

1           **Butanol as cosolvent for transesterification of rapeseed oil by**  
2           **methanol under homogeneous and heterogeneous catalyst**

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**ABSTRACT**

7   The paper is focused on the use of methanol (M) or ethanol together with butanol (B) in the  
8   transesterification of rapeseed oil (O) under homogeneous (KOH) and heterogeneous catalysis  
9   (Mg-Fe mixed oxides). The advantage of using butanol consists in the formation of  
10  homogenous reaction mixture (increases the reaction rate, i.e. decreasing of reaction time) and  
11  higher caloric value of formed esters. The novelty consist in the use of mixture of alcohols. The  
12  ternary plots of reaction components (alcohols and oil) were measured at 25 and 60 °C. For  
13  homogeneous catalyst, the influence of (i) the molar ratios of reaction components, (ii) the  
14  temperature, (iii) the amount of catalyst and (iv) the way of transesterification stopping on the  
15  course of transesterification was studied. The properties of esters phase and also glycerol  
16  phase were determined including ester loss in the glycerol phase. The ester yield was 97 %  
17  after 10 min of reaction for 60 °C and the ratio O:M:B was 1:6:2, which is significantly  
18  decreasing of time in comparison with methanol only (90 min). However, the content of  
19  potassium ions was higher, because butyl ester caused higher solubility of potassium ions. For

20 heterogeneous catalyst, the synthesized materials were characterised by chosen method and  
21 tested in transesterification with methanol, butanol and their combination.

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## 23 **KEYWORDS**

24 transesterification; biodiesel; esters; butanol; methanol

## 25 **NOMENCLATURE**

26	B	butanol
27	BE	butyl ester
28	E	ethanol
29	FAME	fatty acid methyl ester
30	GC	gas chromatography
31	M	methanol
32	ME	methyl ester
33	O	oil
34	EP, GP	the ester phase, the glycerol phase
35	TG, DG, MG	triacylglycerides, diacylglycerides, monoacylglycerides; all of these
36		substances are referred to as glycerides
37		
38	$K$	concentration of potassium ions ( $\text{mg kg}^{-1}$ )
39	$T$	reaction temperature ( $^{\circ}\text{C}$ )
40	$t$	reaction time (min)
41	$w_{\text{water}}$	water content in the EP (ppm)
42	$w_{\text{ester}}^{\text{GP}}$	ester content in the GP (wt.%)
43	$w_{\text{ester}}$	ester content in the EP (wt.%)
44	$w_{\text{glycerol}}$	glycerol content in the GP (wt.%)
45	$w_{\text{Gf}}$	glycerol content in the EP (wt.%)
46	$w_{\text{IS}}$	content of inorganic salts in the GP (wt.%)
47	$w_{\text{MG}}, w_{\text{DG}}, w_{\text{TG}}$	content of MG, DG and TG in the EP (wt.%)
48	$w_{\text{S}}$	soap content (wt.%)
49	$w_{\text{water}}$	water content in the GP

50  $x_B, x_E, x_M, x_O$  mole fraction of butanol, ethanol, methanol and oil in the mixture (-)  
51  $x_{BE}^{EP}$  butyl esters content in the EP (mol.%)  
52  $x_{ME}^{EP}, x_{ME}^{GP}$  distribution of methyl esters in the EP and GP in mole percent (mol.%)  
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## 54 1. INTRODUCTION

55 The mixture of methyl esters of higher fatty acids (biodiesel) is a biofuel for combustion  
56 engines made from biomass. It is produced by the transesterification of triacylglycerides (TG)  
57 contained in vegetable oils or animal fats by low molecular alcohols. The transesterification  
58 has to be catalysed under mild reaction conditions, without any catalyst it proceeds only under  
59 higher temperature and pressure – at the supercritical fluid [1]. A basic homogeneous catalyst  
60 is the most often used [2] [3]. However, the heterogeneous or enzymatic catalysis is also  
61 applicable to ester preparation [4] [5].

62 The most often used alcohol is methanol, the use of other types of alcohols, such as  
63 ethanol [6] or butanol is less common. Methanol and ethanol are immiscible with TG, i.e. the  
64 heterogeneous mixture is formed and the transesterification proceeds only on the interface.  
65 This is in contrast to butanol, which is miscible with TG. To increase the reaction rate (i.e. to  
66 shorten the reaction time) for methanol or ethanol, the reaction mixture has to be intensively  
67 stirred to increase the interface area. Other possibility is the formation of a single phase by  
68 addition of another solvent (called cosolvent), which is inactive to oil and alcohol. The use of  
69 several cosolvents, mostly for homogeneously catalysed transesterification, was published,  
70 such as dimethyl ether [7], di-isopropyl ether, tetrahydrofuran [8], [9], acetone, methyl tert-  
71 butyl ether [10]. Butanol (most often 1-butanol) can be also used as a cosolvent for  
72 transesterification with methanol/ethanol, because dissolves TG and methanol/ethanol.  
73 Moreover, butanol reacts with oil to form butyl esters. The use of butanol was published  
74 almost only as the reaction component for many types of catalysts, such as homogeneous  
75 basic catalyst  $KOCH_3$  or  $KOH$  [11], homogeneous acid catalyst [12] [13] or heterogeneous

76 catalyst [14]. However, the detailed analysis of both phase including ester loss are very often  
77 omitted. For enzymatic catalysis (*Thermomyces lanuginosa*), methanol together with butanol  
78 was published, but without determination of homogeneous region [15]. The transesterification  
79 with only butanol usually proceeded at higher temperature (100-115 °C) and higher molar  
80 ratio of oil to butanol than for methanol [16], because it is less reactive than methanol.  
81 However, the synthesized butyl esters have higher caloric value than methyl esters  
82 (approximately about 7-10%) [17].

83 Almost all papers dealing with transesterification are focused only on the use of single  
84 type of alcohol (some of them with inactive cosolvents) and none of them on the combination  
85 of both alcohols. The novelty of the paper consists in the use of butanol, which was employed  
86 as a cosolvent and also as the reaction component in the transesterification of oil, together  
87 with methanol or ethanol. The relevance of butanol use consists in (i) shortening of the  
88 reaction time and (ii) slightly higher caloric value, because the main product is a mixture of  
89 methyl or ethyl esters with butyl esters. The purpose of ternary plots was to find the region,  
90 where the reaction components were presented in a single phase. The parameters, which can  
91 influence the course of transesterification and properties of ester (EP) and also glycerol phase  
92 (GP), such as the molar ratios of oil, methanol and butanol, the reaction temperatures, the  
93 catalyst amount and the way of transesterification stopping, were studied. The attention was  
94 also paid to the distribution of esters according to alcohols and loss of esters in the GP, which  
95 is often omitted in papers. The use of two types of alcohols together, including determination  
96 of ternary plots, has not been published yet regarding homogeneously or heterogeneously  
97 catalysed transesterification. Its description is the main aim of the paper.

## 98 2. MATERIALS AND METHODS

### 99 2.1. Ternary plot

100 The ternary plot was determined by measuring of transmittance by spectrophotometric  
101 method at wavelength 450 nm at two temperatures (25 and 60°C). The transmittance of pure  
102 oil was 100%. The oil and methanol (or ethanol) were stirred together and heterogeneous  
103 system with low transmittance was formed. Butanol, which is miscible with both liquids, was  
104 successively added and transmittance was monitored. When the transmittance rapidly  
105 increased, the system became homogeneous, which was one point of binodale curve of  
106 ternary plot. This method was used for determination of each binodal point. The molar ratios  
107 of components were used for formation of the final plot in program Origin 9.1. The rapeseed  
108 oil (molar mass 879.1 g mol<sup>-1</sup>) was considered as a chemical individuum.

### 109 2.2. Transesterification of oil

110 Homogeneous catalyst: The rapeseed oil (free of erucic acid, acid number 0.2 mg KOH g<sup>-1</sup>,  
111 water content 650 mg kg<sup>-1</sup> and density 920 kg m<sup>-3</sup> (15°C), produced by Lukana, Czech  
112 Republic) was put into the reaction vessel and thermostated to the reaction temperature. The  
113 catalyst KOH (purity 85 wt.%, Lach-Ner, Neratovice, The Czech Republic) was dissolved in  
114 mixture of methanol (p.a., Penta, The Czech Republic) with butanol (purity 99.5%, Penta, The  
115 Czech Republic) and mixture were also thermostated to the temperature of reaction. The  
116 mixture of alcohols with catalyst was quickly added into the reaction vessel. Throughout the  
117 reaction time, the reaction mixture was sampled and the content of mono-, di- and  
118 triacylglycerides was determined. The reaction was stopped by catalyst neutralization by (i)  
119 gas carbon dioxide as a weak acid [18] or (ii) phosphoric acid as a strong acid [19]. The acids  
120 had been dosed approximately for 5 min until the pH fell to the minimum value, which was  
121 approximately 8 for carbon dioxide and 10.5 for phosphoric acid. The paddle stirrer was set to

122 300 rpm during the reaction and neutralization. The alcohols excess was removed by  
123 distillation; the reaction mixture had been evaporated for 40 min at 100°C at the pressure of  
124 approximately 3 kPa. The mixture was put into a separatory funnel and separated by gravity  
125 for 24 h and then both formed phases (the ester and glycerol) were analysed.

126 Heterogeneous catalyst: Mg-Fe mixed oxides were synthesized from hydrotalcite by heating  
127 (calcination) to 450 °C for 3 h. The hydrotalcite was synthesis by co precipitation from  
128 nitrates of magnesium and iron according to [20]. Moreover, the active coal (1.25 wt% to  
129 amount of precursors) was added during synthesis to increase the specific surface area. The  
130 reaction was carried out in stainless steel batch autoclave (300 ml, Parr company, USA)  
131 equipped with shaft stirrer. The transesterification was carried in 300 ml batch reactor (Parr,  
132 USA). The reaction conditions were: molar ratio alcohol to oil 24:1, 1 wt% of catalyst to input  
133 rapeseed oil, reaction temperature 120 °C and stirring speed 300 rpm. After heating to the  
134 reaction temperature, the stirring was switched on and the reaction was initiated. After  
135 reaction time, the catalyst was removed by filtration and methanol by distillation from the  
136 mixture (75 °C, 3 kPa) and formed phases was analysed, especially ester content in the EP.

### 137 **2.3. Analytical method**

138 The contents of glycerides were determined by gas chromatography (GC) with flame  
139 ionization detector by the method according to EN 14105 by Shimadzu GC-2010 with the  
140 help of linear calibration curves (monoolein, diolein and triolein were used as standards), the  
141 determination is described in detailed [19].

142 The content of potassium ions in the EP were determined by flame photometry (Flame  
143 photometer 410, Sherwood Scientific Ltd, United Kingdom). The flash point of the EP was  
144 measured by the Pensky-Martens closed-cup method (EN ISO 2719) with the instrument OB-  
145 305 (MIM Fabri, Hungary). The water content in both phases was determined according to

146 EN ISO 12937 (TitroLine® 7750) and the alcohol content also in both phases was determined  
147 by GC [21].

148 The contents of basic matter (potassium hydrogen carbonate, potassium carbonate,  
149  $K_2HPO_4$  and soaps) were determined in the GP by acidimetric titration by HCl ( $0.1 \text{ mol dm}^{-3}$ )  
150 with potentiometric identification. The content of glycerol and esters (i.e. esters loss)  
151 including the distribution according to alcohols (methyl and butyl esters) in the GP was  
152 determined by HPLC [19].

153 The heterogeneous catalyst was characterised by X-ray Powder Diffraction (XRD) with  
154 the help of JCPDS database for confirmation of structure of material, inductively coupled  
155 plasma (ICP) to determine the real content of metals and  $N_2$ -isotherme to determine the  
156 surface area [20].

### 157 **3. RESULTS AND DISCUSSION**

#### 158 **3.1. Ternary plots**

159 Firstly, the ternary plots for methanol (M) or ethanol (E), rapeseed oil (O) and butanol (B)  
160 were determined at two temperatures 25 and 60 °C (Fig. 1). The reason was to find the molar  
161 ratios of components, so that the reaction mixture was homogeneous, because the miscibility  
162 depends on the molar ratio of components.

163 The heterogeneous region was larger for methanol than for ethanol at both temperatures.  
164 The reason is that the properties of butanol are more similar to ethanol than to methanol,  
165 especially the dipole moment, which reflects the polarity of chemicals. The dipole moment of  
166 butanol ( $5.54 \cdot 10^{-30} \text{ C.m}$ ) is approximately the same as of ethanol ( $5.84 \cdot 10^{-30} \text{ C.m}$ ) and  
167 different from methanol ( $9.57 \cdot 10^{-30} \text{ C.m}$ ) [22]. The heterogeneous region was larger at 25 °C  
168 for methanol and also ethanol, which was expectable, because the miscibility usually

169 increases with increasing temperature. For ethanol at 60 °C, the mixture was homogeneous at  
170 almost all molar ratios.

171 Moreover, the molar ratios of oil to methanol (from 1:3.6 to 1:6) or oil to ethanol (1:7),  
172 which were used for transesterification, were plotted (Fig. 1).

### 173 **3.2. Transesterification by homogeneous catalyst**

174 The transesterification depends on the various reaction conditions, such as alcohol type, the  
175 reaction temperature and time, the molar ratio of initial components and the amount of  
176 catalyst.

177 Firstly, the transesterification with ethanol and butanol together was carried out at 25 °C, at  
178 molar ratio O:E:B 1:7:3.5 and 1 wt% of catalyst (KOH) to oil. The lower temperature (25 °C)  
179 was chosen, because the undesired oil saponification proceeds less than at 60 °C [23]. The  
180 molar ratio of reaction components was based on ternary plot (Fig. 1B), so the reaction  
181 mixture was in the single phase. After separation, both phases were analysed. However, the  
182 content of potassium ions in the EP was very high (15 g kg<sup>-1</sup>), which was about 1000 times  
183 more than potassium content for ethanolysis itself (10-20 mg kg<sup>-1</sup>) [23]. The formed butyl  
184 ester caused high solubility of potassium soaps in the EP. Similar effect was also observed for  
185 methyl esters, but much less intensively (please refer to section 3.2.1). For this reason, ethanol  
186 for transesterification was not studied in detailed (as for methanol).

#### 187 **3.2.1. The influence of various molar ratios of oil : methanol : butanol**

188 The various molar ratios of O:M:B were used for transesterification. The molar ratios were  
189 found in the ternary plot (Fig 1A) so that the reaction mixture was homogeneous with  
190 minimum alcohol use. For all molar ratios, the amount of catalyst was 0.8 wt% to oil and the  
191 temperature 60 °C, because it is the usual temperature of transesterification with methanol



192 only. Moreover, the reaction was stopped by two different ways. The dependency of  $w_{ester}$  in  
193 the EP on the reaction time was determined and compared with methanolysis itself (Fig 2).

194 If the molar ratio O:M:B was 1:6:2.3, which is the same as is usually used for single  
195 methanol (O:M = 1:6), the  $w_{ester}$  in the EP was 97 % after 10 min. In the case of  
196 transesterification with only methanol, the same yield was achieved after 80 min of reaction  
197 (under the same reaction conditions). Therefore, the reaction time was rapidly decreased by  
198 butanol addition, because butanol acted as a cosolvent. Moreover, butanol also reacted with  
199 oil, because 15 mol% of butyl ester was found in the EP. For lower molar ratios, the  
200 transesterification was slower, because methanol was presented in lower amount. For molar  
201 ratio O:M:B 1:4.6:1.5 (molar ratio of oil to alcohol M:B 1:6.1), the reaction was slightly faster  
202 than reaction with only methanol. For the lowest molar ratio of alcohols (1:4.7), which was  
203 less than for methanol itself, the reaction was the slowest and  $w_{ester}$  in the EP was lower than  
204 for only methanol. However, for lower molar ratios of alcohols, the content of butyl esters in  
205 the EP was also lower (between 7-9 mol%), because less amount of butanol was used.  
206 Boocok, et al. published methyl terc-butyl ether as cosolvent for transesterification with  
207 conversion 95 % after 20 min.

208 Moreover, the properties of the EP and GP were determined. The acid number of the EP  
209 was always less than 0.2 mg KOH g<sup>-1</sup>, because both ways of transesterification stopping  
210 ensure low acid number [19]. The density of EP was in the range 0.874-0.880 g cm<sup>-3</sup> for all  
211 molar ratios and ways of stopping. The viscosity was determined 5.1 mm<sup>2</sup> s<sup>-1</sup>, which was  
212 higher than for pure methyl esters, because the EP contains mixture of methyl and butyl  
213 esters. This was proved by the determination of viscosity of the mixture of methyl and butyl  
214 esters (as molar percent of butyl esters in the mixture -  $x_{BE}^{EP}$ ) (Fig. 3A). The viscosity  
215 increased with increasing butyl ester content and viscosity of butyl ester was about 32 %  
216 higher than methyl esters. The flash point higher than 130 °C of the EP was also determined,

217 which means that the residual content of alcohols is less than 0.08 wt% for methanol and  
218 0.13 wt% for butanol (both were determined by GC). The content of butanol was higher  
219 because is less volatile than methanol.

220 The water content and content of potassium ions were quite high (Table 1) in comparison  
221 with transesterification with only methanol, but the purification step was not used. Higher  
222 water content was also determined for pure butyl ester (1360 ppm) than for pure methyl esters  
223 (650 ppm) without drying. The amount of water was higher for stopping by  $H_3PO_4$  than by  
224  $CO_2$ . The relatively high content of these impurities was caused by formed butyl ester. The  
225 reason is that the potassium ions are more soluble in butyl esters than in methyl ester, which  
226 was confirmed by independent experiments: the potassium soaps were solved in the esters,  
227 which were prepared by mixing of pure methyl and pure butyl esters with various esters  
228 compositions. The content of solved potassium ions was determined by flame photometry  
229 (Fig. 3B). The content of potassium increased with increasing content of butyl esters in the  
230 mixture and was approximately 3.5 times higher for pure butyl ester than for methyl esters.  
231 Therefore, the presence of butyl esters increase the potassium and water content in EP without  
232 purifications. Note: the exact content of potassium and water content depends also on the  
233 separation and purifications steps.

234 The side GP was also analysed in detail (Table 1), including the content of esters in the  
235 GP, i.e. esters loss ( $w_{ester}^{GP}$ ), which is different from other papers. The content of ester in the GP  
236 (19-25 wt%) was higher than in the GP prepared by transesterification with only methanol,  
237 where it was approximately 10 wt% [18]. For butanol, the ester content in the GP has not  
238 been published yet. Moreover, the ester content was higher for stopping by  $H_3PO_4$  than by  
239  $CO_2$ . The GP contains also inorganic salts ( $w_{IS}$ ), which were formed by catalyst neutralization  
240 and depend on the type of reaction stopping ( $K_2HPO_4$  for stopping by  $H_3PO_4$  and  $K_2CO_3$ ,  
241  $KHCO_3$  for stopping by  $CO_2$ ). The content of these salts was low, which detected that almost

242 no catalyst remained at the end of the reaction, i.e. almost all was consumed by side reaction –  
243 saponification. The content of water was quite low, from 0.3 to 0.9 wt%.

### 244 **3.2.2. The influence of reaction temperature**

245 The influence of temperature was also studied: two temperatures were chosen (25 and 60 °C)  
246 and appropriate molar ratios of alcohol to oil, minimum so that mixture was homogeneous,  
247 were determined from the ternary plot (Fig. 1A). For 25 °C, the amount of butanol has to be  
248 higher (molar ratio O:M:B 1:5:4.7, i.e. approximate molar ratio M to B was 1:1) than for  
249 60 °C (molar ratio O:M:B 1:6:2.3, i.e. molar ratio M to B was 2.6:1). The dependency of ester  
250 content in the EP ( $w_{ester}$ ) on the reaction time was determined (Fig. 4) and compared with  
251 single methanol used. For 60 °C, the ester content was 97 wt% after 10 min, while only  
252 methanol was 88.3 wt%. The difference of ester content was greater for lower temperature  
253 (25 °C), where the miscibility of the reaction mixture has stronger influence (85% after 80  
254 min for methanol only). The mixture of methyl and butyl esters was formed.

255 The analysis of both phases was also carried out (Table 2). The viscosity, water content  
256 and potassium content were higher than for pure methyl esters, because the butyl ester caused  
257 higher solubility of potassium ions, which was discussed above (Fig. 3). The content of ester  
258 in the GP was higher for higher temperature, because higher temperature caused higher  
259 solubility.

### 260 **3.2.3. The influence of catalyst amounts**

261 The influence of catalyst (in the range 0.7-0.9 wt% to oil) was studied (Table 3). Moreover,  
262 the reaction was stopped by two ways as in previous cases. Higher catalyst amount means  
263 higher amount ester in the EP. On the other hand, higher catalyst amount caused higher  
264 saponification, which was expected, and so higher content of ester in the GP (ester loss). The

265 content of potassium ions was lower for stopping by  $\text{H}_3\text{PO}_4$  than  $\text{CO}_2$ , which is in accordance  
266 with previous papers, where the similar phenomena was also described [19].

#### 267 **3.2.4. Ester loss and distribution of esters**

268 The ester loss (determined as the content of esters in the GP in wt%) was analysed, which is  
269 very often omitted in papers. The content of esters was approximately in the range 15-25 wt%  
270 (Table 4), which was higher than for pure methyl esters (9-10 wt%). Therefore, the formed  
271 butyl ester caused higher ester loss.

272 Moreover, the distribution of esters according to alcohols, i.e. methyl esters (ME) and  
273 butyl esters (BE), was also determined for both phases (Table 4). The content of methyl ester  
274 in the EP was in the range from 85 mol% to 92 mol% at 60 °C, while at 25 °C it was lower,  
275 around 80 mol%. However, the initial molar ratio of methanol to butanol used for the  
276 transesterification was 52.4 mol% at 25 °C and 73-77.8 mol% at 60 °C of methanol in the  
277 alcohols mixture. According to stoichiometry of transesterification, one mole of alcohol forms  
278 one mole of ester. The ratio between molar percent of methyl esters in EP and molar percent  
279 of methanol in alcohol mixture was calculated. The ratio “one” means the same molar ratio of  
280 methanol and formed methyl ester. For lower temperature (25 °C), more methyl esters were  
281 formed from methanol than butyl esters from butanol: 80 mol% of methyl ester in the EP was  
282 formed from 52.4 mol% of methanol, the ratio was 1.52. For higher temperature (60 °C), the  
283 ratio was lower, 1.19. This ratio depends only on the temperature and not on other reaction  
284 conditions.

285 Only smaller amount of butanol was converted to butyl esters and butanol acted mainly  
286 as a cosolvent. Therefore, for lower temperature, the methyl esters are easily formed than  
287 butyl esters. The reason is probably lower activation energy for transesterification by  
288 methanol than by butanol. However, it is inconclusive, because the activation energy was  
289 published in a wide range, which depends on the simplification of kinetic model, type of oil,

290 type of catalyst and transesterification conditions. The activation energy was published for  
291 methanolysis from 12 to 104 kJ mol<sup>-1</sup> [24] and for ethanolysis from 3.4 to 70.6 kJ mol<sup>-1</sup> [25].  
292 The activation energy for transesterification with butanol was not published. Moreover, the  
293 formed oil is immiscible with methanol, while miscible with butanol, which complicated the  
294 calculation. The positive correlation between content of methyl esters in GP and content of  
295 methyl esters in EP was found (Fig. 5).

296 The dependency of distribution of methyl and butyl ester in the EP and GP on the  
297 transesterification stopping (CO<sub>2</sub> or H<sub>3</sub>PO<sub>4</sub>) was determined. In the case of stopping by CO<sub>2</sub>,  
298 the distribution of methyl and butyl esters between the EP and GP was approximately the  
299 same, i.e. the relative content of methyl esters in the EP and GP was almost the same. The  
300 relative content did not depend on the reaction conditions. However, the distribution was  
301 different for stopping by H<sub>3</sub>PO<sub>4</sub>: more methyl esters were presented in the GP than in the EP.  
302 Therefore, the stopping by H<sub>3</sub>PO<sub>4</sub> caused more solubility of methyl ester in the GP than  
303 stopping by CO<sub>2</sub>.

### 304 **3.3. Transesterification by heterogeneous catalyst**

305 The transesterification with heterogeneous catalyst was also tested. The Mg-Fe mixed oxide  
306 with molar ratio Mg/Fe 3:1 was used as heterogeneous catalyst. The active coal, which was  
307 added during synthesis of hydrotalcite, was removed by calcination at 450 °C. The  
308 determination by XRD (Fig. 6) confirmed the structure of mixed oxide by presentation of  
309 typical diffraction lines for mixed oxide (JCPDS database). In hydrotalcite, the real molar  
310 ratio of magnesium to iron 2.9 was determined by ICP analysis (1.55 mol Mg and 0.53 mol  
311 Fe), i.e. almost as the same as expected. The specific surface area was calculated by fitting of  
312 experimental data determine by nitrogen adsorption–desorption isotherms with use BET  
313 isotherm. The surface area of Mg/Fe 3:1 with 1.25 wt% of coal was 132 m<sup>2</sup> g<sup>-1</sup> which was

314 compared with hydrotalcite Mg/Fe 3:1 without addition of active coal ( $101 \text{ m}^2 \text{ g}^{-1}$ ). The high  
315 surface area is important, because transesterification carried out on the surface of catalyst.

316 The catalyst activity was tested in transesterification of rapeseed oil with (i) only methanol,  
317 (ii) only butanol and (iii) various ratios of methanol to butanol. The best results were achieved  
318 with methanol and mixture of methanol and butanol in molar ratio 1:1. The content of esters  
319 in the EP reached 97.5 wt.% after 4 h of reaction, which is much faster than published in [20],  
320 where it was only 70 wt.% after the reaction time of 6 h. In the case of using only butanol, the  
321 ester content in the EP was 59.4 wt.%, because butanol is less reactive than methanol. The  
322 addition of butanol increase the reaction rate and so decrease the reaction time.

#### 323 **4. CONCLUSIONS**

324 This work described the use of butanol as the cosolvent for transesterification of oil by  
325 methanol or ethanol under homogeneous and also heterogeneous catalyst. The ternary plots  
326 with binodal curve for reaction components (oil, methanol/ethanol and butanol) were  
327 determined for two temperatures (25 and 60 °C) to find the homogeneous region. For  
328 homogeneous catalyst, the transesterification was carried out with various reaction condition.  
329 The ester yield was 97 % after 10 min of reaction for 60 °C and ratio O:M:B 1:6:2. However,  
330 the viscosity and content of potassium ions were higher than for pure methyl ester (without  
331 purification), because the solubility of potassium soaps increased with increasing butyl ester  
332 content in the mixture of esters. The distribution of methyl and butyl esters in both phases was  
333 determined. It was found, that the content of methyl esters was higher than corresponding  
334 methanol in the alcohol mixture, especially at lower temperature. The attention was also  
335 focused on the detailed analysis of the side GP where the content of esters was higher for  
336 higher temperature.

337 The use of butanol decrease the production cost and improves the total energy balance of  
338 biodiesel production and so increases sustainability, because transesterification proceeds in  
339 single phase and moreover formed butyl ester has higher caloric value.

#### 340 **ACKNOWLEDGEMENTS**

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

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423



424 **Figure captions**

425

426 Fig. 1: The ternary plots of M:O:B (A) and E:O:B (B) at two temperatures

427 Fig. 2: The dependency of  $w_{ester}$  in the EP on the reaction time for different molar ratios of  
428 alcohols to oil at 60 °C and 0.8 wt% of catalyst to oil

429 Fig. 3: The dependency of viscosity (A) and content of potassium ions (B) on the molar ratios  
430 of butyl esters in the mixture of methyl and butyl esters

431 Fig. 4. The dependency of  $w_{ester}$  on the reaction time for different reaction temperatures at  
432 0.8 wt% of catalyst to oil, molar ratio O:M:B 1:5:4.7 for 25 °C and 1:6:2.3 for 60 °C

433 Fig. 5: The correlation of methyl esters between the EP and GP

434 Fig. 6: The diffractogram of Mg-Fe mixed oxides

Table 1: The properties of the EP and the GP after transesterification with different molar ratios of O:M:B (temperature 60 °C, time 80 min, catalyst 0.8 wt% to oil)

Stop by	Molar ratio O:M:B	The ester phase						The glycerol phase				
		$w_{ester}$ , wt. %	$water$ , ppm	$K$ , mg kg <sup>-1</sup>	$w_{MG}$ , wt. %	$w_{DG}$ , wt. %	$w_{TG}$ , wt. %	$w_{glycerol}$ , wt. %	$w_{ester}^{GP}$ , wt. %	$w_S$ , wt. %	$w_{IS}$ , wt. %	$w_{water}$ , wt. %
CO <sub>2</sub>	1:6.0:2.3	98.7	960	100	0.78	0.31	0.25	61.5	21.0	14.8	2.48	0.47
	1:4.6:1.5	96.7	600	168	2.05	0.56	0.72	64.8	20.8	16.9	1.58	0.29
	1:3.9:1.1	96.1	720	259	1.71	1.11	1.03	62.4	18.7	16.5	1.71	0.66
H <sub>3</sub> PO <sub>4</sub>	1:6.0:2.3	97.9	1090	22	1.84	0.24	0.07	62.3	21.8	19.8	0.49	0.51
	1:4.6:1.5	95.7	1068	100	3.54	0.71	0.09	56.7	24.5	18.3	0.62	0.56
	1:3.9:1.1	95.1	1114	136	3.53	1.03	1.32	43.7	37.9	15.2	0.59	0.43

Table 2: The properties of the EP and the GP after transesterification at different temperature and reaction stopping (time 80 min, catalyst 0.8 wt% to oil)

Stop by	Molar ratio O:M:B	$T$ , °C	The ester phase						The glycerol phase				
			$w_{ester}$ , wt. %	$water$ , ppm	$K$ , mg kg <sup>-1</sup>	$w_{MG}$ , wt. %	$w_{DG}$ , wt. %	$w_{TG}$ , wt. %	$w_{glycerol}$ , wt. %	$w_{ester}^{GP}$ , wt. %	$w_S$ , wt. %	$w_{IS}$ , wt. %	$w_{water}$ , wt. %
CO <sub>2</sub>	1:5:4.7	25	97.74	1310	238	2.05	0.20	0.01	82.1	5.7	7.17	4.61	0.49
	1:6:2.3	60	98.66	960	110	0.78	0.31	0.26	61.5	21.0	14.78	2.49	0.47
H <sub>3</sub> PO <sub>4</sub>	1:5:4.7	25	97.37	670	176	2.26	0.34	0.34	77.3	12.0	12.10	0.99	0.26
	1:6:2.3	60	98.02	700	102	1.71	0.24	0.03	60.1	20.3	19.28	0.21	0.28

Table 3: The properties of the EP and the GP after transesterification with different catalyst amount (temperature 60 °C and time 80 min)

Stop by	Catalyst amount, wt. %	The ester phase						The glycerol phase				
		$w_{ester}$ , wt. %	$water$ , ppm	$K$ , mg kg <sup>-1</sup>	$w_{MG}$ , wt. %	$w_{DG}$ , wt. %	$w_{TG}$ , wt. %	$w_{glycerol}$ , wt. %	$w_{ester}^{GP}$ , wt. %	$w_S$ , wt. %	$w_{IS}$ , wt. %	$w_{water}$ , wt. %
CO <sub>2</sub>	0.7	96.30	960	104	2.34	0.58	0.78	63.8	16.6	16.2	2.17	0.32
	0.8	96.67	600	168	2.05	0.56	0.72	62.8	17.5	17.9	1.57	0.29
	0.9	97.28	720	111	2.04	0.35	0.34	57.8	23.0	19.2	1.49	0.20
H <sub>3</sub> PO <sub>4</sub>	0.7	95.35	1179	43	3.80	0.62	0.22	67.5	14.0	16.6	1.18	0.77
	0.8	96.12	1075	34	2.93	0.49	0.46	65.9	15.3	17.5	0.37	0.92
	0.9	96.84	798	38	2.85	0.25	0.06	52.5	23.9	20.9	0.08	0.55

Table 4: The loss of esters in the GP ( $w_{ester}^{GP}$ ) including the distribution according to methyl and butyl esters

Way of stop	$T, ^\circ\text{C}$	Molar ratio of M:B	Molar percent of methanol in alcohols	$w_{ester}^{GP}$ , wt. %	Distribution of ME in the EP, mol, %		Ratio between ME in the EP and M in alcohols
CO <sub>2</sub>	25	5.0:4.7	52.4	5.7	79.5	76.8	1.5
CO <sub>2</sub>	25	5.0:4.7	52.4	7.9	79.9	77.3	1.5
H <sub>3</sub> PO <sub>4</sub>	25	5.0:4.7	52.4	12.0	80.9	83.4	1.5
H <sub>3</sub> PO <sub>4</sub>	25	5.0:4.7	52.4	10.9	80.8	76.4	1.5
CO <sub>2</sub>	60	6.0:1.5	73.0	21.0	85.1	85.4	1.2
CO <sub>2</sub>	60	4.6:1.5	75.6	18.7	92.7	92.8	1.2
CO <sub>2</sub>	60	3.9:1.1	77.8	20.8	92.4	91.8	1.2
CO <sub>2</sub>	60	4.6:1.5	75.6	19.6	90.3	88.7	1.2
CO <sub>2</sub>	60	4.6:1.5	75.6	23.0	92.3	92.4	1.2
H <sub>3</sub> PO <sub>4</sub>	60	6.0:2.3	73.0	20.3	86.1	87.8	1.2
H <sub>3</sub> PO <sub>4</sub>	60	6.0:2.3	73.0	21.8	84.8	91.6	1.2
H <sub>3</sub> PO <sub>4</sub>	60	4.6:1.5	75.6	24.5	89.9	94.8	1.2
H <sub>3</sub> PO <sub>4</sub>	60	3.9:1.1	77.8	37.9	91.9	97.4	1.2
H <sub>3</sub> PO <sub>4</sub>	60	4.6:1.5	75.6	14.0	87.6	96.6	1.2
H <sub>3</sub> PO <sub>4</sub>	60	4.6:1.5	75.6	23.9	89.3	96.4	1.2

Figure 1  
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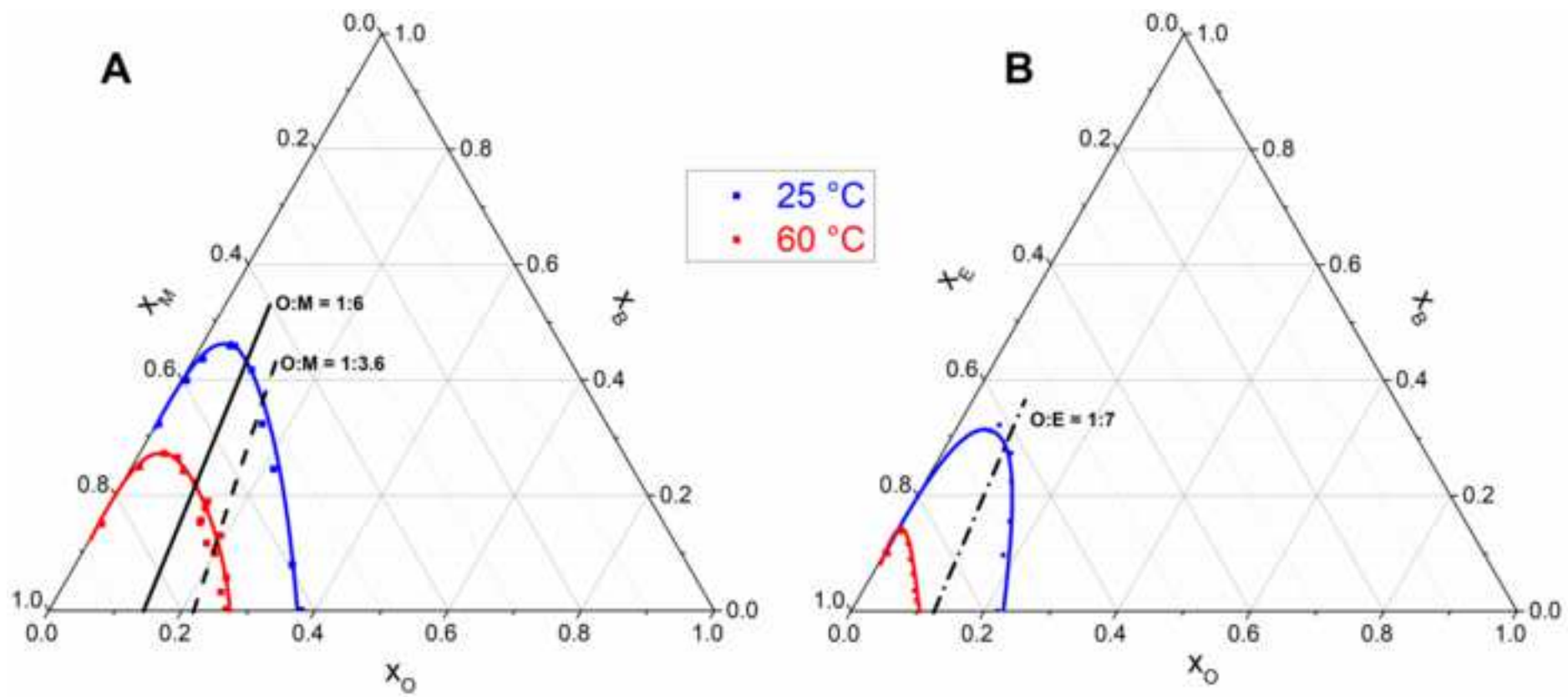


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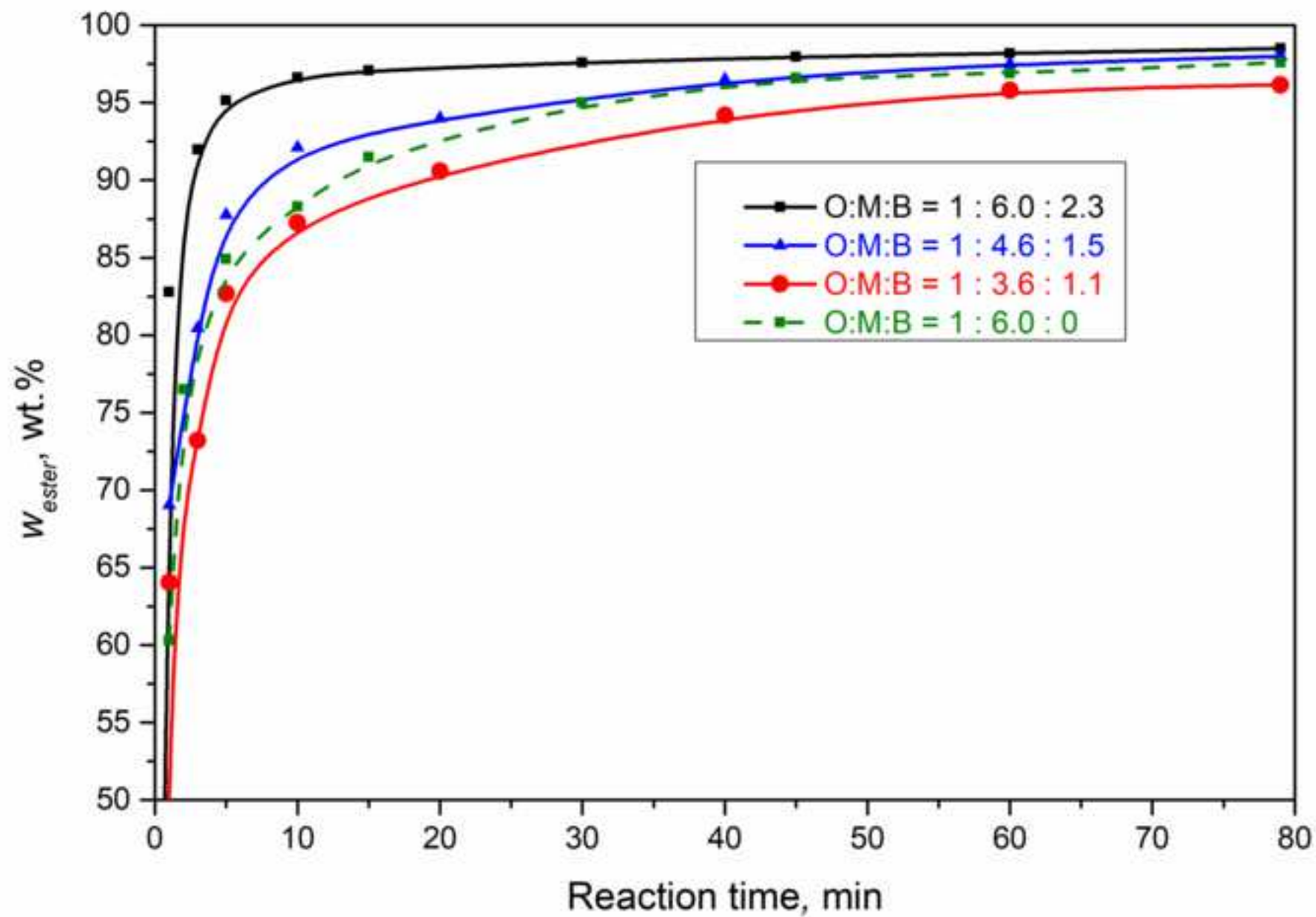


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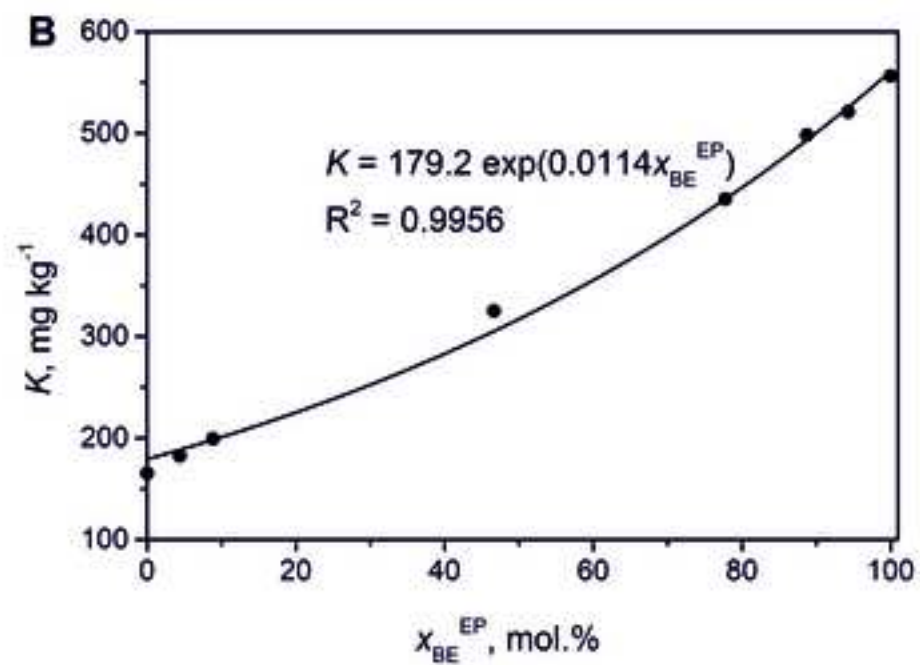
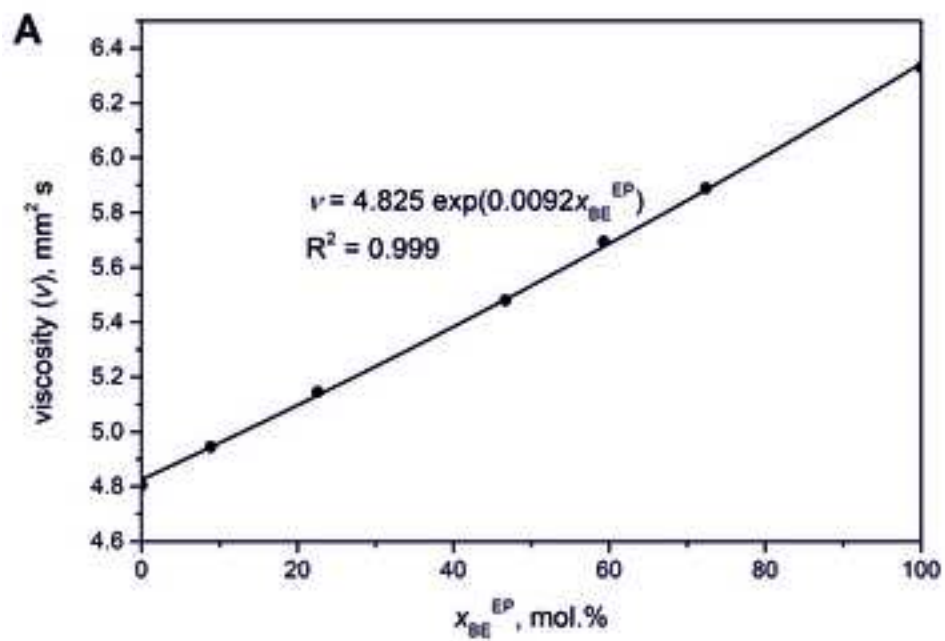




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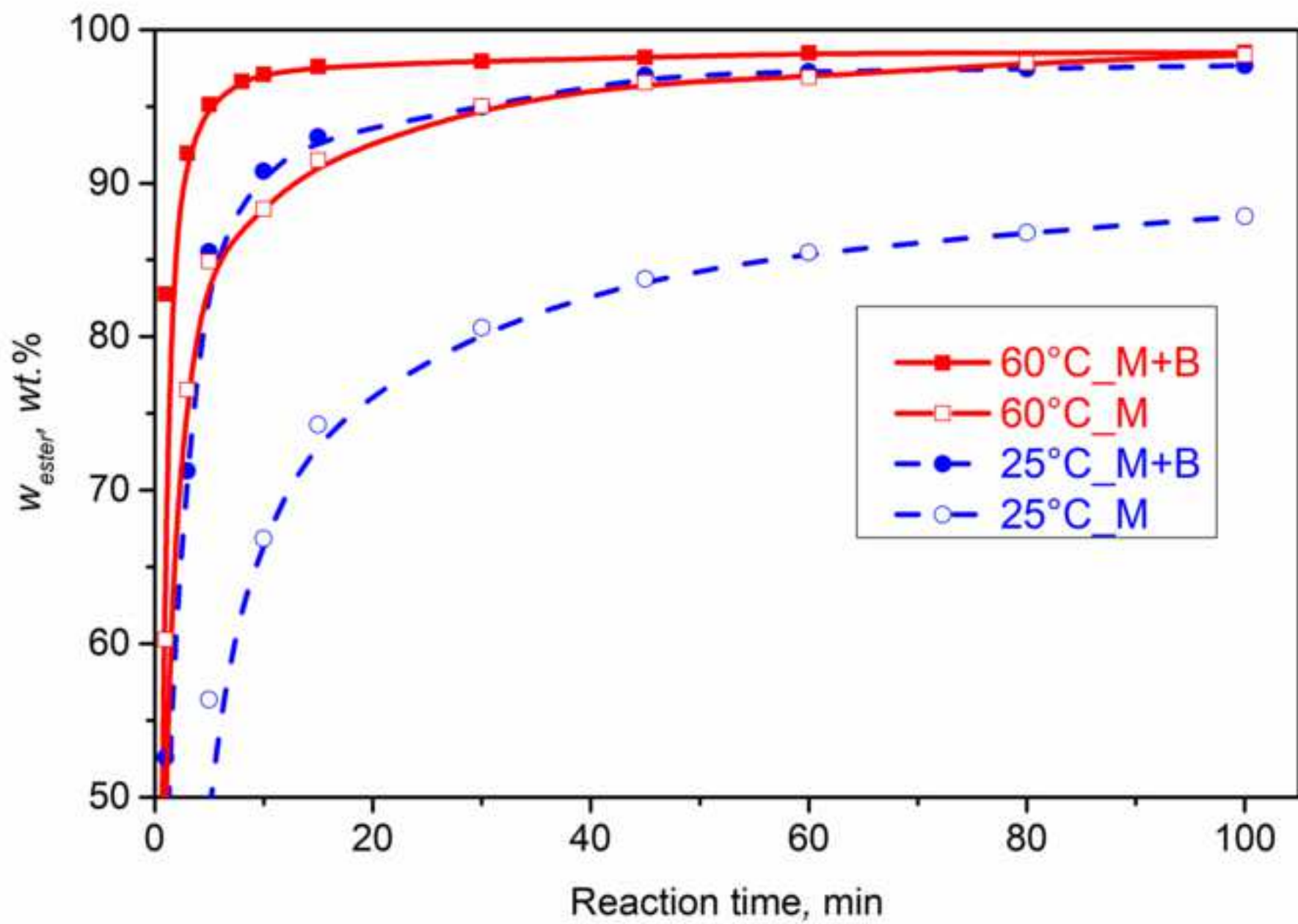


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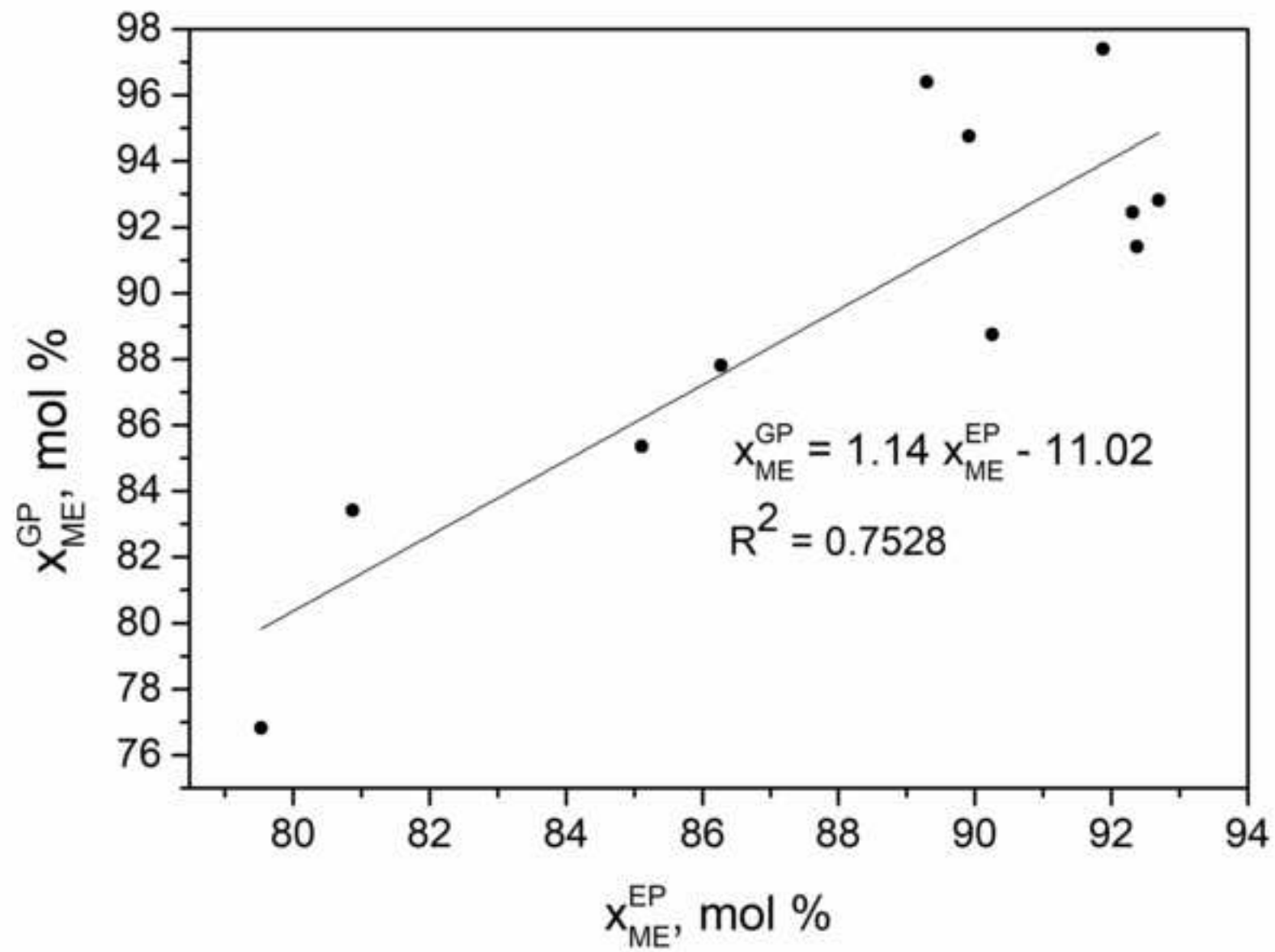


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