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SYNTHESIS OF HETEROGENEOUS CATALYST FOR THE PRODUCTION OF BIODIESEL FROM SOYBEAN OIL

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ABSTRACT

This study explore the comparison of a suitable heterogeneous catalyst for conversion of triglyceride into fatty acid methyl ester. A series of heterogeneous cerium, manganese, and zinc oxide catalyst supported at mixture of cinder was prepared by co-precipitation and applied for conversion of triglyceride in oil to biodiesel using methanol as solvent. Results showed that a maximum TG conversion of 99% was obtained in the transesterification reaction catalyzed by $CeSO_4$+$MnSO_4$+K_2CO_3 catalyst calcinated in 5 h at 600^oC under the optimal conditions as catalyst amount of 3%, Ce:Mn:K molar ratio of 1:1:1. The catalytic activity of catalyst at 70 ºC reaction temperature was over 90% after 6h. The experimental data were satisfactorily predicted at 99% confidence level. However, due to high and efficient yield $CeSO_4$+$MnSO_4$+K_2CO_3 catalyst was identified as the most potential catalyst.

Keywords: biodiesel fuel; heterogeneous; trans-esterification; rare earth metals; eco-friendly regent; used oil.

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1. INTRODUCTION

Biodiesel is a marginal fuel for compressed and ignition engines that is gaining consideration in terms of the reducing fossil energy resources of the world and the mitigation of greenhouse special effects due to carbon dioxide [1]. Biodiesel offers noteworthy impacts in lessening motor emanations at 80– 90% reduction [2]. Biodiesel is a renewable source of energy that

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can help reduce greenhouse gas emissions and minimize the "carbon footprint" of agriculture. It contributes less to global warming because the carbon in the fuel was removed from the air by the plant feedstock [3]. In addition, biodiesel produces less air pollution (exhaust emissions) than diesel made from fossil fuels. A 1998 study by the USDA and US DOE found that using pure biodiesel in urban buses "results in substantial reductions in life cycle emissions of total particulate matter, carbon monoxide and sulfur oxides (32%, 35% and 8% reductions respectively, relative to petroleum diesel's life cycle)".

1.1. Global Energy Crises Situation

The interest and development of biofuels has grown exponentially over the last few years in response to the need to develop sustainable energy resources and to address climate change [1]. Expanding ecological issue and risk of draining petroleum derivative stores coupled to increase demand for diesel and vulnerability in their accessibility has elevated logical scientists to discover alternative potential wellsprings of considerable energy production [4].

A large portion of the sustainable power sources depends on sunlight light [5]. This form utilizes the gravitational capability of raised water that was lifted from the seas by sunlight [6-7]. Wind imperativeness can be utilized to pump water or produce power, but requires extensive areal coverage to produce significant amounts of energy [8-9]. In specific ranges, the geothermal slope (increment in temperature with profundity) is sufficiently high to adventure to produce power [10]. Biodiesel has good lubricant properties compared to petroleum diesel oil. Biodiesel can be mixed with petroleum diesel, allowing biodiesel to be introduced gradually to build up the industry [11].

1.2. Importance of Biodiesel

As being renewable and suitable source of energy, it is practical and suitable for agricultural countries [12]. Biofuels on account of its low instability and vitality substance can be utilized as a part of pressure start (diesel) motors with next to zero alterations [13].

1.3. Synthesis of Biodiesel

Traditional feed stocks for biodiesel production is plant oils, animal fats especially waste cooking oil. Typically, fats with high triglyceride contents are used for synthesis of biodioesel

The non-edible vegetable oils such as Madhucaindica, Jatropha curcas, Pongamiapinnata looks suitable for biodiesel production [14]. Homogeneous catalysis is catalysis in a solution by a soluble catalyst. Strictly speaking, homogeneous catalysis refers to catalytic reactions where the catalyst is in the same phase as the reactants. Homogeneous catalysis applies to reactions in the gas phase and even in solids.

The homogeneous catalyst for biodiesel process is divided into two categories, which are acid and base catalysts. Sulphuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid are the most common acid catalysts being used in biodiesel production [15]. According to [11], the most effective base catalysts are potassium hydroxide, potassium meth oxide, and sodium hydroxide and sodium meth oxide. Sodium meth oxide (CH3ONa) and potassium meth oxide (CH3OK) were claimed to perform better compared to sodium hydroxide (NaOH) and potassium hydroxide (KOH).

1.4. Impacts of Homogeneous Catalyst on Environment

Homogeneous catalyst poses some serious impacts on the environment:

1. They are prone to leaching and difficult to remove.
2. Cost ineffective because we have to add catalyst very often in order to replenish the drained amount.
3. Separation of catalyst from product is water consuming process which causes a lot of waste water production [16-17].

The great majority of practical heterogeneous catalysts are solids and the great majority of reactants are gases or liquids.

Heterogeneous catalysis is a substance term, which portrays a catalysis response where the reagent is in a dissimilar stage to the reactants. Like a homogeneous catalyst, the heterogeneous catalyst is additionally separated into two classifications, i.e. the strong base and the strong acid catalyst. The prevalence of heterogeneous catalyst these days is because of the impediments caused by homogeneous catalyst. The traditional homogeneous catalyst is prescribed to be supplanted by earth well disposed of a heterogeneous catalyst. Being in an alternate stage, heterogeneous catalyst has the advantage of simple separation and reuse [18-22].

In [23] used soybean oil for trans-esterification reaction with MgO supported at silica as a solid heterogeneous catalyst at 220°C for 5h with 96% biodiesel yield. Many authors reported the use of animal shells such as oyster, sea shells, crab shells and egg shells etc. as a source of CaO with different edible and non-edible oil feed stocks [23].

In past MgO, CaO, SrO, were are used by different researcher for biodiesel productions and they exhibit the conversion efficiency ranging from 90% to 95%. In [30] reported the use of SrO for transesterification of soybean oil. It is examined that SrO give 95% yield just 30 minutes reaction time at 65^{o}C reaction temperature was reported by [31] 95% yield was obtained in 30 minutes at 65°C reaction temperature [24-26]. In recent work, four different

alkaline earth metal oxides i.e. $ZnCO_3$, $CeSO_4$, K_2CO_3 and $MnSO_4$ were used to prepare heterogeneous catalysts using wet impregnation dn co-precipitation method [27-28].

In the present paper, four different alkaline earth metal oxides i.e. ZnCO3, $CeSO_4$, K_2CO_3 and $MnSO_4$ were used as heterogeneous catalysts for biodiesel production from soybean oil. Effects of critical process variables i.e. reaction time, methanol to oil ratio and temperature were investigated. The results were then fitted to a historical design to study the Analysis of Variance (ANOVA), to characterize interactions between variables and to simulate the process.

2. RESULTS AND DISCUSSION

Effect of reaction temperature on the TG conversion was presented in Fig. 1. It was observed that the reaction temperature had an influence on TG conversion. As reaction temperature increased from 50^{O}C to 70^{O}C, TG conversion for all catalysts evidently increased from 63% and 99.4%. No further TG conversion increase was observed when the reaction temperature increased to 100^{O}C. The optimum reaction temperature was suggested to be 70^{O}C in the experiment.

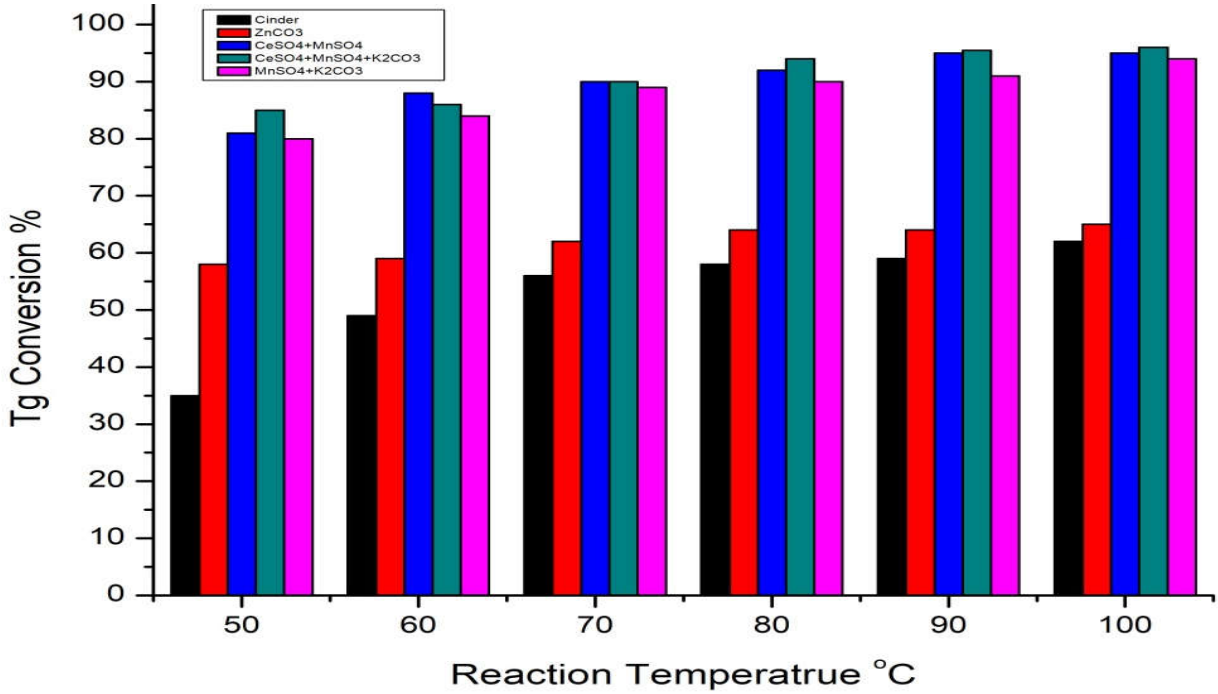

Fig.1. Effect of reaction temperature

The reaction time also affects the conversion efficiency of the process. Fig. 2 shows the effect of reaction time on subcritical heterogeneous transesterification. Initially, the TG conversion increased rapidly with reaction time. The reaction reached its highest TG conversion when the reaction time increased to 6h. Thereafter, TG conversion started to slightly increase but in

order to save time and resources 6h was selected for further reactions [32].

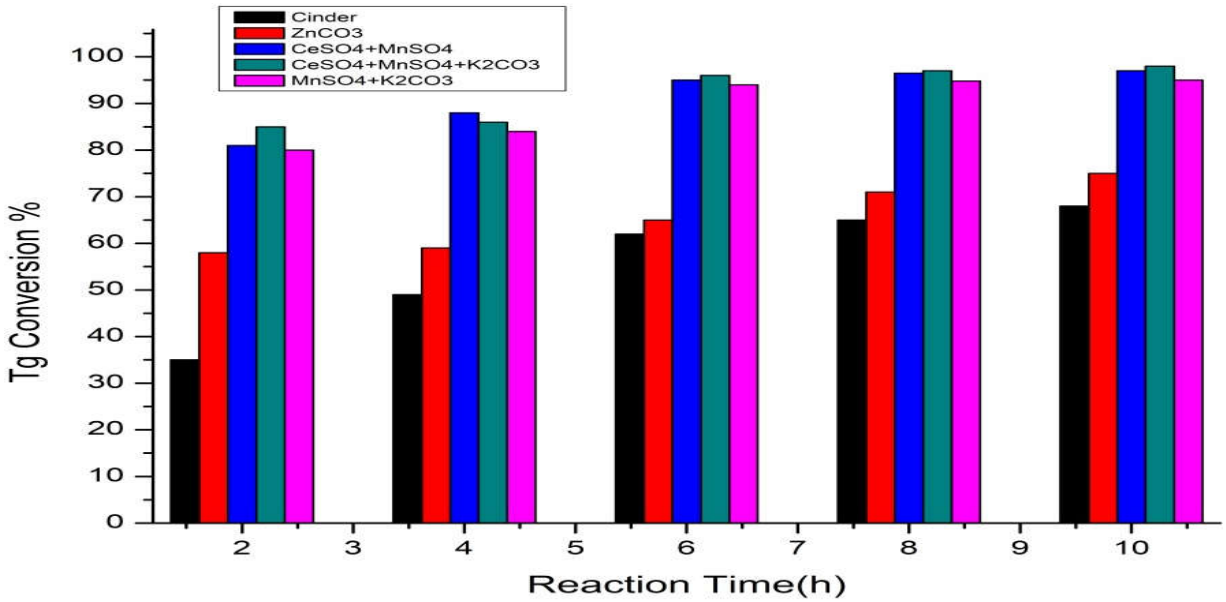

Fig.2. Effect of reaction time

Fig. 3 reveals TG conversion was less than 40% when1% catalyst with respect to Oil and methanol was used in the transesterification reaction. TG conversion evidently increased when the catalyst amount increased from 1% to 3%. A highest conversion of more than about 90% was obtained when catalyst amount was 4%, and no obvious increase was detected with further addition of catalyst. Generally, the increased usage of basic catalyst is favorable for the transesterification reaction [33]. However, too much catalyst used will increase the cost of biodiesel production. The experiment shows that the 3% catalyst is enough for further transesterification reactions.

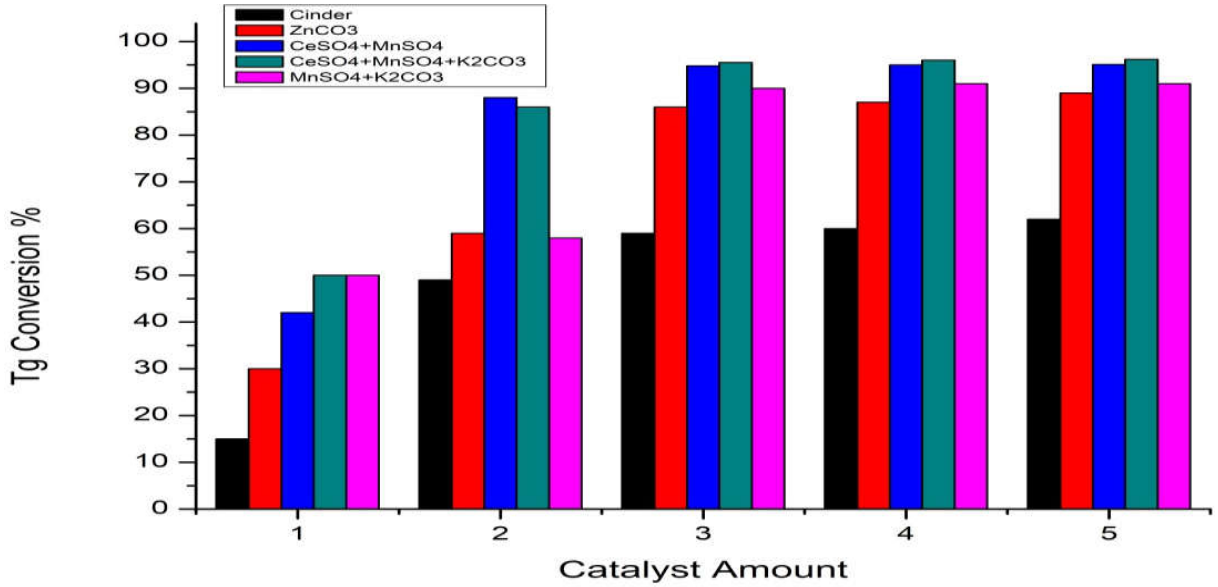

Fig.3. Effect of catalyst amount

Experiments performed in this study showed (Fig. 4) that the novel cinder supported

$CeSO_4$+$MnSO_4$+K_2CO_3 (1:1:1) catalyst calcinated at 600^{O}C exhibited high TG conversion (99%) while $MnSO_4$+K_2CO_3 (1:1) showed TG conversion up to 97%, and $CeSO_4$+$MnSO_4$95% and all catalyst sustained catalytic activity in the subcritical transesterification reaction. The TG conversion of the transesterification reaction catalyzed by catalysts achieved in 6h under the optimized catalyst preparation and transesterification reaction conditions.

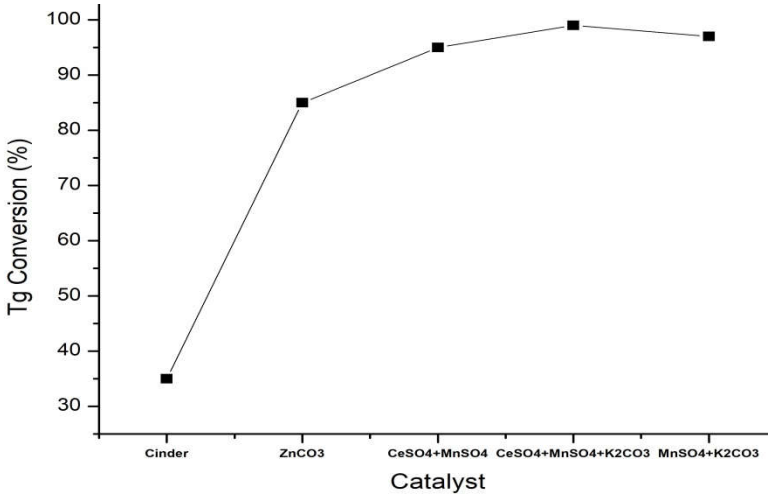

Fig.4. Effect of catalyst amount

3. METHODOLOGY

3.1. Catalyst Preparation

Raw soybean oil, analytical grade methanol $ZnCO_3$, $CeSO_4$, K_2CO_3 and $MnSO_4$ and Cinder (diameter 2.0-5.0 mm) are taken from specified sources for research continuation. Series of catalysts were prepared to by dissolving calculated amount of $ZnCO_3$, $CeSO_4$, K_2CO_3 (Table 1) and $MnSO_4$ into deionized water then an aqueous solution of KOH was slowly added under vigorous stirring at room temperature.

Table 1. Composition of reactants

Composition	Ratio	Amount (g)
$CeSO_4$+$MnSO_4$	1:1	1.66+0.845
$CeSO_4$+K_2CO_3	1:1	1.66+0.691
$CeSO_4$+MnSO4 +K_2CO_3	1:1:1	1.66+0.845+0.691
$MnSO_4$+K_2CO_3	1:1	0.691+0.845
$ZnCO_3$	1	1.25
Support	6.9g	6.9

The mixture was then aged for 2 h at room temperature. The solid product was washed and filtered and drying in an oven at 50℃. The resultant product was calcinated at 600℃ in a

muffle furnace and used in transesterification reactions in Scheme 1 (Fig. 5).

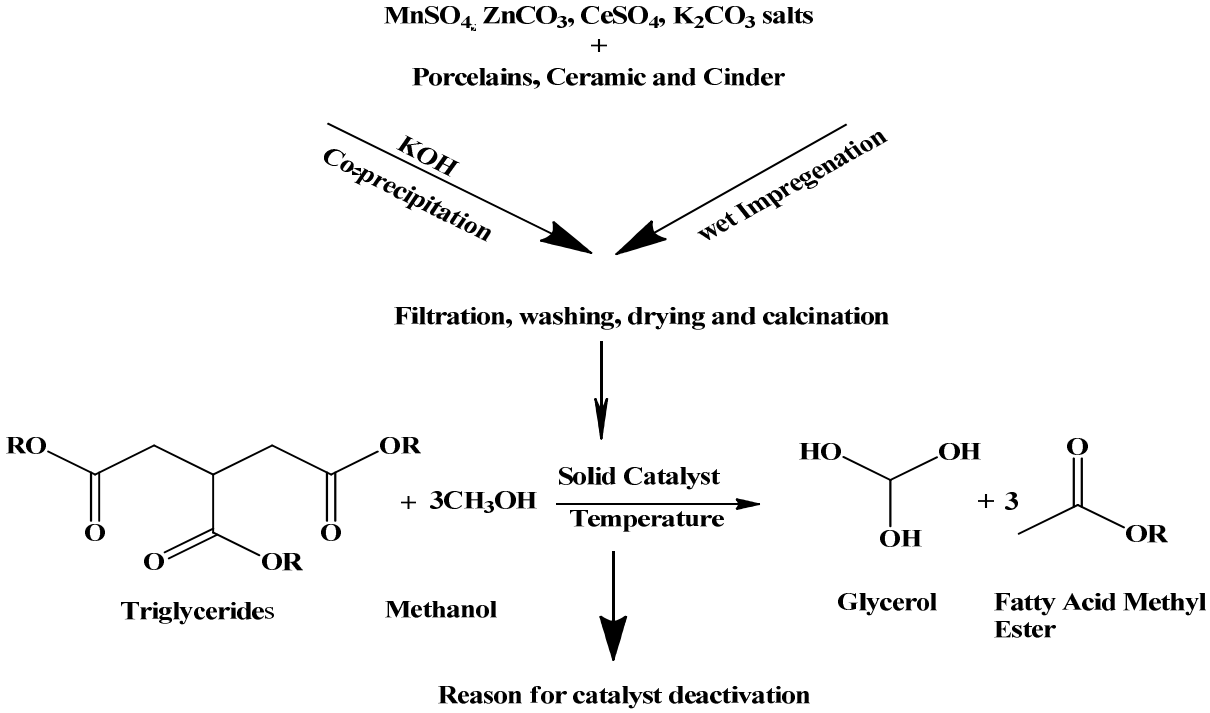

Fig.5. Schematic diagram

3.2. Trans-Esterification Reactions

Ester conversions were determined using procedure written in literature [29-31]. A 500 mL two neck glass flask fitted with condenser, paraffin oil bath and hot plate with a stirrer was used as the reactor.

The reaction temperature inside the reactor was measured with a thermocouple and was controlled by hotplate. For transesterification reaction, soybean oil, methanol and catalyst with certain amount were put into flask and then heated to the pre-set temperature (70°C). The reaction time was counted from the reactor reached the pre-set reaction temperature. After the expected reaction time (6h), the transesterification reaction was stopped and the product inside were poured into a beaker. After the reactions were done, mixture was filtered and TG conversion was analyses by using HPLC. This provided a detailed info about the catalyst activity and oil quality.

4. CONCLUSION

On the basis of analysis catalyst $CeSO_4$+$MnSO_4$+K_2CO_3(1:1:1), $MnSO_4$+K_2CO_3(1:1) $CeSO_4$+$MnSO_4$ supported on 20g cinder are batter then other catalyst to produce more efficient and economical biodiesel. It can be said that this research was successful endeavor. The comparative studies shows that all newly synthesis catalysts were performing efficiently

and were giving us an optimum yield at minimal conditions as compared to existing industrial expenses. Above given stats show that this method can me mass produced and can achieve success by ridding us of all the unnecessary water and catalysts wastes while improving oil.

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