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Choline chloride-based deep eutectic solvents in CaO-catalyzed ethanolysis of expired sunflower oil

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Abbreviations: ChCl:DMU - choline chloride:1,3-dimethylurea; ChCl:EG - choline chloride:ethylene glycol; ChCl:G - choline chloride:glycerol; ChCl:PG - choline chloride:propylene glycol; ChCl:TU - choline chloride:thiourea, ChCl:U - choline chloride:urea; DES - deep eutectic solvent; FAEE - fatty acid ethyl ester; HBD - hydrogen bond donor; TAG - triacylglycerol.

Abstract

Choline chloride (ChCl)-based deep eutectic solvents (DESs) with different amides or polyols as hydrogen bond donors were tested as cosolvents in the ethanolysis of expired sunflower oil catalyzed by either calcined or non-calcined CaO. These cosolvents promoted the ethanolysis by a successful activation of non-calcined CaO, which was ascribed to the $CaCO_3$ and $Ca(OH)_2$ dissolution from the surface of the solid catalyst particles. With both calcined and non-calcined CaO, the polyol-based solvents gave higher fatty acid ethyl esters (FAEE) content than the amide-based solvents. Among the amide-based DESs, choline chloride:urea (ChCl:U) was the most efficient activator of non-calcined CaO. Choline chloride:ethylene glycol (ChCl:EG) and choline chloride:propylene glycol (ChCl:PG) were more efficient than choline chloride:glycerol (ChCl:G) even with non-calcined CaO. However, ChCl:G might be more suitable than the others since the use of glycerol, a by-product of the ethanolysis, could reduce the overall biodiesel production costs. FTIR and XRD analyses of the used and separated CaO were performed in order to get more insight into the catalytically active phase(s). Also, the mechanisms of the CaO activation in the presence of the DESs were considered. The phase separation of the reaction mixture was faster in the presence of the DESs. Since ChCl:U and ChCl:G DESs are nontoxic, biodegradable, biorenewable and „green" solvents and provide the elimination of the calcination step of CaO, thus reducing the overall process costs, the non-calcined CaO catalytic systems with these DESs are recommended for further optimization.

Keywords: calcium oxide; choline chloride; cosolvent; deep eutectic solvent; ethanolysis

1. Introduction

Biodiesel represents a promising alternative energy source to petro-diesel because of its biodegradability, lower toxicity, CO_2 and sulfur emission, the possibility of being used as a fuel alone or mixed with diesel, etc. Most commonly, it is produced by transesterification (alcoholysis) of vegetable oils or animal fats with methanol or ethanol in the presence of homogeneous catalysts. The growing demand for biodiesel requires improving its manufacturing process through the use of large production capacity, new catalytic systems, non-edible vegetable oils as feedstocks and simplified process operations. Heterogeneous (solid) catalysts used in biodiesel production provide number of benefits, compared to homogeneous catalysts, like simpler and cheaper catalyst separation and product purification. Also, the heterogeneous catalyst can be used repeatedly, thus lowering the operating costs. In addition, they have low corrosion risk and low environmental threats. Besides their benefits, solid catalysts have some drawbacks, such as lower reaction rate, possible deactivation and leaching. CaO possesses many desirable properties of heterogeneous catalysts for the production of biodiesel, such as tolerance to moisture and free fatty acids present in the low-quality feedstocks, low solubility in alcohols, low cost, noncorrosivness, environmentally-friendly nature, production from waste and natural materials and reusability [1,2]. However, when exposed to the air, CaO adsorbs CO_2 and water, forming $CaCO_3$ and $Ca(OH)_2$ at the surface of catalyst particles, which inhibit its catalytic activity [3]. Therefore, CaO should be activated by calcination at a high temperature [1] or by washing with methanol [4], glycerol [5], biodiesel [6], or biodiesel containing small amounts of acylglycerols and methanol [7]. Glycerol washing is more efficient in CaO activation than calcination or methanol washing [8].

In the last decade, ethanol has frequently been explored as the acyl acceptor in the biodiesel production [9-11]. Compared to methanol, ethanol is less toxic, has higher dissolving power

3

67 in vegetable oils and can be produced from agricultural renewable resources. Moreover, fatty

68 acid ethyl esters (FAEEs) have higher heat capacity and cetane number, higher oxidative

69 stability, lower iodine value, better lubricity properties, lower cloud point and pour point than

70 fatty acid methyl esters (FAMEs) [9,11]. Furthermore, the environmental advantages of

71 FAEEs, compared to FAMEs, are less exhaust gas emissions [11] and higher biodegradability

72 in water [9]. An additional advantage of ethanolysis is a higher esters yield [9]. However,

73 ethanol is more expensive than methanol, has lower transesterification reactivity caused by

74 steric hindrance of the longer carbon chain, and forms an azeotrope with water, making its

75 separation more difficult. Besides that, the ethanolysis demands more energy, FAEEs yield

76 depends significantly on the presence of water in the reaction mixture, and more stable

77 emulsions are formed. Also, viscosity and the acid value of FAEEs are higher than those of

78 FAMEs [11].

79 Since oil and alcohol are immiscible, the biodiesel production system consists of at least two

80 phases. Different organic solvents, added as cosolvents to a transesterification reaction

81 system, increase miscibility of the reactants, thus providing a pseudo-homogeneous reaction

82 system [12]. Their use is recommended for the reaction performed at a lower temperature

83 when the mass transfer limits the chemical reaction [13]. The added cosolvent should be inert

84 to the reactants, the products, and the catalyst. Besides organic solvents, ionic liquids (ILs)

85 and deep eutectic solvents (DES) can be used in biodiesel production as cosolvents and

86 catalysts [14]. While ILs are organic salts that contain only ions, DESs are generally prepared

87 by combining two classes of compounds, namely hydrogen bond acceptors (HBAs) and

88 hydrogen bond donors (HBDs), in different molar ratios. The resulting DES has lower

89 melting point because of hydrogen bonding [14]. Most commonly used HBAs are substituted

90 quaternary ammonium salts, such as choline chloride (ChCl) [15]. HBDs are usually different

91 organic compounds, such as organic acids, polyols, amides, sugars etc. In comparison with

92 the conventional ILs, DESs are cheaper, less toxic, biodegradable, and easy to be prepared

93   from available and inexpensive precursors. Additional beneficial properties of DESs are wide

94   liquid range, low vapor pressure, non-flammability, and compatibility with water. These

95   properties make DESs useful in biodiesel production and purification as catalysts and

96   solvents, respectively [14].

97   ChCl-based DESs have mostly been applied in homogeneously-catalyzed methanolysis and

98   ethanolysis [16-19], while their use in heterogeneously-catalyzed transesterification reactions

99   is rare [20]. The addition of the ChCl:glycerol (ChCl:G) DES (molar ratio 1:2) as a cosolvent

100   to the homogeneously-catalyzed rapeseed oil methanolysis system favors the production of

101   methoxide ions by the higher effective dissolution of the base catalyst (NaOH) in the

102   DES/methanol mixture [16]. Also, this DES reduces the soap formation in the

103   homogeneously-catalyzed ethanolysis of palm oil [17,18], thus making the separation and

104   purification stages easier. The same result was observed with ChCl:ethylene glycol

105   (ChCl:EG) [19]. Heterogeneous ethanolysis of vegetable oils in the presence of a DES used as

106   a cosolvent has not been studied so far. However, ChCl:G DES activates CaO in the

107   methanolysis of rapeseed oil, thus eliminating calcination, and makes its separation from the

108   reaction mixture faster [20].

109   The present study investigates the effects of different ChCl-based DESs on the expired

110   sunflower oil ethanolysis over non-calcined and calcined CaO. These DESs were prepared

111   from ChCl and the selected HBDs, such as amides (urea, 1,3-dimethylurea and thiourea) and

112   polyols (propylene glycol, ethylene glycol and glycerol). For comparison, the CaO-catalyzed

113   reactions were also carried out in the presence of ChCl and individual HBDs, while the

114   control reactions were performed in the presence of only non-calcined or calcined CaO,

115   $CaCO_3$ or $Ca(OH)_2$. Besides that, the reusability of non-calcined CaO catalyst activated by the

116   prepared DESs and the ChCl:G DES coupled with either recovered or fresh CaO, as well as

117   the separation of the phases at the end of the reaction were investigated. After the optimal 2 h

118   reaction time, the used separated CaO was analyzed by FTIR and XRD in order to get a better

119 understanding of the catalytically active phase(s). The mechanisms of the CaO activation in

120 the presence of the DESs were also considered. The main goal was to compare the catalytic

121 activities of non-calcined and calcined CaO in the absence and the presence of the prepared

122 DESs used as cosolvents and CaO activators. To the best of authors' knowledge, ChCl:1,3-

123 dimethylurea (ChCl:DMU) and ChCl:propylene glycol (ChCl:PG) DESs have not been used

124 yet in transesterification reactions, while ChCl:urea (ChCl:U), ChCl:DMU, ChCl:thiourea

125 (ChCl:TU) and ChCl:PG DESs (all in the molar ratio of 1:2) have not been applied in the

126 ethanolysis of sunflower oil.

127 **2. Materials and methods**

128 *2.1 Materials*

129 Expired commercial sunflower oil (Dijamant, Zrenjanin, Serbia) was provided from a local

130 shopping store. The acid, saponification, iodine and peroxide values of the oil, determined

131 according to the AOCS official methods [21], were 0.64 mg KOH/g, 191 mg KOH/g, 126 g

132 I_2/100 g and 7.25-11.97 mEq/kg, respectively. Density of 907.1 kg/m^3 was determined

133 picnometrically at 25 °C. Dynamic viscosity, determined by a rotational viscometer (Visco

134 Basic Plus v. 0.8, Fungilab S.A., Barcelona, Spain) at 25 °C was 72.70 mPas. Its fatty acid

135 composition is as follows: C-16:0 (5.41±0.08%), C-18:0 (3.19±0.04%), C-18:1

136 (25.23±0.47%), C-18:2 (63.07±0.37%), C-22:0 (1.31±0.13%), C-22:1 (0.55±0.03%) and C-24

137 (0.52±0.06%), i.e. saturated (10.77±0.04%), mono-unsaturated (25.93±0.58%) and poly-

138 unsaturated (63.21±0.39%) fatty acids. Absolute ethanol (99.5%) was provided by Lachema

139 (Neratovice, Czech Republic). Choline chloride (≥ 98.0%), 1,3-dimethylurea (≥ 98.0%),

140 ethylene glycol (≥ 99.0%), CaO (≥ 99.0%) CaCO$_3$ (≥ 99.0%) and Ca(OH)$_2$ (≥ 99.0%) were

141 provided by Sigma Aldrich (St. Louis, USA). Urea and thiourea (both 99.5%) were purchased

142 from Zorka-Pharma (Šabac, Serbia) while propylene glycol and glycerol (both Ph Eur grade)

143 were from MeiLab (Belgrade, Serbia). Also, the following solvents were used: ethyl acetate

6

144 (99.5%, Merck Millipore, Darmstadt, Germany), *n*-hexane (99%, HPLC grade, LGC

145 Promochem, Wesel, Germany) and HPLC grade, JT Baker, Center Valley, Pennsylvania),

146 glacial acetic acid (Zorka-Pharma, Šabac, Serbia) and 2-propanol (HPLC grade, JT Baker,

147 Center Valley, Pennsylvania), and methanol (HPLC grade, LGC Promochem, Wesel,

148 Germany). NaOH pellets (98.0%) and HCl (36 wt.%) were from Sigma Aldrich and

149 Centrohem (Stara Pazova, Serbia), respectively. A standard mixture of ethyl esters of

150 palmitic, stearic, oleic, linolenic and linoleic acids (20.0% of each ester), triolein, diolein and

151 monoolein were purchased from Sigma Aldrich (St. Louis, USA).

152 *2.2 Preparation of deep eutectic solvents*

153 ChCl was mixed with an HBD (urea, 1,3-dimethylurea, thiourea, propylene glycol, ethylene

154 glycol or glycerol) at the 1:2 molar ratio in a round-bottomed flask, as described elsewhere

155 [22]. The prepared DESs were stored in well-closed glass bottles in a desiccator containing

156 $CaCl_2$. The physical and thermodynamic properties of the DESs can be found elsewhere [22].

157 *2.3 Ethanolysis: equipment, reaction conditions and procedure*

158 The ethanolysis reaction was conducted in a batch reactor at atmospheric pressure. The

159 reactor (250 mL two-neck round-bottomed flask) was equipped with a magnetic stirrer (600

160 rpm) and a condenser. It was placed in a glass chamber kept at the constant temperature of

161 70±0.5 °C by circulating water from a water bath by a pump. Two series of experiments were

162 conducted, namely with non-calcined and calcined CaO. First, CaO from a commercial

163 package was calcined at 550 °C for 2 h, as recommended elsewhere [23]; the activated CaO

164 was cooled and kept until the use in a well closed, glass bottle in a desiccator containing

165 $CaCl_2$ and KOH. Also, non-calcined CaO was used directly from the same commercial

166 package, without any pretreatment. Additionally, $CaCO_3$ and $Ca(OH)_2$, taken directly from

167 the commercial packages, were used to evaluate their catalytic effect on the reaction in the

168 absence of the cosolvent or CaO. For all experiments, ethanol, the catalyst and the cosolvent

169   (DES or their individual components when used) in amounts of 14.38, 3.80 and 4.60 g,

170   respectively were added to the reactor. The ethanol-to-oil molar ratio was 12:1, as suggested

171   elsewhere [10,24,25]. The amount of the cosolvent was 20% of the mass oil in all

172   experiments, as recommended elsewhere [12]. This suspension was stirred for 30 min. After

173   turning off the magnetic stirrer, the oil (22.98 g), previously preheated at 70 °C in a stirred

174   glass beaker, was added to the reaction flask. Then, the magnetic stirrer was switched on and

175   the reaction was timed. During the reaction, samples were taken from the reaction mixture,

176   immediately quenched by adding a required amount of the aqueous 5 M HCl solution to

177   neutralize the catalyst and centrifuged (Sigma 2-6E, Germany; 3500 rpm, 10 min). The upper

178   layer (ester/oil fraction) was withdrawn, dissolved in the 2-propanol/n-hexane (5:4 v/v)

179   mixture in an appropriate ratio (1:10 or 1:200 for qualitative TLC or quantitative HPLC

180   analysis, respectively), and filtered through a 0.45 μm Millipore filter. The resulting filtrate

181   was used for thin layer (TLC) and liquid chromatography (HPLC) analyses. All experiments

182   were run in duplicate.

183   *2.4 Separation of FAEEs*

184   After the reaction was completed, the reaction mixture was poured into a separatory funnel

185   and allowed to settle at the room temperature. Three layers were formed during the separation

186   stage. The top layer consisted mostly of FAEEs and smaller amounts of triacylglycerols

187   (TAGs), diacylglycerols (DAGs), monoacylglycerols (MAG) and CaO, the middle layer

188   contained a mixture of excess ethanol, glycerol and the used cosolvent (DES, ChCl or

189   individual HBDs), and the bottom layer was the precipitated CaO.

190   *2.5 Reusability of the non-calcined CaO catalyst activated by different DESs*

191   The CaO catalyst was separated from the reaction mixture with different DESs after 2 h by

192   centrifugation and used without any treatment (no addition of DES, washing and

193   recalcination) in the next five batches under the same reaction conditions.

194 *2.6 Reusability of the ChCl:G DES with recovered or fresh CaO*

195 The ChCl:G DES was recovered from the reaction mixture after the 2 h reactions catalyzed

196 with the recovered or fresh CaO. The reaction mixture was first centrifuged at the room

197 temperature, and the upper and middle layers were separated from the CaO precipitate by

198 decantation. The middle layer was first evaporated to remove excess ethanol and then dried at

199 110 °C until constant weight; hence, the resulting product contained mainly the ChCl:G DES

200 and glycerol extracted by the DES (here called the recovered ChCl:G DES/glycerol product).

201 To test the reusability of the ChCl:G DES coupled with either recovered or fresh CaO, three

202 series of experiments were conducted following the above-described procedure (Section 2.3)

203 using: (1) the recovered ChCl:G DES/glycerol product and the recovered CaO; (2) the

204 recovered ChCl:G DES/glycerol product and fresh CaO; and (3) the treated recovered ChCl:G

205 DES/glycerol product and fresh CaO. For the third series, the recovered ChCl:G DES/glycerol

206 product was treated with an appropriate amount of ChCl for 1 h at 70 °C to prepare the

207 ChCl:G DES in the 1:2 molar ratio.

208 *2.7 Analytical methods*

209 *2.7.1 FAEE content determination*

210 The chemical composition of each sample of the reaction mixture was first estimated

211 qualitatively by TLC and then quantitatively by the HPLC method described elsewhere [25].

212 The TAG conversion degree, x_A, was calculated from the percentage of TAGs in the ester/oil

213 fraction of the reaction mixture at the beginning, c_{A0}, and after a certain time, c_A, of the

214 reaction:

215
$$x_A = 1 - \frac{c_A}{c_{A0}} \tag{1}$$

216 The calibration curves, prepared by using the standard mixture of FAEEs and the standard

217 TAGs, as described elsewhere [24], were used for the quantification of FAEEs and TAGs.

9

218   The contents of TAGs, DAGs, MAGs and FAEEs were calculated from the corresponding

219   peak areas using the calibration curves.

220   *2.7.2 FTIR analysis*

221   The FTIR spectra of the catalysts were recorded at the room temperature by a Michaelson

222   Bomen MB-series spectrophotometer, using the KBr pellet (1.5 mg/150 mg) technique, in the

223   range of 4000–400 cm^{-1} and with the 2 cm^{-1} resolution. The mixture of a catalyst and KBr

224   was vacuumed and pressed (200 MPa) in order to form a thin, permeable pastille.

225   *2.7.3 XRD analysis*

226   The X-ray powder diffraction measurements were performed by a Philips PW 1050 X-ray

227   powder diffractometer using Ni-filtered Cu $K\alpha_{1,2}$ ($\lambda = 1.54178$ Å) radiation and the Bragg–

228   Brentano focusing geometry. Measurements were done at room temperature over the 2θ range

229   of 7–70° with a scanning step width of 0.05° and a counting time of 3 s per step.

230   *2.7.4 Solubility of CaCO₃ and Ca(OH)₂ in deep eutectic solvents*

231   The solubility of $CaCO_3$ and $Ca(OH)_2$ in DESs was determined by the acid-base (HCl/NaOH)

232   titration [20]. The saturated solutions of $CaCO_3$ and $Ca(OH)_2$ in the DESs were prepared.

233   Then, 2 mL of HCl (0.01 $mol \cdot dm^{-3}$) were added into 4 mL of the saturated solution of $CaCO_3$

234   or $Ca(OH)_2$. NaOH (0.015 $mol \cdot dm^{-3}$) was used to neutralize excess HCl. The measured

235   solubility of $CaCO_3$ and $Ca(OH)_2$ in the DESs at 70 °C are given in **Table 1**.

236

Table 1 Solubility (in wt %) of $CaCO_3$ and $Ca(OH)_2$ in the DESs at 70 °C.[a]

DES	$CaCO_3$	$Ca(OH)_2$
ChCl:U	0.44±0.11	8.03±0.07
ChCl:TU	0.34±0.08	4.67±0.09
ChCl:DMU	0.16±0.05	3.85±0.13
ChCl:PG	0.90±0.13	0.30±0.09
ChCl:EG	0.47±0.10	1.84±0.12
ChCl:G	0.89±0.09	2.09±0.06

[a] Mean of three measurements ± standard deviation.

3. Results and discussion

3.1 Ethanolysis of expired sunflower oil

3.1.1 Catalytic activity of CaO, Ca(OH)₂ and CaCO₃

Both non-calcined and calcined CaO, $CaCO_3$ and $Ca(OH)_2$ were tested as catalysts in the

ethanolysis of expired sunflower oil in the absence of any DESs, HBDs or ChCl. Both types

of CaO and $Ca(OH)_2$ showed the observable catalytic activity of different intensity while

$CaCO_3$ had no catalytic activity (**Fig. S.1, Supplementary material**). Due to an increased

number of available active centers on the surface of catalyst particles, calcined CaO was more

active than non-calcined CaO. The sigmoidal dependence of FAEE content on time could be

attributed to the mass transfer limitation at the beginning of the reaction, as it was observed

for CaO-catalyzed methanolysis [4,8,23] and ethanolysis [10,26] reactions. The FAEE content

increased slowly during the initial stage of the reaction on account of slow TAG conversion.

The FAEE content of 48.9±1.4% was obtained in 3 h using calcined CaO, which was four

times higher than that in the reaction catalyzed by non-calcined CaO. Higher FAEE content

(97.8±2.1%) was achieved with calcined CaO in 5 h than with non-calcined CaO

11

254 (84.5±1.4%). These results were similar to those reported for the CaO-catalyzed ethanolysis

255 reactions [10,26]. $Ca(OH)_2$ was much less active than CaO, which agreed with the previous

256 studies on the $Ca(OH)_2$-catalyzed ethanolysis [26,27], because of its less basicity [28]. While

257 Gryglewicz [29] reported no catalytic activity of $Ca(OH)_2$ in the methanolysis of rapeseed oil,

258 several other studies demonstrated its catalytic activity in the transesterification reactions

259 [3,8,30-32]. No catalytic activity of $CaCO_3$ has already been reported [8,20,30]. As a

260 conclusion, $CaCO_3$ and $Ca(OH)_2$ layers formed on the surfaces of CaO particles will reduce

261 its catalytic activity [3,20].

262 *3.1.2 Catalytic activity of choline chloride, hydrogen bond donors and DESs in the absence of*

263 *CaO*

264 The ethanolysis of expired sunflower oil was conducted in the presence of ChCl, the HBDs

265 (urea, 1,3-dimethylurea, thiourea, propylene glycol, ethylene glycol or glycerol) or the DESs

266 (ChCl:U, ChCl:DMU, ChCl:TU, ChCl:PG, ChCl:EG and ChCl:G) and in the absence of CaO.

267 No reaction between the oil and ethanol indicated that the tested compounds had no catalytic

268 activity.

269 *3.1.3 Catalytic activity of CaO in the presence of amide-based hydrogen bond donors and*

270 *DESs*

271 The variations of FAEE content with the progress of the CaO-catalyzed ethanolysis of expired

272 sunflower oil in the presence of ChCl, the amide-based HBDs (urea, 1,3-dimethylurea and

273 thiourea) and the amide-based DESs (ChCl:U, ChCl:DMU and ChCl:TU) are shown in **Fig. 1**.
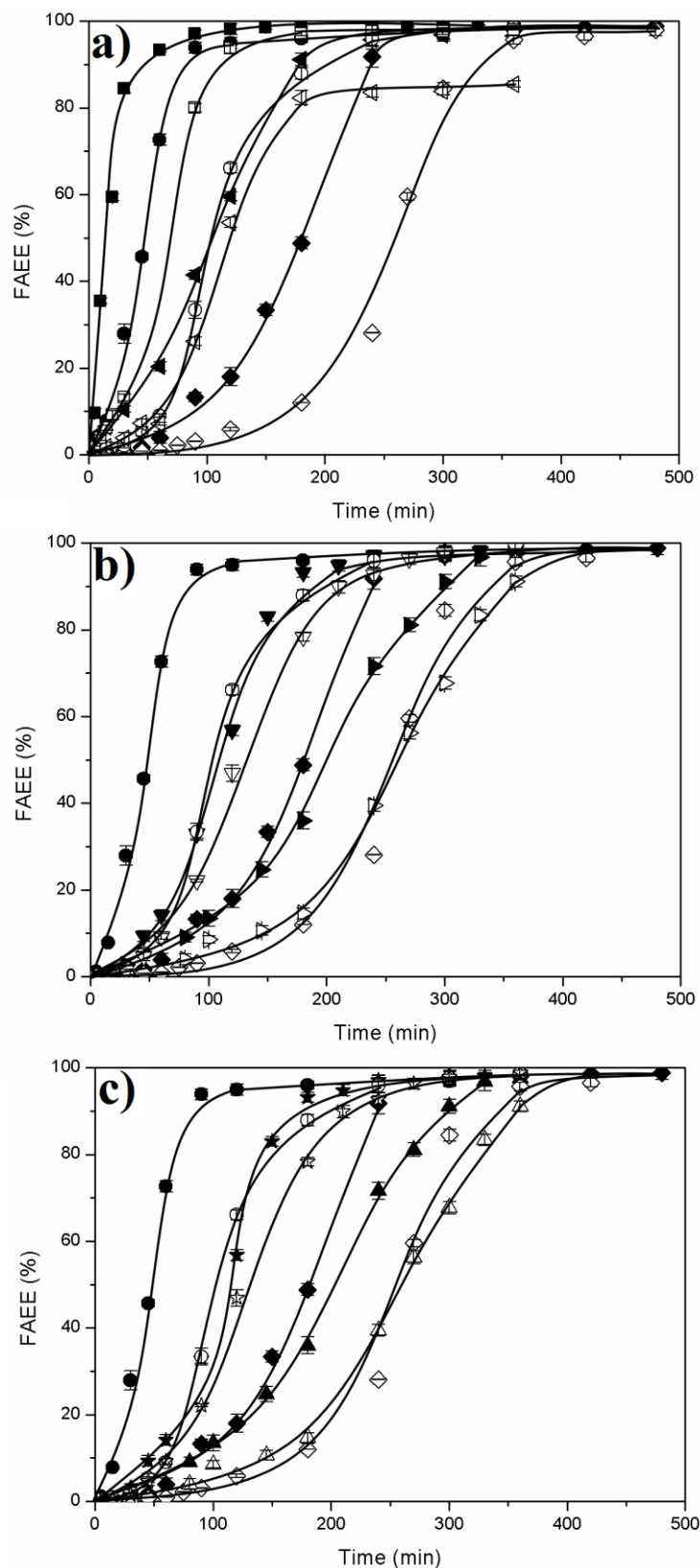
274

Fig. 1. The variations of the FAEE content with the progress of expired sunflower oils ethanolysis catalyzed by calcined (black symbols) or non-calcined (open symbols) CaO with no addition of HBDs or DESs (rhomb) and with addition of ChCl (circle) (**a-c**), urea (left triangle), ChCl:U (square) (**a**), 1,3-dimethylurea (right triangle), ChCl:DMU (down triangle) (**b**), thiourea (up triangle) and ChCl:TU (star) (**c**).

13

The presence of ChCl significantly accelerated the reaction over calcined or non-calcined

CaO but calcined CaO was more active. The addition of urea, 1,3-dimethylurea or thiourea

also accelerated the reaction over both non-calcined and calcined CaO and calcined CaO

systems provided a faster reaction and a higher final FAEE content compared to the

corresponding non-calcined CaO systems. Among the amide-based HBDs, the 1,3-

dimethylurea/calcined CaO system was the most effective. The amide-based DESs gave even

better results than the amides or ChCl, the results being better in combination with calcined

CaO than with non-calcined CaO. The efficiency of the amide-based DESs with both calcined

and non-calcined CaO decreased in the following order: ChCl:U > ChCl:DMU > ChCl:TU.

Since all of them could remove $CaCO_3$ and $Ca(OH)_2$ from the surface of catalyst particles,

thus increasing catalytic activity of CaO (**Table 1**), the differences in their efficiency might be

attributed to their different viscosity, which decreased in the same order (**Fig. S.2,**

Supplementary material) [22,33]. Among these DESs, only ChCl:U is liquid at room

temperature, while others are solids, so despite heating and mixing with ethanol under

stirring, the ChCl:DMU and ChCl:TU DESs have a strong effect on the mass transfer.

3.1.4 Catalytic activity of CaO with polyol-based hydrogen bond donors and DESs

The variations of the FAEE content with the progress of expired sunflower oil ethanolysis in

the presence of ChCl, the polyol-based HBDs (propylene glycol, ethylene glycol and

glycerol) and the polyol-based DESs (ChCl:PG, ChCl:EG and ChCl:G) are shown in **Fig. 2**.
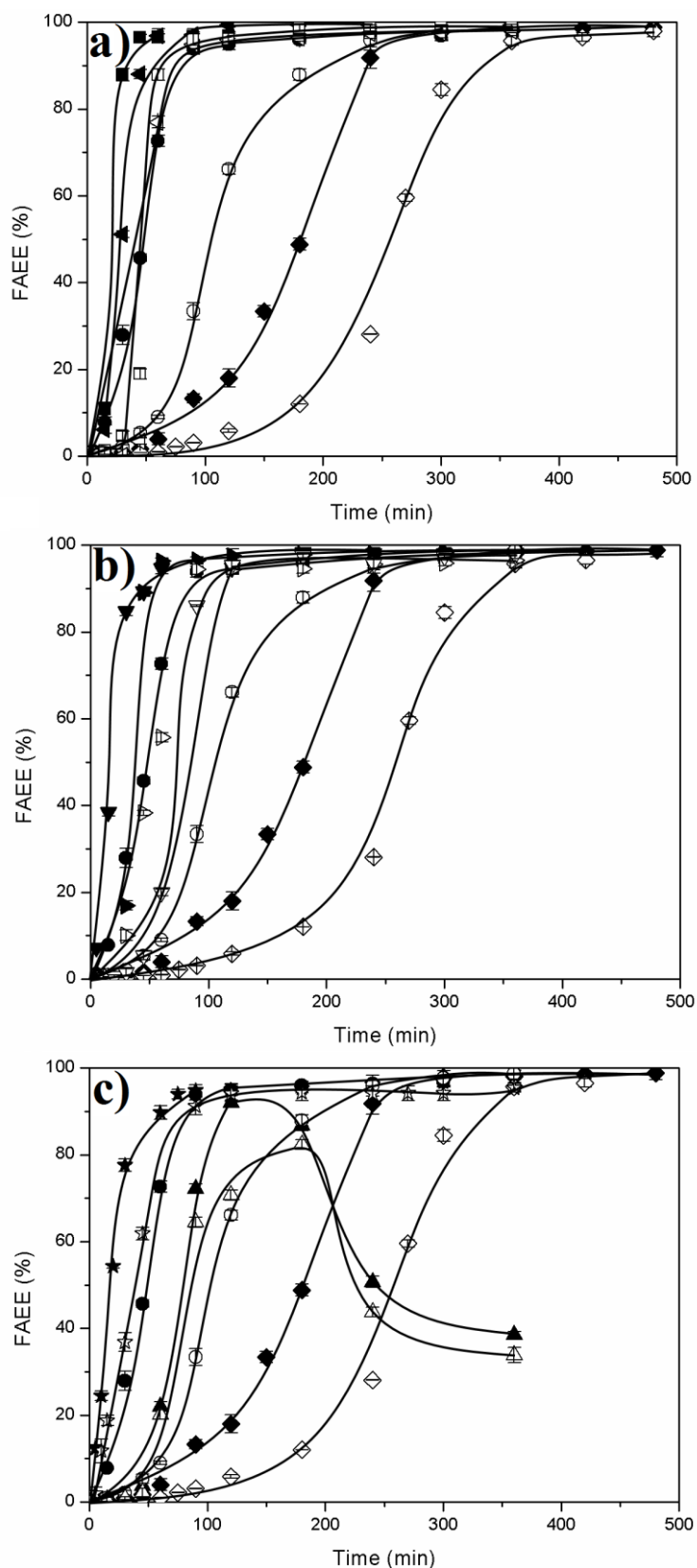
299

Fig. 2. The variations of the FAEE content with the progress of expired sunflower oils ethanolysis catalyzed by calcined (black symbols) or non-calcined (open symbols) CaO with no addition of HBDs or DESs (rhomb) and with addition of ChCl (circle) (**a-c**), ethylene glycol (left triangle), ChCl:EG (square) (**a**), propylene glycol (right triangle), ChCl:PG (down triangle) (**b**), glycerol (up triangle) and ChCl:G (star) (**c**).

15

305 All three polyol-based HBDs accelerated the ethanolysis of expired sunflower oil over both

306 calcined and non-calcined CaO, compared to the reactions in the presence of only CaO or

307 ChCl. The positive influence of all three DESs on the reaction was more pronounced with

308 calcined CaO than with non-calcined CaO. In the presence of glycerol, the decrease of FAEE

309 content in the final stage of the reaction was attributed to the reverse reaction favored by the

310 increased concentration of glycerol by-product. Lower viscosity of ethylene glycol and

311 propylene glycol compared to that of glycerol might also contribute to their more efficient

312 effect on the reaction rate. All three polyol-based DESs also gave better results with calcined

313 CaO than with non-calcined CaO, which could be explained in the same way as it was done

314 for the amide-based DESs. In these DESs the solubility of $CaCO_3$ and $Ca(OH)_2$ is higher

315 (**Table 1**).

316 *3.1.5 Selection of the "best" cosolvent*

317 Although the reactions with calcined CaO combined with HBDs or DESs provided better

318 results, they are economically and energetically more demanding than the reactions catalyzed

319 by non-calcined CaO. From this point of view, the system with non-calcined CaO should be

320 looked for potential commercial utilization. Moreover, the polyol-based DESs were superior

321 over the amide-based DESs. The same was also observed for the enzyme-catalyzed biodiesel

322 production with [34] or without microwave irradiation [35]. However, no report in the

323 available literature has compared so far the polyol- and amide-based DESs used in

324 heterogeneously catalyzed transesterification reactions.

325 Among the amide-based DESs, the most optimal choice is ChCl:U DES, while among the

326 polyol-based HBDs, the best choice should be either ChCl:EG or ChCl:PG. However, from

327 ecological point of view, PG is preferred than toxic EG. Taking into account the fact that

328 glycerol is the by-product of the transesterification, the less active ChCl:G DES might also be
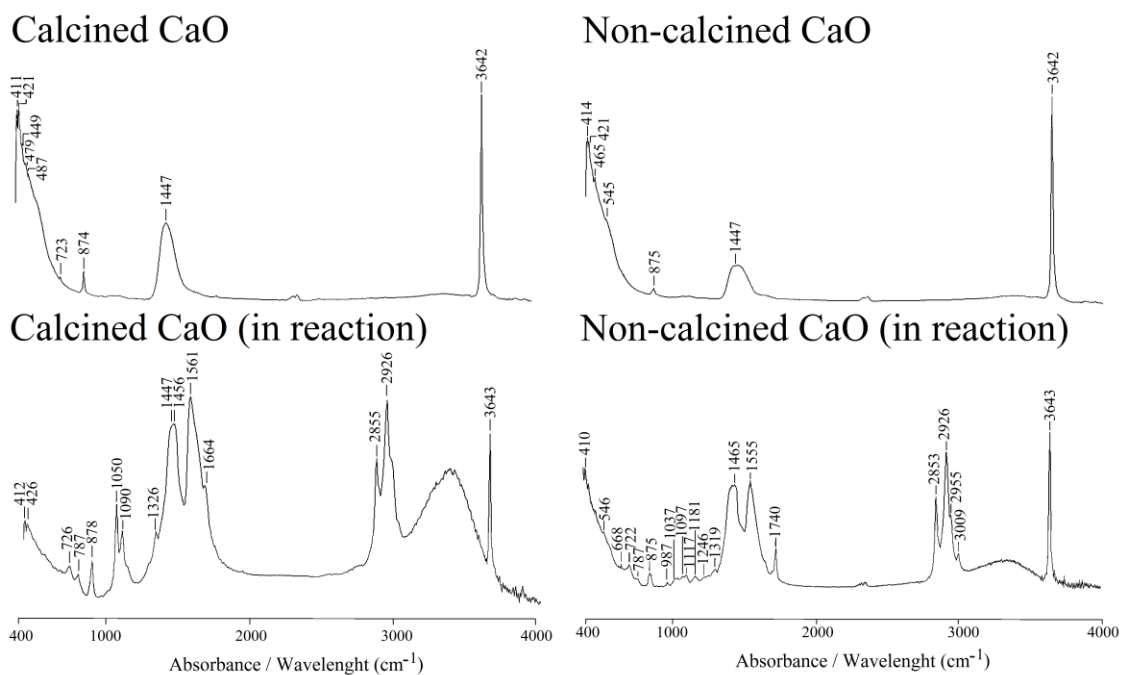
329   a very promising choice, as its use may reduce the overall costs of the process. Therefore, the

330   non-calcined CaO/ChCl:G DES system is also suggested for further optimization.

3.2 Characterization of the used CaO

332   In order to get more insight into the catalytically active phase(s), the used CaO was separated

333   from the reaction mixtures after the optimal 2 h reaction and analyzed by FTIR and XRD. For

334   comparison, commercial non-calcined CaO was also analyzed.
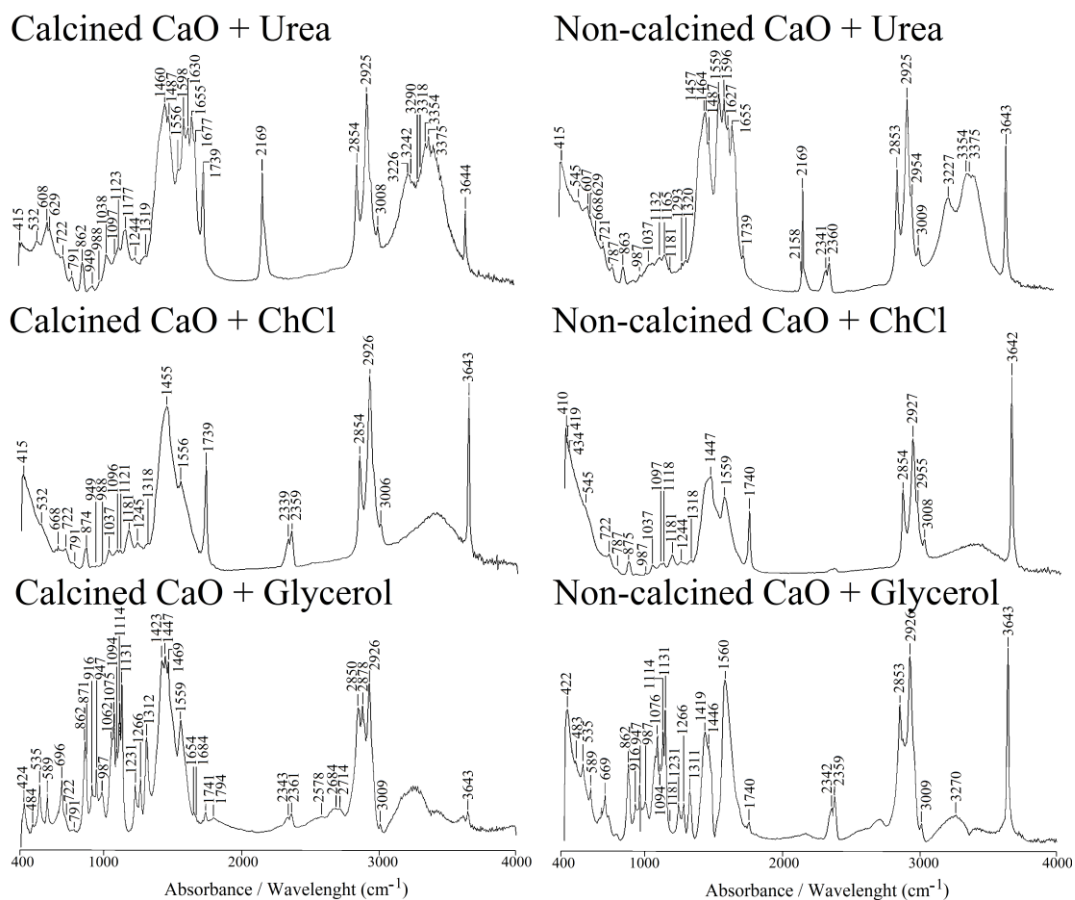
3.2.1 FTIR of CaO

336   In the FTIR spectrum of original non-calcined CaO (**Fig. 3**), the sharp peak at 3642 cm^{-1} can

337   be attributed to the O–H stretching from $Ca(OH)_2$ [20] while the bands at 1447 and 875 (874)

338   cm^{-1} are assigned to the v_3 asymmetric stretching and the v_2 symmetric deformation of

339   carbonate groups of $CaCO_3$ [20,36,37], respectively clearly indicating the presence of $CaCO_3$.

340   During storage, CaO absorbs moisture and CO_2 from the air, so its surface is being covered

341   with hydroxide and carbonate [8]. During calcination, CaO starts to lose carbonate and

342   hydroxide, so their absorption bands are less pronounced [38], as it can be seen in the FTIR

343   spectrum of calcined CaO. In all FTIR spectra of both non-calcined and calcined CaO

344   collected from the reaction mixtures, either without or with DESs or its constituents (**Figs. 3-**

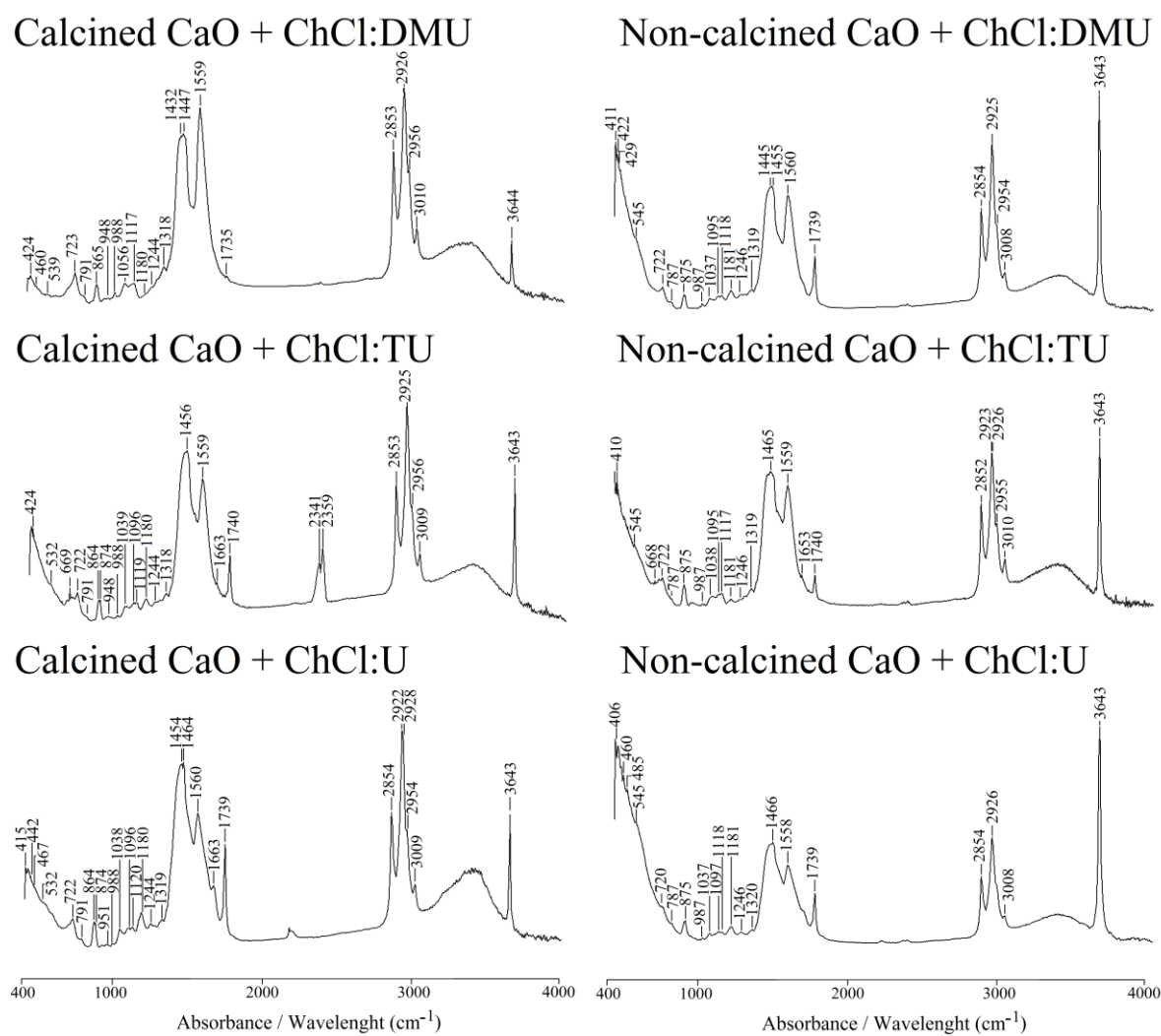345   **6**), some common bands could be identified.

Fig. 3. FTIR spectra of the original non-calcined and calcined CaO and the CaO pastes recovered from the reaction mixture after 2 h.
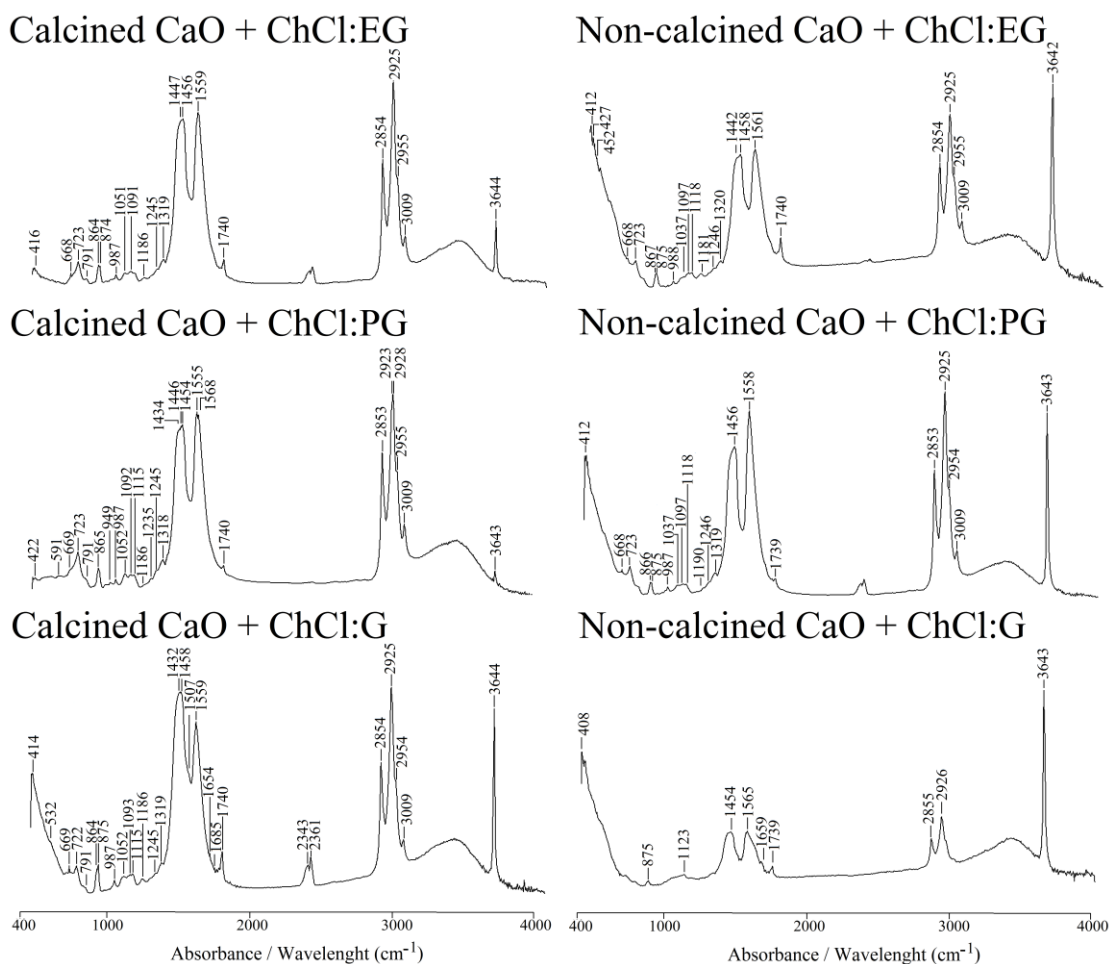

Fig. 4. FTIR spectra of the original non-calcined and calcined CaO and the CaO pastes recovered from the reaction mixture after 2 h of the reaction carried out in the presence of the DESs' constituents.

18

Fig. 5. FTIR spectra of the original non-calcined and calcined CaO and the CaO pastes recovered from the reaction mixture after 2 h of the reaction carried out in the presence of the the amide-based DESs.

19

Fig. 6. FTIR spectra of the original non-calcined and calcined CaO and the CaO pastes recovered from the reaction mixture after 2 h of the reaction carried out in the presence of the polyol-based DESs.
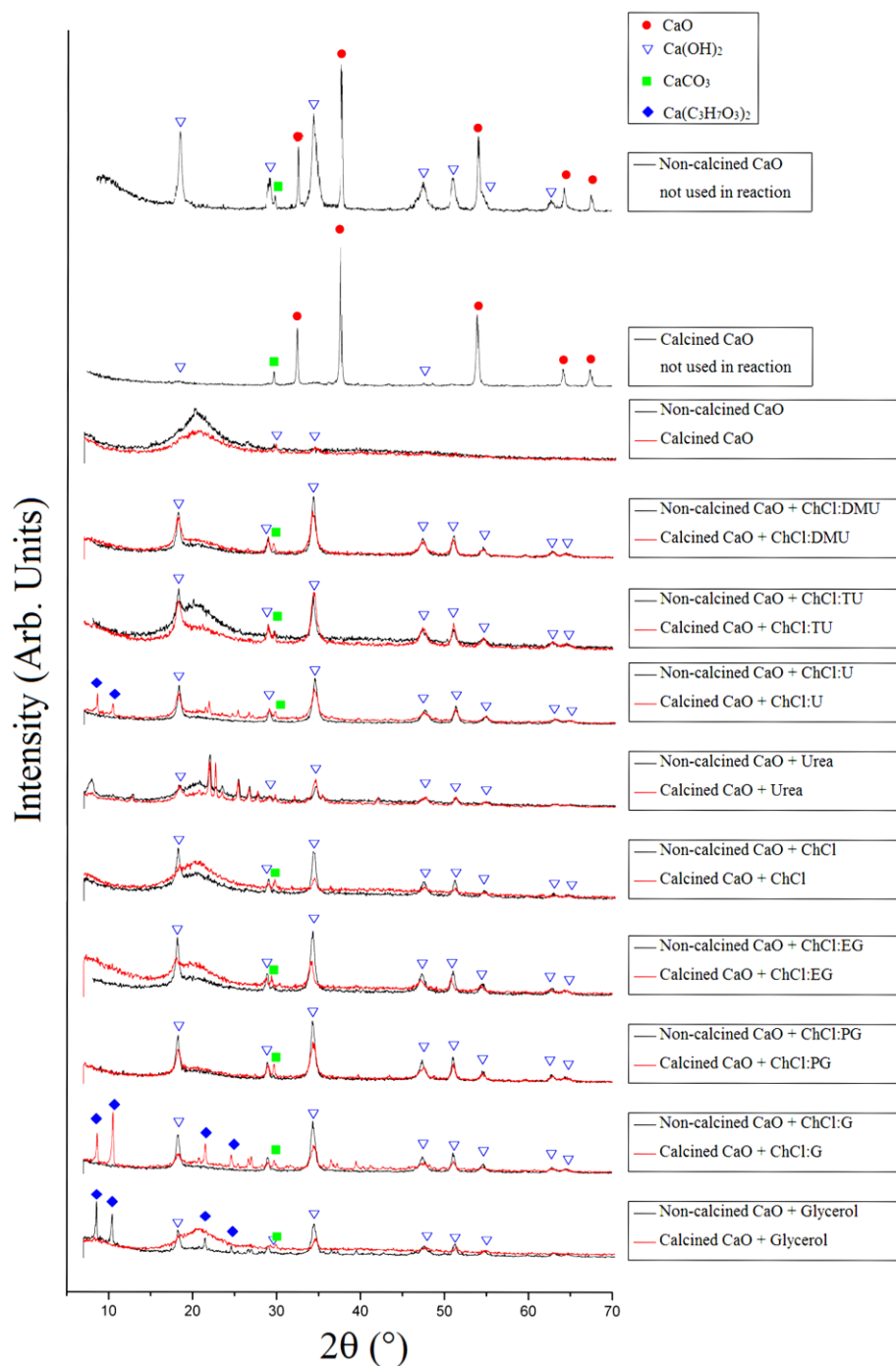
A strong, sharp and very pronounced band at 3643 cm^{-1} represents the v(O–H) stretching vibration of the –Ca–OH groups from $Ca(OH)_2$, derived from $Ca(OH)_2$ present in the sample [36] or by hydration of the CaO surface by water from the Ca-ethoxide synthesis [8]. It was also speculated that this band could be related to the C–OH groups of glyceroxide units bonded to the Ca atoms in Ca-diglyceroxide [39,40]. However, since this band is not present in the FTIR spectrum of clean Ca-diglyceroxide [8], it indicates the presence of $Ca(OH)_2$. A broad band in the range of 3000–3600 cm^{-1} arises from the O–H stretching vibrations from $Ca(OH)_2$ [36] or from the hydrogen bond of the O–H group [20,40]. This suggests adsorption of ethanol molecules on the surface of CaO via O–H group [8] and/or the possible contribution of water physisorbed on the surface of the CaO [39,41]. Sharp bands in the range

371   of 2800–3000 cm^{-1} are due to the v(C–H) stretching vibrations of –CH_3 and –CH_2 groups.

372   These bands are a characteristic of Ca-ethoxide [36,42,43] but they also appear in the

373   spectrum of Ca-diglyceroxide [20,39-41]. Sharp bands in the range of 1400–1600 cm^{-1}

374   correspond to the v(C–H) bending vibrations from Ca-diglyceroxide [20,39,40], as well as the

375   bands around 1460 cm^{-1} in the Ca-ethoxide spectrum [43]. Sharp but weak band around 1319

376   cm^{-1} can be assigned to the C–O–H bending modes of glyceroxide units from Ca-

377   diglyceroxide [8,39]. However, in the FTIR spectrum of pure Ca-diglyceroxide, another

378   characteristic band for this bending mode is seen around 1380 cm^{-1} [8,39], which cannot be

379   revealed in our spectra. Many sharp and weak bands in the ranges of 1200–1350 cm^{-1} and

380   700–1000 cm^{-1} arise from various bending modes of C–H bonds, typically seen in the Ca-

381   diglyceroxide spectrum [8,39,44]. Sharp and weak bands for the stretching vibration of –C–O

382   in the C–OH group of primary alcohol (in the 1050–1085 cm^{-1} range) and in C_2OH group of

383   secondary alcohol (in the 1125–1205 cm^{-1} range) are also noticeable. These bands appear in

384   the spectrum of Ca-diglyceroxide [8,20,39,44]. However, band for the –C–O (primary

385   alcohol) stretching can also arise from Ca-ethoxide [43]. Sharp and weak bands around 860–

386   870 cm^{-1} arise from the v(C–C) stretching vibration [8,39]. The sharp, small and weak band

387   around 875 cm^{-1} arise from the v_2 symmetric deformation of carbonate groups of $CaCO_3$

388   [8,20,36,37] while the other band at around 1447 cm^{-1} can be assigned to the v_3 asymmetric

389   stretching of carbonate groups of $CaCO_3$ [36] overlapped with surrounding stronger bands.

390   This indicates the presence of small amounts of $CaCO_3$.

391   *3.2.2 XRD of CaO*

392   The XRD analysis of non-calcined CaO (**Fig. 7**) reveals the peaks at 32.4, 37.55, 54.05, 64.35

393   and 67.55° 2θ and the peaks at 18.15, 34.25, 47.3, 51, 62.75 and 64.35° 2θ that could be

394   assigned to the CaO phase (PDF#82-1690) and $Ca(OH)_2$ (PDF#84-126), respectively while

395   the peak at about 29.5° and a very weak peak at 43.14° 2θ indicate the presence of $CaCO_3$

396   phase (PDF#85-1108), which proves the sensitivity of CaO to CO_2 and moisture from the

atmosphere. For the calcined CaO sample (**Fig. 7**), the dominant phase is CaO while very

broad peaks at about 18, 34 and 50.9° 2θ suggest the presence of $Ca(OH)_2$ phase in a small

amount. In addition, the peak at 29.45° 2θ may be attributed to the $CaCO_3$ phase. This

suggests that CaO has successfully been activated by calcination.

Fig. 7. XRD patters of non-calcined and calcined CaO combined with different DESs (ChCl:DMU, ChCl:TU, ChCl:U, ChCl:EG, ChCl:PG and ChCl:G) or combined with constituents of DESs' (urea, ChCl and glycerol), all used as catalysts in ethanolysis.

22

405 In the XRD patterns of non-calcined and calcined CaO combined with different DESs or with

406 their constituents (**Fig. 7**), the presence of $Ca(OH)_2$ and $CaCO_3$ phase is proven by its

407 characteristic peaks at about 18.15, 28.85, 34.2, 47.35, 51.05 and 54.55° 2θ and the peaks at

408 about 29.4° 2θ. In the samples of non-calcined or calcined CaO with amide- or polyol-based

409 DESs or with constituents of DESs (ChCl, urea and glycerol), the presence of $Ca(OH)_2$ with

410 little $CaCO_3$ is obvious. Ca-diglyceroxide can be identified by its most intensive peaks at 8.5

411 and 10.4 and 21.3° 2θ (PDF#21-1544) only in the samples of the following systems: calcined

412 CaO/ChCl:G, calcined CaO/ChCl:U and non-calcined CaO/glycerol. The broad peak

413 (amorphous hump) with a maximum at about 20.5° 2θ plausible arises from complex

414 mixtures of organic compounds occurring during the reaction. The intensity of this

415 amorphous hump in some cases is very pronounced (for example, calcined CaO/ChCl:EG and

416 non-calcined CaO/ChCl:TU) while for same samples (non-calcined CaO and calcined CaO),

417 it becomes dominant at XRD patterns. In the samples of non-calcined or calcined CaO

418 collected after the reaction without or with DESs, no XRD peaks of CaO can be seen because

419 of the hydration of CaO during the catalyst collection step [20].

420 The dominant broad peak at about 20.5° 2θ in the samples of non-calcined or calcined CaO

421 collected from the reaction mixtures can be explained easily. Since the FAEE content after 2 h

422 in these reactions was very low (5.9±0.3% and 18.0±2.1%, respectively), it was clear that the

423 amount of glycerol (a by-product) was too low to react with CaO and produce enough amount

424 of catalytically active Ca-diglyceroxide. This was in accordance with Kouzu et al. [44] who

425 reported that after 0.25 h of the CaO-catalyzed methanolysis of soybean oil, the XRD patterns

426 indicated the presence of only CaO and $Ca(OH)_2$ while the XRD patterns of $Ca(C_3H_7O_3)_2$

427 were noticeable after 2 h (when the reaction was completed). The amorphous hump could also

428 originate from Ca-ethoxide produced in the earlier stage of the reaction. The presence of Ca-

429 diglyceroxide in the XRD pattern of the calcined CaO/ChCl:U and CaO/ChCl:G system was

430 correlated with their high FAEE contents of 98.1±1.2% and 94.9±1.4%, respectively. Among

431   non-calcined CaO/amide-based DESs, only the non-calcined CaO/ChCl:U system provided

432   high FAEE content of 93.8±1.3%, unlike the systems with ChCl:DMU and ChCl:TU (FAEE

433   content of 36.1±1.4% and 47.0±1.9%, respectively). On the other hand, the non-calcined

434   CaO/polyol-based DESs systems provided FAEE contents higher than 94%. In the systems

435   with constituents of DESs, Ca-diglyceroxide was present only in the XRD pattern of the non-

436   calcined CaO/glycerol system, which was understandable since glycerol reacted with CaO

437   and $Ca(OH)_2$ and provided Ca-diglyceroxide before the start of ethanolysis. The FAEE

438   content with non-calcined or calcined CaO with glycerol was 70.7±1.2% and 92.0±0.5%,

439   respectively. When ChCl was present in the reaction medium, it could interact with glycerol,

440   forming ChCl:G DES (first in 1:1 and later in 1:2 ChCl-to-glycerol molar ratio). However, the

441   reaction with the non-calcined/ChCl system was not as efficient as the reaction where the

442   already prepared ChCl:G DES was added as a cosolvent. In the case of urea, a lower FAEE

443   content was reported (53.6±1.2% and 59.6±1.1% with the non-calcined and calcined

444   CaO/urea systems, respectively).

445   Additional facts need to be taken into consideration. The catalytically active phase cannot be

446   identified as Ca-diglyceroxide solely on the basis of the XRD pattern [5]. Sánchez-Cantú et

447   al. [45] reported that in the XRD of the catalyst used in the methanolysis of castor oil only

448     $Ca(OH)_2$ and $CaCO_3$ could be identified after the first use while characteristic reflections of

449   Ca-diglyceroxide almost disappeared, showing the easy dissolution of Ca-diglyceroxide

450   crystalline phase. This finding was also reported by Granados et al. [46], who ascribed it to

451   lixiviation of the active phase, causing the deactivation of the catalyst. Produced Ca-

452   diglyceroxide could also be partially solubilized in ethanol during the transesterification,

453   providing a soluble precursor, which was then transformed into the final solid base catalyst,

454   e.g. in the methanolysis of oil carried out at 60 °C this precursor was $CH_3O-Ca-O(OH)_2C_3H_5$

455   (named "calcium-X") [47]. Based on these considerations, the amount of Ca-diglyceroxide

456   crystals was possibly too small to exceed the XRD apparatus limit detection, but they were

active in transesterification, as noted by Sánchez-Cantú et al. [45]. Also, according to

Rodriguez-Navarro et al. [36], when the $Ca(OH)_2$ particles were transformed into Ca-

ethoxide, there were no XRD peaks that corresponded to crystalline alkoxide and newly

formed Ca-ethoxide was amorphous. Amorphization resulted from desolvation during oven-

drying of the sample of the produced Ca-ethoxide, so only $Ca(OH)_2$ and trace amounts of

$CaCO_3$ are seen in the XRD patterns.

3.3 Mechanisms of activation of CaO in the presence of DESs

Calcined and non-calcined CaO reacted with ethanol and glycerol, forming Ca-ethoxide [43]

and Ca-diglyceroxide [44,46,48], efficient catalysts for transesterification reaction [43,49].

$Ca(OH)_2$ present in the CaO samples can also react with ethanol and glycerol, forming Ca-

ethoxide [43] and Ca-diglyceroxide [50]. Ca-alkoxides can significantly reduce the rate of

$Ca(OH)_2$ transformation into the cemented $CaCO_3$ [36]. Mechanism pathways of CaO and

$Ca(OH)_2$ activation with alcohol or glycerol are well explained in the literature [8,50].

For both calcined and non-calcined CaO used as a catalyst, the induction period, characterized

by a low FAEE production rate, was observed but it was shorter in the case of calcined CaO

due to the increased number of available active centers on the catalyst particles released by

degradation of $Ca(OH)_2$ and $CaCO_3$. In the presence of the DESs, the induction period was

further reduced while the initial FAEE production rate significantly increased (**Figs. 1 and 2**).

This was attributed to the Ca-ethoxide formation from CaO, $Ca(OH)_2$ and $CaCO_3$ during

preheating of the catalyst, ethanol and the DES at 70 °C, which was promoted by their

dissolution into the DES. Therefore, in the beginning of the reaction, the initial concentration

of Ca-ethoxide (i.e. ethoxide ions, the first catalytic specimen) in the reaction mixture was

higher than in the absence of the DES, causing a faster ethanolysis reaction. As the reaction

progresses, the produced glycerol reacted with CaO and $Ca(OH)_2$, forming Ca-diglyceroxide

(the second catalytic specimen), which contributed to the further acceleration of the

ethanolysis. Among the amide-based DESs, CaO (either calcined or non-calcined) in the

25

483 presence of ChCl:U provided the highest FAEE content within 2 h of the reaction, probably

484 because it was less viscous than ChCl:DMU and ChCl:TU DESs, providing less mass transfer

485 limitations. All tested polyol-based DESs were less viscous than ChCl:DMU and ChCl:TU

486 [22], implying their better efficiency in the ethanolysis. It might be speculated that ChCl:G

487 DES was the most efficient system probably because Ca-diglyceroxide had already been

488 formed during preheating of the mixture of CaO, ethanol and ChCl:G DES, thus being present

489 in the reaction mixture from the beginning of the ethanolysis.

490 *3.4 Reusability of the non-calcined CaO catalyst activated by different DESs*

491 Both the catalytic activity and reusability of the non-calcined CaO catalysts activated by

492 different DESs are important for their potential industrial application. To test the activation

493 effect of the DESs on non-calcined CaO and the reusability of the activated CaO, the CaO

494 catalyst was separated from the reaction mixture with different DESs after 2 h by

495 centrifugation and used without any treatment (no addition of DES, washing and

496 recalcination) in the next five batches under the same reaction conditions. The ChCl:U DES

497 was found to be superior among the amide-based DESs (**Fig. S.3, Supplementary material**).

498 The FAEE content with ChCl:U DES was 85.5±1.57% after five time reuses. Similar results

499 were observed with different polyol-based DESs (**Fig. S.3, Supplementary material**). The

500 FAEE content achieved with ChCl:EG, ChCl:PG and ChCl:G after five time reuses was

501 86.2±0.90%, 85.2±0.72% and 83.4±1.06%, respectively. The decrease of FAEE content with

502 catalyst reuse could be due to the uncomplete CaO separation from the reaction mixture, the

503 partial loss of CaO due to its leaching and the deactivation of CaO during the reaction and

504 separation. Besides that, the reaction products might cover the surface of CaO catalyst, thus

505 reducing number of active sites [37].

3.5 Reusability of the ChCl:G DES recovered from the final reaction mixture

The reusability of the ChCl:G DES recovered from the final reaction mixture, coupled with either recovered or fresh CaO, was tested in four consecutive batch reactions, and the resulting FAEE contents found after 2 h reactions are shown in **Fig. S.4 (Supplementary material)**. The amount of the recovered ChCl:G DES in all experiments was constant (20% of the mass oil). In the first and second series of experiments, the mass of the recovered ChCl:G DES/glycerol product was increased because of glycerol extraction by ChCl:G DES [51,52].

In the first series, where the recovered ChCl:G DES/glycerol product and the recovered CaO were used, the FAEE content in the second batch (96.4±2.8%) was slightly higher than in the first batch (94.5±2.6%). This was ascribed to the presence of a higher amount of Ca-diglyceroxide originating from the recovered catalyst and the reaction between CaO and glycerol present in the recovered ChCl:G DES/glycerol product. However, the FAEE content decreased drastically in the third run (16.7±2.4%) because of the incomplete separation of the catalyst from the reaction mixture and the reduction of its catalytic activity caused by covering the surface of the catalyst by the reaction products [37].

In the second series, the recovered ChCl:G DES/glycerol product and fresh CaO were used. The FAEE content decreased steadily, being high after the third run (85.3±1.8%). Fresh CaO reacted with glycerol from the recovered ChCl:G DES/glycerol product during the preparation step, providing Ca-diglyceroxide that promoted the FAEE formation.

In the third series, where the treated recovered ChCl:G DES/glycerol product was coupled with fresh CaO. After the second batch, the FAEE content of 83.7±2.2% was smaller than that achieved in the second series, which was attributed to a lower amount of glycerol present in the treated recovered ChCl:G DES/glycerol product, leading to a lower amount of Ca-diglyceroxide.

27

3.6 Separation of fatty acid ethyl esters

Separation of the phases of the final reaction mixture into the separatory funnel at the room

temperature was much faster in the presence of the DES, for instance, ChCl:U, ChCl:PG,

ChCl:EG or ChCl:G for 1 min and ChCl:DMU or ChCl:TU for 10 min, than in its absence.

This phenomenon might be attributed to the reduction of soap formation in the presence of

these DESs, as it was observed for the homogeneously-catalyzed ethanolysis of palm oil in

the presence of ChCl:G [17,18] or ChCl:EG [19]. On the other hand, the very viscous systems

containing CaO and urea, 1,3-dimethylurea, thiourea, propylene glycol, ethylene glycol,

glycerol or ChCl did not separate even after 24 h.

4. Conclusions

Different ChCl-based DESs were tested as cosolvents in the ethanolysis of the expired

sunflower oil catalyzed by either calcined or non-calcined CaO. Among the amide-based

DESs, the ChCl:U/non-calcined CaO combination was the best choice. The polyol-based

DESs were more efficient than the amide-based. Although ChCl:EG and ChCl:PG were more

efficient, ChCl:G is more attractive because the use of glycerol as a by-product of the

transesterification will reduce the process expenses. The non-calcined CaO catalysts activated

by ChCl:U, ChCl:EG, ChCl:PG and ChCl:G DESs can be reused five times. Moreover, the

recovered ChCl:G DES coupled with fresh CaO can be used in four consecutive batches. The

phase separation at the end of the reaction occurred much faster with DES-containing

systems. Both ChCl:U and ChCl:G DESs are safe, cheap, nontoxic, biodegradable,

biorenewable and „green" solvents and provide the elimination of the calcination step of CaO,

thus reducing the overall process costs, so the non-calcined CaO catalytic systems with these

DESs are suggested for further optimization.

Appendix. Supplementary material

554

555 Supplementary material of this work can be found in online version of the paper.

Acknowledgements

556

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702

Artwork with Captions

704 **Figure Captions**

705 **Fig. 1.** The variations of the FAEE content with the progress of expired sunflower oils

706 ethanolysis catalyzed by calcined (black symbols) or non-calcined (open symbols) CaO with

707 no addition of HBDs or DESs (rhomb) and with addition of ChCl (circle) (**a-c**), urea (left

708 triangle), ChCl:U (square) (**a**), 1,3-dimethylurea (right triangle), ChCl:DMU (down triangle)

709 (**b**), thiourea (up triangle) and ChCl:TU (star) (**c**).

710 **Fig. 2.** The variations of the FAEE content with the progress of expired sunflower oils

711 ethanolysis catalyzed by calcined (black symbols) or non-calcined (open symbols) CaO with

712 no addition of HBDs or DESs (rhomb) and with addition of ChCl (circle) (**a-c**), ethylene

713 glycol (left triangle), ChCl:EG (square) (**a**), propylene glycol (right triangle), ChCl:PG (down

714 triangle) (**b**), glycerol (up triangle) and ChCl:G (star) (**c**)**.**

715 **Fig. 3**. FTIR spectra of the original non-calcined and calcined CaO and the CaO pastes

716 recovered from the reaction mixture after 2 h.

717 **Fig. 4**. FTIR spectra of the original non-calcined and calcined CaO and the CaO pastes

718 recovered from the reaction mixture after 2 h of the reaction carried out in the presence of the

719 DESs' constituents.

720 **Fig. 5**. FTIR spectra of the original non-calcined and calcined CaO and the CaO pastes

721 recovered from the reaction mixture after 2 h of the reaction carried out in the presence of the

722 the amide-based DESs.

723 **Fig. 6**. FTIR spectra of the original non-calcined and calcined CaO and the CaO pastes

724 recovered from the reaction mixture after 2 h of the reaction carried out in the presence of the

725 polyol-based DESs.

726 **Fig. 7**. XRD patters of non-calcined and calcined CaO combined with different DESs

727 (ChCl:DMU, ChCl:TU, ChCl:U, ChCl:EG, ChCl:PG and ChCl:G) or combined with

728 constituents of DESs' (urea, ChCl and glycerol), all used as catalysts in ethanolysis.

729

Supplementary material

731

732 **Choline chloride-based deep eutectic solvents in CaO-catalyzed ethanolysis of**

733 **expired sunflower oil**

734

735 Dragan Z. Troter [a], Zoran B. Todorović [a,], Dušica R. Đokić-Stojanović [b], Ljiljana M.

736 Veselinović [c], Miodrag V. Zdujić [c], Vlada B. Veljković [a,*]

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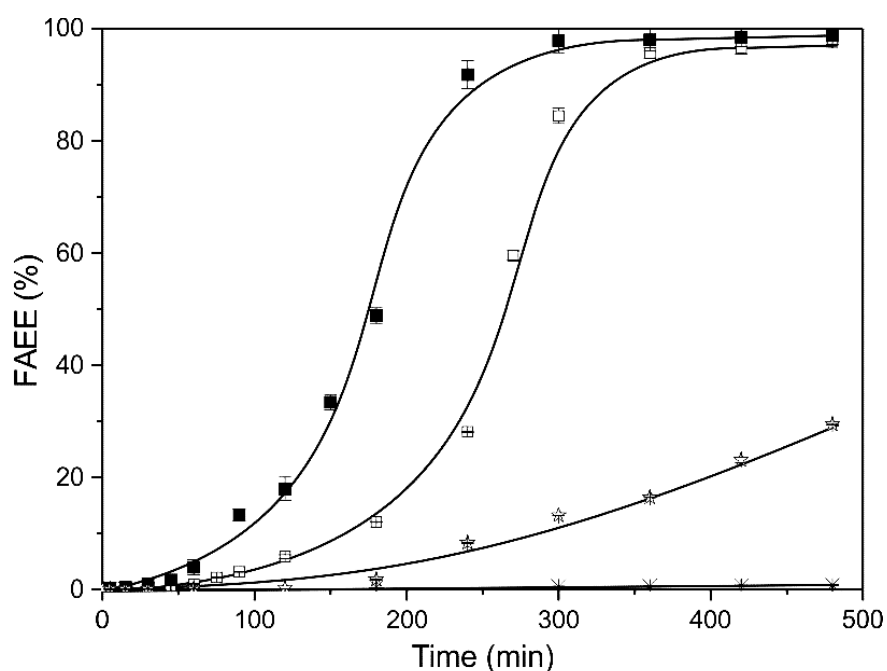741 Mihailova 35, 11000 Belgrade, Serbia

742

743 **Fig. S.1** The variations of the FAEE content with the progress of expired sunflower oils

744 ethanolysis catalyzed by non-calcined CaO (□), calcined CaO (■), Ca(OH)$_2$ (✮) and CaCO$_3$

745 (✲).

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Abbreviations: ChCl:DMU - choline chloride:1,3-dimethylurea; ChCl:EG - choline chloride:ethylene glycol; ChCl:G - choline chloride:glycerol; ChCl:PG - choline chloride:propylene glycol; ChCl:TU - choline chloride:thiourea, ChCl:U - choline chloride:urea; DES - deep eutectic solvent; FAEE - fatty acid ethyl ester.
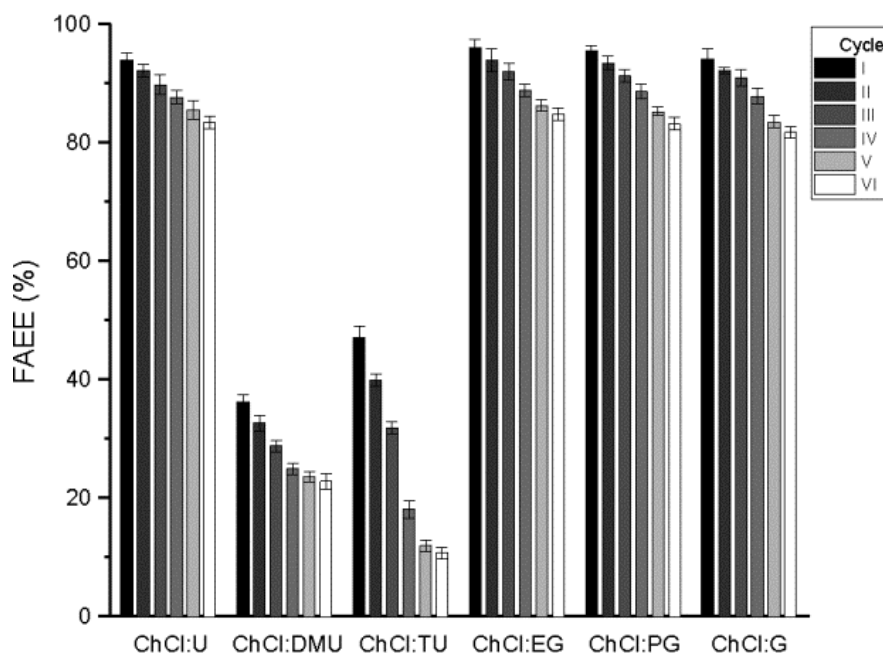
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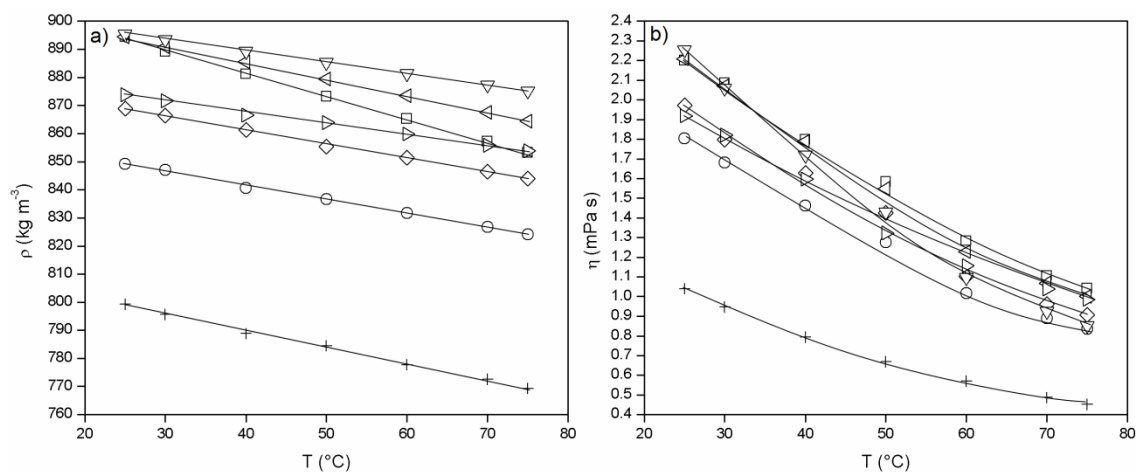
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748 **Fig. S.2** Temperature dependence of the density (**a**) and the viscosity (**b**) of ethanol ($+$) and

749 ethanol mixed with the studied DESs: ChCl:EG ($\bigcirc$), ChCl:PG ($\diamond$), ChCl:G ($\square$), ChCl:U

750 ($\triangleleft$), ChCl:DMU ($\triangleright$) and ChCl:TU ($\triangledown$).
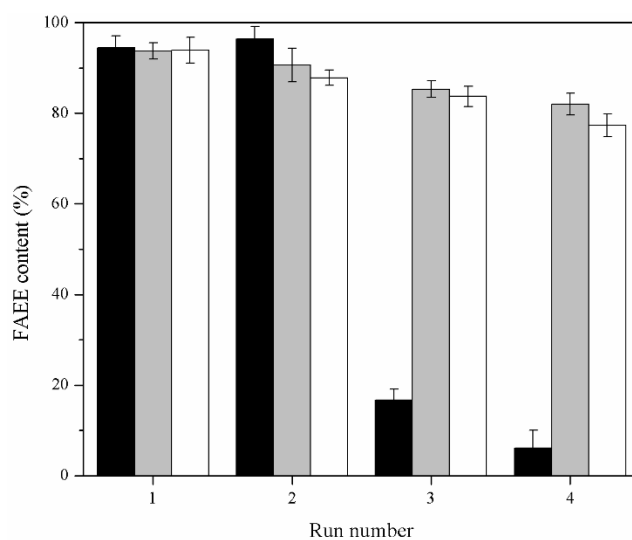
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752

753 **Fig. S.3** Reusability of non-calcined CaO catalyst activated by different DESs. CaO activated

754 with a DES was used in the first batch, while only the recovered CaO was used in the other

755 batches.

756

757

Fig. S.4 The FAEE content after 2 h reaction in four consecutive batches of the sunflower oil

758

ethanolysis catalyzed by either fresh or recovered CaO catalysts in the presence of the

759

recovered ChCl:G DES as a cosolvent (70 °C and the ethanol-to-oil molar ratio was 12:1;

760

reaction systems: recovered ChCl:G DES/glycerol product and recovered CaO - black

761

rectangles, recovered ChCl:G DES/glycerol product and fesh CaO - white rectangles, and

762

treated recovered ChCl:G DES/glycerol product was coupled with fresh CaO - gray

763

rectangles)

764