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

2 **hydroxide**

3 Lubomír Šánek*, Jiří Pecha, Karel Kolomazník, Michaela Bařinová

4 Tomas Bata University in Zlín, Faculty of Applied Informatics, nám. T.G.Masaryka 5555, 760 01

5 Zlín, Czech Republic

6 *E-mails:* sanek@fai.utb.cz, pecha@fai.utb.cz, kolomaznik@fai.utb.cz, barinova@fai.utb.cz

7 *Corresponding author:* sanek@fai.utb.cz, tel. +420 576 038 145, fax. +420 576 032 716, postal

8 address: Lubomír Šánek, Faculty of Applied Informatics, Nad Stráněmi 4511, 76005 Zlín, Czech

9 Republic

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.

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^{-1} (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 ($NaOCH_3$, 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 $KOH.g^{-1}$. 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 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 H_2SO_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 at 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. Sanchéz 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 103Standard. 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 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.

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 °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 °C), and the temperature at which the samples became clarified was thus obtained.

222 The procedure was repeated three times for each sample.

3.   Results and discussion

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 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 °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 mg $KOH.g^{-1}$), significantly exceeded

269 the optimal value of 2 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 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).

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°C, the mixture CP of 0 °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

388   °C, 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.

References

Abdullah, N.H., Hasan, S.H., Yusoff, N.R.M., 2013. Biodiesel Production Based on Waste Cooking Oil (WCO). International Journal of Materials Science and Engineering 1.

Alptekin, E., Canakci, M., Sanli, H., 2012. Evaluation of leather industry wastes as a feedstock for biodiesel production. Fuel 95, 214-220.

Alptekin, E., Canakci, M., Sanli, H., 2014. Biodiesel production from vegetable oil and waste animal fats in a pilot plant. Waste Management 34, 2146-2154.

Canakci, M., Van Gerpen, J., 1999. Biodiesel production via acid catalysis. Transactions of ASAE 42, 1203-1210.

Canakci, M., Van Gerpen, J., 2001. Biodiesel production from oils and fats with high free fatty acids. T Asae 44, 1429-1436.

Canakci, M., Van Gerpen, J., 2003. A Pilot Plant to Produce Biodiesel from High Free Fatty Acid Feedstocks. Transactions of the American Society of Agricultural Engineers 46, 945-954.

Carlini, M., Castellucci, S., Cocchi, S., 2014. A Pilot-Scale Study of Waste Vegetable Oil Transesterification with Alkaline and Acidic Catalysts. Energy Procedia 45, 198-206.

Cmolik, J., Pokorny, J., 2000. Physical refining of edible oils. Eur. J. Lipid Sci. Technol. 102, 472-486.

Čerče, T., Peter, S., Weidner, E., 2005. Biodiesel-transesterification of biological oils with liquid catalysts: Thermodynamic properties of oil-methanol-amine mixtures. Industrial & Engineering Chemistry Research 44, 9535-9541.

423 Da Cunha, M.E., Krause, L.C., Moraes, M.S.A., Faccini, C.S., Jacques, R.A., Almeida, S.R.,
424   Rodrigues, M.R.A., Caramão, E.B., 2009. Beef tallow biodiesel produced in a pilot scale. Fuel
425   Processing Technology 90, 570-575.

426 De Moura, J., Goncalves, L.A.G., Petrus, J.C.C., Viotto, L.A., 2005. Degumming of vegetable oil
427   by microporous membrane. Journal of Food Engineering 70, 473-478.

428 Demirbas, A., 2007. Importance of biodiesel as transportation fuel. Energy Policy 35, 4661-4670.

429 Dias, J.M., Alvim-Ferraz, M.C.M., Almeida, M.F., 2009. Production of biodiesel from acid waste
430   lard. Bioresour. Technol. 100, 6355-6361.

431 Freedman, B., Butterfield, R.O., Pryde, E.H., 1986. Transesterification kinetics of soybean oil.
432   Journal of the American Oil Chemists Society 63, 1375-1380.

433 Freedman, B., Pryde, E.H., Mounts, T.L., 1984a. Variables affecting the yields of fatty esters
434   from transesterified vegetable-oils. J. Am. Oil Chem. Soc. 61, 1638-1643.

435 Freedman, B., Pryde, E.H., Mounts, T.L., 1984b. Variables affecting the yields of fatty esters
436   from transesterified vegetable oils. J. Am. Oil Chem. Soc. 61, 1638-1643.

437 Gerpen, J.V., 2005. Biodiesel processing and production. Fuel Processing Technology 86, 1097-
438   1107.

439 Haas, M.J., McAloon, A.J., Yee, W.C., Foglia, T.A., 2006. A process model to estimate biodiesel
440   production costs. Bioresour. Technol. 97, 671-678.

441 Hoekman, S.K., Broch, A., Robbins, C., Ceniceros, E., Natarajan, M., 2012. Review of biodiesel
442   composition, properties, and specifications. Renewable and Sustainable Energy Reviews 16,
443   143-169.

444 Challinor, J.M., 1996. A rapid simple pyrolysis derivatisation gas chromatography-mass
445   spectrometry method for profiling of fatty acids in trace quantities of lipids. Journal of
446   Analytical and Applied Pyrolysis 37, 185-197.

447 Chitra, P., Venkatachalam, P., Sampathrajan, A., 2005. Optimisation of experimental conditions
448   for biodiesel production from alkali-catalysed transesterification of Jatropha curcus oil.
449   Energy for Sustainable Development 9, 13-18.

450   İşler, A., Sundu, S., Tüter, M., Karaosmanoğlu, F., 2010. Transesterification reaction of the fat
451   originated from solid waste of the leather industry. Waste Management 30, 2631-2635.

452   Karavalakis, G., Anastopoulos, G., Karonis, D., Stournas, S., 2010. Biodiesel production using
453   tetramethyl- and benzyltrimethyl ammonium hydroxides as strong base catalysts. Fuel
454   Processing Technology 91, 1585-1590.

455   Kolomaznik, K., Barinova, M., Furst, T., 2009. Possibility of using tannery waste for biodiesel
456   production. J. Am. Leather Chem. Assoc. 104, 177-182.

457   Kolomazník, K., Klein, K., Vašek, V., Janáčová, D., Uhlířová, M., Mynařík, A., 2013. Method
458   for biodiesel production from fats and oils, p. Patent EP 2 238 224 B231.

459   Kolomaznik, K., Pecha, J., Barinova, M., Sanek, L., 2010. Economic aspects of biodiesel
460   production from tannery waste fats. J. Am. Leather Chem. Assoc. 105, 327-333.

461   Leung, D.Y.C., Guo, Y., 2006. Transesterification of neat and used frying oil: Optimization for
462   biodiesel production. Fuel Processing Technology 87, 883-890.

463   Likozar, B., Levec, J., 2014. Transesterification of canola, palm, peanut, soybean and sunflower
464   oil with methanol, ethanol, isopropanol, butanol and tert-butanol to biodiesel: Modelling of
465   chemical equilibrium, reaction kinetics and mass transfer based on fatty acid composition.
466   Appl Energ 123, 108-120.

467   Marchetti, J.M., Miguel, V.U., Errazu, A.F., 2007. Possible methods for biodiesel production.
468   Renew. Sust. Energ. Rev. 11, 1300-1311.

469   Meher, L.C., Vidya Sagar, D., Naik, S.N., 2006. Technical aspects of biodiesel production by
470   transesterification—a review. Renewable and Sustainable Energy Reviews 10, 248-268.

471   Moraes, M.S.A., Krause, L.C., da Cunha, M.E., Faccini, C.S., de Menezes, E.W., Veses, R.C.,
472   Rodrigues, M.R.A., Caramão, E.B., 2008. Tallow biodiesel: properties evaluation and
473   consumption tests in a diesel engine. Energy & Fuels 22, 1949-1954.

474   Ong, L.K., Kurniawan, A., Suwandi, A.C., Lin, C.X., Zhao, X.S., Ismadji, S., 2013.
475   Transesterification of leather tanning waste to biodiesel at supercritical condition: Kinetics and
476   thermodynamics studies. The Journal of Supercritical Fluids 75, 11-20.

477 Panter, R., Archer, T., Schroetter, A., Ricci, J., Smith, R., B., Dooling, T., A., Tirla, C., 2012.
478   TMAH-catalyzed biodiesel production for greater energy independence. . Abstract for ACS
479   National Meeting.

480 Pecha, J., 2009. Possibilities of Biodiesel Production from Leather Industry Waste Fats, Master
481   thesis, Faculty of technology. Thomas Bata University, Zlin.

482 Ramesh, D., Samapathrajan, A., Venkatachalam, P., 2006. Production of biodiesel from Jatropha
483   curcas oil by using pilot biodiesel plant. The Jatropha Journal 18, 1-6.

484 Ramos, M.J., Fernández, C.M., Casas, A., Rodríguez, L., Pérez, Á., 2009. Influence of fatty acid
485   composition of raw materials on biodiesel properties. Bioresour. Technol. 100, 261-268.

486 Sánchez, B.S., Mendow, G., Levrand, P.G., Querini, C.A., 2013. Optimization of biodiesel
487   production process using sunflower oil and tetramethyl ammonium hydroxide as catalyst. Fuel
488   113, 323-330.

489 Singh, S.P., Singh, D., 2010. Biodiesel production through the use of different sources and
490   characterization of oils and their esters as the substitute of diesel: A review. Renewable and
491   Sustainable Energy Reviews 14, 200-216.

492 Šánek, L., Pecha, J., Kolomazník, K., 2013. Simultaneous determination of main reaction
493   components in the reaction mixture during biodiesel production. Journal of Separation Science
494   36, 1029-1036.

495 Šánek, L., Pecha, J., Kolomazník, K., Bařinová, M., 2015. Biodiesel production from tannery
496   fleshings: Feedstock pretreatment and process modeling. Fuel 148, 16-24.

497 Tanaka, J., Dunning, J.E., Carter, J.C., 1966. Thermal Decomposition of Quaternary Ammonium
498   Hydroxides. Synthesis and Properties of Tri(2H3-methyl)amine. The Journal of Organic
499   Chemistry 31, 3431-3433.

500 Torres, E.A., Cerqueira, G.S., M. Ferrer, T., Quintella, C.M., Raboni, M., Torretta, V., Urbini,
501   G., 2013. Recovery of different waste vegetable oils for biodiesel production: A pilot
502   experience in Bahia State, Brazil. Waste Management 33, 2670-2674.

503   Van Gerpen, J., 2005. Biodiesel processing and production. Fuel Processing Technology 86,
504   1097-1107.

505   Wang, Y., Ou, P.L.S., Zhang, Z., 2007. Preparation of biodiesel from waste cooking oil via two-
506   step catalyzed process. Energy Conversion and Management 48, 184-188.