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# Biodiesel production by esterification of oleic acid over zeolite Y prepared from kaolin

Aidan M. Doyle<sup>1\*</sup> Talib M. Albayati<sup>2\*</sup> Ammar S. Abbas<sup>3</sup> Ziad T. Alismaeel<sup>4</sup>

1. Division of Chemistry and Environmental Science, Manchester Metropolitan University, Chester St., Manchester, M1 5GD, United Kingdom. email: a.m.doyle@mmu.ac.uk

2. Department of Chemical Engineering, University of Technology, 52 Alsinaa St., PO Box 35010, Baghdad, Iraq. email: talib\_albyati@yahoo.com.

3. Department of Chemical Engineering, College of Engineering, University of Baghdad, Al-Jadryah, P.O. Box 47221, Baghdad, Iraq. email: dr\_ammarr19@yahoo.com.

4. Department of Biochemical Engineering, Al-Khwarizmi College of Engineering, University of Baghdad, Al-Jadryah, P.O. Box 47008, Baghdad, Iraq. email: ziadalismaeel@yahoo.com.

\* Corresponding authors: a.m.doyle@mmu.ac.uk; talib\_albyati@yahoo.com

## Abstract

Zeolite Y, with a Si/Al ratio 3.1, was prepared using Iraqi kaolin and tested as a catalyst in the liquid-phase esterification of oleic acid (a simulated free fatty acid frequently used as a model reaction for biodiesel production). XRD confirmed the presence of the characteristic faujasite structure of zeolite Y, and further analysis was conducted using BET adsorption, FTIR spectroscopy, XRF, DLS particle size and SEM. A range of experimental conditions were employed to study the reaction; alcohol/oleic acid molar ratio, temperature, and catalyst mass loading. The optimum conditions for the reaction were observed at 70 °C, 5 wt% catalyst loading and 6:1 ethanol to oleic acid molar ratio. The oleic acid conversion using the zeolite prepared from kaolin was 85% after 60 min, while the corresponding value for a commercial sample of HY zeolite was 76%. Our findings show that low Si/Al ratio zeolite Y is a suitable catalyst for esterification, which is in contrast to the widespread view of the unsuitability of zeolites, in general, for such applications.

**Keywords;** Biodiesel, esterification, Y zeolite, kaolin, Si/Al ratio.

37 **1. Introduction**

38 Biodiesel is an alternative fuel produced from natural sources such as vegetable oils and animal  
39 fats [1-4]. Vegetable oils were first used as fuels over a century ago by Rudolf Diesel but this  
40 source of fuel has been replaced by cheaper petroleum oil fractions that are reformed to diesel  
41 using heterogeneous catalysts. Despite the continuing widespread use of fossil fuels, and recent  
42 technologies that allow increasing amounts of extraction from previously unavailable sources, the  
43 total amount of petroleum oil that is available is limited and will someday expire. Vegetable oils  
44 are extracted from plants and are therefore an almost limitless means of storing solar energy.  
45 Natural oils typically comprise mostly glycerides/triglycerides and suffer from high viscosity and  
46 inappropriate burning rate (cetane number), both of which render them less than ideal as fuels for  
47 transportation.

48  
49 The (trans)esterification of natural oils using heterogeneous catalysis overcomes these problems  
50 by generating alkyl esters that are much more suited to use as fuels, and a number of reviews have  
51 been published on the use of solid-acid catalysts in such applications [5-10 and references therein].  
52 However, there appears to be a general consensus in such reports that microporous zeolites are  
53 unsuitable catalysts for fatty acid esterification. Some reports base this conclusion on a  
54 disproportionately small number of publications whereas others mistakenly exclude the field of  
55 microporous zeolites altogether. While Corma and co-workers accurately proved that pores with  
56 diameter  $< 2$  nm impose a diffusion limitation for reactant molecules above a crucial dimension [  
57 11] we find that certain zeolites are active in oleic acid esterification if sufficiently low Si/Al ratios  
58 are employed.

59  
60 Kaolin clay is a cheap and plentiful raw material found in numerous geographical locations and  
61 has been used successfully in the synthesis of mesoporous aluminosilicates [12] and various  
62 microporous zeolite frameworks; ZSM-5, X/Y,  $\beta$ , and A [13-22]. A large part of these studies was  
63 the removal of impurities in the clays (typically quartz) via the thermal transformation of the  
64 untreated clay into metakaolin, which is itself catalytically active in the transesterification of waste  
65 cooking oil to alkyl esters [23]. The same transesterification reactions were conducted using  
66 metakaolin that was transformed to zeolite A by hydrothermal activation with NaOH [24]. The  
67 liquid-phase acid catalysed esterification of free fatty acids is another important reaction to

68 produce biodiesel. Li et al. reported a lanthanide ion-containing ZSM-5/MCM-41 composite  
69 material, prepared from kaolin, that was active in the esterification of ethanoic acid with n-butyl  
70 alcohol [25]. Da RochaFilho and co-workers investigated the esterification of oleic acid using a  
71 catalyst prepared from Amazon flint kaolin, which was converted to metakaolin and subsequently  
72 treated with sulphuric acid. The as-prepared materials were catalytically active but, to our  
73 knowledge, no studies were reported to investigate whether the acid content is leached during  
74 reaction so it is unclear how stable the catalyst is and whether the system is truly heterogeneous  
75 [26-29].

76  
77 Kaolin from Iraq has been used to prepare zeolite A for desulfurization of liquified petroleum gas  
78 (LPG) and zeolite Y for catalytic cracking (FCC) of cumene [30-32]. Here we prepare zeolite Y  
79 from Iraqi kaolin and test its catalytic activity in the liquid-phase esterification of oleic acid over  
80 a range of experimental conditions; ethanol to oleic acid ratio, catalyst loading and temperature.  
81 The acidic groups are generated by the charge imbalance of Al bonded to the framework of the  
82 zeolite and is therefore more stable than those attached using the relatively simple loading method  
83 for the Amazon flint kaolin [26-29]. Our findings demonstrate that the activity of the prepared  
84 catalyst in oleic acid esterification compares favourably with that of a commercially available Y  
85 zeolite.

86

## 87 **2. Experimental**

### 88 **2.1 Materials**

89 The following is a list of the materials' purity and source/supplier; kaolin clay, State Company of  
90 Geological Surveying and Mining, Iraq; oleic acid ( $C_{17}H_{33}COOH$ ), Thomas Baker; sodium  
91 hydroxide (NaOH) pellets, extra pure, Scharlau; absolute ethanol ( $C_2H_6O$ ), >99.8% GC, Sigma  
92 Aldrich; sodium silicate ( $Na_4SiO_4$ ), 99% purity, BDH Chemicals Ltd.; ammonium nitrate  
93 ( $NH_4NO_3$ ), Hopkin & Williams; oxalic acid dihydrate ( $H_2C_2O_4 \cdot 2H_2O$ ), >99% purity, Fluka  
94 Chemika; phenolphthalein, 2% in ethanol, Sigma-Aldrich. HY-commercial zeolite was purchased  
95 from Qingdao Wish Chemicals Co. Ltd.

96

### 97 **2.2 Catalyst preparation**

98 Zeolite Y was prepared using the method described in Abbas and Abbas whereby NaY was first  
99 prepared and then converted to HY zeolite (HY-kaolin) by ion exchange [33].

100

### 101 **2.3 Preparation of NaY zeolite**

102 1 part (by mass) 45-75  $\mu\text{m}$  (by sieve fraction) kaolin clay was mixed with 1.5 parts (by mass) of  
103 40 wt % aqueous NaOH solution and the mixture was heated at 850  $^{\circ}\text{C}$  for 3 hours in a furnace to  
104 get fused kaolin. The fused kaolin was then milled to get fused kaolin in powder form. 50 g of the  
105 prepared kaolin and 63 g of sodium silicate were dispersed in 500 ml of deionized water by stirring  
106 at 50  $^{\circ}\text{C}$  for 1 hour giving a slurry of approximate pH 13.3. The slurry was aged at 50  $^{\circ}\text{C}$  for 24 h  
107 under static conditions in a polypropylene bottle, and then crystallized at 100  $^{\circ}\text{C}$  for 48 h. The  
108 solid was recovered by filtration, washed with deionized water and dried in an oven at 100  $^{\circ}\text{C}$  for  
109 16 h. Finally, the dried powder was calcined in air at 500  $^{\circ}\text{C}$  for 1 h.

110

### 111 **2.4 Preparation of HY zeolite**

112 100 g of prepared NaY zeolite were mixed with 600 ml of 1 M ammonium nitrate at 100  $^{\circ}\text{C}$  for 4  
113 h and stirred in a round bottom flask fitted with a reflux condenser.  $\text{NH}_4\text{Y}$  zeolite was recovered  
114 by filtration, washed with deionized water and dried at 100  $^{\circ}\text{C}$  for 6 h. HY zeolite was prepared  
115 by stirring 40 g of the prepared  $\text{NH}_4\text{Y}$  zeolite with 800 ml of 0.5 N oxalic acid at room temperature  
116 for 8 h. HY zeolite was recovered by filtration, washed with deionized water, dried at 100  $^{\circ}\text{C}$  and  
117 calcined in air at 550  $^{\circ}\text{C}$  for 5 h.

118

### 119 **2.5 Catalyst characterization**

120 X-Ray diffraction (XRD) was conducted in ambient conditions using a Panalytical X'Pert Powder  
121 diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). All powder diffraction patterns were recorded  
122 from 4-50 $^{\circ}$   $2\theta$  with step size 0.026 and step time 50 s, using an X-ray tube operated at 40 kV and  
123 30 mA with fixed 1/4 $^{\circ}$  anti-scatter slit. Nitrogen adsorption/desorption measurements were carried  
124 out using a Micromeritics ASAP 2020 Surface Analyser where samples were degassed under  
125 vacuum ( $p < 10^{-5}$  mbar) for 12 h at 350  $^{\circ}\text{C}$  prior to analysis. BET-surface areas of the samples were  
126 calculated in the relative pressure range 0.05–0.30 and total pore volume was determined from the  
127 adsorption branch of the  $\text{N}_2$  isotherm as the quantity of liquid nitrogen adsorbed at  $p/p_0 = 0.995$ .  
128 Microscopic images were recorded using a Jeol JSM-5600LV scanning electron microscope  
129 (SEM). Chemical compositions were determined by X-Ray Fluorescence (XRF) using a Spectro  
130 XEPOS instrument with X-LAB Pro software; all measurements were done in He.

131

## 132 2.6 Catalytic test

133 The esterification reaction of oleic acid with ethanol was performed by reflux in a 500 ml batch  
134 reactor placed in a thermostatic oil bath under stirring. The desired amount of catalyst was dried  
135 before reaction at 130 °C for 2 h. The reactor was loaded with 50 ml (44.75 g) of oleic acid and  
136 the desired amount of pre-heated ethanol (3/1, 6/1 or 9/1 ethanol to oleic acid by molar ratio) was  
137 then added. Esterification was carried out over a range of catalyst loadings (2, 5 and 10 wt% with  
138 respect to oleic acid) and reaction temperatures (40, 50, 60 and 70 °C). 5 ml samples were  
139 withdrawn from the reaction mixture at 15 minute intervals, and centrifuged for 10 min at 3000  
140 rpm to separate the solid zeolite from the liquid phase. The supernatant layer was analysed by  
141 titration with 0.1 N KOH, using phenolphthalein indicator, to evaluate the acid value (AV) as  
142 shown in the following equation;

143

$$144 \quad AV = \frac{\text{ml of KOH} \times N \times 56}{\text{Weigth of Sample}} \quad (1)$$

145

146 From the acid value, the conversion of oleic acid can be calculated for each amount of the catalyst  
147 as shown in the following equation;

148

$$149 \quad \text{conversion} = \frac{AV_{t0} - AV_t}{AV_{t0}} \quad (2)$$

150

151 where:

152  $AV_{t0}$  (acid value of the reaction product at time 0)

153  $AV_t$  (acid value of the reaction product at time t)

154

155 The esterification of oleic acid was conducted in the absence of zeolite to determine the extent of  
156 any homogeneous reaction. The conversion after 90 minutes was 12% for an ethanol/oleic acid  
157 molar ratio 6:1 at 70 °C, showing that while there is some homogeneous contribution the  
158 reaction is predominantly due to heterogeneous catalysis by zeolite.

159

## 160 3. Results and Discussion

161

### 162 3.1 Catalyst characterization

163  
 164 The XRD powder pattern of HY-kaolin is shown in Fig. 1. The three most intense peaks of the  
 165 prepared HY-kaolin, located at angles  $6.34^\circ$ ,  $15.76^\circ$  and  $23.77^\circ$  2-theta, confirm the presence of  
 166 the characteristic faujasite structure of zeolite Y according to the Commission of the International  
 167 Zeolite Association (IZA) [34, 35]. Additional comparison with the corresponding pattern of  
 168 commercial HY clearly supports the presence of zeolite Y in the prepared sample, while the  
 169 absence of additional peaks in the HY-kaolin pattern confirms that the prepared sample did not  
 170 contain any detectable quantity of non-zeolitic crystal phases.

171  
 172 Nitrogen adsorption porosimetry results are summarised in Table 1. The BET surface area of the  
 173 HY-kaolin,  $390 \text{ m}^2/\text{g}$ , was lower than that for HY-commercial zeolite,  $625 \text{ m}^2/\text{g}$ . Similar  
 174 differences were observed for the micropore surface areas,  $A_\mu$ , and micropore volumes,  $V_{\mu P}$ , of  
 175 both samples. When combined with the XRD findings in Fig. 1, the porosimetry results confirm  
 176 the presence of micropores in HY-kaolin, whereby the reduced surface area/micropore volume  
 177 complements the reduced intensities of the characteristic diffraction peaks. Based on micropore  
 178 surface areas, the HY-kaolin contains approximately 65% zeolite Y. The remainder is attributed  
 179 to the presence of impurities in the kaolin source, which are not transformed into zeolite and, thus,  
 180 contribute to the final product as amorphous, non-zeolitic impurities. The total pore volumes,  $V_P$ ,  
 181 of both samples are shown for clarity; readings taken close to  $p_0$  will inevitably include intra-  
 182 particular condensation, so the higher value attributed to the HY-kaolin ( $0.853$  vs.  $0.783 \text{ cm}^3/\text{g}$ ),  
 183 while numerically accurate, is not indicative of the faujasite structure.

184  
 185 Table 1: BET adsorption analysis of HY-kaolin and HY-commercial.

Sample	$A_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$A_\mu$ ( $\text{m}^2/\text{g}$ )	$V_P$ ( $\text{cm}^3/\text{g}$ )	$V_{\mu P}$ ( $\text{cm}^3/\text{g}$ )
HY-kaolin	390	235	0.853	0.113
HY-commercial	625	355	0.783	0.258

186  $A_{\text{BET}}$  and  $A_\mu$  are the BET and micropore surface areas, respectively.  $V_P$  and  $V_{\mu P}$  are the total pore volume (at  
 187 relative pressure 0.995) and micropore volume, respectively.

188  
 189 Elemental compositions were determined by XRF, Table 2. HY-kaolin contains somewhat  
 190 similar amounts of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  to that in zeolite Y; this is not surprising given that the prepared  
 191 sample is predominantly aluminosilicate zeolite Y. The Si/Al ratio of the HY-kaolin was found to

192 be 3.1, which is similar to the value of 2.8 in a similar study using Nigerian Ahoko kaolin [16].  
 193 Zeolite X has a Si/Al ratio < 1.5, which means that the more catalytically active and stable form  
 194 of faujasite, zeolite Y, is formed here [36]. Major differences in the elemental makeup of the  
 195 samples were seen in the relative concentrations of Fe, Na, K, Mg and Ca oxides, which were all  
 196 vastly greater in HY-kaolin. These oxides, or various combinations thereof, are hereby assigned  
 197 to be the non-zeolitic impurities that are either X-ray amorphous or too dilute to be seen with XRD.

198  
 199 Table 2: Elemental compositions determined by XRF.

Mass/wt%	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	MgO	K <sub>2</sub> O	CaO	P <sub>2</sub> O <sub>5</sub>
HY-kaolin	15.92	58.11	3.191	0.147	1.222	0.067	4.112	0.6448
HY-commercial	13.66	69.74	0.051	0.032	< 0.0034	< 0.0012	0.151	0.5853

200  
 201 SEM images, Fig. 2, confirm the characteristic micron sized particles of the faujasite structure in  
 202 the HY-commercial and the corresponding agglomeration between such particles for the HY-  
 203 kaolin samples. It is possible that the impurities in the HY-kaolin have contributed to the  
 204 agglomeration in a similar manner to how binders e.g. alumina, are used in the stabilization of bulk  
 205 zeolite powders.

### 206 207 **3.2 Esterification reactions**

208 The esterification of oleic acid with ethanol is a reversible reaction so an excess quantity of ethanol  
 209 is commonly used to enhance conversion. Three ethanol/oleic acid molar ratios were employed;  
 210 3/1, 6/1 and 9/1. The fractional conversion of oleic acid, Fig. 3, increases, as expected, with  
 211 reaction time and decreases slightly due to catalyst deactivation after 45 min. The conversion is  
 212 also found to increase with increasing molar ratio of ethanol to oleic acid; conversions after one  
 213 hour were 69% and 85% for ratios 3/1 and 6/1, respectively. There was only a minimal further  
 214 increase in conversion for the reaction at 9/1 molar ratio. These results agree with those reported  
 215 by SathyaSelvabala et al. who also determined an identical optimum molar ratio of 6:1 in the  
 216 esterification of Neem oil using H-mordenite modified with phosphoric acid [37].

217  
 218 The influence of catalyst loading at oleic acid/ethanol molar ratio of 6/1, Fig. 4, shows an increase  
 219 in maximum conversion from 70 to 85% after 60 min going from 2 to 5 wt% but only a small

220 improvement thereafter. A progressive, although slight, decrease in conversion was seen for all  
221 catalyst loadings during the second hour of reaction.

222  
223 Fig. 5 shows the oleic acid conversion over the temperature range 40-70 °C. The conversion of  
224 oleic acid is highly dependent on reaction temperature whereby the maximum conversion increases  
225 from approximately 40% at 40 °C to 85% at 70 °C.

226  
227 The recyclability of HY-kaolin was examined. Briefly, when the reaction was finished, the catalyst  
228 was recovered by filtration, dried at 100 °C, calcined in air at 550 °C for 5 h, and used in a new  
229 identical reaction for one hour reaction time. The conversion decreased from 85% to 77%, possibly  
230 due to adsorption of water released during esterification, but still retains catalytic activity.

### 231 232 **3.3 Comparison between HY-kaolin and HY-commercial in esterification reaction**

233 Fig. 6 compares the oleic acid conversion of HY-kaolin with that of the commercially sourced HY  
234 zeolite. The difference in activity between zeolites is interesting; the HY-kaolin is somewhat more  
235 active in the early stages of reaction, but reduces to the same conversion as the commercial sample  
236 after two hours. The difference may be due to impurities in the HY kaolin zeolite which initially  
237 enhance the esterification reaction; however, it is difficult to assign such causation with certainty  
238 without further exploration and, therefore, this will not be considered further here. Alternatively  
239 the effect may be due to the different Si/Al ratios of the sample; 3.1 for HY kaolin versus 4.5 for  
240 HY commercial. It is well known that an increase in Si/Al ratio for zeolite Y over the range 2.5-  
241 10 causes increases in Bronsted acid strength and catalyst hydrophobicity and a decrease in the  
242 acid site density/number [36]. Chung and Park showed that the activities of oleic acid esterification  
243 on ZSM-5 and mordenite improved as the number of acid sites increased i.e. with lower Si/Al ratio  
244 [38]. A similar increase in activity is observed in this paper for HY-kaolin, which contains a greater  
245 number of acid sites than HY commercial, during the early stages of reaction. Chung and Park also  
246 reported a conversion of 57% for the same reaction using Y zeolite, Si/Al ratio 3, but did not  
247 present any results regarding changes in this ratio. Overall, the findings presented here are in  
248 contrast to the claims made in many review papers that microporous zeolites are universally  
249 unsuited to the esterification reactions used in biodiesel production, certainly so in the case of oleic  
250 acid [5-10].

251

#### 252 **4. Conclusion**

253 Iraqi kaolin was used to prepare Y zeolite in H form. This material was found to be an active  
254 catalyst in the esterification of oleic acid with conversion 85% obtained after 60 min reaction time  
255 using a 6/1 molar ratio of ethanol/oleic acid at 70 °C. The activity, which was comparable to a  
256 commercially sourced zeolite Y, was attributed to a high density of acid sites provided by the low  
257 Si/Al ratio (3.1).

258

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260

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265

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