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PRODUCTION OF BIO-DIESEL FROM PONGMIA PINNATA AND GUIZOTIA ABYSSINICA SEED OIL USING CRYSTALLINE MANGANESE CARBONATE ($MnCO_3$) AND NANO ZINC OXIDE (ZnO) – A GREEN CATALYSTS

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Abstract
Important aspects of commercial viability of biodiesel production depends upon the price of catalyst and feed stock. Crystalline manganese carbonate and Nano zinc oxide were found to be low cost, non corrosive and a versatile green catalysts. This communication explores the feasibility of biodiesel production from a plant Pongmia Pinnata and Guizotia abyssinica seed oils. Biodiesel, an alternate fuel has attracted considerable attention during the past decade as a renewable, biodegradable and non-toxic fuel. As a future prospective fuel, biodiesel has to compete economically with petroleum diesel fuels. One way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids. The availability and sustainability of sufficient supplies of less expensive feedstock will be a crucial determinant delivering a competitive biodiesel price. Recent food verses fuel controversy makes edible oil not an ideal feed stock for biodiesel production. In this competition the non edible oil sources are preferred as feed stock for the production of biodiesel. The use of the demand for biodiesel is expected to increase sharply in the near future. Increasing demand about global energy production and supply, environmental concerns due to the use of fossil fuels, rising petroleum prices may drive to search for alternative source of energy. Commercial viability of biodiesel production mainly depends upon the cost of catalyst and a diesel substitute. Moreover, biodiesel fuel has become more attractive because of its environmental benefits. In the present study, transesterification process involving methanol and seed oil of Pongmia Pinnata (Karanji) and

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Guizotia abyssinica were carried out. Crystalline manganese carbonate and Nano zinc oxide (25-40nm) were found to be a low cost, non-corrosive and a versatile green catalysts. The chemical composition of the biodiesel product was examined by GC-MS analysis. A comparative study of catalysts were studied, analyzed and reported for biodiesel yields. The effect of methanol quantity, catalyst properties, catalyst amount, reaction time and temperature on the production of biodiesel was determined. Important conclusions are presented.

Keywords: Transesterification process, Pongmia Pinnata, Guizotia abyssinica, Crystalline manganese carbonate and Nano zinc oxide, Fatty acid methyl esters, Bio-diesel, Green Catalyst.

I. Introduction:

Alternative fuels from the renewable source that are environmentally acceptable has been the focus ofextensive research in view of increasing demand for enrgy and environmental awareness.Bio-diesel an alternative renewable fuel substitute made from transesterification of vegetable oil with alcohol, has been accepted for use in blends with conventional petroleum fuel for transportation applications. However, even during times of shootup crude oil prices. soybean and rapeseed are common feedstock for biodiesel production in USA and Europe, respectively. Likewise, palm is being exploited in South East Asia [1]. It is estimated that even if all the edible oils are used for biodiesel production, even then they will not be sufficient in order to meet fuel demand [2]. In addition, it will lead to inflationary pressures in vegetable oil market. The energy demand of Indian industry is also increasing due to growing economic activities and India is not self sufficient in edible oils. Therefore, there is a need to find alternate feedstocks. In order to explore additional oil resources, the study on potential of pongmia pinnata and Guizotia abyssinica seed oils as bio-diesel resource is reported here.

Guizotia abyssinica is annual herbaceous plant cultivated in Ethiopia and India in rotation with cereals and pulses. The plant grows to a height of 0.5-1.5 m and maturtes in 110 to 120 days. The crop is widely adapted to all types of soil and is commonly grown in India on poor and acidic soils or on hilly slopes that are low in fertility. It requires moderate rainfall and grows in temperate and topical areas. Yield levels are reported to be 200- 300 kg/ha, although they can reach 500-600 kg/ha with good management. In north America and Europe, due to high oil content niger seed is considered as a primary energy packed food for the birds. Guizotia abyssinica seeds are sown in the spring season in warm and dry soils, enough for seed germination and emergence. The seeding rate vary from 5 to 10 kg/ha in Ethiopia and from 5 to 8 kg/ha in India [3] seeds are shinning black in appearance and are very light in weight as one-thousand –seed weigh 3- 5g. The seed contains about 30% oil with 25% oleic and 55% linoleic acid in fatty acid composition. Niger oil is used in manufacture of paints, soaps and as illuminant [4]. The seed is usually dried and used for oil extraction, while the protein rich meal, which remains after oil extraction is used as an animal feed manure or fuel, it is also used around the border of cereal field to prevent animal from damaging the cereal crop.

Biodiesel was produced from Niger oil by transesterification of crude oil with various catalysts. In many research publications, biodiesel is produced from the refined edible oil using menthol and alkaline catalysts. Alkaline hydroxides are the most effective transesterification catalysts as compared to acid catalysts. However the problem with alkaline catalyzed transesterification of vegetable oils is possible only if the acid value of oil is less than four[5] – high percentage of free fatty acid in oil reduces the yield of esterification process: such oils are mainly used for making low cost soap. The purpose of this study is to develop a method for transesterification of high FFA vegetable oils as it is considered as potential feedstock for biodiesel production. Heterogeneous pure manganese carbonate base catalyst has many advantages in biodiesel production, with vegetable oils containing high FFA[6]. Biodiesel fuel is considered to be the environmentally friendly fuel because of its renewability, high biodegradability, low pollutant emission, high flash point and excellent lubricity. It is well known that 3.2kg of CO_2 could be reduced by 1kg of biodiesel fuel atomization, incomplete combustion and carbon deposition on the injector and valve seats leading to severe engine problems, all this is due to the viscosity of vegetable oil that is greater than the viscosity of diesel oil. There are three well known procedures such as pyrolysis, cracking and transesterification processes to lower the viscosity of vegetable oil[7]. Transesterification is the chemical reaction between triglycerides and alcohol in the presence of the catalyst to produce mono esters. The long and branched chain triglyceride molecule are transformed to monoester and glycerides. Transesterification process consists of three consecutive reactions i.e., conversion of triglycerides to diglycerides followed by the conversion of diglycerides to monoglycerides. The overall transesterification reaction can be represented by the following.

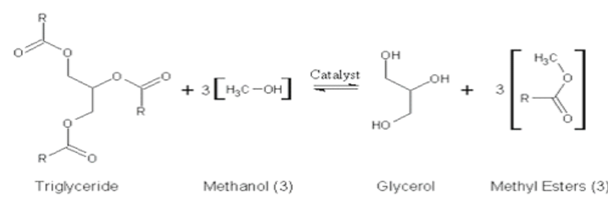

Figure.**1**:Transesterification of triglycerides with alcohol

The major factors affecting the conversion efficiency of the process are molar ratio, amount of catalyst and reaction time. The heterogeneous manganese carbonate base catalyst is active for high molecular weight alcohol achieving conversion to 90% and produces neither corrosion nor emulsion making it easier to separate the product obtained. The activity of manganese carbonate is similar with the traditional NaOH and H_2SO_4 catalyst under the reaction conditions [6].

Various attempts are being made for the search of new catalysts and vegetable oil sources in transesterification reactions, for the production of biodiesel [8-10]. Biodiesel synthesis using solid catalysts instead of homogeneous catalysts could potentially lead to cheaper production cost by enabling reuse of the catalyst. Biodiesel is produced by the transesterification of triglycerides of refined or edible and non-edible oils by using alcohol and alkaline catalyst.

The transesterification of oils is also carried out by solid super acids such as tungustated zirconia-alumina (WZA), sulphated tin oxide (STA) and sulphated zirconia-alumina (SZA), of which the WZA catalyst was the most effective achieving conversion >90% at temperature above 250^0C after 20 h [11]. Current industrial catalysts for bio-diesel are based on the basic catalyst mentioned above require pretreatment of the feedstock to remove impurities, water and the free fatty acids (which precludes the use of low quality feedstocks such as waste oils) [12,13]. They also lead to saponification (i.e. soap formation) of vegetable oil, which occur as an undesired side reaction and necessities lengthy after process separation procedures. These production steps negate the low price of the catalyst and are energy intensive. It is therefore necessary to develop new environmentally benign, inexpensive and effective catalysts which avoid the costly saponification reaction. A wide range of alternatives have been proposed but to date none are ideal. Manganese carbonate ($MnCO_3$) was found to be a versatile catalyst in transesterifiction reaction to produce monoalky1ester (biodiesel). In this communication manganese carbonate was found to be a versatile catalyst with 80% - 95% conversion rate in the production of biodiesel involving vegetable oils like palm oil, Rapeseed oil, groundnut oil, coconut oil and castor oil. Although palm oil and rape seed oil are extensively used for biodiesel production [14].

Along with the cost reduction factors for Bio-diesel production one should look at the greener side of the catalyst. The catalyst choosen in this process crystalline manganese carbonate and zinc oxide are versatile because they are easy to handle non-corrosive and produce good yields. The properties of vegetable oil can be improved to result in low viscosity and high volatility by either of the following methods.

Blending Micro emulsification Transesterification Thermal cracking. Out of these four methods Transesterification is widely used to reduce viscosity of vegetable oil. The conventional catalysts that are being used for Transesterification are corrosive and produce emulsification. Biodiesel fuel is made from vegetable oils, animal fats, and microbial oil (algae, yeast, bacteria, and fungi).The most common method of biodiesel preparation is the transesterification reaction, where the triglycerides present in oil react with monohydric alcohol in the presence of a catalyst, such as sodium hydroxide, sodium methoxide, potassium hydroxide, and potassium methoxide.

Biodiesel synthesis necessarily needs a catalyst to attain the equilibrium in a practical manner. Edible oil as a feedstock for biodiesel production is not encouraged since it is used for consumption it cannot be made commercial.. Acid catalysts take more time for biodiesel synthesis and are also corrosive in nature .Although alkaline catalysts take less time, they increasethe pH of the biodiesel, which thus requires thorough rinsing withwater to remove the left over catalyst, resulting in waste water generation and loss of methyl esters (MEs), and consequently resulting in the loss of yield. In future the demand for liquid fuels in transportation sector is going to increase rapidly than in any other sector.

To overcome the above constraints, research has focused on finding a suitable heterogeneous catalyst that could potentially lead to cheaper production cost by enabling reuse of the catalyst and gives a high yield and conversion without compromise. Hence much effort has been devoted to develop new biodiesel production processes by using cheaper feedstocks and catalysts which gives high yield.

Keeping in view the significance of non conventional feedstock for biodiesel production, an attempt has been made to produce biodiesel from pongmia pinnata and Guizotia abyssinica oil. since nano (10^{-9}m) catalysts are taking a significant place in every field major part of the experiments are carried out using certain nano catalysts.

II. Materials and Methods:

The Guizotia abyssinica seed were collected from Araku, Vaizag of A.P., Koraput, Orissa and hilly regions of Karnataka, India. Ash colored, crystalline manganese carbonate was purchased from Chemical Corporation of India, Mumbai. Methanol, chloroform, petroleum ether, sodium sulphate, and silica gel for TLC were purchased from Sarabhai Division. Fine Chemicals, Mumbai, India. Pongmia oil is purchased from local market in AfzalGunz, Hyderabad.

Experimental:

Oil extraction: The oil extraction process in the laboratory using soxhlet extractor and hexane as solvent is as follows. Finely ground seeds dried in oven at 100 °C for 2 h were subjected to extraction with hexane for a period of 24 h. Removal of solvent by rotary evaporation and drying afforded oil and yield is to be calculated on dry weight basis.

Analysis of oils:

The extracted oil is then subjected to Gas chromatography to find out the fatty acid composition. The samples should be analyzed with a gas chromatograph equipped with a split-split less injection system.

Name of fatty acid	Molecular formula	Percentage (%)composition
Palmitic	$C_{16}H_{32}O_2$	11.65
Stearic	$C_{18}H_{36}O_2$	7.50
Oelic	$C_{18}H_{34}O_2$	51.59
Linoleic	$C_{18}H_{32}O_2$	16.64
Eicosanioc	$C_{20}H_{40}O_2$	1.35
Dosocasnoic	$C_{22}H_{44}O_2$	4.45
Tetracosanoic	$C_{24}H_{48}O_2$	1.09

Table**2**: Fatty acid composition of Guizotia abyssinica oil [15]:

Nam of fatty acid	Percentage (%)composition
Palmitic (C16/0)	9.2
Stearic (C18/0)	10.1
Oleic (C18/1)	9.0
Linoleic (C18/2)	71.7

Catalyst Preparation:

Zinc oxide preparation by Sol-Gel Method:

Synthesis of ZnO nano powder is as follows: Zinc nitrate (0.5 M) and NaOH (1 M) solutions were prepared separately in 100 ml standard flasks. Sodium hydroxide solution was heated to 40^{o}C under constant stirring, the zinc nitrate solution was added slowly (drop wise for 30 min) to the NaOH solution. After 2 hours of stirring, the white precipitate deposited in the bottom of the flask was collected and washed several times with absolute ethanol and distilled water. The ZnO samples were obtained by dehydration of the precipitate. The obtained ZnO was calcined at 400^{o}C for 4 hours.

Reaction Mechanism:

Addition of zinc nitrate to NaOH solution results in the formation of Zn $(OH)_2$ colloids, as shown in equation 1. During this process, part of the Zn $(OH)_2$ colloids dissolves as shown in equation2. When the concentration of Zn^{2+} and OH^- reaches the super saturation degree of Zn $(OH)_4^{2-}$, ZnO nuclei will form according to equation 3.

$$Zn(NO_3)_2.6H_2O + 2NaOH = Zn(OH)_2(gel) + 2NaNO_3 + 6H_2O \quad (1)$$

$$Zn(OH)_2\ (gel) + 2H_2O = Zn^{2+} + 2OH^- + 2H_2O = Zn(OH)_4^{2-} + 2H^+ \quad (2)$$

$$Zn(OH)_4^{2-} = ZnO + H_2O + 2OH^- \quad (3)$$

Procedure:

Optimum conditions for catalyst to oil ratio and methanol to oil ratio were investigated. The crude oil was taken into the reaction fl ask and heated at 70^{o}C. The catalyst mixed in methanol at different concentrations was used for the conversion of extracted oil to FAME (Fatty Acid Methyl Esters).

Table**1**: Fatty acid composition of Pongmia pinnata oil data from literature.

The reaction conditions such as the amount of catalyst and the oil-methanol ratio were optimized. The transesterification reactions were performed in a 250ml round bottom flask with a reflux condenser, stirring was provided with a magnetic stirrer. This was set at a constant speed throughout the experiment. Initially, the oil was heated at a desired temperature. A known amount of catalyst was mixed in the required amount of methanol and was stirred separately for half an hour. This methanolic catalyst was then added to the round bottom flask containing oil and desired temperature is set.

Recovery of Catalyst

The catalyst thoroughly washed 4 - 5 times with water for 35 hrs. After complete drying, the catalyst was re-used for transesterification reaction. The obtained results showed

a catalytic efficiency of 95% and decreased after 7 times uses.

XRD of ZnO.

The most widespread use of x-ray powder diffraction, and the one we focus on here, is for the

- Identification of crystallinity of ZnO, by their diffraction pattern.
- Study of thermal expansion in crystal structures of ZnO using in-situ heating stage equipment.

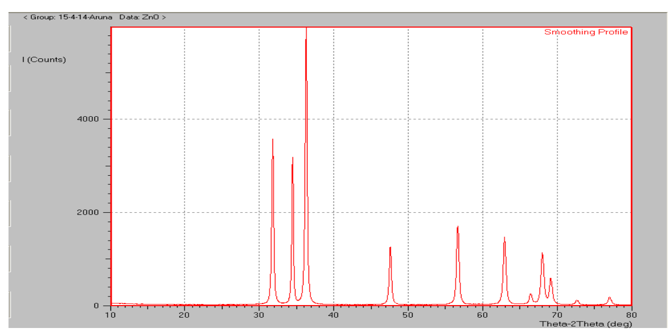

Figure.**2**: XRD of ZnO nano catalyst

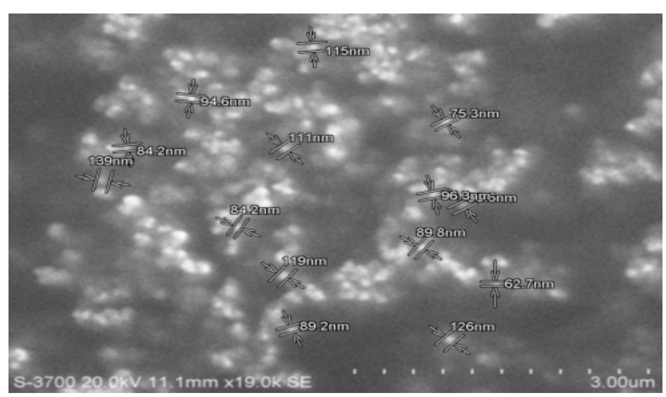

Figure.**3**: Scanning electron micrograph of ZnO

Analysis of Fatty Acid Methyl Esters:

The fatty acid methyl esters are analysed primarily using TLC test. In this test TLC glass plates are prepared by using chloroform, silica gel and glass plates. During the experiment the product sample is spotted along with raw material spot beside and it is allowed to run in petroleum ether (n-hexane) and then the spots are observed in iodine environment.

Gas chromatography:

Gas chromatography has been to date the most widely used method for the analysis of biodiesel due to its higher accuracy in quantifying minor component. The samples were analyzed with GCMSQP2010, SHIMADZU gas chromatograph equipped with a split-split less injection system. Helium was used as a carrier gas. The conditions of the instrument were: Column temperature 135^{o}C, injection temperature set at 250^{o}C, split flow (100ml/min),carrier flow rate 2.4123 ml/min .An FID detector is used with its temperature at 325^{o}C. The samples were prepared for analysis by adding approximately 0.05 g of FAME to 5 ml of n-Hexane. About 1ml of this mixture was put in to GC auto sampler vials. Two micro liters of the sample were injected into the column.

Following is the GC-MS of a sample:

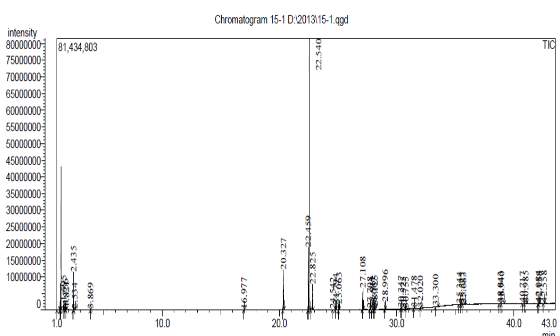

Figure.**4**: GC-MS of sample prepared from pongmia oil using manganese carbonate as catalyst

III. Results and Discussion:

Guizotia abyssinica oil

1. Effect of methanol to oil ratio:

Methanol to oil ratio is one of the most important variables in methyl ester production. Stoichiometrically 3 mol of methanol is required for each mole of triglyceride, but in practice large quantity of methanol is required to shift the equilibrium favorably.

Figure.**5**: shows that conversion increases directly with increase in methanol quantity at different catalyst to oil ratios. Excess methanol facilitates separation of glycerol from methyl ester phase. From Figure.**5** it may be concluded that use of methanol to oil ratio higher than 5:1 is not advantageous in terms of methyl ester yield, although it may facilitate easy separation of glycerine.

2.Effect of catalyst percentage:

In this work, the activity of $MnCO_3$ in Guizotia abyssinica oil transesterification was studied in the range of 0.5 to 3 wt% of the catalyst. The highest biodiesel yield - 95% was obtained at 1wt% catalyst (shown in Figure.6) in 180 min. A further increase of catalyst quantity shows decrease in biodiesel yield. All the reactions were carried out with 5:1 alcohol to Guizotia abyssinica oil molar ratio under reflux condition. It was observed that the yield of biodiesel decreases with increase in manganese carbonate quantity because of emulsification, which hinders the glycerin separation and reduces the ester yield. The yield of biodiesel increases with increased catalyst quantity at lower methanol to oil ratio. In practice, however, it was also observed that transesterification could not proceed well with an unsufficient amount of catalyst.

3. Effect of Temperature:

The reaction temperature is one of the main parameters which effect the biodiesel yield. This was studied in the range of 25-75°C at atmospheric pressure. The maximum yield was achieved at 65°C because of the emulsification of the glycerides by $MnCO_3$.

The methanol to oil molar ratio was 5:1 and the catalyst concentration was 1% in all the experiments. The temperature dependence of biodiesel yield is presented in Figure 7.

4. Effect of time:

For the complete conversion of oil to biodiesel during transesterification reaction, it must be stirred thoroughly at a constant rate. Experiments were carried out at a speed of 350-450 rpm between 30-180 min. The experiments showed that conversion of Guizotia abyssinica oil to biodiesel yield of 95% was achieved in 180 min at reflux condition. However, the reaction was carried out at the temperature close to the boiling point of methanol (60-68°C) at atmospheric pressure for a given time. As time increases, the yield of biodiesel decreases. The effect of reaction time on biodiesel yield is shown in Figure 8.

The same procedure is followed for Pongmia pinnata and their results are shown in Figures. 9,10,11,&12

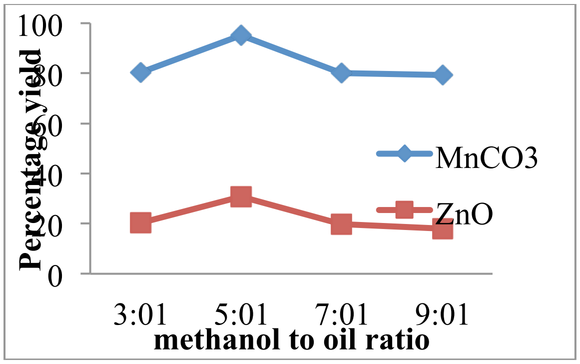

Figure.5: **Effect of methanol to oil ratio**

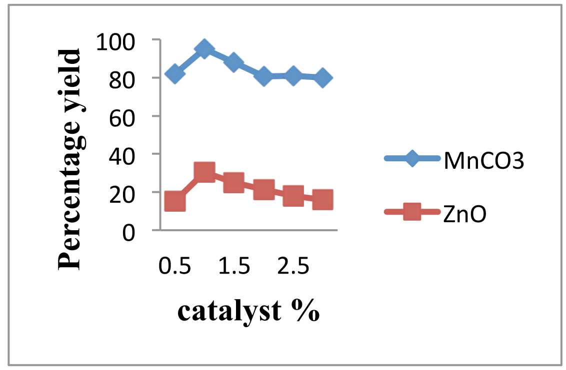

Figure.6. **Effect of catalyst percentage**

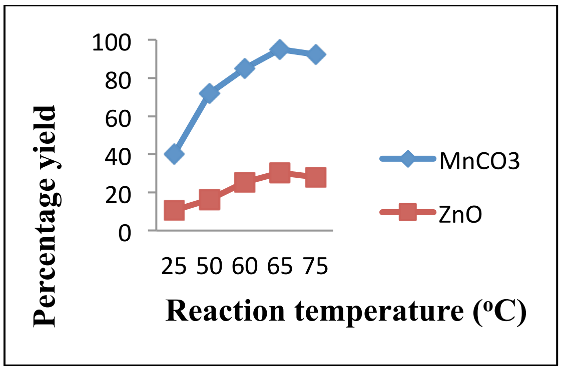

Figure.7. **Effect of Temperature**

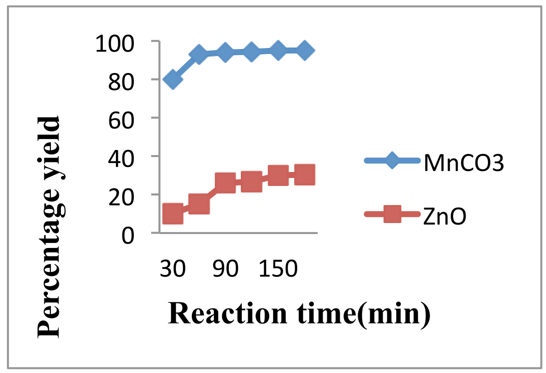

Figure.8. **Effect of time:**

Pongmia pinnata oil:

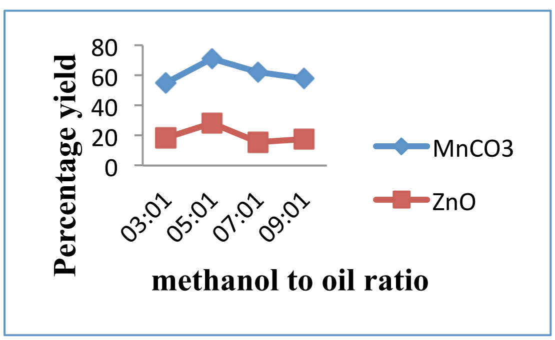

Figure.9. **Effect of methanol to oil ratio**

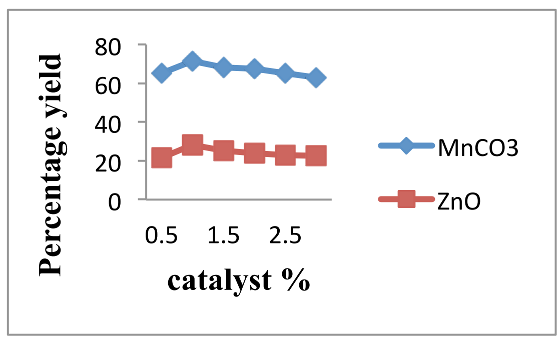

Figure.10. **Effect of catalyst**

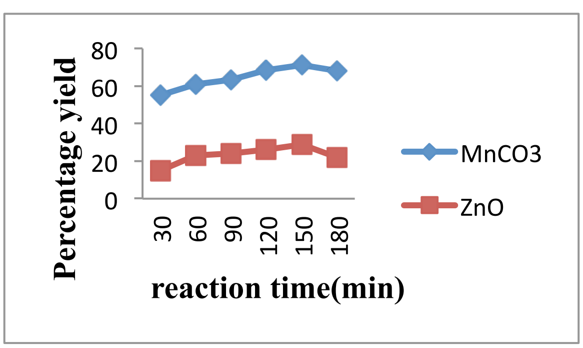

Figure.11. **Effect of Time**

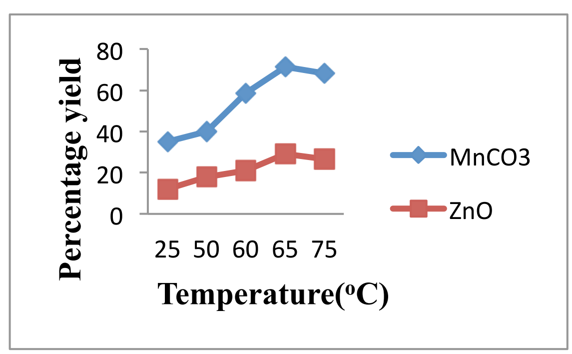

Figure.12. **Effect of Temperature**

IV. Conclusions:

- The results show that a 5:1 ratio of methanol to oil at 70^{o}C, and catalyst weight of 1% gives the highest yield(95%) of methyl ester phase for any oil(Pongmia and Guizotia) used.
- Manganese carbonate gave higher yield (i.e.,95%) than other catalyst used.
- Among nano zinc oxide and Manganese carbonate nano zinc oxide gave good yield.

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