



KINETICS AND THERMODYNAMIC STUDIES OF BIODIESEL PRODUCTION FROM USED SUN FLOWER OIL

Manisha Mahatale^a, Sushil Kapoor^b, Dilip Patil^c

^aDept. of Chemistry, Janata Mahavidyalaya, Chandrapur-442401, M.S., India

^bDept. of Chemistry, Art, Commerce and Science College, Tukum, Chandrapur-442401, M.S., India

^cDept. of Chemistry, Govt. Institute of science, Nagpur-440001, M.S., India

Abstract

Kinetics of biodiesel production from used sunflower oil (USO) was carried out by potassium hydroxide as catalyst, prior to kinetics, optimum parameter under different reaction condition were determined. The condition, oil(100g), oil to methanol ratio (1:03, 1:04, 1:05, 1:06, 1:07, 1:08, 1:09 and 1:10) potassium hydroxide concentration (0.25wt. % , 0.50 wt. % , 0.75 wt. % , 1.00 wt. % , 1.25 wt. % , 1.50 wt. % , and 2.00 wt %) and temperature (35°C, 40°C, 45°C, 50°C, 55°C, 60°C, 65°C and 70°C) were used for optimization study. Chemical Kinetics of this reaction shows that it is pseudo first order reaction with respect to USO concentration with rate constant $7.72 \times 10^{-3} \text{ min}^{-1}$ at 60°C. The activation energy and Arrhenius constant is obtained by Arrhenius plot were 19.7 KJ^{-1} and $3.55 \times 10^{-3} \text{ min}^{-1}$ respectively. The other thermodynamic parameters such as enthalpy of activation (ΔH^\ddagger), entropy of activation (ΔS^\ddagger) and free energy of activation (ΔG^\ddagger) were 17.044 KJ g^{-1} , $797.6 \text{ JK}^{-1} \text{ g}^{-1}$, and $-248.56 \text{ KJ g}^{-1}$ respectively. The catalytic constant K_{KOH} for biodiesel production from USO is 4.75×10^{-3}

Keywords: Activation energy, Biodiesel, Kinetics, Pseudo first order, Sunflower oil

1. Introduction

Biodiesel is an eco-friendly, alternative fuel prepared from edible or non-edible vegetable oils and animals fat. These vegetable oils and animal fat are made up mainly of triglycerides. Those triglycerides when reacts with lower alcohol in presence of acid, alkaline and

enzyme catalyst results in biodiesel¹ i.e. long chain fatty acid alkyl ester²⁻⁵. These esters are very similar to petroleum derived diesel. It has following main advantage⁶⁻¹⁷ over petroleum based diesel: biodegradability, non-toxicity, low emission profile, reduced level particulates, carbon monoxide, sulfur oxide, atmospheric hydrocarbon and soot particles, environmentally beneficial and balance carbon dioxide cycle in atmosphere. Biodiesel is produced by alcoholysis of tryglycerides with methanol in presence of acid or base or enzyme as catalyst, with glycerol as by product¹⁸⁻²⁰. Several studies have been reported on the production of biodiesel in presence homogeneous catalyst such as sodium hydroxide (NaOH), sodium methoxide (NaOCH₃), potassium hydroxide (KOH), potassium methoxide (KOCH₃), sodium car carbonate (Na₂CO₃), potassium carbonate (K₂CO₃), and among heterogeneous catalyst, alkaline earth metal oxide^{21,22} and zeolites²³⁻²⁸.

Seed of high oil content, like sunflower oil, have attracted much attention over few decades as renewable energy source both because of its relative high yield and production. Hence, kinetic and thermodynamic study of production of biodiesel from used sunflower oil has been carried out in present investigation. Kinetics of this reaction is very important due to wide industrial uses of biodiesel. So the kinetics of this reaction has extensively been studied due to process design reaction²⁹⁻⁴⁰. Although this reaction has been known for some time, quantitative kinetic and thermodynamic data is still lagging behind.

In present study, there is no intention to describe the fundamental mechanism of the reaction or to analyze the product yield. Rather, in present work the focus is on the measurement of observed kinetic and thermodynamic parameter.

2. Materials and Methods

Materials:

The used sunflower oil was obtained from restaurants of Chandrapur City, of Maharashtra, India. To remove the impurities USO were sieved and filtered under vacuum pressure. Methyl alcohol of 99.9% purity was purchased from S. D. Fine chemicals, Mumbai and KOH pellets of 98.2% purity were from E. Merck.

Apparatus:

Three vertical-neck flat bottom (0.5L) was fitted with reflux water condenser, an internal digital temperature measurement probe and microcontroller based vertical type stirrer is used as reaction vessel.

Optimum parameter:

The optimum parameters for production of biodiesel from used sunflower oil were determined by measuring volume of biodiesel produced. Potassium hydroxide (0.25g to 2.0g) was added in various amount of methanol (10g to 33.3g). Dissolution of potassium hydroxide in methanol was ensured. This mixture was added in 100g of used sunflower oil and ratio of oil to methanol (1:03 to 1:10) was maintained. The reaction mixture was reflux at 35°C to 70°C for 15-120 minutes in 0.5L three vertical-neck flat bottom flask equipped with a reflux water condenser, microcontroller base stirrer and internal digital temperature measurement prob.

After refluxing for 15-120 minutes, flat bottom flask removed and mixture poured in a beaker and cooled suddenly. Then the reaction mixture was allow to stand overnight while phase separation occurred by gravity setting in pale yellow liquid biodiesel on the top with light brown glycerol at the bottom of the beaker. The used sunflower oil biodiesel was carefully decanted into a hard glass test tube leaving glycerol at the bottom of the beaker. The biodiesel was washed with water as explained by Alamu et-al.⁴¹

The procedure was repeated by varying parameters which controls the biodiesel production. In each case biodiesel yield was measured and recorded. The optimum

parameter determined were further used for kinetic study

Since the aim of the work is to determine the kinetic and thermodynamic parameters, the temperature stability and its measurement are more important. Hence high precision thermostat and digital temperature measurement probe were used in this study.

Kinetic Measurements:

Kinetic measurements were carried out at optimum parameters to determine the average reaction rate constant. 100g of used sunflower oil was added to the reaction flask placed in a thermostat. The tip of the temperature measurement probe was adjusted so that it is not struck by vertical stirrer bar. Previously stirred 1.0 g potassium hydroxide and 14.3 g of methanol was added in reaction flask containing oil. The reaction mixture was refluxed at 60°C; simultaneously stop was started. The reaction flask was removed and cooled suddenly at various time intervals (15 to 90 minutes) by carrying out numerous experiments. At each time interval biodiesel was obtained as explained earlier. From the volume of biodiesel weight of biodiesel was determined, the amount of biodiesel weight of biodiesel was determined, the amount of used sunflower oil reacted and unreacted were calculated.

The order of reaction was confirmed by different methods. Further, the pseudo first order reaction rate constant, activation energy, frequency factor (Arrhenius constant) activation entropy, activation enthalpy and free energy of activation were evaluated. Various amount of catalyst, i.e. potassium hydroxide (0.25 g to 2.0 g) was used to evaluate the catalytic constant.

3. Result and Discussion

Optimization parameter for biodiesel production:

Production of biodiesel from used sunflower oil was studied using various amount of potassium hydroxide (0.25 g to 2.0 g) in methanol with oil to methanol ratio of 1:07 (Table 1). Result show an increase in the biodiesel production to 95.00% with increase in amount of potassium hydroxide up to 1.00 g. There after a sharp decrease is observed in biodiesel production with increase in amount of potassium hydroxide, Use of 1.25 g, 1.50 g, 1.75 g and 2.00 g. of potassium hydroxide shows 90.00%, 86.00%, 82.00% and 78.00 %

production of biodiesel, respectively. Thus 1.00 g of potassium hydroxide is an optimum amount. Biodiesel production was carried out at 1.00g of potassium hydroxide, 1:07 oil to methanol ratio and temperature 60° C by varying the reaction time from 15 minutes to 120 minutes. It was found that the percentage yield of product increases 65.00% to 95.00% upto 90 minutes. After 90 minutes it decreases to 85.00 % at 120 minutes. It indicates, 90 minutes as optimum reaction time (Table 2).

The reaction temperature was varied from 35° C to 70°C. It was noticed that the maximum yield of biodiesel was obtained at 60°C. Above 60°C the percentage yield decreases. Similarly the biodiesel production was studied at various oil to methanol ratio. It was found that 1:07 is the highest ratio for biodiesel production (Table -2).

Kinetics of biodiesel production:

The kinetics of biodiesel production was carried out at optimum parameters. The study was undertaken on the basis of amount of biodiesel produced. From the weight of biodiesel produced the amount of used sunflower oil reacted and

unreacted were evaluated. The kinetics of biodiesel production is treated as pseudo first order reaction. Thus the equation of biodiesel production kinetics can be given as below:

$$-\frac{d[\text{USO}]}{dt} = k [\text{USO}][\text{methanol}] \quad (1)$$

Due to excess amount of methanol, the equation can be reduced as follow :

$$-\frac{d[\text{USO}]}{dt} = k' [\text{USO}] \quad (2)$$

If the initial amount of used sunflower oil is expressed as $[\text{USO}]_0$ and amount at some time interval is expressed as $[\text{USO}]_t$, then integral of equation (2) can be written as :

$$\ln \frac{[\text{USO}]_0}{[\text{USO}]_t} = k't \quad (3)$$

The amount of USO is expressed as weight. Therefore, the expression of $[\text{USO}]_0/[\text{USO}]_t$ where $[\text{USO}]_0/[\text{USO}]_t$ are initial weight and weight at some time interval, respectively. Thus equation (3) can be simplified as follow:

$$k' = \frac{2.303}{t} \log \frac{[\text{USO}]_0}{[\text{USO}]_t} \quad (4)$$

From equation (4), observed rate constant, k , at each time interval was determined and finally average rate constant was evaluated.

Order of reaction

The order of reaction was determined by different methods. The order of reaction was determined by carrying out kinetics of biodiesel production at optimum conditions set previously. The reaction was carried out by changing the amount of reactant. The amount of biodiesel produced was determined at particular time interval. The data is recorded. It was observed that if the differences in consecutive values of weight of initial weight of reactant are similar then the reaction follows zero order kinetics. If the differences in consecutive values of natural logarithm of weight of reactant are similar then the reaction is of first order nature. On the other hand, if the differences in the consecutive value of natural logarithm of reciprocal of weight of reactant are similar then the reaction is of second order. Data shows similarities between the consecutive values of natural logarithm of reactant weight and proves the first order nature of biodiesel production (Table. 3).

The rate equation of first order reaction is

$$k = \frac{2.303}{t} \log \frac{[\text{USO}]_0}{[\text{USO}]_t};$$

if this equation is rearranged as $\log [\text{USO}]_t = -kt/2.303 + \log [\text{USO}]_0$, mathematically it is an equation of the type $y = m x + c$. when the graph was plotted between $\log[\text{USO}]_t$ and time in minutes a straight line with negative slope is obtained which proves the first order nature of the reaction (Table-4 and figure 1).

Similarly, when the above equation is rearranged as

$$\log \frac{[\text{USO}]_0}{[\text{USO}]_t} = -\frac{kt}{2.303},$$

mathematically, it is an equation of the type $y = mx$. when the graph is plotted between $\log \frac{[\text{USO}]_0}{[\text{USO}]_t}$ and time in minutes,

a straight line passing through origin is obtained. This again confirms the first order nature of biodiesel production reaction (Table.5 and figures. 2).

The amount of methanol used was in large excess and its weight was not altered in reaction. Thus the reaction is a pseudo first order reaction.

Our result shows that production of biodiesel from used sunflower oil is a first order reaction with respect to used sunflower oil weight, as the weight of methanol does not change appreciably as the reaction proceeds.

The average reaction rate constant recorded is $7.72 \times 10^{-3} \text{ min}^{-1}$ at 60°C . The average reaction rate constant is evaluated at various temperatures i.e. 35°C to 70°C (Table .6).

On increasing reaction temperature upto 60°C , the average rate constant of the reaction increases upto $2.82 \times 10^{-3} \text{ min}^{-1}$. After 60°C the average rate constant decreases to $2.60 \times 10^{-3} \text{ min}^{-1}$ at 70°C . Thus optimum condition obtained at 60°C for the average rate constant of reaction.

Kinetics parameters of biodiesel production:

The average rate constant for biodiesel production from used sunflower oil were determined at temperature ranging from 35°C to 70°C . The Arrhenius equation, $k = Ae^{-E_a/RT}$ is used to evaluate activation energy. Where k is the average rate constant of biodiesel production, A is the frequency factor (Arrhenius constant), R is the gas constant and T is the temperature in Kelvin. Taking natural logarithm on both sides of Arrhenius equation,

$$\ln k = -E_a/RT + \ln A \quad (5)$$

This is an equation of straight line. The Arrhenius plot can be drawn using values of natural logarithm of average rate constant versus $1/T$. The activation energy obtained from the slope is 19.7 KJg^{-1} (Table. 6 and Figure 3)

From intercept of the plot Arrhenius constant is found to be $3.55 \times 10^{-3} \text{ min}^{-1}$.

Thermodynamic parameters:

The thermodynamic parameters such as activation entropy and activation enthalpy were evaluated using the general form of Eyring- polanyi equation⁴²:

$$k = k_b T/h e^{\Delta G^\ddagger/RT}$$

Where k is average rate constant of biodiesel production, k_b is the boltzman constant, T is the temperature in Kelvin , h is the plancks constant, ΔG^\ddagger is the free energy of activation and R is the gas constant. As $-\Delta G^\ddagger = -\Delta H^\ddagger + T\Delta S^\ddagger$ by substituting and rearranging, the equation can be converted to straight line equation as follow;

$$\ln k/T = -\Delta H^\ddagger/R \cdot 1/T + \ln k_b/h + \Delta S^\ddagger/R \quad (7)$$

Plotting the graph of $\ln k/T$ versus $1/T$ gives straight line with slope $\Delta H^\ddagger/R$ and intercept $\ln k_b/h + \Delta S^\ddagger/R$ from which ΔS^\ddagger and ΔH^\ddagger can be evaluated. The activation entropy and activation enthalpy obtained are $797.6 \text{ JK}^{-1}\text{g}^{-1}$ and 17.04 KJg^{-1} respectively (Table 7. and figure 4). The value of free energy of activation is determined by using the equation $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ at 60° and found to be -248.56 KJg^{-1}

Table. 1: Optimum amount of potassium hydroxide

Weight of sunflower Oil : 100 g

Oil to methanol ratio : 1:07

Temperature : 60°C

Amount of potassium Hydroxide /g	Volume of biodiesel /ml	% yield
0.25	65.00	65.00
0.50	75.00	75.00
0.75	85.00	85.00
1.00	95.00	95.00
1.25	90.00	90.00
1.50	86.00	86.00
1.75	82.00	82.00
2.00	78.00	78.00

The optimum amount of potassium hydroxide = 1.0 g.

Table 2 : Kinetics of biodiesel production from used sun flower oil : optimum parameters

Sr. No.	Parameters	Optimum value
1	Amount of used sunflower oil	100 g
2	Reaction time	90 minutes
3	Oil to methanol ratio	1:07
4	Weight of potassium hydroxide	1.0 g wt%
5	Temperature	60°C

Table 3 : Kinetics of Biodiesel production from used sunflower oil : order of reaction

Weight of used sunflower oil	: 100 gm
Oil to methanol ratio	: 1:07
Weight of potassium hydroxide	: 1.0 wt %
Temperature	: 60°C

Time /Min	Amount of oil Reacted /g	Amount of Oil unreacted /g [A]	ln [A]	Difference in successive ln [A]
0	-	100	4.6052	-
15		92.26	4.5246	0.0806
30		84.53	4.4371	0.0875
45		77.63	4.3519	0.0852
60		71.45	4.2690	0.0829
75		65.46	4.1814	0.0876
90		60.25	4.0985	0.0829

Difference in successive ln [A] is almost constant

Table : 4 Kinetics of biodiesel production from used sunflower oil : order of reaction

Weight of used sunflower oil	:	100g
oil to methanol ratio	:	1:07
Weight of potassium hydroxide	:	1.0 wt %
Temperature	:	60°C

Time / min	[USO]t /g	log [USO]t
0	a=100	2.0000
15	92.26	1.9650
30	84.53	1.9270
45	77.63	1.8900
60	71.45	1.8540
75	65.46	1.8160
90	60.25	1.7800

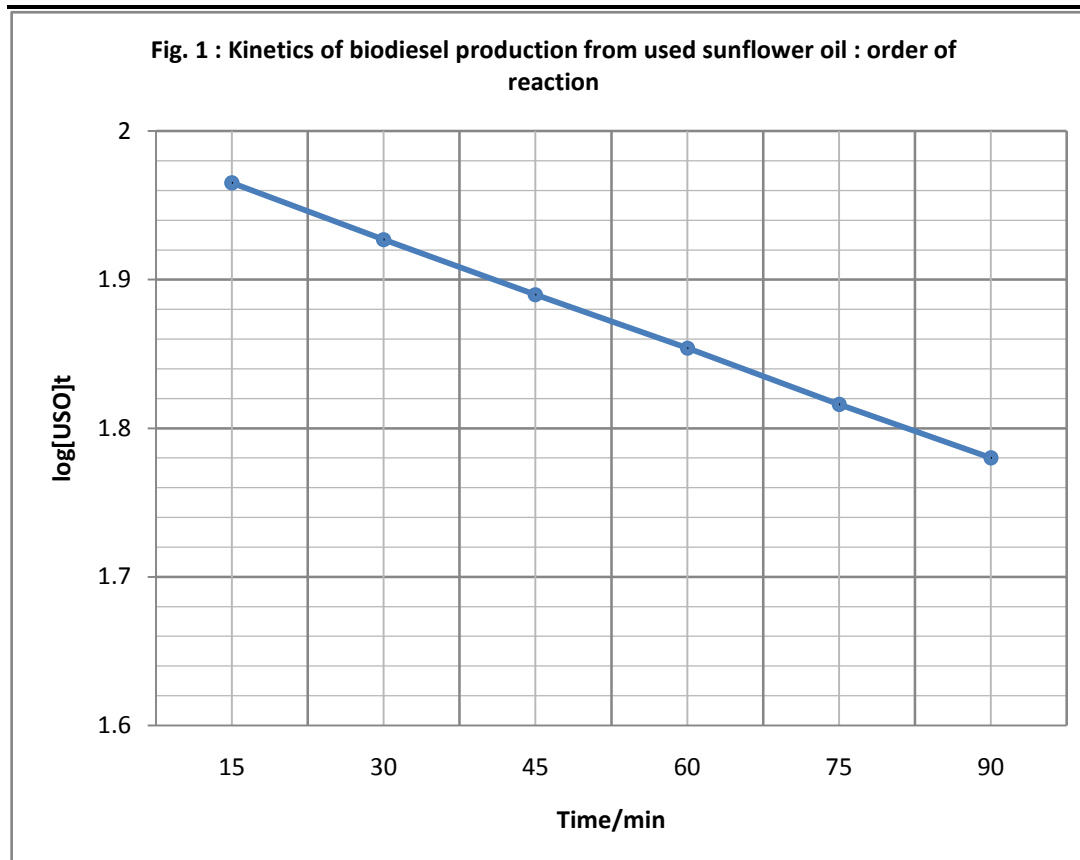


Table : 5 Kinetics of biodiesel production from used sunflower oil : order of reaction

Weight of used sunflower oil	:	100g
oil to methanol ratio	:	1:07
Weight of potassium hydroxide	:	1.0 wt %
Temperature	:	60°C

Time / min	[USO]t /g	[USO] / [USO]t	log [USO]0 / [USO]t
0	[USO]0=100	1.0000	00.00
15	92.26	1.0839	0.0350
30	84.53	1.1830	0.0728
45	77.63	1.2882	0.1099
60	71.45	1.3996	0.1460
75	65.46	1.5276	0.1840
90	60.25	1.6597	0.2200

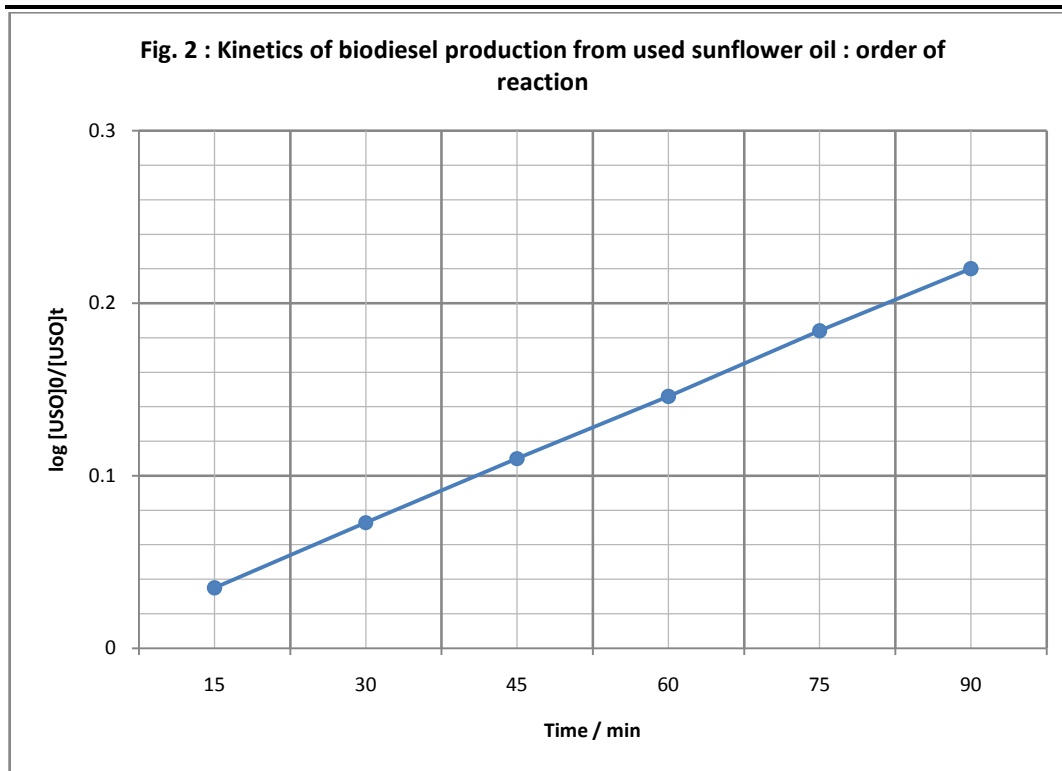


Table : 6 Kinetics of biodiesel production from used sunflower oil : activation energy.

Weight of used sunflower oil : 100g
 oil to methanol ratio : 1:07
 Weight of potassium hydroxide : 1.0 wt %

Temperature t/°C	T/K	Average rate constant k/10 ⁻³ min ⁻¹	1/T/ 10 ⁻³ k ⁻¹	ln k
40	313	5.68	3.19	-5.17
45	318	6.14	3.14	-5.09
50	323	6.70	3.09	-5.00
55	328	7.21	3.05	-4.93
60	303	7.72	3.00	-4.86

Activation energy, $E_a = 13.7 \text{ KJ g}^{-1}$

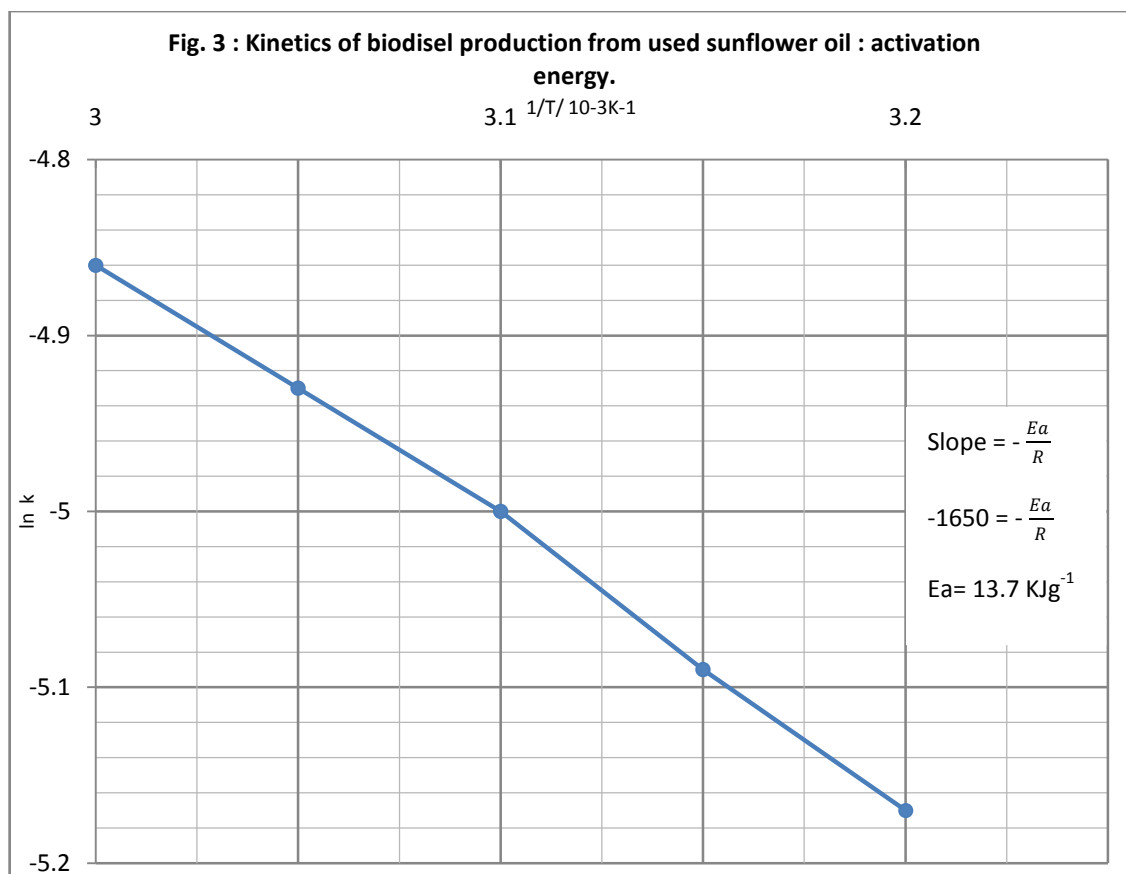
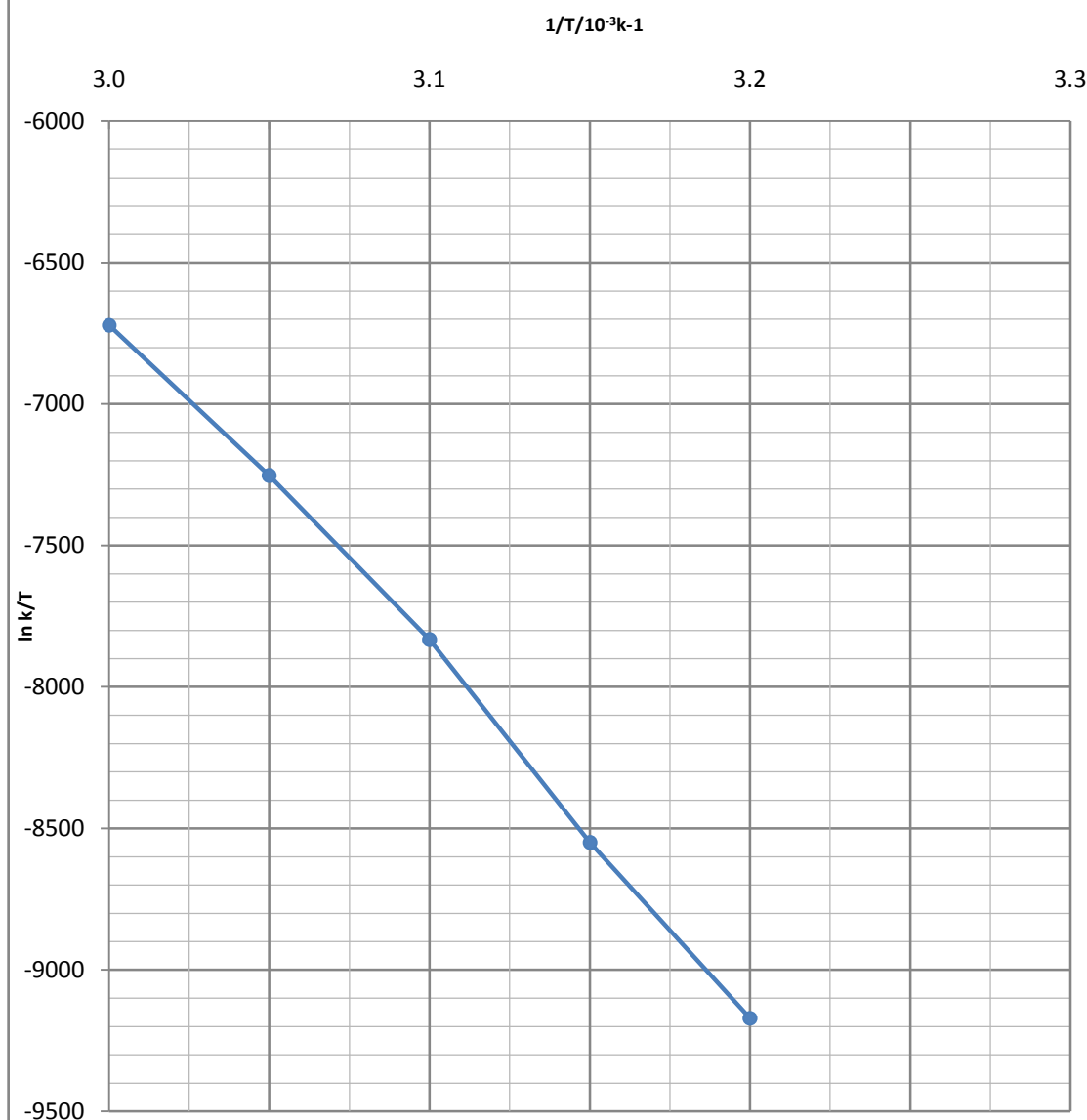


Table no 7: Kinetics of biodiesel production from used sunflower oil : thermodynamic parameters

Temperature $t/^{\circ}\text{C}$	T/K	$1/T/ 10^{-3}\text{k}^{-1}$	Average rate constant $\text{k}/10^{-3} \text{ min}^{-1}$	ln k	$\text{k}/T/10^{-5}$	ln k/T
40	313	3.19	5.68	-5.17	1.8147	-10.9170
45	318	3.14	6.14	-5.09	1.9308	-10.8550
50	323	3.09	6.70	-5.00	2.0743	-10.7833
55	328	3.05	7.21	-4.93	2.1982	-10.7253
60	333	3.00	7.72	-4.86	2.3183	-10.6721

Fig. 3: Kinetics of biodiesel production from used sunflower oil : thermodynamic parameters



References:

- [1] Ma F, Hanna M.A., Biodiesel production: a review. *Biores Technol.*,1999,70, 1-15.
- [2] Kumar D., Ali A., *Biomass Bioenerg.* 2012,46,459-468
- [3] Patil P., Gude V.G., Pinappa S., Dong S. *Chem. Eng. J.*,2011, 168,1296- 1300.
- [4] Zhang L., Sheng B., Xin Z., Liu Q., Sun S., *Bioresourcetechnol.*,2010 101, 8144 - 8150
- [5] Deshmane V.G., Adewuyi Y.G., *Fuel*, 2013,107,474-482
- [6] O. Ilgaon, *Fuel Process Technol*, 2012, 95, 62-66.
- [7] Oliveira Lima J. R., GhaniY. A.,Da Silva R. B, Bastita F. M, Bini R .A., L.C. Varanda L .C., De Olivera J. E., *Appl. Catal. A*, 2012, 445, 62-66
- [8] Rashtizadeh E., Fareaneh F., Taiwan J., *Inst. Chem.Eng.*, 2013,44, 917-923.
- [9] Boey P. L., Maniam G. P., Hamid S. A., *Chem. Eng. J.*, 2011, 168, 15-22
- [10] Borges M. E., Diur L., *Renew. Sust. Energ.Reg.*, 2012, 16, 2839-2849.
- [11] Chen X,Du W., Liu D., Ding F., *J. Chem. Technol Biotechnol.*,2008, 83, 71:76.
- [12] Reyes J.F., Sepulveda M.A., *Fuyel*, 2006, 85, 1714-1719

- [13] Meher L.C. Vidyasagar D, Naik S.N., *Renew. Sustain Energy Rev.*,2006, 10, 248-268.
- [14] Du. W., Xu Y.Y., Liu D.H., Zeng J., *J. Mol. Catal B: Enzymatic*, 2004 30, 125-129
- [15] Ma F, Hanna M.A., *Biodiesel Production: a Review. Biores Techno.*,1999,70, 1-15.
- [16] Wardle D.A., *Renew sustain. Energy Review*, 2003,7, 1-64.
- [17] Agrawal A.K. and Das L.M., *J. Eng. Gas Turbines Power*, 2001 123, 440-447
- [18] Di. Serio M., Tesser R., Pengmei L., Santacesaria E., *Energ. Fuel*,2008, 22,2007-2017.
- [19] Dong X., Fang Z., Liu Y. H., Yu C. L., *Energy*, 2011, 36, 777-784.
- [20] Wen L. ,Wang, Lu D., Hu S., Han H., *Fuel*, 2002 89, 2267-2271.
- [21] Liu X., Piao X, Wang V., Zhu S., *Energ Fuel*, 2008, 22, 1313-1317.
- [22] De Moura C. V., De Castro A.G., De Moura E. M., Dos Santos J. R., Moita Neto J. M., *Energ Fuel*, 2010, 24, 6727-6532
- [23] Shu Q., Yang T., Yuan H., Quing S., Zhu G., *Catal.Comm.*,2007, 8, 2159-2165.
- [24] Wu H., Zhang J., Wei Q., Zheng J., *Fuel Process Technol*, 2013, 109,,13-18.
- [25] Vieira S. S., Magriotis Z. M., Santos N. A., Saczk A. A., Hori C. E, Arroyo P. A, *Bioresource Technol*, 2013, 133, 248-255.
- [26] Carreo A., Vicente G., Rodriguez R., Linares M., Depeso G. L., *Catal. Today* 2011, 167, 148-153.
- [27] Borges L.D., Moura N.N, Costa A. A., Braga P. R., Dias J. A., Dias S.C, De Mededo J. L., G.F.Ghesti G. F.,*VAppl Catal*. 2013, A 450, 114-119.
- [28] Kusuma R. I., Hadinoto J. P., A Ayucitra F.E.Soetaredjo, S.Ismadji,*Appl. clay Sci.*,2013, 74, 121-126.
- [29] Birla A., Singh B.,Upadyas S. N., Y.C. Sharma, *Bioresource Technol* 2012, 106, 95-100.
- [30] Jain S., Shama M. P., *Bio resource Technol.*, 2010, 101, 7701-7706.
- [31] Jain S., Sharma M. P., Rajvanshi S., *Fuel Process Technol.*, 2011, 92, 32-38.
- [32] Joelianingsih A., Maeda H., Hagiwara S., Nabetani H., Sagara Y, Soerawidjaya T. H., Tambunan A. H., Abdulah K., *Renew Energ.*,2008, 33, 1629-1636.
- [33] Choi C. S., Kin J. W., Jeong C. J., Kim H., Yoo K. P., J., *Supercrit. Fuludis*, 2011, 58, 365.370.
- [34] Shivakumar P., Sindhanaiselvan S., Gandhi N. N., Devi S. S, Renganathan S., *Fuel*, 2013, 103, 693-698.
- [35] Stamenkovic O. S., Todororic Z. B., Laric M.L., Velikoric V. B., Skala D. U., *Bioresource Technol.*, 2008, 99, 1131-1140
- [36] Veljkoric V. B., O.S. Stamenkric O. S., Todororic Z. B., Lazic ML. , Skalu P. U. *fuel* , 2009, 88, 1554-1562.
- [37] Marjanovic A.V., Stamenkaric O. S., Todorivic Z. B., Mazic M. L., Veljkovic V. B., *Fuel*, 2010, 89, 665-671
- [38] Lukic I., Kesic Z., Maksimovic S., Zdujic M., Liu H, J. Kvstic J., D. Skala D.,*Fuel*, 2013, 113, 367-378.
- [39] Santos A. G., Araujo A. S., Caldeira V.P, Fernandes V. J., L.D. Sourea L. D.,Barras A. K., *Thermochim, Acta*, 2010, 506, 57-61.
- [40] Stamenkovic O.S., Veljkric V. B., Tadorivic Z. B., Laxic M. L., Bankovic I. B. , Skala D. U., *Bioresource Technol*, 2001 101,4423,4430.
- [41] Alamu O. J., Waheed M. A., Jekeyinta S. O., *Agricultural EngineeringInternational; the CIGR E Journal .Manuscript Number EE 07009.2007 Vol. IX July.*
- [42] Puri B.R., Sharma L.R., Pathania M. S., *Principles & Physical Chemistry Vishal Publishing, Jalandhar India*, 2005.