

9 Abstract

10 The current research article addresses the ability of heterogeneous Amberlyst 16 to catalyze
11 the esterification reaction between acetic acid and ethanol, as well as the modelling of the chemical
12 kinetics. The effects of pretreatment, reaction temperature, ethanol-to-acid molar ratio, catalyst
13 dose and time on the rate of ethyl acetate production were systematically investigated.
14 Furthermore, the recyclability of Amberlyst 16 to accelerate the esterification reaction was
15 carefully examined. Amberlyst 16 was found to be a suitable catalyst for this process giving a final
16 conversion of 93.3 % using reaction temperature of 60 °C, ethanol-to-acid molar ratio of 6:1,
17 catalyst dose of 10 wt. % and 200 rpm stirring intensity after 1680 min, and can be successfully
18 utilized for 4 recycle tests. A detailed kinetic model has been developed and tested for the
19 described process, which was based on a four-step mechanism equivalent to the Langmuir-
20 Hinshelwood one. It was found that that the esterification reaction occurred between ethoxide ions
21 and acetic acid chemisorbed on the neighboring catalytic surfaces, whereas, the overall process
22 was controlled by the surface reaction step.

23

24

25 **Keywords:** Acetic acid; Amberlyst 16; Esterification; Ethyl acetate; Kinetic modeling.

26

27 1. Introduction

28 Carboxylic acid esters are commercially important fine chemicals that have a wide range
29 of applications. Ethyl acetate finds its high relevance as biodiesel and an intermediate in food,
30 paints, coatings, inks and adhesives industries [1, 2]. The demand for ethyl acetate was augmented
31 by more than 80 % from 2004 to 2011. The global ethyl acetate production in 2012 has been
32 recognized to be 3.12 million tonnes. China is the dominant producer of ethyl acetate followed by
33 India, United Kingdom, Japan and Brazil. These five nations together produced over 2.57 million
34 tonnes of ethyl acetate in the year 2012 [3, 4]. Its increasing utilization is in favor with the
35 ecosystem by minimizing the usage of aromatic compounds such as, toluene that has hazardous
36 effects on the environment and human health [5]. There are several routes tested for both
37 laboratory- and industrial-scale production of ethyl acetate [6]. One of the possible methodologies
38 for the synthesis of this valuable chemical is the esterification process between acetic acid and
39 ethanol. The acetic acid esterification process is valuable also in upgrading of pyrolysis bio-oils.
40 The removal acetic acid impurities is reported to improve bio-oil stability [7, 8]. Esterification is
41 a single-step reaction in which an acid molecule reacts with a molecule of alcohol to yield a single
42 molecule of both esters and water [8]. In general, a catalytic material is utilized to accelerate the
43 rate of ethyl acetate production. The rate of the acid-catalyzed esterification reaction is faster than
44 that of the non-catalytic process because the acid catalyst functions as a proton donor for the
45 protolysis of the carboxylic acid [8, 9]. The available literature suggests the use of either inorganic
46 mineral acids such as, sulfuric acid, hydrochloric acid, or organic acids such as, *p*-toluene sulfonic
47 acid to catalyze the esterification processes [8-13]. Although the ability of homogeneous catalysts
48 to promote the generation of reaction products using mild operating parameters have resulted in
49 their widespread utilization, they generally are miscible in the reaction mixture; and therefore, are

50 difficult to be removed and recycled. Moreover, use of homogeneous acid catalysts might also
51 evolve human safety and corrosion of equipment related concerns. For these reasons, there has
52 been reducing interest for homogeneous catalysts in the chemical industries. The technical hurdles
53 related to the use of homogeneous catalysts is anticipated to be minimized by its replacement with
54 a heterogeneous catalytic system. Consequently, serious scientific efforts are engaged in finding
55 active and stable heterogeneous catalysts which would not leach into the reaction medium and
56 be used for several reaction cycles [14].

57 Heterogeneous catalysis significantly contributes to strengths of the modern chemical
58 technology. This is because the advent of metals or other elements from the catalyst into the
59 reaction products could be notably minimized, thus quenching multiple separation and purification
60 steps. Examples of solid catalysts employed to catalyze the acetic acid esterification processes
61 include: ion-exchange resins [15-17], acid-functionalized silica [18, 19], zeolites [20, 21] and
62 supported heteropolyacids [22]. Ion-exchange resins have been established to be potential
63 heterogeneous catalyst for the esterification processes because the selective adsorption of reactants
64 and swelling nature of these materials not only accelerate the esterification reaction but also affect
65 the equilibrium conversion. Peters et al. [20] presented a study focused on the comparison of
66 efficiency of eight commercial acid catalysts for esterification between acetic acid and butanol,
67 wherein it was concluded that cation-exchange resins (Smopex 101 and Amberlyst 15) displayed
68 superior catalytic performance than sulfated zirconia and zeolites. Izci and Bodur [23] concluded
69 that strongly acidic cation-exchange Dowex 50 Wx2 presented better catalytic performance than
70 Amberlite IR-120 for the acetic acid butanolysis reactions because of its higher total exchange
71 capacity, surface area and pore volume. de la Iglesia et al. [24] utilized zeolite membrane reactors
72 packed with Amberlyst 15 for the continuous production of ethyl acetate. The reported study

73 suggested that Mordenite membranes displayed high resistance to acidic reaction medium and
74 enabled about 90 % acetic acid conversion for five days of experiment. With upgrading the
75 esterification process, the necessity to understand the reaction pathway and modeling the reaction
76 kinetics becomes of high importance because the design of an industrial-scale reactor could be
77 based on the rate equations. Pöpken et al. [25] performed the mathematical modeling for
78 Amberlyst 15 catalyzed production of methyl acetate, in which an independent adsorption
79 experiments were incorporated to the kinetic expression due to swelling nature of cation-exchange
80 resins. The Langmuir-Hinshelwood-Hougen-Watson kinetic model has been previously reported
81 to display good fit with the experimental data for the methanolysis and butanolysis of acetic acid
82 catalyzed by Amberlyst 15. Whereas, Tsai et al.[17] suggested that both Eley-Rideal and
83 Langmuir-Hinshelwood-Hougen-Watson kinetic models were equally good to describe the
84 reaction kinetics of esterification between acetic acid and methanol catalyzed by Amberlyst 36.
85 Though literature on Amberlyst 15 and Amberlyst 36 catalyzed esterification of acetic acid with
86 different short-chain alcohols and mathematical modeling of the respective alcoholysis process are
87 available [17, 24-26], no studies on the use of another macroreticular strongly acidic ion-exchange
88 resins (Amberlyst 16) to catalyze esterification between acetic acid and ethanol has been so far
89 reported.

90 The endeavor of the present study is to investigate the catalytic performance of commercial
91 cation-exchange Amberlyst 16 resins for the esterification reaction between acetic acid and
92 ethanol. The impact of pretreatment, reaction temperature, ethanol-to-acid molar ratio, catalyst
93 dose and time on this esterification reaction was systematically studied. The recyclability of
94 Amberlyst 16 resins for the esterification reaction was also carefully examined. Furthermore, a

95 mathematical model was established to describe the reaction kinetics of ethanolysis of acetic acid
96 over the applied range of experimental conditions.

97

98 2. Materials and Methods

99 2.1. Materials

100 Amberlyst 16 (wet form) was supplied by the Dow Chemical Company (Philadelphia,
101 USA). Its properties provided by the supplier are listed in the Table 1. Ethanol with 99.9 and 96
102 % purity, respectively, were purchased from Kemetyl Norge AS. Acetic acid, diethyl ether,
103 potassium hydroxide (KOH) and phenolphthalein indicator with around 99.7 % purity were
104 purchased from Sigma-Aldrich and utilized as received.

105 **Table 1:** Physical characteristics for Amberlyst 16 resins.

106	Parameters	Value
107	Type	Strong acid
	Matrix	Macroreticular
	Functional group	Sulfuric acid
108	Active sites concentration (dry weight)	$\leq 4.8 \text{ eq kg}^{-1}$
	Cross-linking degree	Medium (8-14 %)
109	Harmonic mean size ¹	0.6 to 0.8 mm
	Physical form	Opaque beads
110	Surface area ²	$30 \text{ m}^2 \text{ g}^{-1}$
	Average pore diameter	25 nm
111	Moisture content	52 to 58 %
	Thermal stability	130 °C

112 ¹Beads size that is close to the median diameter but a little smaller, and is calculated from the distribution function.

113 ²Nitrogen BET.

114 2.2. Catalyst pretreatment

115 For test experiments purpose, a section of commercial Amberlyst 16 resins were dried in
116 an oven (Narbetherm P300, Germany) at 65°C for 24 h. This pre-treatment method of the material
117 was adapted from the data sheet from the Dow Chemical Company, and as applied in the previous
118 study [27]. To test catalytic leaching, approximately 0.5 g of dried and wet resins were transferred
119 into different beakers containing 15 ml of ethanol solutions having different purity. The mixtures

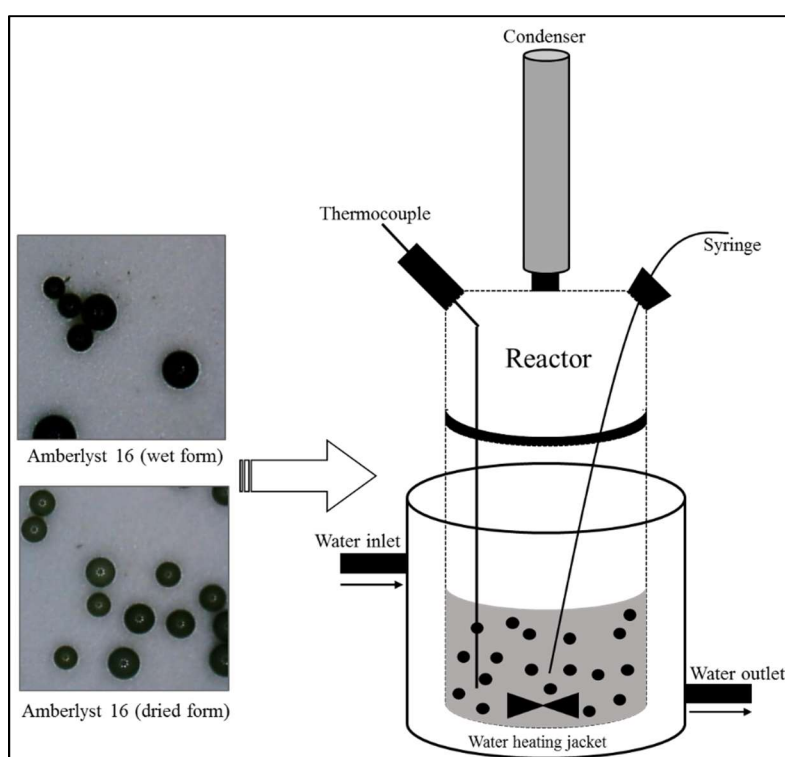
120 of resins and ethanol were stirred at 200 rpm at ambient temperature and atmospheric pressure for
121 2 h. Apart from absolute and rectified ethanol, the material leaching was also tested in water and
122 the esterification reaction mixture.

123 **2.3. Reaction**

124 Amberlyst 16 catalyzed esterification reaction of acetic acid with ethanol was performed
125 in a three-neck glass reactor (Quark glass, New Jersey, USA) of 500 cm³ volume capacity. The
126 diameter and length of the glass reactor is equivalent to 10 and 12.5 cm, respectively. The middle
127 neck of the reactor was connected with the water cooling condenser to minimize the evaporation
128 of reaction solvent, while the side necks were fitted with rubber cork through which the aliquots
129 of the reaction mixture were periodically withdrawn using a plastic syringe. The glass reactor was
130 equipped with a jacket through which a stream of water flows continuously from thermostatically
131 controlled water bath (VWR International, USA), the temperature of which is regulated by a PID
132 controller with 1 °C precision. A magnetic stirrer with dimensions of 5 cm length and 0.8 cm
133 diameter was utilized for all experiments, and the glass reactor was placed on a magnetic plate that
134 controlled the speed of stirring. The experimental scheme is shown in Figure 1. The stirring
135 intensity was maintained at 200 rpm for all experiments.

136 Initially, measured amounts of acetic acid and ethanol were added to the reactor and heated
137 to the desired temperature. Once the system temperature reached the set point, sample aliquot
138 (approximately 1 mL) was withdrawn. Then, an appropriate weight of catalyst was introduced and
139 stirring of the reaction was instantaneously started; this was considered as the starting time of the
140 ethanolysis reaction. The aliquots of reaction mixture withdrawn at specified time intervals (0, 15,
141 30, 90, 120, 180, 240, 360, 480, 600, 720, 840, 960, 1140, 1320, 1500 and 1680 min) to study the
142 progress of the reaction. The reaction volume is 400 ml; therefore, removing around 17 ml aliquots

143 (4.25 %) of total reaction mixture is assumed to not significantly affect the reaction balance as the
144 aliquots removed would contain fraction of all reactants, intermediates, formed product and by-
145 product. The stirring of the reaction mixture was stopped approximately 10 seconds prior to aliquot
146 extraction to avoid the ejection of catalytic materials, and started immediately after the extraction.
147 All experiments were replicated twice to obtain the reproducibility, and an average of the
148 experimental values were presented in the graphical representations.



149 Figure 1: Experimental scheme for Amberlyst 16 catalyzed acetic acid esterification.

150 2.4. Reusability of catalyst

151 The degree of catalyst decay was tested through the recyclability tests. After the first run
152 of esterification reaction, Amberlyst 16 resins were separated from the post-reaction mixture
153 through filtration using the Whatmann filter paper. The catalysts were then washed with 5 mL of
154 ethanol four times to remove the attached reaction mixture from previous runs. The catalyst, which

155 is in the wet form, was then immediately used for the next cycle of esterification reaction. The
 156 aliquots of reaction mixture withdrawn at specified time intervals (0, 15, 60, 120, 240, 480, 920,
 157 1500 and 1680 min). The procedure for the extraction of reaction aliquots was as previously
 158 mentioned. The design of experiments showing reaction temperature, catalyst dose and initial
 159 acetic acid concentration is presented in Table 2.

160 **Table 2:** Design of experiments for Amberlyst 16 catalyzed esterification of acetic acid.

Run	Catalyst form (cycle)	Temperature (°C)	Ethanol-to-acid molar ratio	Catalyst dose (wt.%)	Acid initial conc. (mol dm ³)
1	Dried	60	6:1	5	2.38
2	Wet	60	6:1	10	2.38
3	Wet	40	6:1	5	2.38
4	Wet	50	6:1	5	2.38
5	Wet	70	6:1	5	2.38
6	Wet	60	3:1	5	4.09
7	Wet	60	9:1	5	1.68
8	Wet	60	6:1	15	2.38
9	Wet	60	6:1	5	2.38
10	Wet, recycle-1	60	6:1	5	2.38
11	Wet, recycle-2	60	6:1	5	2.38
12	Wet, recycle-3	60	6:1	5	2.38
13	Wet, recycle-4	60	6:1	5	2.38

161

162 2.5. Analysis

163 The acid value of withdrawn reaction samples were determined in accordance to the EN
 164 14104 official method [27].

165 The acid value (AV) is expressed as:

166
$$AV = \frac{V_{KOH} \times C_{KOH} \times M_{KOH}}{W_R} \quad (1)$$

167 V_{KOH} is the volume of KOH (mL), C_{KOH} is the concentration of KOH in moles per liter,
168 M_{KOH} is the molar mass, W_R is the weight of sample added to the titration in grams.

169 The acetic acid conversion (A_x) is expressed as:

170
$$A_x = \frac{\text{Initial moles of acid} - \text{Final moles of acid}}{\text{Initial moles of acid}} \times 100 \% \quad (2)$$

171 The titration method determining the concentration of sulfonic acid species is employed to
172 investigate the leaching phenomenon of Amberlyst 16 resins in the reactants.

173 **2.6. Kinetic modelling: theoretical background**

174 In a stoichiometric esterification reaction, a molecule of carboxylic acid reacts with a single
175 molecule of ethanol to produce a single molecule of both fatty acid ethyl esters (FAEEs) and water.
176 The overall esterification of acetic acid with ethanol is represented as:

177 For the kinetic modeling purpose, following commonly applied assumptions were taken
178 into consideration [16, 28]:

179 (1) The reaction mixture was perfectly mixed, and its composition, catalyst distribution and
180 temperature were uniform throughout the process because the reaction was performed in a
181 batch reactor under continuous vigorous stirring.

182 (2) The contribution of homogeneous (leaching of solid catalyst in the reaction mixture) and
183 thermal catalysis (reaction without catalyst) is insignificant because ion-exchange resins
184 are poorly soluble in the reaction mixture and acts as heterogeneous catalyst.

185 The curve fitting procedure was performed using the Aspen custom modeler software
186 (version 8.4, Aspen Technology, Inc., USA). The selection of an appropriate mathematical model

187 for the described ethanolysis process was based on the statistical parameters, such as the sum of
188 weighted errors and the model selection criteria (MSC). The mathematical expression for the MSC
189 is presented as:

$$190 \quad MSC = \ln \left[\frac{\sum(\beta_{exp,i} - \beta_{exp,a})^2}{\sum(\beta_{exp,i} - \beta_{pre,i})^2} \right] - \frac{2p}{n} \quad (3)$$

191

192 where, $\beta_{exp,i}$ is the experimental data at i^{th} reaction time; $\beta_{exp,a}$ is an average of the
193 experimental data; $\beta_{pre,i}$ is the predicted values at i^{th} reaction time; p is the number of the parameter
194 involved in the model; n is the number of the experimental data.

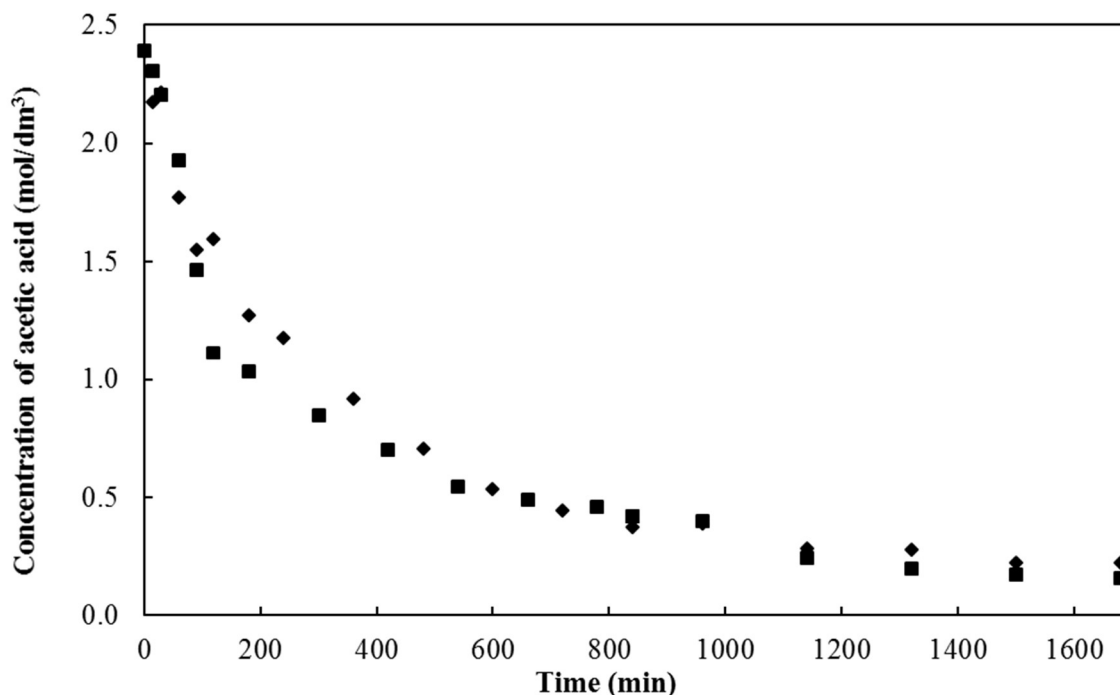
195

196 3. Results and discussion

197 3.1. Pretreatment effects

198 The pretreatment of ion-exchange resins has been proven to significantly affect their
199 performance as catalysts. Pretreatment experiments were performed to investigate not only the
200 leaching of ion-exchange resins in reactants but also on their performance as catalyst. Previous
201 studies reported that different wet Amberlyst resins were dried before testing its catalytic
202 performance [29-31]. Therefore, this study started with testing and comparing the efficacy of
203 Amberlyst 16 as received wet and laboratory-dried form to assist the esterification of acetic acid
204 with ethanol. For the drying pretreatment, Amberlyst 16 were kept in an oven, set at 65 °C, for
205 24h. The catalyst dose applied for the esterification reaction is based on the number of resins beads
206 and the mass balance was carried out. Therefore, catalyst dose of 5 and 10 wt. % (with respect to
207 acetic acid) for dried and wet Amberlyst 16 resins, respectively, was used to catalyze the
208 ethanolysis reaction. This is because the drying pretreatment resulted in around 50 % weight loss
209 of the wet resins. The application of such method enables the access of reactant molecules to an
210 equal number of catalytic sites. The esterification reaction was performed at 60 °C using 6:1
211 ethanol-to-acid molar ratio, 200 rpm stirring intensity and 1680 min reaction time. The graphical
212 representation indicating a drop in the concentration of acetic acid with time is shown in Figure 2.
213 The rate of the reaction in the case of dried catalyst was better than that of weight catalyst during
214 the initial 30 minutes of the reaction, after which the resins catalyst in wet form displayed slightly
215 better reaction rate but no significant impact on the final acid conversion was observed. The acetic
216 acid conversion after 1680 min of esterification reaction performed using wet and dried Amberlyst
217 16 was 93.3 and 90.7 %, respectively. Furthermore, the dried Amberlyst 16 slightly leached in
218 ethanol solution, while, its wet form displayed no lixiviation phenomenon. Furthermore,

219 Amberlyst 16 was stable in absolute ethanol, rectified ethanol and water. Therefore, Amberlyst 16
220 resins in its wet form was further used in all experiments.



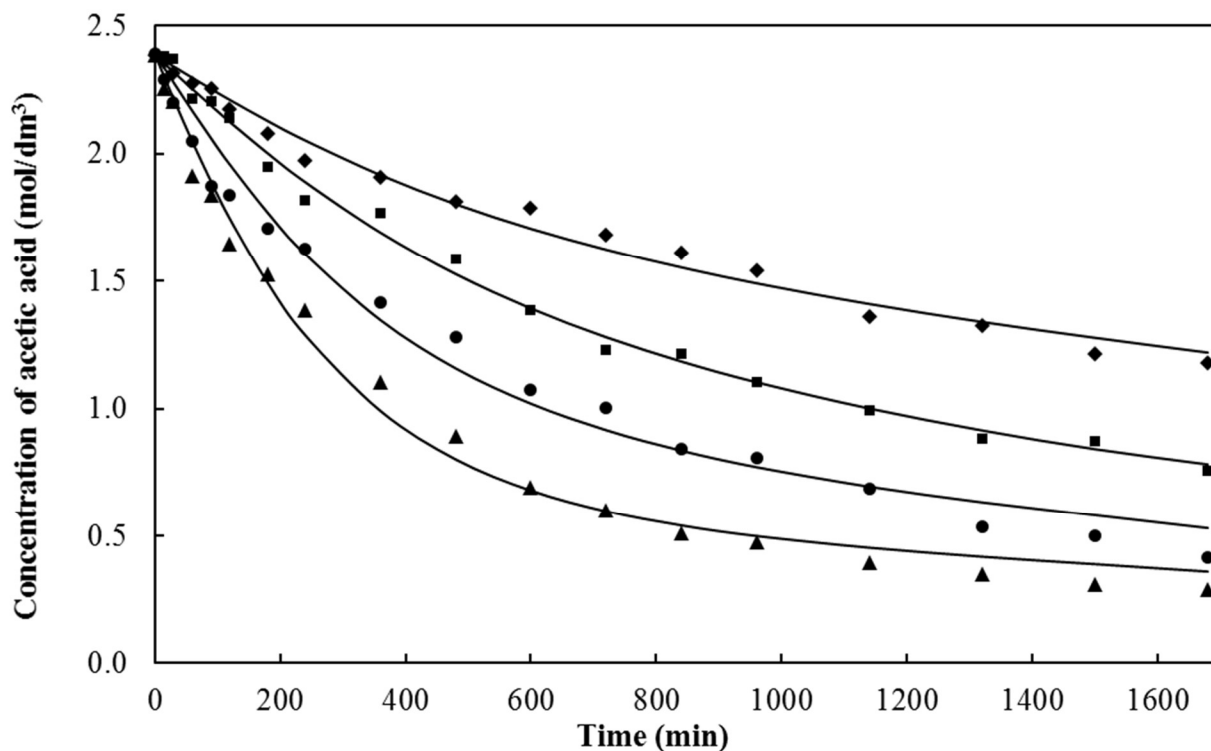
221
222 Figure 2: Catalytic performance of wet and dried Amberlyst 16 ion-exchange resins for the
223 esterification process. ■- wet form, ◆- dried form. Reaction temperature-60 °C, ethanol-to-acetic
224 acid molar ratio- 6:1, stirring intensity- 200 rpm.

225

226 3.2. Temperature effects

227 The effects of different reaction temperatures on Amberlyst 16 resins catalyzed
228 esterification reaction between acetic acid and ethanol was studied because the rise in temperature
229 is anticipated to accelerate the reaction rate. The increase in temperature is said to improve the
230 miscibility as well as reactivity between reactants [28]. The effects of four reaction temperatures
231 (40, 50, 60 and 70 °C) on the above-mentioned ethanolysis process was studied keeping constant
232 ethanol-to-acid molar ratio of 6:1, catalyst dose of 5 wt. %, stirring intensity of 200 rpm and 1680
233 reaction time. Further higher temperatures were not applied to eliminate the possibility of ethanol

234 evaporation. The experimental results for the effect of temperature on the variation in acetic
 235 concentration are presented as symbols in Figure 3. The experimental findings indicated that an
 236 increase in temperature had a positive impact on the rate of the described esterification reaction.
 237 To achieve approximately 50 % acid conversion, the reaction time reduced from 1500 to 360 min
 238 when temperature was raised from 40 to 70 °C. The acid conversion after 1680 reaction time
 239 augmented from 50.2 to 87.8 % when temperature was raised from 40 to 70 °C. The obtained
 240 experimental findings were in close agreement with the previously reported Amberlyst 16 resins
 241 catalyzed esterification processes [29, 30]. The final acid conversion increased by 18 and 14 %
 242 when temperature was raised from 40 °C to 50 and 60 °C, respectively; however, further increasing
 243 reaction to 70 °C resulted only in rise of 5 % acid conversion. Therefore, reaction temperature of
 244 60 °C was used for further experiments.



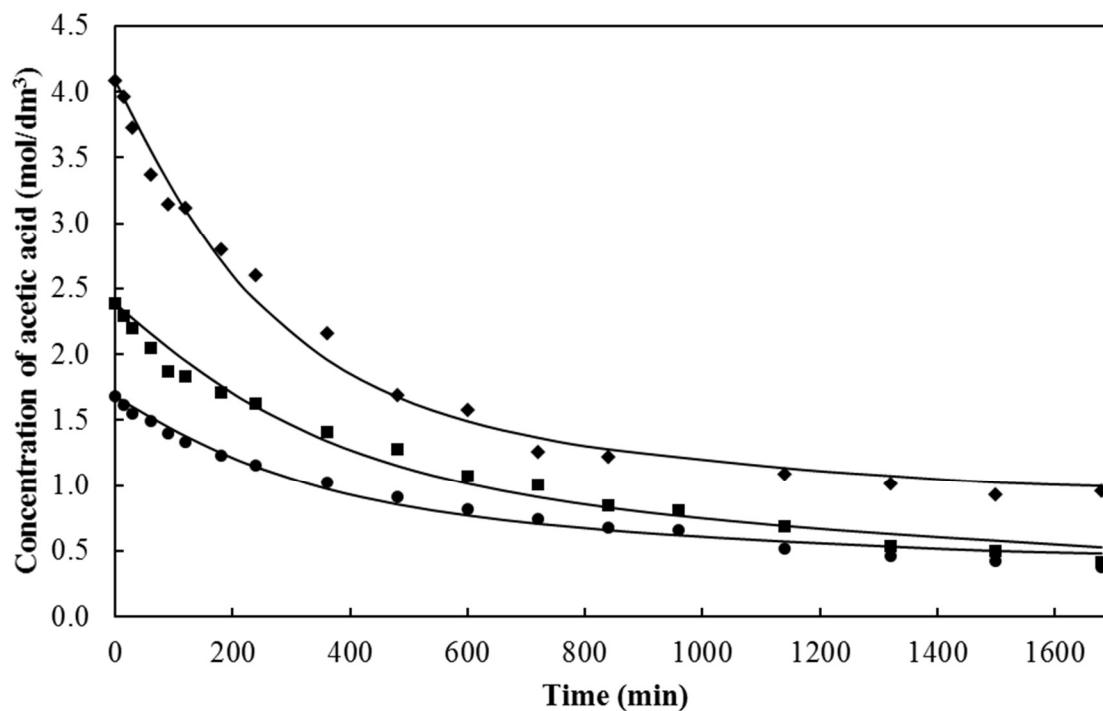
245
 246 **Figure 3:** Comparison between experimental and predicted values for the variation in acetic acid
 247 concentration with time due to the impact of reaction temperatures. ◆- 40, ■- 50, ●- 60, ▲- 70 °C.

248 Experimental data: symbols, kinetic model: lines. Ethanol-to-acetic acid molar ratio- 6:1, catalyst
249 dose- 5 wt. %, stirring intensity- 200 rpm.

250

251 **3.3. Ethanol-to-acid molar ratio effects**

252 The other important variable affecting the esterification reaction is the alcohol-to-acid
253 molar ratio. Since the esterification is an equilibrium reaction, use of an excess alcohol would be
254 beneficial to shift the reaction towards the product formation. The effects of different ethanol-to-
255 acid molar ratio (3, 6 and 9:1) on the Amberlyst 16 resins catalyzed esterification reaction of acetic
256 acid with ethanol was investigated keeping fixed temperature of 60 °C, catalyst dose of 5 wt. %,
257 stirring intensity of 200 rpm and 1680 reaction time. The experimental findings for the effect of
258 ethanol-to-acid molar ratio on the variation in acetic concentration are presented as symbols in
259 Figure 4. The obtained results suggested that increasing alcohol-to-acid molar ratio had a negative
260 impact on the rate of the esterification reaction. Use of higher ethanol concentration slightly
261 lowered the reaction rate. The acquired trend of results could be due to dilution of reaction mixture
262 that minimized the acetic acid-catalyst interaction. The usage of very high amount of ethanol could
263 also direct the dissociation of acetic acid and the reacting species, thus minimizing the rate of
264 formation of the product. The achieved results were in close agreement with the previously
265 reported esterification process, where in increasing methanol-to-acid molar ratio from 1 to 3:1
266 positively affected the esterification process; however, further increase in mole ratio of methanol-
267 to-acid reduced oleic acid conversion from around 85 to 72 % [16]. Hykkerud and Marchetti
268 reported similar pattern of results and explained that such behavior is because the reaction was in
269 its initial stage and the equilibrium state was not applicable [27]. In the present study, highest
270 acetic acid conversion of 82.6 % was obtained using 6:1 ethanol-acid molar ratio.



271

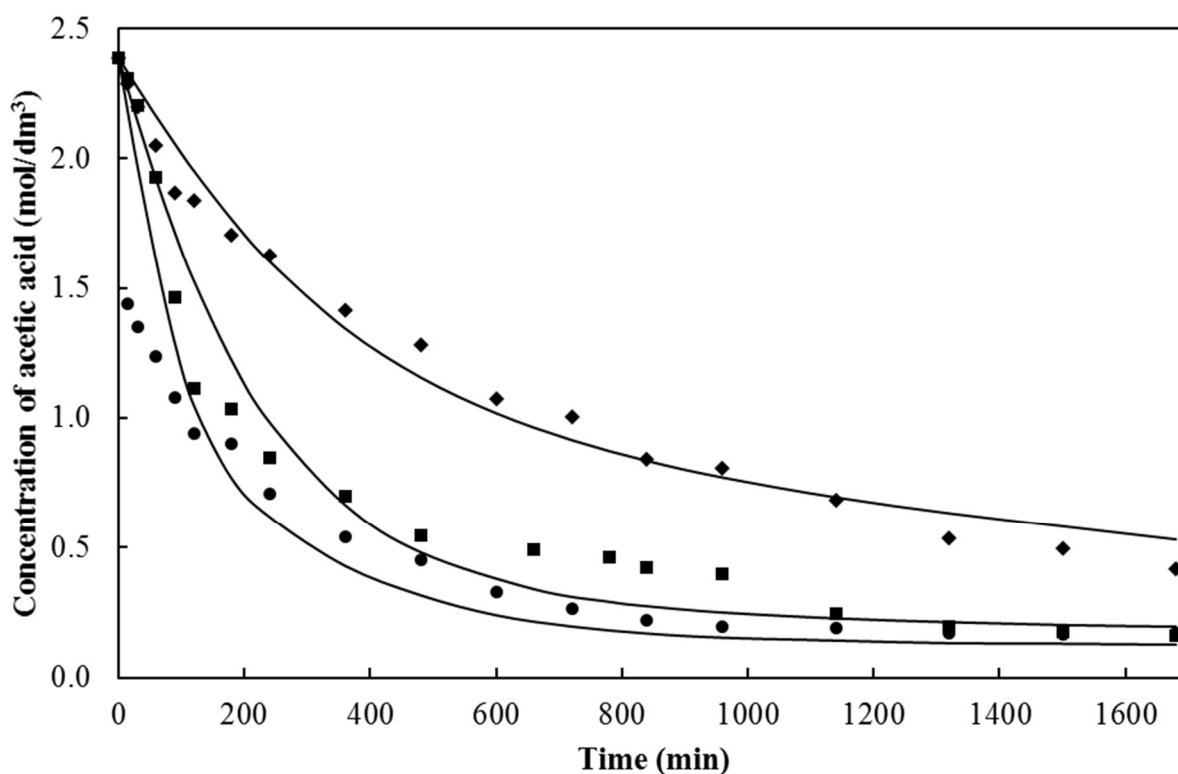
272 **Figure 4:** Comparison between experimental and predicted values for the variation in acetic acid
 273 concentration with time due to the impact of ethanol-to-acid molar ratio. ◆- 3, ■- 6, ●- 9:1.
 274 Experimental data: symbols, kinetic model: lines. Reaction temperature-60 °C, catalyst dose- 5 wt.
 275 %, stirring intensity- 200 rpm.

276

277 3.4. Catalyst dose effects

278 The dependence of acetic acid conversion on the catalyst dose was further investigated. The
 279 effects of three catalysts amounts (5, 10 and 15 wt. %) on the change in the acetic acid
 280 concentration was studied setting the constant reaction temperature of 60 °C, ethanol-to-acid molar
 281 ratio of 6:1, stirring intensity of 200 rpm and 1680 reaction time. The experimental results for the
 282 study evaluating the effects of catalyst dose on the variation in the concentration of acetic acid are
 283 shown as symbols in Figure 5. A faster drop in the acid concentration was observed with increasing
 284 catalyst dose. Increasing catalyst dose from 5 to 15 wt. % resulted in reducing reaction time from
 285 600 to 90 min, respectively, to achieve around 55 % acetic acid conversion. This is attributed to

286 an increase in the availability of active catalytic centers. Though increase in the catalyst amount
287 accelerated the rate of the esterification reaction, no significant difference in the final acid
288 conversion was observed. The highest acetic conversion of 93.3 % was recorded using 10 wt. %
289 catalyst dose.



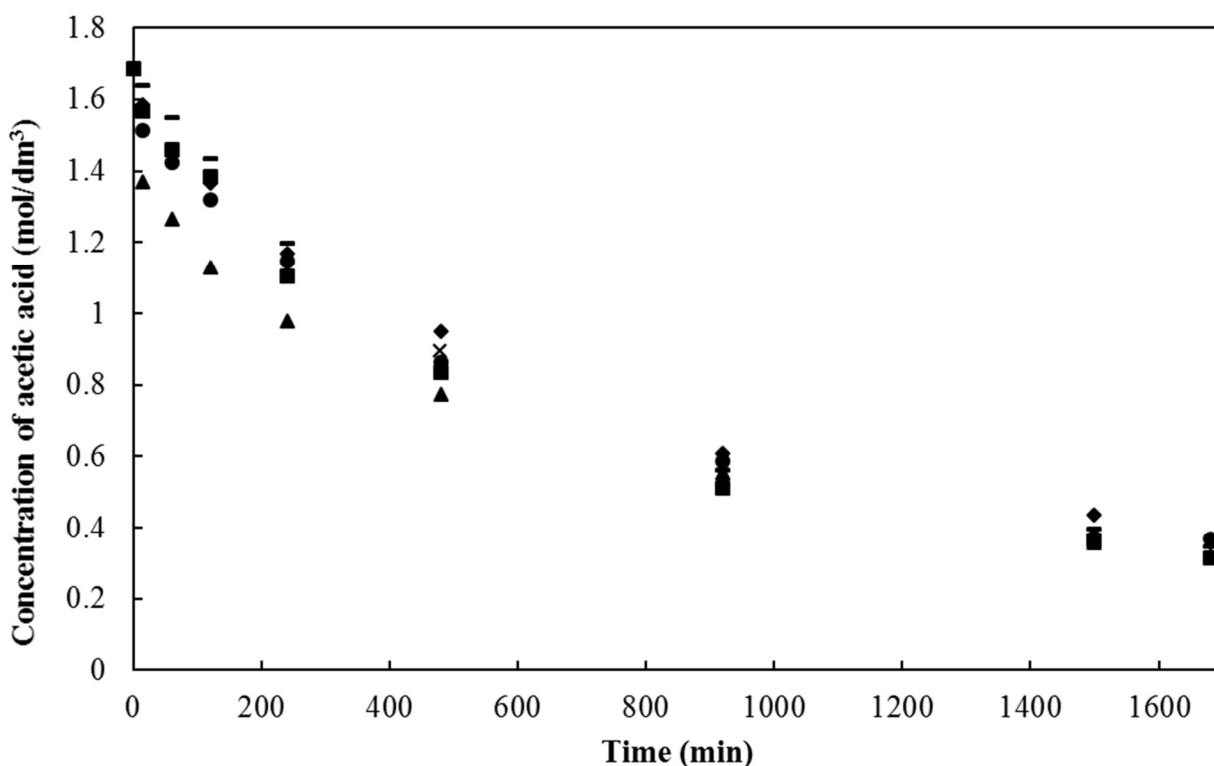
290
291 **Figure 5:** Comparison between experimental and predicted values for the variation in acetic acid
292 concentration with time due to the impact of catalyst dose. \blacklozenge - 5, \blacksquare - 10, \bullet - 15 wt. %. Experimental
293 data: symbols, kinetic model: lines. Reaction temperature-60 °C, ethanol-to-acid molar ratio- 6:1,
294 stirring intensity- 200 rpm.

295

296 3.5. Catalyst recyclability

297 From a chemical engineering perspective, reutilization of heterogeneous catalysts is an
298 important aspect for the large-scale production of valuable chemicals. In this study, the
299 recyclability of wet Amberlyst 16 cation-exchange resins to catalyze the esterification reactions of

300 acetic acid with ethanol was investigated keeping constant reaction temperature of 60 °C, ethanol-
301 to-acid molar ratio of 6:1, catalyst dose of 5 wt. %, stirring intensity and 1680 min reaction time.
302 The change in both reaction rate and final acetic acid conversion with time was monitored. The
303 experimental findings for the catalyst recycle tests are presented in Figure 6. Reusing the catalyst
304 slightly lowered the rate of reaction, but showed insignificant variation in the final acetic acid
305 conversion. After four catalyst recycle tests, the final acetic acid conversion dropped only by 3.2
306 % indicating that commercial wet Amberlyst 16 is a suitable heterogeneous catalyst that could be
307 reutilized at least four times for the ethyl acetate production under the studied range of
308 experimental conditions.



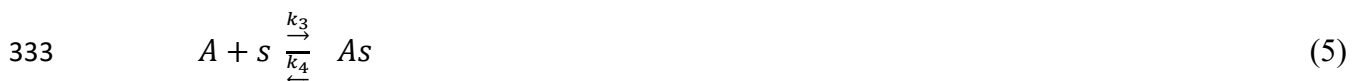
309
310 **Figure 6:** Recyclability tests of the wet Amberlyst 16 resins for the acetic acid esterification with
311 ethanol. ▲- fresh, ●- reuse 1, ■- reuse 2, ◆- reuse 3, x- reuse 4. Reaction temperature-60 °C,
312 ethanol-to-acid molar ratio- 6:1, catalyst dose- 5 wt. %, stirring intensity- 200 rpm.

314 **3.6. Kinetic modeling of esterification process**

315 To develop a mathematical model that appropriately describes the chemical kinetics of
316 Amberlyst 16 catalyzed esterification of acetic acid with ethanol, the adsorption of reactant
317 molecules on the catalytic sites, surface chemical reaction and product desorption steps were taken
318 into consideration. The rate-controlling step for this reversible reaction was determined, and rate
319 constants for the overall reaction were evaluated. A total of 12 different kinetic models were tested,
320 and the selection of the best mathematical model was based on the parameters such as MSC and
321 sum of weighed errors. By fitting the model with the experimental data, the appropriate kinetic
322 model for the current esterification reaction included following features:

- 323 (1) Both ethanol and acetic acid molecules are absorbed on the solid catalytic surface due to
324 their polar nature.
- 325 (2) The esterification reaction occurred between ethanol and acetic acid molecule
326 chemisorbed on the neighboring sites of the catalyst surface.
- 327 (3) The overall process rate is controlled by the surface reaction between chemisorbed
328 ethoxide and acetic acid molecules.
- 329 (4) The overall Amberlyst 16 assisted esterification of acetic acid with ethanol follows
330 Langmuir-Hinshelwood reaction mechanism.

331 The esterification reaction steps involved in the reaction pathway could be presented as:





336 where, E is ethanol, A is acetic acid, s is the catalytic active sites, EA is ethyl acetate and
 337 W is water.

338 When the surface reaction was proposed to be the rate-limiting step, the fractional
 339 conversion of acetic acid can be expressed as:

340
$$\frac{dX_A}{dt} = m^2 \left[\frac{[k_1 k_3 k_5 C_E C_A]}{k_2 k_4} - \frac{[k_6 k_8 C_{EA} C_W]}{k_7} \right] \quad (9)$$

341
$$k = A e^{-E_a/RT} \quad (10)$$

342 The equation for the mass balance of the catalyst is presented as:

343
$$m = \frac{m_0}{\left[1 + \left[\frac{k_1 C_E}{k_2} \right] + \left[\frac{k_3 C_A}{k_4} \right] + \left[\frac{k_8 C_W}{k_7} \right] \right]} \quad (11)$$

344 while,

345
$$C_A = C_{A0} [1 - X_A] \quad (12)$$

346
$$C_E = C_{E0} - C_{A0} * X_A \quad (13)$$

347
$$C_{EA} = C_W = C_{A0} * X_A \quad (14)$$

348 where, k_1, k_3, k_5 and k_7 are the specific rate constants for reaction in the forward direction;
 349 k_2, k_4, k_6 and k_8 are the specific rate constants for reaction in the reverse direction; ($k_1, k_3, k_5, k_8 =$
 350 $\text{ltr mol}^{-1}\text{t}^{-1}$; $k_2, k_4, k_7 = 1 \text{ t}^{-1}$; $k_6 = \text{ltr}^2(\text{mol}^2)^{-1}\text{t}^{-1}$); C_{E0} is the ethanol initial concentration (mol L^{-1}); C_E

351 is the ethanol concentration at time t (mol L^{-1}); C_{A0} is the acetic acid initial concentration (mol L^{-1}); C_A is the acetic acid concentration at time t (mol L^{-1}); C_W is the concentration of water (mol L^{-1}); C_{EA} is the concentration of ethyl acetate (mol L^{-1}); m_0 is the initial mass of the catalyst (g); m is the mass of the catalytic sites involved in the reaction (g); A is the pre-exponential factor of the Arrhenius equation (min^{-1}); E_a is the activation energy (cal mol^{-1}); R is the universal gas constant ($1.98 \text{ cal K}^{-1} \text{ mol}^{-1}$); T is the absolute temperature (K).

357 The discussed kinetic model provided a good correlation between the experimental
358 findings and predicted values, with sum of weighed square error and MSC for the change in acetic
359 acid concentration of $6.72 \text{ E-}2$ and 3.79 , respectively. The achieved low value of sum of weighed
360 square error and high value of MSC validated the proposed kinetic model based on the Langmuir-
361 Hinshelwood reaction mechanism to be appropriate to predict the wet Amberlyst 16 assisted
362 esterification of acetic acid with ethanol under the studied range of experimental conditions. The
363 kinetic parameters for the acetic acid esterification process with ethanol in the presence of wet
364 Amberlyst 16 cation-exchange resins are presented in Table 3. The achieved results were in
365 agreement with previously reports, which concluded that the acetic acid esterification process
366 follows the Langmuir-Hinshelwood type reaction mechanism [17, 19]. The activation energy
367 values obtained for the current process were compared with those catalyzed using different
368 Amberlyst resins, and were found to be in reasonable agreement with the previously reported
369 studies [17, 23, 25]. The simulation curves for the experimental change in the acetic acid
370 concentration at different temperature, ethanol-to-acid molar ratio and catalyst dose are presented
371 as solid lines in Figure 3, 4 and 5, respectively.

372

373

374 **Table 3:** Kinetic parameters for the acetic acid esterification process with ethanol in the presence
 375 of wet Amberlyst 16 cation-exchange resins.

376

377

Parameters	Value	Unit
A ₁	7133.17	min ⁻¹
E _{a1}	2215.14	cal mol ⁻¹
A ₂	126.74	min ⁻¹
E _{a2}	3619.35	cal mol ⁻¹
A ₃	5008.52	min ⁻¹
E _{a3}	1506.69	cal mol ⁻¹
A ₄	11.99	min ⁻¹
E _{a4}	1953.84	cal mol ⁻¹
A ₅	219.35	min ⁻¹
E _{a5}	6438.3	cal mol ⁻¹
A ₆	4005.27	min ⁻¹
E _{a6}	4877.57	cal mol ⁻¹
A ₇	972.99	min ⁻¹
E _{a7}	9800.75	cal mol ⁻¹
A ₈	597.74	min ⁻¹
E _{a8}	4177.3	cal mol ⁻¹

378 4. Conclusion

379 The current research article presents the experimental as well as simulation investigations
380 for the esterification reaction of acetic acid with ethanol in the presence of the strongly acidic
381 Amberlyst 16 ion-exchange resins. The obtained experimental findings suggested that the drying
382 of Amberlyst 16 before its application for the esterification reaction displayed slight leaching as
383 well as insignificant impact on the final acetic acid conversion, when compared with those using
384 wet resins. Therefore, Amberlyst 16 could be applied directly in its available wet form to catalyze
385 the acetic acid esterification reaction with ethanol. Increase in both reaction temperature and
386 catalyst dose resulted in the acceleration in the rate of ethyl acetate generation. However,
387 increasing ethanol-to-acid molar ratio slightly lowered the rate of reaction. The application of
388 reaction temperature of 60 °C, ethanol-to-acid molar ratio of 6:1, catalyst dose of 10 wt. % and
389 200 rpm stirring intensity resulted in 93.3 % acetic acid conversion after 1680 min of esterification
390 reaction catalyzed by Amberlyst 16 cation-exchange resins. The catalyst was found to be active
391 and stable under mentioned experimental conditions, and can be reutilized at least for four reaction
392 cycles without any pretreatment. The proposed kinetic model suggested that the reaction followed
393 Langmuir-Hinshelwood mechanism. The esterification reaction occurred between ethoxide and
394 acetic acid molecules both chemisorbed on the neighboring catalytic active surface, the rate of
395 which was controlled by the surface reaction step. The proposed kinetic model presented a good
396 agreement between the predicted values and the experimental data under the studied range of
397 experimental conditions. Based on the experimental as well as simulation investigations, it could
398 be concluded that Amberlyst 16 cation-exchange resins is active, stable and reusable
399 heterogeneous catalyst for the ethyl acetate production through the esterification route.

400 **References**

- 401 [1] Gaspar AB, Esteves AML, Mendes FMT, Barbosa FG, Appel LG (2009) Chemicals from
402 ethanol-The ethyl acetate one-pot synthesis. *Applied Catalysis A: General* 1-2: 109
- 403 [2] Nielsen M, Junge H, Kammer A, Beller M (2012) Towards a green process for bulk-scale
404 synthesis of ethyl acetate: Efficient acceptorless dehydrogenation of ethanol. *Angewandte Chemie*
405 *International Edition* 23: 5711
- 406 [3] PRWEB. Global ETAC Production to Exceed 3.5 Mln Tonnes in 2015.
407 <http://www.prweb.com/releases/2014/02/prweb11619424.htm> (Accessed 21.08.18)
- 408 [4] Merchant Research & Consulting Ltd. Ethyl Acetate (ETAC): 2016 World Market Outlook
409 and Forecast up to 2020. <https://mcgroup.co.uk/researches/ethyl-acetate-etac> (Accessed 21.08.18)
- 410 [5] Inui K, Kurabayashi T, Sato S (2002) Direct synthesis of ethyl acetate from ethanol over Cu-
411 Zn-Zr-Al-O catalyst. *Applied Catalysis A: General* 1-2: 53
- 412 [6] Inui K, Kurabayashi T, Sato S (2002) Direct synthesis of ethyl acetate from ethanol carried out
413 under pressure. *Journal of Catalysis* 212(2): 207
- 414 [7] Manayil JC, Inocencio CVM, Lee AF, Wilson K (2016) Mesoporous sulfonic acid silicas for
415 pyrolysis bio-oil upgrading *via* acetic acid esterification. *Green Chemistry* 18: 1387
- 416 [8] Bennett JA, Parlett CMA, Isaacs MA, Durndell LJ, Olivi L, Lee AF, Wilson K (2017) Acetic
417 acid ketonization over Fe₃O₄/SiO₂ for pyrolysis bio-oil upgrading. *ChemCatChem* 9(9): 1648
- 418 [9] Rönneck R, Salmi T, Vuori A, Haario H, Lehtonen J, Sundqvist A, Tirronen E (1997)
419 Development of a kinetic model for the esterification of acetic acid with methanol in the presence
420 of a homogeneous acid catalyst. *Chemical Engineering Science* 52(19): 3369
- 421 [10] Mäki-Arvela P, Salmi T, Sundell M, Ekman K, Peltonen R, Lehtonen J (1999) Comparison
422 of polyvinylbenzene and polyolefin supported sulphonic acid catalysts in the esterification of
423 acetic acid. *Applied Catalysis A: General* 184(1): 25
- 424 [11] Jafar JJ, Budd PM, Hughes R (2002) Enhancement of esterification reaction yield using
425 zeolite A vapour permeation membrane. *Journal of Membrane Science* 199(1-2): 117

- 426 [12] Marchetti JM, Errazu AF (2008) Esterification of free fatty acids using sulfuric acid as
427 catalyst in the presence of triglycerides. *Biomass and Bioenergy* 32(9): 892
- 428 [13] Marchetti JM, Pedernera MN, Schbib NS (2011) Production of biodiesel from acid oil using
429 sulfuric acid as catalyst: kinetics study. *International Journal of Low-Carbon Technologies* 6(1):
430 38
- 431 [14] Avhad MR, Marchetti JM (2016) Innovation in solid heterogeneous catalysis for the
432 generation of economically viable and ecofriendly biodiesel: A review. *Catalysis Reviews: Science and Engineering* 58(2): 157
- 434 [15] Marchetti JM, Errazu AF (2008) Comparison of different heterogeneous catalysts and
435 different alcohols for the esterification reaction of oleic acid. *Fuel* 87(15-16): 3477
- 436 [16] Ilgen O (2014) Investigation of reaction parameters, kinetics and mechanism of oleic acid
437 esterification with methanol by using Amberlyst 46 as a catalyst. *Fuel Processing Technology* 124:
438 134
- 439 [17] Tsai Y-T, Lin H-m, Lee M-J (2011) Kinetics behavior of esterification of acetic acid with
440 methanol over Amberlyst 36. *Chemical Engineering Journal* 171(3): 1367
- 441 [18] Jermy BR, Pandurangan A (2005) A highly efficient catalyst for the esterification of acetic
442 acid using n-butyl alcohol. *Journal of Molecular Catalysis A: Chemical* 237(1-2): 146
- 443 [19] Miao S, Shanks BH (2011) Mechanism of acetic acid esterification over sulfonic acid-
444 functionalized mesoporous silica. *Journal of Catalysis* 279(1): 136
- 445 [20] Peters TA, Benes NE, Holmen A, Keurentjes JTF (2006) Comparison of commercial solid
446 acid catalysts for the esterification of acetic acid with butanol. *Applied Catalysis A: General*
447 297(2): 182
- 448 [21] Corma A, Garcia H, Iborra S, Primo J (1989) Modified faujasite zeolites as catalysts in organic
449 reactions: Esterification of carboxylic acids in the presence of HY zeolites. *Journal of Catalysis*
450 120(1): 78
- 451 [22] Verhoef MJ, Kooyman PJ, Peters JA, van Bekkum H (1999) A study on the stability of MCM-
452 41-supported heteropoly acids under liquid- and gas-phase esterification conditions. *Microporous and Mesoporous Materials* 27(2-3): 365
- 453

- 454 [23] Izci A, Bodur F (2007) Liquid-phase esterification of acetic acid with isobutanol catalyzed by
455 ion-exchange resins. *Reactive and Functional Polymers* 67(12): 1458
- 456 [24] de la Iglesia Ó, Mallada R, Menéndez M, Coronas J (2007) Continuous zeolite membrane
457 reactor for esterification of ethanol and acetic acid. *Chemical Engineering Journal* 131(1-3): 35
- 458 [25] Pöpken T, Götze L, Gmehling J (2000) Reaction kinetics and chemical equilibrium of
459 homogeneously and heterogeneously catalyzed acetic acid esterification with methanol and methyl
460 acetate hydrolysis. *Industrial & Engineering Chemistry Research* 39(7): 2601
- 461 [26] Gangadwala J, Mankar S, Mahajani S, Kienle A, Stein E (2003) Esterification of acetic acid
462 with butanol in the presence of ion-exchange resins as catalysts. *Industrial & Engineering
463 Chemistry Research* 42(10): 2146
- 464 [27] Hykkerud A, Marchetti JM (2016) Esterification of oleic acid with ethanol in the presence of
465 Amberlyst 15. *Biomass and Bioenergy* 95: 40
- 466 [28] Avhad MR, Sánchez M, Peña E, Bouaid A, Martínez M, Aracil J, Marchetti JM (2016)
467 Renewable production of value-added jojobyl alcohols and biodiesel using a naturally-derived
468 heterogeneous green catalyst. *Fuel* 179: 332
- 469 [29] Tesser R, Casale L, Verde D, Di Serio M, Santacesaria E (2010) Kinetics and modeling of
470 fatty acids esterification on acid exchange resins. *Chemical Engineering Journal* 157(2-3): 539
- 471 [30] Özbay N, Oktar N, Tapan NA (2008) Esterification of free fatty acids in waste cooking oils
472 (WCO): Role of ion-exchange resins. *Fuel* 87(10-11): 1789
- 473 [31] Leveneur S, Murzin DY, Salmi T, Mikkola J-P, Kumar N, Eränen K, Estel L (2009) Synthesis
474 of peroxypropionic acid and hydrogen peroxide over heterogeneous catalysts. *Chemical
475 Engineering Journal* 147: 323

476 **Acknowledgement**

477 The authors would like to express their gratitude to the Norwegian University of Life
478 Sciences (Project no. 1301051406) for the financial support.

479

480 **Competing financial interests**

481 The authors declare no competing financial interests.

482

