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HETEROGENEOUS CATALYSIS OF BIODIESEL PRODUCTION BY CORN OIL TRANSESTERIFICATION USING A CALCIUM OXIDE - CD AL LDH COMPOSITE SYNTHESIZED VIA RDF

by

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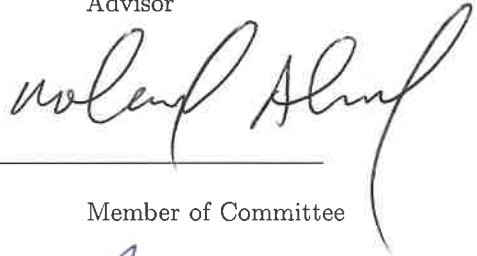
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Abstract
of the Thesis of

George Karim El Labaki   for   <u>Master of Science</u>
<u>Major</u>: Chemical Engineering

Title: <u>Heterogeneous Catalysis of Biodiesel Production by Corn Oil</u>
<u>Transesterification using a Calcium Oxide - Cd Al LDH Composite</u>
<u>Synthesized via RDF</u>

In this study, a CdAl LDH precursor synthesized by RDF was impregnated with calcium nitrate and calcinated to obtain Ca/CdAl oxide. This was used as a heterogeneous base catalyst in the transesterification of corn oil with methanol for the purpose of biodiesel production. The catalyst was characterized by SEM/EDX, powder XRD, and BET nitrogen adsorption-desorption technique. Thermogravimetric analysis was carried out on its LDH precursor. Transesterification reactions were carried out using the prepared catalyst and commercially obtained calcium oxide to compare their activity in the reaction. Proton NMR was used to examine the obtained biodiesel product. The fatty acid methyl ester yield was measured under a series of different reaction durations, with a 4wt% catalyst loading at 11:1 methanol:oil ratio at 62°C. The optimal biodiesel yield was determined to be 93%. The Ca/CdAl oxide catalyst was also tested in the transesterification of waste cooking oil, where a 72.4% yield was observed.

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ABBREVIATIONS

Al	Aluminum
Ba	Barium
BET	Brunauer–Emmett–Teller
C	Carbon
Ca	Calcium
Cd	Cadmium
Ce	Cerium
Cr	Chromium
Cu	Copper
EDX	Energy Dispersive X-ray
Fe	Iron
FFA	Free Fatty Acid
H	Hydrogen
^1H NMR	Proton Nuclear Magnetic Resonance
HT	Hydrotalcite
K	Potassium
La	Lanthanum
LDH	Layered Double Hydroxide
Li	Lithium
Mg	Magnesium
N	Nitrogen
Na	Sodium
O	Oxygen
PDF	Powder Diffraction File
R	Alkyl Chain
RDF	Reaction-Diffusion Framework
rpm	revolutions per minute
S	Sulfur
SEM	Scanning Electron Microscopy
Si	Silicon
Sr	Strontium
TGA	Thermogravimetric Analysis
wt%	Percent by Weight
XRD	X-ray Diffraction
Zn	Zinc

Chapter 1

Introduction

Coal, natural gases, and petrochemical resources make up the major factor supplying the world's energy demands. This is a cause of concern, as these sources are finite and unsustainable. Their depletion and their greenhouse gas emissions present quite a dilemma, as it is clear that the world cannot rely on them indefinitely. This has led to great interest in conducting research initiatives to find new means to supplement fossil fuel energy sources. Ideally these new means should have a lesser environmental impact and come from renewable sources for the sake of sustainability. New alternative fuels must be readily sourced, feasible to mass-produce, economically competitive with currently preferred energy sources, and environmentally friendly. Chemical fuels sourced from plants and biomass have caught the attention of many. It is important to note that these renewable sources such as edible oils must not compete with food demands to avoid food shortages caused by the allocation of arable land specifically for energy production. Nonetheless, vegetable oils and seed oils have been utilized to produce biodiesel, an environmentally benign substitute of petroleum diesel. Biodiesel is non-toxic and releases far less emissions than conventional diesel [1]. The oils and fats used to produce biodiesel are chemically classified as triglycerides. This chemical species is comprised of a glycerol group connected to three fatty acid chains that differ in length, orientation, and number of unsaturated carbon double bonds. In the process of transesterification, these triglycerides transform into fatty acid alkyl esters.

CHAPTER 2

LITERATURE REVIEW

Transesterification (also referred to as alcoholysis) is a reversible reaction, and usually it is desired to shift the reaction equilibrium in the forward direction. This acceleration of the conversion can be achieved by using excess alcohol according to Le Chatelier's principle. In this particular reaction, the transesterification of triglycerides involves the sequential displacement of the alcohol groups of the ester, producing diglycerides and monoglycerides as intermediates. Figure 2.1b shows these stages.

First, the triglyceride reacts with the alcohol to produce a diglyceride and a fatty acid alkyl ester. Then, the diglyceride molecule further reacts with the alcohol to produce another fatty acid alkyl ester molecule and a monoglyceride. Finally, the monoglyceride reacts with the alcohol to produce glycerol and a fatty acid alkyl ester [2].
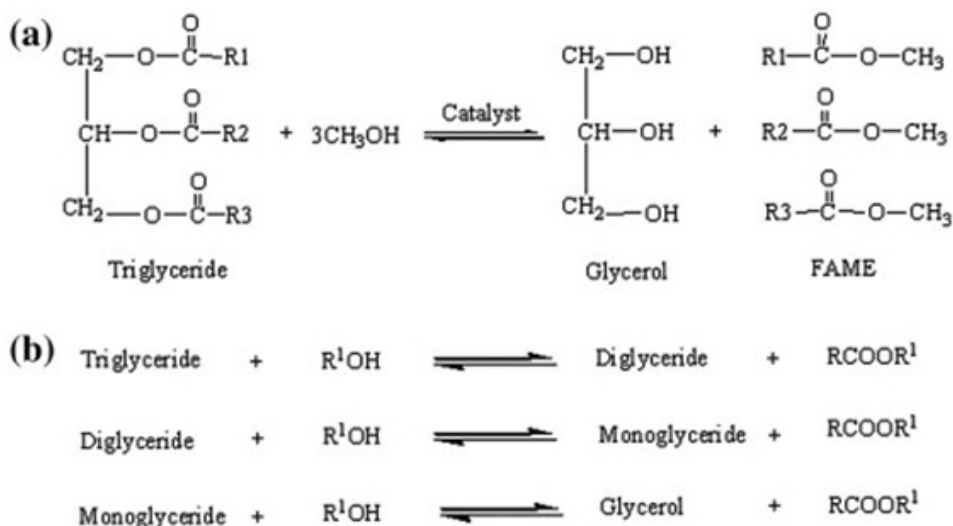

Figure 2.1: The transesterification of a triglyceride using methanol [3]

The forward reaction rate is observed to behave as pseudo-first order, and the reverse reaction rate is observed to be second order [3]. An excess of alcohol is encouraged, but a high molar ratio of alcohol to vegetable oil leads to an increase in

the solubility of glycerol, thus hindering its separation. When glycerol remains in the reaction mixture, it helps shift the equilibrium backward, ultimately breaking down the fatty acid alkyl esters and decreasing the yield. A study by Encinar, Gonzalez, Rodriguez, *et al.* [4] investigated the effect of varying the cynara oil to ethanol ratio on the reaction yield. The transesterification of cynara oil was carried out at molar ratios ranging between 3:1 and 15:1. It was found that the ester yield increased to a maximum in the range of 9:1 and 12:1. For low molar ratios (less than 6:1), the reaction was incomplete. As for a molar ratio as high as 15:1, certain quantities of glycerol remained in the biodiesel phase due to the aforementioned increase in solubility, which decreased the yield of the esters and made the separation of glycerol more difficult.

As for the choice of alcohol, in the case of base catalysis using ethanol is less preferable than methanol. This is because of the formation of a stable emulsion. Methanol and ethanol are immiscible with triglycerides at ambient temperature, which usually necessitates mechanical stirring to enhance mass transfer. In the case of methanolysis, the emulsions that form are unstable and readily break down to form a lower glycerol rich layer and upper methyl ester rich layer. In ethanolysis on the other hand, these emulsions are more stable [3]. The formation of the mono-glyceride and diglyceride intermediates contribute to the formation of emulsions because of their polar hydroxyl groups and non-polar hydrocarbon chains. Emulsions are unstable when the concentrations of the intermediates are low enough but stabilize when the concentrations reach a threshold. The larger non-polar group in ethanol, relative to methanol, is regarded as the main factor in stabilizing the emulsions.

2.1 On Homogeneous Acid & Base Catalysts in Transesterification

During acid-catalyzed transesterification, a carbocation is formed when the ester's carbonyl group is protonated. This weakens the carbon oxygen π bond, making the carbonyl carbon a good electrophile. When the alcohol is introduced, it conducts a nucleophilic attack on the carbocation to produce a tetrahedral intermediate. The acid is then regenerated as water is eliminated and the new ester is formed [5]. The schematic in figure 2.2 describes this mechanism.

In homogeneous base catalysis of transesterification, the mechanism is described as follows. The alkoxide ion (RO^-) conducts a nucleophilic attack on the carbonyl group of the triglyceride, leading to the formation of a tetrahedral intermediate. Then, the intermediate rearranges and produces one methyl ester molecule and a diglyceride ion, with a further nucleophilic attack occurring to produce glycerol and a fatty acid methyl ester (figure 2.3)[5].

2.1.1 *Problems of Homogeneous Catalysts*

The homogenous nature of these catalystss presents difficulty in the recovery of the catalyst, namely the occurrence of saponification causing issues in the separation of
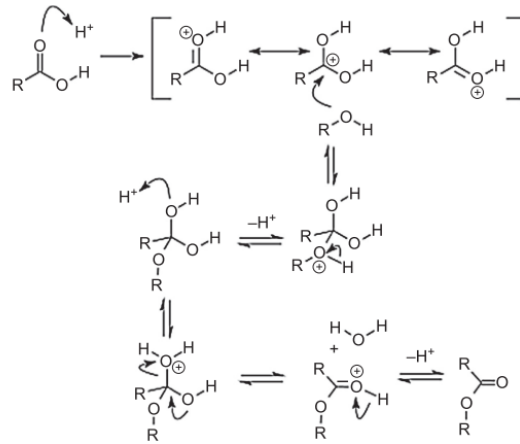
Figure 2.2: Homogeneous acid-catalyzed transesterification mechanism [5]
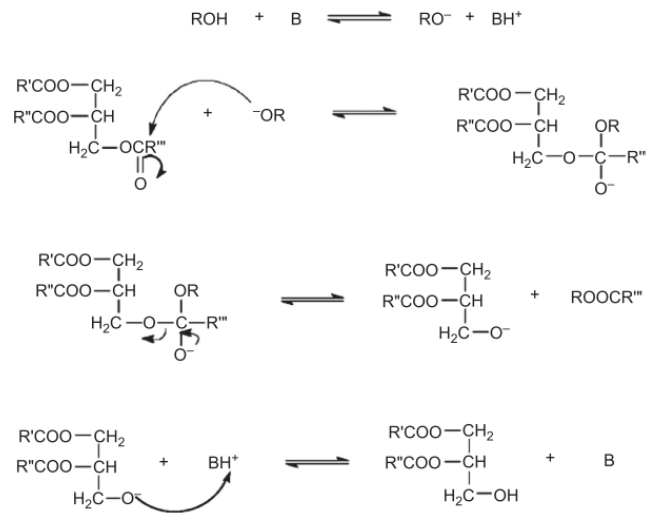
Figure 2.3: Homogeneous base-catalyzed transesterification mechanism [5]

the product [6]. The final reaction mixture containing biodiesel and glycerol must be washed extensively. This is a time-consuming, energy intensive processing step that generates a large amount of wastewater. Homogeneous catalysts have been found to be quite sensitive toward water content and free fatty acid (FFA) content in the triglycerides [7]. The common homogeneous catalysts such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) tend to form soap and water in a saponification reaction when the FFA content in the feedstock is 3% or higher [3]. The acid catalysts have been known to corrode engine components if not properly separated from the biodiesel product [8]. Subsequent research has investigated solid catalysts in transesterification and deemed them more preferable as they cause less damage to the environment. Being a heterogeneous medium, the downstream operations are simpler as the solid catalyst is more easily separated. However it is still essential that the catalyst is stable and does not leach any of its active chemical species onto the reaction phase [6].

2.2 Solid Base Catalyzed Transesterification

In the example of transesterification catalyzed by a solid base SrO [9], the reactions take place on the surface of solid (figure 2.4). At first, surface O^{2-} ions extract H^+ from methanol (CH_3OH) to produce surface methoxide (CH_3O^-), a species with strong basicity and high catalytic activity. Then, the triglyceride's carbonyl carbon atom attracts a methoxide anion from the surface of the SrO catalyst, and a tetrahedral intermediate is formed. Then, the intermediate obtains H^+ from the surface of the strontium oxide catalyst (3rd step) and reacts with methanol to produce methoxide anions (4th step). Finally, the tetrahedral intermediate rearranges into a fatty acid methyl ester, biodiesel.
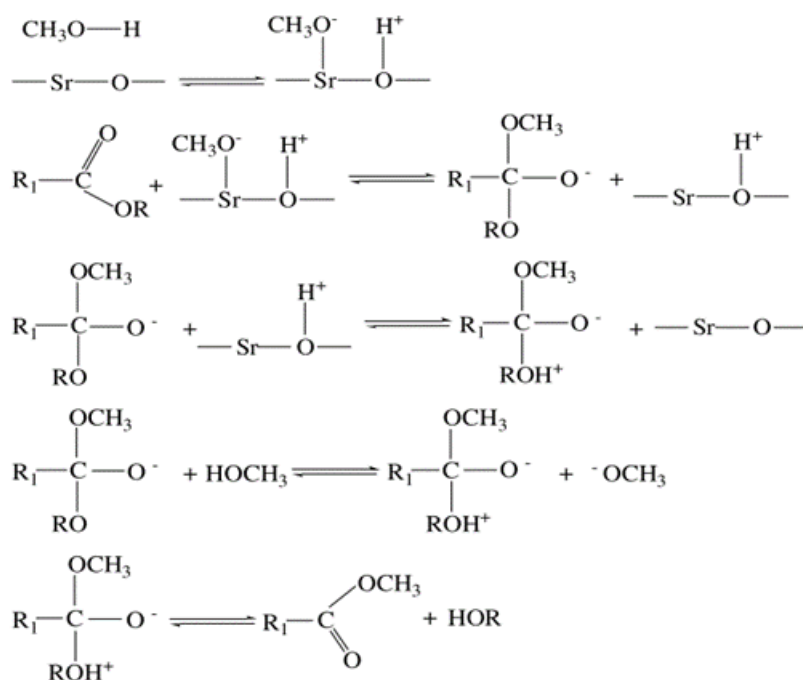
Figure 2.4: Mechanism of solid base catalysis of transesterification using strontium oxide[9]

2.2.1 *Hydrotalcites*

Hydrotalcites (HT) are one type of solid base catalyst that have good anion-exchange properties and adjustable base strength, thus attracting much attention in biodiesel production. Hydrotalcite-like compounds belong to a group of anionic clays known as layered double hydroxides (LDH) and resemble brucite ($Mg(OH)_2$) in their structure [26]. They are formed by the stacking of positively charged sheets where the divalent metal cations are partially substituted by trivalent cations [27]. The excess in positive charge is balanced by the intercalation of anions in the inter-gallery region. Hydrotalcites are represented by $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}_{x/n})$. mH_2O

with M(II) being divalent anions (eg. Mg^{2+}, Zn^{2+}, $Mn^{2+}+$, Ni^{2+}), M(III) being trivalent metal ions (eg. Al^{3+}, Cr^{3+}, Fe^{3+}) and A^{n-} being the interlayer anion [28].

Magnesium-Aluminum HTs for example have been employed in triacylglycerol transesterification of oil feedstocks[29]. Increasing Mg:Al cationic ratio to a certain extent showed an increase in the surface charge of the layers, which higher base strength and higher transesterification rate of fatty acid esters [23]. As triglycerides may contain fatty acid chains of varying lengths, the bulkier compounds may present mass-transport limitations, which hinder their access to the base sites in the HT. To investigate this, Tajuddin, Lee, and Wilson [5] prepared macroporous Mg-Al hydrotalcites in a procedure that utilizes size-controlled polystyrene nanospheres as a physical template for the macropores. This macroporous hydrotalcite showed a 10-times improvement in the normalized activity for the transesterification of long-chain triglycerides (C12 and C18) with respect to regular hydrotalcites, since the base sites in the macropores are more accessible. As for shorter-chain C4 triglycerides, the microporous aspect did not have a significant impact because these short triglycerides diffuse more easily due to their smaller size.

In order to form a stable LDH, divalent and trivalent metal cations should fall in a certain size range. Their ionic radii should between 64 pm and 88 pm and between 62 pm and 69 pm, respectively[28]. Even though cadmium cations, which have an ionic radius of 109 pm, are reported to be incompatible with the formation of stable brucite-like sheets, Saliba and Al-Ghoul [30] managed to synthesize a stable CdAlCl

Catalyst	Yield (%)	Oil	Me:Oil Ratio	Catalyst Loading (wt%)	Reaction Conditions	Ref
CaO-ZnO	97.5	sunflower	10:1	2	60°C, 4h	[10]
$CaO/Al/Fe_3O_4$	98.7	rapeseed	15:1	6	3h	[11]
LaMgO	96	cottonseed	54:1	5	65°C, 0.33h	[12]
MgO	93.69	moringa oleifera	12:1	1	45°C, 4h	[13]
CuO/Mg	82.83	sunflower	6:1	0.25	60°C, 0.5h	[14]
$CaO-Al_2O_3$	98.64	palm	12:1	6	65°C, 5h	[15]
$KAlSiO_4$	98.9	sesame	6:1	5	75°C, 3h	[16]
ZiO_2 + Li,Na,K	99	soybean	8:1	6	65°C, 4h	[17]
$g-C_3N_4$	96	canola	24:1	1	150°C, 3h	[18]
$BaCeO_3$	98.3	karanja	19:1	1.2	65°C, 0.67h	[19]
$CaSO_4/Fe_2O_3-SiO_2$	94	jatropha	9:1	12	120°C, 4h	[20]
CdO	94	linseed	6:1	0.1	100°C, 3h	[21]
MgO , ZnO / Al_2O_3	94	castor	6:1	5	60°C, 2h	[22]
MgAlO	67	soybean	15:1	7.5%	9h	[23]
CaMgZnO	97.5	palm	20:1	6	60°C, 3h	[24]
LaMn	99	soybean	12:1	3	180°C, 1h	[25]

Table 2.1: Mixed metal oxide catalysts for biodiesel production

LDH via RDF using an agar gel matrix.

2.2.2 *Reaction Diffusion Framework*

The reaction-diffusion framework presents a facile method to produce self-assembling porous layered double hydroxide nanoparticles of spherical shape. The desired metal cations at desired ratios are dissolved into an agar gel matrix, forming the inner electrolyte, and are set to react with the outer electrolyte consisting of a strong or weak base. At the interface between the electrolyte and the gel, a supersaturation gradient of the base is created as it starts diffusing downward through the gel. The gel serves as a framework to eliminate solid sedimentation and convection currents, leading to a more crystalline structure [28].

2.3 Objective

The objective of this work is to present another application for the novel, versatile [28], [31] CdAl LDH synthesized by Saliba & Al Ghoul. The implementation of this compound in the purpose of catalyzing the transesterification reaction of vegetable oil is explored. Multiple characterization techniques will be carried out as well as a comparison in biodiesel production yield using this catalyst and and a commercially obtained alternative. The catalyst will also be tested on waste cooking oil in the interest of making use of waste biomass and conserving edible oil. The irony of using toxic cadmium metal in the environmentally friendly field of biodiesel is not lost, but this study proceeds in the pursuit making of new, small contributions.

Chapter 3

Materials and Methods

3.1 Catalyst Synthesis

3.1.1 *Layered Double Hydroxide Synthesis using RDF*

The layered double hydroxide precursor was synthesized using the reaction-diffusion framework method described by Saliba [30], [32].

An aqueous 0.5mol/L solution of cadmium and aluminum at a 1:1 ratio is prepared by mixing $Cd(NO_3)_2$. $4H_2O$ and $Al(NO_3)_3$. $9H_2O$ at the appropriate amounts. An agar solution is prepared by dissolving 0.5g of lennox agar in 40mL of water. It is heated to 90°C and kept under constant stirring until the solution becomes consistent and relatively clear. Then, 10mL of the cadmium-aluminum solution is added to the agar for mixing. The final mixture is then transferred into glass tubes where it is left to gel at room temperature for 5 hours. The gel stiffens by the end of this period.

Then, a 1mol/L aqueous solution of NaOH is gently transferred to the tubes onto the surface of the gel in order to commence the reaction. The reaction is allowed to progress for 3 days. White and yellow bands will form in the gel which contain CdOH and the desired CdAl LDH respectively. It must be noted that the procedure yields a small amount per tube and must be scaled up by running parallel reactions in multiple tubes in order to obtain sufficient product.

The yellow LDH band is manually extracted and washed twice with hot water in order to dissolve away the attached agar particles. The solution is centrifuged and then freeze-dried for 24 hours to obtain the Cd-Al LDH powder, the precursor for the catalyst.

3.1.2 *LDH Impregnation with Calcium*

In order to achieve any success in transesterification of the corn oil, the obtained precursor must be futher modified. The CdAl LDH was impregnated with calcium in a procedure outlined by Castro, Garcia, and Assaf [33]. A catalyst of 40wt% calcium loading (wt Ca / wt Ca + wt calcined hydrotalcite) was prepared by immersing the CdAl LDH in an aqueous solution of $CaNO_3$. The mixture is set to stir at 80°C until all the water evaporates. After that, it is dried at 110°C in an oven overnight.

In order to obtain the desired Ca/CdAl oxide catalyst, the dried powder is calcinated at 600°C for 30 minutes at a heating rate of 10°C/min. The catalyst must be stored in a dessicator to protect it from humidity, which will lead to formation of unwanted $Ca(OH)_2$ and $CaCO_3$ sites [33].

3.2 Characterization

Several characterization techniques were carried out on the catalyst. Scanning electron microscopy was used to examine the morphology of the catalyst and its LDH precursor at the nano scale with a 5kV electron beam. SEM samples were coated with a layer of gold 10nm thick via sputtering.

Energy-dispersive X-ray spectroscopy at 20kV allowed the quantification of the atomic weights and atomic compositions of the catalyst. The results quantify the atomic ratio relating the amounts of Cd and Al present in the LDH as well as show how much Ca is present in the catalyst after the impregnation procedure.

Thermogravimetric analysis was conducted to observe the percentage mass change of the catalyst sample at increasing temperatures under an inert nitrogen atmosphere. The temperature ranges from room temperature to upwards of 700°C and varies at a rate of 5K/min. The change in mass as the temperature increases sheds light on the possible decomposition reactions that the sample goes through as the temperature increases.

BET method was carried out to the quantify key physical properties such as surface area, pore volume, and pore size by examining the amount of nitrogen adsorbed/desorbed at different values of partial pressure.

Powder X-ray Diffraction was employed in order to characterize both the CdAl LDH precursor and the Ca/CdAl oxide catalyst. Cu kα radiation was utilized at $(\lambda) = 1.5406$ Å.

3.3 Transesterification experiments

The transesterification reactions of corn oil and methanol was carried out as follows. 5g of oil is first preheated to 62°C in a silicon oil bath. The Ca/CdAl oxide catalyst and excess methanol are then added. A methanol:oil molar ratio of 11 was used throughout. With the mean molecular weight of the corn oil taken as 872.33 g/mol [34], 2.55mL of methanol is required for a 5g oil sample. The mixture is stirred at 600 rpm for the duration of the reaction. After the reaction is stopped, the final mixture is centrifuged in order to separate the solid catalyst. The liquid phase is poured into a separatory funnel and allowed to separate into two phases. The lower phase consists of glycerol and the upper phase consists of the fatty acid methyl esters and excess methanol. The upper phase is recovered and placed in a rotary evaporator at 42°C under vacuum in order to evaporate the excess alcohol present.

The transesterification reaction was carried out for both the Ca/CdAl oxide catalyst and commercially obtained CaO for comparison. Multiple experiments

were conducted where the reaction duration was varied while the catalyst loading was kept at 4wt% of the mass of oil.

^{1}H NMR was used to examine the stock corn oil and the obtained biodiesel sample. It was used to compare the existence of the peaks that correspond to the specific carbon atoms that substitute upon undergoing transesterification

One of the key factors affecting the ability to transesterify waste cooking oils is their content of free fatty acids. These single fatty acid chains, originally bonded to a glycerol group as a triglyceride, diglyceride, or monoglyceride, become detached during exposure to high temperatures and other species present in food during frying and other cooking procedures. The Ca/CdAl oxide catalyst was also tested on waste cooking oil under similar reaction conditions to check for the ability to tolerate a FFA content value above the minimal amount of FFA in refined edible vegetable oil.

In this work, waste corn oil was tested for FFA content using the British-Adopted European Standard (BS EN 14104:2003)[35]. This is accomplished by titrating it a strong base, sodium hydroxide. A sample of 15g of waste oil was recorded. A volume containing 50mL of ethanol and a few drops of phenolphtalein indicator was neutralized with the titration solution of sodium hydroxide 0.1mol/L in water. When a faint, pink color persists, the sample of waste oil is added to the mixture. Heating and stirring is applied in order to thoroughly mix the oil into the solution. The obtained homogeneous mixture is then titrated with the NaOH solution until the persistent light pink color reemerges.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization

4.1.1 *Scanning Electron Microscopy & EDX*

Electron micrographs were obtained for obtained for 3 samples (figure 4.1). The first is the CdAl LDH precursor. The second is the oxide obtained by calcination of the precursor without any calcium impregnation. The third is the finished Ca/CdAl oxide catalyst. One can observe the near-spherical, flower-like morphology of the precursor. The structure of the nanosheets provides many pores and high surface area for calcium to be situated on during the wet impregnation procedure. The micrograph of the calcium-free CdAl oxide is observed to lose the flowery shape as the evaporation of the contents of the inter-gallery region leads to a collapse of the nanosheets. In the third figure the morphology of the catalyst features the calcium sites situated around and underneath the collapsed nanosheets.
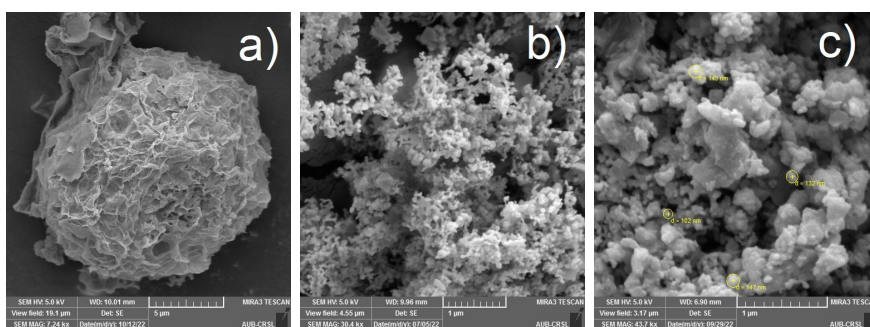

Figure 4.1: SEM micrographs for (a) CdAl LDH precursor, (b) CdAl oxide, and (c) Ca/CdAl oxide

The EDX spectrum of the CdAl LDH showed a cationic ratio of 0.36. The cationic ratio is defined as the fraction of aluminum ions with respect to the sum of aluminum and the divalent ion of the hydrotalcite structure (eq 4.1). The EDX result of the Ca/CdAl oxide catalyst can be found in table 4.1.

Element	Atomic wt%
Cd	7
Al	3
Ca	17
O	73

Table 4.1: Average atomic wt% of Ca-CdAl oxide catalyst

$$\text{cationic ratio } x = \frac{Al}{Al + Cd} \tag{4.1}$$

4.1.2 *Thermogravimetric Analysis*

The TGA graph of the CdAl LDH can be found in figure 4.2 and is seen to be in line with the general shape of TGA curves of layered double hydroxides [36]. The first stage sees the elimination of any water on the surface of the catalyst. In the second stage, the intercalated water inside the inter-gallery region is released. The third stage sees the dehydroxylation of Cd-OH bonds, and the final stage is where the Al-OH bonds undergo dehydroxylation [31].
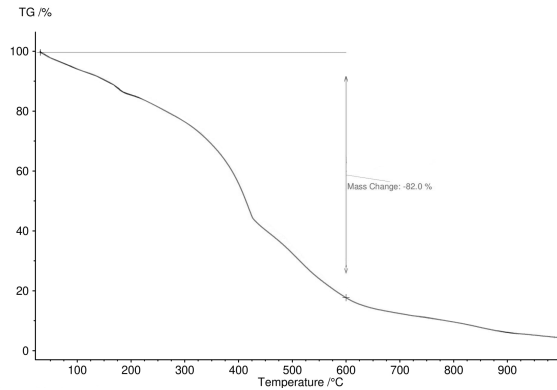

Figure 4.2: TGA graph of CdAl LDH precursor

4.1.3 *BET Nitrogen Physisorption Method*

The adsorption-desorption isotherm in figure 4.3a is a type IV isotherm indicative of a mesoporous structure. A hysteresis loop of type H2b is observed, indicating a complex pore structure with non-uniform pore opening sizes. The catalyst has a small surface area of 3.1 m^2/g, implying that it facilitates the transesterification reaction through its chemical activity, not through its physical adsorptive properties. The pore width of 133 Å confirms its mesoporous structure.
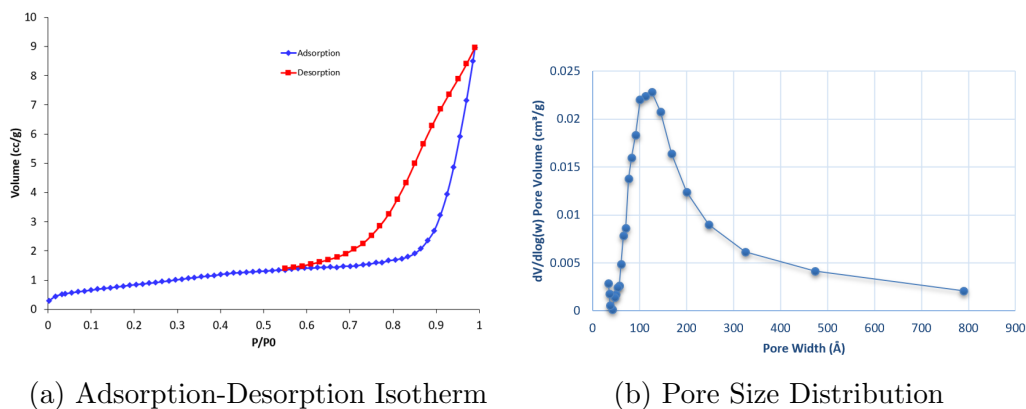
(a) Adsorption-Desorption Isotherm   (b) Pore Size Distribution

Figure 4.3: BET results for Ca/CdAl oxide catalyst

BET Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	BJH desorption pore width (Å)
3.1	0.013	133

Table 4.2: Surface area, pore volume, and pore width of Ca/CdAl oxide

4.1.4 *Powder X-Ray Diffraction*

XRD spectra were obtained for the CdAl LDH precursor (figure 4.4) and the Ca/CdAl oxide catalyst (figure 4.5). The CdAl LDH is shown to have the structure of a hydrotalcite, which is characterized by the characteristic peaks at 2θ=12°and 2θ=23°. These values of 2θ correspond to an interplanar distance of 7.37 Å and 3.86 Å via Bragg's law (equation 4.2) .The LDH was matched with the MgAl hydrotalcite (PDF 1-070-2151) shown in blue and CdAl hydoxide nitrate hydrate (PDF 01-080-7110) shown in red (figure 4.4).

The Ca/CdAl oxide catalyst showed a pattern (figure 4.5) exhibiting features of both calcium oxide at 2θ=32°and 2θ=37.5°(PDF 00-02-1088) (in red) and calcium cadmium oxide at 2θ=33 and 2θ=38 (PDF 00-061-0464) (in blue). The interplanar distances of these lattices at the indicated peaks can be found in table 4.3. Because the catalyst was prepared by adsorbing calcium onto its surface and then collapsing the structure of the hydrotalcite upon calcination, the resulting catalyst appears to be a composite of the two matched oxide structures.

Material	2θ (°)	d (Å)
Calcium oxide	32	2.79
	37	2.43
Calcium cadmium oxide	33	2.71
	38	2.37

Table 4.3: Interplanar distance values for materials matched for Ca/CdAl oxide catalyst

$$\text{Bragg's law: } n\lambda = 2dsin\theta \tag{4.2}$$

where
λ is the wavelength of the x-ray (1.5406 Å)
d is the distance between the planes in the crystal structure in Å
θ is the diffraction angle
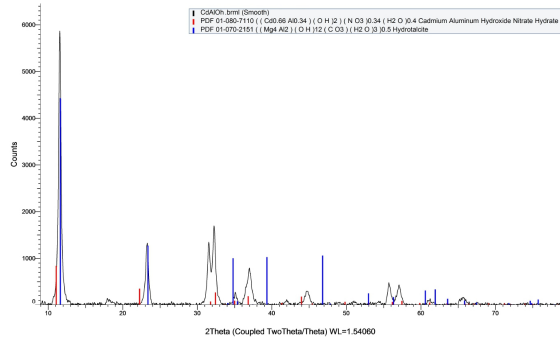n = 1

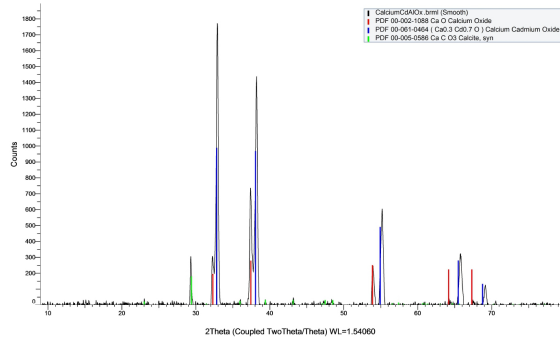Figure 4.4: X-ray diffraction pattern for CdAl LDH precursor

Figure 4.5: X-ray diffraction pattern for Ca/CdAl oxide catalyst

4.2 Transesterification of corn oil with methanol

4.2.1 *Transesterification experiments*

The biodiesel yield was defined as:

$$\text{Yield \%} = \frac{\text{weight of biodiesel}}{\text{weight of oil}} * 100 \tag{4.3}$$

The results of the transesterification reactions at 62°C, 11:1 methanol:oil ratio, 4wt% loading can be found in figure 4.8. The optimal biodiesel yield obtained from the Ca/CdAl oxide catalyst was designated at 93% after 3 hours of reaction time, with almost no worthwhile increases observed with higher reaction duration.

It is clear that the prepared catalyst exhibits a noticeable increase in catalytic activity compared to the commercial CaO, as the reaction yield sharply increases significantly sooner.

The biodiesel conversion, representing the purity of the biodiesel end sample, was calculated from the NMR spectrum using equation 4.4 [37] on the NMR curve in figure 4.7. The conversion at 3h, 62°C, 4wt% loading of Ca/CdAl oxide catalyst, 11:1 methanol:oil molar ratio was found to be 96%.

$$C = \frac{2 * A_{Me}}{3 * A_{\alpha CH_2}} * 100 \tag{4.4}$$

where
C is the conversion % of fatty acid methyl esters
A_{Me} is value obtained by integrating the area under the NMR curve indicated by the peak at 3.6 ppm, which corresponds to the methyl ester's methoxy group
$A_{\alpha CH_2}$ is value obtained by integrating the area under the NMR curve indicated by the peak 2.3 ppm, which corresponds to the methylene protons

As stated, the methoxy group at 3.6 ppm corresponds to the lone carbon atom in the fatty acid methyl ester [37]. Therefore it is not present in the NMR spectrum of the corn oil (figure 4.6) and only appears in figure 4.7 after transesterification has taken place.

Under the same reaction conditions, transesterification of waste cooking oil was also carried out and yielded 72.4%. This decrease in yield in comparison to the transesterication of the uncooked corn oil is to be expected, since the increase in FFA content upon frying the corn oil is bound to hinder the reaction rate. The fact that it still presented a worthwhile yield value likely implies that the free fatty acid content in the waste cooking oil is not too high so that the reaction was still feasible. The FFA content of the waste oil was quantified later.
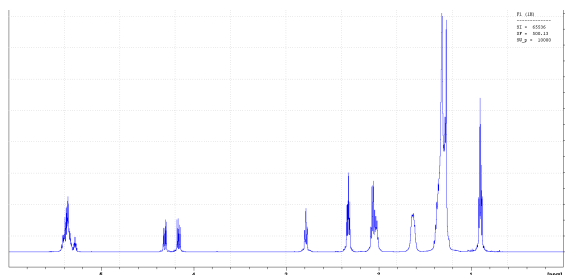

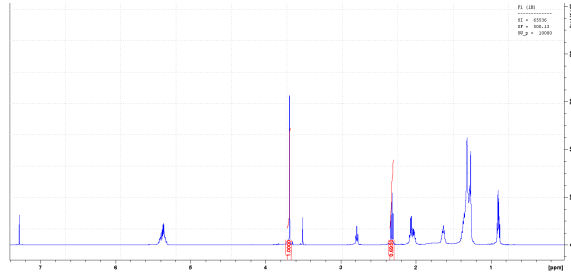Figure 4.6: ^1H NMR spectrum of corn oil

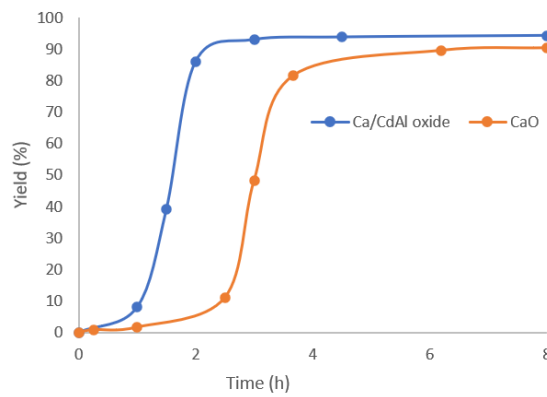Figure 4.7: ^{1}H NMR spectrum obtained biodiesel sample

Figure 4.8: Variation of biodiesel yield as a function of reaction time, for Ca/CdAL catalyst and commercial CaO

4.2.2 *FFA content in Waste Cooking Oil*

The FFA content (as oleic acid) can be calculated as [38]

$$\%FFA = \frac{282 * v * c * 100}{m * 1000} = \frac{28.2 * 0.65 * 1.003}{15.11} = 1.217\% \tag{4.5}$$

where
v is the amount of titrant (in mL) needed to reach equivalence
c is the concentration of the titrant (in mol/L)
m is the mass of the oil sample (in grams)
282 is the molecular weight of oleic acid(g/mol)

As prieviously mentioned, the prepared catalyst was able to present a biodiesel yield above 70% due to an expected relatively low FFA content in the waste cooking oil. It should be noted that the waste oil was obtained by frying corn oil 3 times. That is enough for it to count as waste cooking oil in this case, but in industrial cases the vegetable oil would be fried much more thoroughly and likely would exhibit significantly higher FFA content.

Chapter 5

Conclusion

In this study, a CdAl LDH precursor synthesized by RDF was impregnated with calcium nitrate and calcined to obtain Ca/CdAl oxide. This was used as a heterogeneous base catalyst in the transesterification of corn oil with methanol for the purpose of biodiesel production. The catalyst was characterized by SEM/EDX, powder XRD, and BET nitrogen adsorption-desorption technique. Thermogravimetric analysis was carried out on its LDH precursor. Transesterification reactions were carried out using the prepared catalyst and commercially obtained calcium oxide to compare their activity in the reaction, and the synthesized catalyst showed a noticeable increase in activity. The fatty acid methyl ester yield was measured under a series of different reaction durations, with a 4wt% catalyst loading at 11:1 methanol:oil ratio at 62°C. The optimal biodiesel yield was determined to be 93% at 3 hours of reaction time. The Ca/CdAl oxide catalyst was also tested in the transesterification of waste cooking oil, where a 72.4% yield was observed. Future work would investigate the quantification of catalyst basicity, recyclability of the catalyst, and quantification of leaching of calcium into the reaction medium, as the latter is a common problem with heterogeneous alkaline catalysts.

Bibliography

[1] L. C. Meher, D. Vidya Sagar, and S. N. Naik, "Technical aspects of biodiesel production by transesterification—a review," *Renewable and Sustainable Energy Reviews*, vol. 10, no. 3, pp. 248–268, 2006, 21, ISSN: 1364-0321. DOI: https://doi.org/10.1016/j.rser.2004.09.002. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S1364032104001236.

[2] T. F. Dossin, M.-F. Reyniers, R. J. Berger, and G. B. Marin, "Simulation of heterogeneously mgo-catalyzed transesterification for fine-chemical and biodiesel industrial production," *Applied Catalysis B: Environmental*, vol. 67, no. 1, pp. 136–148, 2006, 19, ISSN: 0926-3373. DOI: https://doi.org/10.1016/j.apcatb.2006.04.008. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0926337306001329.

[3] M. Koberg and A. Gedanken, "Chapter 9 - using microwave radiation and sro as a catalyst for the complete conversion of oils, cooked oils, and microalgae to biodiesel," in *New and Future Developments in Catalysis*, S. L. Suib, Ed. Amsterdam: Elsevier, 2013, pp. 209–227, 2, ISBN: 978-0-444-53878-9. DOI: https://doi.org/10.1016/B978-0-444-53878-9.00010-2. [Online]. Available: https://www.sciencedirect.com/science/article/pii/B9780444538789000102.

[4] J. Encinar, J. Gonzalez, J. Rodriguez, and A. Tejedor, "Biodiesel fuels from vegetable oils: Transesterification of cynara c ardunculus l. oils with ethanol," *Energy fuels*, vol. 16, no. 2, pp. 443–450, 2002, ISSN: 0887-0624.

[5] N. A. Tajuddin, A. F. Lee, and K. Wilson, "6 - production of biodiesel via catalytic upgrading and refining of sustainable oleagineous feedstocks," in *Handbook of Biofuels Production (Second Edition)*, R. Luque, C. S. K. Lin, K. Wilson, and J. Clark, Eds. Woodhead Publishing, 2016, pp. 121–164, 1, ISBN: 978-0-08-100455-5. DOI: https://doi.org/10.1016/B978-0-08-100455-5.00006-0. [Online]. Available: https://www.sciencedirect.com/science/article/pii/B9780081004555000060.

[6] I. Atadashi, M. Aroua, and A. A. Aziz, "Biodiesel separation and purification: A review," *Renewable Energy*, vol. 36, no. 2, pp. 437–443, 2011, ISSN: 0960-1481.

[7] Y. M. Sani, W. M. A. W. Daud, and A. A. Aziz, "Activity of solid acid catalysts for biodiesel production: A critical review," *Applied Catalysis A: General*, vol. 470, pp. 140–161, 2014, ISSN: 0926-860X.

[8] E. Lotero, Y. Liu, D. E. Lopez, K. Suwannakarn, D. A. Bruce, and J. G. Goodwin, "Synthesis of biodiesel via acid catalysis," *Industrial engineering chemistry research*, vol. 44, no. 14, pp. 5353–5363, 2005, ISSN: 0888-5885.

[9] X. Liu, H. He, Y. Wang, and S. Zhu, "Transesterification of soybean oil to biodiesel using sro as a solid base catalyst," *Catalysis Communications*, vol. 8, no. 7, pp. 1107–1111, 2007, 22, ISSN: 1566-7367. DOI: https://doi.org/10.1016/j.catcom.2006.10.026. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S1566736706003931.

[10] Ž. Kesić, I. Lukić, D. Brkić, *et al.*, "Mechanochemical preparation and characterization of cao·zno used as catalyst for biodiesel synthesis," *Applied Catalysis A: General*, vol. 427-428, pp. 58–65, 2012, ISSN: 0926-860X. DOI: https://doi.org/10.1016/j.apcata.2012.03.032. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0926860X12001755.

[11] S. Tang, L. Wang, Y. Zhang, S. Li, S. Tian, and B. Wang, "Study on preparation of ca/al/fe3o4 magnetic composite solid catalyst and its application in biodiesel transesterification," *Fuel Processing Technology*, vol. 95, pp. 84–89, 2012, ISSN: 0378-3820. DOI: https://doi.org/10.1016/j.fuproc.2011.11.022. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0378382011004097.

[12] V. Mutreja, S. Singh, and A. Ali, "Potassium impregnated nanocrystalline mixed oxides of la and mg as heterogeneous catalysts for transesterification," *Renewable Energy*, vol. 62, pp. 226–233, 2014, ISSN: 0960-1481. DOI: https://doi.org/10.1016/j.renene.2013.07.015. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0960148113003601.

[13] H. Esmaeili, G. Yeganeh, and F. Esmaeilzadeh, "Optimization of biodiesel production from moringa oleifera seeds oil in the presence of nano-mgo using taguchi method," *International Nano Letters*, vol. 9, no. 3, pp. 257–263, 2019, ISSN: 2228-5326. DOI: 10.1007/s40089-019-0278-2. [Online]. Available: https://doi.org/10.1007/s40089-019-0278-2.

[14] R. Varghese, S. Jose, H. Joyprabu, and I. Johnson, "Ultrasonication assisted production of biodiesel from sunflower oil by using cuo: Mg heterogeneous nanocatalyst," *IOP Conference Series: Materials Science and Engineering*, vol. 225, no. 1, p. 012213, 2017, ISSN: 1757-899X 1757-8981. DOI: 10.1088/1757-899X/225/1/012213. [Online]. Available: https://dx.doi.org/10.1088/1757-899X/225/1/012213.

[15] M. Zabeti, W. M. A. W. Daud, and M. K. Aroua, "Biodiesel production using alumina-supported calcium oxide: An optimization study," *Fuel Processing Technology*, vol. 91, no. 2, pp. 243–248, 2010, ISSN: 0378-3820. DOI: https://doi.org/10.1016/j.fuproc.2009.10.004. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0378382009003051.

[16] M. Mahloujifar and M. Mansournia, "A comparative study on the catalytic performances of alkali metals-loaded kalsio4 for biodiesel production from sesame oil," *Fuel*, vol. 291, p. 120 145, 2021, ISSN: 0016-2361. DOI: https://doi.org/10.1016/j.fuel.2021.120145. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0016236121000211.

[17] Y.-M. Dai, Y.-Y. Li, L. Jia Hao, B. Y. Chen, and C.-C. Chen, "One-pot synthesis of acid-base bifunctional catalysts for biodiesel production," *Journal of Environmental Management*, vol. 299, p. 113 592, 2021, ISSN: 0301-4797. DOI: https://doi.org/10.1016/j.jenvman.2021.113592. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0301479721016546.

[18] T. V. de Medeiros, A. Macina, and R. Naccache, "Graphitic carbon nitrides: Efficient heterogeneous catalysts for biodiesel production," *Nano Energy*, vol. 78, p. 105 306, 2020, ISSN: 2211-2855. DOI: https://doi.org/10.1016/j.nanoen.2020.105306. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S2211285520308831.

[19] S. Sahani, T. Roy, and Y. Chandra Sharma, "Clean and efficient production of biodiesel using barium cerate as a heterogeneous catalyst for the biodiesel production; kinetics and thermodynamic study," *Journal of Cleaner Production*, vol. 237, p. 117 699, 2019, ISSN: 0959-6526. DOI: https://doi.org/10.1016/j.jclepro.2019.117699. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0959652619325491.

[20] S. H. Teo, A. Islam, E. S. Chan, *et al.*, "Efficient biodiesel production from jatropha curcus using caso4/fe2o3-sio2 core-shell magnetic nanoparticles," *Journal of Cleaner Production*, vol. 208, pp. 816–826, 2019, ISSN: 0959-6526. DOI: https://doi.org/10.1016/j.jclepro.2018.10.107. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0959652618331214.

[21] M. Tariq, A. K. Qureshi, S. Karim, *et al.*, "Synthesis, characterization and fuel parameters analysis of linseed oil biodiesel using cadmium oxide nanoparticles," *Energy*, vol. 222, p. 120 014, 2021, ISSN: 0360-5442. DOI: https://doi.org/10.1016/j.energy.2021.120014. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0360544221002632.

[22] M. B. Navas, J. F. Ruggera, I. D. Lick, and M. L. Casella, "A sustainable process for biodiesel production using zn/mg oxidic species as active, selective and reusable heterogeneous catalysts," *Bioresources and Bioprocessing*, vol. 7, no. 1, p. 4, 2020, ISSN: 2197-4365. DOI: 10.1186/s40643-019-0291-3. [Online]. Available: https://doi.org/10.1186/s40643-019-0291-3.

[23] W. Xie, H. Peng, and L. Chen, "Calcined mg–al hydrotalcites as solid base catalysts for methanolysis of soybean oil," *Journal of Molecular Catalysis A: Chemical*, vol. 246, no. 1, pp. 24–32, 2006, ISSN: 1381-1169. DOI: https://doi.org/10.1016/j.molcata.2005.10.008. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S1381116905007211.

[24] S. Limmanee, T. Naree, K. Bunyakiat, and C. Ngamcharussrivichai, "Mixed oxides of ca, mg and zn as heterogeneous base catalysts for the synthesis of palm kernel oil methyl esters," *Chemical Engineering Journal*, vol. 225, pp. 616–624, 2013, ISSN: 1385-8947. DOI: https://doi.org/10.1016/j.cej.2013.03.093. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S138589471300418X.

[25] S. Nasreen, H. Liu, D. Skala, A. Waseem, and L. Wan, "Preparation of biodiesel from soybean oil using la/mn oxide catalyst," *Fuel Processing Technology*, vol. 131, pp. 290–296, 2015, ISSN: 0378-3820. DOI: https://doi.org/10.1016/j.fuproc.2014.11.029. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0378382014005086.

[26] Y.-B. Wang and J.-M. Jehng, "Hydrotalcite-like compounds containing transition metals as solid base catalysts for transesterification," *Chemical Engineering Journal*, vol. 175, pp. 548–554, 2011, ISSN: 1385-8947.

[27] D. Saliba and M. Al-Ghoul, "Kinetics of intercalation of fluorescent probes in magnesium–aluminium layered double hydroxide within a multiscale reaction–diffusion framework," *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 374, no. 2080, p. 20 160 138, 2016, ISSN: 1364-503X.

[28] D. Saliba, A. Ezzeddine, R. Sougrat, N. M. Khashab, M. Hmadeh, and M. Al-Ghoul, "Cadmium–aluminum layered double hydroxide microspheres for photocatalytic co2 reduction," *ChemSusChem*, vol. 9, no. 8, pp. 800–805, 2016, ISSN: 1864-5631.

[29] J. Mittal, "Recent progress in the synthesis of layered double hydroxides and their application for the adsorptive removal of dyes: A review," *Journal of Environmental Management*, vol. 295, p. 113 017, 2021, ISSN: 0301-4797.

[30] D. Saliba and M. Al-Ghoul, "Stability and particle size control of self-assembled cadmium–aluminum layered double hydroxide," *CrystEngComm*, vol. 18, no. 43, pp. 8445–8453, 2016.

[31] D. Saliba, S. E. El Jamal, A. Jonderian, M. Ammar, M. Hmadeh, and M. Al-Ghoul, "Tuning the structural properties of cadmium–aluminum layered double hydroxide for enhanced photocatalytic dye degradation," *RSC Advances*, vol. 10, no. 70, pp. 43 066–43 074, 2020.

[32] D. Saliba, A. Ezzeddine, A.-H. Emwas, N. M. Khashab, and M. Al-Ghoul, "Dynamics and mechanism of intercalation/de-intercalation of rhodamine b during the polymorphic transformation of the cdal layered double hydroxide to the brucite-like cadmium hydroxide," *Crystal Growth Design*, vol. 16, no. 8, pp. 4327–4335, 2016, ISSN: 1528-7483.

[33] C. S. Castro, L. C. F. Garcia, and J. M. Assaf, "The enhanced activity of ca/mgal mixed oxide for transesterification," *Fuel Processing Technology*, vol. 125, pp. 73–78, 2014, ISSN: 0378-3820. DOI: https://doi.org/10.1016/j.fuproc.2014.03.024. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0378382014001209.

[34] E. Truzzi, L. Marchetti, S. Benvenuti, *et al.*, "A novel qnmr application for the quantification of vegetable oils used as adulterants in essential oils," *Molecules*, vol. 26, no. 18, 2021, ISSN: 1420-3049. DOI: 10.3390/molecules26185439.

[35] *En 14104:2003 fat and oil derivatives - fatty acid methyl esters (fame) - determination of acid value.*

[36] R. Yahyaoui, P. E. S. Jimenez, L. A. P. Maqueda, K. Nahdi, and J. M. C. Luque, "Synthesis, characterization and combined kinetic analysis of thermal decomposition of hydrotalcite (mg6al2 (oh) 16co3· 4h2o)," *Thermochimica Acta*, vol. 667, pp. 177–184, 2018, ISSN: 0040-6031.

[37] F. Kesserwan, M. N. Ahmad, M. Khalil, and H. El-Rassy, "Hybrid cao/al2o3 aerogel as heterogeneous catalyst for biodiesel production," *Chemical Engineering Journal*, vol. 385, p. 123 834, 2020, ISSN: 1385-8947.

[38] S. Nielsen, *Food Analysis*. Springer US, 2014.