higher reaction rates and the mild reaction conditions as compared to acid-catalyzed transesterifications. Nowadays, biodiesel is conventionally produced through a batch or continuous transesterification of highly refined vegetable oils with methanol by using homogeneous alkaline catalysts such as sodium or potassium hydroxides or methoxides. This conventional, industrial technology is not compatible with oils which have

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Nomenclature specific surface area particle $(m_{particle}^2 k g_{cat}^{-1})$ activity of component *i* (mol m⁻³) a' a_i pre-exponential factor ($m^3 kg_{cat}^{-1} mol^{-1} s^{-1}$) Α surface peak area of component i (V s⁻¹) A_{peak,i} parameter estimate b bulk fluid concentration (mol m_{gas}^{-3}) C_b concentration at external particle surface (mol m_{gas}^{-3}) C_{S} Са Carberry number CF_i calibration factor of component *i* with respect to *n*octane C_i \hat{C}_i observed concentration of component $i \pmod{m^{-3}}$ predicted concentration of component $i \pmod{m^{-3}}$ De effective diffusion coefficient ($m^2 s^{-1}$) activation energy (kJ mol⁻¹) EA reaction rate coefficient ($m^3 kg_{cat}^{-1} mol^{-1} s^{-1}$) mass transfer coefficient ($m s^{-1}$) k kg equilibrium coefficient of the overall reaction Keq K_i adsorption equilibrium coefficient of component *i* $(m^3 mol^{-1})$ characteristic particle size (m) L likelihood function Lmax mass of component i (kg) m_i order of the reaction п number of moles of component *i* (mol) n_i Ν total number of experimental points or components number of parameters р reaction rate (mol $kg_{cat}^{-1} s^{-1}$) observed volumetric reaction rate (mol $m^{-3} s^{-1}$) r r_{obs} gas constant ($J mol^{-1} K^{-1}$) R net production rate of component *i* (mol kg_{cat}⁻¹ s⁻¹) Ri regression sum of squares REG RSSQ residual sum of squares S objective function time (s) t Т temperature (K) W weight of catalyst (kg_{cat}) X_i conversion of component i Greek symbols parameter β activity coefficient of component i γi effectiveness factor n θ_i fractional coverage of catalyst surface Λ likelihood ratio stoichiometric coefficient for component i v_i Φ Weisz modulus reaction enthalpy $(kJ mol^{-1})$ ΔH_r Subscripts and superscripts 0 initial conditions adsorption site Α model A В model B

cat catalyst

- eq at equilibrium
- i component i

a free fatty acids (FFAs) content exceeding a threshold value of about 0.5 wt%. The development of new technologies, enabling to employ waste raw materials such as fried oils or mixtures of oils from various sources that cannot be treated in the conventional

process for their high content in free fatty acids, would, hence, offer an enormous strategic advantage. Innovative biodiesel production processes may be based on supercritical methanol or a two-stage process including esterification prior to transesterification. The esterification pre-treatment aimed at the abatement of FFAs is generally promoted by homogeneous acids or by solid acid ion-exchange resins. Strong sulfonic acid ion-exchange resins are promising candidates for catalyzing the complete esterification of FFAs and a first part of the transesterification [2,8–11]. Zielinska-Nadolska et al. [9], e.g., proved that the strong acid ion-exchange resin Lewatit K1221, modified potassium carbonate and the superacid ion-exchange resin Nafion SAC-13, gave the highest ethyl methyl carbonate yield in the transesterification of dimethyl carbonate with ethanol. Therefore, Lewatit K1221 catalyst was selected in this work.

Pseudo-homogeneous (PH) and adsorption-based mechanisms have been used to describe heterogeneously catalyzed transesterification. Adsorption-based mechanisms include the Eley-Rideal (ER) and the Langmuir-Hinshelwood (LH) mechanisms. Saha and Streat [12] have evaluated different heterogeneous acid catalysts including ion-exchange resins as catalysts for the transesterification of cyclohexyl acrylate with *n*-butanol and 2-ethylhexanol. The experimental results were best described by a kinetic model based on a Langmuir-Hinshelwood-Hougen-Watson mechanism. Jimenez et al. [13] studied the transesterification of *n*-butyl acetate and methanol catalyzed by ion-exchange resin Amberlyst 15 and found the pseudo-homogeneous model as the best description for the experimental data. Bożek-Winkler and Gmehling [14] and Steinigeweg and Gmehling [15] studied the kinetic behavior of the reaction of methyl acetate and butanol catalyzed by the ion-exchange resin Amberlyst 15. Two different kinetic models, pseudo-homogenous and Langmuir-Hinshelwood, were used to describe the reaction rate. The simpler pseudo-homogeneous model provided similar results as the Langmuir-Hinshelwood model [14].

The objective of this work is to investigate the transesterification kinetics of ethyl acetate (EtOAc) with methanol (MeOH) to form methyl acetate (MeOAc) and ethanol (EtOH) catalyzed by Lewatit K1221. Experiments in a perfectly mixed batch reactor have been performed. These experimental data have been modeled to obtain more insight in the reaction mechanism and a potential rate-determining step. Pseudo-homogeneous and different adsorption-based models, such as Eley–Rideal and Langmuir–Hinshelwood, have been used. This work fits into an overall strategy for the adequate simulation of a two-stage biodiesel manufacturing process. Base catalyzed transesterification kinetics have been previously studied [3], acid catalyzed transesterification kinetics are the subject of the present study, while the acid catalyzed esterification kinetics will be studied in the future.

2. Procedures

2.1. Materials

Methanol (Fiers, purity >99.85%) and ethyl acetate (Fiers, purity \geq 99.5%) were used as reagents. *n*-Octane (Acros Organics, purity >99%) was used as internal standard. Lewatit K1221 (Lanxess) is a strongly acidic, dark brown translucent, polymer-based resins in spherical bead form, with sulfonic acid groups. This gel-type resin is moderately crosslinked (4%) with polystyrene. The bead size varies between 0.4 and 1.2 mm. Lewatit K1221 contains minimal 1.2 mol H⁺/L. The resin is heat-sensitive and experiences a loss of activity above 398 K. Prior to transesterification, the catalyst was dried under vacuum at 233 K for 24 h to completely remove any moisture.



Fig. 1. Experimental setup.

2.2. Experimental setup

The transesterification of ethyl acetate with methanol was carried out in a three-necked glass flask of 180 mL capacity equipped with a reflux condenser, a thermocouple and a sampling port, see Fig. 1. The temperature in the reactor was maintained within 0.5 K from the set point using a PID-controller (Lauda Proline RP845). The reaction mixture was stirred with a magnetic stirrer and set at a constant speed of 500 rpm throughout the experiment. The reactor was first loaded with methanol and catalyst and then heated to the reaction temperature. The gas volume of the reactor was minimal, hence the loss to the vapor phase could be neglected.

When the reactor mixture reached the desired temperature. preheated ethyl acetate and *n*-octane were added through the sampling port in order to have a well determined starting point of the experiment without disturbing the reactor temperature. *n*-Octane was used as internal standard for analytical purposes and for obtaining a constant reaction volume. The *n*-octane content ranged from 56 to 3 mol%, depending on the molar ratio 1:1 to 10:1. All experiments have been performed at atmospheric pressure. Each experiment was performed at least quadruple with an experimental error below 5%. The range of experimental conditions is given in Table 1. A reference experimental data set consisting of 1012 points from 68 experiments has been used for initial model regression. It has subsequently been extended with 270 data points according to a D-optimal design, see Section 2.6, for more precise parameter estimation and conclusive model discrimination.

Table 1

Range of experimental conditions.

Temperature (K)	303.15-333.15
Pressure (MPa)	0.1
Initial MeOH:EtOAc molar ratio	1:1 to 10:1
Mass of catalyst (10 ⁻³ kg)	0.5-5.0
Batch time ^a (kg s)	12.6-126

^a Defined as the product of experiment time and the mass of catalyst.

2.3. Sampling and analysis

Samples of the reaction mixture were withdrawn through the sampling port every 1800 s. The samples were analyzed by gas chromatography using a Focus GC, equipped with an AS3000 auto sampler, a Stabilwax capillary column ($30 \text{ m} \times 0.32 \text{ mm}$, 0.25μ m thickness) and a flame ionization detector. The injector and detector temperatures were both set at 523 K. The oven temperature program started at 313 K for 300 s, then increased to 343 K at a rate of 6.0 K s^{-1} , further increased to 473 K at a rate of 50.0 K s^{-1} and finally held constant at 473 K. The Chromchard 2.3.2 software was used to analyze the gas chromatography data. No by-product formation was observed. No conversion was observed when the reaction was performed in the absence of the catalyst. No catalyst activity decay, e.g., due to leaching, was observed in successive runs on the same catalyst batch.

Quantification of the reaction components was performed by relating the peak surface areas to the mass of *n*-octane, the internal standard:

$$\frac{A_{peak,ref}}{A_{peak,i}} = CF_i \frac{m_{ref}}{m_i} \tag{1}$$

where $A_{peak,i}$ and $A_{peak,ref}$, are the peak surface area of component *i* and *n*-octane, and CF_i the calibration factor of the component *i* with respect to *n*-octane.

Conversions were calculated as follows:

$$X_{i} = \frac{C_{i,0} - C_{i,t}}{C_{i,0}}$$
(2)

where X_i is the conversion of reactant *i*, $C_{i,0}$ the initial concentration of *i* and $C_{i,t}$ the concentration of *i* at time *t* [16].

Only experiments with a mass balance deviation below 5% were used in the kinetic modeling. Prior to any regression, the corresponding experimental results were scaled to obey a 100% mass balance.

2.4. Intrinsic kinetics measurements

In order to ascertain that the obtained data represent intrinsic kinetics, they should be free from deviations due to non-ideal reactor behavior and interference with transport phenomena. Two types of mass-transfer resistance have been verified, one across the solid-liquid interface and the other in the intraparticle space. Quantitative criteria have been developed to verify the absence of mass transfer limitations, such as the Carberry number C_a for external mass transfer and the Weisz modulus Φ for internal diffusion. These parameters were calculated using the appropriate correlations (Table 2) [16,17].

In addition to these quantitative criteria, also some qualitative tests have been performed to verify the importance of transfer phenomena and the ideality of the reactor flow pattern. To evaluate the significance of external mass transport phenomena, transesterification experiments were performed at different agitation speeds. When external mass transport is not rate limiting, there is no effect of the agitation speed [16]. It is clear that the external masstransfer resistance is negligible between 200 and 1000 rpm, see Fig. 2. Hence, all further experiments were conducted at a stirrer

Table 2

Criteria for the absence of transport limitations for a catalyst particle under steadystate operation.

Transport phenomenon	Criterion	Calculation
Extraparticle mass transport ('Carberry number')	$Ca = \frac{r_{obs}}{k_g a' c_b} < 0.05$	Ca = 7.7E - 03
Intraparticle mass transport ('Wheeler-Weisz criterion')	$ \Phi = rac{r_{obs}L^2}{\eta_{in}Dec_s} \left(rac{n+1}{2}\right) < 0.1 $	Φ = 7.5E – 02



Fig. 2. Effect of the agitation speed (legend) on the conversion of EtOAc (T=333 K, W=0.58 × 10⁻³ kg, initial MeOH:EtOAc molar ratio = 10:1).

speed of 500 rpm to ensure that the reaction rate was not limited by external diffusion. This was also observed by Sanz et al. [18]. These authors indicate that external diffusion does not usually control the overall rate in the reactions catalyzed by ion-exchange resin unless the agitation speed is very low or the reaction mixture is very viscous.

The possible effect of internal mass-transfer was verified by using different catalyst particle sizes [16]. The commercial Lewatit K1221 resin was screened into four different size ranges. As shown in Fig. 3, no significant differences were found in the reaction rate for the different catalyst sizes, i.e., the effect of internal mass transfer on the reaction kinetics could be considered negligible. Hence, all experiments were conducted with the ion-exchange resin as supplied by the manufacturer without any size screening.



Fig. 3. Effect of the particle size (legend) on the conversion of EtOAc (T=333 K, W=0.58 × 10⁻³ kg, initial MeOH:EtOAc molar ratio = 10:1).

2.5. Thermodynamic calculations

The reaction enthalpy was calculated based on thermodynamic data obtained form the tabulated values of the ASPEN engineering suiteTM 11.1, and was found to vary from -4.20 at 303 K to -0.50 kJ mol⁻¹ at 333 K, showing a slightly exothermic reaction. The corresponding equilibrium coefficient K_{eq} :

$$K_{eq} = K_C K_{\gamma} = \frac{C_{\text{MeOAc}} C_{\text{EtOH}}}{C_{\text{MeOH}} C_{\text{EtOAc}}} \frac{\gamma_{\text{MeOAc}} \gamma_{\text{EtOAc}}}{\gamma_{\text{MeOH}} \gamma_{\text{EtOAc}}}$$
(3)

ranges from 1.59 at 303 K to 1.46 at 333 K, which is similar to values reported in previous transesterification studies [7]. The equilibrium conversion of ethyl acetate X_{eq} varies from 58 to 94% depending on the initial molar ratio of methanol to ethyl acetate (MeOH:EtOAc), i.e., ranging from 1:1 to 10:1.

The non-ideal character of the reaction mixture was assessed and activity coefficients γ_i for each component *i* were calculated at temperatures ranging from 303.15 K to 333.15 K with the UNIFAC group contribution method [19]. The molecular activity coefficient, see Eq. (4), is separated into two parts: the combinatorial part provides the contribution due to differences in molecular size and shape, and the residual part provides the contribution due to energy interactions, functional group sizes and interactions of surface areas:

$$\ln \gamma_i = \frac{\ln \gamma_i^c}{\text{combinatorial residual}} + \frac{\ln \gamma_i^R}{residual}$$
(4)

Table 3 shows the activity coefficients of each component for all the experimental conditions, at the start of the reaction and at thermodynamic equilibrium. Since the activity coefficients were different from 1.0, the reaction mixture clearly exhibits non-ideal behavior. Deviations from ideality were found to be most pronounced in the experiments with a high initial molar methanol to ethyl acetate ratio.

2.6. Modeling and regression analysis

The mass balance for species *i* in a batch reactor, which is considered to be spatially uniform in composition and temperature, is given by

$$\frac{1}{W}\frac{dn_i}{dt} = R_i = v_i r \tag{5}$$

with R_i the net production rate of component *i*, *W* the catalyst mass in the reactor, v_i the stoichiometric coefficient of component *i*, n_i the number of moles of component *i* in the reaction mixture, and *t* the time. In Eq. (5), the net production rate is calculated according to equations derived from the various mechanisms that are proposed, i.e., pseudo-homogeneous (PH), Langmuir–Hinshelwood (LH) and Eley–Rideal (ER).

The net production rate is a function of the reaction rate coefficient, temperature, activities and equilibrium coefficients. The reaction rate coefficient is described by the Arrhenius law, which is reparameterized according to Kittrell [20] in order to avoid strong binary correlation between the Arrhenius parameters:

$$k = k_{T_{ref}} \exp\left[-\frac{E_A}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$
(6)

with E_A the activation energy, R the universal gas constant and $k_{T_{ref}}$ the reaction rate coefficient at the reference temperature. The activation energy and the rate coefficient at the reference temperature as well as the adsorption equilibrium coefficient for the adsorption-based mechanisms have been determined from regression, see

Table 3

...

Activity coefficients of MeOH, EtOH, MeOAc, EtOAc and *n*-octane at different temperatures and different initial MeOH:EtOAc molar ratios, at the start of the reaction and at equilibrium. C_{EtOAc.0}=1.79 M except at 333 K and initial MeOH:EtOAc molar ratio = 1:1 where C_{EtOAc.0}=5.79 M.

Temperature	303 K				313 K		323 K		333 K					
MeOH:EtOAc ratio	1:1		10:1		10:1		10:1		1:1		5:1		10:1	
Conversion (%)	0	56	0	94	0	94	0	94	0	56	0	89	0	94
MeOH	1.47	1.52	1.02	1.02	1.02	1.02	1.02	1.02	1.45	1.51	1.29	1.31	1.02	1.02
EtOH	-	1.41	-	1.19	-	1.18	-	1.18	-	1.39	-	1.28	-	1.17
MeOAc	-	1.27	-	2.12	-	2.08	-	2.05	-	1.25	-	1.62	-	2.02
EtOAc	1.25	1.25	2.27	2.27	2.24	2.24	2.21	2.20	1.23	1.23	1.59	1.57	2.17	2.17
n-Octane	4.84	4.57	17.39	17.22	16.58	16.42	15.82	15.67	4.51	4.29	4.02	4.01	15.10	14.96

Table 5. The latter was performed by minimizing the following objective function *S*:

$$S = \sum_{k=1}^{N} (C_{\text{EtOAc},k} - \widehat{C}_{\text{EtOAc},k})^2 \xrightarrow{b} \text{minimum}$$
(7)

with $C_{\text{EtOAc},k}$ the experimentally observed concentration of ethyl acetate in the *k*th experiment and $\widehat{C}_{\text{EtOAc},k}$ the corresponding model calculated value, *N* the total number of experimental measurements and *b* the parameter vector [14,16]. The minimization was achieved by a single response Levenberg–Marquardt algorithm. The residual sum of squares (*RSSQ*) equals the final value of *S* of Eq. (7). The regression sum of squares (*REG*) is given by

$$REG = \sum_{k=1}^{N} \hat{C}^2 \tag{8}$$

The estimated parameters were subsequently evaluated based on their physicochemical and statistical significance. The reaction rate coefficients have to increase with temperature, i.e., the activation energy and the rate coefficient at the reference temperature have to be positive and, based on the Van't Hoff equation, the adsorption equilibrium coefficients have to decrease with temperature. The statistical significance of the parameter estimates was assessed with the Student *t*-test:

$$t = \frac{b_i - \beta_i}{s(b_i)} > t_{tab}(N - p, 95\%)$$
(9)

with b_i the estimated parameter value, β_i , the proposed value, c.q., zero, for parameter *i*, and $s(b_i)$ an estimate of the standard deviation [16,21].

The global significance of the regression was assessed with the *F*-test:

$$F = \frac{REG/p}{RSSQ/(N-p)} > F_{tab}(p, N-p, 95\%)$$
(10)

with *p* the number of model parameters [16,22].

Apart from the statistical and physical significance of the regression and the corresponding model parameters, discrimination between rival models can also be performed based on the so-called likelihood ratio. The likelihood ratio Λ is the ratio of the maximum in the likelihood function, L_{max} obtained with the rival models A, with p_A parameters and $RSSQ_A$, and B, with p_B parameters and $RSSQ_B$:

$$L_{\max} = \frac{(N-p)^{N/2}}{\left(\sqrt{2\pi RSSQ}\right)^N} \exp\left(-\frac{N-p}{2}\right)$$
(11)

$$\Lambda = \frac{(L_A)_{\max}}{(L_B)_{\max}} = \left[\frac{N - p_A}{N - p_B}\right]^{N/2} \exp\left(\frac{p_A - p_B}{2}\right) \left[\frac{RSSQ_B}{RSSQ_A}\right]^{N/2}$$
(12)

For a high ratio, model *A* has a higher probability to adequately describe the experimental data than model *B* and vice versa for a small ratio.

In case the likelihood ratio does not lead to a decisive discrimination, a design of experiments (DOE) can be performed to obtain more precise parameter estimates and, hence, to allow a better discrimination. In this work, a D-optimal experimental design is used, which minimizes the joint confidence interval of the model parameters and, hence, maximizes the determinant of the parameter estimation covariance matrix [16,23,24].

3. Kinetic model

The kinetic model for the transesterification of ethyl acetate with methanol can be expressed according to either a pseudohomogeneous or an adsorption reaction based reaction mechanism such as Langmuir–Hinshelwood (LH) or Eley–Rideal (ER) [14,25–27].

The pseudo-homogeneous kinetic model is given by

$$r = k_{PH} \left(a_{\text{MeOH}} a_{\text{EtOAc}} - \frac{1}{K_{eq}} a_{\text{EtOH}} a_{\text{MeOAc}} \right)$$
(16)

with k_{PH} the reaction rate coefficient, a_i the activity of component i and K_{eq} the equilibrium coefficient of the overall reaction.

For the adsorption-based models, the various LH mechanisms consist of five elementary steps, while the ER mechanisms consist

Table 4

Elementary steps and reaction mechanism for the kinetic modeling of transesterification of ethyl acetate with methanol. * = active site.

Elementary reactions	Reaction me	echanism	nism				
	PH	LH	ER				
			Alcohol adsorption	Ester adsorption			
$CH_3OH + * \rightleftharpoons CH_3OH^*$		1	1				
$CH_3CH_2COOCH_3 + * \rightleftharpoons CH_3CH_2COOCH_3^*$		1		1			
$CH_3OH + CH_3CH_2COOCH_3 \rightleftharpoons CH_3COOCH_3 + CH_3CH_2OH$	1						
$CH_3OH^* + CH_3CH_2COOCH_3^* \rightleftharpoons CH_3COOCH_3^* + CH_3CH_2OH^*$		1					
$CH_3OH + CH_3CH_2COOCH_3^* \rightleftharpoons CH_3COOCH_3^* + CH_3CH_2OH$				1			
$CH_3OH^* + CH_3CH_2COOCH_3 \rightleftharpoons CH_3COOCH_3 + CH_3CH_2OH^*$			1				
$CH_3CH_2OH^* ightarrow CH_3CH_2OH + *$		1	1				
$CH_3COOCH_3^* \rightleftharpoons CH_3COOCH_3^* + ^*$		1		1			

Table 5

Reaction rates based on the mechanism and rate-determining step (with $K'_i = K_i a_i$).

Abbreviation	Rate-determining step	Rate equation
LH mechanism LH-MeOH	$CH_3COOH + * \rightleftharpoons CH_3COOH^*$	$r = \frac{k_{\text{MeOH}}(a_{\text{MeOH}} - (1/K_{eq})(a_{\text{MeOAc}}a_{\text{EtOH}}/a_{\text{EtOAc}}))}{1 + (K_{\text{MeOH}}/K_{eq})(a_{\text{MeOAc}}a_{\text{EtOH}}/a_{\text{EtOAc}}) + K'_{\text{EtOAc}} + K'_{\text{MeOAc}} + K'_{\text{EtOH}}}$
LH-EtOAc	$CH_3CH_2COOCH_3 + * \rightleftharpoons CH_3CH_2COOCH_3 *$	$r = \frac{k_{\text{EtOAc}}(a_{\text{EtOAc}} - (1/K_{eq})(a_{\text{MeOAc}}a_{\text{EtOH}}/a_{\text{MeOH}}))}{1 + K'_{\text{MeOH}} + (K_{\text{EtOAc}}/K_{eq})(a_{\text{MeOAc}}a_{\text{EtOH}}/a_{\text{MeOH}}) + K'_{\text{MeOAc}} + K'_{\text{EtOH}}}$
LH-SR	$CH_3COOH^* + CH_3CH_2COOCH_3^* \rightleftarrows CH_3COOCH_3^* + CH_3CH_2OH^*$	$r = \frac{k_{\text{SR}} \kappa_{\text{MeOH}} \kappa_{\text{EtOAc}} (a_{\text{MeOH}} a_{\text{EtOAc}} - (1/\kappa_{eq}) a_{\text{MeOAc}} a_{\text{EtOH}})}{(1 + K'_{\text{MeOH}} + K'_{\text{EtOAc}} - K'_{\text{MeOAc}} + K'_{\text{EtOH}})^2}$
LH-EtOH	$CH_3CH_2OH^* ightarrow CH_3CH_2OH + ^*$	$r = \frac{k_{\text{EtOH}} K_{eq}((a_{\text{MeOH}} a_{\text{EtOAc}}/a_{\text{MeOAc}}) - (1/K_{eq})a_{\text{EtOH}})}{1 + K'_{\text{MeOH}} + K'_{\text{EtOAc}} + K'_{\text{MeOAc}} + K_{\text{EtOH}} K_{eq}(a_{\text{MeOH}} a_{\text{EtOAc}}/a_{\text{MeOAc}})}$
LH-MeOAc	$CH_3COOCH_3^* \rightleftharpoons CH_3COOCH_3 + ^*$	$r = \frac{k_{\rm MeOAc}K_{\rm eq}((a_{\rm MeOH}a_{\rm EtOAc}/a_{\rm EtOA}) - (1/K_{\rm eq})a_{\rm MeOAc})}{1 + K'_{\rm MeOH} + K'_{\rm EtOAc} + K'_{\rm EtOH} + K_{\rm MeOAc}K_{\rm eq}(a_{\rm MeOH}a_{\rm EtOAc}/a_{\rm EtOH})}$
ER mechanism with acetate adsor	ption	
ER-EtOAc	$CH_3CH_2COOCH_3 + * \rightleftharpoons CH_3CH_2COOCH_3 *$	$r = \frac{k_{\text{EOAc}}(a_{\text{EOAc}} - (1/K_{eq})(a_{\text{MeOAc}}a_{\text{EtOH}}/a_{\text{MeOH}}))}{1 + (K_{\text{EtOAc}}/K_{eq})(a_{\text{MeOAc}}a_{\text{EtOH}}/a_{\text{MeOH}}) + K'_{\text{MeOAc}}}$
ER-EtOAc-SR	$CH_3CH_2COOCH_3^* + CH_3OH \rightleftharpoons CH_3CH_2OH + CH_3COOCH_3^*$	$r = \frac{k_{\text{SR}} \kappa_{\text{EtOAc}} (a_{\text{MeOH}} a_{\text{EtOAc}} - (1/K_{eq}) a_{\text{MeOAc}} a_{\text{EtOH}})}{1 + \kappa'_{\text{EtOAc}} + \kappa'_{\text{MeOAc}}}$
ER-MeOAc	$CH_3COOCH_3^* \rightleftharpoons CH_3COOCH_3 + ^*$	$r = \frac{k_{\text{MeOAc}} K_{\text{eq}}((a_{\text{MeOH}a_{\text{EtOAc}}/a_{\text{EtOA}}) - (1/K_{eq})a_{\text{MeOAc}})}{1 + K'_{\text{EtOAc}} + K_{\text{MeOAc}} K_{eq}(a_{\text{MeOH}a_{\text{EtOAc}}/a_{\text{EtOA}})}$
ER mechanism with alcohol adsor	ption	
ER-MeOH	$CH_3COOH + * \rightleftharpoons CH_3COOH^*$	$r = \frac{k_{\text{MeOH}}(a_{\text{MeOH}} - (1/k_{eq})(a_{\text{MeOAc}}a_{\text{EtOH}}/a_{\text{EtOAc}}))}{1 + (K_{\text{MeOH}}/k_{eq})(a_{\text{MeOAc}}a_{\text{EtOH}}/a_{\text{EtOAc}}) + K'_{\text{EtOH}}}$
ER-MeOH-SR	$CH_3COOH^* + CH_3CH_2COOCH_3 \rightleftharpoons CH_3CH_2OH^* + CH_3COOCH_3$	$r = \frac{k_{\text{SR}}K_{\text{MeOH}}(a_{\text{MeOH}}a_{\text{EtOAc}} - (1/K_{\text{eq}})a_{\text{MeOAc}}a_{\text{EtOH}})}{1 + K'_{\text{MeOH}} + K'_{\text{EtOH}}}$
ER-EtOH	$CH_3CH_2OH^* ightarrow CH_3CH_2OH + ^*$	$r = \frac{k_{\text{EtOH}} K_{eq}((a_{\text{MeOH}} a_{\text{EtOAc}} / a_{\text{MeOAc}}) - (1/K_{eq}) a_{\text{EtOH}})}{1 + K'_{\text{MeOH}} + K_{\text{EtOH}} K_{eq}(a_{\text{MeOH}} a_{\text{EtOAc}} / a_{\text{MeOAc}})}$

of three elementary steps. The steps considered according to the rival mechanisms are summarized in Table 4. For the LH mechanisms, both reactants are adsorbed on a catalytically active site. Adsorbed ethyl acetate reacts with adsorbed methanol to form adsorbed methyl acetate and adsorbed ethanol. Methyl acetate and ethanol finally desorbs from the active sites.

For the ER mechanisms, ethyl acetate or methanol first adsorbs on a catalytically active site. Then the adsorbed reactant reacts with the other reactant from the bulk phase to form methyl acetate and ethanol. One of these products is adsorbed. In the third step, the adsorbed product, methyl acetate or ethanol, desorbs.

Each step in the LH and ER mechanism can be considered as potentially rate determining, leading to 11 rival expressions for the corresponding reaction rates, see Table 5. The concentrations of the surface species are obtained assuming quasi equilibration of the other elementary steps in the reaction mechanism. In combination with a balance over the active sites, analytical expressions are derived for the reaction rate equations as a function of the activities of the reaction components, the reaction rate coefficient and the adsorption and surface reaction equilibrium coefficients (Table 5).

4. Results and discussion

4.1. Experimental

4.1.1. Temperature effect

The temperature effect on the transesterification reaction rate was studied by conducting experiments between 303 and 333 K. In accordance with the Arrhenius law, a higher temperature results in a higher transesterification rate and a correspondingly higher ethyl acetate conversion at the same batch time, see Fig. 4. The final, equilibrium conversion is practically temperature independent, which is a logic consequence of the limited reaction enthalpy of the investigated transesterification reaction (not shown) [14].

4.1.2. Initial reactant molar ratio effect

The effect of the initial molar methanol to ethyl acetate ratio in the range of 1:1 to 10:1 is shown in Fig. 5. Higher initial molar ratios result in higher ethyl acetate conversions. Because the EtOAc/catalyst amount ratio was kept constant in these experiments, this also corresponds to higher reaction rates. Also, the equilibrium conversion increases with increasing initial reactant molar ratio, see Fig. 5 and Table 3. For lower MeOH:EtOAc ratios, longer batch times are needed to reach thermodynamic equilibrium.

4.2. Model discrimination

The model parameters of the rival models reported in Table 5 have been estimated by regression. Model discrimination is performed in order to determine the best performing model and, correspondingly, the most likely reaction mechanism, including the rate-determining step. Prior to regression and discrimination, initial parameter estimates have been determined.



Fig. 4. Simulated (lines) and experimental (symbols) conversion of ethyl acetate versus batch time at different temperatures (legend) (initial MeOH:EtOAc molar ratio = 1:1, simulation model = ER-MeOH-SR).



Fig. 5. Simulated (lines) and experimental (symbols) conversion of ethyl acetate versus batch time at different initial MeOH:EtOAc molar ratios (legend) (temperature = 333 K, simulation model = ER-MeOH-SR).

4.2.1. Initial parameter estimates

Values for the rate coefficient at each investigated temperature were estimated by isothermal regressions using the *PH* model, see Fig. 6. A linear regression of the obtained values to the Arrhenius relationship resulted in initial estimates of the activation energy E_A amounting to 50.3 kJ mol⁻¹ and of the rate coefficient at reference temperature of 328.38 K amounting to 2.62 × 10^{-6} m³ kg⁻¹_{cat} mol⁻¹ s⁻¹.

Initial values for the different adsorption equilibrium coefficients were taken from the literature and set equal to $0.1 \text{ m}^3 \text{ mol}^{-1}$ [28]. From initial regression efforts, it was clear that, in the rather narrow temperature range that has been investigated, the temperature dependence of the adsorption coefficients K_i would be practically impossible to estimate significantly. Hence, in an effort to reduce the number of adjustable parameters, the determination of adsorption coefficient values, K_i , has been limited to an average value over the investigated temperature range.

4.2.2. Performance evaluation between all rival models

The model regression and discrimination results are shown in Table 6. The obtained F values for the global significance of the



Fig. 6. Arrhenius diagram for the transesterification reaction of methanol and ethyl acetate using Lewatit K1221 catalyst (symbols obtained by isothermal regression with the *PH* model, line obtained by linear regression).

Table 6

Statistical evaluation of all models (1012 experimental points, experimental conditions as reported in Table 1).

Model	Number of statistically significantly estimated (total) parameters	RSSQ	F
ER-EtOAc/LH-EtOAc ^a	3 (4)/3 (6)	5	31,000
ER-MeOH-SR	4(4)	5	21,000
ER-EtOAc-SR	4(4)	7	15,000
PH	2(2)	8	41,000
ER-EtOH/LH-EtOH ^a	3 (4)/3 (6)	9	20,000
ER-MeOAc/LH-MeOAc ^a	3 (4)/3 (6)	9	18,000
ER-MeOH/LH-MeOH ^a	3 (4)/3 (6)	25	8000
LH-SR	4(6)	59	1000

^a Models have become mathematically equivalent because of the not statistically significantly estimated parameters

regression range from 1008 to 40,650. Typically, only one or two of the adsorption equilibrium coefficients could be estimated significantly different from zero. As a result, various ER and LH models, such as ER-EtOAc and LH-EtOAc, LH-EtOH and ER-EtOH, and ER-MeOH and LH-MeOH, became mathematically equivalent to each other.

The best performing models, i.e., those with the lowest residual sum of squares and the higher F value (31,000), correspond to an Eley-Rideal or a Langmuir-Hinshelwood mechanism with ethyl acetate adsorption as the rate-determining step (ER-EtOAc/LH-EtOAc). Model ER-MeOH-SR, corresponding to an Eley-Rideal mechanism with methanol adsorption and with the reaction of ethyl acetate from the bulk with adsorbed methanol on the catalyst surface as rate-determining step, has also a good performance in terms of the residual sum of squares. Because it contains an additional, significantly estimated parameter compared to the two previously discussed models, the corresponding F value is limited to about 20,000, however. Similarly, the ER-EtOAc-SR model has a lower F value for the global significance of the regression, and moreover, the corresponding residual sum of squares is about 50% higher than that obtained with the above discussed models. The PH-model has an even higher residual sum of squares, but because this model has only two adjustable parameters, it has the highest F value for the global significance of the regression. The next four models that still perform reasonably well, i.e., ER-EtOH/LH-EtOH, ER-MeOAc/LH-MeOAc, all contain 3 significantly estimated parameters and correspond to Eley-Rideal mechanisms with ethanol desorption (LH-EtOH is mathematically equivalent to ER-EtOH), resp. methyl acetate desorption as rate-determining steps (LH-MeOAc is mathematically equivalent to ER-MeOAc). However, the combination of (1) F values for the global significance of the regression below 20,000 and (2) RSSQ exceeding 8, is clearly inferior compared to the just described models. The likelihood ratios of these 4 models compared to the best performing models exceed 18 and, hence, they can be rejected with a probability of 90%. The other models, i.e., ER-MeOH/LH-MeOH, LH-SR, all have significantly higher residual sum of squares and corresponding F values below 10,000 and, hence, will not be further considered either.

Table 7

Statistical evaluation of the 4 best performing models (1282 experimental points, experimental conditions as reported in Table 1).

Model	Number of statistically significantly estimated (total) parameters	RSSQ	F
ER-MeOH-SR	4(4)	27	62,000
ER-EtOAc-SR	3 (4)	35	78,000
PH	2(2)	36	149,000
ER-EtOAc/LH-EtOAc ^a	3 (4)/3 (6)	48	47,000

^a Models have become mathematically equivalent because of the not statistically significantly estimated parameters

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Parameter estimates with their 95% confidence interval, obtain	ed by regression of 128	S2 experimental points (T_{ref} = 328.38 K).
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	ER-EtOAc/LH-EtOAc	ER-MeOH-SR	ER-EtOAc-SR	PH
$k_{T_{ref}} (10^{-3} \text{ m}^3 \text{ kg}_{cat}^{-1} \text{ mol}^{-1} \text{ s}^{-1})$	0.053 ± 0.002	0.259 ± 0.052	67.130 ± 0.719	0.003 ± 0.00003
E_A (kJ mol ⁻¹)	52.538 ± 1.542	50.190 ± 0.940	49.328 ± 0.995	49.405 ± 0.967
$K_{\rm EtOAc}(10^{-3} {\rm m}^3 {\rm mol}^{-1})$	2.643 ± 0.194	n.a. ^a	n.s.	n.a.
$K_{\rm EtOH}$ (10 ⁻³ m ³ mol ⁻¹)	n.a. ^a /n.s. ^b	0.233 ± 0.040	n.a.	n.a.
K_{MeOH} (10 ⁻³ m ³ mol ⁻¹)	n.a./n.s.	0.015 ± 0.004	n.a.	n.a.
$K_{\rm MeOAc} (10^{-3} {\rm m}^3 {\rm mol}^{-1})$	n.s./n.s.	n.a. ^a	0.052 ± 0.019	n.a.

^a not applicable

^b not significantly estimated

The physical meaning of the remaining models (ER-EtOAc/LH-EtOAc, ER-MeOH-SR, ER-EtOAc-SR and PH) is explained below.

ER-EtOAc corresponds to an Eley–Rideal mechanism with ethyl acetate adsorption as rate-determining step. Ethyl acetate adsorption is then followed by reaction with methanol from the bulk (Table 5). The 4 adjustable parameters in this model are the activation energy and the rate coefficient $k_{\text{EtOAcT}_{ref}}$ at the reference temperature, the adsorption equilibrium coefficient of respectively ethyl acetate and methyl acetate, K_{EtOAcT} and K_{MeOAc} . The first three model parameters are estimated statistically significantly different from zero, while the adsorption equilibrium coefficient of methyl acetate is not. The final rate expression, hence, becomes:

$$r = \frac{k_{\text{EtOAc}}(a_{\text{EtOAc}}a_{\text{MeOH}} - (1/K_{eq})(a_{\text{MeOAc}}a_{\text{EtOH}}/a_{\text{MeOH}}))}{1 + (K_{\text{EtOAc}}/K_{eq})(a_{\text{MeOAc}}a_{\text{EtOH}}/a_{\text{MeOH}})}$$
(17)

ER-MeOH-SR also corresponds to an Eley–Rideal mechanism but with the reaction of ethyl acetate from the bulk with adsorbed methanol on the catalyst surface as rate-determining step, see Table 5. The 4 model parameters are the activation energy and the rate coefficient k_{sr} at reference temperature, the adsorption equilibrium coefficients of respectively ethanol and methanol, K_{EtOH} and K_{MeOH} . All these model parameters are estimated significantly different from zero. The corresponding rate expression is given in Table 5.

ER-EtOAc-SR also corresponds to an Eley–Rideal mechanism with the reaction of adsorbed ethyl acetate with methanol from the bulk as rate-determining step (Table 5). The 4 model parameters are the activation energy and the rate coefficient k_{sr} at reference temperature, the adsorption equilibrium coefficients of respectively ethyl acetate and methyl acetate K_{EtOAc} and K_{MeOAc} and are all estimated significantly different from zero. The corresponding rate expression is given in Table 5.

The *PH* model does not take any adsorption into account. Ethyl acetate and methanol react from the bulk to form ethanol and methyl acetate in the bulk. The corresponding rate expression and the explanation of the parameters is given in Eq. (16) in Section 3.

4.2.3. Discrimination between best performing models using an experimental design

A D-optimum design of experiments has been performed aiming at a more precise parameter estimation in the remaining 4 rival models. This design is expected to simultaneously allow further model discrimination. It proposes experiments in the outer range of the operating conditions, in particular at a molar ratio of 1:1, a temperature of 303 K and a catalyst amount of 4.0×10^{-3} kg. These experiments were performed. Subsequently, regression has been performed for the rival models using the enlarged dataset. The statistical performance of the models is shown in Table 7, while the corresponding parameter estimates are reported in Table 8.

The obtained F values range from 62,000 to 149,000.

ER-MeOH-SR has the lowest residual sum of squares (27) with all four adjustable parameters being estimated significantly. With one parameter less, ER-EtOAc-SR has a higher *F* value but also a higher RSSQ (35). The *PH*-model only has 2 adjustable parameters, which are both estimated significantly. This results in the highest *F* value among the considered models, despite the RSSQ which is about one third bigger of the lowest RSSQ, obtained with ER-MeOH-SR. Due to the absence of any adsorption related terms in the PH-model, it cannot account for any surface coverage effects, however. ER-EtOAc/LH-EtOAc, with only 3 parameters that are estimated significantly different from zero, has an even higher RSSQ. Hence, this model is considered to describe the experimental data set not adequately.

The likelihood ratio of ER-MeOH-SR and ER-EtOAc-SR (Eq. (12)) is higher than 18, showing that there is a higher probability that the ER-MeOH-SR-model describes the data set better than the ER-EtOAc-SR-model.

Activation energies of about 50 kJ mol⁻¹ are obtained, irrespective of the model used. For a transesterification catalyzed with an acid ion-exchange resin similar results were published in literature [14,27–29], e.g., López et al. [28] found an activation energy of 48.5 kJ mol⁻¹ for the transesterification of triacetin to diacetin on a Nafion[®] SAC-13 ion exchange resin, which was comparable with that for H₂SO₄ (46.1 kJ mol⁻¹). An activation energy of 20 kJ mol⁻¹ was determined by Dossin et al. [3] for the transesterification of ethyl acetate with methanol on a base MgO catalyst.

The $k_{T_{ref}}$ at 328.38 K varies between 0.003×10^{-3} and 67.130×10^{-3} m³ kg_{cat}⁻¹ mol⁻¹ s⁻¹, depending on the model used. This value is similar to the one published by Bożek-Winkler and Gmehling [14] for the transesterification of methyl acetate and *n*-butanol catalyzed by Amberlyst 15.

The estimated values of the adsorption equilibrium coefficients for the transesterification with acid ion-exchange resins are quite similar with the published ones [14,28,29]. Based on the structural similarity and on the acid dissociation coefficient of MeOH and EtOH, which are rather close to each other, Dossin et al. [7] decided to estimate a single adsorption equilibrium coefficient for both alcohols. Results published by Bożek-Winkler and Gmehling [14] and Tesser et al. [2] indicate that the alcohol adsorption equilibrium coefficient values are indeed relatively close to each other, but that the one corresponding to methanol has the lowest value. The ratio of the adsorption coefficients as determined from the ER-MeOH-SR model amounts to 15. In particular the value obtained for K_{EtOH} significantly exceed the one reported in literature, i.e., $0.233 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ versus $0.0289 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ [14]. As a result, a refined version of this model has been tested, in which this ratio has been fixed to 2. The remaining 3 adjustable parameters have been determined by regression. With an RSSQ of 31 and an *F* value amounting to 80,000 with only 3 adjustable parameters, this refined version performs statistically better than the original ER-MeOH-SR model but is still inferior to the PH model. Hence, an ultimate model refinement consisted of fixing the adsorption coefficients for methanol and ethanol at their literature determined values, i.e., $0.0140 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ and $0.0289 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$, respectively [14]. With an RSSQ amounting to 36 and a corresponding F value of 142,000, this ultimate version of the ER-MeOH-SR model is statistically practically identical to the PH model.

Besides the statistical significance of the models, the models are also evaluated on their physicochemical significance. Sulfonic acid ion-exchange resins show a higher affinity for alcohols than for esters [14,18,30-33]. This indicates that methanol will adsorb more strongly than ethyl acetate, which is in line with the assumptions made in ER-MeOH-SR but in clear contrast with the assumptions made in ER-EtOAc/LH-EtOAc and ER-EtOAc-SR. These physicochemical considerations, combined with the higher RSSO of the latter models, see Table 8, lead to the elimination of ER-EtOAc/LH-EtOAc and ER-EtOAc-SR from the list of rival models. The PH-model lacks any adsorption effect. The good statistical performance of the PH-model, in terms of F value for the significance of the regression is an indication that the partial replacement of adsorbed methanol reactant by adsorbed ethanol product has only a limited effect on the simulated ethyl acetate concentration at the investigated operating conditions. Fixing the adsorption coefficient values K_{MeOH} , K_{FtOH} in ER-MeOH-SR at literature reported values, the corresponding F value and RSSQ of ER-MeOH-SR become comparable with the statistical results of the PH model. Hence, because of the additional physicochemical phenomena accounted for in the former model based on literature reported parameter values, ER-MeOH-SR is selected from the rival models as the most adequate model.

Fig. 7 shows the residual diagram of the experimental and calculated ethyl acetate concentration using ER-MeOH-SR. The diagram shows a good agreement between experimental and simulated values and is not indicative of any systematic deviation. The agreement between ER-MeOH-SR model calculations and the experimental data is also evident from Figs. 4 and 5.

4.3. Selected model assessment

4.3.1. Further considerations on the actual reaction mechanism

Homogeneous acid catalyzed transesterification has a mechanism that is equivalent to hydrolysis [5]. The mechanism, see Fig. 8, starts with the protonation of the carboxyl group of the ethyl



Fig. 7. Residual figure for the concentration of ethyl acetate for the complete set of 1282 data points. The simulated values are obtained using Eq. (16) with the estimated model parameters of ER-MeOH-SR (Table 8). Range of experimental conditions (Table 1).

acetate, step 1, followed by a nucleophilic attack of the methanol on this protonated ethyl acetate, step 2, yielding a tetrahedral intermediate. In step 3, the proton migrates from the reacting methanol oxygen atom to the product ethanol oxygen atom after which the tetrahedral intermediate decomposes into a protonated methyl acetate and ethanol, step 4. The fifth and last step in the reaction mechanism is the regeneration of the acid site [5,28,34–39].

According to the selected ER-MeOH-SR model, the transesterification mechanism on Lewatit K1221, would be clearly distinct from the mechanism presented in Fig. 8. Methanol should be adsorbed on the catalyst's active site with ethyl acetate reacting from the bulk, see Table 4 and Section 4.2.3, while, according to the homogeneously catalyzed mechanism, it should be ethyl acetate which is adsorbed, c.q., protonated on the acid sites with



Fig. 8. Homogeneous acid-catalyzed reaction mechanism for the transesterification of ethyl acetate with methanol.



Fig. 9. Heterogeneous acid ion-exchange resin catalyzed reaction mechanism for the transesterification of ethyl acetate with methanol.

methanol reacting from the bulk. This apparent contradiction can be explained by invoking a physical adsorption step in the mechanism, which is preceding any chemical elementary step on the acid sites. In this mechanism including reactant physical adsorption, both methanol and ethyl acetate are physisorbed in the pores of the resin. The physisorption of methanol being more pronounced than that of ethyl acetate, the physisorption of methanol is more likely to experience saturation effects, while that of ethyl acetate is situated in the Henry regime. Starting from these physically adsorbed reactants, the homogeneous acid catalyzed mechanism can occur within the resin's pores, i.e., ethyl acetate protonation followed by reaction with methanol. As a result, an overall rate equation for transesterification on Lewatit K1221 will require an adsorption term for methanol but not for ethyl acetate. if in addition to the physisorption in the Henry regime, also the chemisorption/protonation of ethyl acetate is not suffering from saturation effects. Given the pK_a values of methanol and ethyl acetate, i.e., 16 vs. 21, it is indeed the protonation of ethyl acetate, which is expected to be more pronounced than that of methanol.

The above considerations about the reaction mechanism are in agreement with the results obtained by López et al. [28]. These authors identified a methanol partial reaction order, which tends to zero at high methanol concentrations [40]. It indicates the importance of accounting for methanol adsorption in the reaction mechanism, even if methanol is unlikely to interact directly with the acid sites. As a result, Lopez et al. [28] ultimately derived a rate equation starting from a classical Eley–Rideal mechanism with ester adsorption on the active sites and reaction with methanol from the bulk that was extended with a methanol adsorption term $K_{MeOH}C_{MeOH}$. An adsorption term corresponding to the product ester was not included. The adsorption coefficients for methanol and the reacting ester, K_{MeOH} and K_{TG} , were small and similar. However, due to the significantly higher methanol concentration than ester concentration, only the methanol adsorption term was mathematically significant, as it is the case in the model developed as part of the present work.

The view on the acid catalyzed transesterification by ion exchange resins developed in this work also agrees with the interpretation by Alonso et al. [34]. Their principal peculiarities between heterogeneous and homogeneous mechanisms refer to the following two aspects: firstly, the activation of the carbonyl group of the ester comes with the chemisorption of the ester molecule on the Brønsted active site. The second aspect refers to the methanol involved in the reaction, which is the rate-determining step in the Eley–Rideal model. The methanol is not chemisorbed, although methanol can also be chemisorbed on the Brønsted acid sites, but the methanol is available in the liquid medium present in the pores of the solid catalyst [34] (Fig. 9).



Fig. 10. Calculated physisorbed fractions as a function of the batch time at 333 K, and with initial MeOH:EtOAc molar ratio = 10:1 and 1:1 (MeOH* and EtOH* physisorbed fractions of methanol and ethanol, respectively; (*) fraction of free physisorption sites).

4.3.2. Evolution of the physisorbed fractions in the catalyst pores

The evolution of the physisorbed methanol and ethanol fractions, i.e., θ_{MeOH^*} and θ_{EtOH^*} , as well as the fraction of free physisorption sites, θ_* , as a function of batch time at different experimental conditions has been calculated using the site balance and the quasi-equilibrium assumption for methanol and ethanol adsorption and are shown in Fig. 10:

$$1 = \theta_* + \theta_{\text{MeOH}^*} + \theta_{\text{EtOH}^*} \tag{20}$$

$$\theta_* = \frac{1}{1 + K_{\text{MeOH}} a_{\text{MeOH}} + K_{\text{EtOH}} a_{\text{EtOH}}}$$
(21)

$$\theta_{\text{MeOH}^*} = \frac{K_{\text{MeOH}} a_{\text{MeOH}}}{1 + K_{\text{MeOH}} a_{\text{MeOH}} + K_{\text{EtOH}} a_{\text{EtOH}}}$$
(22)

$$\theta_{\text{EtOH}*} = \frac{1 - K_{\text{MeOH}} a_{\text{MeOH}}}{1 + K_{\text{MeOH}} a_{\text{MeOH}} + K_{\text{EtOH}} a_{\text{EtOH}}}$$
(23)

At 333 K and an initial molar methanol to ethyl acetate ratio of 10:1, about 80% of the physisorption sites is free while 20% is occupied by methanol at the start of the experiment. Near completion of the experiment, the fraction of free sites is reduced to about 60%, while 25% is occupied by ethanol and 15% by methanol. The fraction of free physisorption sites on the catalyst decreases with increasing batch time, because ethanol physisorbs more strongly in the catalyst's pores than methanol. As a result, rather than saturation effects by methanol physisorption, some product inhibition effect will occur, because the product ethanol is occupying about one fourth of the available pore volume of the catalyst. At lower initial molar methanol to ethyl acetate ratios, this product inhibition effect will, accordingly, be more pronounced, because of the higher ester and, hence, product ethanol concentration. Given the dominance of the fraction of free sites, the above described inhibition effects are only having a moderate effect on the simulated reaction rates. This is in agreement with the model discrimination on a statistical basis, in which the PH model was considered equivalent to the ER-MeOH-SR model.

5. Conclusions

Acid catalyzed transesterification reactions occur via a mechanism involving ester protonation followed by reaction with the alcohol. The use of sulfonic acid ion-exchange resins such as Lewatit K1221, induces a physisorption step prior to the chemical elementary steps of the reaction mechanism. Because the physisorption of alcohols is more pronounced than that of esters, a model discrimination between a pseudo-homogeneous model and Langmuir–Hinshelwood and Eley–Rideal models with varying assumptions related to the rate-determining step and reactant and product adsorption, resulted in the selection of an Eley–Rideal mechanism considering methanol adsorption with subsequent reaction with ethyl acetate from the bulk as rate-determining step as the most adequate model. No adsorption term related to ethyl acetate protonation had to be incorporated, indicating that the resin's acid sites were mainly unoccupied at the investigated operating conditions.

The model discrimination as performed in this work demonstrates the need of an assessment of the physical significance of the model and the corresponding parameters. This can be achieved by comparison with literature reported information on the various elementary steps in the reaction mechanism. The combined information about the homogeneously acid catalyzed transesterification reaction mechanism and physical adsorption measurements of alcohols and esters on resins have allowed an advanced interpretation of the selected model based on typical discrimination activities.

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