Process Optimisation and Kinetics Study of Biodiesel Production from Dairy Waste Scum Using ZnO Heterogeneous Nanocatalyst

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Abstract. The present paper describes about the biodiesel production from diary waste using zinc oxide as a heterogeneous catalysts. The bio-oil from dairy waste scum was collected and used for biodiesel production. Zinc oxide nanostructures was synthesised by sol-gel method and characterised using particle size analyser, X-ray diffractometer and thermogravimetric analyser. The synthesised heterogeneous ZnO nanocatalyst was used for transesterification of dairy waste scum. The maximum biodiesel yield of 94.8% was obtained at the optimised reaction conditions, 0.8 wt. %, and methanol to oil molar ratio 9:1, reaction time 40 min, reaction temperature 65 °C, and mixing speed 300 rpm. The fatty acid methyl ester production reaction follows a first order reaction rate. This research work shows that synthesised ZnO nanocatalyst was an effective catalyst to produce biodiesel from dairy waste scum.

Key Words: Dairy waste, Scum oil, Transesterification, Kinetics, ZnO nanocatalyst.

1. Introduction

In the past decade, our environment has been polluted to a higher level, due to the increase in the consumption of non-renewable fuels. Consequently, Energy produced from non-renewable resources such as, coal and crude oil releases higher amount of toxic gases into the environment. These toxic gases can produce pollution creating activities resulted in global warming and ozone layer depletion [1]. The exhaust gases from vehicles and automobiles can also causes pollution in the environment. To minimize the pollution levels, alternative energy sources are preferred. These sources are locally available and causes lesser amount of gas emission. Such sources reduces pollution caused due to the chemical wastes and radioactive wastes [2]. Always, Renewable resources can provide clean and unlimited energy. Biodiesel is a long chain fatty acids comprising of mono methyl (or) ethyl esters. Biodiesel is a liquid fuel produced from oils, fats and lipids. These oils, fats and lipids are from renewable resources such as plants, animals and algae. Biodiesel can be used as a substitute for conventional petro diesel fuel. In a transesterification reaction, the triglycerides react with alcohol to form alkyl esters and glycerol as a byproduct. In the reaction mechanism, three moles of alcohol is required to react with one of triglyceride mole and form three moles of alkyl ester. It is a reversible reaction as shown in Eqn. 1. The reaction stoichiometry is 3:1 alcohol to oil. Usually alcohol is used in excess amount to shift the reaction equilibrium towards the product side [3]. Practically alcohol to oil molar ratio is more than 3:1 to increase the yield of the product.

$$TG + 3\,CH_3OH \xleftrightarrow{Catalyst} 3RCOOCH_3 + GL \qquad (1)$$

Biodiesel is non-toxic to the environment. It is a clean and completely burning fuel and also has high lubricity. The diesel engines can be directly fueled with biodiesel without any engine modifications. Biodiesel during combustion reaction produces lesser amount of air polluting substances compared to conventional diesel [4]. The word biodiesel itself implies that it is easily biodegradable and safer to the environment as it is from renewable resources. Biodiesel production activities encourages growth of local and rural economy. The production activity does not create any pollution. Several organizations promote the use of biodiesel. The physical and chemical properties of biodiesel matches with all international standards and it can be used directly (or) blended with diesel in any proportion from B0 to B100. The alternative fuels derived from oil from seeds, fat from animals and lipids from algae has a good scope in future due to the increasing pollution problems from petroleum resources. According to Knothe *et al.,* (2005), fueled an IC compression ignition engines with biodiesel proved that it is cleaner and safer than diesel [5]. The scarcity of fossil fuel motivates the researches to search a new biomass as a source of energy. The first generation feedstocks poses a threat to the food supply [6] and [7]. Anil Kumar Sarma *et al.,* (2005) reported that the preparation of biodiesel from Koroch (Pongamia glabra, another species under genus Pongamia) seed oil with 6:1 molar ratio and 1 g of $NaOCH_3$ [8]. Viscosity, density, cetane number, calorific value, IBP/FBP etc of resultant biodiesels was also evaluated. Vincent and Chakravarthi (2009) reported a novel method for improved manufacture of green biodiesel for which one or more solid metallic oxide base catalysts were selected from CaO, CaO-Al_2O_3, $CaTiO_3$, $BaTiO_3$, MgO-Al2O_3, Ti oxide, V oxide, Co oxide, Fe oxide, Hydrotalcite $Mg_6Al_2(CO_3)(OH)16.4H_2O$, Magnetite, Mg silicate and Ca silicate [9]. Kawashima *et al.,* (2009) reported that metal oxides of Ca, Mg and Zn are effective heterogeneous catalytic system for biodiesel preparation [10]. Research has been carried out in the field of CaO activity enhancement by pretreatment of CaO with methanol. The maximum yield of 90% was achieved when 0.1 g CaO was used as a catalyst. The most widely used heterogeneous catalysts for transesterification of triglycerides are metal oxides and mixed metal oxides. Kouzu *et al.,* (2008) investigated the catalyst activity of CaO, Ca $(OH)_2$ and $CaCO_3$ towards the transesterification of triglycerides of soybean oil and reported that CaO shows better activity [11]. Albuquerque *et al.,* (2008) synthesized MgO, CaO and tested for transesterification of ethyl butyrate [12]. Deepanraj *et al.,* (2017) reported biofuel from the blends of Jatropha (*Jatropha curcas*) and Karanja (*Pongamia pinnata*) oil were evaluated for their combustion properties. The biodiesel blends, the thermal efficiencies were 29.0% and 28.6%, respectively. The prolonged combustion was observed for Karanja oil blend in comparison to *Jatropha* oil blend [13]. Deepanraj *et al.,* (2012) reported performance and emission analyses for rice bran oil methyl ester (biodiesel) blends with diesel. The results reveal that blends of rice bran methyl ester with diesel up to 20% by volume (ZOBD) provide better engine performance and improved emission characteristics [14]. The present research work is mainly based on the biodiesel production from diary waste using a heterogeneous catalysts as ZnO.

2. Materials and Methods

2.1 Dairy Waste Scum Collection: The scum was collected from the area where the wash waters enter the effluent treatment section of the industry. Top layer is collected in glass beaker. Beaker was heated to a temperature of 60 °C to melt the fat into liquid phase. The heated oil was filtered to remove any suspended foreign particles from the sample. The Filtered oil was then centrifuged at 5000 rpm to remove water layer. The oil is then heated to remove any moisture content present in the oil.

2.2 Synthesis of ZnO nanocatalyst: The zinc Oxide nanoparticles was synthesized by sol-gel method. The zinc acetate and sodium hydroxide was used as precursors. 3 grams of $Zn(COOCH_3)_2$ was dissolved in 20 ml of deionized water. 15 ml of 0.1 M sodium hydroxide solution was prepared separately and poured dropwise into the zinc acetate solution under constant stirring for 30 minutes. After the addition of NaOH, 100 ml of ethanol was slowly added to the mixture and a white precipitate was formed. This precipitate was washed with distilled water and with ethanol. The ZnO

nanoparticles were obtained after drying at 110 °C for 10 hours. The synthesis of ZnO nanoparticles is chemically given by Eqn. 2.

$$Zn(CH_3COO)_2.2H_2O + 2NaOH \longrightarrow ZnO + 2NaCH_3COO + H_2O \quad (2)$$

2.3 Characterization of ZnO nanocatalyst: A Mastersizer laser diffraction particle size analyzer (Malvern Instruments, Worchestershire, UK) was used. About 0.1 g of nanoparticle was analyzed at ambient temperature (20±2 °C). Crystallographic analysis of the nanoparticles was obtained by an X-ray powder diffractometer STADI P (STOE) with Ge (1 1 1) monochromatized Cu Kα radiation (λ = 1.54187A˚). Diffraction data were collected at scanning speed of 2°/min over the 2θ range of 10-80°. XRD involves the diffraction of X-rays by the lattice of crystalline materials. In addition to the measurement of small crystallite sizes, X-ray diffraction can also be used to identify the crystalline phases, to measure the amount of those phases in the mixture, to determine crystal structures, and to determine the unit cell size of the crystalline material. Thermal stability of the nanoparticles was determined using TGA 7 (Perkin-Elmer) instrument operating in dynamic mode (heating rate = 10 °C/min under helium gas), was employed. The samples of less than 3 mg were placed.

2.4 Transesterification Reaction: A double necked one litre round bottomed reaction flask is placed over a magnetic stirrer with hot plate. One neck was used for reflux condenser and thermometer was inserted through the other neck to measure the reaction temperature. The heating mantle temperature can be adjusted as per the desired reaction temperature with a temperature controller of accuracy ± 0.5 °C. The magnetic pellet is taken inside the round bottom flask and the stirring speed of the reaction mixture can be adjusted with a control knob provided in the magnetic stirrer. The condenser is connected to a running water to reflux the methanol used. For each experimental study, the reaction flask was filled with 500 ml of dairy waste scum oil and then heated to the required reaction temperature. Transesterification reaction was conducted by the addition of a specified quantity of methanol and ZnO nanocatalyst. After addition of all reactants into the reactor, it was left undisturbed until the desired reaction time. The percentage of biodiesel yield was calculated by the volume of biodiesel produced divided by the volume of oil used, multiplied by 100.

3. Results and Discussion

3.1 Characterization Studies of ZnO Nanocatalyst

3.1.1 Nano Particle Size Analysis: The average particle size of the ZnO nanoparticle was found using the data from a particle size analyser. The size and intensity data was plotted as shown in the figure 1. The average particle size was 83.12 nm. This result shows that synthesised ZnO is crystalline in nature. The peak starts at 60 and ends at 100 nm which shows that the particle size is distributed between this specified ranges. The narrow peak indicates that the size range is not wider and all particles are similar in its dimensions and proves that the method used for synthesis process is good.

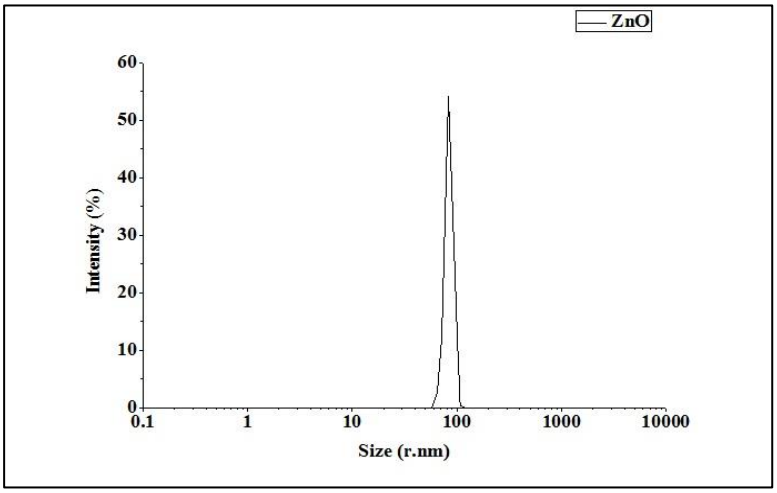

Figure 1: Particle Size Analyser for ZnO nanocatalyst

3.1.2 XRD Analysis: XRD patterns of the synthesized ZnO nanoparticles is shown in the figure 2. XRD pattern shoes that five different peaks were obtained at different 2 theta values. The highest peak is at angle 33.92° at (101) plane with 4781 intensity and at angle 36.40° with intensity 4085. These peaks corresponding to the standard peaks for ZnO nanoparticles as mentioned in JCPDS card no 36-1451. The sharper peaks shows that the particles are in nanosize as well as crystalline in nature. The crystalline structure of ZnO nanoparticles is again confirmed with these results.

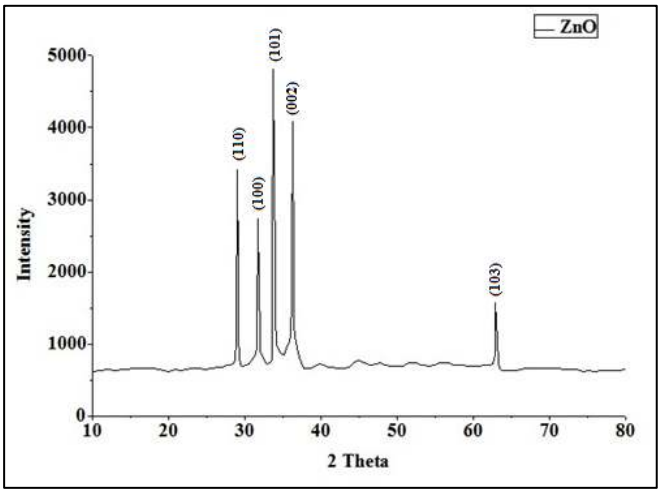

Figure 2: XRD Patterns for ZnO

3.1.3 Thermo-Gravimetric Analysis: The thermal stability of ZnO nanoparticles can be easily studied with the help of a thermogravimetric analysis. A plot between the temperature and the weight of the sample is shown in the figure 3. There is no weight loss till the temperature of 300 °C which indicates that the drying step was completely done and there is no moisture content in the nanoparticles. After 300 °C a sharp decrease of about 23% in the weight of the sample is due to the presence of zinc acetate precursor present in the sample. After this weight loss, the weight of the ZnO sample loaded is constant throughout the analysis which shows that it can withstand even at a temperature of 800 °C.

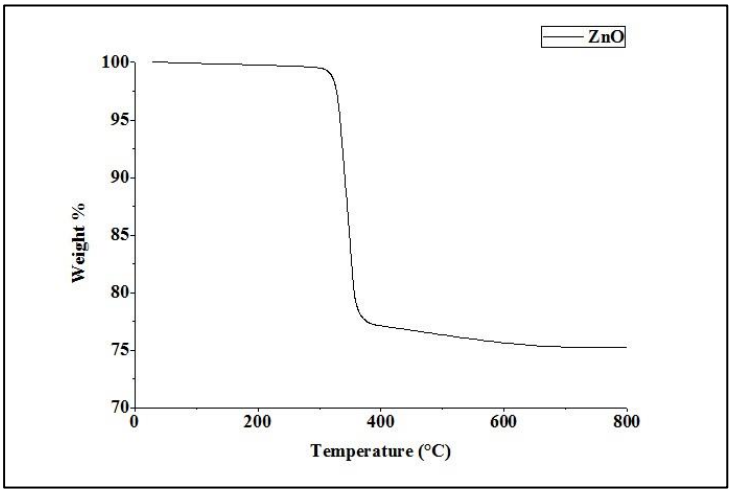

Figure 3: TGA Plot for ZnO

3.2 Biodiesel production

3.2.1 Catalyst optimisation: The catalyst quantity used in this reactions affects the reaction rate drastically though it doesn't alter the equilibrium conversion of the reversible reactions. If the catalyst is having more activity, less amount of the catalyst is required. In order to scrutinize the activity of ZnO catalyst, different weight ratios of catalyst to oil were used for the catalyst optimization studies of transesterification of a variety of mass ratios of catalyst to oil were used for transesterification process. Reactions were carried at constant parameters of reflux temperature, reaction time, molar ratio of methanol to oil and stirring speed. Figure 4 shows the effect of mass ratio of ZnO catalyst to oil on the transesterification reaction. 90.1% conversion was obtained when 0.8 wt. % of catalyst was used.

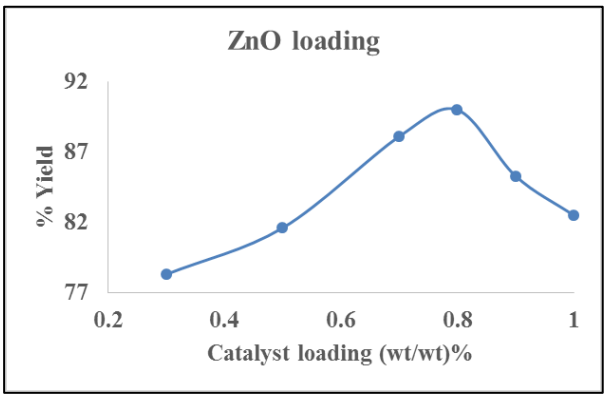

Figure 4: Effect of catalyst loading

3.2.2 Reaction temperature optimisation: The carbonyl activity of triglyceride have a tendency to improve its activity to initiate the reaction. The long chains of triglyceride restricts the carboxylic group activation. It is a complex reaction attained by the nucleophilic attack of the alcohol used. The carbonyl group activation can be done only at a temperature ranging the boiling point of methanol. Further, the reactions were conducted at different temperature using ZnO catalyst and with optimized values of catalyst loading. Figure 5 shows how the biodiesel yield varies at different

reaction temperatures. From this figure, it is clear that biodiesel yield increases with the temperature. Higher yields of biodiesel 92.4 wt. % was achieved at 65 °C for ZnO catalysed reaction.

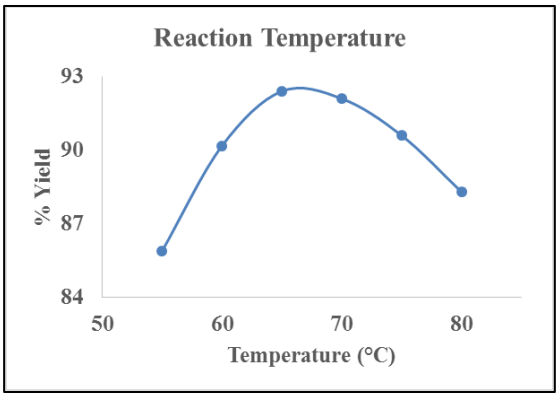

Figure 5: Effect of reaction temperature

3.2.3 Reaction time optimisation: The behaviour of reaction completion time was studied at different time intervals ranging from 20 to 70 min for ZnO catalysed reactions is shown in figure 6. The catalyst amount and reaction temperature values were previously optimized. The optimum conversion of 92.4 was observed at 40 min, when ZnO catalyst was used as a catalyst. When the reaction temperature increases, the rate of the reaction also increases and thus reducing the overall time consumed for the completion of reaction. Maximum biodiesel yield can be achieved if sufficient contact time is given for the reactants to collide [15].

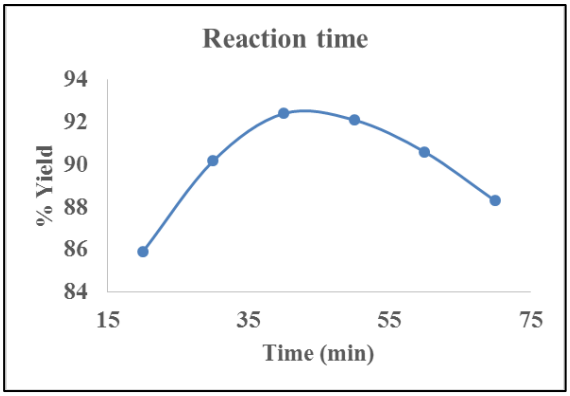

Figure 6: Effect of reaction time

3.2.4 Alcohol optimisation: The methanol to oil molar ratio is the most important parameter that influences the conversion of oil into ester. As per the stoichiometric calculations, 3 moles of methanol are required per mole of triglyceride. In practical, the molar relative amount of methanol is always maintained more than the stoichiometric ratio to drive the transesterification reaction to achieve complete conversion [16]. In this examination, the effect of molar ratio of methanol to dairy waste scum oil was investigated with different molar ratios of 3:1 to 15:1. Each reaction was run at individual optimized parameter values of catalyst concentration, reaction temperature and time for each catalyst. The changes in biodiesel yield according to the methanol oil molar ratio is shown in the figure 7. When ZnO catalyst was used, the conversion of triglyceride was observed as 94% at the 9:1 molar ratio of methanol to dairy waste scum oil with 40 min reaction time. The conversion of triglyceride was found to be increased with increase in molar ratio from 3:1 to 9:1. Further

increase in molar ratio from 9:1 to 12:1 leads to decrease in the conversion of triglyceride. This is due to the presence of mass transfer limitation during the transesterification reaction.

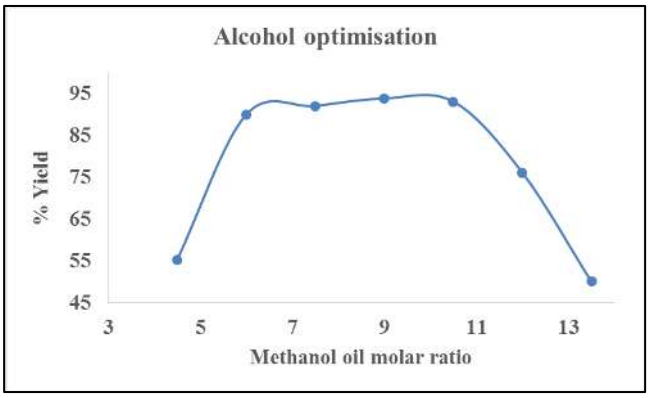

Figure 7: Effect of methanol oil molar ratio

3.2.5 Stirring speed optimisation: The experimental studies were done at different rpm, such as, 150, 200, 250, 300, 350 and 400 to optimize the stirring rate of the reactants. From figure 8 the mixing speed of 300 rpm produced 94.8% of FAME for ZnO catalyst. Therefore, 300 rpm mixing intensity can be maintained for dairy waste scum biodiesel production. Sivakumar et al. (2011) obtained similar results in stirring speed optimization studies [17]. They reported that 350 rpm mixing intensity was suitable for the production of dairy waste scum oil methyl ester.

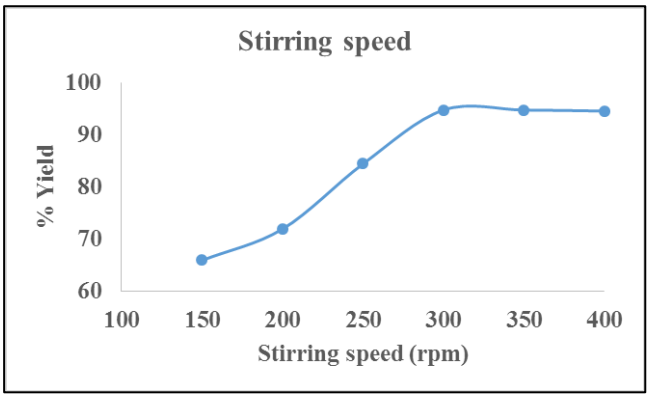

Figure 8: Effect of stirring speed

3.3 Kinetics of transesterification of dairy waste scum oil: The kinetic studies was carried out for the transesterification of dairy waste scum oil at the optimum reaction conditions. The reaction is based on first order and followed by the function of concentration of methyl ester. The rate constant of the reaction was determined based on the amount of the product take place at the reaction time interval [18]. In the present work, the increased amount of methyl ester reactant was selected for the kinetics study. Consequently the first order rate constant of the reaction was expressed in the Eqn. 3.

$$\boldsymbol{Rate} = \frac{\boldsymbol{d(ME)}}{\boldsymbol{dt}} \qquad (3)$$

Supplementary, a plot of dME/dt vs yield using log graph gives straight line involved in the transesterification reaction shows first order as shown in the figure 9. The R^2 value of the straight line found to be 94% good agreement and then additionally shows that the speed of reaction varies linearly with yield.

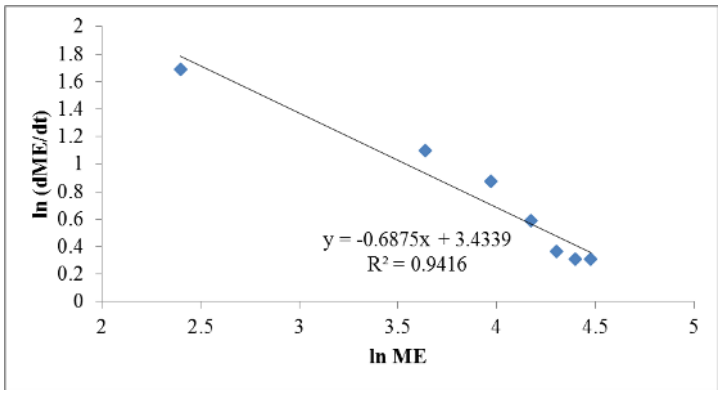

Figure 9: A linear graph reaction rate vs yield on logarithmic graph (%) for transesterification of dairy waste scum oil.

A plot relating ln k and inverse of temperature was plotted as shown in figure 10. This plot is used to determine the activation energy required using Arrhenius equation.

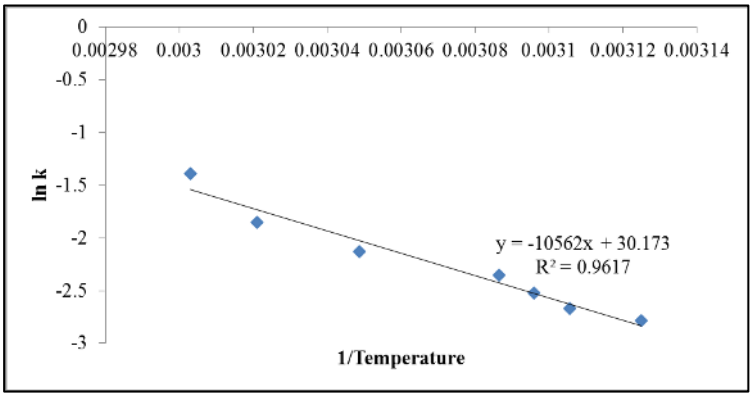

Figure 10: A linear graph of Arrhenius equation (ln k v/s 1/T)

Conclusion: The ZnO nanocatalyst was synthesised via sol-gel method and characterized using three different analysis. The synthesised heterogeneous catalyst was used to produce biodiesel from dairy waste scum oil. The transesterification reaction parameters were optimized and the optimum conditions are 0.8 wt. % ZnO nanocatalyst, 9:1 methanol to oil molar ratio, reaction completion time of 40 min, reaction temperature of 65 °C and stirring speed of 300 rpm. These conditions are similar to those reported previously [19] and [20]. The maximum yield of 94.8% was achieved when nano ZnO was used as a catalyst and the reaction follows first order kinetics.

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