

The Use of Cosolvents in Heterogeneously and Homogeneously Catalyzed Methanolysis of Oil

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ABSTRACT

1 The paper describes transesterification of oil by methanol with use of cosolvents such as ethyl
2 acetate, tetrahydrofuran, hexane, acetone and diethyl ether at catalyst homogeneous (potassium
3 hydroxide) and heterogeneous (mixed oxides). The cosolvents dissolve oil and methanol to form
4 a single (homogeneous) phase, which increases the reaction rate. Therefore, the biodiesel
5 production will be environmentally friendly because less energy is consumed, which increases
6 sustainability. The whole binodal curve of ternary plots of oil, methanol and cosolvent was
7 determined to find the molar ratio, in which the reaction mixture forms a single phase. The ethyl
8 acetate and tetrahydrofuran have relatively small heterogeneous region, because of the similarity
9 of their electric dipole moment with methanol. After transesterification, the detailed analysis of
10 ester and also glycerol phase was carried out. For homogeneous catalyst, the highest esters
11 content in the ester phase was achieved with tetrahydrofuran. For heterogeneous catalyst, the
12 ester content was lower with cosolvent than without cosolvent, probably due to dilution of
13 reaction components by cosolvent or bonding of cosolvent to the active sites of the catalyst.

14 KEYWORDS

15 methyl ester; transesterification; cosolvents; ternary plot; heterogeneous catalyst;
16 homogeneous catalyst

17 NOMENCLATURE

18	AC	Acetone
19	DEE	Diethyl ether
20	DG	Diacylglycerides
21	ETAC	Ethyl acetate
22	EP	Ester phase
23	FAME	Fatty acid methyl ester
24	GC	Gas chromatography
25	GP	Glycerol phase

26	HEX	Hexane
27	MET	Methanol
28	MG	Monoacylglycerides
29	O	Oil
30	TG	Triacylglycerides
31	THF	Tetrahydrofuran
32		
33	<i>an</i>	Acid number (mg g^{-1})
34	<i>K</i>	Concentration of potassium ions (mg kg^{-1})
35	w_{water}^{EP}	Content of water in the EP (ppm)
36	w_{water}^{GP}	Content of water in GP (wt%)
37	w_{ester}	Ester content in the EP (wt%)
38	w_{MG}	Content of MG (wt%)
39	w_{DG}	Content of DG (wt%)
40	w_{TG}	Content of TG (wt%)
41	w_{ester}^{GP}	Ester content in the GP (wt%)
42	$w_{glycerol}$	Content of glycerol in the GP (wt%)
43	$w_{K_2CO_3}$	Content of potassium carbonate in the GP (wt%)
44	w_{KHCO_3}	Content of potassium bicarbonate in the GP (wt%)
45	$w_{K_2HPO_4}$	Content of dipotassium phosphate in the GP (wt%)
46	w_S	Content of soap in the GP (wt%)
47	ν	Viscosity of EP ($\text{mm}^2 \text{s}^{-1}$)
48	ρ	Density of EP (g cm^{-3})

49 **1 Introduction**

50 Biodiesel – the mixture of methyl esters of higher fatty acids is an alternative fuel for
51 combustion engines. It belongs to the renewable resources of energy and can be used in
52 current diesel engines without any modification. The carbon balance of biodiesel is zero,
53 because carbon dioxide formed by combustion is removed by photosynthesis of plants and
54 converted back into oil. Therefore it is sustainable source of energy. Moreover, biodiesel is

55 nontoxic ecological fuel, which does not contain sulphur or aromatic hydrocarbons and it is
56 also biodegradable (Yildiz et al., 2019).

57 It is usually synthesized by transesterification of triacylglycerides (TG) with low molecular
58 alcohols (most often methanol – MET), which is mostly catalyzed by homogeneous (Gardy et
59 al., 2019). The use of heterogeneous catalysts such as mixed metal oxide (Banerjee et al.,
60 2019) is also possible. The sources of TG are vegetable oils, animal fats or waste cooking oils
61 (Cordero-Ravelo and Schallenberg-Rodriguez, 2018). The use oils from algae was published
62 (Passell et al., 2013). The TG and methanol are immiscible liquids, i.e. heterogeneous mixture
63 is formed and the reaction proceeds on the interface. To increase the reaction rate (i.e. to
64 shorten the reaction time): (i) the reaction mixture has to be intensively stirred or (ii) a
65 cosolvent can be added. The cosolvents are inactive to reaction components and solve both
66 raw materials to single phase, i.e. homogeneous mixture is formed. The use of cosolvents
67 decreases the production costs by decreasing of (i) reaction time or (ii) reaction temperature.
68 Total production process will consume less energy and so be more sustainable.

69 The most commonly used cosolvents are organic solvents with relatively similar boiling
70 point to methanol. The use of several cosolvents, mostly for homogeneously catalysed
71 transesterification, could be found in the literature, such as acetone (AC), ethyl acetate
72 (ETAC), tert-butyl methyl ether dimethyl ether, di-isopropyl ether, tetrahydrofuran (THF)
73 (Ataya et al., 2006). Todorovic et al. published use of THF (from 0% to 50% based on the oil
74 mass) as a cosolvents for transesterification of sunflower oil catalysed by potassium
75 hydroxide (KOH) at 10 °C. They found that maximum yield of fatty acid methyl ester
76 (FAME) was 90 wt% for optimum 50 wt% of THF to make the reactants completely miscible
77 at the reaction temperature of 20 °C (Todorovic et al., 2013). Alhassan et al. tested three types
78 of cosolvents (DEE, dichlorbenzene and AC) in transesterification of cotton oil with methanol
79 and KOH as the catalyst. The optimal volume of cosolvents added to methanol was found

80 10 vol% for dichlorbenzene and AC and about 30 vol% for DEE. The authors also found that
81 the addition of cosolvents does not affect the properties of the fuel (Alhassan et al., 2014).
82 Another author, also used AC as the cosolvent for homogeneous transesterification of canola
83 oil with methanol catalysed by KOH and found that optimal reaction conditions were 25 wt%
84 of AC, 1 wt% of KOH and a molar ratio of methanol to oil of 4.5:1 (Thanh et al., 2013). Guan
85 et al. carried out transesterification of sunflower oil with methanol (the molar ratio methanol
86 to oil 6:1) by using KOH as the catalyst in the presence of various cosolvents (dimethyl ether,
87 tert-butyl methyl ether, DEE and THF) at 25 °C. They determined minimum molar ratio of
88 cosolvent and methanol for each cosolvent necessary for total dissolution of methanol and
89 sunflower oil. The oil was completely converted into biodiesel after 20 minutes in comparison
90 with 78% without cosolvents. Moreover, they found, that the addition of excess cosolvents
91 decreased the reaction rate due to high dilution of the reaction mixture (Guan et al., 2009).

92 For heterogeneous catalyst, the cosolvent is also applicable. The calcium dioxide was used
93 as heterogeneous catalyst of sunflower oil by methanol, where the crude biodiesel was used as
94 cosolvent (Todorovic et al., 2019).

95 The aim is to describe and compare the influence of cosolvents on the course of
96 transesterification and properties of both phases. The novelty especially consists in (i) the
97 measurement of ternary plots including binodal curve for all molar ratios of oil, methanol and
98 cosolvent such as tetrahydrofuran (THF), acetone (AC), ethyl acetate (ETAC), diethyl ether
99 (DEE), hexane (HEX) and (ii) the detailed analysis of formed ester and glycerol phase
100 including the ester losses (for homogeneous catalyst) after transesterification. The
101 measurement of ternary plots and properties of both phases, which are very often omitted, are
102 different from other papers. The importance lays in potential decreasing of transesterification
103 time and temperature, which can improve economic and environmental impact of biodiesel
104 production.

105 **2 Materials and methods**

106 **2.1 Ternary plot**

107 The points of binodal curve at ternary plots were determined by spectrophotometric method
108 by measuring of the transmittance at constant wavelength 567 nm at laboratory temperature
109 (25 °C), for 100% of transmittance, pure oil was used. The mixture of oil and methanol (in
110 certain molar ratio) was added into cuvette and stirred at 25 °C. The formed heterogeneous
111 mixture had low transmittance. The inert cosolvent, which is miscible with both liquids, was
112 consecutively added (the amount added was 100 µl) until the transmittance sharply increased
113 (almost at 100 %), as shown at Fig. 1.

114 Thus, one point of the binodal curve of the ternary plot was obtained. All binodal points for
115 all cosolvents, i.e. ethyl acetate, THF, hexane, acetone and diethyl ether (all p.a., Penta, Czech
116 Republic) at different molar ratios of oil and methanol were determined by this method. The
117 chosen properties of cosolvents are stated in Table 1. The final plots were created in program
118 Origin 9.1. Note that the oil is composed of many types of triacylglycerides with very similar
119 properties, which are not possible to separate. Hence oil was considered as chemical
120 individuum with molar mass of 879.1 g mol⁻¹ (Komers et al., 2001).

121 **2.2 Transesterification of oil**

122 For homogeneous catalyst, 400 g of rapeseed oil (acid number 0.23 mg KOH g⁻¹, water
123 content 338 mg kg⁻¹ produced by Ceresol, Czech Republic) was put into the reaction vessel.
124 The amount of 0.8 wt% of catalyst KOH (purity 85 wt%, Lach-Ner, Neratovice, Czech
125 Republic) to oil was dissolved in the mixture of methanol (p.a., Penta, Czech Republic) and
126 cosolvents (one of the ETAC, THF, HEX, AC and DEE). The exact cosolvent amount was
127 added so that the reaction mixture was in single phase. The mixture was thermostated to 25°C
128 (at atmospheric pressure) and then poured into the reaction vessel and stirred at 200 rpm; this

129 point was considered as the start of transesterification. The reaction mixture was sampled at
130 time intervals (10, 20, 30, 50 and 90 min) and analysed with a respect to reaction
131 intermediates (mono-, di-, and triglycerides) and the main reaction product (esters). The
132 reaction was stopped by immediate neutralization of the catalyst by addition of 5 ml of
133 0.2 mol dm^{-3} hydrochloric acid (HCl).

134 After reaction time (90 min), the reaction was stopped by neutralization of the catalyst by
135 gaseous carbon dioxide (weak acid) (Hajek et al., 2012) or phosphoric acid (relatively strong
136 acid). For neutralization by CO_2 , pH was monitored and when decreased to constant value
137 (approximately 9), the catalyst was neutralized. For neutralization by H_3PO_4 , the amount of
138 catalyst remaining after reaction was necessary to determine by potentiometric titration and an
139 equivalent amount of acid was added (Vavra et al., 2018). The excess of alcohol and
140 cosolvents was removed by distillation under reduced pressure (approximately 3 kPa) and
141 higher temperature (70 °C). Then, the mixture was separated by gravity for 24 h in the
142 separatory funnel. After separation, both formed phases (the ester and glycerol phases) were
143 analysed.

144 For heterogeneous catalyst – Mg-Al mixed oxides were synthesized from hydrotalcites by
145 heating (calcination) to 450 °C for 3 h , the detailed synthesis process was described (Hajek et
146 al., 2015). The real molar ratio Mg:Al was 4.5:1. The reaction was carried out in stainless
147 steel batch autoclave (300 ml, Parr company, USA) equipped with shaft stirrer. The amount
148 of 30 g of rape seed oil, 32 ml of methanol (PENTA s.r.o., p.a.), 12 ml of cosolvent and 1 g of
149 catalyst were placed to the reactor. After heating to the reaction temperature (120 °C), the
150 stirring was switched on (300 rpm) and the reaction, which takes 6 hours, was initiated. After
151 reaction time, the catalyst was removed by filtration and methanol by distillation from the
152 mixture (70 °C, 3 kPa). The mixture was analysed.

153 **2.3 Analytical method**

154 The contents of glycerides were determined by gas chromatography with flame ionization
155 detector (GC-2010, Shimadzu, Japan) according to EN 14105 with the help of linear
156 calibration curves (monoolein, diolein and triolein were used as standards). The content of
157 esters in the EP (w_{ester} in wt%) was calculated as the difference of 100% minus the sum of
158 concentrations of all glycerides in the EP (providing that the concentrations of other
159 substances in the EP are insignificant).

160 For homogeneous catalyst, the content (mg/kg) of potassium ions in the EP was
161 determined by flame photometry (Flame photometer 410, Sherwood Scientific Ltd, United
162 Kingdom). The flash point of the EP was measured by the Pensky-Martens closed-cup method
163 (EN ISO 2719) with the instrument OB-305 (MIM Fabri, Hungary). The water content in both
164 phases was determined according to EN ISO 12937 (TitroLine® 7750). In the GP, the
165 contents of basic matter (potassium hydrogen carbonate, potassium carbonate, K_2HPO_4 and
166 soaps) were determined by acidimetric titration by HCl (0.1 mol dm^{-3}) with potentiometric
167 identification (Kwiecien et al., 2009). The content of glycerol and esters (i.e. esters loss) in
168 the GP was determined by HPLC (Hajek et al., 2010).

169 The heterogeneous catalyst was characterised by XRD and TGA to confirm the successful
170 synthesis (Hajek et al., 2015).

171 **3 Results and discussion**

172 **3.1 Ternary plots**

173 The main reaction components methanol and oil are immiscible liquids (i.e. heterogeneous
174 system is formed), so the transesterification proceeds on the interphase. The addition of
175 cosolvent, which is miscible with oil and also with methanol, forms the homogeneous mixture
176 (single phase).

177 Firstly, the ternary plots for methanol, rapeseed oil (Oil) and all cosolvents (ETAC, THF,
178 HEX, AC and DEE) were determined at constant temperature 25 °C (Fig 2). Moreover, the
179 molar ratio of oil to methanol 1:6, which is the most often used, was also marked in the plots
180 (red line). The chosen properties of cosolvents (Rumble, 2019) including the minimum molar
181 ratio of components for the mixture in the single phase are stated in Table 1.

182 The aim was to find the molar ratio between methanol, oil and cosolvent, so that the
183 reaction mixture was in single phase (homogeneous). The binodal curve of ternary plots was
184 completely determined, which enabled to find homogeneous region for any molar ratio of
185 methanol to oil. This is the difference from paper published by Todorovic et al., where
186 authors used sunflower oil and determined single “region” only for one molar ratio of
187 methanol to oil at 60 °C (Todorovic et al., 2013). Authors Khang et al. determined the ternary
188 plot for methanol, oil and THF (in volume percent), but only for quite narrow part of binodal
189 curve: from 0.1 to 0.25 vol% of coconut oil in mixture (Khang et al., 2014). The ternary plots
190 especially for THF as cosolvent with different types of oil such as canola, soybean and palm
191 were determined (in volume percent) at 23 °C. Another authors used visual indication of
192 cloud point, which is less precisely than indication by transmittance. Moreover, they used
193 volume ratio methanol/oil from 0.1 to 0.9, so without determination of the lowest ratios. The
194 superimposition of ternary diagrams revealed that for some oils were virtually identical.
195 Authors carried out on transesterification of soybean oil, but without any analysing of product
196 in detail (Boocock et al., 1996).

197 The heterogeneous region was smaller for ETAC, THF and DEE in comparison with HEX
198 and AC (Fig 2). The reason is the electric dipole moment, which corresponds to the polarity of
199 chemical substances (Table 1). The dipole moments for ETAC (1.78 C m), THF (1.63 C m)
200 and DEE (1.15 C m) have similar value as the methanol itself (1.69 C m), so these solvents are
201 relatively miscible, i.e. small amount of cosolvent has to be added to reaction mixture to form

202 single phase. The dipole moments of cosolvents HEX (0.08 C m) and AC (2.91 C m) are
203 significantly different from dipole moment of methanol (1.69 C m), which has smaller single
204 region, i.e. large amount of cosolvent has to be added to reaction mixture so it was
205 homogeneous. Todorovic at al. published lower molar ratio so that the mixture was
206 homogeneous, but at higher temperature (60 °C) and standard pressure. This finding corresponds
207 with the fact that solubility usually increases with increasing temperature, i.e. heterogeneous
208 region is smaller. However, there is not described in detail how the molar ratio was found out,
209 especially for DEE which has boiling point at 34.5 °C (at standard pressure), i.e. at 60 °C has to
210 be huge amount of this matter in gas phase (Todorovic et al., 2013).

211 3.2 Transesterification – homogeneous catalyst

212 The transesterification with addition of cosolvent was tested at homogeneous catalyst (KOH).
213 The course of transesterification, i.e. the dependency of the content of formed ester (w_{ester}) on
214 time was determined for cosolvents and compared with the course without cosolvents under
215 the same reaction conditions (Fig. 3). The relatively low temperature (25 °C) was chosen
216 because (i) the reaction mixture is not possible to heat more than the boiling point of less
217 volatile component, e.g. boiling point of DEE is 34.5 °C (at standard pressure) (ii) the reaction
218 rate decreases with decreasing temperature so at lower temperature the courses are better
219 comparable (reaction is relatively slow).

220 In addition, the transesterification was stopped by neutralisation of remained catalyst by
221 two types of acids: gas CO₂ as weak acid (Hajek et al., 2012) and by concentrated H₃PO₄ as a
222 relatively strong acid (Vavra et al., 2018). After separation, the properties of the ester phase
223 and glycerol phase were determined including ester losses in the GP.

224 The highest content of ester in the EP (w_{ester}) for all reaction times was achieved with THF
225 (more than 90 wt% after 90 min of reaction). The complete transformation of oil to ester was

226 not achieved because low temperature (25 °C) was chosen. The EP, formed by
227 transesterification with cosolvents ETAC and DEE, has slightly less ester content than the EP
228 formed without cosolvents (approximately 85 wt%). The lowest ester content was achieved
229 with acetone and hexane, because huge amount of these cosolvents had to be added so that the
230 mixture was in the single phase (table 1). This caused decreasing of concentration of oil and
231 methanol decrease and thereby decreased of reaction rate. However, Alhassan et al. carried out
232 the transesterification with diethyl ether and acetone as cosolvents at 60 °C (at standard
233 pressure) with bath reactor equipment by condenser unit. They achieved high yield of esters
234 90-100 wt%, which depended on concrete reaction conditions (Alhassan et al., 2014). Higher
235 content of ester was caused by higher temperature. Although authors used condenser unit, the
236 boiling point of reaction mixture had to be similar as boiling point of the least volatile
237 component i.e. diethyl ether (boiling point 34.5 °C at standard pressure). Therefore, the reaction
238 mixture cannot be heated to 60 °C with diethyl ether (real temperature has to be much lower),
239 or diethyl ether has to be present in vapour and not in liquid phase (it is not specified how much
240 the reactor was filled with liquid phase and how much “empty” space remained for gas phase).
241 Similarly for acetone (boiling point at 56.5 °C).

242 The properties of the EP are stated in Table 2. The content of mono-, di- and triglycerides is
243 relatively high, which is consistent with the ester content; higher content of glycerides means
244 lower content of esters. The density (ρ) of EP was in the range 0.82-0.89 g cm⁻³ for all types of
245 cosolvents and ways of stopping. The viscosity (ν) was determined 5.1-5.5 mm² s⁻¹, which
246 was slightly higher than for methyl esters prepared without cosolvents (4.9 mm² s⁻¹), because
247 the EP contains glycerides, which increase the viscosity. Moreover, viscosity is slightly lower
248 for stopping by phosphoric acid than by gas carbon dioxide. The acid number (*an*) is less than
249 0.4 mg KOH g⁻¹, because both ways of catalyst neutralisation ensure low acid number, i.e. the
250 transformation of soap (formed by side reaction) to higher fatty acid does not proceed (Vavra et

251 al., 2018). The flash point of the EP was more than 120 °C for all cosolvents, which means
252 almost no methanol or cosolvent were presented. The content of water in the EP (w_{water}^{EP}) was
253 higher than for transesterification without the cosolvent (650 ppm), because the cosolvents
254 contain small amount of water, which was presented in reaction mixture and remained after
255 methanol removal by distillation. The highest water in the EP was for AC because (i) AC
256 contains the highest water content and (ii) there was added the most amount from all cosolvents.
257 The content of potassium ions (K) was also quite high. Note: The content of w_{water}^{EP} and K were
258 determined directly in EP after separation without any purification steps. Their content strongly
259 depends on the purification process and are not usually determined (Alhassan et al., 2014).

260 Moreover, the distribution of methyl esters according to higher fatty acid in the EP for
261 cosolvents was determined (Table 3). The content of methyl esters of linolenic acid is
262 approximately the same for THF and DEE and slightly higher for AC and ETAC than without
263 cosolvent. On the other hand, the content of methyl esters of linoleic acid was almost the
264 same for all cosolvents and also without cosolvent (ca 21 %). The content of the methyl esters
265 of oleic acid was the highest, which corresponds with the fatty acid profile of rapeseed oil.
266 The highest differences were for methyl esters of palmitic acid, where without cosolvent it
267 was 5.2 %, but for DEE the content was almost double (10.4 %). The differences in
268 distributions of methylesters are probably caused by the different polarity of cosolvents and
269 esters. The composition of the GP as a side product was also determined (Table 4).

270 The GP contains, besides glycerol ($w_{glycerol}$), the formed soaps (w_s), the products of catalyst
271 neutralisation, water (w_{water}^{GP}) and esters (w_{ester}^{GP}). The product of catalyst neutralisation
272 depends on the type of neutralisation: carbonates ($w_{K_2CO_3}$ and w_{KHCO_3}) were formed by
273 neutralisation of CO_2 and phosphates ($w_{K_2HPO_4}$) by H_3PO_4 . The ester loss (determined as
274 content of ester in the GP) was higher for transesterification stopped by H_3PO_4 for all
275 cosolvents except ETAC. This is different from our previous finding regarding

276 transesterification without cosolvent, where the ester content in the GP was higher just for
277 transesterification stopped by CO₂ (Vavra et al., 2018). Therefore, the presence of cosolvents
278 in reaction mixture changes the amount of losses according to the way of transesterification
279 stop. The content of soaps was higher than without cosolvent (approximately 15 wt%), which
280 indicates a side reaction process. The reason is probably that the reaction proceeds in a single
281 phase. Note: the total summa of weight percent is not exactly 100%, because (i) the GP
282 contains small amount of other substances, such as methanol and vegetable dyes, which were
283 not determined and (ii) every analysis has some error (the highest error has glycerol
284 determination, because its concentration is high). However, the composition is not possible to
285 compare with other studies, because the GP is usually omitted.

286 **3.3 Transesterification – heterogeneous catalyst**

287 The Mg-Al mixed oxides with molar ratio Mg/Al 4.5 were used as heterogeneous catalyst.
288 This molar ratio was chosen because the activity of transesterification was quite high and not
289 significantly changed by molar ratio increasing. The structures of Mg-Al hydrotalcite (as
290 precursor) and also mixed oxides were confirmed by XRD analysis, where the characteristic
291 diffraction lines were found (Fig. 4). The temperature stability of hydrotalcite was described
292 by thermogravimetric analysis with mass detection (Fig. 5). Hydrotalcite are usually
293 decomposed in two or three consecutive steps (Yang et al., 2002). Our catalyst was
294 decomposed in two steps. In the first step (100-250 °C), only mass signal of water was found
295 and therefore the surface water was desorbed. During the second step (250-500 °C)
296 carbonates from anion layer and another water were desorbed, for this reason mass signal of
297 carbone dioxide and water were determined. The third did not occur. The total loss of mass
298 during the TGA analysis was approximately 46%.

299 The content of ester in the ester phase was 42 wt.% for tetrahydrofuran, 39.5 wt% for ethyl
300 acetate and diethyl ether and 29.6 wt% for hexane and acetone, which is lower than without

301 cosolvent (72 wt%). The decreasing is much lower than for homogeneous catalyst (section
302 3.2). The probable reason for so low ester content is (i) bonding of cosolvent to the active
303 sites of catalyst, which are not available for transesterification or (ii) dilution of reaction
304 components (methanol and oil) by cosolvent, which corresponds with the fact that hexane and
305 acetone had to be added in higher amount than acetate and diethyl ether.

306 **4 Conclusions**

307 The work described the use of various cosolvents (form single phase) for transesterification of
308 oil by methanol. At first, the ternary plots including binodal curve for all molar ratios of oil to
309 methanol were determined. The lower molar ratios (mixture was in single phase) were
310 determined for ethyl acetate, tetrahydrofuran and diethyl ether, because their dipole moments
311 are relatively similar to dipole moment of methanol. The formation of esters and also final
312 content of ester in the ester phase was similar for all cosolvents except ethyl acetate.
313 However, the highest ester content was achieved for tetrahydrofuran (93.2 wt%). The use of
314 cosolvents does not significantly change the distribution of methyl esters according to higher
315 fatty acid (except methyl esters of palmitic acid). It was also found, that the cosolvents change
316 the amount of ester losses, which depends on the way of transesterification stop. The use of
317 cosolvent can decrease the production cost and improves the total energy balance of biodiesel
318 production, because it proceeds at lower temperature and shorter time. On the other hand, the
319 ester yield is slightly lower, because saponification is more intensive.

320 For heterogeneous catalyst, the ester content was lower with cosolvent than without
321 cosolvents, probably due to dilution of reaction components.

322

323 **Acknowledgements**

324 This work was supported by the Czech Science Foundation, Project No. 19-00669S.

325 **REFERENCES**

- 326 Alhassan, Y., Kumar, N., Bugaje, I.M., Pali, H.S., Kathkar, P., 2014. Co-solvents
327 transesterification of cotton seed oil into biodiesel: Effects of reaction conditions on quality
328 of fatty acids methyl esters. *Energy Convers. Manage.* 84, 640-648.
329 <https://doi.org/10.1016/j.enconman.2014.04.080>
- 330 Ataya, F., Dube, M.A., Ternan, M., 2006. Single-phase and two-phase base-catalyzed
331 transesterification of canola oil to fatty acid methyl esters at ambient conditions. *Ind. Eng.*
332 *Chem. Res.* 45, 5411-5417. <https://doi.org/10.1021/ie060152o>
- 333 Banerjee, S., Sahani, S., Sharma, Y.C., 2019. Process dynamic investigations and emission
334 analyses of biodiesel produced using Sr-Ce mixed metal oxide heterogeneous catalyst. *J.*
335 *Environ. Manage.* 248. <https://doi.org/10.1016/j.jenvman.2019.06.119>
- 336 Boocock, D.G.B., Konar, S.K., Sidi, H., 1996. Phase diagrams for oil/methanol/ether
337 mixtures. *J. Am. Oil Chem. Soc.* 73, 1247-1251. <https://doi.org/doi.10.1007/Bf02525453>
- 338 Cordero-Ravelo, V., Schallenberg-Rodriguez, J., 2018. Biodiesel production as a solution to
339 waste cooking oil (WCO) disposal. Will any type of WCO do for a transesterification
340 process? A quality assessment. *J. Environ. Manage.* 228, 117-129.
341 <https://doi.org/10.1016/j.jenvman.2018.08.106>
- 342 Gardy, J., Rehan, M., Hassanpour, A., Lai, X.J., Nizami, A.S., 2019. Advances in nano-
343 catalysts based biodiesel production from non-food feedstocks. *J. Environ. Manage.* 249.
344 <https://doi.org/10.1016/j.jenvman.2019.109316>
- 345 Guan, G.Q., Sakurai, N., Kusakabe, K., 2009. Synthesis of biodiesel from sunflower oil at
346 room temperature in the presence of various cosolvents. *Chem. Eng. J.* 146, 302-306.
347 <https://doi.org/10.1016/j.cej.2008.10.009>
- 348 Hajek, M., Kutalek, P., Smolakova, L., Troppova, I., Capek, L., Kubicka, D., Kocik, J.,
349 Thanh, D.N., 2015. Transesterification of rapeseed oil by Mg-Al mixed oxides with various
350 Mg/Al molar ratio. *Chem. Eng. J.* 263, 160-167. <https://doi.org/10.1016/j.cej.2014.11.006>
- 351 Hajek, M., Kwiecien, J., Skopal, F., 2012. Biodiesel: The influence of dealcoholization on
352 reaction mixture composition after neutralization of catalyst by carbon dioxide. *Fuel* 96, 85-
353 89. <https://doi.org/10.1016/j.fuel.2012.01.037>
- 354 Hajek, M., Skopal, F., Kwiecien, J., Cernoch, M., 2010. Determination of esters in glycerol
355 phase after transesterification of vegetable oil. *Talanta* 82, 283-285.
356 <https://doi.org/10.1016/j.talanta.2010.04.035>
- 357 Khang, D.S., Razon, L.F., Madrazo, C.F., Tan, R.R., 2014. In situ transesterification of
358 coconut oil using mixtures of methanol and tetrahydrofuran. *Chem. Eng. Res. Des.* 92,
359 1512-1518. <https://doi.org/10.1016/j.cherd.2014.01.002>
- 360 Komers, K., Stloukal, R., Machek, J., Skopal, F., 2001. Biodiesel from rapeseed oil, methanol
361 and KOH 3. Analysis of composition of actual reaction mixture. *Eur. J. Lipid Sci. Technol.*
362 103, 363-371. [https://doi.org/10.1002/1438-9312\(200106\)103:6<363::Aid-
363 Ejlt363>3.0.Co;2-3](https://doi.org/10.1002/1438-9312(200106)103:6<363::Aid-Ejlt363>3.0.Co;2-3)
- 364 Kwiecien, J., Hajek, M., Skopal, F., 2009. The effect of the acidity of rapeseed oil on its
365 transesterification. *Bioresour. Technol.* 100, 5555-5559.
366 <https://doi.org/10.1016/j.biortech.2009.06.002>
- 367 Passell, H., Dhaliwal, H., Reno, M., Wu, B., Ben Amotz, A., Ivry, E., Gay, M., Czartoski, T.,
368 Laurin, L., Ayer, N., 2013. Algae biodiesel life cycle assessment using current commercial
369 data. *J. Environ. Manage.* 129, 103-111. <https://doi.org/10.1016/j.jenvman.2013.06.055>
- 370 Rumble, J., 2019. *Handbook of Chemistry and Physics*, 100 ed.
- 371 Thanh, L.T., Okitsu, K., Sadanaga, Y., Takenaka, N., Maeda, Y., Bandow, H., 2013. A new
372 co-solvent method for the green production of biodiesel fuel - Optimization and practical
373 application. *Fuel* 103, 742-748. <https://doi.org/10.1016/j.fuel.2012.09.029>

374 Todorovic, Z.B., Stamenkovic, O.S., Stamenkovic, I.S., Avramovic, J.M., Velickovic, A.V.,
375 Bankovic-Ilic, I.B., Veljkovic, V.B., 2013. The effects of cosolvents on homogeneously and
376 heterogeneously base-catalyzed methanolysis of sunflower oil. *Fuel* 107, 493-502.
377 <https://doi.org/10.1016/j.fuel.2012.11.049>

378 Todorovic, Z.B., Troter, D.Z., Dokic-Stojanovic, D.R., Velickovic, A.V., Avramovic, J.M.,
379 Stamenkovic, O.S., Veselinovic, L.M., Veljkovic, V.B., 2019. Optimization of CaO-
380 catalyzed sunflower oil methanolysis with crude biodiesel as a cosolvent. *Fuel* 237, 903-910.
381 <https://doi.org/10.1016/j.fuel.2018.10.056>

382 Vavra, A., Hajek, M., Skopal, F., 2018. Acceleration and simplification of separation by
383 addition of inorganic acid in biodiesel production. *J. Clean. Prod.* 192, 390-395.
384 <https://doi.org/10.1016/j.jclepro.2018.04.242>

385 Yang, W.S., Kim, Y., Liu, P.K.T., Sahimi, M., Tsotsis, T.T., 2002. A study by in situ
386 techniques of the thermal evolution of the structure of a Mg-Al-CO₃ layered double
387 hydroxide. *Chem. Eng. Sci.* 57, 2945-2953. [https://doi.org/10.1016/S0009-2509\(02\)00185-9](https://doi.org/10.1016/S0009-2509(02)00185-9)

388 Yildiz, I., Acikkalp, E., Caliskan, H., Mori, K., 2019. Environmental pollution cost analyses
389 of biodiesel and diesel fuels for a diesel engine. *J. Environ. Manage.* 243, 218-226.
390 <https://doi.org/10.1016/j.jenvman.2019.05.002>
391

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393

394 **Figure caption**

395 Fig. 1: The dependency of transmittance on time for determination of points of binodal curve

396 Fig. 2: The ternary plots of methanol, oil with various cosolvents: ETAC (A), THF (B), HEX
397 (C), AC (D), DEE (E) at 25 °C and atmospheric pressure; the molar ratio of oil to
398 methanol 1:6 is marked by red line

399 Fig. 3: The dependency of content of ester in the EP (w_{ester}) on the reaction time for various
400 cosolvents at 25°C and 0.8 wt% of catalyst to oil

401 Fig. 4: The diffractogram of Mg-Al hydrotalcites (HT) and mixed oxides (HTc)

402 Fig. 5: TGA of Mg-Al hydrotalcites

403

Figure 1
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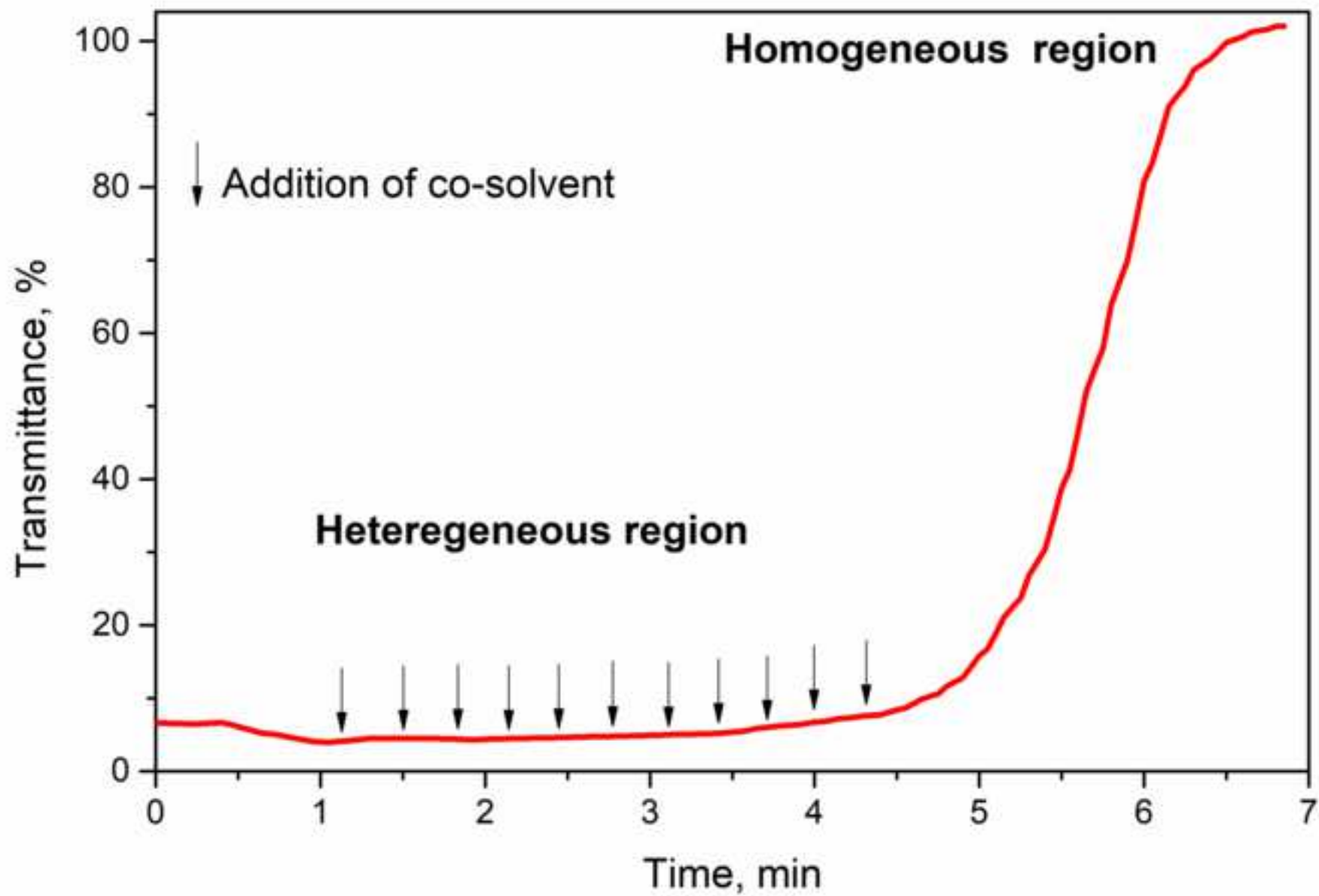


Figure 2

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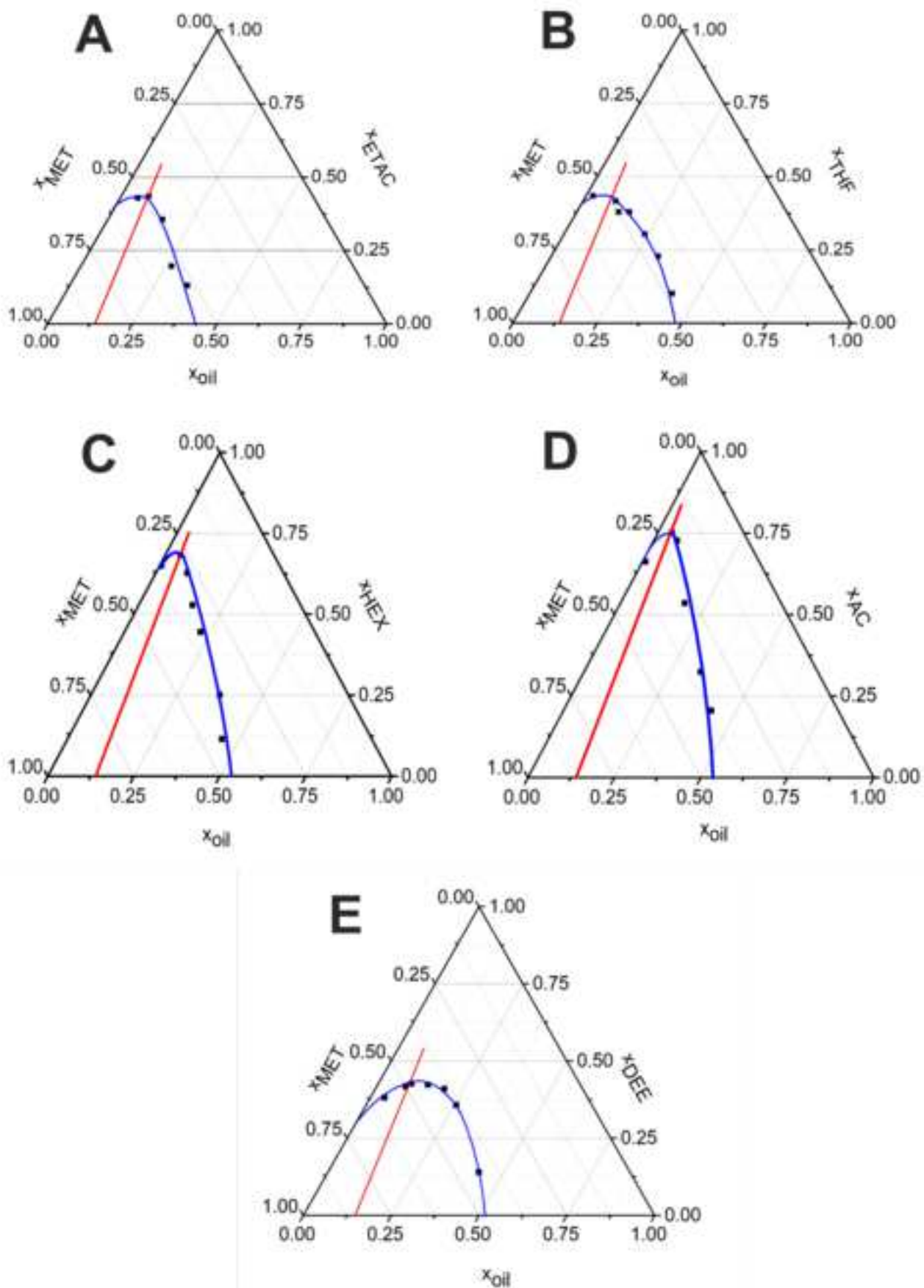


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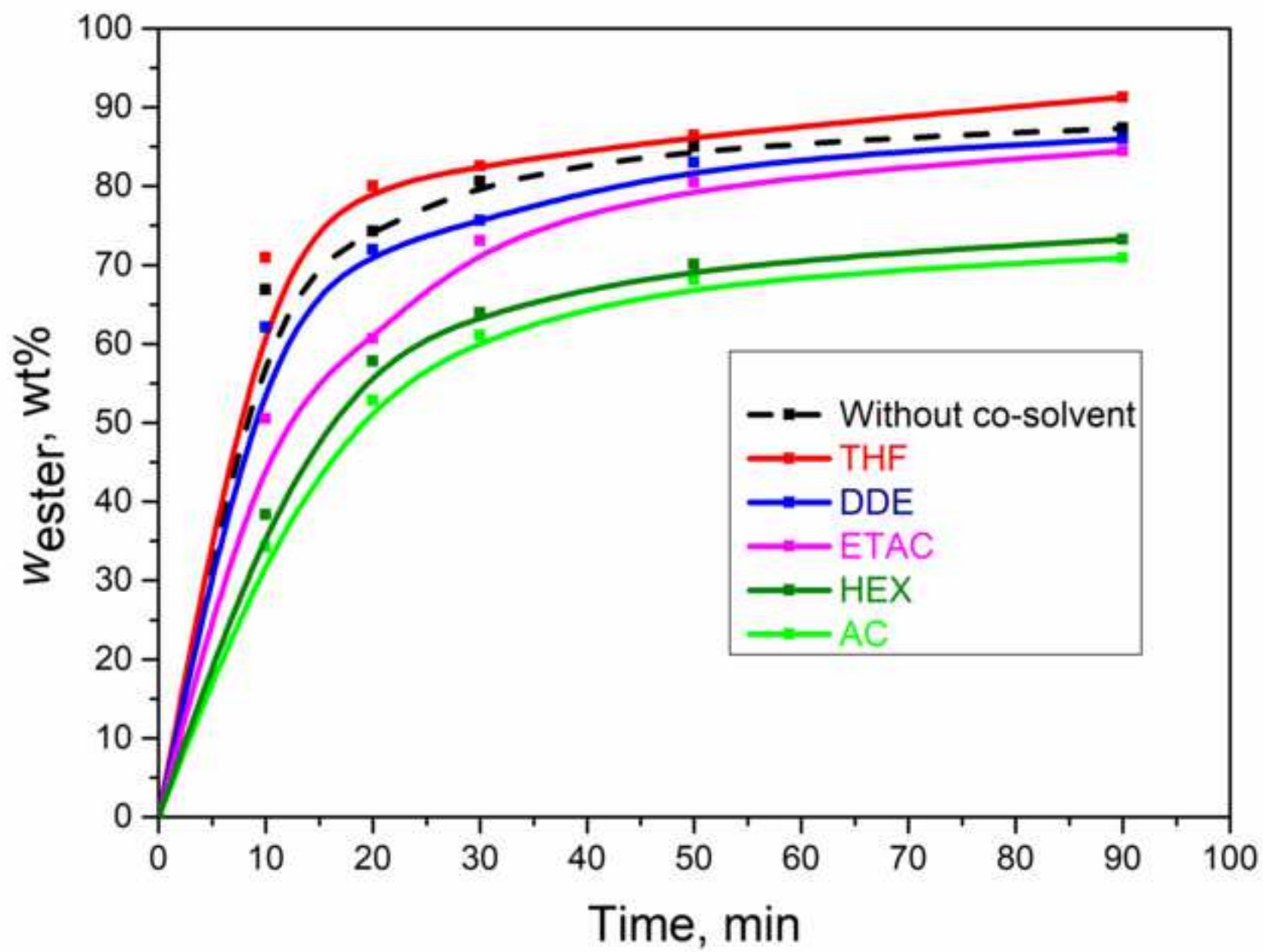


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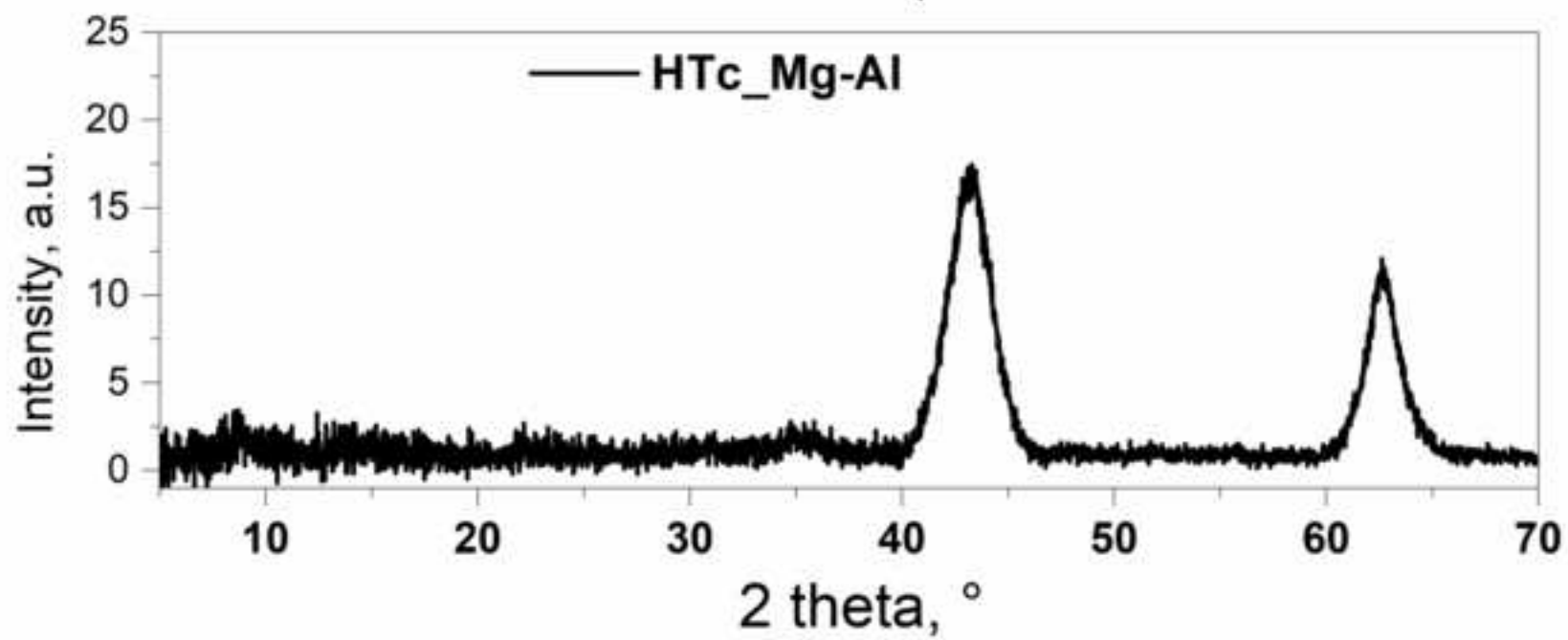
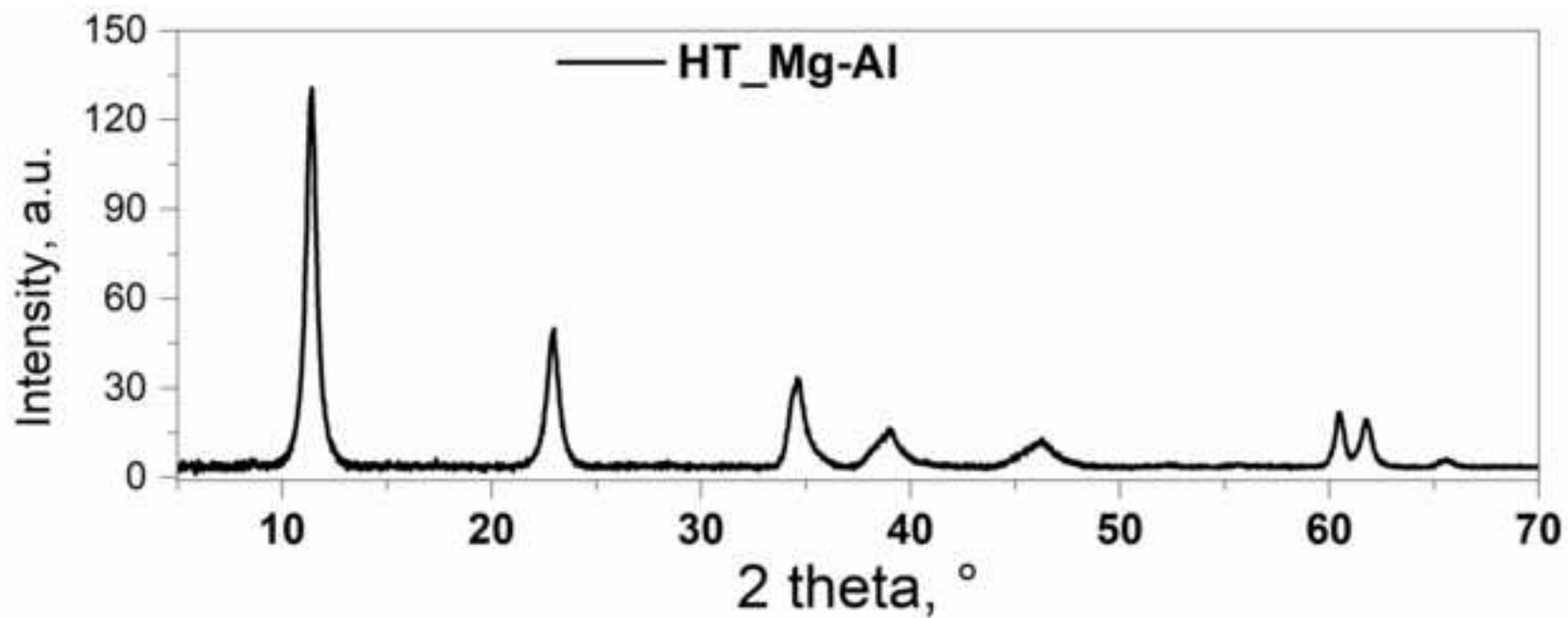
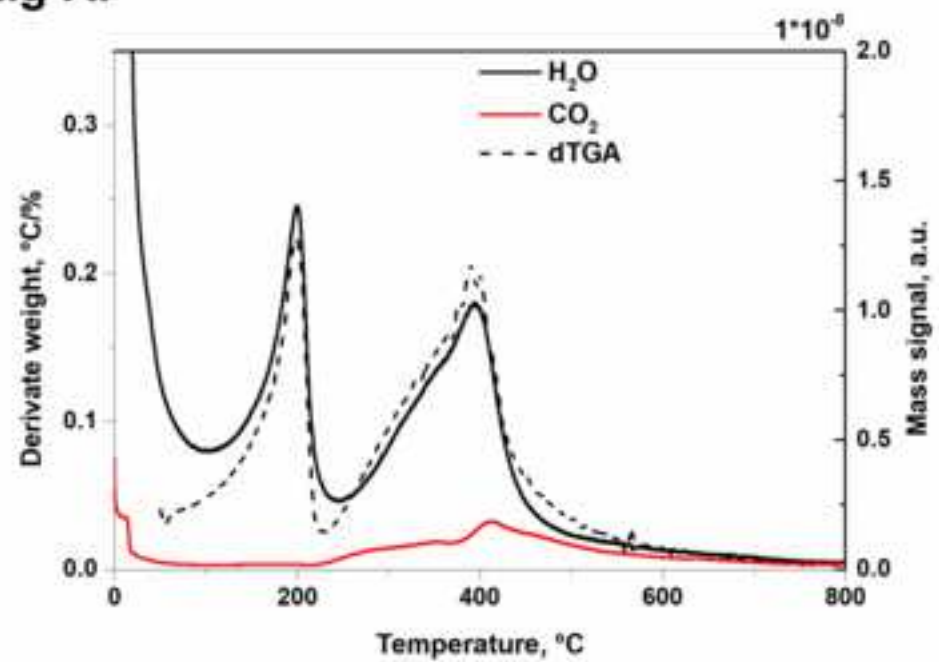
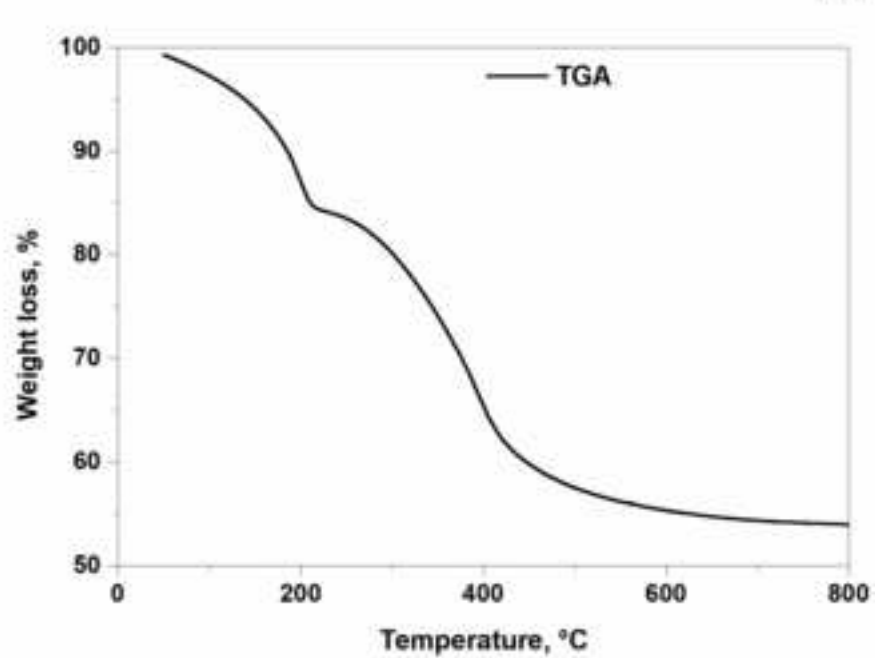


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HT_Mg-Al



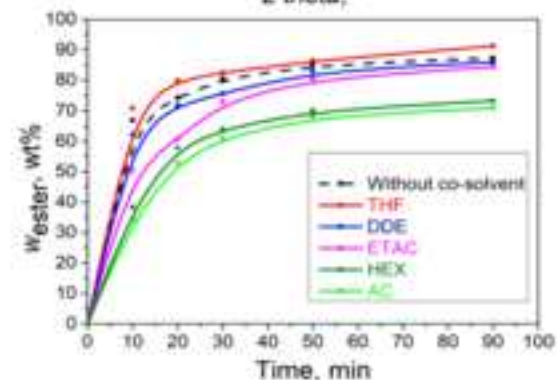
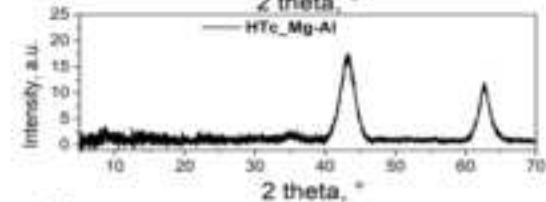
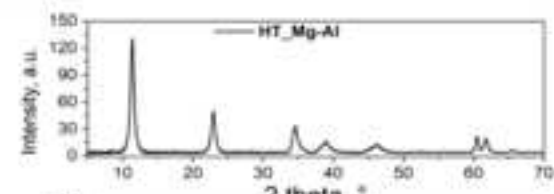
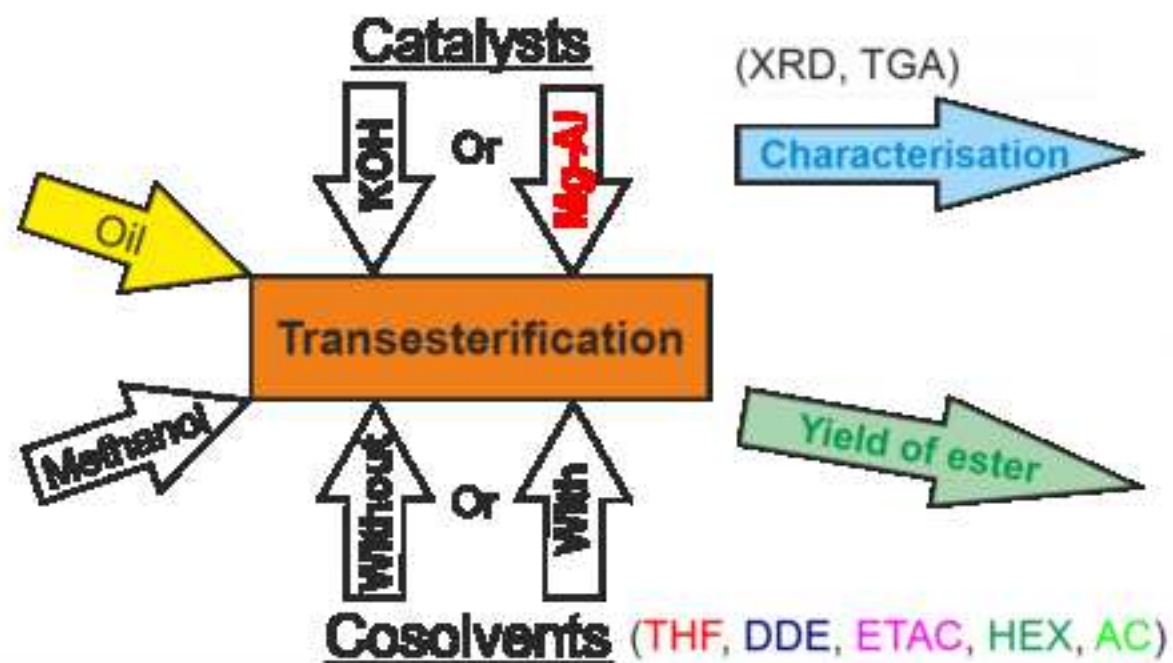


Table 1: The chosen properties of cosolvents and methanol including the minimum molar ratio of components for the mixture is in the single phase

Type of cosolvent	Methanol	ETAC	THF	AC	DEE	HEX
Boiling point at standard pressure, °C	64.7	77.1	66	56.5	34.6	68.5
Density (20 °C), g cm ⁻³	0.79	0.89	0.89	0.79	0.71	0.66
Dynamic viscosity (20 °C), mPa s	0.59	0.45	0.55	0.32	0.24	0.31
Electric dipole moment, C m	1.69	1.78	1.63	2.91	1.15	0.08
Relative permittivity (20 °C), -	32.7	1.37	7.58	20.7	4.33	1.89
Water content, wt%	0.03	0.02	0.03	0.25	0.15	0.05
Molar ratio oil:MET:cosolvent, -	-	1:6:5.5	1:6:6	1:6:24.5	1:6:5	1:6:15

Table 2. The properties of the EP after transesterification with various cosolvents

Type of cosolvent	ETAC		THF		AC		DEE		HEX	
Way of stop	CO ₂	H ₃ PO ₄	CO ₂	H ₃ PO ₄	CO ₂	H ₃ PO ₄	CO ₂	H ₃ PO ₄	CO ₂	H ₃ PO ₄
w_{MG} (wt%)	12.35	12.55	5.18	4.59	4.06	4.39	11.10	10.75	3.92	3.85
w_{DG} (wt%)	7.85	7.55	2.28	2.47	4.33	4.60	3.82	2.41	4.40	4.21
w_{TG} (wt%)	8.99	8.66	1.26	1.31	5.58	5.11	2.51	2.37	5.08	4.95
w_{ester} (wt%)	70.8	71.2	91.3	91.6	86.0	85.9	82.6	84.5	86.6	87.0
ρ (g cm ⁻³)	0.84	0.88	0.82	0.88	0.86	0.89	0.89	0.89	0.87	0.88
ν (mm ² s ⁻¹)	5.45	5.29	5.20	5.11	5.38	5.26	5.50	5.38	5.41	5.32
an (mg KOH g ⁻¹)	0.10	0.25	0.24	0.24	0.11	0.31	0.31	0.30	0.12	0.25
w_{water}^{EP} (ppm)	800	700	800	650	900	700	1000	1100	1000	800
K (mg kg ⁻¹)	97	84	72	60	250	240	66	57	220	230

Table 3. The distribution of methyl esters according to higher fatty acid in the EP

Type of cosolvent	Methyl esters of higher fatty acids (100%)			
	Linolenic (%)	Linoleic (%)	Oleic (%)	Palmitic (%)
Without	11.00	21.70	62.10	5.21
THF	11.10	20.07	64.77	4.07
AC	14.50	21.11	58.41	5.98
DEE	10.78	21.37	57.49	10.35
ETAC	13.37	21.03	62.92	2.68
HEX	13.40	21.50	58.03	7.07

Table 4. The composition of the GP after transesterification with various cosolvents

Type of cosolvent	ETAC		THF		AC		DEE		HEX	
Way of stop	CO ₂	H ₃ PO ₄	CO ₂	H ₃ PO ₄	CO ₂	H ₃ PO ₄	CO ₂	H ₃ PO ₄	CO ₂	H ₃ PO ₄
$w_{glycerol}$ (wt%)	67.5	68.5	43.8	46.1	41.5	71.3	65.9	60.2	56.1	70.5
w_{ester}^{GP} (wt%)	3.8	2.8	9.0	13.3	5.9	6.4	7.2	13.1	7.1	5.9
w_{water}^{GP} (wt%)	0.41	0.48	0.24	0.68	0.88	1.04	0.69	0.79	0.85	0.99
w_S (wt%)	33.3	35.6	30.3	31.9	29.2	18.4	28.7	22.2	28.3	19.5
$w_{K_2CO_3}$ (wt%)	3.1	-	4.8	-	5.5	-	5.6	-	5.2	-
w_{KHCO_3} (wt%)	0.19	-	0.45	-	0.43	-	0.36	-	0.51	-
$w_{K_2HPO_4}$ (wt%)	-	1.9	-	2.38	-	0.6	-	2.38	-	1.1