

Transesterification of Waste Cooking (Vegetable)Oils for Glycerol Production:A Kinetic study

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ABSTRACT

In the present investigation the kinetics of transesterification of three wastecooking (vegetable) oils vizwaste soybean oil,waste groundnut oil andwaste sunflower oilwith methanolwere studied using KOH as catalyst. Transesterification of fatty acids generate fatty acid esters (biodiesel) and glycerol.The emphasis was given to the production of glycerol due to its high commercial value (may be utilized as raw material for variety of other valuable products). The transesterificationreaction was found to be second order when concentration of methanolwas limited.The effect of temperature on the conversion of glycerol werestudied and rate constant were determined for all threewaste cooking (vegetable) oils. The maximum conversion was achieved at 60°C in all cases. Upon comparison of values of % conversion of glycerol, rate constant and activation energy for the reaction, waste soybean oil transesterification was found to be better among all three waste vegetable oils studied with the 70% conversion to glycerol, higher rate constant and lower value of activation energy for thereaction.

Keywords: glycerol, kinetics,transesterification,waste vegetable oils.

I. INTRODUCTION

On the increasing demand of transportation fuel and its degradability concern with environment, biodiesel is accepted as an alternate and renewable fuel in place of crude diesel oil. Unfortunately its commercial production is low due to its high overall cost of production. There are some options to lower down the production cost of biodiesel and one of them is the use of cheap or waste substrates for its production and other is utilization of its by-product[1]. Waste raw material like waste frying vegetable oils(soybean,groundnut and sunflower) can be used for the production of biodiesel via transesterification reaction [2,3].

The glycerol is the main by-product generated during the manufacturing of biodiesel. A commercial biodiesel generate 87% glycerol, 9% water, 0.03% methanol, 1.26% Na, with 3,625 kcal/kg gross energy[4,5]. Approximately every 45.3 kg of biodiesel generate 4.53 kg of crude glycerol[6]. The low-priced glycerol thus generated may be used for production of high value products [7]like production of biosurfactant by microorganism used in detergent industry [8].

The kinetics of transesterification of vegetable oils have been reported by several authors [9,10]. However, very limited literature is available for the kinetic study of transesterification waste frying/cooking oils. The kinetic study is essentially required for any new set of reactants for the determination of rate constant, activation energy

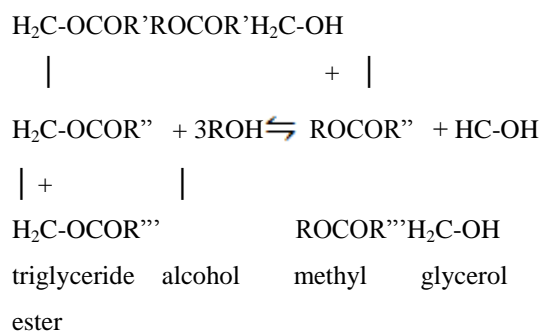
and conversion rate to final product. Finally kinetic study of the reaction is helpful in optimizing the production process and to remove or reduce undesirable side reactions/products.

1.1 Transesterification of oil

In the transesterification of oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol.

1.1.1 Base catalysed process

The following transesterification reaction of vegetable oils mediated by base catalyst is found rapid and beneficial in contrast to that with the acid mediated reaction [11]:



A number of kinetic studies on the transesterification of esters and vegetable oils with alcohol are reported in the literature [9,10,12]. These studies include, the determination of reaction rate constant, the equilibrium constant and the activation energy for the reaction. The existing methods include GLC [13], FTIR [14], NMR [15], measuring of refractive index [16], determination of hydroxyl group in glycerol [16], spectroscopic [17], viscosity methods [18,19] and pH monitoring [20]. Most of these methods require taking samples for off-line analysis or require expensive instruments and complex data analysis.

1.2 Theoretical Background

The transesterification of vegetable oil can be presented [12] as:



where TG, MG and GL represent triglyceride, diglyceride, monoglyceride and glycerol, respectively.

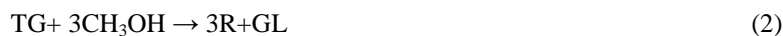
The overall vegetable oil transesterification reaction can be given [9] as:



where R represent fatty acid methyl ester (FAME).

In excess of methanol where the triglyceride is the limiting reagent, the reaction has been considered as pseudo-first order by most of the investigators [21,22,23]. However, when methanol is not in excess, the

transesterification may be considered a second order reaction and the rate constant may be determined from the following reaction type as the rate determining step:



The second order rate constant (k_{obs}) for this reaction may be given as,

$$K_{\text{obs}} = \frac{1}{t} \left[\frac{1}{(a-x)} - \frac{1}{a} \right]$$

$$\text{OR } \frac{1}{(a-x)} = k_{\text{obs}}t + \frac{1}{a} \quad (3)$$

where a is the initial concentration of TG while $(a-x)$ is the concentration of TG at any time t . Taking x as the weight % of glycerol at any time t , the remaining wt% of TG, i.e. $(a-x)$ at that time may be obtained.

According to equation (3) a plot of $1/(a-x)$ versus time will give a straight line with a positive intercept ($1/a$) and a slope (k_{obs}). Thus the value of second order rate constant (k_{obs}) may be evaluated.

1.3 Activation energy

The Arrhenius equation for estimation of activation energy [12] is given in equation 4:

$$K(T) = ATe^{-E_a/RT} \quad (4)$$

Where, K is the rate constant, E_a is the activation energy, R is the gas constant, T is temperature in Kelvin and A is frequency factor constant or also known as pre-exponential factor or Arrhenius factor.

The purpose of the present work was to use a simple method to study the kinetics of the transesterification especially of waste frying/cooking (vegetable) oils with alcohol. In present study the kinetics of the transesterification of three waste vegetable oils viz. waste cooking (vegetable) soybean oil (WSB), waste groundnut oil (WGN) and waste sunflower oil (WSF) with methanol in presence of KOH as catalyst have been studied.

II. MATERIALS AND METHODS

2.1 Materials

The analytical grade chemicals viz. potassium hydroxide, methanol, etc. were procured from Thomas Baker, Mumbai (India). Waste cooking soybean oil, groundnut oil and sunflower oil samples were collected from different sources (locally available hotels and fast food shops) and used as such.

2.2 Methods

250 ml of waste cooking (vegetable) oil (known weight) was heated at a temperature of $30^\circ \pm 0.1^\circ\text{C}$ in constant temperature bath. 2.5 g of potassium hydroxide (KOH) was dissolved in 50 ml of methanol. It was agitated till the catalyst (KOH) gets completely dissolved in methanol and then it was heated separately at same temperature at $30^\circ \pm 0.1^\circ\text{C}$. When both the solutions i.e. oil and (methanol+KOH) attained the temperature in water bath, the contents were mixed thoroughly. 60 ml of this mixture was measured and transferred to each of the four round bottom flasks fitted with condenser and placed in the same bath at $30^\circ \pm 0.1^\circ\text{C}$. After an interval of 10 minutes the first flask was withdrawn from the temperature bath assembly and kept in ice mixture to arrest the reaction. The second, third and fourth flask were withdrawn at time intervals of 20, 30 and 40 minutes, respectively. The mixture

was poured into separating funnel and allowed to stand for separating in two layers. The bottom layer of crude glycerol was collected and weight of glycerol was determined in each set of experiments.

The procedure was repeated as above at 40°, 50° and 60°C and % conversion of glycerol was determined. From the percentage conversion versus time data, the kinetic data i.e. the order of reaction, rate constants, and activation energy of reaction have been evaluated. All the experiments were performed in triplicate and the results shown are the mean of three independent experiments.

2.3 Characterization of Glycerol

The Characterization of glycerol obtained by transesterification of waste cooking (vegetable) oils was done by FTIR (Perkin Elmer Spectrum Version 10.03.06) and was compared with that of an authentic sample of glycerol. The viscosity (in accordance with ISO/DIS 3105, ASTM D 2515, ASTM D 446), density and surface tension of crude glycerol were estimated using automatic tensiometer (Kyowa Japan make, DY 500).

III. RESULTS AND DISCUSSION

3.1 Transesterification of waste vegetable oils

The crude glycerol obtained via transesterification reaction of three different waste cooking (vegetable) oils viz. waste soybean oil (WSB), waste groundnut oil (WGN) and waste sunflower oil (WSF). The waste cooking oils were collected from the nearby hotels and shops. In the presence of alkali (KOH) the transesterification reaction of methanol and waste cooking oils were carried out at different temperatures and the weight % of crude glycerol thus generated was determined. The weight % of crude glycerol produced via transesterification of waste cooking oils at different temperature are shown in Fig. 1a, 1b, 1c. The maximum conversion of glycerol was obtained from the transesterification of WSB at 60°C after 40 minutes and it was 5% more in comparison to that obtained from WGN and WSF at the same temperature and time of reaction. Above 60°C the conversion of glycerol was found to be lower (data not shown). This indicates that the rate of glycerol production increases as time increases. After 40 minutes an increase in % conversion of glycerol was negligible.

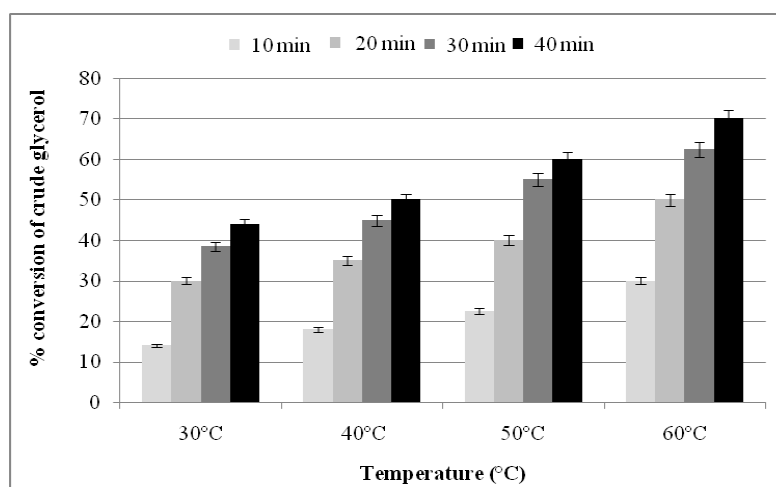


Fig 1a: % conversion of crude glycerol produced from transesterification of WSB at different temperatures.

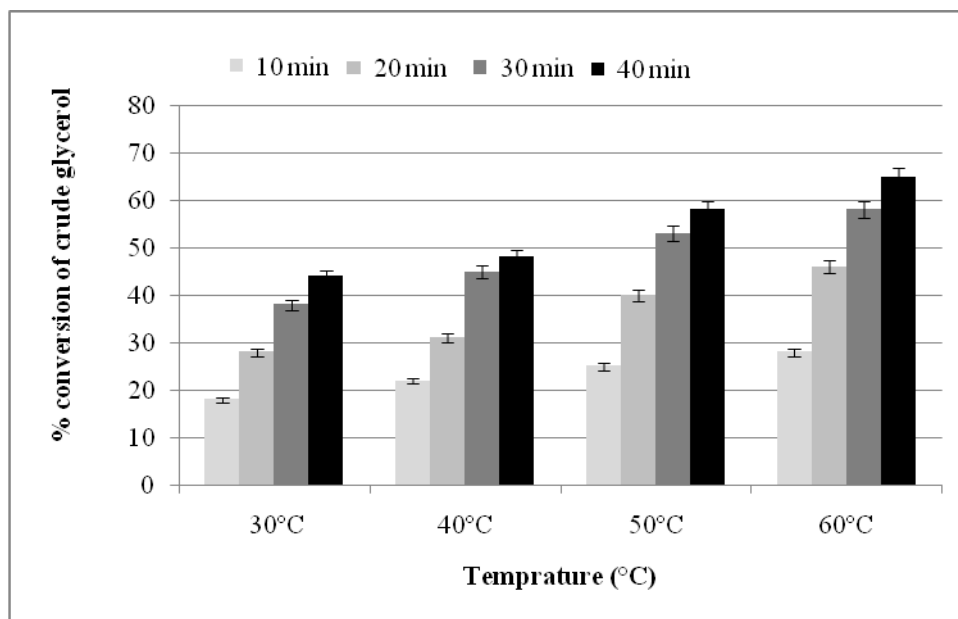


Fig 1b: % conversion of crude glycerol produced from transesterification of WGN at different temperatures.

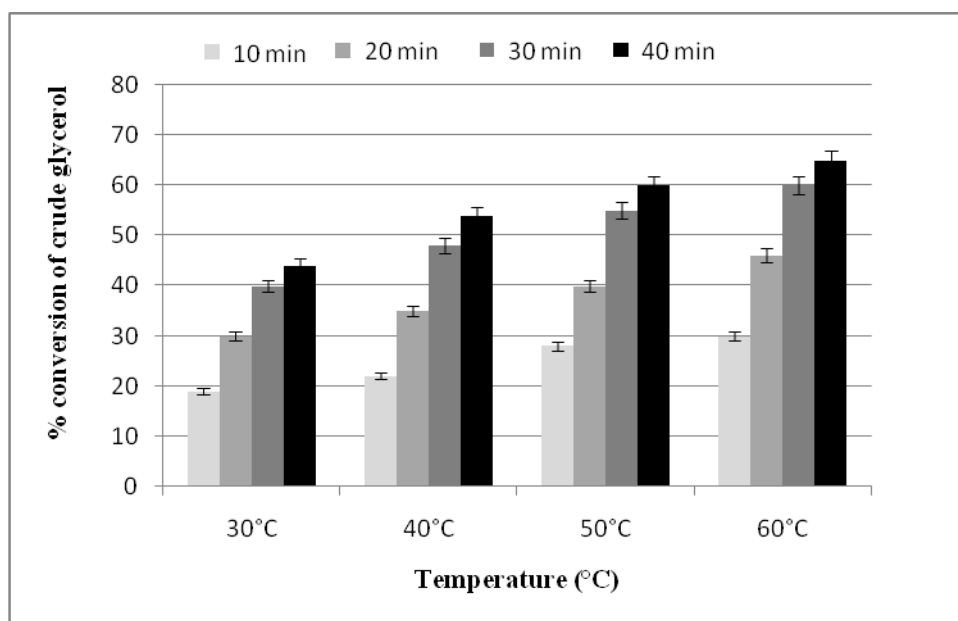


Fig 1c: % conversion of crude glycerol produced from transesterification of WSF at different temperatures.

3.2 FT-IR spectra

The Fourier Transform Infrared spectra of pure glycerol and transesterified crude glycerol are shown in Fig.2a and 2b. The band at 3300-3400 cm^{-1} was due to OH stretching modes of water and crude glycerol whereas the band at 1640-1650 cm^{-1} was mainly due to OH bending mode of water. The peaks around 2800-2900 cm^{-1} were due to the CH stretching modes of crude glycerol whereas the peaks between 1500-700 cm^{-1} were due to CH bending (1500-1200 cm^{-1}) and C-O stretching (1200-900 cm^{-1}) modes of glycerol. The peaks of crude glycerol

were confirmed by running the spectrum of pure glycerol that is shown in Fig.2a. Similar spectrum analysis was presented by[24].

The density, viscosity and surface tension of crude glycerol in each case were also determined and reported in Table 1. The viscosity, density and surface tension of glycerol obtained from transesterification of waste vegetable oils WSB, WGN, WSF were ranged between 14.5×10^{-3} to 16.4×10^{-3} mPa.s, 0.9179 to 0.9273 kg/cm³ and 31.09 to 32.10 mN/m respectively.

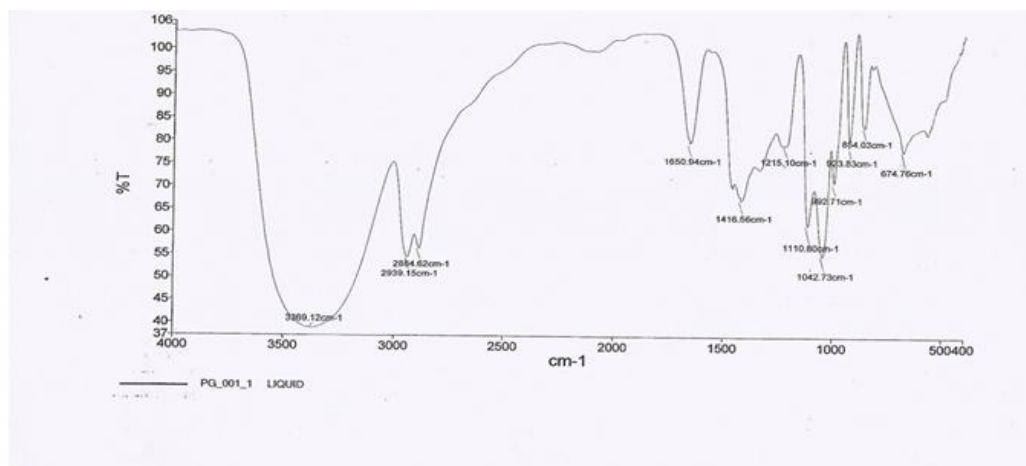


Fig 2a: FTIR spectrum of pure glycerol.

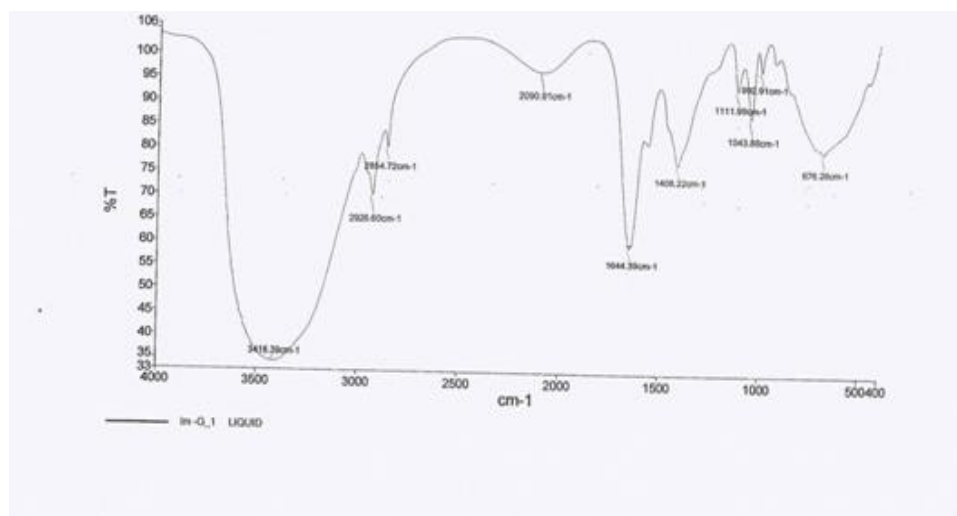


Fig 2b: FTIR Spectrum of crude glycerol obtained from transesterification of WSB.

Table 1: Density, viscosity and surface tension of crude glycerol obtained via transesterification of waste vegetable oils at 60°C.

Waste vegetable oil	Density (Kg/m ³)	Viscosity (mPa.s)x10 ⁻³	Surface tension (mN/m)
WSB	0.9273±0.0420	16.40±0.85	32.10±0.42
WGN	0.9179±0.0435	14.50±0.71	31.09±0.38
WSF	0.9212±0.0418	16.10±0.78	31.43±0.40

3.3 Determination of rate constant

The transesterification of Nigerian *Jatropha curcas* oil with butanol and found that the forward reactions obey second order reaction at 6:1 and pseudo first order at 30:1 [25]. In the present study it was assured that the transesterification reaction was irreversible with the order of two. To determine the rate constants for the conversion of crude glycerol, the plots of $1/(a-x)$ versus time plots should give a straight line passing through the origin. The second order plots i.e. $1/(a-x)$ versus time plots at different temperatures in case of WSB, WGN and WSF are shown in Fig. 3a, 3b, 3c respectively. These relationships are useful in a variety of ways, if we only know the concentration at specific time for a reaction and graph yields straight line, then the reaction must be second order. The second order rate constant have been evaluated by calculating the slope of the plot of $1/(a-x)$ versus time. The observed rate constant for glycerol conversion from transesterification of WSB, WGN and WSF were found to be 1.28, 1.13 and 1.26 L mol⁻¹sec⁻¹ respectively at 60°C.

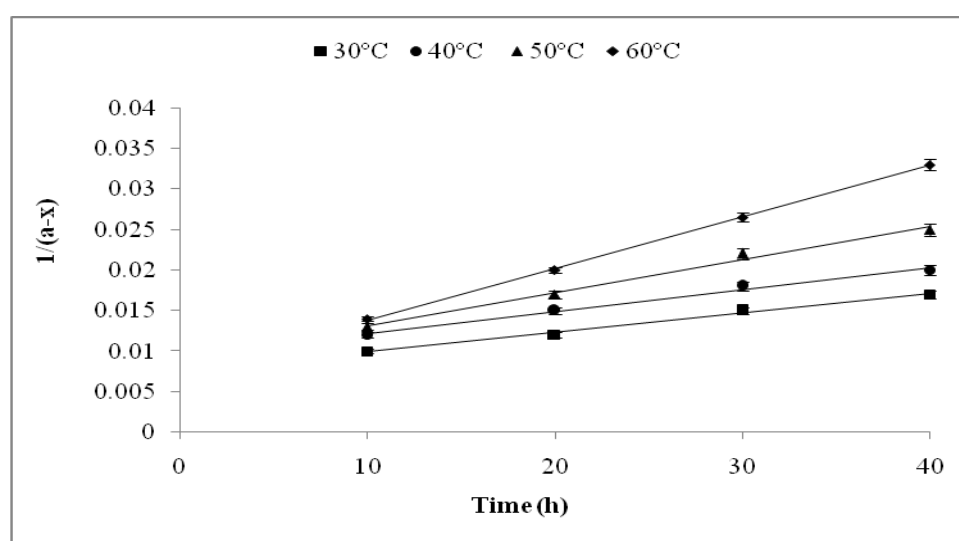


Fig 3a: Second order plots at different temperatures for production of crude glycerol in transesterification of WSB.

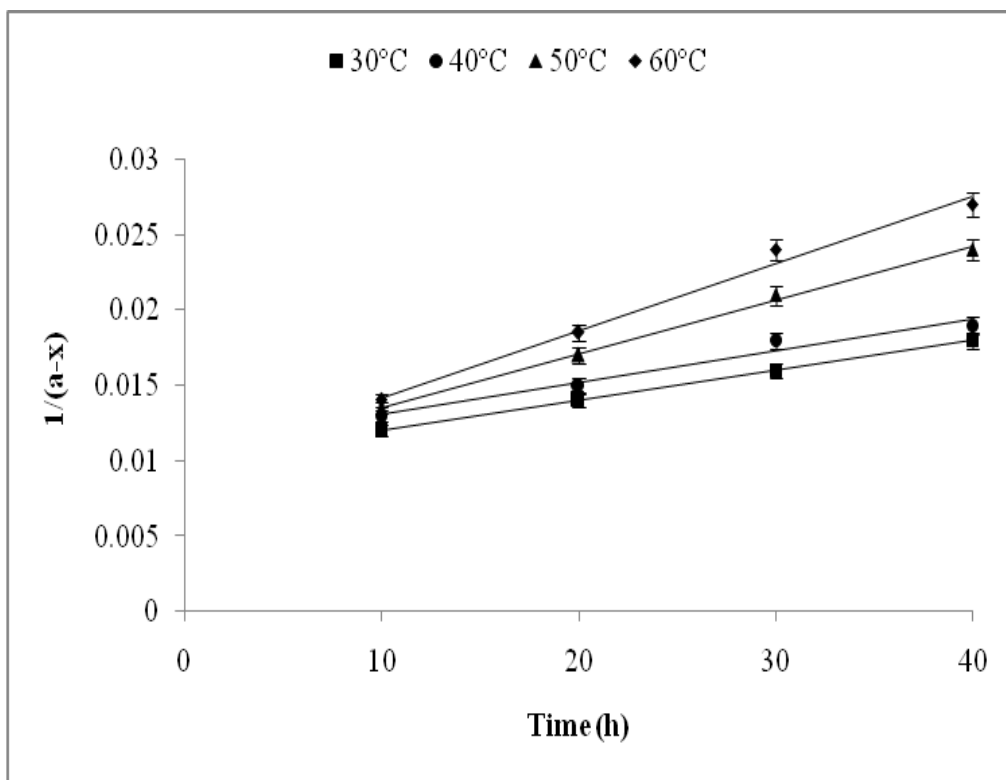


Fig 3b:Second order plots at different temperatures for production of crude glycerol transesterification of WGN.

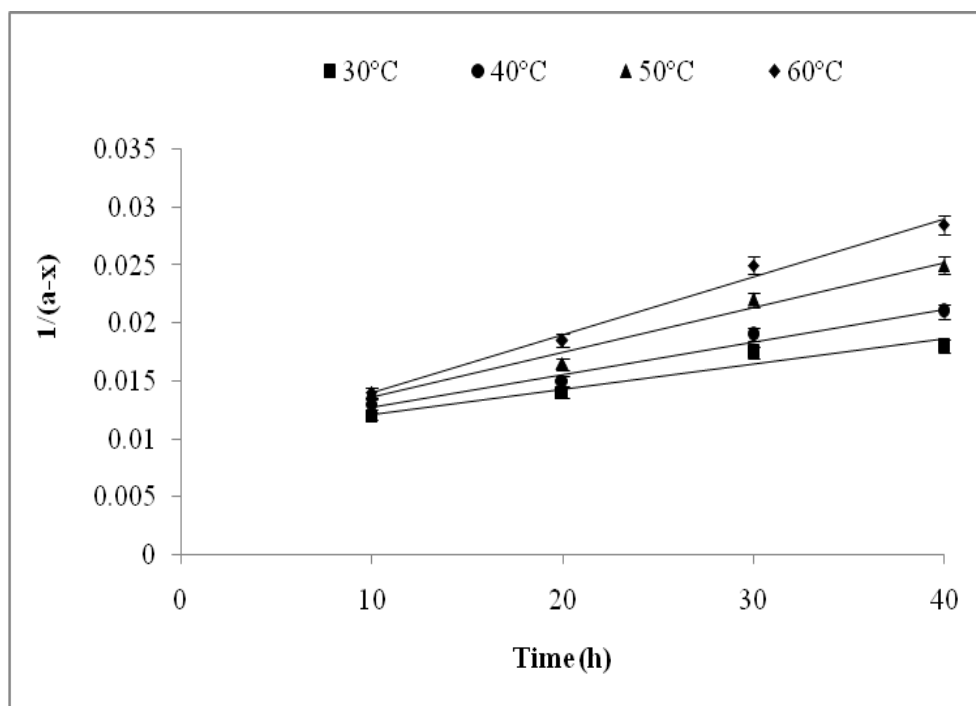


Fig 3c:Second order plots at different temperatures for production of crude glycerol in transesterification of WSF.

3.4 Determination of activation energy:

Activation energies were determined by the Arrhenius equation (Equation 4). The value of energy of activation in each case evaluated with the help of Arrhenius plot i.e. plot of $\log(k_{\text{obs}})$ versus $1/T$ (Fig 4). Activation energies of WSB, WGN, WSF for transesterification reactions in the present study were found to be 22.45 KJmol^{-1} , 23.18 KJ mol^{-1} and 27.00 KJmol^{-1} respectively. Activation energies reported by [25] ranged from 19.12 KJ.mol^{-1} to 34.92 KJ mol^{-1} for refined *Jatropha curcus* oil for conversion of triglyceride to diglyceride. The present results are similar to the existing literatures for the different transesterification studies. From Fig.4 it was observed that the activation energy of transesterification of WSB is the lowest among all the waste vegetable oils studied. Therefore, WSB was found a better source for the transesterification reaction to produce glycerol. Thus the kinetic study of transesterification of waste vegetable oils is useful for the studies like utilization of waste oil for the efficient production of valuable product like glycerol besides biodiesel.

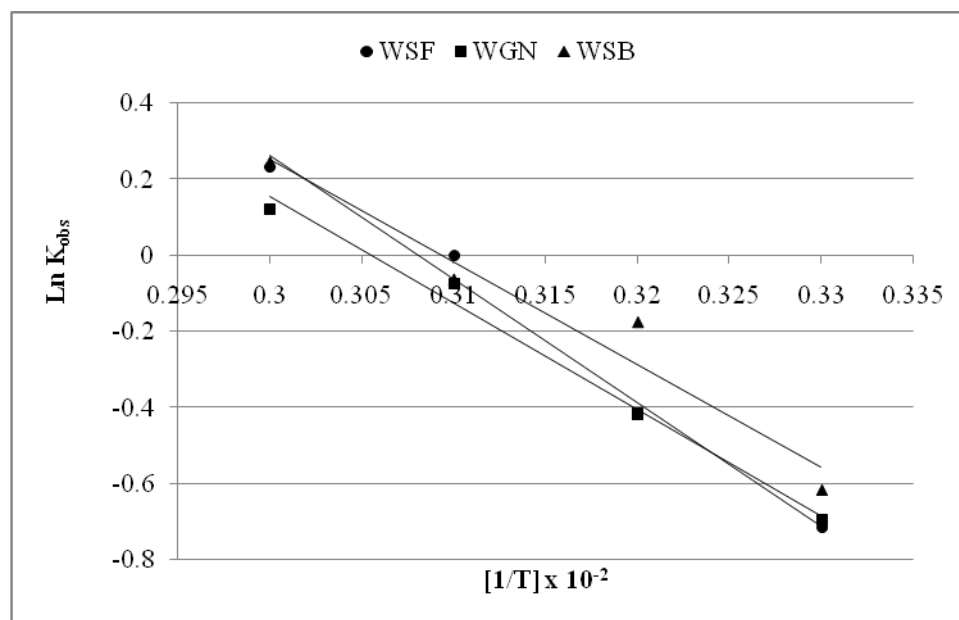


Fig 4: Arrhenius plots for production of crude glycerol in transesterification of waste cooking (vegetable) oils.

IV. CONCLUSION

In view of the above results, it was observed that when methanol is not in excess, the transesterification of waste cooking (vegetable) vegetable oils in presence of alkali behave like a second order reaction. Among the three waste cooking (vegetable) oils studied WSB was found to be more suitable for the conversion of glycerol via transesterification reaction using KOH as catalyst. At 60°C maximum conversion of glycerol was achieved with the rate constant 1.28 $\text{L mol}^{-1}\text{sec}^{-1}$ and the activation energy for the reaction was found to be 22.45 KJ mol^{-1} . This study is useful for further investigations on utilization of crude glycerol for the production of various value added products.

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