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Qualitative treatment of catalytic hydrolysis of alkyl formates

Olatunde Jogunola[a,*], Tapio Salmi[a], Kari Eränen[a], J.-P. Mikkola[a,b]

[a] *Åbo Akademi, Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering, FI-20500 Åbo/Turku, Finland*
[b] *Umeå University, Technical Chemistry, Chemical-Biological Centre, Department of Chemistry, SE-90187 Umeå, Sweden*

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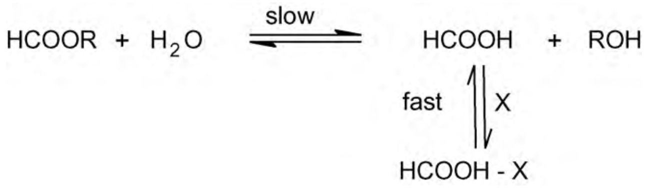
ABSTRACT

Liquid-phase hydrolysis of alkyl formates was performed in a stirred batch reactor using formic acid as a homogenous catalyst, cation exchange resin as heterogeneous catalyst and an additive as a complexation agent. The catalysts increased the rate of the reaction considerably, but the equilibrium conversion was slightly suppressed by the homogenous catalyst. The additive not only accelerated the reaction rate, but also improved the yield significantly. The effect of external and internal mass transfer limitations present in the heterogeneous reaction steps was investigated and it was observed that there is the existence of internal diffusion limitation for the largest catalyst particles. Other parameters such as temperature, catalyst pre-treatment, catalyst loading and stirring speed were investigated in order to optimize the process. The experiments also demonstrated that the ion exchange resin can be reused more than once.

1. Introduction

The hydrolysis of alkyl formates (particularly methyl formate, MeFo) has been of particular interest to the fine chemical industry because one of the products, formic acid (FA) has found a wide market in agricultural sector as silage additives [1]. Other major applications include leather tanning, textile dyeing and finishing, carpet printing, chemical synthesis and pharmaceuticals, food chemicals, formate salts, rubber chemicals (antiozonants and coagulants), catalysts, plasticizers, fuel cell (direct formic acid fuel cell), chemical pulping and regulation of pH in chemical processes [1–3]. Alkyl formates hydrolysis process is an endothermic reversible reaction with a low equilibrium constant (e.g. $K_C \leq 0.2$ for ethyl or methyl formate). The hydrolysis equilibrium is relatively unfavourable and thus excess water is required to shift the equilibrium towards the products. This leads to operational problems in terms of cost in removing the excess water and finding a cost effective corrosion-resistant material for process equipment. Other methods to improve the equilibrium conversion are the removal of the methanol product from the reaction system and the complexation of the acid product with an additive. The reaction involved in this complexation step is denoted as



where R = CH_3 or C_2H_5, X = additive and HCOOH–X = acid–additive complex

The additive is an organic base such as an imidazole derivative [4]. It shifts the equilibrium conversion towards the product as well as increases the reaction rate when added to the reaction mixture. It does not react with the reactants but forms a not too strong adduct with the carboxylic acid product so as to enhance the easy recovery of the acid and facilitate a more straightforward recycling of the organic base. Hence, with a stronger acid–additive complex, the acid will not be easily recovered, while a weaker adduct is incapable of shifting the equilibrium towards the product.

Furthermore, the alkyl formate hydrolysis reaction is slow at neutral pH but can be enhanced by an acid catalyst. A typical reaction involving the acid-catalyzed hydrolysis of alkyl formate is expressed as

$$\mathrm{HCOOR} + \mathrm{H_2O} \overset{\mathrm{H^+}}{\rightleftharpoons} \mathrm{HCOOH} + \mathrm{ROH}$$

Both homogenous and heterogeneous catalysts can be used to speed up the reaction rate. Typical homogenous catalysts include mineral acids such as H_2SO_4 [5] and HCl [6–8]. However, H_2SO_4 promotes the decomposition of the formic acid produced to car-

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Abbreviations: AMR, amberlite IR-120 resins; CX, adduct (complex formed between formic acid and additive); DVB, divinyl benzene; EFH, ethyl formate hydrolysis; MFH, methyl formate hydrolysis; EtFo (A), ethyl formate; EtOH (D), ethanol; FA (C), formic acid; FAC, formic acid-catalyzed; FID, flame ionization detector; GC, gas chromatograph; H_2O (B), water; MeFo (A), methyl formate; MeOH (D), methanol; meq, milliequivalent; NC, non-catalytic; PS, polystyrene; rpm, revolution per minute; TOF, turnover frequency; X, additive.

* Corresponding author. Tel.: +358 2 2154431; fax: +358 2 2154479.
E-mail address: jolatund@abo.fi (O. Jogunola).

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Nomenclature

a	shape factor
a_p	interfacial area-to-volume (m^{-1})
C	concentration (mol/kg)
D_i	molecular diffusion coefficient ($m^2 s^{-1}$)
D_{ei}	effective diffusion coefficient ($m^2 s^{-1}$)
d_p	particle diameter (mm)
E_a	activation energy of the formic acid-catalyzed reaction (kJ mol^{-1})
E_a^o	activation energy for the uncatalyzed reaction (kJ mol^{-1})
E_a'	activation energy for the autocatalytic reaction (kJ mol^{-1})
E_a''	activation energy for the additive-enhanced step (kJ mol^{-1})
Eq	activation parameter of the equilibrium constant
f	rate function
K_C	concentration-based equilibrium constant
k°	rate constant due to dissociation of B (kg $mol^{-1} min^{-1}$)
k	rate constant of the formic acid-catalyzed reaction ($kg^2 mol^{-2} min^{-1}$)
k'	rate constant of the autocatalytic reaction ($kg^2 mol^{-2} min^{-1}$)
k''	rate constant of the complexation step ($kg^2 mol^{-2} min^{-1}$)
M_B	molar mass of the solvent (kg mol^{-1})
N	flux (mol $m^{-2} s^{-1}$)
pH	power of hydrogen
R	gas constant (J $mol^{-1} K^{-1}$)
R_j	radius of the particle (mm)
r	reaction rate (mol $kg^{-1} min^{-1}$)
T	temperature (K)
t	time (min)
V	volume (cm^3)
V_A	molar volume of the solute ($m^3 mol^{-1}$)
X_A	equilibrium conversion
X	dimensionless coordinate
Y	frequency function for particle size distribution
x_j	ratio of particle radius to average radius
Greek letters	
α	stoichiometric ratio of the additive
β_{LS}	liquid–solid mass transfer coefficient (m s^{-1})
η	effectiveness factor
ε_p	porosity of the particle
θ	association factor of the solvent
τ_p	tortuosity of the particle
ρ_p	density of the particle (kg m^{-3})
μ_m	viscosity of the mixture (g $cm^{-1} s^{-1}$)
Subscripts and superscripts	
DR	dry resin
eqm	equilibrium
SR	swollen resin
0	initial value
i	component
j	particle size fraction

bon monoxide and water. Nevertheless, HCl has been reported to catalyze the reaction efficiently without decomposition. Another disadvantage of homogenous catalysts is their miscibility with the reaction medium, which might lead to separation and corrosion related problems. This can be overcome by the use of formic acid to catalyze its own reaction and there have been reports of such process in the chemical industry [9,10]. Furthermore, heterogeneous catalyst provides an attractive alternative to homogenous catalyst. The main advantage of a heterogeneous catalyst is that a catalyst-free product can be obtained simply by filtration, which is incorporated in the process.

Over the past few years, considerable research efforts have been devoted to the liquid-phase hydrolysis of esters (particularly alkyl acetates) using hydrophobic solid acid catalysts such as cation exchange resins, heteropolyacids, zeolites and zirconium phosphonates [11]. This is due to the fact that many inorganic solid acid catalysts are hydrophilic, thus limiting the accessibility of the organic substances to the acid sites. However, there are few reports on the catalytic hydrolysis of alkyl formates and some of these reports used catalysts such as activated charcoal [12,13] and ion exchange resins [14–16]. Ion exchange resins are highly ionic, covalently cross-linked, insoluble polyelectrolytes and a typical one is the PS-DVB resin, in which sulphonic acid is fixed to a polymer carrier such as polystyrene (PS) cross-linked with divinylbenzene (DVB). These solid resins as catalyst have a lot of advantages: the problems associated with separation and corrosion encountered in homogenous catalysts is eliminated and they can be used in continuous mode to achieve high product purity [11,17]. More so, the resins can discriminate between small and large molecules [18].

Most of the research work found in the open literature on hydrolysis of alkyl formates using activated charcoal and ion exchange resins have been performed in a chromatographic reactor [12,13,16,17]. This is due to the fact that alkyl formate hydrolysis is an equilibrium limited reaction and the properties of the heterogeneous catalysts as an adsorbent can be utilized in a chromatographic reactor to separate different components and achieve higher conversion of the alkyl formate. Thus, the reverse reaction is prevented and the reaction is shifted towards the products by removing the product components from the reaction mixture [13].

There have been very few reports in the literature concerning the study of alkyl formate hydrolysis using a heterogeneous catalyst in a stirred batch reactor. This might be due to the fact that in a batch reactor, the property of an ion exchange resin to separate the reaction products cannot be utilized. Therefore, no conversion greater than the equilibrium conversion, is possible. One representative report (Metwally et al. [19]) used cation resin for the hydrolysis of ethyl formate (EtFo). They reported the activation parameters for the resin-catalyzed ethyl formate hydrolysis in water–acetone mixture. Nevertheless, no detailed study has been published in the literature concerning the kinetics of alkyl formate (particularly methyl formate) resin-catalyzed hydrolysis in a stirred batch reactor. Furthermore, to the best of my knowledge, there has not yet been a report in the open literature concerning alkyl formate hydrolysis in the presence of formic acid catalyst or an additive.

In this work, we have studied the thermodynamics and kinetics of alkyl formate hydrolysis using formic acid and Amberlite IR-120 resin as acid catalysts, and an organic base as an additive in a stirred batch reactor. Furthermore, the three processes were compared qualitatively. Also, the mass transfer limitations using heterogeneous catalyst were investigated and the effect of other parameters such as catalyst pre-treatment, stirring speed, catalyst loading and temperatures on both kinetics and thermodynamics equilibrium were included in the study.

2. Experimental section

2.1. Experimental set-up, procedure and matrix

All experiments were carried out in a conventional 500 ml Parr autoclave made of zirconium metal. The reactor consists of feeding and reaction vessels, a heating unit, a sampling line and a stirrer.

Table 1
Experimental details.

	Heterogeneous catalyst C_{0A} (mol/kg)	Homogenous catalyst C_{0A} (mol/kg)	Organic base C_{0A} (mol/kg)
Methyl formate hydrolysis			
$[MeFo]_0$	10.49	9.91	4.42–7.94
$[H_2O]_0$	18.87	17.83	7.91–17.43
$[MeOH]_0$	0.94	1.03	0.46–0.82
$[FA]_0$		0.00–1.11	0.49–0.89
$[X]_0$			0.00–4.43
Catalyst loading	0.00–16.67 g/kg on dry basis		
Ethyl formate hydrolysis			
$[EtFo]_0$	9.04	8.64	4.15–8.64
$[EtOH]_0$	0.44	0.42	0.2–0.42
$[H_2O]_0$	16.28	15.56	7.47–15.90
$[FA]_0$		0.00–0.97	0.46–0.97
$[X]_0$			0.00–4.15
Catalyst loading	0.00–66.67 g/kg on dry basis		

The sampling line was equipped with a cooling bath and a filter. A precise temperature control required two thermocouples and cooling air. The reaction was performed at a nitrogen-pressure of 20 bar and isothermally at temperatures of 60 and 90 °C for heterogeneous catalyst (Amberlite IR-120 and Dowex 50Wx8), 80–110 °C for the homogenous catalyst (formic acid) and 80–110 °C for the additive-enhanced reaction, respectively. Distilled water with or without the catalyst was placed in the reaction vessel. In the case of the additive-enhanced reaction; distilled water, the additive ((Alfa Aesar, ≥98.87) and formic acid (Sigma–Aldrich, 99.5%) were placed in the vessel. Methanol (Baker, >99 wt.%) and methyl formate (Sigma–Aldrich, 97 wt.%) in the case of methyl formate hydrolysis (MFH) or ethanol (Altia, 99.5%) and ethyl formate (Sigma–Aldrich, 97 wt.%) in the case of ethyl formate hydrolysis (EFH) were discharged into feeding vessel with the aid of a dropping funnel. Nitrogen line to the reactor and the vent lines were connected to the system. The stirred reaction vessel was heated until it reached the desired temperature. The content in the feeding vessel was discharged into the reaction vessel as quickly as possible using nitrogen-pressure and the reaction commenced immediately. The initial total amount of the hydrolysis mixture was close to 0.3 kg, while a stirring rate of 300 rpm was used for all the experiments except the one involving the investigation of external mass transfer limitation in which 700 rpm was used instead. Table 1 shows the experimental matrix.

2.2. Gas chromatographic analysis

Samples were withdrawn at defined sampling intervals (5, 10, 15 or 20 min) using the reactor system internal pressure and were analyzed off-line with a gas chromatograph (GC): 6890N, injection port temperature 150 °C, oven temperature 150 °C, HP-PLOT U column, 250 m × 530 μm × 20 μm, carrier gas helium (15 ml/min at 1 min), detector FID (250 °C, H_2 flow 40 ml/min, air flow 450 ml/min). The calibration was performed using acetonitrile (Labscan, >99%) as an internal standard. The calibration of the internal standard solution was always done immediately before the analysis of any sample. The analysis time for a sample was between 6 and 11 min. The experimental results were based on alcohol analysis (methanol in case of MFH and ethanol in case of EFH) due to the volatility of methyl formate and the difficulty in getting a reliable analysis method for ethyl formate and formic acid.

2.3. Catalyst properties and characterization

The properties of the solid catalysts supplied as beads by the manufacturer are shown in Table 2. The particle diameter, d_p of Amberlite IR-120 is 0.3–1.2 mm, while Dowex 50Wx8 with a mesh of 50 (d_p = 0.3–0.84 mm); 100 (d_p = 0.15–0.3 mm); and 400 mesh (d_p = 0.04–0.08 mm).

The catalyst was pre-treated by washing with distilled water, decanted and then dried in an oven at 99 °C for 2 days until a constant mass was obtained. Our group has shown that the nature of the pre-treatment has no effect on the reaction kinetics [20]. After the hydrolysis reaction, the catalyst was washed with water and dried at 99 °C for subsequent reuse.

The swelling ability of the resin in different liquids was studied at 25 °C. About 1 g of the catalyst was placed in a bottle and 25 ml of the liquid was added to it. The mixture was shaken intermittently and allowed to settle overnight so that equilibrium would be reached. The liquid not absorbed was separated from the catalyst and the volume occupied by the catalyst was measured accordingly.

The acidic capacity was measured by a conventional titration method [21]. About 0.5 g of the resin was added to 50 ml of NaCl solution (200 g/l) and stirred. The system was allowed to stand for 1 day so that cation exchange between the H^+ and Na^+ could take place. The mixture was titrated with a 0.1 N NaOH solution.

3. Mathematical modelling

A reversible reaction similar to the hydrolysis of alkyl formate can be represented as

$$A + B \rightleftarrows C + D$$

where A = ethyl formate (EtFo) or methyl formate (MeFo), B = water, C = formic acid (FA) and D = ethanol (EtOH) or methanol (MeOH).

In the modelling, the system is considered as a pure liquid-phase. The vapourization of the components was surpassed by carrying out the reaction under pressure, so the role of the gas-phase, including the volatilization of the components can be ignored. The gas volume is quite small compared to the liquid volume in the reactor.

Table 2
Properties of the solid catalysts as given by the manufacturer.

Properties	Amberlite IR-120	Dowex 50Wx8-50, -100, -400 mesh
Bead type	Gel	Gel
Cross linking (%)	8	8
Particle size range (μm)	300–1200	Depend on the mesh
Moisture content (% mass)	45	54
Density of wet catalyst (g/cm^3)	1.26	–
Max. operating temperature (°C)	120	150
Capacity by dry weight (meq/g)	4.4	4.8

Max. = maximum.

The reaction rate in the absence of catalyst (neutral medium) is expressed as

$$r_i = f\left(C_AC_B - \frac{1}{K_C}C_CC_D\right) \tag{1}$$

where $f = k^\circ + k'C_C$

For the heterogeneous catalyst, during the course of study of the hydrolysis process, internal diffusion affected the kinetics. A mathematical model, which incorporates the particle size distribution of the solid catalyst, was developed to reveal the kinetics and internal mass transfer effects of the porous particles. The mass balance for the bulk phase is

$$\frac{\partial C_i}{\partial t} = a_p\sum_j y_jN_{ij}x^2 + r_i \tag{2}$$

The mass balance for the catalyst particles is

$$\frac{\partial C_{pi}}{\partial t} = r_i + \frac{\dot{r}_i\rho_p}{\varepsilon_p} + \frac{D_{ei}}{\varepsilon_pR_j^2}\left(\frac{\partial^2 C_{pi}}{\partial X^2} + \frac{a-1}{X}\frac{\partial C_{pi}}{\partial X}\right) \tag{3}$$

with the boundary conditions $C_{i(X=1)} = C_{pi}$ at the particle surface and $(\partial C_{pi}/\partial X)_{X=0} = 0$ at the centre of the particle. r_i is the reaction rate of the homogenous catalytic part of the system in mol min^{-1} m^{-3} and $\dot{r}_i$ is the reaction rate of the heterogeneous system in mol min^{-1} kg^{-1}.

The shape factor, a is 3 (sphere) for the resin. The effective diffusion coefficient is given as: $D_{ei} = \varepsilon_pD_i/\tau_p$. The diffusion coefficient, D_i can be calculated from Wilke–Chang equation

$$D_i = \frac{7.4\times10^{-12}\sqrt{\theta M_B}}{\mu_mV_A^{0.6}}$$

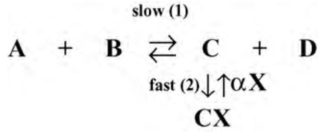
In the presence of formic acid catalyst, we assumed that the rate constant of the non-catalyzed reaction is negligible compared to the rate constant of the catalytic reaction. Thus, we have

$$r'_i = kC_{H^+}\left(C_AC_B - \frac{C_CC_D}{K_C}\right) \tag{4}$$

Since formic acid catalyzed its own reaction, $C_{H^+} = C_C$. It is important to note that C_C comprises the added acid and the acid generated due to autocatalysis. Thus Eq. (3) becomes

$$r'_i = kC_C\left(C_AC_B - \frac{C_CC_D}{K_C}\right) \tag{5}$$

For the additive-enhanced reaction, the reaction involved two steps: the slow uncatalyzed process and the fast complexation step. The reactions involved in the process are expressed as:



$$\begin{array}{c} \mathbf{A} + \mathbf{B} \overset{\text{slow (1)}}{\rightleftarrows} \mathbf{C} + \mathbf{D} \\ \text{fast (2)}\downarrow\uparrow\alpha\mathbf{X} \\ \mathbf{CX} \end{array}$$

where A = ethyl or methyl formate, B = water, C = formic acid, D = ethanol or methanol, X = additive and CX = acid–additive complex (adduct). The stoichiometric coefficient of the additive α is not unity.

The reaction rate for the alkyl formate hydrolysis in the presence of an additive can be expressed as

$$r''_i = f\left(C_AC_B - \frac{1}{K_C}C_CC_D\right) \tag{6}$$

where $f = k^\circ + k'C_C + k''C_X$

The hydrolysis reaction depends on temperature, thus Arrhenius equation can be used. The reaction rate in neutral medium (Eq. (1)) becomes:

$$r_i = k^oe^{-E_a^o/RT} + k'C_Ce^{-E'_a/RT}(C_AC_B - \frac{1}{K_C}C_CC_D) \tag{7}$$

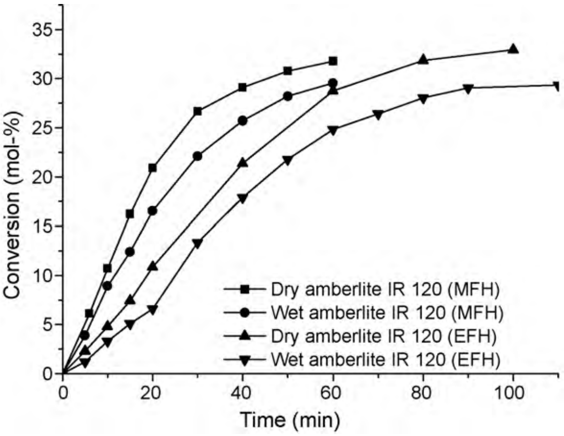


Fig. 1. The effect of the catalyst pre-treatment on the kinetics of alkyl formate hydrolysis at 60 °C; B/A molar ratio = 1.8.

Eq. (5) becomes:

$$r'_i = kC_Ce^{-E_a/RT}(C_AC_B - \frac{1}{K_C}C_CC_D) \tag{8}$$

The additive enhanced reaction rate Eq. (6) takes the form:

$$r''_i = k^oe^{-E_a^o/RT} + k'C_Ce^{-E'_a/RT} + k''C_Xe^{-E''_a/RT}(C_AC_B - \frac{1}{K_C}C_CC_D) \tag{9}$$

The temperature dependence of the equilibrium constant can be described as:

$$K_{eqi} = K_oe^{-Eq_i/RT} \tag{10}$$

4. Results and discussion

4.1. Catalyst characterization and properties

4.1.1. The effect of the pre-treatment

Often, dried catalysts are necessary for enhanced reactivity and conversion rates or if the addition of water is a problem. In our case, the aim of the pre-treatment was to remove water, corresponding to 45% of the total weight (see Table 2) of the wet Amberlite IR-120 resins. Therefore, the exact amount of water in the reaction system is known since water is one of the reactants. The pre-treatment of the resins modified its structure and increased its activity slightly because in the dry form, the diffusion properties of these resins are quite different from the wet type [20]. This is exemplified by the differences in kinetic experiments carried out with the dry and wet resins as shown in Fig. 1.

4.1.2. The swelling ratio of the resins

When polymer materials such as ion exchange resins come in contact with a liquid, they absorbed the liquid and swelled. The swelling kinetics is linked with the diffusion of liquids. The nature of the solvent determines the extent of swelling and the swelling degree decreases with the reduction in polarity of the solvent [22]. The resin was left in water overnight (24 h) for it to attain equilibrium. The extent to which Amberlite IR-120 resin swelled in pure solvents at 25 °C was investigated using the concept of swelling ratio:

$$\text{Swelling ratio} = \frac{\text{Volume of swollen resin at equilibrium}}{\text{Volume of dry resin}} = \frac{V_{SR}^{eqm}}{V_{DR}^0} \tag{11}$$

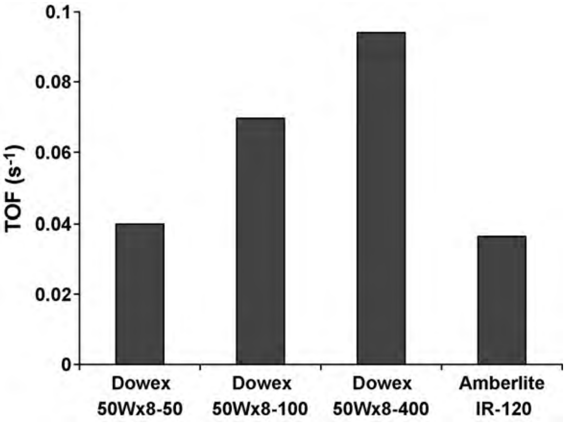


Fig. 2. The catalytic activity of different dry resins at 60 °C.

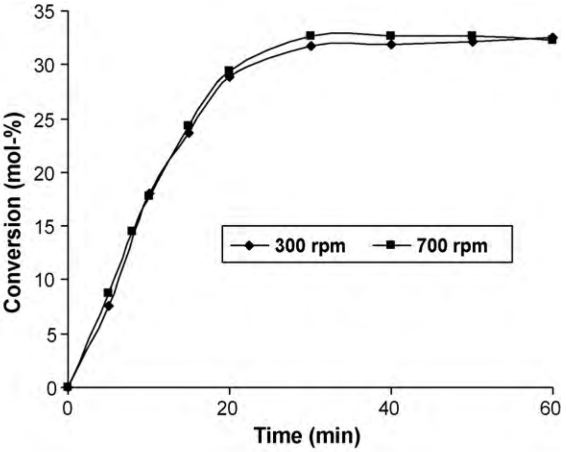


Fig. 3. The effect of external mass transfer around the catalyst particles at 60 °C; H_2O/MeFo molar ratio = 1.8.

The swelling ratio of the resin at 25 °C after equilibrium has been attained was found to be: H_2O 2.94; MeFo 1.66; EtFo 1.60; MeOH 2.33, EtOH 2.37 and FA 2.00. Water has the highest swelling ratio, while the two esters (MeFo and EtFo) have the lowest swelling ratio. The same sequence was obtained by Mai et al. [15]. Since water is one of the reactants, the swelling behaviour of the liquid mixture was assumed to follow that of water for the sake of simplicity.

4.1.3. The catalytic activity of different resins

The catalytic activity of 5 g Amberlite IR-120 resin on dry basis was compared with three different size ranges of the same amount of Dowex 50Wx8 at 60 °C using the concept of turnover frequency (TOF). Both catalysts are microporous cation exchange resins with the same percentage of cross-link.

$$\text{TOF} = \frac{\text{Initial rate of FA formation}}{\text{No. of Brønsted acid sites}}$$

The number of Brønsted acid sites was estimated based on the cation exchange capacity of the resin. The initial TOF for the different resins is displayed in Fig. 2.

It can be deduced that catalysts with the same particle size has almost the same initial reaction rate. For example, Amberlite IR-120 (d_p = 0.3–1.2 mm) has similar catalytic activity as Dowex 50Wx8-50 (d_p = 0.3–0.84 mm), even though their capacities according to the manufacturer is slightly different (see Table 2). However, Amberlite IR-120 was selected for further experimental matrix because of its affordability and wider particle size range. The exchange capacity of the resin on dry basis, determined by titration method was found to be 4.7 meq/g. This value was obtained as the average of three different measurements. This is different from the one obtained by the manufacturer (4.4 meq/g) because of experimental error and probably the non-ideality of the titration mixture. The apparent Brønsted acid concentration $[H]^+$ is calculated based on the cation exchange capacity by dry weight (meq/g):

$$[\text{H}]^+ = \frac{4.7 \times 10^{-3} \times \text{mass of catalyst}}{\text{Volume of solution}}$$

4.1.4. Mass transfer limitation effects (batch-mode)

4.1.4.1. The effect of stirring speed. Two experiments were performed at stirring speeds of 300 and 700 rpm, respectively in order to investigate the effect of agitation speed and external mass transfer on the overall reaction rate of methyl formate hydrolysis using 2.5 g of Amberlite IR-120 resin. The anticipated external mass transfer limitations were characterized by a liquid–solid mass transfer coefficient β_{LS}, which depends mainly on the diameter of the catalyst particle; thus Amberlite IR-120 with a larger particle size should offer stronger external mass transfer resistances. This is illustrated in Fig. 3.

In fact, we can conclude that no external mass transfer limitations were present in the case of the dry resin at the stirring speed range of 300–700 rpm (Fig. 3). Also, no attrition of the catalyst occurred under the chosen operating conditions. Therefore, 300 rpm was used for all additional experiments to avoid external mass transfer limitations and to suppress attrition. Also, a stirring speed of 300 rpm was enough for the hydrolysis of the two alkyl formates using a homogenous catalyst and an additive.

4.1.4.2. The effect of catalyst particle sizes. Kinetic experiments were carried out for 2.5 g of dry Dowex 50Wx8 using three different particle size ranges (d_p = 0.04–0.08, 0.15–0.3 and 0.3–0.84 mm) in order to ascertain the influence of the internal mass transfer limitation. The effect of the particle size on hydrolysis of methyl formate is presented in Fig. 4.

The observed difference in the reaction rate under identical experimental conditions was due to the internal diffusion present inside the catalyst particles, provided that the concentration of the acid sites does not depend on the particle size. It was assumed that accessibility of these sites do not depend on the particle size since the resin swelled well in water before the reaction commenced. Thus, the smallest beads (d_p = 0.04–0.08 mm) exhibited the fastest rate at 60 °C. Assuming these particles have the limiting rate (without internal diffusion limitation); the effectiveness factor η can be estimated as

$$\eta = \frac{\text{Observed rate of MeFo disappearance}}{\text{Rate in the absence of internal diffusion}}$$

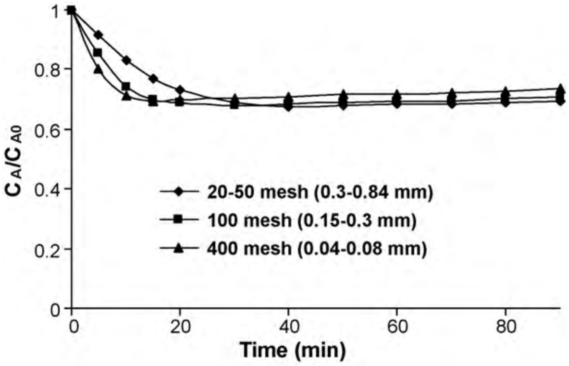


Fig. 4. The effect of internal diffusion inside the catalyst particles at 60 °C; H_2O/MeFo molar ratio = 1.8.

Table 3
Effectiveness factor for different size ranges.

Particle size (mm)	η	
	$t = 0$ min	$t = 15$ min
0.04–0.08	1.00	1.00
0.15–0.3	0.75	0.98
0.3–0.84	0.43	0.75

$$\eta = \frac{(dC_A/dt)_{\text{particle-size in question}}}{(dC_A/dt)_{d_p=0.04-0.08\,\text{mm}}} \tag{12}$$

From Eq. (12), one can estimate the effectiveness factor for the particle size ranges in question. This is presented in Table 3.

Thus, one can deduce that internal diffusion limitation effects were significant in these particles. The internal mass transfer affected the observed overall reaction rates at the beginning of the reaction and the effect diminished as the equilibrium is approached (see Fig. 4). The same is true for Amberlite IR-120 resin (d_p = 0.3–1.2 mm) too.

4.1.5. The effect of catalyst loading

The amount of catalyst was varied over a range of 1.67–66.67 g of dry catalyst per kg of the solution, while keeping other parameters constant in order to determine the effect of catalyst loading on the hydrolysis kinetics. The procedure was applied for both ethyl and methyl formates. The results are shown in Fig. 5.

It can be observed that the initial reaction rate is linearly increasing with the catalyst loading for both ethyl formate and methyl formate hydrolyses, since the active site, the sulphonic acid groups ($-SO_3H$) are directly proportional to the amount of catalyst present in the solution. Thus, more suphonic acid group is readily available as the amount of catalyst increases, which leads to the formation of larger amount of carbonium ions per unit time. This in turn, increases the reaction rate. However, the reaction rate curve of MFH is not as perfectly linear as that of EFH.

4.1.6. Catalyst reuse

The main obstacle encountered in the study of catalyst deactivation was the repeatability of the experimental conditions. The main goal of this study was to determine whether the resin can be used more than once without a significant decrease in activity. The apparent Brønsted acid concentration $[H^+]$ was calculated based on the dry weight capacity (meq/g) of the catalyst, given by the manufacturer and this capacity was assumed to remain constant from batch-to-batch. The catalyst deactivation was investigated using 2.5 g of Amberlite IR-120 four times consecutively at 60 °C under the same reaction conditions. After each run, the catalyst was washed with water and dried at 99 °C for almost 48 h until a constant mass is obtained. The result is depicted in Fig. 6.

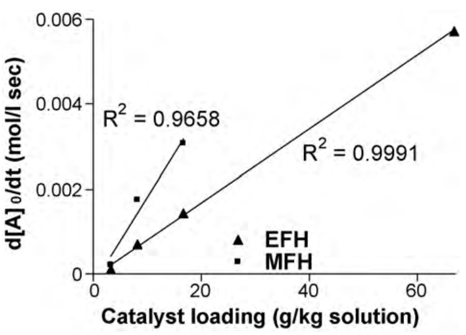


Fig. 5. The effect of catalyst loading on alkyl formates hydrolysis at 60 °C; B/A molar ratio = 1.8.

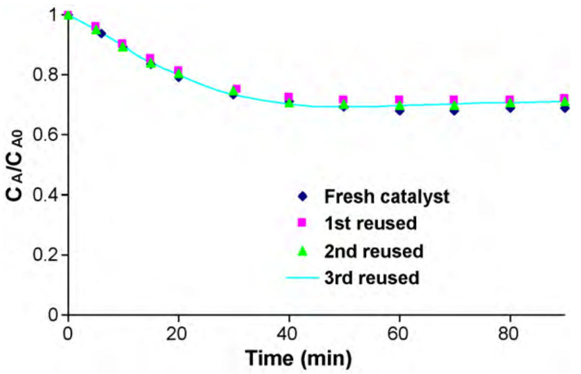


Fig. 6. Deactivation studies of Methyl formate hydrolysis over Amberlite IR-120 at 60 °C; H_2O/MeFo molar ratio = 1.8.

It can be concluded that the deterioration of the catalyst activity was negligible after three batches since the conversion curves are practically overlapping one another. All curves in Fig. 6 are the same, within experimental accuracy. Similar results have been reported by Altiokka and Çitak [23] for Amberlite IR-120 during the esterification of acetic acid with isobutanol. So, the resin may be used repeatedly since the capacity of the catalyst remains virtually the same. Indeed, that the catalyst can be used repeatedly is one of the most important prerequisites for green chemistry.

4.2. Qualitative analysis of reaction rate and chemical equilibrium

4.2.1. The effect of water on equilibrium conversion

The presence of excess water in alkyl formate hydrolysis improves formic acid yield in the absence of any additive. This is also true in the presence of a suitable additive. The purpose of this study is to find the optimum molar ratio of water that will be needed to give a reasonable conversion. The molar ratio of water-to-ester was varied from 1.0 to 3.0 at 90 °C, while additive-to-ester molar ratio was kept constant at 0.40. The value of the equilibrium conversion was obtained by taking the average of the experimental conversions when the reaction had attained chemical equilibrium. The increment is the difference between the succeeding and preceding values of the equilibrium conversions. The result is shown in Table 4 for both methyl formate and ethyl formate hydrolyses.

It can be deduced that the equilibrium conversion increases as the amount of water increases in the presence of the additive. However, the increment increases initially but decreases as more water is added to the system. Therefore, it is not economically viable to increase the amount of water just to get a minor change in the conversion. So, there should be a point of process optimization in terms of capacity and energy requirement in water removal. From Table 4, the optimum water-to-ester molar ratio is between 1.5 and 2.0. It can be concluded that less excess water is needed in the hydrolysis

Table 4
The effect of excess water on equilibrium conversion at 90 °C.

H_2O/ester molar ratio	Equilibrium conversion (mol%)		Increment	
	MeFo	EtFo	MeFo	EtFo
1.00	–	0.51	–	–
1.50	0.56	0.56	–	0.05
2.00	0.64	0.62	0.08	0.06
2.50	0.68	0.64	0.04	0.02
3.00	0.70	0.65	0.02	0.01

Table 5
The effect of the initial FA charge on equilibrium composition and conversion.

Temperature (°C)	C_{0A} (mol/kg)	Equilibrium concentration (mol/kg) $[FA]_0 = 0.0$ mol/kg					C_{0A} (mol/kg)	Equilibrium composition (mol/kg) $[FA]_0 = 1.11$ mol/kg				
		MeFo	H_2O	FA	MeOH	X_A		MeFo	H_2O	FA	MeOH	X_A
90	10.49	6.853	15.237	3.637	4.577	.347	9.907	6.882	14.808	4.135	4.053	.305
100	10.49	6.760	15.147	3.727	4.667	.355	9.907	6.859	14.785	4.158	4.076	.308
110	10.49	6.843	15.067	3.807	4.750	.363	9.907	6.840	14.766	4.177	4.093	.31
Temperature (°C)	C_{0A} (mol/kg)	Equilibrium concentration (mol/kg) FA = 0.0 mol/kg					C_{0A} (mol/kg)	Equilibrium composition (mol/kg) FA = 1.11 mol/kg				
		EtFo	H_2O	FA	EtOH	X_A		EtFo	H_2O	FA	EtOH	X_A
90	9.043	5.653	12.892	3.391	3.828	.375	8.643	5.900	12.813	3.707	3.159	.317
100	9.043	5.613	12.853	3.430	3.865	.379	8.643	5.851	12.764	3.757	3.208	.323
110	9.043	5.583	12.822	3.460	3.895	.383	8.643	5.818	12.731	3.789	3.241	.327

A = MeFo or EtFo; X = conversion.

of alkyl formate in the presence of an additive in order to achieve a reasonable conversion.

4.2.2. *The effect of the additive or formic acid catalyst on the equilibrium composition and reaction rate*

The effect of the FA-catalyzed hydrolysis reaction on the chemical equilibrium was investigated by maintaining the molar ratio of water-to-ester constant at 1.8, while the molar ratio of acid-to-ester is 0.0 for the neutral aqueous solution hydrolysis (uncatalyzed reaction) and 0.1 for the acid-catalyzed reaction. The results at three different temperatures can be seen in Table 5.

It was observed that the initial FA charge acting as a catalyst decreased the equilibrium conversion slightly for both ethyl formate and methyl formate hydrolysis. For methyl formate hydrolysis at 90 °C, the equilibrium conversion decreased from 34.7 to 30.5%. This is due to the presence of more formic acid as catalyst and product in the reaction solution and this accumulation of the acid favours the backward reaction. Therefore, it is imperative to use moderate amount of formic acid as catalyst in the system in order not to reduce its yield drastically.

In the case of the additive-enhanced hydrolysis process, the additive-to-ester molar ratio was varied from 0.0 to 1.0, while the others parameters were kept constant. The results for ethyl formate hydrolysis are depicted in Fig. 7.

The equilibrium conversion increases as the amount of the additive in the mixture increases. The additive forms a complex with formic acid by removing the free acid as it is being formed, thus preventing the backward reaction (re-esterification of the acid). However, it is not economically viable to increase the amount of additive without getting an appreciable increase in the equilibrium conversion, since its increment decreases as the molar ratio of X/ester increases. Therefore, there should be an optimum amount of X in the system for an efficient process. This could be between the additive-to-ester molar ratios of 0.40–0.60.

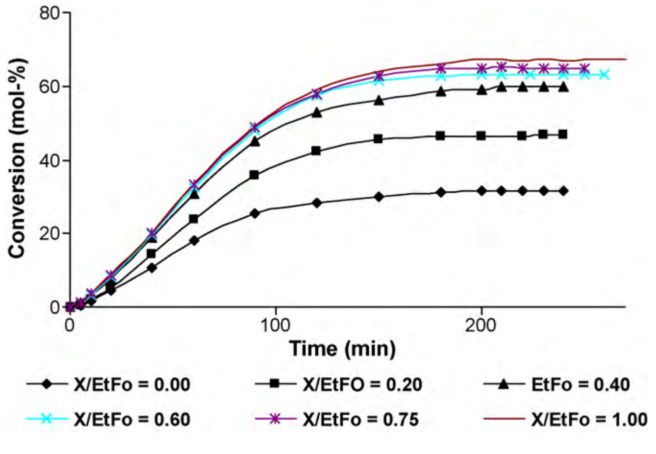


Fig. 7. The effect of the additive on equilibrium conversion and reaction rate at 90 °C; H_2O/EtFo molar ratio = 1.8.

Also, the reaction rate increases as the amount of the additive increases (see Fig. 7) especially when the molar ratio, X/EtFo = 0.2 and 0.4 compared to when there was no additive (X/EtFo = 0.0). The difference in kinetics is relatively small at the initial stage of the reaction, but becomes prominent as the reaction proceeds towards chemical equilibrium. At the initial stage of the reaction, less FA is formed and the reaction is slow. But, as the reaction progresses, more H^+ accumulate and it is being taken up as quickly as possible by X. Thus, the frequency of reactants collision increases and the reaction rate increases. The noticeable difference between the two reaction rates as the reaction progresses might be due to the fact that at X/EtFo = 0.2, there might be some free (uncaptured) formic acid left in the mixture due to the unavailability of enough X to complex the acid product in the mixture. However, as more X is added (X/EtFo = 0.4), the percentage of formic acid left unattached to the additive reduced drastically.

Furthermore, as more additive is added to the system (i.e. when X/EtFo = 0.60, 0.75 and 1.0), there is no appreciable increase in the reaction rate since the curves have almost the same gradient. This can be attributed to the fact that there is no more free formic acid left to be captured by the additive in the reaction mixture. The same effect is observed in methyl formate hydrolysis.

4.2.3. *The effect of temperature*

The influence of temperatures was investigated by performing experiments under the same reaction conditions (e.g. water-to-ester ratio of 1.8) but at temperatures of 60 and 90 °C in the case of the heterogeneous catalyst and 80–110 °C for the formic acid-catalyzed (FAC) reaction. 1.11 mol of FA/kg of solution and 0.1 mol SO_3H^+/kg solution were used as catalysts, respectively. As expected, the rate of reaction increases as temperature increases for both methyl formate and ethyl formate hydrolyses. Some of the results for the purpose of clarity are illustrated in Fig. 8 for the homogenous and heterogeneous catalysts.

Methyl formate hydrolysis was found to be faster than ethyl formate hydrolysis under similar reaction conditions for both homogenous and heterogenous catalysts. This is due to steric effects present in ethyl formate. In acid-catalyzed hydrolysis, the susceptibility of the reaction to polar effects is very low and the relative rates are determined by steric factors only [24]. There is the presence of steric hindrance in the intermolecular motion of ethyl formate hydrolysis.

Also, an increase in the temperature enhances the reaction rate of the additive-enhanced process for alkyl formate hydrolysis. This is displaced in Fig. 9 for methyl formate hydrolysis.

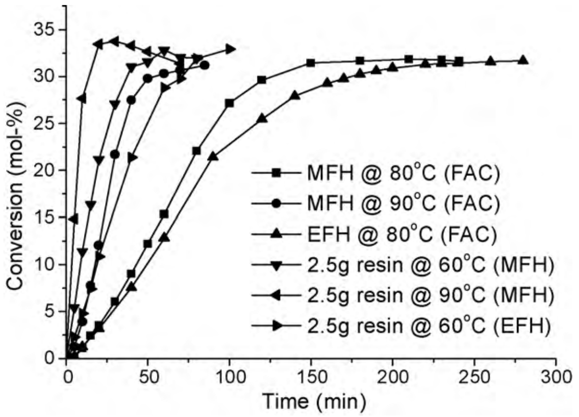


Fig. 8. The effect of temperatures on the kinetics of alkyl formate hydrolysis for acid-catalyzed reaction; B/A molar ratio = 1.8.

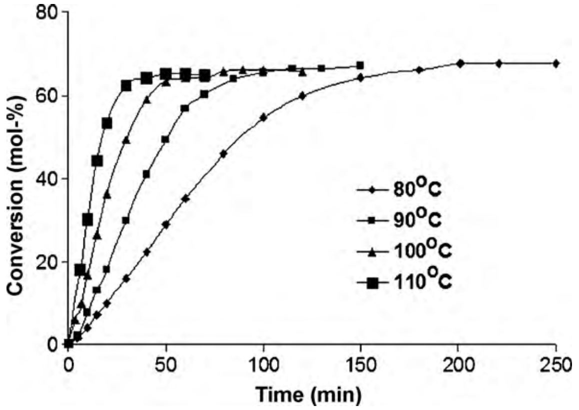


Fig. 9. The effect of temperature on kinetics of methyl formate hydrolysis in the presence of the additive; X/MeFo molar ratio = 0.6; H_2O/MeFo molar ratio = 1.8.

At higher temperature (e.g. 110 °C), there is more energy in the system and this results in earlier accumulation of H^+, which is taken up by X as fast as it is being formed and this leads to more reactants particle collisions. However, these reactions cannot be performed at a very high temperature because it favoured the decomposition of FA. Furthermore, it can be deduced from Fig. 9 that temperature has no effect on equilibrium conversion since alkyl formate hydrolysis has weak temperature dependence.

The pH of the hydrolysis process at 90 °C in the presence of the additive, formic acid and Amberlite IR-120 resin (AMR) was monitored during the course of the reaction. As expected, the pH decreases as formic acid is formed and remains virtually constant at equilibrium. This is shown in Table 6 for both methyl formate hydrolysis (MFH) and ethyl formate hydrolysis (EFH) under similar reaction conditions.

The pH of the homogenous catalyst was as measured about 0.33 and 0.37 units lower than that of the heterogeneous catalyst for MFH and EFH, respectively at the end of the reaction. Also, the additive-enhanced hydrolysis process took place under acidic conditions.

Table 6
pH of the hydrolysis processes.

Catalyst type	MFH		EFH	
	$t = 0$	$t = t_{eqm}$	$t = 0$	$t = t_{eqm}$
FAC	1.87	0.96	1.66	0.87
AMR	4.26	1.29	3.65	1.24
X	6.64	5.20	6.46	4.80

AMR = Amberlite IR-120 resin; FAC = formic acid-catalyzed reaction; X = additive. 0 = initial; eqm = equilibrium.

4.2.4. *The effect of the additive or catalysts on initial rate and equilibrium time*

Nevertheless, it is difficult to compare formic acid as a catalyst with Amberlite IR-120 resins since their intrinsic acidities are at different levels. Sulphonic acid is a much stronger acid than its corresponding carboxylic acid. Arbitrarily, for the purpose of this work, we consider the optimum molar ratios of acid-to-ester of 0.1 (0.33 mol H^+) and water-to-ester of 1.8 at 80–110 °C, which enhances the reaction rate without drastically affecting the formic acid yield for the homogenous catalyst. For the heterogeneous catalyst, we use 2.5 g (0.031 mol SO_3H^+) of Amberlite resins with the same water-to-ester ratio at 60 and 90 °C but without initial FA charge. In case of the additive-enhanced reaction, we consider the following optimum amount: X/MeFo of 0.6 (1.02 mol X/kg), FA/MeFo of 0.1 with the same water-to-ester ratio at 80–110 °C. This was done for the purpose of comparison (see Table 1). All other experimental conditions remain unchanged. The results of the initial reaction rate r_i^0 per mole of H^+, SO_3H^+ or X are presented in Table 7.

From Table 7, we can observe that the reaction rate was quite slow in the absence of the catalyst especially at the lowest temperature (60 °C) and increased significantly as expected when catalyst was added to the system. Also, the time required to attain chemical equilibrium reduced drastically from 8 h for the non-catalytic reaction to an hour for the resin-catalyzed reaction. At higher temperature (e.g. 90 °C), the hydrolysis rate was faster for the Amberlite-catalyzed reaction compared to the formic acid-catalyzed reaction and additive-enhanced system. In addition, the time needed to attain equilibrium reduced significantly especially for the resin-catalyzed reaction. Therefore, with the solid catalyst, one has the luxury of saving time and operating at milder reaction conditions (e.g. lower reaction temperature), which leads to a reduction in energy cost.

However, there is the problem of formic acid separation from water in the two catalytic processes because formic acid formed an azeotropic mixture with water. And separation cannot be effected by simple distillation. This problem is overcome by the use of the additive X, since formic acid binds weakly to the additive and the acid can be recovered and the additive recycled by simple distillation.

Table 7
The effect of the additive or catalysts on the initial reaction rate and the equilibrium time for MFH.

Temperature (°C)	r_i^0 (10^{-2} mol/kg min)				Time to reach equilibrium (min)			
	r_i^0/mol H^+	r_i^0/mol SO_3H^+	r_i^0/mol X	r_i^0 NC	FAC	AMR	X	NC
60	–	369.4	–	0.10	–	60	–	480
80	7.21	–	1.88	0.27	150	–	190	200
90	11.72	1008	2.29	0.53	70	25	100	120
100	19.22	–	8.05	1.50	50		70	80
110	34.45	–	16.88	4.33	40		50	55

NC = non-catalytic reaction; AMR = Amberlite IR-120 resin; FAC = formic acid-catalyzed reaction; X = additive.

5. Conclusions

The hydrolysis of alkyl formate was studied using formic acid as the homogenous catalyst, Amberlite IR-120 resin as the heterogeneous catalyst and an additive as the complexation agent and the three systems were compared arbitrarily under the same experimental conditions. Both catalysts and the additive improved the reaction rate significantly and reduced the time required to reach the equilibrium. The equilibrium conversion remains unchanged in the case of the heterogeneous catalyst but it was slightly reduced when formic acid was used as the catalyst. However, the equilibrium conversion improved significantly when the hydrolysis reaction was carried out in the presence of the additive. Furthermore, the need for the separation of the formic acid product from water is eliminated if the additive is used instead of the catalysts. Nevertheless, the three hydrolysis processes took place in an acidic medium.

Also, the catalytic activity of Amberlite IR-120 resins was compared with different size ranges of Dowex 50Wx8 with the same percentage of cross link and it was observed that Dowex 50Wx8-50 has almost the same activity as Amberlite IR-120. In addition, there was the presence of internal mass transfer limitation for the larger catalyst particles of Amberlite IR-120 resins and it was found that the resins can be reused more than once without any significant reduction in its activity. Thus, the cost of the resins per product kilogram is significantly reduced. Furthermore, a reduction in the energy cost was noticeable by operating at a lower temperature with more catalyst.

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References

[1] Kirk-Othmer Encyclopaedia of Chemical Technology, vol. 11, John Wiley & Sons, New York, 1993, pp. 951–959.

[2] Ullmann's Encyclopaedia of Industrial Chemistry, vol. 15, Wiley-VCH, Weinhein, 2003, pp. 49–70.

[3] A. Aguilo, T. Horlenko, Hydrocarb. Process 59 (1980) 120–130.

[4] H. Hohenschutz, J.E. Schmidt, H. Kiefer, EP 1432 (1978), to BASF (translated from German to English).

[5] J.F. Eversole, US Patent 2,160,064 (1939), to Carbide and Carbon Chemicals.

[6] F.A. Long, M.A. Paul, Chem. Rev. 57 (1957) 946–950.

[7] R.P. Bell, A.L. Dowding, J.A. Noble, J. Am. Soc. 9 (1955) 3106–3110.

[8] W. Newling, C. Hinshekwood, J. Chem. Soc. (1936) 1357–1361.

[9] J.D Leonard, EP 5998 (1979).

[10] J.B. Lynn, O.A. Homberg, A.H. Singleton, US Patent 3,907,884 (1975), to Bethlehem Steel Corp.

[11] Y. Izumi, Catal. Today 33 (1997) 371–409.

[12] B.K. Cho, W.R. Carr, R. Aris, Chem. Eng. Sci. 35 (1980) 74–81.

[13] R. Wetherold, E. Wissler, K. Bischoff, Adv. Chem. Ser. 133 (1974) 181–190.

[14] K. Saari, E. Tirronen, A. Vuori, M. Lahtinen, US Patent 6,429,333 B1 (2002), to Kemira Chemicals Oy.

[15] P.T. Mai, T.D. Vu, K.X. Mai, A. Seidel-Morgenstern, Ind. Eng. Chem. Res. 43 (2004) 4691–4702.

[16] C.W. Davies, G.G. Thomas, J. Chem. Soc. (1952) 1607–1610.

[17] T. Falk, A. Seidel-Morgenstern, Chem. Eng. Sci. 57 (2002) 1599–1606.

[18] R. Roy, J. Bhatia, J. Chem. Tech. Biotechnol. 37 (1987) 1–10.

[19] M.S. Metwally, A. Abel Razik, M.F. El Hadi, M.A. El-wardany, React. Kinet. Catal. Lett. 49 (1) (1993) 151–159.

[20] S. Leveneur, J. Wärnå, T. Salmi, D. Murzin, L. Estel, Chem. Eng. Sci. 64 (2009) 4101–4114.

[21] Z.P. Xu, K.T. Chuang, Chem. Eng. Sci. 52 (1997) 3011–3017.

[22] A.A. Zagorodini, Ion Exchange Materials Properties and Application, Elsevier, Amsterdam, 2007.

[23] M.R. Altiokka, A. Çitak, Appl. Catal. A: Gen. 239 (2003) 141–148.

[24] K.J. Laidler, Chemical Kinetics, Harper & Row, New York, 1987.