



Preparation of Poly (AAc/AAM)/NaOH Hydrogel as a Catalyst for Electrolysis Production of Biodiesel from Waste Cooking Oil

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Abstract

Biodiesel has been considered to be the best substitute for diesel due to its unique qualities which contribute to environmental conservation. This work was undertaken to transesterification process and the production of biodiesel from waste cooking oil by electrolysis with a novel catalyst poly (AAc/AAM)/NaOH hydrogel. The catalyst was prepared by trapping sodium hydroxide in polyacrylic acid and acrylamide poly (AAc/AAM) to be used as a strong basic heterogeneous catalyst. The swelling of prepared hydrogel with different doses of cross-linker were examined. The Scanning electron microscopy (SEM) as well as the energy-dispersive X-ray spectroscopy (EDX) were employed to characterize the prepared catalyst. The degree of conversion of WCO to biodiesel expressed as fatty acid methyl esters (FAMES) was determined via high performance thin layer chromatography (HPTLC), as well as the composition of FAMES by gas chromatography mass spectrometry (GC/MS). Technical Details and Standards of biodiesel prepared from WCO were also characterized. Optimization of the electrolysis catalyzed process revealed that the optimum conditions employed for electrolysis process to produce the most promising results 92.8 % for biodiesel yield were oil: methanol molar ratio 1:35, dose of electrolyte salt (NaCl) 0.7g / 40 g oil, water dose used to dissolve the electrolyte salt 1.6 % related to oil volume and electrical potential required was 30 volt and catalyst dose 20% related to oil weight over a reaction duration of 60 minutes under ambient reaction conditions.

Keywords: biodiesel, waste cooking oil, electrolysis, transesterification, hydrogel.

1. Introduction

Energy consumption has significantly grown during the past century as a result of alterations in lifestyle and population growth. The usage of energy resources is required for human survival. The vast majority of the world's energy is consumed for industry, power, transportation, and household consumption as a result of ongoing population growth. The most obvious explanation is the rising need for fossil fuels across all industries [1]. Growing energy consumption caused a severe destruction to the environment like the excess CO₂ and the global warming, acid rain and greenhouse gas emissions, as well as carcinogenic illnesses [2-3].

According to some reports, if consumption continues at its current rate, the remaining gas and oil reserves would be depleted in 41 to 63 years [4]. The availability of fossil fuels is not renewable and will soon run out, according to the second argument [5]. On other respect, it is anticipated that conventional fuels would become more expensive as petroleum

supplies are used up in the next decades [6]. Furthermore, the unstable cost of crude oil puts nations with little resources in grave peril [7].

In addition to grave environmental concerns, declining crude oil reserves, increasing petroleum fuel prices, and overconsumption of liquid fuels, primarily for transportation, have necessitated the development of alternative "eco-friendly," economically and environmentally sustainable sources of competitive and readily available energy. Researchers have been focused their efforts on finding an appropriate alternative for fossil fuels in recent years since it is predicted that various forms of renewable energy resources will play a big part in alleviating the world's future power dilemma. It has been suggested that using renewable energy sources like biofuels, hydropower, wind and solar energy could be a viable replacement to reduce complete dependency on fossil fuels [8, 9].

Vegetable oils are catalytically transesterified with short- or medium-chain alcohols to produce

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biodiesel. Biodiesel has the most energy potential and will be the focus of this research. Because it is biodegradable, nontoxic, renewable, and totally compatible with diesel engines, this type of fuel shows great potential as a petro-diesel substitute [10]. Biodiesel is becoming more popular as a substitute for diesel fuel because of its superior exhaust quality, sustainability and biodegradability. In the presence of catalysts, lower molecular weight alcohols, vegetable oil and animal fats are combined to produce biodiesel, sometimes referred to as mono alkyl esters. Generally speaking, animal fats and vegetable oil are hydrophobic substances that are present in both animals and plants. They are insoluble in water. These compounds consist of three moles of fatty acids and one mole of glycerol [11 - 14]. Biodiesel is one of these substitutional fuels that is marketed as an additional fuel for diesel engines [15].

Because the manufacturing of biodiesel from edible oils is not economically feasible and cannot compete with diesel fuel derived from petroleum, it is vital to look for inexpensive oil feedstock. For a while now, scientists have been looking into the possibility of producing biodiesel at a lower cost by using non-edible vegetable oils. Recently, Waste cooking oil has been utilized as a feedstock to lower the price of producing biodiesel [16]. There are many inexpensive sources such as inedible oils, animal fats, Waste cooking oils (WCOs) and by-product oil residues from edible oil refineries can be used to manufacture ecologically friendly and sustainable goods [17]. WCO is two to three times cheaper than vegetable oils, in addition to saving money on waste disposal and treatment [18].

Edible oils are used for cooking by people all over the world, but the oil is eventually discarded, posing a significant hazard to the environment. Oil that enters water sources pollutes the environment by generating oil layers on the water surface that block oxygen exchange and degrade the ecology. In addition, dumping spent oil in drain pipes causes problems by clogging them and causing foul odours, raising the expense of wastewater treatment. For these reasons, it was necessary to develop a method for recovering and reusing this oil [19].

Homogenous alkali catalysis (NaOH, KOH, and CH₃-ONa) is used in conventional biodiesel transesterification processes because it is both affordable and widely accessible [20, 21]. However, there are several drawbacks to the process, including high levels of energy consuming, which raises the cost of capital equipment significantly, and safety issues. Furthermore, the feedstock's water and free fatty acid (FFA) concentration are extremely important in this process. High water content can cause saponification, which results in lower ester yields, more difficult glycerol separation from methyl ester, increased viscosity, and the formation of

emulsions, dimeric and polymeric acids, and glycerides [22, 23]. They all result in difficulties with the recapture of methyl ester and the purification of downstream. Meanwhile, soap creation uses up some of the catalyst, lowering the final yield.

When compared to other biodiesel production techniques, electro-chemical synthesis (also known as electrolysis or electrosynthesis) has many advantages. It can be carried out at ambient conditions and is suitable for oil feedstocks with high water content. It also requires less operational energy, doesn't require a co-solvent, and has a high potential for enhancing performance through the addition of heterogeneous catalysts. [24]. Electrolysis is a type of non-spontaneous redox reaction that happens when an external voltage is applied. Electrical energy was used to electrolytically dissociate water molecules in an electrolyte, resulting in the formation of hydrogen and oxygen molecules. Excess water in the reactant mixture has been shown in several studies to slow the conversion rate of biodiesel from feedstock oil and to degrade the characteristics of fatty acid methyl esters. A continuous electric field applied to the reactant combination throughout the transesterification process could limit water production and potentially electrolyze away pre-existing water molecules in the mixture. [25]. The stimulus to use heterogeneous catalysts for biodiesel synthesis is the potential to avoid the saponification and neutralization steps [26 - 28].

The present work is concerned with preparation of poly (AAc/AAm)/NaOH hydrogel as a heterogeneous catalyst during electrolysis of biodiesel from used cooking oil.

2. EXPERIMENTAL WORK

2.1. Materials and equipment

Waste cooking oil (WCO) is a blend of used cooking oil from several sources, including sunflower oil, corn oil, soybean oil, etc. This oil comes from domestic use which collected from various homes in Egypt. Methanol, sodium chloride extra pure, N, N'-methylene bis acrylamide (MBA), potassium persulphate (KPS) were supplied by Sigma – Aldrich, Inc. Acrylic acid (AAc) and Acrylamide (AAm) monomers were provided by Sisco Research Lab. PVT. LTD, India.

2.1.1. Electrolysis Cell

The electrolysis cell is the primary device utilized in biodiesel manufacturing process. The electrolysis cell includes a DC current source as well as positive and negative electrodes that are coupled to graphite electrodes. Graphite is inexpensive and corrosion-resistant as well as its atomic structure strengthen its electrical conductivity.

2.2 EXPERIMENTAL PROCEDURE

2.2.1. Electrolysis of WCOs

The reactants are filled in the electrolysis cell. The reaction was carried out in a batch glass reactor (capacity of 500 ml) including oil, water, alcohol, NaCl as an electrolyte and the catalyst. The magnetic stirrer, which is set to a medium speed, and the power supply are both turned on. The electrolysis process was carried out at ambient conditions. At the end of the experiment, biodiesel and glycerol are detached in two stages by casting.

Different doses of cross-linker used for preparing poly (AAc/AAm) hydrogel as well as, the catalyst doses applied to biodiesel production were studied. The resultant mixture is put into a separating column after reaction for a predetermined time to detach the biodiesel from the glycerol.

Evaporation was done for two hours at a temperature of 70°C to get the product free of methanol. Gas chromatography mass spectrophotometry (GC/MS) was used to analyze the biodiesel that was manufactured to specify composition and types of FAMES components. In order to calculate the yield % of FAMES, High performance thin layer chromatography (HPTLC) was also employed.

2.2.2. Enhancement of Electrolytic Process

The aim of this study is to upgrade the efficiency of electrolysis process of WCO using polymeric heterogeneous catalysts namely poly (acrylic acid/acrylamide). This work was undertaken to produce biodiesel from used cooking oil by electrolysis method utilizing a novel heterogeneous catalyst. The catalyst [poly (AAc/AAm)/NaOH] was prepared by trapping sodium hydroxide in poly (acrylic acid / acrylamide) hydrogel to be used as a strong basic heterogeneous catalyst.

2.2.2.1. Preparation of poly (acrylic acid / acrylamide) Hydrogel

A modified procedure was followed for the preparation of poly(acrylic acid / acrylamide) hydrogel [29]. A mixed solution of acrylic acid monomer and acrylamide monomer in distilled water was prepared by agitating the monomers, and then a decided amount of N, N-methylene bis-acrylamide dissolved in distilled water was added to the reactants as a cross-linker under ambient conditions. The blend solution was agitated and heated in a water bath to 80 °C for 15 minutes before the initiator was added. The reaction blend was stirred for a short period of time to finish the polymerization reaction. The prepared hydrogel was then immersed in excess distilled water to remove any impurities then air dried at room temperature then crushed to particles (≈3 to 5 ml). Additionally, the produced polymer was swelled in a NaOH solution. The swelled polymer was washed then air dried at room temperature to be used as a heterogeneous catalyst. The swelling of prepared hydrogel was affected by the cross-linker dose which

added to the reactants medium. So, the quantity of trapped sodium hydroxide varied according to degree of swelling. The effect of trapped NaOH amount on the transesterification process was studied thoroughly.

2.3. Characterization

2.3.1. Scanning Electron Microscopy (SEM)

The morphology of the prepared dry poly (acrylic acid / acrylamide)/NaOH has been characterized using scanning electronic microscopy technique (Quanta fig. 250 micro analyzer) at central laboratories of National Research Centre, Egypt. Under SEM, EDX was utilized to examine the chemical components of a SAP/NaOH. This technique discovers the X-rays generated by means of the electron beam interactions with the sample. It is possible to map the distribution of the various chemical components that make up the material. The processed X-ray data is used to compute the fraction of each measured element contained in the individual particles. Following that, the compositional and morphological data are integrated for exploratory data analytics.

2. 3.2. CHARACTERIZATION OF WCO AND BIODIESEL

2.3.2.1. Quantitative Analysis of WCO and biodiesel

The components of both WCO and prepared biodiesel were performed utilizing High Performance Thin Layer Chromatography, (CAMAG TLC SCANNER 3), (CAMAG AUTOMATIC TLC SCANNER 4) and (CAMAG ADC2) at Centre of Drug Discovery Research and Development at Faculty of Pharmaceutical, Ein Shams University, Egypt **Figure 1**. To start with, the plate was cut into 10 x 20 cm. Hexane was used to dilute the sample 40 times before the automatic spotting of 2 µl on a TLC plate. Then, at a distance of 1 cm and in separate lanes, the sample and standards were spotted. After the pre-saturation of TLC chamber for 15 minutes with the mobile phase of hexane, diethyl ether, and glacial acetic acid the plate was allowed to develop in the TLC chamber. The mobile phase mixture was permitted to migrate up to 9 cm from the plate's base. The plate was air-dried following development. The air-dried plate was scanned using the win CATS software at the HPTLC scanner 3 under UV at 203.5 nm to quantify the methyl esters in terms of yield percentage [30].



Figure 1: High Performance Thin Layer Chromatography Apparatus

2.3.2.2. Qualitative Analysis of biodiesel (Fatty Acid Methyl Esters)

At the Central Laboratories Network, National Research Centre, Giza, Egypt, a Gas chromatography-mass spectrometry (GC/MS) system (Agilent Technologies) was outfitted with a gas chromatograph (7890B) and a mass spectrometer detector (5977A). The (GC) was outfitted with (DB-WAX) column (30 m x 250 μ m interior diameter and 0.25 μ m film thickness). Helium was used as the carrier gas during analyses performing, with a flow rate of 1.9 ml/min at a split of 1:10, an injection volume of 1 μ l, and the following temperature programme: 50 °C for 1 minute; 25 °C/min rise to 200 °C and hold for 5 minutes; 3 °C/min rise to 220 °C maintained for 10 minutes; 5 °C/min rise to 240 °C and kept for 8 minutes. At 250 and 290°C, respectively, the injector and detector were maintained running. By using a spectral range of m/z 60-400 and solvent retardation for 6 min, mass spectra were obtained by electron ionization (EI) at 70 eV. To determine the various components, the spectrum fragmentation pattern was compared to the Wiley and NIST Mass Spectral Library data.

2.4. Technical Details and Standards of biodiesel prepared from WCO

Fuel products must meet quality criterion in order to be used commercially. They act as manufacturing process guidelines, ensure that customers receive high-quality fuel, and give authorized instruments for evaluating safety hazards and environmental pollutants. In order to verify that biodiesel meets and maintains a continuously high level of quality in line with industry requirements, frequent testing must be performed on the fuel.

2.4.1. Viscosity

Viscosity is a gauge of a substance's ability to flow, so it is an essential feature of any fuel. A fuel that is overly viscous might make it difficult for an engine to operate. Kinematic viscosity gauges how easily a fluid will move while exerting force. Dynamic viscosity is divided by fluid density to get kinematic viscosity. Viscosity of both WCO and prepared biodiesel were measured. Determination viscosity of WCO and prepared biodiesel were conducted by using a rotating viscometer.

2.4.2. Specific gravity of WCO and biodiesel

To calculate the specific gravity of biodiesel and WCO, divide the density of the biodiesel or oil by the density of water (1 g/ml).

Following are the steps to determine the density of biodiesel and WCO:

1. Using the weighing balance, the weight of a 50 ml beaker was measured and the result was recorded.

2. The weighted beaker is filled with 25 ml of the substance, and it is then weighed.
3. The beaker's weight after filling it with the substance is noted. Equation below is used to compute density:

$$\frac{\text{Mass with material (g)} - \text{Mass of beaker (g)}}{\text{Volume of material (ml)}} = d_m \quad (1)$$

The following formula is used to calculate the specific gravity of both WCO and biodiesel.

$$SG = \rho_m / \rho_w \quad (2)$$

2.4.3. Cetane number

Cetane Number ((CN)) indicates the readiness of the fuel for self-ignition after the injection to a diesel engine. The Cetane number of biodiesel is determined by ASTM D 976 at Central Analytical Labs of Egyptian Petroleum Research institute (EPRI). CN is a measure of the igniting performance of the diesel fuel oil. CN of fuels reveal their ignition capabilities or ability to automatically ignite following injection.

2.4.4. Flash point

The fuel's flash point is the temperature at which it transforms into a mixture and will ignite just being in contact with a flame or spark. ASTM D 93 is used to determine the biodiesel flash point at Central Analytical Labs of Egyptian Petroleum Research institute (EPRI). The flash point is significant for safety reasons associated with handling and storing diesel as well as for compliance with regulatory regulations.

2.4.5. Pour point

The term "pour point" refers to the temperature at which "fuel stops to flow when cooled under circumstances specified in ASTM D 97". The D-97 is used for the calculation of pour point at Central Analytical Labs of Egyptian Petroleum Research institute (EPRI).

2.4.6. Cloud point

Cloud point takes place at a higher temperature than the pour point. The cloud point is that temperature at which wax crystals initially begin to be formed in the liquid if it is being cooled in accordance with ASTM D 97 requirements by which cloud point are calculated at Central Analytical Labs of Egyptian Petroleum Research institute (EPRI).

3. Results and Discussion

3.1. Transesterification

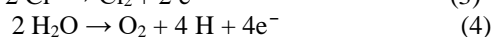
One of the most recent methods utilized to produce biodiesel is the electrolysis process. Many advantages through this process are the ability to exploit the feedstock's high-water content directly in the electrolytic process (i.e., the hydrolysis of water at the cathode and anode) and the ability to operate at

room temperature. Electric current flowing through an electrolyte solution will cause a chemical reaction when electrical energy is transformed into chemical energy (redox reaction).

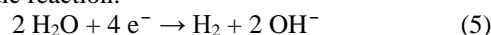
On the other hand, the problem derived from the presence of FFA can be solved by electrolysis method [31]. Japanese Researchers have reported the first application of an electrolysis technique to manufacture biodiesel from maize oil and waste cooking oil at ambient temperature [32]. In the transesterification of vegetable oils, when an alcohol reacts with a triglyceride compound, fatty acids alkyl esters and glycerol are produced [33]. The most common alcohols utilized in transesterification are methanol and ethanol. Methanol has more favourable economic, physical, and chemical characteristics than ethanol, making it a better choice for transesterification reactions. In the electrolysis process of transesterification an electrolyte solution is electrically charged through electrode rods, causing the ions present inside the electrolyte solution to migrate to the electrode that has a different or opposite charge. When electrical energy is transformed into chemical energy and flows through an electrolyte solution, a chemical reaction will take place (redox reaction). The electrolysis process has three properties, which are as follows: Free ions in an electrolyte solution have the ability to provide, accept, or remove electrons, allowing electrons to move through the solution and an electrical source from outside (DC power supply).

At the cathode, in presence of alcohol the hydroxyl ions are formed which are the responsible for the producing of nucleophilic methoxide ions. consequently, these ions attack the carbon in triglycerides (TG), resulting in the production of biodiesel during the transesterification process. Three alcohol molecules are required for every one triglyceride molecule to carry out the transesterification process under stoichiometric conditions [33]. Because in the transesterification process the reaction is reversible, the excess alcohol is necessary to drive the reaction toward the generation of biodiesel and glycerol [34]. Even with a relatively high-water proportion, this innovative method produced a high fatty acid methyl ester (FAME) yield. As illustrated in equations (3) and (4), the evolution of chlorine or oxygen on the anode may occur when the reaction mixture including NaCl and H₂O was supplied into the electrolysis cell. On the cathode, on the other hand, hydroxyl ions and hydrogen are produced (equation 5). To produce an acceptable FAME yield, transesterification of triglycerides (TG) with methanol requires an active species, methoxide ion (CH₃O⁻).

Anodic reaction:

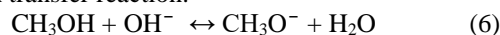


Cathodic reaction:



Methoxide ion is generated when methanol combines with hydroxyl ions (OH⁻) as in equation (6). Once generated, the methoxide ion is extremely nucleophilic and attacks the carbonyl moiety in glyceride molecules to produce FAME and glycerol (equation 7). As a consequence, the electrolysis process could be used to produce biodiesel fuel.

Proton transfer reaction:



Transesterification reaction:



3.2. Characterization of Poly(acrylic acid / acrylamide)/NaOH Hydrogel

The prepared poly (acrylic acid / acrylamide) hydrogel was swelled in NaOH solution. Figure 2 shows the dry hydrogel before (a) and after (b) swelling in NaOH solution. The presence of NaOH incorporated in the hydrogel matrix was attributed as the cause of this. The presence of NaOH in the hydrogel networks was confirmed by the whitest color of sample b.

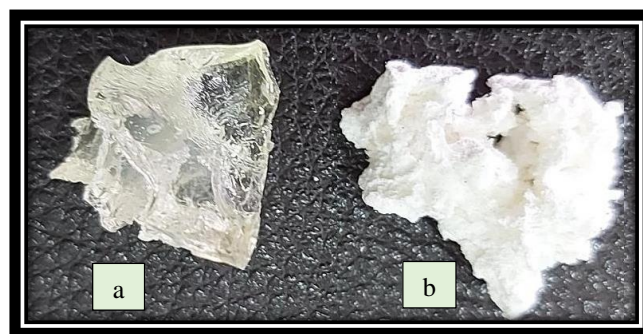


Figure 2: poly (acrylic acid / acrylamide)/NaOH hydrogel (a) blank and (b) containing NaOH

3.2.1. Scanning Electron Microscopy

The surface morphology of dry hydrogel which prepared by different doses of methylene bis acrylamide (the cross-linker) was evaluated through the use of scanning electronic microscopy (SEM). Increasing the amount of the cross-linker up to the optimum dose enhanced the swellability of the hosting hydrogel [35], and by extension, increasing the amount of sodium hydroxide trapped in the hydrogel.

Figures 3 (a, b, and c), represent the surface morphology of dry hydrogel in which NaOH was trapped. Sodium hydroxide appears on the polymer surface as white portions. The amount of NaOH depends on the degree of swelling, which in turn is related to the number of cross-links added to the hydrogel during its preparation.

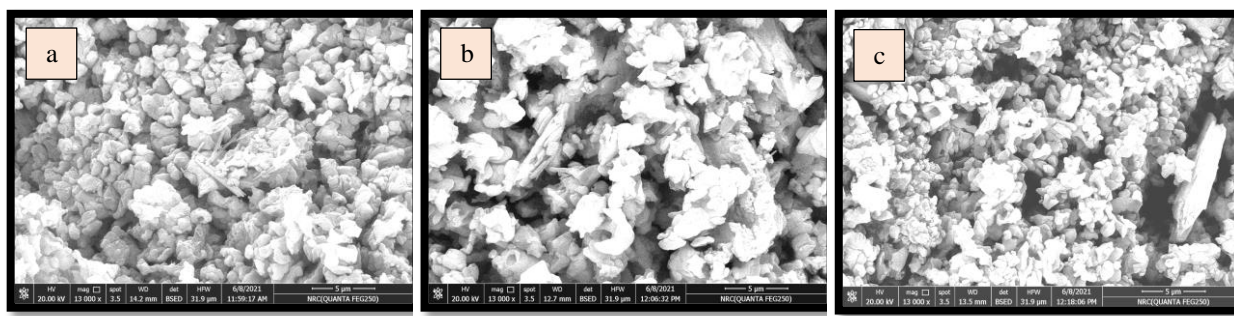


Figure 3: SEM images of prepared dry hydrogel with different amounts of MBAAm (a) 0.08 g (b) 0.12 (c) 0.16 g and loaded with NaOH

On the other hands, the amount of sodium hydroxide trapped in prepared hydrogel was examined by EDX as shown in Figures 4 (a, b and c). the results revealed that the weight percentage of each Na and O are followed the order, $a \geq b > c$.

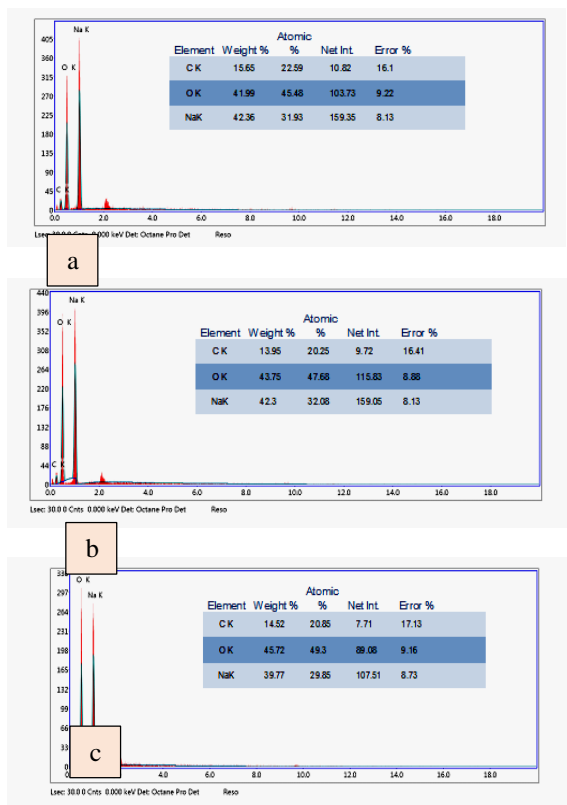


Figure 4: EDX images of prepared dry hydrogel with different amounts of MBAAm (a) 0.08 g (b) 0.12 g (c) 0.16 g and loaded with NaOH.

Swelling of prepared hydrogel was sensitive to cross-linker dose [34]. Figure 5 shows that, the swellability of the hydrogel increased from 135 g/g to 177 g/g by increasing the amount of the cross-linker from 0.13 % to 0.26 % of reactants weight. Further increase of cross-linker dose which used for preparing the poly (AAC/AAm) hydrogel declines its swellability. The

optimum dose of the cross-linker employed to prepare the poly (AAC/AAm) hydrogel was 0.26 %. As a result, this hydrogel was utilized as a catalyst to create biodiesel from WCO with trapped sodium hydroxide, as it was predicted to load more sodium hydroxide than other hydrogels made by using different amounts of cross-linker.

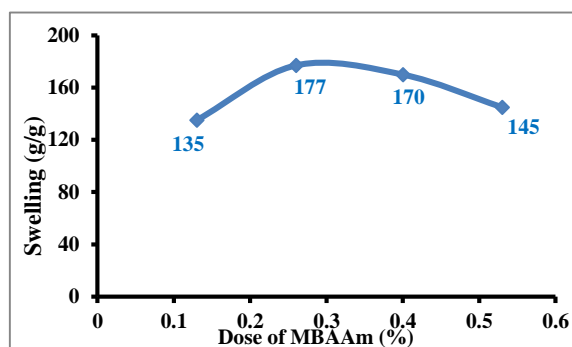


Figure 5: Relation between cross-linker dose and swellability of the prepared hydrogel.

3.3. Application of poly (acrylic acid / acrylamide) hydrogel as carrier of sodium hydroxide to enhance electrolysis process

Figure 6 depicts the relationship between catalyst doses and biodiesel yield. The results demonstrated that the prepared catalyst had a positive effect. According to the findings in Figure 6 the biodiesel yield softly increased as the catalyst dose was raised. The catalyst dose that produced the best production of biodiesel (92.8 %) was 20% of oil weight. On the other hand, increasing the dose of the prepared catalyst into the reaction medium to 25%, the biodiesel yield roughly leveled off to 92.55 %.

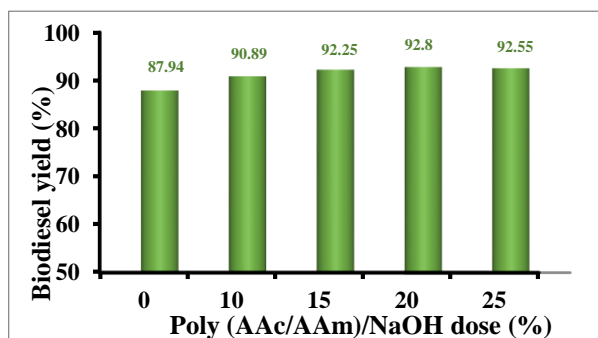


Figure 6: Effect of poly (AAc/AAM)/NaOH dose on biodiesel yield percent by using graphite/graphite electrodes.

3.3.1. WCO components

The components of the used oils were quantitatively analyzed using HPTLC. On scanning, λ_{max} for the biodiesel product was found to be 203.5 nm. Consequently, all of the samples were analyzed at 203.5 nm. Figure 7 shows the present peaks of monoglycerides (MG), diglycerides (DG), free fatty acids (FFA) and triglycerides (TG). The R_f for MG was less than 0.1 as per (peak1). The (peaks 2, 3, 4, 5 and 6) that corresponded to R_f between 0.15 and 0.3 represented DG. While (Peak 7) represented the free fatty acids ($R_f = 0.4-0.5$). The last peak (peak 8) with R_f 0.6-0.8 was of TG.

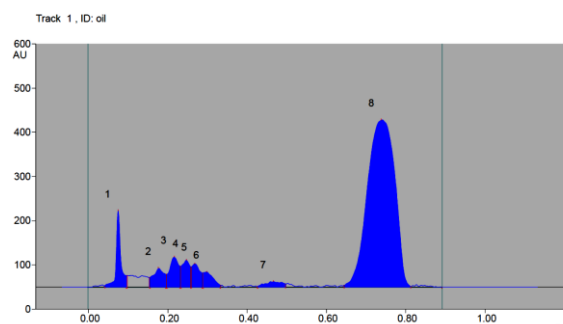


Figure 7: Two dimensional HPTLC chromatogram of different glycerides present in WCO

3.3.2. Biodiesel components and yield

High performance thin layer chromatography (HPTLC) was used in the study to provide a quick and repeatable method for accurately measuring the yield % of triglycerides into biodiesel (FAME). The oil substrate was transesterified by a novel process using electrolysis in the presence and absence of the prepared catalyst. HPTLC was used to analyze the monoglycerides, diglycerides, unreacted triglycerides, free fatty acids, and biodiesel (FAME) product. The yield % was estimated using the peak regions of the glycerides and biodiesel products. As previously explained in the previous section, the percentage of used oil conversion to biodiesel can be determined.

3.3.3. Transesterification of WCO via electrolysis without using a catalyst

Figure 8 represents the conversion of WCO to methylated esters and biodiesel (FAMES) yield via electrolysis without using a catalyst. Figure 8 revealed that the presence of MG, DG and TG is about 12.07 % while biodiesel (FAME) is 87.94%. On the other hand, there is no presence of TG and FFA in the ingredients, meaning that all of WCO has been converted to MG, DG and FAMES; this explains why saponification does not take place. Also, Table 2 illustrates different percentage values of biodiesel analyzed through HPTLC scanning.

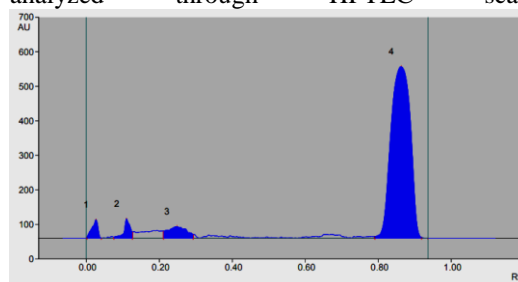


Figure 8: Two dimensional HPTLC chromatogram of different methyl esters present in transesterified WCO via electrolysis without using a catalyst

Table 1: Statistical analysis of different percentage values of WCO analyzed through HPTLC scanning.

Peak	Start Rf	Start hight AU	Max. position Rf	Max. hight AU	Max. %	End Rf	End hight AU	Area	Area %
1	0.04 Rf	2.4	0.07	172.9	21.09	0.10	25.7	1695.1	5.64
2	0.15 Rf	21	0.18	42.1	5.14	0.20	28.1	1024.8	3.41
3	0.20 Rf	28.3	0.22	67.3	8.21	0.23	46.7	1367.3	4.55
4	0.23 Rf	46.7	0.25	60.5	7.38	0.26	45.4	1053.0	3.5
5	0.26 Rf	45.7	0.27	52.4	6.39	0.29	31.5	954.6	3.18
6	0.29 Rf	31.9	0.3	34.0	4.15	0.33	3.9	743.6	2.47
7	0.43Rf	102	0.47	12.2	1.49	0.50	6.7	454.5	1.51
8	0.64 Rf	3.8	0.74	378.3	46.15	0.81	0.8	22771.2	75.74

Table 2: Statistical analysis of FAMEs values present in transestrified WCO via electrolysis without using a catalyst.

Peak	Start Rf	Start hight AU	Max. position Rf	Max. hight AU	Max. %	End Rf	End hight AU	Area	Area %
1	0.05	1.6	0.09	45.3	8.20	0.10	16.3	859.3	4.04
2	0.22	20.6	0.23	29.7	5.37	0.29	0.2	1077.2	5.07
3	0.78	2.3	0.85	477.7	86.43	0.90	0.1	19329.1	90.89

3.3.4. Transestrification of WCO via electrolysis by using a catalyst

A novel application of hydrogels can be used as a carrier to sodium hydroxide trapped in poly (PAAc/PAAM) during biodiesel manufacturing. The trapping of sodium hydroxide transforms the homogeneous catalyst into a heterogeneous catalyst, allowing for easy separation after the reaction is completed. The influence of different percentages of the prepared catalyst (related to WCO, namely 10, 15, 20, and 25 percent) on biodiesel yield was investigated. The effect of poly (PAAc/PAAM) /NaOH hydrogel on biodiesel yields were studied by utilizing graphite electrodes.

Figure 9 depicts the conversion of WCO into methylated esters and biodiesel (FAME) yield via electrolysis by using a catalyst dose of 10 %. Figure 9 and table 3 revealed that the presence of MG and DG is about 9.11 % while biodiesel (FAME) is 90.89%. On the other hand, there is no presence of TG and FFA in the ingredients, meaning that all of WCO has been converted to MG, DG and FAMEs (100 % conversion). As shown in Figures 10 and 11, the same behaviors were holds true for the conversion and biodiesel yield, when 15 % and 20 % of the prepared catalyst were used. Biodiesel yield was increased to 92.25 % and 92.8 respectively. Also,

tables 3 and 4 represent MG, DG and FAME yields.

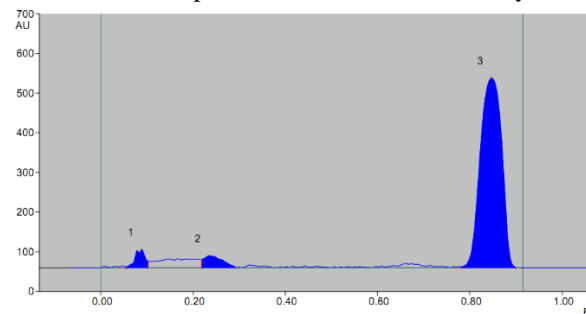


Figure 9: Two dimensional HPTLC chromatogram of different methyl esters present in transestrified WCO via electrolysis by using 10 % catalyst.

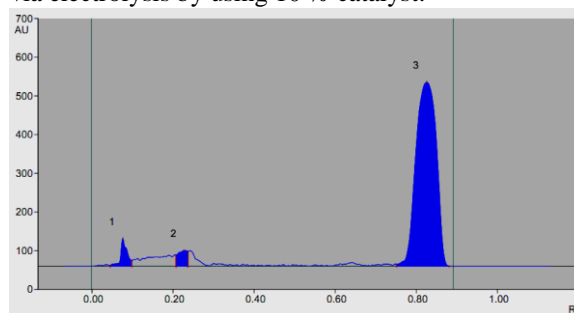


Figure 10: Two dimensional HPTLC chromatogram of different methyl esters present in transestrified WCO via electrolysis by using 15 % catalyst

Table 3: Statistical analysis of FAMEs values present in transestrified WCO via electrolysis by using 10 % catalyst.

Peak	Start Rf	Start hight AU	Max. position Rf	Max. hight AU	Max. %	End Rf	End hight AU	Area	Area %
1	0.00	2.5	0.03	53.2	8.30	0.04	0.3	770.6	2.91
2	0.07	3.7	0.11	56.6	8.82	0.13	18.3	840.1	3.17
3	0.21	21.1	0.25	34.0	5.30	0.29	11.0	1587.3	5.99
4	0.79	5.2	0.86	497.4	77.57	0.92	2.6	23310.8	87.94

Table 4: Statistical analysis of FAMEs values present in transestrified WCO via electrolysis by using 15 % catalyst.

Peak	Start Rf	Start hight AU	Max. position Rf	Max. hight AU	Max. %	End Rf	End hight AU	Area	Area %
1	0.04	2.9	0.08	71.5	12.17	0.10	14.9	978.3	4.20
2	0.21	29.2	0.23	40.5	6.90	0.24	39.1	847.4	3.55
3	0.75	5.3	0.83	475.2	80.93	0.88	0.2	20944.7	92.25

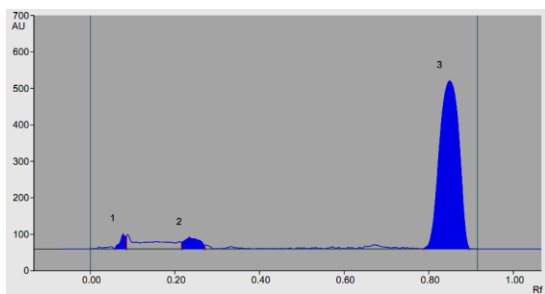


Figure 11: Two dimensional HPTLC chromatogram of different methyl esters present in transesterified WCO via electrolysis by using 20 % catalyst. Therefore, from the perspective of economics, the optimum dose of the prepared catalyst to be employed for manufacturing biodiesel by electrolysis was 15%.

3.1. Quantitative Analysis of Fatty Acids Methyl Esters

Table 5: Statistical analysis of FAMES values present in transesterified WCO via electrolysis by using 20 % catalyst.

Peak	Start Rf	Start height AU	Max. position Rf	Max. height AU	Max. %	End Rf	End height AU	Area	Area %
1	0.06	0.4	0.08	40.0	7.54	0.09	35.5	476.6	2.39
2	0.22	18.7	0.23	30.8	5.81	0.27	9.3	1000.7	4.81
3	0.79	0.3	0.85	460.2	86.66	0.90	0.0	18358.9	92.8

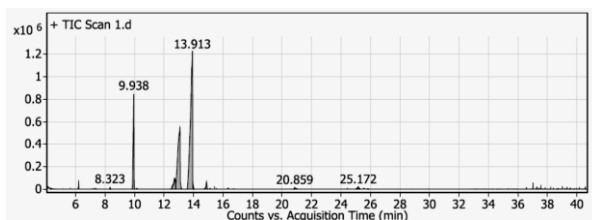


Figure 12-a: FAMES retention time as given by GC/MS.

Using the aforementioned GC-MS analytical technique, quantitative measurement of FAMES in the biodiesel samples was conducted. According to the GC-MS of the FAMES, the mixture is made up of nine distinct esters of fatty acids with retention time 8.323, 9.938, 10.15, 12.724, 13.066, 13.913, 13.973, 14.872 and 20.859 minutes (Figure 12 - a). There are nine major peaks observed and six peaks were corresponded to the ester group. All peaks appeared were corresponds to different type of ester. On the other hand, (Figure12 - b) represents the entire FAME components and the percentage of each of them.

Comparing the MS-data of the sample with the inbuilt database in the computer, the esters were identified as methyl esters of Tetradecanoic acid, Hexadecanoic acid, 9-Hexadecenoic acid, Methyl stearate, 9-Octadecenoic acid (Z), 9,12-Octadecadienoic acid (Z,Z)-, 9,12-Octadecadienoic acid, 9,12,15-Octadecatrienoic acid and Docosanoic acid as summarized in Table 5.

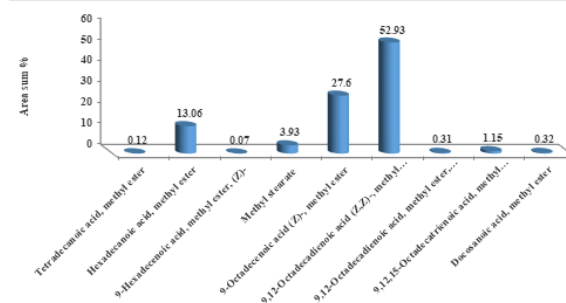


Figure 12-b: GC/MS excel data of FAME types and yield.

Table 6: RT & MW of FAMES

RT	Name	Common name	Formula	Molecular Weight
8.323	Tetradecanoic acid, methyl ester	Methyl tetradecanoate	C ₁₅ H ₃₀ O ₂	242.40
9.938	Hexadecanoic acid, methyl ester	Methyl palmitate	C ₁₇ H ₃₄ O ₂	242.40
10.15	9-Hexadecenoic acid, methyl ester, (Z)-	Methyl palmitoleate	C ₁₇ H ₃₂ O ₂	254.41
12.724	Methyl stearate	Methyl stearate	C ₁₉ H ₃₈ O ₂	298.5
13.066	9-Octadecenoic acid (Z)-, methyl ester	Methyl oleate	C ₁₉ H ₃₆ O ₂	296.5

13.913	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	Methyl linoleate	C ₁₉ H ₃₄ O ₂	294.47
13.973	9,12-Octadecadienoic acid, methyl ester, (E,E)-	Methyl linoleate	C ₁₉ H ₃₄ O ₂	294.47
14.872	9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-	Methyl Linolenate	C ₁₉ H ₃₂ O ₂	292.5
20.859	Docosanoic acid, methyl ester	Methyl Docosanoate	C ₂₃ H ₄₆ O ₂	354.61

3.2. WCO and biodiesel characteristics

Biodiesel has a substantially lower viscosity than the oil from which it is derived. Viscosity has an impact on fuel atomization and injector lubrication in diesel engines. Density and Specific gravity were crucial factors for diesel fuel injection systems. Density is correlated with numerous performance factors, including cetane number and heating value [35]. The effectiveness of fuel atomization is impacted by this feature. Specific gravity and Density were measured at room temperature.

3.3. Technical Details and Standards of biodiesel prepared from WCO

Transesterification of vegetable oils is the most used method for biodiesel manufacture. In contrast to those of pure vegetable oil, the biodiesel (methyl esters) produced by vegetable oil transesterification has a higher cetane number, lower viscosity, and elevated calorific value. This leads a shorter ignition delay and longer combustion duration, and therefore reduced particle emissions. Utilizing it reduces the amount of carbon residues on injector nozzles [36].

An important characteristic of diesel fuels is the ability to auto ignites which is quantified by the cetane number. In addition to having a greater cetane number than petroleum diesel, biodiesel also performs better and safer due to its higher flash point.

3.3.1. Viscosity

The primary factor in fuel combustion that matters is viscosity of the fuel. The engine's thermal efficiency and ease of combustion are assessed by the direct injection of fuel through the nozzle into the open combustion chamber. Viscosity that is too low will result in significant internal pump leakage, whilst the system pressure reaches an unacceptably high level, affecting the performance of the injection process when the spray ignites. Viscosity has a crucial impact in low-speed or light-load conditions [37].

Temperature has a significant impact on viscosity; many issues brought on by excessive viscosity are most apparent under cold-start engine conditions and low ambient temperatures [38]. In a fatty ester or an aliphatic hydrocarbon, the chain length of the fatty acid or alcohol component causes the viscosity to rise. Aliphatic hydrocarbons exhibit a smaller increase in viscosity over a given number of carbons than do fatty molecules [36]. Since biodiesel has a

higher lubricity than diesel fuel, it has an advantage over diesel fuel in that it can be used as an additive to increase the fuel's lubricity [39].

3.3.2. Calculation of specific gravity (SG)

- Specific gravity of WCO

Weight of Beaker filled with oil = 65.37g

Weight of empty Beaker = 42.77g

WCO volume = 25ml

$$\text{Density of WCO} = \frac{(65.37-42.77)\text{g}}{25\text{ml}} =$$

0.904 g/ml

Density of water = 1 g/ml

$$\text{SG of WCO} = \frac{0.904\text{g/ml}}{1\text{g/ml}} = 0.904$$

- Specific gravity of biodiesel

Weight of Beaker with biodiesel = 64.27g

Mass of Beaker without oil = 42.77g

Volume of biodiesel = 25ml

$$\text{Density of biodiesel} = \frac{(64.27-42.77)\text{g}}{25\text{ml}} = 0.86\text{ g/ml}$$

$$\text{SG of biodiesel} = \frac{0.86\text{ g/ml}}{1\text{ g/ml}} = 0.86$$

The physical properties of the used-cooking oil and biodiesel were appointed. Density and specific gravity (calculated) dynamic viscosity and kinematic viscosity (calculated), free fatty acid present in WCO (by HPTLC) were determined. Table 6 provided a list of the physical characteristics of WCO and biodiesel (FAMES).

Table 7: Physical properties of used cooking oil and FAME

	Unit	oil	FAMES
Density	g/cm ³	0.904	0.804
Specific gravity	-	0.904	0.89
Dynamic Viscosity at room temperature	mPa.sec	49.5	5.94
Kinematic Viscosity at room temperature	mm ² /sec	54.76	7.39
FFA	%	7.84	-

3.3.3. Cetane number

Fuels' cetane number (CN) reveals their ignition characteristics or ability for automatic ignition

following injection. Higher CN values are also associated with improved ignition efficiency and decreased ignition delay. One of the most important considerations when utilizing biodiesel (ethyl or methyl ester) is CN.

The calculated cetane number of the prepared biodiesels under the studied optimum conditions were 61.23 (ASTM D-976). The majority of refineries produce diesel with cetane ranges of 40 and 45, which is the minimum for diesel fuels, which must have a cetane number greater than 40. The cetane number of biodiesel is higher, as ranging from 46 to 65 (depending on raw material used).

Less delay between ignition and the beginning of fuel injection into the engine combustion chamber is indicated by a greater CN. Biodiesel has higher CN than traditional gasoline, which indicates better performance in combustion [39]. CN is One of the most important manifestation of the presence of ethyl or methyl ester in the biodiesel [40]. The increase of cetane number is related to the length and saturation on the fatty acid chain.

3.3.4. Flash point

Flash point is the lowest temperature at which a liquid fuel will ignite when an ignition source is placed close to its surface and produces a short flash. Regarding regulatory regulations and safety considerations related to handling and storing fuel, the flash point is crucial. [41].

The flash point of the prepared biodiesels under the studied optimum conditions was 183 °C (ASTM D-92). That is meaning there is no remaining methanol in the examined sample [40]. On the other hand, this result is consistent with the findings of previous studies. Flash points of Petroleum-based diesel are ranging from 50 °C to 80 °C which makes them essentially safe [41, 42].

There is substantially less fire risk associated with the use, storage, and transportation of biodiesel than there is with other frequently used fuels since it has a flashpoint of more over 160 °C. The lower flashpoint limit of biodiesel is 93 °C in ASTM D – 92 [43]. Aligning the standards might necessitate a comparable alignment of regulation because flash point is utilised as a regulation for classifying the transport and storage fuels from region to other. For biodiesel storage, handling, and transportation purposes, it must have a flash point that is higher than the requirement for diesel fuel [44].

3.3.5. Pour point, cloud point

Biodiesel's low-temperature characteristics are critical for flow and engine performance because fuel solidification, whether partial or complete, can cause problems with the starter, driving, and engine damage due to insufficient lubrication [45]. The cloud point is the temperature at which the fuel becomes cold and

forms wax crystals, giving off a foggy look [46]. A liquid's pour point is the temperature at which it loses its flow-ability.

The ASTM D-97 is used for the calculation of pour point. The pour point and cloud point of biodiesel are higher than those of petroleum diesel [47]. When operating at low temperatures, fuels thickening create a problem in the flow, affecting engine parts such as fuel supplying lines and fuel injectors. The efficacies of gasoline filtering caps have a greater correlation with biodiesel or petroleum diesel cloud levels.

Pour points of the prepared biodiesel under the studied optimum conditions were calculated according to ASTM D – 97 and it was 0 °C for all biodiesel samples. The cloud points of the prepared biodiesel under the studied optimum condition were calculated according to ASTM D-2500, the results were 6 °C These values revealed that the produced biodiesel is categories as "Biodiesel # 2" which is suitable for use in warm or hot climate [48].

Conclusion

Biodiesel is a promising alternative for other conventional fuels. The use of Waste cooking oils was found to be a cheap alternative feedstock considerably reducing the total production cost of biodiesel and also leads to further water stream pollution should be avoided. Nevertheless, this feedstock plays an important role in biodiesel production, in particular, the choice of the suitable process to be used in transesterification reaction. This work was undertaken to emphasize properties of WCO and production of biodiesel from WCO by electrolysis method using a novel catalyst poly (AAc/AAm)/NaOH hydrogel. Characterization of the biodiesel product was achieved carefully. This involves GC/MS analysis displaying the characteristic peaks of FAMES that ranged between C₁₅ and C₂₃ methyl esters. Also, HPTLC was performed to determine FAMES yield in the product. The catalyst was prepared by trapping sodium hydroxide in poly (AAc/AAm) to be used as a strong basic heterogeneous catalyst. The poly (AAc/AAm)/NaOH hydrogel were characterized via SEM and EDX and apply as a catalyst to enhance electrolysis process. The study demonstrated that the biodiesel yield reached about 92.8 % via electrolysis of WCO in the presence of poly (AAC/AAM)/NaOH as a novel catalyst. Further investigations of these types of polymeric catalysts to be employed in the process of biodiesel production are recommended.

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