

Research Article

Utilization of Modified Eggshells as a Solid Catalyst for the Conversion of Waste Cooking Oil to Biodiesel

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Received: January 17, 2018; Accepted: February 19,
2018; Published: February 26, 2018

Abstract

The search for economic, sustainable and environment friendly alternatives to petroleum fuel, as well as its synthesis and utilization in practical applications is one of the trending fields of research at the moment. Biodiesel is one such fuel capable of meeting all the criteria to be classified as a suitable alternative to petrol or diesel. Production through transesterification of organic oils does not pose doubts about the sustainability and eco-friendliness of this energy source but its production still is a challenging task due to the expenditure involved in its feedstock generation and required catalyst synthesis. Therefore, this research focused onto the utilization of waste eggshells to synthesize highly active, Calcium Oxide based catalyst to catalyze efficient conversion of waste cooking oil to biodiesel. The physically and chemically modified calcium oxide catalysts formed have a BET surface area of 11.8501m²/g and presence of around 81% of elemental calcium as constituent through XRF characterization. In addition to this 1H Nuclear Magnetic Resonance Spectroscopy was used to determine the conversion of biodiesel which revealed a maximum biodiesel production yield of nearly 92% at an optimal condition of 2 hours - catalyst activation time, 25°C - catalyst activation temperature, 5% (of reactant oil weight) – catalyst concentration, 60°C – transesterification reaction temperature, 4 hours – transesterification reaction period and 40% (of reactant oil weight) – methanol content. Fuel properties of the synthesized biodiesel was attained through subjecting it to ASTM D6751 standard test and the evaluation made was comparable to that of conventional fuel which indicates that feasible production of commercial standard biodiesel is possible through the methodology adopted in this study.

Keywords: Biodiesel; Heterogeneous Catalyst; Eggshells; Transesterification; Waste Oil

Introduction

Search for environment-friendly and sustainable energy source alternative to petroleum and fossil fuel is gaining greater attention amongst researchers in recent years. Biodiesel is one such alternative to petroleum fuel which offer significant number of advantages over fossil fuel to be considered as the energy source for future generation. In spite of having valuable benefits biodiesel is still lacking popularity and is considered uneconomical due to its high overall production cost almost (70-95)% of which is constituted that of feedstock production and the rest constituted by the catalyst used for transesterification of the feedstock to biodiesel. Furthermore, the expenditure of biodiesel production is not only concentrated in obtaining the feedstock, but also involves usage of alcohols most often methanol which corrodes the reactor walls and pipes as highlighted [1], thus increasing equipment construction, operative and maintaining cost.

Feedstock for biodiesel production

Conventionally the feedstock's undertaken for biodiesel production usually involve crop oils such as that extracted from rapeseed, sunflower, corn, soya bean, cotton seed, neem [2], palm oil [3], dessert date seed [4], sesame oil and many more sources. At one side where biodiesel can be counted as sustainable fuel due to being able to be produced from almost any vegetable oil whether

edible or non-edible, there on the other hand side the production of feedstock for biodiesel from the mentioned sources include growing, fertilizing and harvesting of crops, extraction of oil from those crops, refining of extracted oil and finally conversion of the refined oil to biodiesel, a long process which includes requirement of large land for the crop harvesting as well as extra cost is required to be invested behind installation of equipment for extraction of oil from the crops and its refining which add on to the high cost involved in the production of biodiesel from vegetable oil. Thus, researchers at present are searching for alternative source of feedstock which can be attained economically and in a feasible manner such as the byproduct of cooking oil deodorizer distillate [5], production of biodiesel from animal fats and waste that are rich in unsaturated lipids such as beef tallow [6], synthesis of biodiesel from carbon dioxide sequestering bacterium [7] through extraction from microalgae [8] and through transesterification of waste cooking oil biodiesel [9].

Catalysts for transesterification of feedstock to Biodiesel

One of the prime factors of the biodiesel production is the requisite of utilization of a suitable catalyst in order to enhance the reaction rate between the waste oil and methanol. Conventional catalysts used are homogenous strong bases or acids, such as Potassium Hydroxide (KOH), Sodium Hydroxide (NaOH), Sulphuric Acid (H₂SO₄) [10] and etc. The key issue of using homogenous catalyst includes:

- Requirement of high temperature in order to carry out the transesterification reaction.
- Recycling and reusing of the catalysts are difficult.
- The catalysts are corrosive in nature thus result in damage of the equipment.
- Equilibrium state for the reaction is attained after long time.

The aforementioned issues pertained mostly with acidic homogenous catalyst. Although basic homogeneous catalyst reaches equilibrium state faster than the acidic ones but its possess all the other issues mentioned as well as reacts with free fatty acid of the feedstock oil resulting in saponification of the mixer, thus, making final separation of the products difficult. Hence heterogeneous catalysts are preferred over homogenous ones to overcome the stated issues. Researchers have continuously worked on searching the alternative to homogenous catalysts, such as biocatalyst – *Rhizopus oryzae* [10], organo-metallic compounds possessing at least one $-OCH_3$ functional group, silicates [11] and more but in most of the cases the formation of catalyst from such sources are cost consuming showing although they are able to overcome the problems associated with homogeneous catalyst. Calcium oxide is one heterogeneous catalyst very commonly considered for biodiesel synthesis since it has shown suitable catalyzing characteristics in terms of purification of the product, reusability, ease of use and its availability vast in natural resources, however here too exist the issue of cost efficiency since untreated (CaO) shows slower reaction rate and hence is not suitable for practical application. There are several projects undertaken worldwide that are focused on enhancement of the catalytic activity of CaO, such as impregnation of CaO catalyst with external support such activated carbon, carbon nanotube, silica or aluminum [12,13], enhancement of the catalytic activity of CaO through calcinations [14] or through calcination-hydration-dehydration treatment [15] as well as through treatment of calcium oxide by methanol prior to transesterification reaction [16]. At one place where impregnation of calcium oxide by other metal or components showed well reactivity but the process being cost consuming makes the whole biodiesel synthesis process uneconomic. On the other side, the calcination treatments are able to overcome all the mentioned issues but it did not attain the product yield as high as that obtained through the process when the catalyst is treated with methanol. Moreover, methanol being already used for the transesterification reduces the requirement for any extra chemical to be used for the activation process which eases the procedure through eliminating the need to separate the catalyst from activating reagent and washing it. Thus, the procedure undertaken in this project is in line with that followed by [16].

Most common sources of calcium oxide for the formation of catalyst involve eggshells of different species [17] Fish bones [18], calcium oxide compounds present in coral reefs (Farm n.d.), limestone ores and many more but this project is focused on catalytic activity of calcium oxide obtained from chicken eggshells due to its greater abundance compared to any other species of eggshells.

Emphasis of the project on waste utilization

The key focuses of this project is on forming heterogeneous catalyst from waste eggshells and modify it for utilization in biodiesel production from waste cooking oil. The inspiration behind utilization

of these two organic wastes came from Caledonian College's girl's hostel. Observing a large consumption of eggs on daily basis as well as production of large quantity of waste oil from frying of food items struck the instinct of utilization of such wastes to something valuable to the mind. Moreover, due to vast consumption of dairy and fried products worldwide, eggshells and waste cooking oil are two of the most abundant waste items produced annually in any country of the world which eventually leads to disposal problem of such wastes. Each year a large amount of untreated waste eggshells is dumped in open landfills despite the fact that eggshells consists of a large amount of Calcium Carbonate that can be useful in manufacture of many valuable products. This dumping of eggshells creates disposal problems as eggshells have a slower decomposing rate and also releases harmful odor upon biodegradation. Similarly, around the world, major quantities of waste frying oil are illegally dumped into landfills and rivers causing environmental pollution and eutrophication. Therefore, this project aims to convert these waste materials which are considered of no use and usually thrown away to something sustainable which may have an impact to solve one of the major issues faced by mankind at present, that of energy and environmental conservation.

Composition of eggshells

Study undertaken by [19] shows that the composition of the eggshell involves approximately 94% of calcium carbonate, 1% each of magnesium carbonate and calcium phosphate and 4% of organic matter while [20,21] investigated the composition of different types of eggshell and found that at an average the organic matter of the eggshell involve highest percentage of Sialic acid and uronic acid. Both inner and outer wall of the eggshell showed less presence of Nitrogen. When the eggshell was subjected to amino acid analysis, presence of hydroxyproline and proline in lower quantity as well as alanine and glycine in higher quantity.

Experimental Procedure

The complete experimental procedure can be explained more precisely through dividing those into the several steps.

Collection and preparation of raw materials for further process

As per prior statement waste chicken eggshells and waste cooking oil would be used as raw materials for the formation of heterogeneous catalyst and followed by biodiesel production respectively. College canteen, hostel consumption and local fast food shall be key sources for collection of both the precursor. Prior to collection of the waste cooking oil, it is important to observe the color of the oil as it is supposed to be darker in color than unused cooking oil, furthermore, any oil which would appear cloudy or milky would be discarded since such an appearance is usually a result of presence of large percentage of water or animal fat content in the oil which may hinder the biodiesel production process. Once a sufficient quantity of the precursor is collected, respective procedures would be carried out in order to prepare those to undergo transesterification process.

The eggshells would be washed two times with tap water in order to remove any dirt particles or impurities remaining on its surface followed by the samples would be washed one time with distilled water to prevent any ions from tap water to remain on surface of the

eggshells and contaminate the further process. The washed eggshells would be allowed to dry naturally in ambient environment. And once dried properly the eggshells would be ground to random particle size using a domestic scale grinder. The preparation of waste cooking oil for biodiesel production would be carried out in three separate steps as per recommended by [22], after each treatment the oil would be transferred and stored in a new clean dust and air free bottle.

Physical modification of precursor through calcinations

The meticulously washed, dried and randomly ground eggshells would be subjected to calcinations in the muffle furnace at different temperatures between (450°C – 550°C) for residence time between (4-6) hours. The reason for using greater residence time and lower calcinations temperature compared to other allied researches are that:

- The longer residence time compensate for lower calcinations temperature in order to allow complete decomposition of calcium carbonate (CaCO_3) constituents of the eggshells.
- Uniform heating for longer period of time allows conservation of energy through even distribution of heat, thus results in achieving the desired standard of the calcined product without consuming greater amount of energy to attain higher temperature.

The purpose behind subjecting the catalyst precursor to calcination has been explained through the followings:

- Calcination allows decomposition of the calcium carbonate to carbon dioxide (CO_2) and calcium oxide (CaO) – which is the key constituent of our desired catalyst. The CO_2 escapes to atmosphere leaving behind the catalyst compounds.
- Escape of CO_2 decreases the carbon content of the catalyst leading eventually to zero percentage of elemental carbon present in the sample, thus can result in better purity of the fuel formed as well as ensure less carbon footprint to atmosphere due to its usage.
- Naturally the CaCO_3 molecules consists of crystalline regions and with heating and escape of carbon dioxide the size of the crystals decreases to almost one-third of its original size, thus increases the surface area of the catalyst and enhances its pore size distribution and pore volume resulting in increased activity of the catalyst.

Chemical activation of calcined catalyst

Evaluation done through prior researches figured out that physical modification of the eggshells can enhance its catalytic activity. However, in order to attain a greater product yield compared to that of non-active calcium oxide or calcined catalyst solely, chemical activation of the calcined samples is imperative and would be done in the following method:

The calcine ground eggshell catalyst sample would be weighed and mixed with methanol in a 1:4 ratio and the mixture would be let to stand for a period of 24 hours with the presence of magnetic stirrer. An excess amount of methanol would be used to ensure a reflux condition between CaO and methanol and the magnetic stirrer has to be applied in order to maintain mixing of the reagents uniformly. After 24 hours, the magnetic stirrer would be removed from the reaction beaker and activated catalyst particles would be allowed to settle down. The supernatant methanol would then be decanted and

the remaining slurry would then be kept open in ambient temperature to allow the entire highly volatile methanol to evaporate naturally leaving behind dried activated catalyst sample.

The mixture cannot be oven dried due to methanol being extremely flammable. The purpose behind selecting methanol as the activating reagent for activation of catalyst and to react with feed oil for biodiesel production would cut off any requirement of washing of the catalyst after activation or separation of the activating agent before the transesterification process, thus again reducing process cost and the obtained catalyst sample can be directly utilized for further process and reacts with the CaO constituents of the calcined eggshells and converts a small amount of the CaO to $\text{Ca}(\text{OCH}_3)_2$ through reacting with it. On the other hand, the reaction mentioned above produces water as a byproduct that reacts with some more CaO to form $\text{Ca}(\text{OH})_2$. The two products $\text{Ca}(\text{OCH}_3)_2$ and $\text{Ca}(\text{OH})_2$ then acts as the initiating reagent for the transesterification of the waste cooking oil. In the reaction glycerin is produced as a byproduct which then reacts with remaining CaO molecules forming a calcium-glycerin complex that accelerates the rate of the reaction by acting as the main catalyst.

Characterization of the chemically activated catalyst samples

In order to characterize the chemically activated catalyst sample, it is significant to utilize the major analytical techniques such as X-Ray Fluorescent (XRF), Brunauer, Emmet, Teller (BET) Analysis and Hammett Indicator.

Utilization of the formed catalyst for the production of biodiesel

The major key aspects related to the utilization of formed catalyst for the production of biodiesel as follows:

- The procedure of biodiesel production starts with esterification of the waste oil through addition of small quantity of sulphuric acid and methanol in a view of modification of the free fatty acids consisted in oil to ease attachment of methanol to the fatty acids for biodiesel production.
- The next stage is transesterification which involves the utilization of the catalyst. The waste oil molecules are eventually broken down by the catalysts forming free fatty acids and glycerol. These free fatty acids then bond with methanol to form biodiesel and glycerol can later be separated from the final product as a byproduct.
- The third and fourth steps separation of glycerol and washing of the biodiesel with water using settling method. Since glycerol being denser than the produced oil could settle down to the bottom of the reactor from where it can easily drop out and can be collected for further processing to form glycerin. In a similar manner when water is added to the biodiesel its impurities are collected by the water which then settle down at the bottom of the settler and can be later on removed leaving behind clean final product.

Evaluation of the product yield

In order to determine the efficiency of the catalyst and the complete system it is imperative to evaluate the yield of the product formed. The result obtained from each analysis can be compared together to obtain an average and more accurate estimation of

the product yield. Since both the techniques to be utilized serves nearly similar purposes, hence depending on the availability of the equipment, only NMR investigation was carried out.

Characterization of product composition

ASTM D6751 [23] standard test has been conducted to test the fuel to meet a set of standards in terms of density, kinematic viscosity, calorific values, flash point and acid value.

Generalization and interpretation of the experimental data

The experimental procedure is exclusively based on collection of data from each of the experimental steps mentioned above and interprets the obtained data into a more understandable form to be able to compare the final evaluation to that of the existing evaluations carried out by similar researches.

Results and Discussion

BET characterization

The most significant parameter for defining the catalytic activity of a catalyst is its surface morphology, including its surface area and porosity which is dependent on a number of factors such as precursor material selected for the catalyst formation, activation agent, method of activation, catalyst preparation and activation temperature and duration. It was found that although the surface area of sample 1 was only around $1.4022 \text{ m}^2/\text{g}$ which is much lower than that of commercial CaO catalyst having a surface area of $3.0022 \text{ m}^2/\text{g}$ (). For sample 2 the surface area was found to increase to $3.5982 \text{ m}^2/\text{g}$ which is almost close to that evaluated by () following same methodology but once activation of the catalyst sample was done, a significant increase in the surface area was observed in sample 3 having a value of $11.8501 \text{ m}^2/\text{g}$ which is comparatively greater than that attained through conventional impregnation of CaO catalyst.

Hammett indicator characterization

Another important aspect of the catalyst surface is its basicity which was tested using the Hammett indicator test. The test was carried out for same three samples and observations noted at the end point of the titration are as follows:

- Indicator 1: 2,4 -dinitroaniline – pKa = 16
- Indicator 2: Indigo Carmine – pKa = 13
- Indicator 3: Phenolphthalein – pKa = 9.7

The basicity of each parameter catalyst was considered to be greater than the weakest indicator which showed any color change and lesser than the strongest indicator which did not show any color change. Hence for untreated uncalcined grinded eggshell is pKa value was within the range of (7 – 9) whereas that of calcined catalyst sample and calcined along with chemically modified sample, the pKa value was found to be within the range of (9.7 – 13) and (13 – 16) respectively.

XRF characterization

XRF analysis for the catalyst sample was carried out at a 1000 Ampere tube current and within around 1-minute acquisition life time, the analysis was complete and showed a presence of around 81% calcium as the major component with other elements present being iron in considerable amount as well as lead, chlorine, terbium and tin

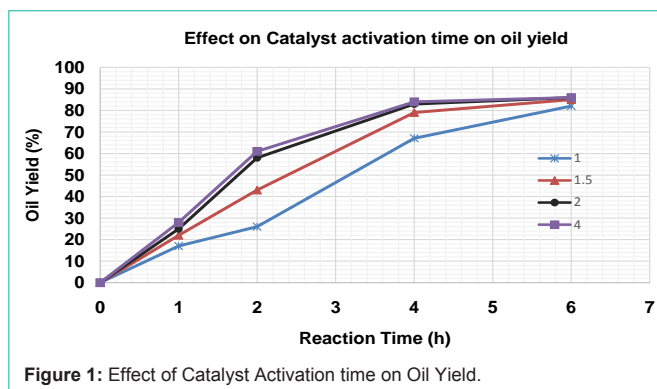


Figure 1: Effect of Catalyst Activation time on Oil Yield.

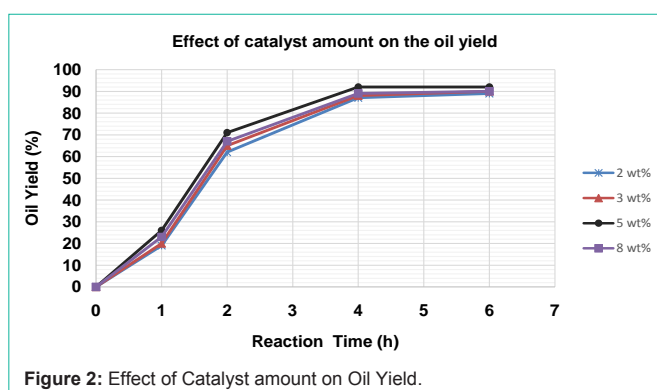


Figure 2: Effect of Catalyst amount on Oil Yield.

in very negligible quantity. The instrument used for this purpose is Philips-PW 2400 model.

NMR analysis of final product

Characterization of the product oil was done through H1 NMR which revealed peaks of alpha-methylene protons in triplet form and methoxy protons in singlet form at 2.35ppm and 3.58ppm respectively. Observations of the mentioned characteristics peaks confirmed the product as a methyl ester. Other peaks that were observed include that of methyl and methylene protons of the carbon chain constituents of the product at 0.750ppm and 1.402ppm respectively. Furthermore, multiple and single signals were observed at 5.872ppm and 1.9ppm arising due to olefinic hydrogen and beta-carbonyl methylene respectively. The H1 NMR spectrum of the biodiesel synthesized was shown in Figure 6.

ASTM standard test of synthesized biodiesel

The results obtained through subjecting the product biodiesel to [23] ASTM D6751 standard test are as follows:

Density of biodiesel (kg/m^3) = $879 \text{ kg}/\text{m}^3$, Kinematic Viscosity (mm^2/sec) = 4.53, calorific Value = 44.8 (kJ/kg) , flash Point = 115°C and acid Value = 0.32.

Optimization of experiment parameters

The yield of product obtained from the experiment is a function of a number of factors such as catalyst activation time by methanol, catalyst activation temperature, amount of catalyst utilized for the reaction, amount of methanol used for the reaction, reaction period and reaction temperature.

Effect of catalyst activation time on the product yield: In order to

evaluate the optimal value of each of the parameters mentioned above, the reaction was at first carried to optimize the catalyst activation time and then each successive parameter was optimized through carrying out further experiments using prior optimized value of the previous parameters. To observe the effect of catalyst activation time on the product yield, the quantity of methanol involved in the reaction was added to 0.5g of catalyst sample before the prime transesterification reaction. The activation of catalyst is carried out in a reflux reactor with magnetic stirrer and once the activation period is over, the waste oil was also added to the reactor and temperature was further adjusted for the transesterification reaction. As per the literature review the quantity of methanol taken for this phase of experiment was 40% of the oil weight, temperature during the activation period was set at 25°C while during the transesterification reaction it was increased to 60°C and a constant oil weight of 25ml was taken for the entire sample. A total of 4 samples were prepared for this phase of experiment and four separate apparatus setups was arranged to carry out simultaneous reactions. For each sample the catalyst activation period was different ranging between 1 – 4 hours. Furthermore, the similar reaction was carried out with 4 different samples as mentioned above each time for 4 different transesterification periods ranging from 1 – 6 hours. Thus, this was the most time-consuming phase throughout the whole experiment was shown in Figure 1.

As can be seen through the plot in Figure 1, that over a period of 6 hours the maximum oil yield attained by utilization of all the catalyst sample are almost similar but for catalyst chemically treated with methanol for a duration of 1 to 1.5 hour showed a slower reaction rate than those treated for 2 hours and longer time. Furthermore, the catalyst treated for longer than 2 hours when utilized for biodiesel formation was able to achieve almost the maximum product yield in 4 hours reaction time. Since catalyst treated for both 2 and 4 hours showed similar reaction rate, thus the optimal catalyst activation time was evaluated as 2 hours.

Effect of catalyst activation temperature on the product yield:

Since from the first phase of the experiment the optimum catalyst activation time was evaluated to be 2 hours, therefore keeping this value and the other parameters constant as previously mentioned, only the activation temperature was varied. Three different catalyst samples were prepared for activation temperatures 25°C, 35°C and 60°C and the other procedures were carried out in similar manner as written before. Although the rate of reaction for all three types of catalyst was observed to be similar but the final oil yield obtained after a reaction period of 6 hours was found to be maximum for catalyst treated at 25°C, this result is in line with the experimental data obtained by [16]. Although in usual cases it is expected that increasing the temperature of a reaction increases the yield of product but in this case increasing the temperature more in the activation phase does increase the collision between Calcium oxide molecules from the catalyst sample with that of methanol thus formation of the intermediate compound $\text{Ca}(\text{OCH}_3)_2$ gets increased as more methanol reacts with Calcium oxide. This is what effects the actual transesterification reaction as the same methanol quantity serves for both the purposes of catalyst treatment and of reacting with fatty acids of the waste oil, thus as more methanol reacts with catalyst molecules lesser molecule of methanol is available for reacting with the waste oil molecules resulting in lesser production of biodiesel through

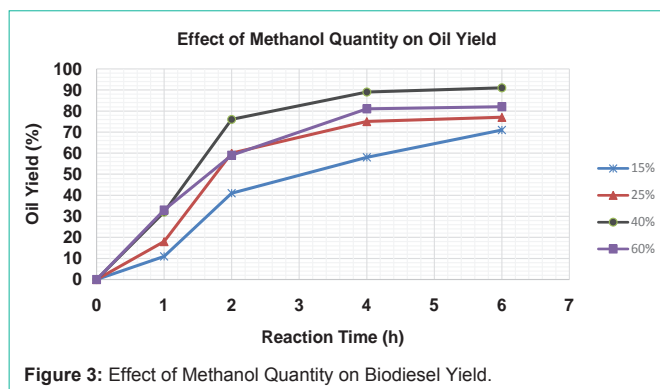


Figure 3: Effect of Methanol Quantity on Biodiesel Yield.

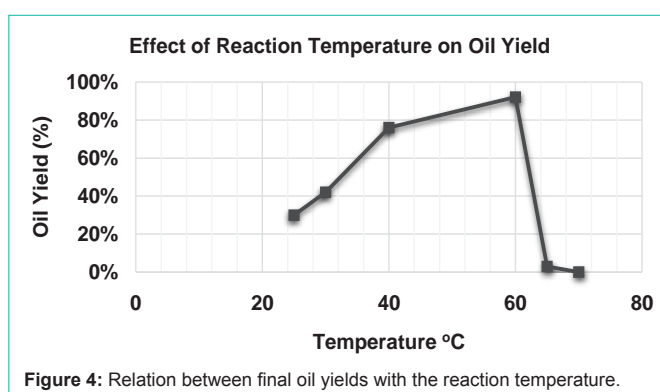


Figure 4: Relation between final oil yields with the reaction temperature.

transesterification of the waste oil since then methanol acts as the limiting reagent despite of high rate of reaction due to the availability of large amount of highly active catalyst compounds.

Effect of catalyst amount on the product yield: In order to observe the trend of any possible variation on biodiesel yield formed as an effect of the catalyst amount utilized, reaction was carried out using catalyst sample activated with methanol at 25°C for 2 hours. 25ml of waste oil was taken and 40% of the oil's weight of methanol (in this case 10 ml) was taken for each sample. The transesterification reaction was carried out at 60°C for four different catalyst amounts – 2, 3, 5 and 8 weight percentage of oil taken for the reaction, thus in this case the quantity of catalyst taken was 0.5g, 0.75g, 1.25g and 2g respectively. For each catalyst loading the reaction was carried out for different durations ranging from 1 – 6 hours. The procedure of this phase of the experiment was in accordance to [24] and the data obtained through the rate of reactions represented in Figure 2

As represented through the plot given above, the maximum oil yield was obtained by 4 hours of reaction period and were not affected by the amount of catalyst loading however increasing the amount of catalyst from 2 weight percentage to 5 weight percentage of oil weight did show an increase in the reaction rate whereas further increasing the catalyst amount resulted in a reduction of the reaction rate. This effect can be summarized by the concept that as catalyst concentration increases the chances of collision between reactant particles and active site of catalyst also increases which in turn results in rise of the reaction rate, however a point comes when the catalyst works at its maximum capacity and beyond this point further increasing the catalyst concentration barely shows any effect on rate of reaction instead if the concentration of catalyst gets too

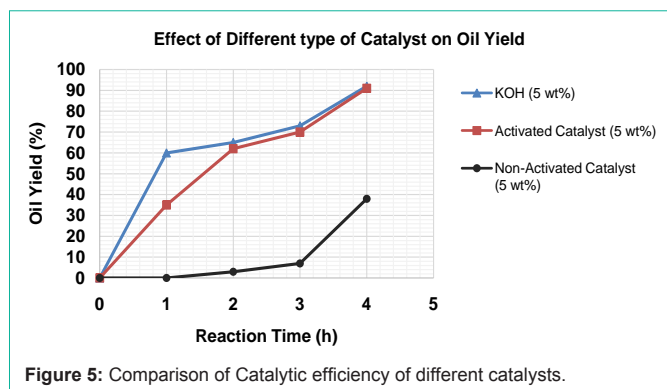


Figure 5: Comparison of Catalytic efficiency of different catalysts.

high, excess collision between catalyst molecules hinders collision between reactant particles to that of the active site of catalyst and thus the excess catalyst particles then provides an inhibition effect on the reaction reducing its rate to some extent. Thus 5 weight percentage of catalyst was taken into account as the optimal catalyst loading for biodiesel production this way [25,26].

Effect of methanol quantity on the product yield: In order to figure out the optimal quantity of methanol for the formation of biodiesel, 25ml of waste oil was reacted with methanol of 15%, 25%, 40% and 60% of oil's weight, thus 3.75ml, 6.25ml, 10ml and 15ml of methanol was separately reacted with 25 ml of waste oil in the presence of 5 oil weight percentage of catalyst loading that was activated with methanol at 25°C for 2 hours. The transesterification reaction is carried out at 60°C. The result from this phase of the reaction is represented through Figure 3.

As the quantity of methanol increases from 15 to 40 weight percent of oil, both the transesterification rate as well as the final product yield increases from 70% to nearly 90%, whereas further increasing the methanol quantity to 60 weight percent of oil results in a decrease of both the reaction rate and oil yield. This effect could be explained as the transesterification being an equilibrium reaction requires high methanol quantity to shift the equilibrium towards the direction of the product whereas increasing the methanol quantity beyond optimal creates a dilution effect which disturbs the triglyceride structure resulting in formation of monoglyceride from triglyceride of waste oil which increases the solubility of glycerol in final product forming soap effect. Thus, the separation of biodiesel from glycerol becomes difficult in presence of excess methanol. Hence methanol quantity 40 weight percent of waste oil was considered to be the optimal.

Effect of reaction period on product yield: Observation of all the previous phases the research showed that, for most samples prepared the maximum biodiesel yield was achieved by reaction period of 4 hours. Further increasing the transesterification reaction period to 6 hours did not show any significant increase of the final product yield. Thus, 4 hours had been taken into account as the optimal reaction period.

Effect of reaction temperature on product yield: Keeping all the other parameters at the optimal values, the effect of reaction temperature was observed for five different temperatures of 25°C, 30°C, 40°C, 60°C and 70°C. The procedure followed during the

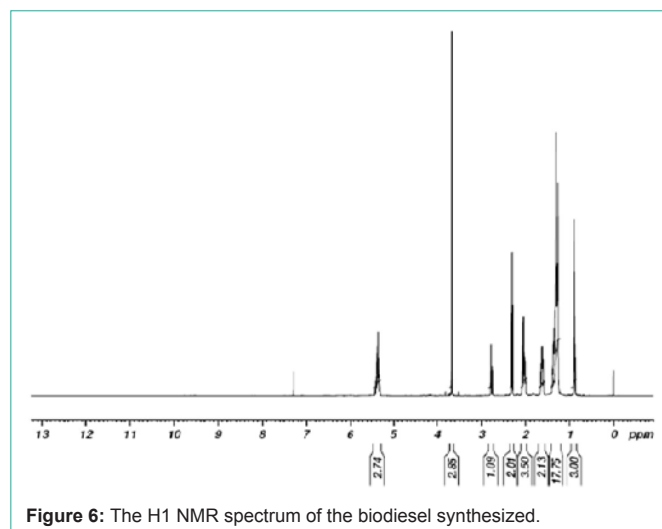


Figure 6: The H1 NMR spectrum of the biodiesel synthesized.

reaction was same as that of other phases of the experiment. Figure 4 shows the relationship of the final oil yield with the reaction temperature.

Although increasing the reaction temperature also showed an increase in the product yield for temperature ranging from (25 – 60) °C but increasing the reaction temperature beyond 60°C to 65°C did bring a drastic decrease in the product yield to reach nearly 3% only and further increase of the temperature value to 70°C showed no reaction at all. This could be because of the fact that at temperature of 35°C to 60°C, according to Boltzmann theory, the greater the temperature of the reaction the more is the collision between reagent particles thus, enhancing the product yield as the equilibrium shifts towards right at higher temperature due to availability of more energy for the activation of the reaction. However, above 60°C and close to 65°C, boiling point of methanol is reached thus resulting in vaporization of methanol which cause methanol to act as the limiting reagent for the transesterification as well as the active site of the catalysts also get disturbed at more than 60°C. This combined effect brings the sudden reduction in product yield. Further at 70°C since no reaction is observed, it can be assumed that the catalyst eventually get deactivated at extreme temperature more than 60°C which can be considered as the optimal reaction temperature for this project.

Comparison of the prepared catalyst sample to that of conventional catalyst: In order to ensure reliability of the formed catalyst to be utilized for conventional purposes, the activity of catalyst sample was compared to that of Potassium Hydroxide (KOH) catalyst which is one of the prime conventional catalyst used for biodiesel production as well as to that of non-activated sample of the catalyst. Transesterification of 25ml waste oil was carried out under optimum condition for each of the three types of catalyst. In case of non-activated eggshell catalyst, the catalyst activation period with methanol before transesterification was omitted and catalyst was directly loaded along with both the reagent for the main conversion reaction. The result obtained through this phase of the experiment was represented through Figure 5.

As depicted through the plot for the three catalysts that although at initial stage of the transesterification the rate of reaction attained

by utilization of activated catalyst sample was comparably lesser than that of potassium hydroxide catalyst but eventually after 2 hours of reaction period, both the KOH catalyst and activated eggshell catalyst sample showed closely similar trend in reaction rate as well as the maximum product yield achieved after four hours was almost near in value whereas the rate of reaction shown by non-activated eggshell catalyst sample was consistently low till 3 hours of reaction period yielding very less product. Although the reaction rate increases after 3 hours for non-activated catalyst but the maximum product yield attained after four hours was only around 38% which is much less than that offered by the other two catalysts. The result obtained through this phase of the reaction was in correlation to that of [16]. The ¹H NMR spectrum of the biodiesel synthesized was shown in Figure 6.

Evaluation of catalyst reusability

One of the most significant properties of a heterogeneous catalyst is its reusability. The reusability of the catalyst sample was evaluated through carrying out transesterification reaction utilizing it until a considerable reduction in the product yield and reaction rate was observed. All the parameters of the reaction condition were kept constant through all the cycles and the catalyst was shaken with methanol and filtered again in order to remove any surface particle, reactivated through reacting with methanol and utilized for transesterification. It was observed that till 5 consecutive cycles the product yield did not show much considerable change from the maximum but after sixth cycle the product yield and reaction rate both decreased eventually yielding only around half of the maximum yield at 7th cycle [27-32].

Conclusions

It had been possible to prove through this project that waste materials such as eggshells and leftover cooking oil which visually have no beneficiary uses as per norm and factually can lead to several hazardous impacts over the environment upon dumping can be turned into highly active catalyst and enormously valuable fuel respectively. This increasing feasibility of cost-effective formation of a highly active solid heterogeneous catalyst for the transesterification of vegetable oil to biodiesel as well as search for suitable and economic feedstock generation from various resources for the same purpose has been the driving force behind numerous researches carried out in this sector. The results obtained through this investigation has summarized below:

- Formation of highly active catalyst from waste eggshells had been possible through implementation of appropriate calcinations temperature and duration in conjunction to usage of suitable chemical reagent for physical and chemical modification of the precursor material.
- A maximum surface area of 11.8501m²/g and 81% elemental calcium constituent of the catalyst has been found through BET and XRF characterization of the formed catalyst and shows its high catalytic efficiency in comparison to conventional Calcium oxide based catalyst as per surface morphology.
- Maximum yield of 92% biodiesel production has been attained as evaluated through ¹H NMR analysis of the product oil.

- Through running a series of experiments with varying parameters, the optimal condition for the production of maximum yield of biodiesel was found to be 2 hours and 25°C of respective time and temperature for chemical activation of catalyst as well as 40% (of reactant oil weight) of methanol content, 5% (of reactant oil weight) of catalyst concentration, 4 hours and 60°C of reaction period and temperature.

- It had been found during the preparation of the catalyst that a mass of around 120 grams of eggshell catalyst was possible to be produced from only 52 eggshells which are not even 15% of the number of eggs normally consumed in an average restaurant or dairy manufacturer on daily basis. Furthermore, only 10% of the total mass of prepared catalyst had been required to be used throughout the complete span of the experimental period of the project.

- Reusability of the prepared eggshell catalyst sample was investigated and it was found that the formed catalyst can be reused for 5 times successfully showing no considerable change in the yield or rate of biodiesel synthesis. However, after reusing for the sixth time, eventual decrease in the product yield was observed for each consecutive run of reaction.

- The produced oil was subjected to ASTM D6751 standard test and its several properties were accessed and found to be as 879 kg/m³ of density, 4.53 (mm²/sec) of kinematic viscosity, 44.8(kJ/kg) of calorific value, 115°C flash point and acid value of 0.32. The evaluated values of all of the parameters were found to be within the standard range of values set for conventional biodiesel.

- The catalytic efficiency of the formed eggshell catalyst was compared to that of potassium hydroxide and non-activated sample of the catalyst through carrying out three separate transesterification reactions under identical reaction condition and the activated catalyst sample was found to show almost similar reaction rate and attained maximum product yield near to that obtained through utilization of conventional grade KOH catalyst over the same time span. Non-activated catalyst was not able to attain even half of the maximum product yield over same time span.

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