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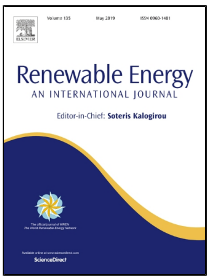

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Investigation of solid base catalysts for biodiesel production from fish oil

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Abstract

A series of composite CaO-$Ca_3Al_2O_6$ mixed oxides were investigated as potential catalysts for biodiesel synthesis from waste fish oil. Different Ca/Al ratios, in the range of 1.5 to 6 were studied, alongside pure CaO. The catalysts were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM) and CO_2-Temperature Program Desorption (TPD). The catalytic activity of the materials was studied for the transesterification reaction of cod liver oil with methanol at 65 °C, with 1:12 oil to methanol molar ratio and 10 wt% of catalyst. Over 97% conversion of the triglycerides to methyl esters was achieved for the 6Ca/Al catalyst after 2 h reaction time. This was similar to the performance of CaO. However, 6Ca/Al catalyst was reused successfully for seven consecutive tests, in contrast to CaO that was reused for only five tests, before it deactivated. Therefore, by incorporating the $Ca_3Al_2O_6$, it was possible to enhance the stability of the catalytically active species and improve the lifetime of the catalyst. Post-test catalyst characterisation showed the formation of an intermediate phase (calcium diglyceroxide) that enhanced the catalyst's performance and tolerance to air exposure and humidity. Finally, the catalyst deactivation, after seven cycles, took place due to the formation of $Ca(OH)_2$ and $CaCO_3$ species.

Keywords: biodiesel, heterogeneous catalyst, waste fish oil, transesterification reaction

1. Introduction

The aquaculture industry produces large amounts of waste which has low commercial value. This waste is produced during food processing, where the main product is the fillet of the fish, which represents only 30% of the wet fish weight and the rest is discarded.[1] This waste has been typically used in animal feed or fertilisers.[1–3] However, there is a significant opportunity to utilise this for the production of renewable fuel. More specifically, as the fish waste that comes from the food processing has high oil content, it is possible to use it as feedstock for the production of biodiesel.[1,4–6] Fish oil extracted from waste not only reduces the amount of waste that is generated, but also reduces the

total cost of biodiesel synthesis.[3] Moreover, this biodiesel can be used by the local farmers in the diesel generators or sold for blending with mineral diesel, allowing them to be energy independent, while reducing their waste disposal burden. Therefore, there is a great opportunity to produce low cost biodiesel from fish waste, produced by an important agricultural industry.

Biodiesel is a biodegradable fuel that is produced from plant- or animal- derived oils or fats. It is comprised of fatty acid alkyl esters, obtained during the transesterification reaction of triglycerides of lipids with low molecular weight alcohols.[7–10] Biodiesel is non-toxic and a cleaner-burning fuel than fossil diesel. It has no aromatics and a higher flash point than petrodiesel.[11] Some of the technical challenges associated with the use of biodiesel are its low oxidation stability, poor cold flow properties and low energy content.[12] These properties are mainly dependent on the fatty acid profile of the biodiesel, which corresponds to that of the feedstock it is obtained from.[11] However, since biodiesel is miscible with fossil diesel, it can be blended in different ratios with it. As a result, the fuel properties can be improved, and it can be used in the existing fuel distribution infrastructure.[11,12]

The transesterification reaction for biodiesel synthesis can be catalysed by both acids and bases, with base catalysis being considerably more rapid.[11] Traditionally, the biodiesel synthesis takes place in moderate reaction conditions (60 °C, 1 atm), in the presence of alkaline homogeneous catalysts such as sodium methoxide and sodium or potassium hydroxide.[11] Although these catalysts demonstrate fast reaction rates, they contaminate the biodiesel and extra separation and purification steps are required, increasing the cost and energy requirements of the production.[9–12] Therefore, different approaches have been investigated to improve the process efficiency for the biodiesel production.

Many studies have focused on improving the heat and mass transfer limitations that take place due to the immiscibility of the oil and methanol phases. The implementation of novel reactor designs,[16–18] the operation at supercritical conditions,[19] the addition of co-solvents[20] and the use of ultrasounds[21] or microwaves[22] have shown promising results. Other approaches have focused on reducing the cost of the separation and purification of the product by performing simultaneous reaction and separation. This was achieved by using membrane reactors[23] or reactive distillation.[24] Finally, a lot of research has been conducted on performing the transesterification reaction heterogeneously, adding an enzymatic or inorganic solid base catalyst.[8] However, enzymatic catalysts are less attractive than the inorganic, due to their high synthesis cost and longer reaction times.[25]

The use of inorganic solid base catalysts offers many benefits for the biodiesel production. These catalysts can be easily separated from the reaction mixture and recycled.[11] As a result, the biodiesel production is more economically feasible and environmentally friendly.[15] In addition to that, the separation of the glycerol from the biodiesel is much simpler and no purification step is required. Moreover, these catalysts can be used in a continuous process, which can further reduce the capital cost of the biodiesel synthesis.[26]

Diverse solid base catalysts have been investigated for this purpose. Scientists have studied alkaline earth oxides, such as CaO, MgO and SrO.[10] These catalysts demonstrate strong basic sites, which are beneficial to the transesterification reaction and show high catalytic activity.[27] Doping the alkaline earth oxides with alkali metals can enhance their basicity and consequently their catalytic activity. For instance, the Li-doped CaO catalysts demonstrated enhanced catalytic activity, but the leaching of the alkali promoters was problematic during repeated cycling.[28] To increase the recyclability of the heterogeneous catalysts, the incorporation of the active phase on a support has been investigated.[26] Typical examples are CaO supported on Al_2O_3[29,30] and KF/Ca–Al hydrotalcites.[31] Finally, the hydrotalcites demonstrate high intrinsic activity for the transesterification reaction of lipids,[32] but they are poorly suited for bulky C16-C18 triglycerides, due to their low surface area.[33]

The CaO-based materials are some of the most promising heterogeneous catalysts for biodiesel production from vegetable oils or animal fats.[34–36] These catalysts are low-cost materials, with high basicity and demonstrate high activity in moderate reaction conditions. However, one of the main limitations of these catalysts is the deactivation during repeated tests, due to leaching of Ca^{2+} ions, which also leads to contamination of the biodiesel.[27] One approach to overcome this issue is to use mixtures of CaO with other metal oxides, which can enhance both the catalysts stability and catalytic activity. Typical examples are studies on CaO and ZrO_2 mixed catalysts,[37] CaO supported on La_2O_3 and CeO_2[38] or composite oxide containing CaO and $Ca_{12}Al_{14}O_{33}$.[39,40]

In this work, the synthesis and characterisation of a series of catalysts, comprising CaO and $Ca_3Al_2O_6$, are investigated for biodiesel production from waste fish oil. Finally, the catalytic activity and reusability of these catalysts are evaluated with cod liver oil, to determine the optimum catalyst in terms of performance and stability for biodiesel production from waste fish oil.

2. Experimental

2.1. Synthesis of the catalysts

The catalysts were prepared by combustion synthesis with ethylene glycol and citric acid. Appropriate stoichiometric ratios of $Ca(NO_3)_2{\cdot}4H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ were diluted in deionised water, with ethylene glycol and citric acid. The solution was heated under stirring at 100 °C to evaporate the water and it was then combusted at 300 °C. The resulting powder was calcined at 1000 °C for 5 h and a mixed oxide phase of CaO and $Ca_3Al_2O_6$ (C3A) was obtained. Different Ca/Al ratios were investigated in the range of 1.5 to 6, which resulted to different CaO/C3A ratios. Moreover, commercial CaO powder was used as reference. The compositions of the catalysts synthesised in this work and their abbreviations are summarised in Table 1.

Table 1 Composition of the synthesised catalysts and their abbreviations

Catalyst abbreviation	Ca/Al molar ratio	CaO (wt.%) *	C3A (wt.%) *
CaO	-	100	0
6Ca/Al	6	65	35
3Ca/Al	3	38	62
2Ca/Al	2	17	83
C3A	1.5	0	100

* Theoretical values

2.2. Characterisation techniques

Room temperature powder X-ray diffraction (XRD) was performed on a PANalytical Empyrean diffractometer operated in reflection mode using Cu-Kα1 radiation. The obtained XRD patterns were analysed with STOE Win XPOW software to determine the crystal structure of the catalysts and the evolution of different phases during testing. The microstructure of the samples was analysed with a JEOL JSM-6700 field emission scanning electron microscope (FEG-SEM). Elemental analysis was performed with an Oxford Inca EDX system. Fourier-transform infrared (FTIR) spectra were recorded using a Shimadzu IRAffinity 1S IR spectrometer. Measurements were conducted in wavenumber range of 4000–600 cm^{-1}. The Ca/Al ratio of the catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Thermo-iCAP 6000 spectrometer. The samples were treated in hydrochloric acid and compared to standards.

The total basicity of the prepared catalysts was measured based on their temperature programmed CO_2 desorption profiles. The catalysts were pre-treated at 800 °C under an Ar flow rate of 50 ml/min to remove any adsorbed CO_2 and water from their surface and then cooled down to 50 °C. At this temperature, the CO_2 chemisorption was carried out in a CO_2 flow rate of 50 ml/min for 2 h. The excess of CO_2 was then desorbed at the temperature of the adsorption in an Ar flow (50 ml/min) for 2 h. Finally, desorption of CO_2 took place with Ar from 100 to 800 °C. The evolution of the mass of the catalysts during these treatments was measured using Thermogravimetric analysis (TGA) in a Netzsch STA 449C instrument. The TGA was equipped with a Pfeiffer mass spectrometer (MS), which analysed the CO_2 evolution during the different steps.

2.3. Physicochemical characterisation of the fish oil

The evaluation of the catalysts' activity for the transesterification reaction was performed with commercial cod liver oil, purchased from Holland and Barrette, UK. Fish oil methyl esters were

analysed with a GC-MS (Agilent, Intuvo 9000 GC), equipped with an Agilent DB-23 column. The free fatty acid composition of the fish oil is presented in Table 2. It consists mainly of palmitic acid (14.2%), oleic acid (13.8%), palmitoleic acid (11.7%), docosahexaenoic acid (11.2%), eicosapentaenoic acid (9.6%) and cis-11-eicosenoic acid (9.1%).

Table 2 Free fatty acid % composition of the cod liver oil

Free Fatty Acids	**Lipid Number**	**Composition (%)**
Myristic acid	C14	8.9
Palmitic acid	C16	14.2
Palmitoleic acid	C16:1	11.7
Stearic acid	C18	5.8
Oleic acid	C18:1	13.8
Linoleic acid	C18:2	3.4
α-Linoleic acid	C18:3	1.7
Stearidonic acid	C18:4	4.3
cis-11-eicosenoic acid	C20:1	9.1
Eicosapentaenoic acid	C20:5	9.6
Erucic acid	C22:1	6.3
Docosahexaenoic acid	C22:6	11.2

The physicochemical properties of the fish oil are summarised in Table 3. The cod liver oil was yellow in colour with typical smell. The density of the oil was 897 kg/m^3 and the boiling point was 420 °C. No impurities or water were present in the fish oil and the acid value was 0.53 mg KOH/g. Therefore, this was a suitable feedstock to perform the transesterification reaction with the synthesised catalysts for biodiesel synthesis.

Table 3 Physicochemical properties of the cod liver oil

Property	Value
Visual observations at 15 °C	Yellow liquid
Density at 15 °C	897 kg/m^3
Boiling point	420 °C
Water content	<0.001 wt.%
Acid value	0.53 mg KOH/g

2.4. The transesterification reaction

The transesterification was performed in a 100 ml three-neck round-bottom flask equipped with a water-cooled reflux condenser and a magnetic stirrer. The temperature was controlled at 65 °C with an oil bath and it was monitored during the reaction with a thermocouple probe that was placed in the reaction mixture. Appropriate amounts of fish oil, methanol and catalyst were used based on the requirements of each experiment and the reaction mixture was stirred at 800 rpm to achieve uniform temperature distribution and suspension of the catalyst in the reaction mixture. Samples from the reaction mixture were collected in different time intervals, for monitoring the evolution of the transesterification reaction. After running the reaction for the desirable duration, the mixture was centrifuged at 1400 rpm, the liquid was decanted, and the remaining catalyst was filtered under vacuum and washed thoroughly with methanol. Then, the recovered catalyst was dried in the oven (80 °C) overnight and it was used for analysis and recyclability tests. No fresh catalyst was added during the catalysts recycling. The reaction was carried out with an oil to methanol ratio of 1 to 12, catalyst loading of 10 wt.% based on the fish oil weight and reaction times of up to 4 h.

The conversion of the fish oil triglycerides to the methyl esters of the biodiesel was determined by H^1 Nuclear Magnetic Resonance (NMR) in a Bruker AVII 400 spectrometer. Figure 1 presents the H^1 NMR spectra of cod liver oil and of the biodiesel produced, when full conversion of the triglycerides (G) to methyl esters (M) took place. The conversion was calculated based on the integration of the signal at 3.68 ppm (M) and at 2.30 ppm (A), according to equation (1).[41] The signal at 3.68 ppm corresponds to the hydrogen of the methoxy groups in the methyl esters and at 2.30 ppm to the hydrogen of the methylene groups of the fatty acid derivatives. Finally, the signals between 4.3-4.1 belong to the glyceride protons and therefore they disappear when full conversion of the fish oil to biodiesel takes place.

166 $$C_{ME} = \frac{2 \cdot I_M}{3 \cdot I_A} \quad (1)$$

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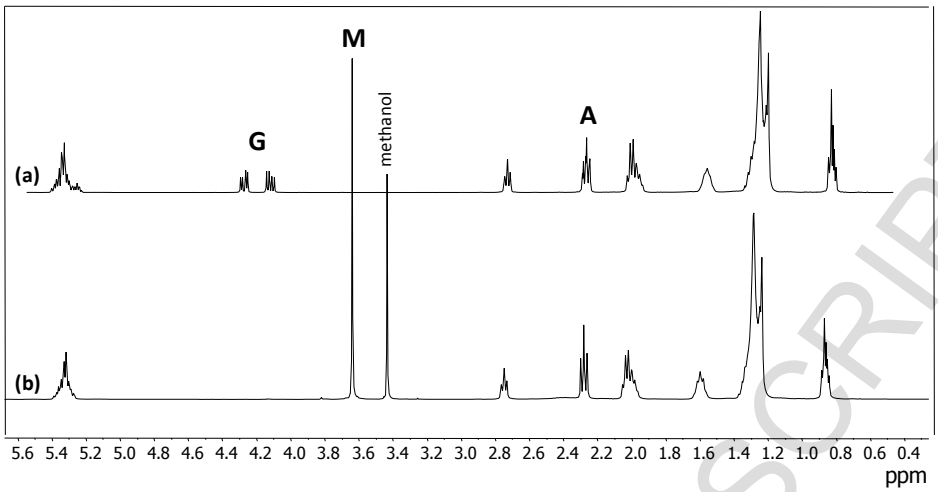

168

169 Figure 1 H^1 NMR spectra of a) cod liver oil and b) biodiesel produced after the transesterification reaction of the
170 fish oil

171

172 # 3. Results and discussion

173 ## 3.1. XRD analysis of the synthesised catalysts

174 The XRD patterns of the synthesised catalysts with the different Ca/Al molar ratios are presented in
175 Figure 2. For a Ca/Al ratio of 1.5, a single phase C3A material was obtained, with cubic structure, *Pa-3*
176 space group and cell volume V=3558.74(5) Å. By increasing the Ca/Al ratio up to 6, a mixed phase of
177 C3A and CaO was obtained. It is worth noting that no other intermediate phases were evident by XRD.
178 According to Figure 2, by increasing the Ca/Al ratio there was an increase in the CaO content and a
179 decrease in the C3A phase.

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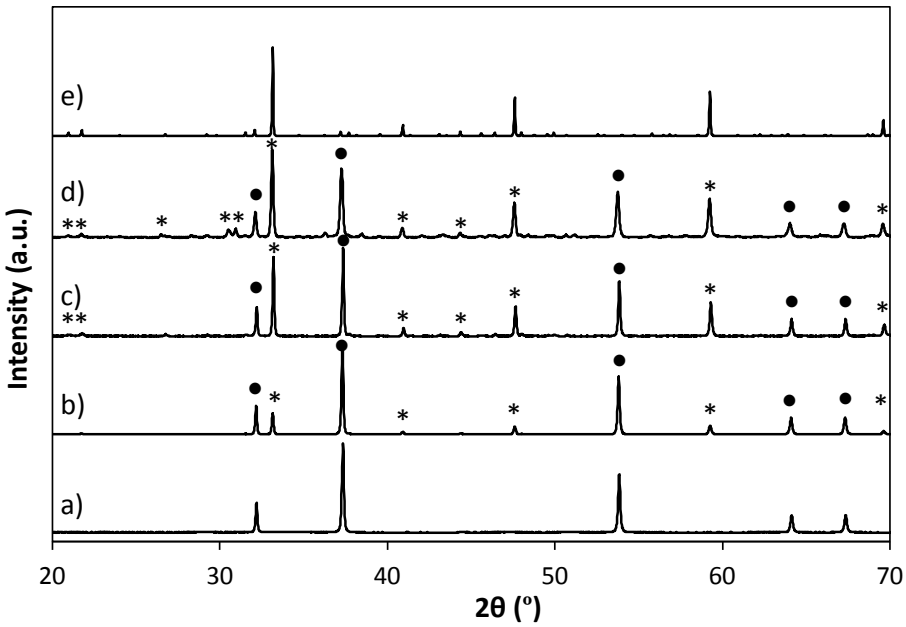


Figure 2 XRD patterns of the synthesised catalysts a) CaO, b) 6Ca/Al, c) 3Ca/Al, d) 2Ca/Al, e) C3A, where (*) corresponds to the C3A phase and (●) to the CaO phase

3.2. Catalysts microstructure

The microstructure of the catalysts was observed by SEM. Figure 3 illustrates the SEM micrographs of the catalysts with the different Ca/Al ratios after calcination at 1000 °C for 5 h. Based on Figure 3, it is evident that the catalyst is a two phase system, where the CaO phase presented smaller particles and the C3A phase formed larger and more agglomerated particles. By increasing the Al content, the formation of the C3A phase was more evident. Consequently, the formation of the CaO phase decreased. Moreover, for high Ca/Al ratios the particles of the catalyst comprised a uniformly dispersed mixture of CaO and C3A (Figure 3 a,b), while for lower Ca/Al ratios the particles of the CaO phase were partially coated on the C3A particles (Figure 3 c). This shows the Ca/Al ratio can influence the distribution of the two phases and the microstructure of the catalyst.

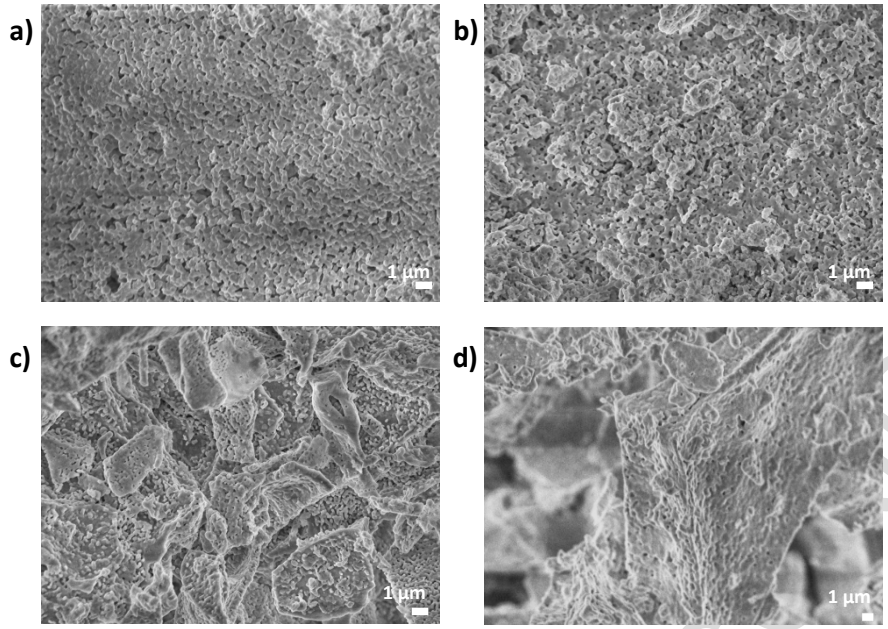


Figure 3 SEM micrographs of the CaO-C3A catalysts a) 6Ca/Al, b) 3Ca/Al, c) 2Ca/Al and d) C3A

3.3. CO_2 desorption profiles of the catalysts

The basicity of the synthesised catalysts was determined from their CO_2 desorption profiles. Figure 4a presents the evolution of the catalysts mass in relation to temperature during the CO_2 desorption step, as recorded by the TGA. The main weight loss occurred in one step between 600 and 700 °C and corresponds to the CO_2 desorbed on the catalyst's basic sites. The largest weight loss was observed for CaO and by decreasing the Ca/Al ratio, the amount of CO_2 desorbed by the catalyst was reduced. Finally, pure C3A with no free CaO demonstrated no weight loss, therefore no CO_2 desorption took place.

Figure 4b shows the CO_2 gas evolution when the CO_2 desorption took place between 100 and 800 °C, as it was recorded by the MS. The temperature where the CO_2 signal was detected corresponded to the temperature where the samples lost mass, due to the CO_2 desorption from the catalysts. The strongest CO_2 signal was detected for pure CaO at approximately 670 °C and was attributed to the strong basic sites corresponding to unbonded O^{2-} anions of CaO. [31,37,42–44] Moreover, no CO_2 signal was observed for pure C3A, as was expected based on the TGA results. By decreasing the Ca/Al ratio from 6 to 2, the CO_2 signal decreased and a slight shift of the desorption temperature from 670 to 610 °C was observed. These results suggest that when larger Ca/Al ratios are used, the number of the basic sites increases. There is more free CaO on the catalyst and therefore the observed CO_2 signal is stronger. This indicates, the CaO phase is the active species in this catalytic system and the C3A phase acts as a support and stabilises the active species. Finally, the shift of the desorption

temperature to lower values can be attributed to the acidic contribution of the C3A phase on the composite catalysts that reduced the basic strength of the catalyst.

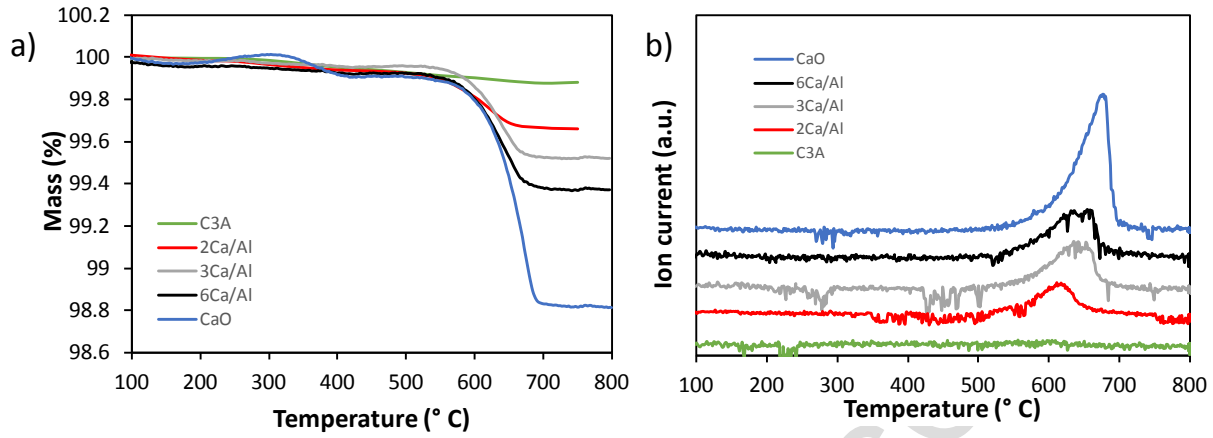


Figure 4 CO_2 desorption profiles of the synthesised catalysts a) mass evolution with temperature b) CO_2 gas evolution with temperature

3.4. The transesterification reaction

3.4.1. Catalysts activity

The catalytic activity of these samples was investigated for the transesterification reaction of cod liver oil to biodiesel. The samples were tested using the same reaction conditions to compare their catalytic activity and the influence of the Ca/Al ratio to the transesterification reaction. The reaction was carried out at 65 °C, with 1:12 oil to methanol molar ratio and a stirring speed of 800 rpm. The amount of catalyst used was fixed at 10 wt.% based on the oil used. Figure 5 presents the evolution of the conversion of the triglycerides to methyl esters with time for each catalyst. The conversion of the cod liver oil triglycerides to methyl esters in different time intervals was calculated by H^1 NMR, according to eq. 1.

According to Figure 5, all the catalysts demonstrated a conversion higher than 95% after a maximum of 4 h reaction time, except C3A. However, it is worth pointing out that the reaction rates differed and were proportional to the Ca/Al ratio. More specifically, no conversion was observed for C3A. The slowest reaction rate was demonstrated by 2Ca/Al and full conversion was achieved after 4 h. Following that, 3Ca/Al showed full conversion after 3 h and then 6Ca/Al after 2 h. Finally, pure CaO demonstrated full conversion after 2 h, which was similar to 6Ca/Al.

The differences in the catalysts' activity was related to their basicity. The more basic sites present on the catalyst, the faster the rate of reaction for biodiesel production is. This coincides with the CO_2 TPD results presented in Figure 4. As previously mentioned, C3A showed no CO_2 adsorption and therefore

it did not demonstrate any triglycerides conversion to biodiesel. By increasing the Ca/Al ratio of the catalyst and consequently creating more basic sites within the catalyst, the catalytic activity increased, and the transesterification reaction occurred at a faster rate. It is worth mentioning that 6Ca/Al catalyst performed with similar reaction rates as pure CaO. Thus, the stability of these two different catalytic systems was investigated, as explained in the following section.

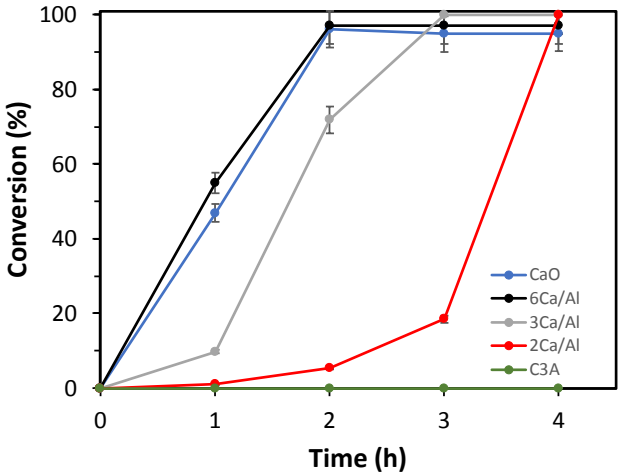


Figure 5 Triglycerides conversion to methyl esters over time for the synthesised catalysts

3.4.2. Catalysts recyclability

The reusability of the catalysts was investigated, by recovering the used catalyst and repeating the transesterification reaction with the same sample. Figure 6 presents the results from the recyclability tests of CaO and 6Ca/Al, the two samples that demonstrated similar catalytic activity and reaction rates. CaO was recycled and performed with over 95% conversion for five tests and was fully deactivated on the sixth test. However, 6Ca/Al catalyst demonstrated better stability than CaO and performed successfully for seven tests and was finally deactivated on the eighth test. An interesting observation was made regarding the changes in the reaction rates of the catalysts during the different tests performed. More specifically, CaO demonstrated roughly 60% conversion during the first hour of the first test. However, on the second test the conversion after the first hour increased to 85%. Then, the conversion in the first hour of each test gradually decreased and the catalyst was deactivated by the sixth test. Similar behaviour was observed for the 6Ca/Al catalyst, which was deactivated on test eight. This is discussed in detail in section 3.6, considering the changes in the catalysts structure. Overall, the recyclability tests showed that by incorporating the C3A phase into the catalyst, the stability of the CaO phase can be enhanced significantly, due to the interaction between the two phases.

According to the literature, the stability of CaO during biodiesel production is limited to approximately five cycles, if no catalyst pre-treatment is performed.[27,45] Many scientists have tried to stabilise CaO by incorporating another oxide phase. Dekhordi *et al.* have prepared CaO and ZrO_2 mixed oxides for the transesterification of waste cooking oil.[37] They found by increasing the Zr:Ca ratios the stability of the catalyst increased but the activity was dependent on the CaO content. The optimum Ca/Zr ratio was 0.5 and when they operated with 10 wt.% catalyst, 30:1 methanol to oil molar ratio and 2 h reaction time, they achieved a biodiesel yield of 92%. However, when the catalyst was recycled, the biodiesel yield decreased to 80% after 10 cycles.[37] Another interesting example is the $Ca_{12}Al_{14}O_{33}$ and CaO mixed oxide catalyst used for the transesterification of rapeseed oil.[39] This catalyst achieved 87% conversion over seven cycles at 65 °C, with a 15:1 methanol to rapeseed molar oil ratio, 6 wt.% of catalyst and 3 h reaction time.[39] In this work, 6Ca/Al demonstrated 97% triglycerides conversion to methyl esters, operating at 65 °C, with 10 wt.% catalyst, 12:1 methanol to oil molar ratio and 2 h reaction time. The conversion was retained above 95% for seven consecutive cycles and no catalyst pre-treatment was performed. This catalyst has demonstrated superior performance and enhanced stability for biodiesel production from cod liver oil.

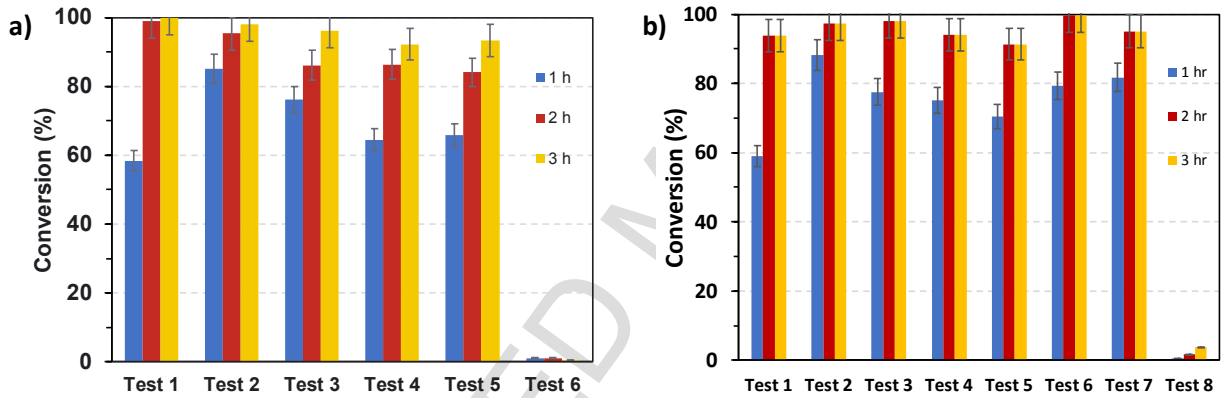


Figure 6 Recyclability tests of a) CaO and b) 6Ca/Al catalysts

3.4.3. Biodiesel properties

The physicochemical properties of the biodiesel produced from cod liver oil with the 6Ca/Al catalyst are presented in Table 4. After the transesterification reaction, the density of the fish oil decreased from 897 kg/m^3 to 888 kg/m^3, the boiling point dropped from 420 to 227 °C and the ester content was 97%. These physicochemical properties meet the EU standard limits. Only the acid value of the fish oil biodiesel was above the EU standard limits and was measured to be 1.06 mg KOH/g. Finally, the cloud point and the pour point of the biodiesel was 0 and -3 °C respectively, indicating this fuel is suitable for relative cold climates.

Table 4 Physicochemical properties of the synthesised biodiesel

Property	Value	EU standard limits
Visual observations at 15 °C	Dark orange liquid	-
Ester content	97%	≥96.5%
Density at 15 °C	888 kg/m^3	860-900 kg/m^3
Acid value	1.06 mg KOH/g	≤0.5 mg KOH/g
Cloud point	0 °C	-
Pour point	-3 °C	-
Boiling point	227 °C	-

3.5. Post-test catalyst characterisation

To understand the changes in the catalyst's activity during the cycling experiments, post-test characterisation of the 6Ca/Al catalyst was performed. Figure 7 shows the room temperature XRD patterns of 6Ca/Al at the end of each test. The catalyst was recovered from the reaction mixture, washed with methanol and dried overnight at 80 °C. For comparison, the XRD pattern of the as-prepared catalyst is presented, which shows the peaks corresponding to the CaO and C3A phases, as discussed in paragraph 3.1.

According to the XRD analysis, the C3A phase was retained during the recycling of the catalyst over all seven tests. There were observed no changes in the peak positions or their intensities. However, after the first test, the intensities of the peaks corresponding to the CaO phase decreased significantly and an additional phase was observed. This phase was identified as calcium diglyceroxide (CaDG).[46–48] The CaDG phase gradually disappeared during the recycling of the catalyst and by the end of test 7, there was no evidence of this phase according to the XRD data. Moreover, the formation of $Ca(OH)_2$ and $CaCO_3$ progressively took place. By the end of test seven, when the catalyst was fully deactivated, the C3A phase was retained, there was no evidence of the CaDG phase and the only Ca species observed were $CaCO_3$ and $Ca(OH)_2$.

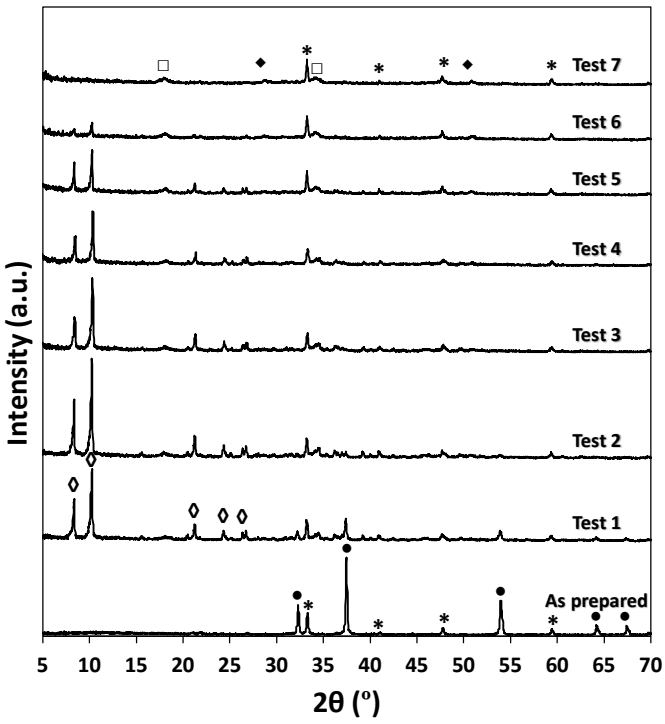
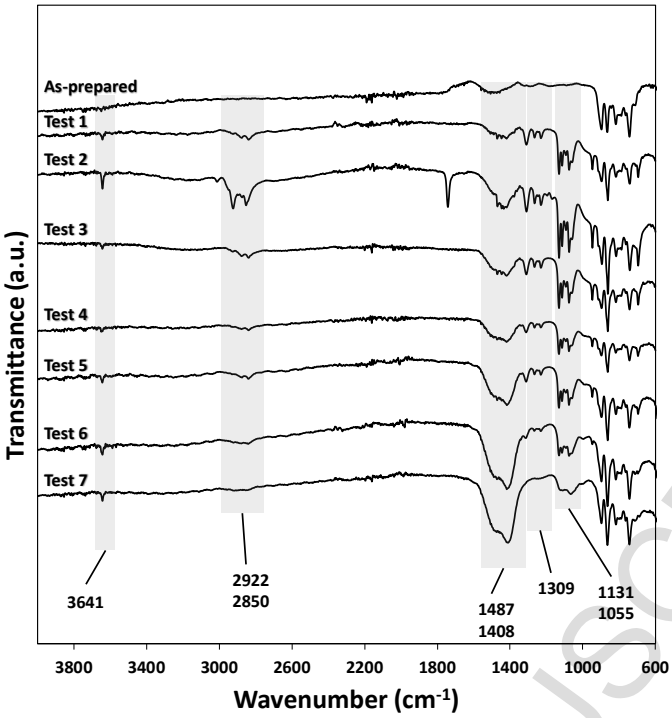


Figure 7 Phase evolution during the recyclability test of the 6Ca/Al catalyst, where (*) corresponds to the C3A phase, (●) to CaO, (◊) to CaDG, (□) to $Ca(OH)_2$ and (♦) to $CaCO_3$

Alongside the XRD analysis, FTIR spectroscopy was performed for the 6Ca/Al catalyst. Figure 8 presents the evolution of the FTIR spectra of the catalyst during the progression of a series of biodiesel tests. After the first test extra transmittance bands appeared, which are characteristic of the CaDG phase.[35,46,47,49–51] More specifically, the bands at 2922 and 2850 cm^{-1} are attributed to the C-H stretching vibration and at 1309 cm^{-1} to the C-H bending vibration. Moreover, the band at 1135 cm^{-1} corresponds to the C-O stretching vibration in the C_2OH group and the band at 1055 cm^{-1} to the stretching vibration of C-O in the COH group of diglyceroxide. Finally, the band at 3641 cm^{-1} can be attributed to the -OH stretching vibration of the COH group of the glyceroxide bonded to the calcium atoms. However, this band can overlap with the bands that correspond to the $Ca(OH)_2$ formation and it can be difficult to distinguish between the two contributions.

During the catalyst's reusability tests, it was noticed that the intensity of the transmittance bands that corresponded to the CaDG phase gradually decreased. Moreover, some transmittance bands in the region of 1408-1487 cm^{-1} progressively appeared. These bands correspond to the formation of $CaCO_3$.[50,52] Therefore, when the catalyst was deactivated after test seven, the main transmittance bands that were evident were the ones in the regions of 3641 cm^{-1} and 1408-1487 cm^{-1}, which can be attributed to the formation of $Ca(OH)_2$ and $CaCO_3$, respectively. These results were in good agreement with the XRD analysis presented in Figure 7.



333

334 Figure 8 FTIR spectra of the 6Ca/Al catalyst after each test during the recyclability test

335

336 Furthermore, the changes in the Ca/Al ratio of the 6Ca/Al catalyst were measured by ICP-OES and
337 EDX, before and after the reusability experiment. As presented in Table 5, the Ca/Al ratio decreased
338 from 6 to approximately 3.5 and the two techniques demonstrated comparable results. The slightly
339 higher Ca/Al ratios detected by EDX, suggested that the surface of the catalyst was Ca-rich. The
340 decrease in the catalyst's Ca/Al ratio is attributed to leaching of Ca ions, and supports the data
341 collected by XRD and IR. More specifically, since the C3A phase was stable according to XRD, the
342 decrease in the Ca/Al ratio was due to the leaching of Ca ions from the CaO phase. Finally, the post-
343 test Ca/Al ratio, that was approximately 3.5, was much higher than the theoretical Ca/Al ratio (1.5) of
344 the pure C3A phase. This suggests there were still free Ca species on the surface of the catalyst.
345 These species are most likely $Ca(OH)_2$ and $CaCO_3$, according to XRD and FTIR. However, these
346 phases are much less active for the transesterification reaction and led to the deactivation of the
347 catalyst.[35]

348 Table 5 Ca/Al ratios of the 6Ca/Al catalyst

	as-prepared	post-test
ICP-OES	5.9	3.3
EDX	7.2	3.7

3.6. Reactions mechanism

Summarising the post-test characterisation performed by XRD, IR, ICP-OES and EDX the phase transformations that took place during these experiments and the catalysts deactivation mechanism can be explained. More specifically, the XRD data alongside the FTIR analysis were a strong indication that the formation of the CaDG phase took place after the first test of the catalyst. The formation of the CaDG phase during the transesterification reaction is not unusual, when CaO species are present. According to the literature, CaO can react with the glycerol produced during the reaction and CaDG is formed with water according to equation 2.[46,47,51]

$$CaO + 2\ C_3H_8O_3 \rightarrow Ca(C_3H_7O_3)_2 + H_2O \quad (2)$$

The formation of the CaDG phase can enhance the catalytic activity of CaO, due to the non-protonated O atoms that can be exposed on the surface of the catalyst[46,47] or it can act as an emulsifier and improve the mass transfer limitations that can occur in the reaction mixture.[51] This can be confirmed by the improved performance of the catalysts observed after the first test (Figure 6), when the CaDG phase formed.

However, based on the XRD and FTIR results, the CaDG progressively disappeared during the recycling of the catalyst indicating potential leaching of this phase. This can occur during the reaction or during the filtration and washing of the catalyst. According to the literature, in the presence of water CaDG can be hydrolysed according to equation 3.[27]

$$Ca(C_3H_7O_3)_2 + 2\ H_2O \rightarrow Ca^{2+} + 2\ OH^- + 2\ C_3H_8O_3 \quad (3)$$

Therefore, when this reaction takes place it can lead to leaching of Ca^{2+} ions, as confirmed by ICP-OES and EDX.

Finally, the disappearance of the CaDG phase was followed by the formation of $Ca(OH)_2$ and $CaCO_3$ species. The formation of the $Ca(OH)_2$ and $CaCO_3$ phases took place due to the catalyst's hydration (Equation 4) and the carbonisation (Equation 5) when the catalyst was exposed to ambient air or to the water produced in the reaction mixture.[27,35]

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (4)$$

$$CaO + CO_2 \rightarrow CaCO_3 \quad (5)$$

This led to the deactivation of the catalyst, as these species are less active for the transesterification reaction than CaO.[35] However, it is worth pointing out that the hydration and carbonisation of CaO took place progressively, while the decrease of the CaDG phase occurred, as it was observed by XRD (Figure 7) and FTIR (Figure 8). This suggests the CaDG can form a protective layer on the surface of the catalyst and hinder its deactivation due to hydration and carbonisation. Similar observations have been reported in the literature by Kouzu *et al.*[46] and Endalew *et al*.[53]

4. Conclusions

In this work, the synthesis and characterisation of a series of CaO-$Ca_3Al_2O_6$ mixed oxides were investigated as potential solid base catalysts for biodiesel production from waste fish oil. The activity of the catalysts for the transesterification reaction of cod liver oil with methanol was evaluated. The 6Ca/Al catalyst was identified as the optimum composition in terms of catalytic activity and stability, as it was reused successfully over seven consecutive tests. This catalyst was more stable than pure CaO, which was reused for five tests, indicating that by incorporating the $Ca_3Al_2O_6$ phase, it was possible to enhance the stability of the catalytically active species. Post-test characterisation of the catalyst suggested that the formation of Ca diglyceroxide took place, which enhanced the reaction rate. However, deactivation of the catalyst, after seven consecutive tests, occurred due to leaching of Ca^{2+} ions from the active phase. Finally, the formation of $Ca(OH)_2$ and $CaCO_3$ species took place due to hydration and carbonisation of the free CaO.

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Highlights

- Investigation of the CaO-$Ca_3Al_2O_6$ catalyst for biodiesel synthesis from fish oil
- The optimum ratio in terms of catalytic activity and recyclability was 6Ca/Al
- The formation of an intermediate, more active phase was identified by XRD and IR
- 6Ca/Al catalyst was recycled successfully for 7 consecutive cycles