Transesterification of Algae Oil using K₂CO₃/ZnO Heterogeneous Base Catalyst

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The objective of the present work was to develop a heterogeneous base catalyst K_2CO_3/ZnO for transesterification of algae oil. This catalyst was prepared by wet impregnation method calcined at high temperature of 600 °C. The catalyst was characterized by X-ray diffraction technique. The crude algae oil was degummed and its free fatty acid was reduced to 2 % by methanol treatment. Methanol was used to convert triglycerides to biodiesel using K_2CO_3/ZnO. The doping of 30 % K_2CO_3 on ZnO calcined at 600 °C was studied on biodiesel yield. The reaction parameters such as temperature, stirring rate, amount of catalyst, methanol to oil molar ratio on the yield of fatty acid methyl ester were investigated. Highest yield was obtained for 7 % catalyst, 9:1 methanol to molar ratio at 80 °C for 30 % K_2CO_3/ZnO. This study proved that the catalyst loading less than 5 % was unsuccessful in biodiesel yield. The physio-chemical properties of the produced algae biodiesel was determined as per ASTM test procedures.

Keywords: Base heterogeneous catalyst, Algae biodiesel, Transesterification, Characterization.

INTRODUCTION

Biodiesel is a viable alternative as petroleum reserves are diminishing. It is produced from vegetable oil through transesterification. Methanol, ethanol, propanol, butanol and amyl alcohol are some of the alcohols used for transesterification process. Presence of catalyst is important during transesterification to increase the reaction rate and the yield. Catalysts are classified as homogeneous and heterogeneous catalyst. Homogenous catalyst function in the same phase as the reactants. However water is formed during esterification with homogeneous catalyst which needs to be removed by drying. Properties of some homogenous catalyst change if stored or remained unused. Researchers are forced towards heterogeneous catalyst transesterification as it has less number of unit operation and simple product separation and purification process.

Heterogeneous catalyst are classified as acid heterogeneous and base heterogeneous. Ion-exchange resins, metal based catalyst and carbon based catalyst are acid heterogeneous. Metal oxide base, carbon group based, boron group based and waste material based are base heterogeneous catalyst. Various solid acid catalysts such as resins, sulfated tungsten and zirconium oxides, heteropoly acids, sulfated polyaniline, metal complexes and zeolites have been employed as heterogeneous catalysts on the biodiesel production reactions. The solid acid heterogeneous catalyst used by many of the researchers are zeolite, mixed oxides, sulfonic acid groups catalysts, sulfonic acid modified mesoporous silica, heteropoly acids and polyoxonetalates, supported and substituted heteropoly acids, solid acid catalysts based in waste carbon. Zeolites are extensively used in industry as they are cost effective and environment friendly. Zeolites have narrow pore size and have diffusion limitations for adsorption of triglycerides on the active sites. This limits its use as a catalyst for transesterification. Brito *et al.* [1] studied fried oil transesterification reactions with methanol using several zeolites Y and interchanged with CaCl₂ and KOH. It was observed that best yield of 98 % fatty acid methyl ester (FAME) was obtained with Y756 zeolite interchanged with KOH. Viscosities of the reaction product obtained reached values next to diesel standard ones. In another study, Wang *et al.* [2] synthesized zeolite MCM-22 and commercial zeolite HY (CBV-780) treated with NaOH were used for transesterification of triolein in excess methanol at lower reaction

temperature of 60 °C. High yield of 98 % and 99 % was obtained within 5.5 h of reaction using NaOH treated CBV-780 and MCM-22 catalyst. Also no saponification was observed with treated zeolites. Recently research was carried out by Damyanova *et al.* [3] using CeO₂-ZrO₂ oxides with different proportions of CeO₂ content by weight. Zirconia surface was enriched with fluorite structure of CeO₂ with 12 % by weight. CeO₂-ZrO₂ oxide systems displayed high surface and good thermal stability which is similar to chemically mixed oxides. Many metal oxide catalyst [4] like alkali earth metal oxides, mixed metal oxides and transition metal oxides, are studied by researchers for transesterification process with high catalyst activity. In metal oxides positive ions behave as electron acceptors and negative ions behave as proton acceptors which results is adsorption process. For transesterification such catalyst provide adsorptive sites for methanol which breaks the O-H bond into methoxide ions and hydrogen cations. Methoxide anions react with triglyceride molecules to yield methyl esters [5,6]. Basic catalysts give a higher reaction rate as compared to acidic catalysts, irrespective of whether they are homogeneous or heterogeneous. The higher activity is due to the generation of highly active alkoxide ion (RO⁻) when the alcohol reacts with the base catalyst. Heterogeneous basic catalysts are sensitive to free fatty acids (FFA) in the feedstock. Soap formation decreases the biodiesel yield if the free fatty acid content in oil exceeds 2 % by mass. Water reacts with alkyl esters to produce carboxylic acids, which react with alkaline metals to form sodium or potassium salts similar to a soap, reducing alkyl ester yield and making glycerol recovery difficult [7]. Zeolite and silica gel have been used in the catalyst to absorb water to offset the adverse effect of water. Liu *et al.* [8] transestrified soybean oil using CaO as a solid base catalyst. The experimental results showed that a 12:1 molar ratio of methanol to oil, addition of 8 % CaO catalyst, 65 °C reaction temperature and 2.03 % water content in methanol gave the best results and the biodiesel yield exceeded 95 % from 3 h reaction process. CaO maintained sustained activity even after being repeatedly used for 20 cycles. Strontium oxides were also used as catalyst [8]. It was noted that yield was more than 95 % and catalyst life was also increased.

EXPERIMENTAL

Spirulina algae oil was extracted by mechanical expeller method. Analytical grade methanol, zinc powder and potassium carbonate was purchased from Lotus Chemicals India Ltd. Two step transesterification process of algae crude oil (ACO) was carried out with K₂CO₃/ZnO as heterogeneous catalyst. All other chemicals were of analytical grade and obtained from Sinopharm Reagent Chemical Co. Ltd.

Pre-treatment of algae crude oil: The crude algae was degummed by adding orthophosphoric acid by 0.6 % (v/v). The mixture was stirred at 1000 rpm by electrical stirrer for 30 min and transferred to decanter and to settle down for about 48 h. All the dust and sediment particles settled down at bottom of the decanter was removed. The degummed algae oil was again preheated at 70 °C on hot surface plate. Water was added by 3 % (v/v) and stirred at 1000 rpm for about 30 min and centrifuged at 6000 rpm. Phosphatides and gums were separated from CaO. The oil was again heated at 100 °C to remove any trace of water. The degummed oil was ready for transesterification [9].

Preparation of K₂CO₃/ZnO heterogeneous catalyst by incipient-wetness impregnation method (IWI): Zinc oxide was prepared by dissolving 10 g of low surface area of zinc oxide in 100 mL of distilled water and the resulting Zn(OH)₂ was stabilized for 20 h at 210 °C to obtain ZnO of high surface area. The zinc oxide was dried and any traces of water on the surface was absorbed. This unmodified zinc oxide was stored in silica gel desiccator prior to its use. Modified ZnO at different loadings of K₂CO₃ was prepared. ZnO was impregnated with 5.4 g of potassium carbonate with aqueous solution and impregnated for 24 h at 110 °C in an oven to ensure proper diffusion of K₂CO₃ on ZnO. The pre-treated samples were calcined at different temperatures ranging from 500-700 °C in muffle furnace. The calcined material were then cooled at room temperature before using in next transesterification process.

Characterization of heterogeneous catalyst: The structure of the synthesized K₂CO₃/ZnO heterogeneous catalyst was investigated by X-ray diffraction technique in the scanning angle 2θ of 5-80°. The successful synthesis of catalyst was confirmed by XRD. The width of the maximum peak represents the size of the crystalline grain. This size and other parameters are given by Scherrer formula [10]:

$$D = \frac{0.9 \times \lambda}{B_p \cos \theta} \tag{1}$$

where D is crystalline grain size, λ is the wave length of the X-ray and B_p is the width of the maximum peak in half height. The grain size is calculated using equation 1.

Preparation of algae biodiesel

Degumming of crude algae oil: Methanol in a molar ratio of 9:1 and 1.5 % H₂SO₄ on volume basis was added to the degummed algae crude oil. The mixture was heated at 70 °C and continuously stirred at 650 rpm for 1 h. The mixture was then transferred to decanter and kept for 24 h. The free fatty acid content of the mixture was determined by titrating 1 g of algae crude oil oil in 0.1 mL of phenolphthalein indicator against NaOH of 0.1 mol concentration. By using the following formula the free fatty acid (FFA) content of algae crude oil was determined by using the following equation.

$$FFA \text{ (g/mL)} = \frac{\text{Titer value} \times \text{Molarity of NaOH} \times \text{m.w. of NaOH}}{\text{Weight of the sample}} \tag{2}$$

At the end of the first stage of treatment the free fatty acid content was found to be 3.65, hence the process was repeated for next stage until its free fatty acid was reduced to 2.0. Transesterification was done for this low free fatty acid algae crude oil using heterogeneous base catalyst K₂CO₃/ZnO. The extracted crude algae oil samples were tested using standard methods of testing to evaluate their properties. The acid value of the oil was determined by the titration method (AOCS official method Cd 3d-63) using a KOH-methanol solution. The saponification value of the oil was determined by AOCS official method Cd 3-25. The iodine value of the algae oil was determined by AOCS (American Oil Chemists' Society) official method Cd 1-25.

Transesterification of degummed algae oil: Initially 50 mL of algae crude oil was poured in to 3 neck conical flask to methanol with a molar ratio of 9:1 and heated at constant temperature of 80 °C in a heating mantel. The molar ratio was decided from the following formula.

Volume of methanol added = Number of moles of methanol × molecular weight of methanol × 50 (for 50 mL)/ Density of methanol × 870

Hence the volume of methanol added = (n × 32.04 × 50)/(0.7918 × 870)

where 'n' is the molar concentration of the catalyst. Molecular weight of methanol $(CH_3OH) = 32.04$, density of methanol = 0.7918 g/m³.

K_2CO_3/ZnO was added as catalyst varying its mass from 7-4 % in this mixture. The mixture was stirred by magnetic stirrer at a speed of 450 rpm. The catalyst was separated from the mixture by decantation. Methanol was removed by distillation and the remaining mixture was allowed to settle down. Biodiesel formed the upper layer and glycerin precipitated at the bottom. The biodiesel was washed with water adding of 3 mL of phosphoric acid and allowed to settle for 24 h in the decanter for the removal of excess methanol. The leftover methanol was separated from oil by centrifuging the mixture at 5000 rpm. The collected biodiesel was heated at 100 °C to remove any traces of water.

RESULTS AND DISCUSSION

X-ray diffraction analysis: Table-1 shows the calculated parameters using Scherrer equations. Figs. 1-3 show that the calcination leads to deposition of K_2CO_3 on ZnO. It can be seen that calcination process of K_2CO_3/ZnO is better at 600 °C as

TABLE-1
SCHERER EQUATION PARAMETERS FOR PREPARED CATALYST AT DIFFERENT TEMPERATURES

Peak No.	2θ (°)	Corresponding element	B_p (2π)	D (nm)
Temperature = 500 °C				
1	56.816	K_2CO_3	0.0299	1.61913
2	63.100	K_2CO_3	0.0298	1.47216
3	68.190	K_2CO_3	0.0295	1.37415
Temperature = 600 °C				
1	35.073	K_2CO_3	0.0309	2.5567
2	36.892	K_2CO_3	0.0309	2.43452
3	46.136	K_2CO_3	0.0306	1.88884
4	57.141	K_2CO_3	0.0302	1.61069
5	63.366	K_2CO_3	0.0298	1.46663
Temperature = 700 °C				
1	34.917	K_2CO_3	0.0309	2.56766
2	36.745	K_2CO_3	0.0308	2.44366
3	57.025	K_2CO_3	0.0301	1.61371
4	63.262	K_2CO_3	0.0298	1.46879

compared to the other temperatures. The presence of ZnO is detected in the XRD patterns at 35.073°, 36.892°, 46.136°, 57.141° and 63.366°. The results confirmed the deposition of K_2CO_3 on ZnO. Hence, the heterogeneous catalyst K_2CO_3/ZnO calcined at 600 °C will be the active site for better transesterification reaction.

Physio-chemical properties of crude algae oil and algae biodiesel: Algae biodiesel was compared with the B100 standards ASTM D6751.The produced biodiesel matches the standard and can be used as blends with diesel. Higher unsaturated fatty acids (UFA) present in the oil give higher iodine values. The intensity of unsaturated fatty acid influences fuel oxidation tendency. The iodine value of algae oil was recorded
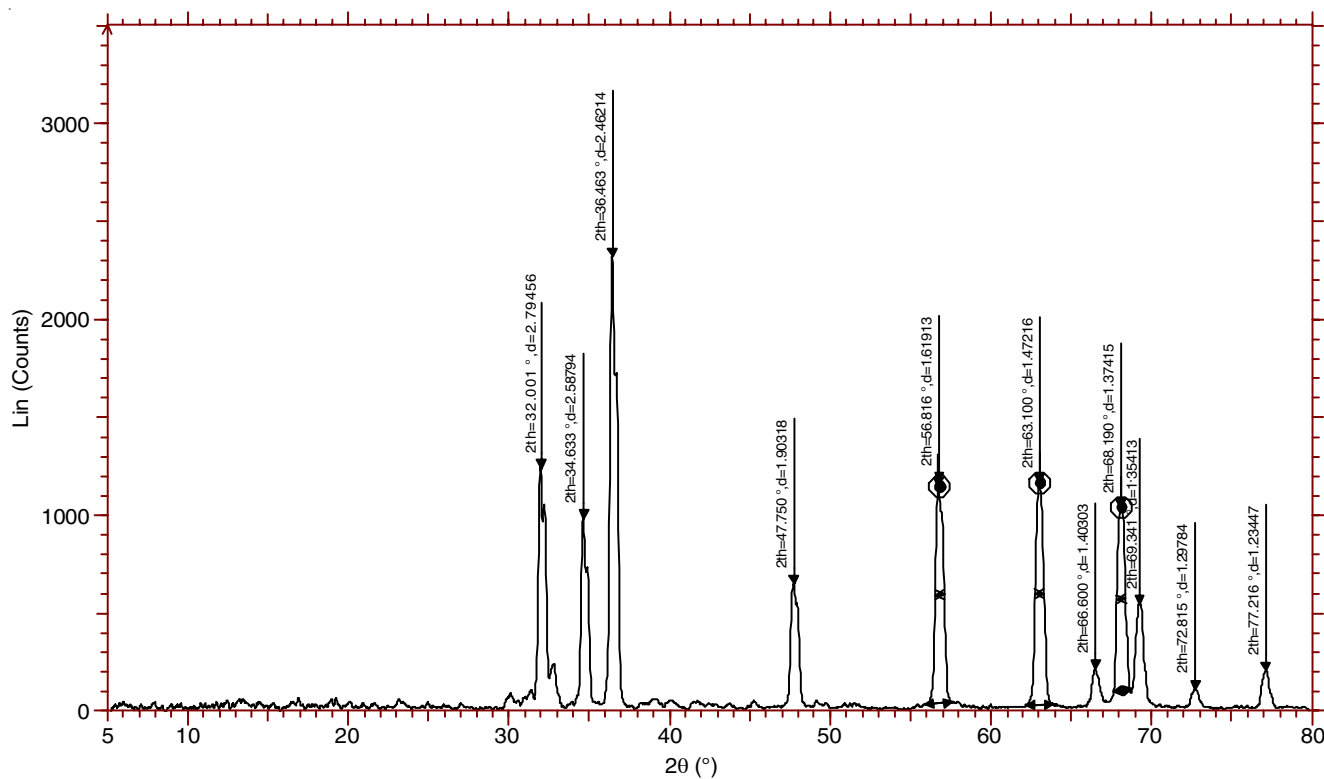

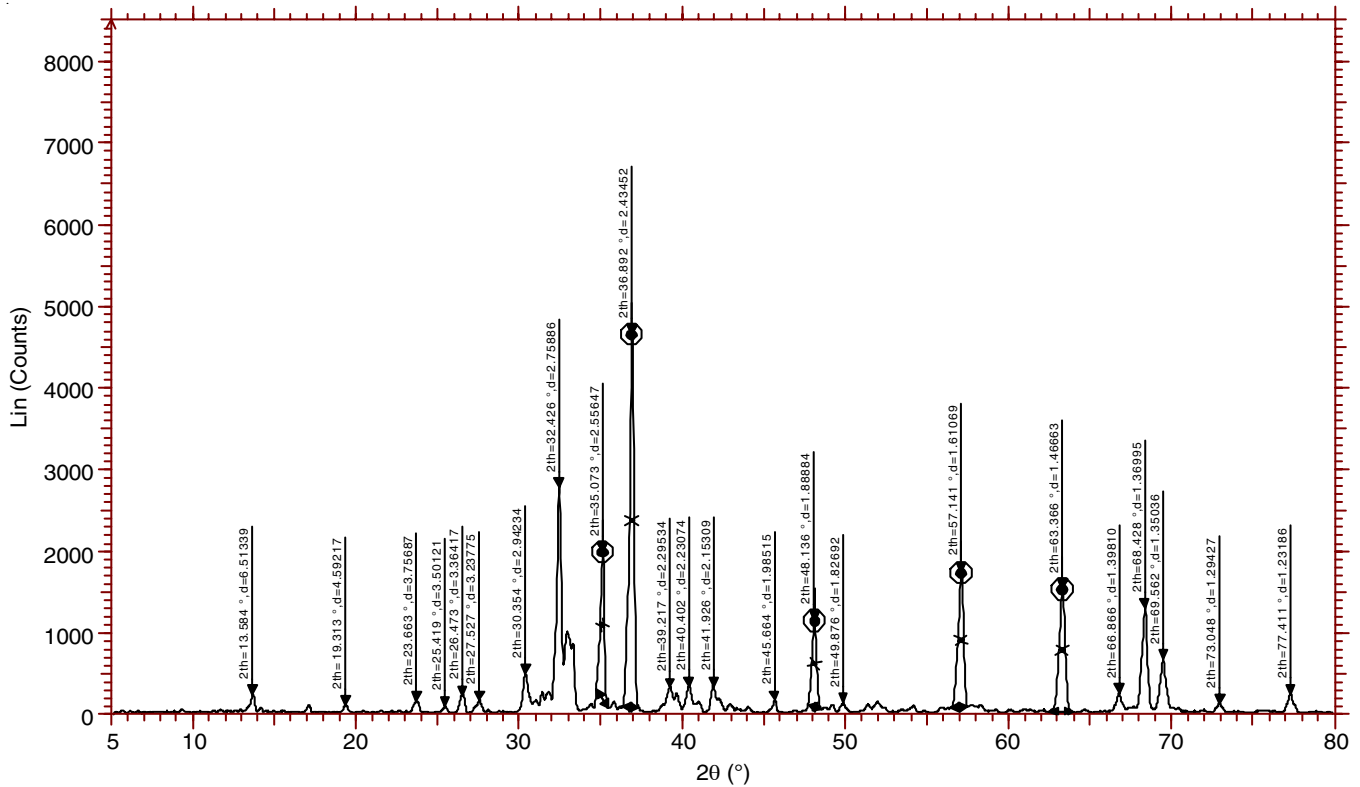Fig 1. XRD pattern of heterogeneous catalyst at 500 °C

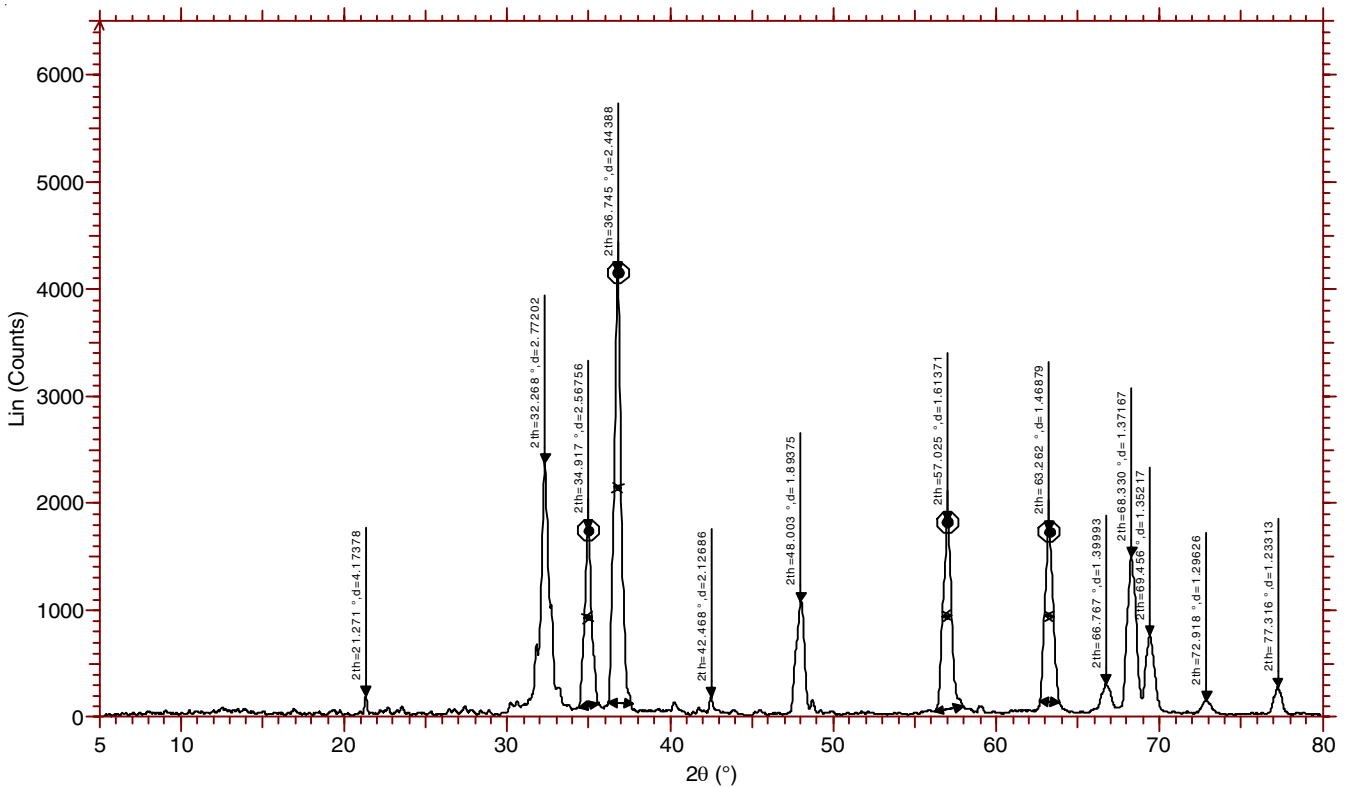Fig 2. XRD pattern of heterogeneous catalyst at 600 °C

Fig 3. XRD pattern of heterogeneous catalyst at 700 °C

as 86 mg I_2/100 g and 80 I_2/100 g for biodiesel. Aging of the fuel depends upon its acid value. The acid value of the algae biodiesel 0.1 mg KOH/g while that of crude oil was 0.57 mg KOH/g. The acid value after transesterification decreased. Low acid value of biodiesel decreases corrosion problems in the engine and ensures smooth operation [11-13]. Both the algae oil and algae biodiesel showed low ash content (approximately 0 %). Ash contents leads to abrasion in engine parts. The density effects the atomization of fuel. The specific gravity of the algae oil was 0.863 and that of algae biodiesel 0.85. Ignition delay

is the time interval between the fuel injection and the first noticeable pressure increase during combustion of fuel. Cetane number is inversely proportional to ignition delay of the engine. The higher the cetane number shorter will be the ignition delay. Fuels with low cetane numbers will cause increased smoke opacity, difficulty in starting, rough operation and noise. The calculated cetane number for algae biodiesel was 53. The calorific value of the produced biodiesel was 41321.63 kJ/kg.

Influence of catalyst concentration on FAME yield: The influence of catalyst concentration on biodiesel yield is shown in Fig. 4. The catalyst concentration is an important factor, which effects the conversion of triglycerides to methyl esters. Higher concentration of heterogeneous catalyst of 30 % doped K_2CO_3/ZnO is necessary for higher yield of algae biodiesel. The results showed that 7 % catalyst concentration yields 77.2 % whereas 5 % catalyst concentration yielded only 67 %. This showed that the biodiesel yield decreases with decrease in catalyst concentration. However on further reduction of catalyst concentration less than 5 % concentration, there was no effect of catalyst on chemical reaction and ultimately lead to soap formation. Hence 5 % concentration of K_2CO_3/ZnO is the limiting value for conversion of algae oil having less than 2 % free fatty acid.
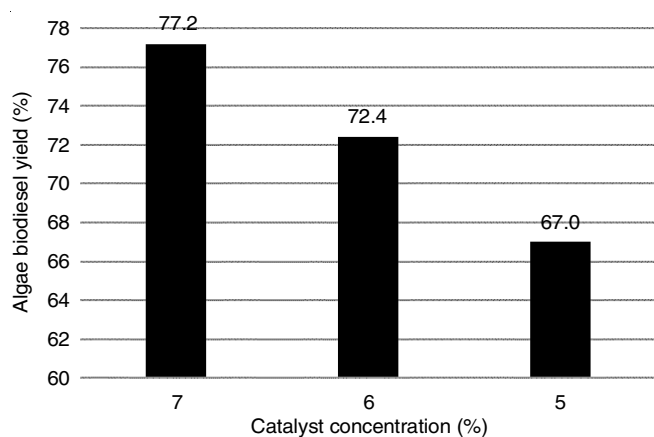

Fig 4. Influence of catalyst concentration on yield

Conclusion

The experimental result concludes that the synthesized K_2CO_3/ZnO heterogeneous base catalyst is with K_2CO_3 as active component on doping with ZnO is active in the transesterification of algae oil. It is also noticed that the calcination temperature is significant in synthesis of heterogeneous catalyst where 600 °C was the optimum temperature for better strength of the catalyst. The biodiesel yield mainly depends on the catalyst concentration and it was found that 7 % catalyst by weight was successful in greater yield compared to 5 % weight catalyst. Catalyst weight less than 5 % was unsuccessful in

biodiesel conversion promoting soap formation. The favourable working conditions for better yield is methanol to molar oil ratio is 9:1, at 80 °C when stirred at constant speed of 450 rpm.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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