SYNTHESIS OF ALGAE BIODIESEL USING K_2CO_3/ZnO HETEROGENEOUS BASE CATALYST AND ITS CHARACTERISATION

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ABSTRACT

The objective of the present work is to produce algae biodiesel with base heterogeneous catalyst K_2CO_3/ZnO . This catalyst is prepared by wet impregnation method calcined at a high temperature of 600°C. 30% doping of K_2CO_3 on ZnO calcined at 600°C was studied for biodiesel yield. Transesterification reaction parameters like catalyst concentration, temperature, stirring speed, the molar ratio of methanol to oil on biodiesel yield were investigated. The produced algae biodiesel was characterized by various techniques such as thermogravimetric and differential thermal analysis (TGA-DSC), Gas Chromatography analysis and Fourier transform infrared (FT-IR) spectroscopy. Gas chromatography (GC) shows the presence of higher Oleic acid content of 90.8% and Linolenic acid of 0.1% in the synthesized algae biodiesel. Differential scanning calorimetric analysis shows that the boiling point off fatty acid methyl esters is 269.5°C. Thermogravimetric analysis reveals that oil decomposition starts at 360°C and maximum weighty loss is observed at 422.5°C.

Keywords: Heterogeneous Catalyst, Algae Biodiesel, Transesterification, Characterization.

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INTRODUCTION

Presently shortage of fossil fuels and environmental air quality degradation are the twin crisis the world is facing. The drastic increase in energy demand and the number of vehicles has led to a severe shortage of petroleum reserves all over the world. The situation has led to exploring for an alternative fuel, which is not only environment-friendly but also renewable and sustainable.¹ For developing countries, fuels such as alcohol, vegetable oils, biomass, biogas, synthetic fuels, etc. are becoming crucial. Such type of fuels can be used directly or some modifications can be done so that they can be used as a substitute for traditional fuels. In developing nations like India, more than 95% of surface transport rely on petroleum products. The policy-makers are forced to explore potential options as alternate fuel.² Biodiesel may be considered as the alternative options for meeting part of India's energy needs. Biodiesel is prepared with transesterification with the help of a catalyst. The reaction rate and increase in biodiesel yield mainly depend on the presence of catalyst during the transesterification process. Transesterification reactions can be accelerated in the presence of a homogeneous or heterogeneous catalyst. The reactants and catalyst will be in the same phase for the homogeneous catalyst.

Heterogeneous catalyst functions in a different phase from the reaction mixture. Homogeneous catalyst is widely used as it gives a high yield at low cost. However, water is formed during esterification with a homogeneous catalyst which needs to be removed by drying. Homogeneous catalyst is difficult to regain and recycle. Properties of some homogeneous catalyst change if stored or remained unused. Heterogeneous catalyst transesterification has simple product separation and purification process as it has less number of unit operation.

Heterogeneous catalyst can be either acid or base type. Acid heterogeneous catalyst grouped in Ion exchange resins, metals and non-metallic such as carbon-based are some of the examples for acid type heterogeneous catalysts. While oxides of metals, carbon and boron group elements are few available base

type heterogeneous catalysts. Oxides of Zirconia, sulfated tungsten, heteropoly acids, metal complexes and zeolites are some of the solid catalysts widely used as heterogeneous catalyst employed in biodiesel reactions.^{3,4,5} Many researchers transesterified the vegetable oils with Zeolites, sulphonic acid groups, mixed metal oxides, polyoxometalates, heteropoly acids as solid acid heterogeneous catalysts. High catalytic reactivity is one of the distinguished property possessed by many alkali metal oxides,⁶ transition oxides, mixed metal oxides. These catalysts are widely studied by researchers for the transesterification process. Positive ions of metal oxides are designated as electron acceptors while negative ions are termed as proton acceptors. These electron and proton acceptors participate in the adsorption process. These catalysts break O–H bonds present in methanol to methoxide ions and hydrogen cations. The triglyceride molecules react with these methoxide anions to yield methyl esters.^{7,8,9} The reaction rate of basic heterogeneous catalysts is higher than acidic catalysts for both homogeneous and heterogeneous type catalysts.¹⁰ Alkoxide ion (RO^-) is highly active which is generated due to the catalyst reaction with alcohols during the transesterification process. The FFA present in the oil feedstocks is highly sensitive to heterogeneous catalysts of basic nature. The biodiesel yield mainly depends on the amount of FFA content in oils. When the FFA content is more than 2% the tendency to soap formation is more and the biodiesel yield decreases. The glycerol recovery becomes difficult whenever the water present in the methyl esters reacts then carboxylic acids generating carboxylic acids. Then these acids react with alkaline metals to produce salts of sodium and potassium reduces biodiesel yield similar to the soap formation.^{11,12} These negative effects of water in the oils can be removed by doping silica gel and zeolites in the catalyst. Hence in the present work, a base heterogeneous catalyst $\text{K}_2\text{CO}_3/\text{ZnO}$ was synthesized and tested to convert algae oil to methyl esters and studied the conditions for maximum yield by optimizing the reaction parameters.

EXPERIMENTAL

Materials and Methods

The dried algae biomass obtained from spirulina species was pressed in mechanical expeller and crude algae oil is extracted. Methanol 99.0% purity of analytical grade, potassium carbonate and Zinc powder were procured from Lotus Chemicals India Pvt Ltd. Transesterification of crude algae oil is carried out by two-step transesterification process with the synthesized heterogeneous base catalyst $\text{K}_2\text{CO}_3/\text{ZnO}$. Analytical grade chemicals are procured from Sinopharm Reagent Chemical Co. Ltd.

Synthesis of Heterogeneous Base Catalyst $\text{K}_2\text{CO}_3/\text{ZnO}$ by Incipient-Wetness Impregnation Method (IWI)

The $\text{K}_2\text{CO}_3/\text{ZnO}$ was synthesized by wet impregnation method by doping ZnO and K_2CO_3 . Zinc oxide was prepared from commercially available zinc powder by taking 10grams of Zinc powder and adding 100ml of distilled water to this and mixture is stirred by mechanical stirrer rotating at 3000rpm for a period of 2 hours until all the zinc powder is dissolved in the solution. Then the resulted slurry is heated at 110°C and then evaporated to remove traces of water for about 24 hours and finally dried such that no trace of water is seen. Then the dried powder is stored in silica gel desiccators before it is used. Then K_2CO_3 was doped with ZnO powder at different loadings of $x\text{-ZnO}/\text{K}_2\text{CO}_3\text{-y}$, where x is the ZnO concentration and y is the calcination temperature. Then 5.4 grams of an aqueous solution of potassium carbonate is mixed with ZnO by wetness impregnation method and the left for 24 hours maintaining the temperature at 110°C in an oven for proper diffusion of ZnO on K_2CO_3 . The prepared catalyst is calcined at different temperatures ranging from 500°C - 700°C in a muffle furnace for a time of 24 hours. The calcined catalyst was cooled to room temperature before prior use.¹³

Transesterification of Algae Oil with $\text{K}_2\text{CO}_3/\text{ZnO}$ Heterogeneous Catalyst

Before the transesterification process, the crude algae oil is degummed. Initially, for degumming the crude algae oil (ACO) was dissolved in methanol in the ratio of 9:1 (molar basis) and poured in a conical flask consisting of 3 neck jar. Then the 3 jar neck is kept on a heating mantel and heated at a constant temperature at 80°C . The prepared heterogeneous base catalyst $\text{K}_2\text{CO}_3/\text{ZnO}$ is then dissolved in the mixture of oil and methanol. Experiments are conducted by varying the catalyst concentration 4% to 7%

on a weight basis in the mixture. The mixture in the flask is stirred at a constant speed of 450rpm by keeping a magnetic stirrer inside the flask. Then a two-layer solution is formed in the flask. The bottom layer is glycerin and the upper layer is algae methyl ester. Then the mixture is transferred to decanter and allowed to settle down. The catalyst is collected from the flask by decantation method. The glycerin is also separated from the decanter and leftover upper layer is algae methyl ester. Any traces of methanol are removed by distillation and this mixture is allowed to settle down. To this mixture, water is added along with 3 ml of phosphoric acid and allowed to settle down for a period of 24 hours in the decanter.¹⁴ Any traces of water and methanol are removed in the centrifuge stirred at 5000rpm. The collected biodiesel is preheated at 100°C to remove any traces of leftover water.

Gas Chromatography(GC) for Fatty Acid Composition Analysis

The Fatty acid composition was analyzed by GC Shimadzu gas chromatography. This GC analyzer is equipped with Agilent 6890N series a flame ionization detector and a capillary column DB-225(30 m × 0.25 mm × 0.25 μm). The initial oven temperature was kept at 160°C for first 2 minutes and further raised to 230°C at 5°C min⁻¹ and final temperature at 230°C for 20 min. An oil sample of 0.25ml crude algae oil is dissolved in a minimum amount of chloroform for analyzing the fatty acid composition. The oxygen-free nitrogen (N₂) is used at a flow rate of 1.0mL/min and the split ratio is kept at 50:1.

Differential Scanning Calorimetric-Thermal Gravimetric Analysis (DSC-TGA)

In the present work for sample analysis, the temperature range was fixed from ambient temperature to 450°C. To enhance the sample throughput, the instrument is equipped with a dual furnace made up of SiC. The heating rate was set as 10°C/min with a continuous flow of nitrogen atmosphere. Heat flow was monitored throughout as the function of temperature.

RESULTS AND ANALYSIS

Effect of Catalyst Loading on Algae Biodiesel Yield

The catalyst loading was found to be the most significant factor during the transesterification reaction for the conversion of triglycerides to monoglycerides. Figure-1 shows the effect of catalyst loading on FAME yield. The results indicate that when enough amount of catalyst is not loaded during the reaction maximum yield of algae biodiesel could not be achieved. A hence a larger concentration of 30% loading of K₂CO₃/ZnO is necessary for increasing the contact between catalyst and reactants participating in the transesterification process. When the catalyst concentration is 5% the algae biodiesel yield is only 67%. But when the catalyst concentration is increased from 5% to 7% the yield is also increased to 77.2%. At the same time when the catalyst concentration is decreased less than 5%, the reaction did not proceed and a large amount of soap is formed. A similar amount of 76.28% yield is observed for transesterification of rice bran oil with NiO-CoO-MoO/CNZ catalyst.¹⁵ Thus it is concluded that for 30% doped K₂CO₃/ZnO, the optimum catalyst loading for better yield is 7%.

Fig.-1: Variation of Algae Biodiesel yield at Different Catalyst Concentration

GC Analysis for Algae Biodiesel

The successful conversion of algae oil into fatty acid methyl esters and its composition was determined by Gas chromatography (GC) analysis as shown in Fig.-2. The amount of unsaturated fatty acids present in a

given amount of oil is an indication of the stability of oil, as most of the chemical reactions take place at double bonds. Oils containing more amount of oleic acid will be more stable and tendency for oxidation is minimized. The Fig.-2 depicts the produced algae biodiesel consisting of nine FAME and is represented in Table-1.

Fig.-2: The GC Analysis of Algae Biodiesel

From Table-1 it is observed that the unsaturated fatty acid methyl oleate(C18:1), methyl linoleate(C18:2), methyl linoleate(C18:3) are present in the biodiesel. Saturated FAME like methyl stearate (C18:0) and methyl palmitate(C: 16) are also observed in the biodiesel. The major fatty acid in algae biodiesel is oleic acid (90.8%).

Table-1: Identified Fatty Acid Methyl Ester (FAME)

Fatty Acid	wt%
Arachidic acid (C20:0)	0.1
Gadoleic acid (C20:1)	1.0
Linoleic acid (C18:2)	5.0
Linolenic acid (C18:3)	0.1
Myristic acid (C14:0)	0.4
Oleic acid (C 18:1)	90.8
Palmitic acid (C16:0)	1.6
Palmitoleic acid (C16:1)	0.3
Stearic acid (C18:0)	0.7

The composition of remaining fatty acids of algae biodiesel are palmitic (1.6%), stearic (0.7%), linoleic (5%), linolenic (0.1%), Arachidic (0.1%) and Myristic acid (0.4%). The kinematic viscosity and ignition delay time (IDT) of biodiesel play a key role in the combustion process.^{16,17,18} Higher saturated content like C18:0 and C16:0 increases the kinematic viscosity which is very less in the produced algae biodiesel. Studies report that C18:3 and C18:2 are the methyl esters responsible for lower kinematic viscosity. This FAMEs result, confirms improved combustion and good fuel-air mixing.

Thermal Gravimetric Analysis- Differential Scanning Calorimetry (DSC-TGA)

TGA method was used to determine the thermal stability of crude algae oil and produced algae biodiesel. The sample was heated at a constant heating rate (10⁰C/min) with a continuous flow of nitrogen atmosphere. Fig.-3(a) shows that moisture content released from oil around 110⁰C to 200⁰C. In the absence of moisture and volatile matter the Fig.-3(b) does not show any degradation between 20⁰C to 225⁰C. The TGA curve shows two-step degradation. Weight loss of the first step started approximately at 225⁰C. This step indicates the volatilization point of the crude algae oil. In the second step TG curve shows the onset of decomposition (temp at which oil starts degrading) at approximately 360⁰C. The DTG

curve shows maximum weight loss at 422.5⁰C. Thermal degradation range was observed from 280⁰C to 450⁰C. In Fig.-4(a) shows two steps, where the initial weight loss started at 164⁰C. This temperature indicates the starting of the volatilization point of algae biodiesel. In the final step, the inflection occurs at 269.5⁰C which indicates the boiling point of the esters. Extent of fuel deterioration, when exposed to air during storage, indicates oxidation stability of a fuel. In Fig.-4(b) the onset of one exothermic thermal event is showing in DSC curve with a change in enthalpy (ΔH) 6246 J/kg which gives confirmation of an oxidation reaction which has been taken place. From the DSC curve oxidative onset temperature of biodiesel is recorded approximately 269.5⁰C.¹⁹ The obtained relatively high onset temperature shows high thermal and oxidation stability of the biodiesel. Similar results are seen in TGA graphs of Magnesium hydroxide fluorides heterogeneous catalyst during transesterification of waste cooking oil where there is no thermal decomposition at 600–700⁰C.²⁰

Fig.-3: (a) TG/DTG Curves (b) DSC/TG Thermographs for Crude Algae Oil

Fourier Transform Infrared (FT-IR) Spectroscopy

The infrared spectrometer is used to study the characterization of prepared algae crude oil and methyl ester of algae. The spectrum was studied for wave numbers ranging between 400–4000 cm⁻¹. The scan resolution was maintained as 4 cm⁻¹ with a rate of 16cm/min. FTIR spectra of crude algae oil and pure

algae bio-diesel are shown in Fig.-5 and Fig.-6. Esters will have stretching of C=O which is depicted by peaks in both the spectra of crude algae oil and algae biodiesel. Peaks are observed at 1747.31 cm^{-1} in fig.5 and 1744 cm^{-1} in Fig.-6.²¹

Fig.-4: (a)TG/DTG Curves (b) DSC/TGA Curves for Algae Biodiesel

Similar absorption peaks are observed at the wave number of 1619.30 cm^{-1} for C=O bonds depicted in spectra of amidation of FAME from coconut oil.²² The characteristic absorption bands for both symmetric and vibration asymmetric modes of C-H for crude algae oil methyl groups were identified at 2924 cm^{-1} and 2926 cm^{-1} . Fig.-6. also shows symmetry and asymmetric vibrations in range 2926 cm^{-1} and 2855 cm^{-1} . Trans isomers contain strong band at 970 cm^{-1} and the weak band at 3012 cm^{-1} which is absent in the fig.6. This confirms cis isomers are present in the algae biodiesel. In fig.5 and fig 6 shows medium bands at 723 cm^{-1} and 3005 cm^{-1} . Biodiesels will have many overlapping peaks from the range from 1000 cm^{-1} to 1300 cm^{-1} . The absorption peak around 1200 cm^{-1} may be evidence to the asymmetric axial stretching vibrations of C(C=O)-O bonds of the esters, while peaks around 1171 cm^{-1} can be attributed to axial stretching of asymmetric O-C-C vibration bonds.^{23,24} Mono alkyl esters are the main constituent of any biodiesel. It was observed that C=O bonds were stretched intensively for methyl esters of algae oil. The bond O-CH₃ appeared around 1747 cm^{-1} and 1163 cm^{-1} for algae crude oil and at 1744 cm^{-1} and 1171 cm^{-1} for algae biodiesel. A weak peak is present at 3468 cm^{-1} in fig 6. Complete transesterification of algae oil can be observed from the wavenumber of 3005 cm^{-1} representing the OH group of carboxylic acid as depicted in fig6. Both the samples of algae oil and biodiesel, stretch bands representing the C-H of aromatic hydrogen and aromatic C=C bonds are absent.²⁵

Fig.-5: FTIR Spectra for Algae Crude Oil

Fig.-6: FTIR Spectra for Algae Biodiesel

CONCLUSION

A heterogeneous base catalyst is formulated by doping K_2CO_3 with ZnO and is successful in transesterification of algae oil. The results report that K_2CO_3 is an active component in the formulation of K_2CO_3 /ZnO. The effect of calcination temperature on catalyst reaction strength, concentration, methanol to molar ratio, transesterification temperature and stirring speed was studied. Calcination temperature proved to be a significant factor in the synthesis of catalyst. The best catalyst strength was obtained for the calcination temperature of 600°C . The algae crude oil is transesterified by using this heterogeneous K_2CO_3 /ZnO and maximum yield is obtained for catalyst concentration of 7% by weight basis and yield is better than 5% catalyst concentration. It was observed that with 5% catalyst concentration the transesterification of algae oil was unsuccessful and soap formation resulted. Maximum algae biodiesel was obtained for 9:1 methanol to the molar ratio for a constant reaction temperature of 80°C carried at 450rpm stirring speed. The synthesized algae biodiesel were characterized by GC, TG & DSC analysis. The thermogram of crude algae oil indicates that the moisture content is released in the temperature range between 110°C to 200°C . The vaporization of crude algae oil starts at 225°C while for algae biodiesel it was noticed at 164°C . The DSC combustion graphs of neat algae biodiesel indicate that all the reactions are exothermic with a change in enthalpy (ΔH) 6246 J/kg dissipating heat to the surroundings. The thermogram of crude algae oil indicates the degradation of the oil is in the range of 280°C to 450°C while

the maximum weight loss is observed at 422.5⁰C. The thermogram of neat algae biodiesel indicates the degradation in the temperature range of 164⁰C to 269.5⁰C. This is an indication of better conversion of FFA to methyl esters. The GC analysis reveals the meager presence of Linolenic and Arahidic acids content of 0.1%. This is an indication of the lower viscosity of synthesized algae biodiesel. Hence the prepared catalyst K₂CO₃ /ZnO is good for the synthesis of algae oil.

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