

# 1 **Pilot-scale production of biodiesel from waste fats and oils using tetramethylammonium** 2 **hydroxide**

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## 10 **Abstract**

11 Annually, a great amount of waste fats and oils not suitable for human consumption or which  
12 cannot be further treated are produced around the world. A potential way of utilizing this low-  
13 cost feedstock is its conversion into biodiesel. The majority of biodiesel production processes  
14 today are based on the utilization of inorganic alkali catalysts. However, it has been proved that  
15 an organic base – tetramethylammonium hydroxide – can be used as a very efficient  
16 transesterification catalyst. Furthermore, it can be employed for the esterification of free fatty  
17 acids - reducing even high free fatty acid contents to the required level in just one step. The work  
18 presented herein, is focused on biodiesel production from waste frying oils and animal fats using  
19 tetramethylammonium hydroxide at the pilot-plant level. The results showed that the process  
20 performance in the pilot unit - using methanol and TMAH as a catalyst, is comparable to the  
21 laboratory procedure, even when the biodiesel is produced from waste vegetable oils or animal  
22 fats with high free fatty acid content. The reaction conditions were set at: 1.5 % w/w of TMAH,

23 reaction temperature 65 °C, the feedstock to methanol molar ratio to 1:6, and the reaction time to  
24 120 min. The conversion of triglycerides to FAME was approximately 98 %. The cloud point of  
25 the biodiesel obtained from waste animal fat was also determined.

26 *Key words:* biodiesel, cloud point, pilot scale, tetramethylammonium hydroxide, waste oil and fat

## 27 **1. Introduction**

28 Recently, biodiesel – as a renewable, non-toxic and biodegradable fuel, has been considered as a  
29 promising liquid fuel that can be used in diesel engines - either separately, or in a mixture with  
30 conventional diesel fuel (Ong et al., 2013; Singh and Singh, 2010). Chemically, biodiesel is  
31 defined as a mixture of long-chain Fatty Acid Methyl Esters (FAME). The most common method  
32 used for biodiesel production is the transesterification of vegetable oils and animal fats with a  
33 short-chain alcohol (e.g. methanol, ethanol) under alkali or acid conditions (Freedman et al.,  
34 1986; Kolomaznik et al., 2010). There are three stepwise reactions, during which triglycerides are  
35 gradually transformed through two intermediates - i.e. diglycerides and monoglycerides, into  
36 three molecules of FAME and one molecule of glycerol (Pecha, 2009; Ramesh et al., 2006).  
37 However, the transesterification reaction is affected by the selected reaction conditions, i.e. the  
38 type and amount of catalyst, the type of alcohol, the alcohol/oil molar ratio, the reaction time, the  
39 reaction temperature and also the feedstock quality (especially dependent on the free fatty acid  
40 content), (Freedman et al., 1984a; Marchetti et al., 2007; Meher et al., 2006).

41 The price of pure vegetable oils and animal fats plays a key role in the whole production process  
42 because it constitutes up to 80 % of the overall production costs (Demirbas, 2007). This makes  
43 biodiesel production - if unsubsidized, economically disadvantageous. Large amounts of fats and  
44 oils (such as waste frying oils, beef tallow, pork lard or tannery waste fats – i.e. fleshings)  
45 unsuitable for human consumption or which cannot be further treated, are produced annually  
46 around the world. These fats and oils have to be disposed of, which is often very costly.

47 One possibility for utilizing such low-cost feedstocks is their conversion into biodiesel (Haas et  
48 al., 2006; Ong et al., 2013). However, the majority of waste fats and oils contain significant  
49 amounts of free fatty acids (FFAs). This prevents the direct conversion of triglycerides into  
50 biodiesel by means of commonly used technologies using inorganic alkalis (e.g. KOH, NaOH or  
51 their methanolates) as transesterification catalysts, since the catalyst is consumed in the FFA  
52 neutralization and thus, the yield of FAME after the transesterification reaction is insufficient  
53 (Freedman et al., 1984a; Van Gerpen, 2005). In the case of acid catalyst transesterification (e.g.  
54 sulfuric or phosphoric acid), the transesterification reaction runs very slowly unless a large excess  
55 of methanol is used - which makes the process economically unfavorable (Canakci and Van  
56 Gerpen, 1999; Van Gerpen, 2005). However, these acid catalysts appear to be effective for FFA  
57 esterification catalysis in the case of the conversion of FFA into esters in the first step of the  
58 acidic waste fats pretreatment process. The choice of a suitable catalyst is especially dependant  
59 on the FFA content. In order to get a high FAME yield, the recommended FFA content in the  
60 feedstock for effective alkali transesterification should not exceed 1 % - which corresponds to an  
61 acid value of less than 2 mg KOH.g<sup>-1</sup> (ideally less than 0.5 %) (Canakci and Van Gerpen, 2001).  
62 In addition to free fatty acids, the waste feedstock (especially waste fats), contain other  
63 components - like proteins, water, oxidation products and phosphatides that also have to be  
64 removed or significantly reduced (de Moura et al., 2005). This can be performed using either  
65 physical or chemical refining processes; and subsequently, the transesterification reaction  
66 catalyzed by homogeneous alkali catalysts, can be applied (Cmolik and Pokorny, 2000).

67 Papers dealing with biodiesel production from waste vegetable oils and animal fats have been  
68 published by many authors. Most of these works are focused on the production of biodiesel on  
69 the laboratory scale (Alptekin et al., 2012; Dias et al., 2009; İşler et al., 2010; Kolomaznik et al.,  
70 2009; Leung and Guo, 2006; Wang et al., 2007). However, only a few papers describe the

71 production of biodiesel in larger scales. In their pilot-plant study, Canakci and Van Gerpen  
72 (2003) used two kinds of animal fats (with FFA contents of 9 and 40 % respectively) for  
73 biodiesel production. A two-step, acid-catalyzed pretreatment process using sulfuric acid, was  
74 used for FFA esterification and the subsequent utilization of an alkali catalyst ( $\text{NaOCH}_3$ , 0.21 %  
75 w/w) enabled the achievement of a good esters yield after transesterification. Chitra et al. (2005),  
76 transferred biodiesel production from the laboratory to the pilot-scale, using non-edible oil from  
77 *Jatropha curcus* (FFA content 3.1 %) as feedstock and methanol (20 % w/w) and NaOH (1 %  
78 w/w) as catalysts for the transesterification reaction. The total biodiesel yield achieved was 96 %.  
79 Da Cunha et al. (2009), studied biodiesel production from a pilot plant using beef tallow and  
80 methanol (1:6), and potassium hydroxide (1.5 % w/w) as an alkali catalyst. From the results, it is  
81 clear that they produced high-quality biodiesel with a good conversion rate. The acid number of  
82 the feedstock ranged from 1.2 to 1.8 mg KOH.g<sup>-1</sup>. Torres et al. (2013), compared the results  
83 obtained in the laboratory with the results from the pilot-scale experiments in their article. The  
84 results showed that the biodiesel quality produced from waste vegetable oil on the pilot scale,  
85 using methanol and KOH and NaOH as catalysts, is comparable with the biodiesel quality  
86 obtained in the laboratory. The total yield of FAME was approximately 90 %. Abdullah et al.  
87 (2013), produced biodiesel from waste cooking oil on the pilot scale using a two-step process  
88 which included FFA esterification with sulfuric acid in the first step, followed by  
89 transesterification using NaOH as an alkali catalyst. The biodiesel produced was then tested for  
90 its physical and fuel properties - using ASTM standard methods for biodiesel fuel quality  
91 assurance. Alptekin et al. (2014), in their pilot plant study, produced biodiesel from vegetable oil  
92 (corn oil) and low-cost animal fats (chicken fat and fleshings oil) with high FFA content. In the  
93 first step, sulfuric acid and methanol were used for the pretreatment of the fleshing oil and  
94 chicken fat that allowed the reduction of the FFA content to below 1 %. After that, it was

95 possible to apply alkali-catalyzed transesterification, using methanol and KOH as a catalyst, with  
96 a satisfactory FAME yield. Carlini et al. (2014), investigated the operating conditions for  
97 biodiesel production from waste cooking oils obtained from households with an acid value of  
98  $2.12 \text{ mg KOH.g}^{-1}$  in their pilot-scale study. The work was focused on the comparison of the  
99 catalyst type - i.e. NaOH and  $\text{H}_2\text{SO}_4$ , at different concentrations; and also, on the concentrations  
100 of the alcohol used. The best reaction conditions with the highest reaction yield (94.3 %), were  
101 obtained using 0.5 % of NaOH and a 100% excess of methanol.

102 Kolomazník et al. (2009), in their work suggested, on the laboratory scale, a refining melting  
103 process as a pretreatment step with the subsequent triglyceride transesterification with a strong  
104 organic catalyst like tetramethylammonium hydroxide (TMAH) for the treatment of acidic waste  
105 fat. TMAH is a strong organic base, and therefore, it can be used simultaneously as an FFA  
106 esterification agent as well as a catalyst for triglyceride transesterification. Moreover, the ash  
107 content in glycerol is substantially lower when organic bases are used - in comparison with  
108 inorganic transesterification catalysts. Likewise, biodiesel production using TMAH as a strong  
109 organic catalyst of the transesterification reaction has been published by other authors - but only  
110 on the laboratory scale. In the biodiesel production process from rapeseed oil, as described by  
111 Čerče et al. (2005), the total conversion of triglycerides to FAME was achieved in 15 min. at the  
112 selected reaction conditions. Karavalakis et al. (2010), focused their work on a comparison of the  
113 reaction conditions to obtain the best yield of methyl esters from waste frying oil using  
114 tetramethyl- and benzyltrimethyl ammonium hydroxides as catalysts of the transesterification  
115 reaction. Panter et al. (2012), optimized the reaction conditions of TMAH-catalyzed biodiesel  
116 production from vegetable oil - where the conversion rate reached nearly 100 % in less than 2  
117 hours under optimal reaction conditions. Sánchez et al.(2013), introduced the optimal reaction  
118 conditions for successful transesterification of sunflower oil - namely, a TMAH concentration of

119 1.76 % w/w TMAH, a reaction temperature of 60 °C, a molar ratio of fat to methanol of 1:6 and a  
120 reaction time of 2 hours, in their work.

121 To the best of our knowledge, biodiesel production using TMAH as a catalyst on a pilot-scale has  
122 yet to have been published. The aim of this work is to present a pilot-scale biodiesel production  
123 process for processing waste frying oils (WFO) and animal fats (WAF), using this novel type of  
124 organic alkali catalyst.

## 125 **2. Materials and methods**

### 126 **2.1 Material**

127 Waste frying vegetable oil and waste pork lard were used as feedstock for biodiesel production.  
128 Waste frying oil was collected from a local catering facility, and waste pork lard was obtained  
129 from a local slaughterhouse. Pure rapeseed oil (Lukana brand) - used for method optimization in  
130 the laboratory, was purchased from a local grocery store. The electro-technical-grade solution of  
131 tetramethylammonium hydroxide (TMAH, 25 wt. % in methanol) was purchased from Sachem,  
132 Inc. Rectified methanol (99.9%) was obtained from Glycona, s.r.o. Adipic acid and butanol were  
133 supplied by the IPL Company, and were of analytical grade. Diesel fuel for the cloud point  
134 determination was purchased from a local fuel station - PRIM, s.r.o. The diesel fuel properties  
135 fulfilled the prescribed EN 590 standard parameters.

### 136 **2.2 Analytical methods**

137 The dry matter was determined in compliance with the EN ISO 662 Standard; the acid value  
138 according to the EN ISO 660 Standard; the saponification value determination conformed to the  
139 ISO 58 8763 Standard; the ash content in line with the CSN 58 8760 Standard; and Total  
140 Kjeldahl Nitrogen (TKN) in harmony with the ISO 1871 Standard. The composition of the  
141 biodiesel reaction mixture, (i.e. content of FAME, glycerol, TG, DG and MG), was determined

142 by gas chromatography (Master GC Fast Gas Chromatograph, DANI Instruments S.p.A.)  
143 according to the method described in (Šánek et al., 2013). The contents of the reaction  
144 intermediates in the crude biodiesel were determined using the EN 14 105 Standard, and the  
145 FAME content according to the EN 14 103 Standard. The fatty acid composition of the feedstocks  
146 was determined according to ISO 12966.

### 147 **2.3 The pretreatment and transesterification process on the pilot-scale level**

148 Biodiesel was produced in a pilot plant with a processing capacity of 100 kg per day. The  
149 flowchart of the biodiesel pilot plant is shown in Fig. 1. The core of the pilot plant is composed  
150 of two stirred 40-l batch vessels, designed for different operations. Both vessels operate at  
151 ambient pressure and at a fixed temperature - managed by a control unit. The first vessel, the  
152 “Extractor”, is used for the reduction of the FFA level of the acidic feedstock, and the second  
153 serves as the “transesterification reactor”. Both units are equipped with heating and agitating  
154 devices and a reflux condenser. After the acidic feedstock extraction, the mixture is transferred  
155 into a separatory funnel and allowed to settle. The refined feedstock (i.e. the lower layer) is  
156 transferred to the reactor, where it is subjected to transesterification. After the completion of the  
157 transesterification process, the reaction mixture is then transferred into a 100-l separatory funnel  
158 and allowed to settle overnight. The glycerol and biodiesel layer separation is followed by batch  
159 vacuum distillation (i.e. pressure is gradually increased to 90 kPa, temperature to 70 °C, with a  
160 distillation time of one 25-l batch per about 30 min.) of the upper FAME layer so as to remove  
161 the remaining methanol. The distillation is performed in a glass vacuum evaporator manufactured  
162 by KAVALIERGLASS, Co., Ltd. The other parts of the pilot plant include storage tanks for the  
163 feedstock (capacity 1000-l), methanol (capacity 50-l) and TMAH (capacity 50-l). The  
164 components dosage can be performed by pumps managed by the control unit, or manually.

165 The processing of waste frying oil into biodiesel did not require any pre-treatment step because  
166 the acid value of the waste oil was  $1.3 \text{ mg KOH.g}^{-1}$ , and it was therefore possible to use the  
167 alkaline catalyst for the transesterification reaction directly. However, the properties of the waste  
168 animal fat were different - and for that reason, a pre-treatment step had to be included. The raw  
169 animal fat was rendered and then the rendered fat was subjected to the pre-treatment step -  
170 carried out according to the method described in our previous publication (Šánek et al., 2015).  
171 The comparison of the waste frying oil and waste animal fat properties used for biodiesel  
172 production on the laboratory and pilot scales is shown in Table 1. All raw feedstock was filtered  
173 before further processing, to avoid contamination of the resultant products. The fatty acid profile  
174 of the feedstocks is shown in Table 2.

#### 175 *Extraction of rendered animal fat*

176 A total of 12.3 kg of rendered fat was mixed intensively with 4.3 kg of methanol and 3.04 kg of  
177 25 wt. % methanolic solution of tetramethylammonium hydroxide for 30 min at 60 °C. After that,  
178 the resultant mixture was allowed to separate for 1 hour and the obtained phases (i.e. the refined  
179 fat and the extract) were subsequently withdrawn. The refined fat was subjected to a  
180 transesterification reaction - according to the reaction conditions as described in the following  
181 subchapter. In the case of the laboratory experiments, the FFA extractions were conducted in a  
182 similar manner: a 1:1 ratio of methanol to rendered fat, the amount of TMAH for the FFA  
183 neutralization depended on the acid value, with an extraction time of 30 min, at 60 °C with the  
184 subsequent separation of the layers.

#### 185 *The transesterification reaction*

186 The reaction conditions were first optimized in the laboratory, using pure rapeseed oil as  
187 feedstock (250 g). For the upscale to the pilot plant purposes, only three concentration levels of



188 TMAH as a catalyst were examined, specifically - 0.5; 1 and 1.5 % w/w (related to the initial  
189 weight of rapeseed oil). The molar ratio of oil to methanol was 1:6 (56.25 g of methanol). The  
190 reaction mixture was stirred intensively for 2 h under reflux at 60 °C. The reaction mixture  
191 samples were periodically withdrawn and analyzed, as described above. The waste fats and oils  
192 laboratory experiments were conducted in a similar manner, i.e. the molar ratio of methanol to fat  
193 was 6, the reaction temperature was 60 °C, the reaction time was 2 hours and the reaction mixture  
194 was intensively stirred. The reaction mixture was then allowed to settle, with subsequent  
195 separation of the upper methyl ester layer. The methanol removal from the separated methyl ester  
196 layer was performed by means of vacuum distillation and the resultant crude biodiesel was  
197 analyzed according to the EN 14 105 Standard, to determine the content of the reaction  
198 intermediates. The FAME content was determined according to the EN 14 103 Standard.

199 The transesterification reaction conditions on the pilot-scale were set depending on the  
200 experiments performed in the laboratory scale, as described above. The feedstock, i.e. extracted  
201 fat (6.35 kg) or waste frying oil (15 kg), was subjected to a transesterification reaction with  
202 methanol (molar ratio of fat to methanol 1:6) and TMAH (1.5% w/w, relative to the initial weight  
203 of fat and oil) as a catalyst. The reaction mixture was stirred intensively for 2 h under reflux at  
204 65 °C. After the completion of the transesterification process, the reaction mixture was  
205 transferred into a separatory funnel, where the hot glycerol and biodiesel (methylesters) layers  
206 were easily separated.

207 Then, the methanol was distilled off the ester layer. The course of the reaction in time was  
208 studied; 2 mL of the reaction mixture were taken at the selected time, and immediately  
209 neutralized with an 0.1 M adipic acid solution in butanol, in order to stop the reaction and then  
210 analyzed using gas chromatography. The preparation of the reaction mixture samples for gas

211 chromatography analysis and chromatographic conditions were set according to (Šánek et al.,  
212 2013), where they are described in detail.

#### 213 **2.4 Determination of the cloud point of biodiesel from WAF**

214 The cloud point of the biodiesel produced from the pilot plant was measured in an 0.5 L Dewar  
215 flask, filled with brine, at a temperature of  $-23\text{ }^{\circ}\text{C}$ . Several samples were prepared for the  
216 determination of the cloud point at different ratios of biodiesel and diesel fuel. A test-tube with  
217 ethanol was inserted into the brine, and then a smaller test-tube with a prepared blend of biodiesel  
218 and diesel fuel, and a thermometer was placed in it so that its level was below the ethanol level.  
219 The sample was then constantly stirred until it reached the temperature at which a cloudy  
220 appearance of the sample was formed. After that, the cooled samples were placed in a lukewarm  
221 water bath ( $24\text{ }^{\circ}\text{C}$ ), and the temperature at which the samples became clarified was thus obtained.  
222 The procedure was repeated three times for each sample.

### 223 **3. Results and discussion**

#### 224 **3.1 Transesterification reaction**

225 Prior to the pilot-scale biodiesel production, the reaction conditions were optimized in the  
226 laboratory, using pure rapeseed oil. After that, it was possible to transfer the results obtained in  
227 the laboratory to the pilot scale. As can be seen in Fig. 2, the highest conversion (98 %) of  
228 triglycerides was achieved after 120 min. from the start of the reaction with 1.5 % w/w of  
229 TMAH; while in case of lower TMAH concentrations (0.5 and 1 % w/w), the conversions of  
230 triglycerides were only 74 % and 90 %, respectively. Therefore, the TMAH concentration of 1.5  
231 % w/w was used for further biodiesel production from waste frying oil and animal fat laboratory  
232 and pilot-scale tests. The aim of the optimization described above was to ensure that the almost  
233 complete conversion of triglycerides to methyl esters is achieved within 120 minutes - which was

234 an acceptable reaction time with regard to reactor productivity. From the economic point of view,  
235 it was necessary to use the lowest catalyst concentration which would also assure the fulfillment  
236 of the said requirement. In spite of the fact that pure rapeseed oil was used for reaction conditions  
237 optimization purposes, the results should also be valid for other vegetable oils and animal fats  
238 because differences in the reaction course and the final conversion especially, are practically  
239 negligible - as reported e.g. by (Freedman et al., 1984b; Likozar and Levec, 2014).

### 240 **3.2 Waste frying oil processing**

241 The acid values of WFO used for biodiesel production at both the laboratory and pilot-plant  
242 scales, were  $1.31 \text{ mg KOH.g}^{-1}$ . Since this figure corresponded to the optimal value suitable for  
243 alkali transesterification, the FFA extraction step was not included. The appropriate reaction  
244 conditions of the transesterification reaction were set according to the experiments previously  
245 carried out on the laboratory scale, using pure rapeseed oil (with the exception of the reaction  
246 temperature - which was increased slightly to  $65 \text{ }^{\circ}\text{C}$ ). The comparison of glycerol and  
247 intermediates content in crude biodiesel from WFO obtained at the laboratory and pilot scales,  
248 respectively, determined as per the EN 14 105 Standard, is shown in Table 3. As can be seen, the  
249 transfer of the experimental conditions from the laboratory to the pilot-scale was highly  
250 successful. The results obtained on both scales were comparable. The reaction intermediates (i.e.  
251 monoglycerides and diglycerides) and the initial triglycerides were present in the final crude  
252 biodiesel in very low contents. It thus follows that there was an almost complete (98 %)   
253 conversion of triglycerides to FAME. The produced crude biodiesel was in compliance with the  
254 requirements prescribed by the European Standard for Commercial Grade Biodiesel - EN 14 214,  
255 related to the content of reaction intermediates, which serves as the main indicator of the overall  
256 biodiesel quality. Only the glycerol content, formed as a by-product in the resulting crude

257 biodiesel was higher, since no subsequent biodiesel purification was carried out, e.g. by using the  
258 common water washing procedure (Gerpen, 2005).

259 The course of triglyceride conversion to FAME on the pilot-scale as compared against the  
260 laboratory scale is plotted in Fig. 3. The results showed that the upscale of the process was also  
261 successful in terms of the reaction kinetics. The slight difference between the data is within the  
262 experimental error and understandable in view of the slight reaction temperature modification  
263 between the laboratory and pilot plant experiments. The monitoring of the reaction process is  
264 important, and essential in view of the investigation of the reaction kinetics, as well as an  
265 understanding of the overall biodiesel production process and its control on the pilot-scale level  
266 and simultaneously, for the evaluation of TMAH catalytic efficiency over time.

### 267 **3.3 Waste animal fat processing**

268 On the other hand, the waste animal fat FFA level ( $37.59 \text{ mg KOH.g}^{-1}$ ), significantly exceeded  
269 the optimal value of  $2 \text{ mg KOH.g}^{-1}$ ; therefore, the pretreatment process had to be included. In our  
270 case, FFA removal was performed with an equimolar amount of TMAH - instead of the more  
271 commonly-used strong mineral acids, since utilization of TMAH allows one to achieve  
272 practically complete removal of the FFAs in only one stage (Šánek et al., 2015). The extract  
273 phase containing TMAH organic soaps, can be processed in a separate step to corresponding  
274 FAME according to the method described in (Kolomazník et al., 2013). The extraction conditions  
275 were set according to the method published in (Šánek et al., 2015). After the reduction of the  
276 FFA level under a specified value, it was possible to complete the transesterification reaction  
277 with an alkaline catalyst - in this case, tetramethylammonium hydroxide, which was confirmed  
278 by the obtained results; which showed that TMAH utilization as an extraction agent allowed  
279 reductions of the acid number to under the recommended value (concretely,  $1.42 \text{ mg KOH.g}^{-1}$ )

280 only in a one-stage extraction procedure. The extracted fat was then subjected to the  
281 transesterification reaction according to the reaction conditions listed above. As can be seen in  
282 Table 1, the waste animal fats' properties were substantially different. This was caused by the  
283 longer storage period of the raw feedstock used for the pilot-scale experiments. However, the  
284 application of TMAH as an extraction agent led once again to the successful reduction of the  
285 FFA content to the desired value (viz Table 1) and the extracted animal fat could be immediately  
286 used for transesterification. The fat (i.e. the sum of glycerides) loss during the pretreatment was  
287 13.5 %. Nevertheless, this figure is dependent on the actual free fatty acid content in the input  
288 feedstock - as was shown in (Šánek et al., 2015).

289 The results after the transesterification reaction show (viz Table 4) that the biodiesel produced  
290 from waste animal fat quality on the pilot-scale is comparable with that of biodiesel produced on  
291 the laboratory scale. The resulting biodiesel composition, i.e. the reaction intermediates' content,  
292 is similar to that of biodiesel produced from waste frying oil - except for the un-reacted initial  
293 triglycerides' content - which was slightly higher; however, extension of the reaction time would  
294 lead to the complete conversion of the triglycerides. The slightly increased glycerol content  
295 resulted from the fact that no crude biodiesel purification step was included. However, the  
296 conversion of triglycerides into FAME exceeded 98 %; which was comparable to the results of  
297 the laboratory scale process - as can also be seen in Fig. 3. In this case, we can conclude that the  
298 quality of biodiesel from WAF produced on the pilot-scale was in compliance with the EN  
299 14 105 Standard for reaction intermediates, i.e. mono- and diglycerides.

### 300 **3.4 Scale-up evaluation**

301 The main goal of our work was to test the TMAH catalyst for different feedstock and to verify  
302 that the scale-up of the process was successful - which means that the suggested procedure is able

303 to convert glycerides present in a broad range of waste feedstock into methyl esters with  
304 sufficiently high reaction conversion achieved in the required time of two hours. As was shown,  
305 this goal was fulfilled - even for feedstock with highly variable initial acid value, i.e. initial FFA  
306 content.

307 Dozens of experiments using different waste frying oil or waste fat were performed in the pilot  
308 plant. Fig. 4 shows the reproducibility of the experimental setup on the pilot-scale by means of  
309 final reaction conversion after 2 hours; which was determined routinely in order to control the  
310 production process. As can be seen, in practically in all cases, the final conversion was close to  
311 98 %, i.e. the final conversion value achieved under laboratory conditions. Nevertheless, the  
312 analyses of the reaction intermediates and TG at low concentrations by the standard method used  
313 for process monitoring and kinetics measurements (see Šánek et. al, 2013) had lower accuracy  
314 (but not lower precision) since the method is designed to capture the reaction mixture  
315 composition in a large range of concentrations. Consequently, the final crude biodiesel after  
316 methanol removal, was analyzed by the EN 14 105 Standard method, which is more suitable for  
317 the accurate determination of glycerides present at low concentrations in the final product. Fig. 5  
318 shows the results of the said analyses for 10 different batches of crude biodiesel. The results are  
319 expressed in the form of total and bound glycerol (i.e. the sum of glycerol in TG, DG and MG). It  
320 can be seen that the bound glycerol content was, in all cases, lower than 0.20 % and thus - the  
321 final reaction conversion was, in fact, higher than 98 %. On the other hand, the reaction may also  
322 proceed further, albeit at a very low rate, during the reaction mixture separation and cooling  
323 phases because the catalyst is not neutralized prior to methyl ester layer separation. However, the  
324 said small difference between the conversions measured after 2 hours from the reaction start and  
325 after methanol removal are within the experimental error margins of the routine method. In  
326 addition, Fig. 5 confirms that this crude biodiesel was able to fulfill the limit set by the EN 14214

327 Standard regarding the total glycerol level in most cases, even without implementation of  
328 standard water washing. The removal of catalyst from biodiesel is not necessary in the TMAH  
329 case, since this catalyst and also its salts with fatty acids are decomposed into volatile compounds  
330 (Challinor, 1996; Tanaka et al., 1966) at high temperatures and consequently does not form  
331 deposits in diesel engines.

332 The aim of the final biodiesel analysis was to confirm that its composition (especially, the content  
333 of MG, DG and TG) fulfills the related parts of the European Biodiesel Quality Standard:  
334 EN 14214. It was shown that many properties (e.g. viscosity, density, etc.) are fulfilled when  
335 sufficiently high reaction conversion is achieved; this is demonstrated for example, in the  
336 comparison of biodiesel properties prepared from different vegetable oils in the work of (Ramos  
337 et al., 2009). Some properties are, of course, dependent on the degree of feedstock un-saturation –  
338 especially the cold flow properties. The detailed fatty acid composition of the feedstock is shown  
339 in Table 2. As can be seen, the WAF has a relatively high saturated fatty acid content. Since cold  
340 flow properties usually represent the most problematic issue when feedstock with a low degree of  
341 unsaturation is used for biodiesel preparation, this is discussed in detail in the next chapter. Other  
342 properties - like water or methanol content, are dependent on the biodiesel production process. In  
343 the case of the technology discussed for utilizing TMAH as a catalyst and neutralization agent, a  
344 detailed list of biodiesel properties prepared from tannery waste fat was published in (Šánek et  
345 al., 2015).

346 The usual yield of biodiesel was around 90 %, this figure was calculated from the initial weight  
347 of fat or oil fed into the transesterification reactor and the final weight of biodiesel obtained after  
348 methanol removal. The losses are caused by the fact that the glycerol layer, which contains part  
349 of the FFA in the form of corresponding soaps and also FAME, was not further processed in our  
350 pilot plant - as is clear from its scheme (Fig. 1). Furthermore, a thin layer of the FAME phase was

351 always left above the glycerol phase during product separation in order to ensure that all glycerol  
352 was separated from the FAME. In addition, part of the products remained in the piping and  
353 pumps during batch manufacturing.

354 Please note that the processing costs are dependent on the feedstock composition in the suggested  
355 method, the details of the process economy are given in (Kolomaznik et al., 2010).

### 356 **3.5 Cold flow properties of biodiesel**

357 As pointed out above, when a feedstock with a relatively high degree of saturation is  
358 transesterified, the resulting biodiesel has unfavorable cold flow properties - which substantially  
359 limit the usability of such biodiesel at low temperatures. On the other hand, it was reported by  
360 (Moraes et al., 2008), that methyl esters produced from animal fat (i.e. feedstock with a low  
361 degree of unsaturation) has higher oxidation stability when compared to the esters generated from  
362 vegetable oils (i.e. a feedstock with a higher degree of unsaturation). It follows from what has  
363 been said above, that the usability of biodiesel from WFO at low temperatures is usually not  
364 associated with major obstacles. The exceptions are caused by a high concentration of saturated  
365 fatty acids (e.g. palm oil) or the content of saturated fatty acids with long carbon chains (e.g.  
366 peanut oil, Ramos et al., 2009). For this reason, we were focused on finding the cloud point of  
367 biodiesel from waste animal fat produced on the pilot-scale level and the blending of this  
368 biodiesel with conventional diesel fuel. The saturated fatty acid content in WAF is more than 40  
369 % (see Table 2). The Cloud Point (CP), is one of the quantities needed to measure a diesel fuel's  
370 cold-weather characteristics (Moraes et al., 2008), this is specified by report in the ASTM D6751  
371 Standard, and is correlated with other usual cold flow properties (Hoekman et al., 2012). The CP  
372 of pure biodiesel from the said feedstock is approximately 16.5 °C, which implies that this kind  
373 of biodiesel cannot be used at low temperatures. However, simple dilution of the biodiesel



374 produced with conventional diesel fuel (or biodiesel from vegetable oils) represented an available  
375 and effective way of cold flow properties' improvement. The comparison of the results obtained  
376 according to Chapter 2.4, is plotted in Fig. 6. The figure shows that the CP is defined as a linear  
377 function of the diesel fuel content in the mixture. Although the diesel fuel used for the CP  
378 determination had a CP of only  $-8^{\circ}\text{C}$ , the mixture CP of  $0^{\circ}\text{C}$  was achieved at a FAME  
379 concentration of 35 % (v/v) in the mixture.

#### 380 **4. Conclusion**

381 The work presented herein is focused on the processing of waste oil and fat into biodiesel on the  
382 pilot-scale. The preliminary experiments in the laboratory revealed that the selected reaction  
383 conditions could be scaled up to pilot-plant level. Based on the data discussed above, utilization  
384 of TMAH as an extraction agent makes it possible to ensure the practically complete removal of  
385 the FFAs in only one step - and thereafter, the extracted fat can be directly subjected to  
386 transesterification. The reaction conditions used for transesterification were: 1.5 % w/w of the  
387 catalyst (related to the weight of the initial amount of feedstock), the reaction temperature of  $65^{\circ}\text{C}$ ,  
388 the feedstock to methanol molar ratio of 1:6, and the reaction time of 2 h. The results clearly  
389 demonstrated that using an organic alkali (i.e. tetramethylammonium hydroxide) as a  
390 transesterification catalyst for waste frying oil and waste pork lard with methanol allowed the  
391 production of high quality biodiesel - even from highly acidic feedstock. The conversion  
392 achieved in all cases exceeded 98 %, and the laboratory data transfer was also successful in terms  
393 of the reaction kinetics. It was also established that, in order to achieve the desired CP value, the  
394 biodiesel produced from waste animal fat need merely be mixed with conventional diesel fuel.  
395 The results demonstrated that crude biodiesel produced from waste oil and fat fulfills the key  
396 requirements prescribed by the European Standard for Commercial Grade Biodiesel: EN 14 214,  
397 as related to the FAME content and the reaction intermediates.

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