World Applied Sciences Journal 9 (11): 1306-1312, 2010
ISSN 1818-4952

Esterification of Free Fatty Acids by Heterogeneous γ-Alumina-Zirconia Catalysts for Biodiesel Synthesis

[1]J.K. Heydarzadeh, [2]G. Amini, [3]M.A. Khalizadeh, [4]M. Pazouki,
[2]A.A. Ghoreyshi, [5]M. Rabeai and [2]G.D. Najafpour

[1]Department of Chemical Engineering, Islamic Azad University of Shahrood Branch, Shahrood, Iran
[2]Faculty of Chemical Engineering, Babol Noshirvani University of Technology, Babol, Iran
[3]Department of Applied Chemistry, Islamic Azad University of Ghaemshahr Branch, Ghaemshahr, Iran
[4]Materials and Energy Research Center, Meshkindasht, Karaj, Iran
[5]Faculty of Mechanical Engineering, Babol Noshirvani University of Technology, Babol, Iran

Abstract: An alternative energy for the replacement of fossil fuels has been developed. Biodiesel synthesis as a renewable energy was derived in a continuous packed column reactor. Free fatty acids (FFA) were esterified with ethanol in a heterogeneous catalytic reaction. The catalytic reactor had great potential as FFA introduced to the top of column, flow down ward, reached to catalyst surface and interacted with ethanol on the active site. The ester product was instantaneously formed. In this catalytic reaction, effects of mass ratio of the free fatty acids/ethanol and reaction temperature in the range of 150-250°C were investigated. As the reaction temperature increased, the esterification reaction was enhanced. The obtained data showed that at optimal conditions (mass ratio of 3:5 and reaction temperature 250°C), the FFA conversion to ethyl ester was 90%.

Key words: Biodiesel · Free fatty acid · Esterification · Sol-gel method · Alumina-zirconia catalysts

INTRODUCTION

Energy is the most basic necessity of all industrial activities in civilized societies. It is often used in transportation as well as power generation. It has been reported that about 88% of world energy production are derived from fossil fuels including petroleum, coal and natural gas [1]. In response to the world wide awareness about the impacts of fossil fuels emissions on global warming, rising prices of petroleum fuels and conservation of natural resources, the principles of green energy and alternative fuels gain popularity [2-4]. The economic issue of biofuel may encourage new research to be developed for the replacement of fossil fuel. Use of renewable sources, waste bioresources and low cost raw material may boost the economics of the biodiesel production.

Biodiesel used in diesel engine, is one of the alternative fuels which is defined as monoalkyl esters of long chain fatty acids derived from animal fats, vegetable oil, waste cooking oil, seaweeds and algae oils. The characteristics of biodiesel are similar to diesel fuels and they can be used either pure or blended with diesel fuel [5]. Therefore, biodiesel is a suitable substitution for fossil fuel. Two useful methods exist for biodiesel production. Transesterification of triglycerides and esterification of free fatty acids (FFAs) are commonly used for biodiesel synthesis [6, 7]. In the case of enriched FFA as raw materials, to avoid soap formation and loss of deactivated catalyst, esterification of FFA is preferred [8]. The esterification reaction is summarized as follows:

Free fatty acids + ethanol ↔ fatty acid ethyl esters + water

The main steps and basic technology for production of biodiesel is illustrated in Fig. 1. Generally, various methods are implemented to produce biodiesel from oils and fats. Base catalyzed transesterification [9-11], acid-catalyzed transesterification [12,13], enzymatic transesterification [14,15], heterogeneous catalyst [16, 17] and supercritical esterification [18] are the five main processes in biodiesel synthesis. Disadvantages of alkaline solution in estrification reaction at low temperature (80°C) were saponification reaction of FFA

Corresponding Author: J.K. Heydarzadeh, Department of Chemical Engineering, Islamic Azad University of Shahrood Branch, Shahrood Iran. E-mail: najafpour@nit.ac.ir.

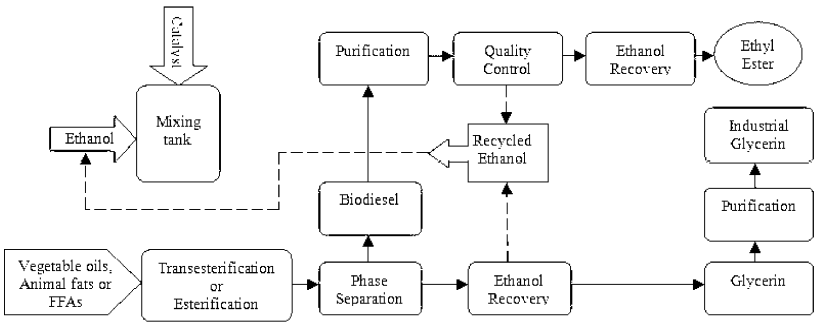

Fig. 1: Main steps of biodiesel production

and separation of desired from undesired products. However, heterogeneous catalyst esterification process is expected to be an effective method because of the process advantages in compare with the other existing processes such as reusability, elimination of washing step, process simplification, easier catalyst and product separation [19]. Numerous investigations were carried out to discover the suitable solid catalyst and the effect of operational variables such as feed temperature, reaction temperature, molar ratio of alcohol to oil, intensity of mixing, purity of reactant and types of catalysts on reaction yield and residence time.

Vujicic *et al.* have investigated the Kinetics of biodiesel synthesis from sunflower oil using CaO heterogeneous catalyst [20]. They have found that in a continuous stirred tank reactor (CSTR), with methanol:oil ratio of 6:1, CaO catalyst is capable of esterification process under defined operating condition. For 5.5 h reaction time and at 80°C, the highest yield (91%) of fatty acid methyl ester (FAME) was achieved. Kawashima *et al*. have focused on the development of heterogeneous base catalysts for biodiesel production [21]. They have prepared thirteen different kinds of metal oxides containing calcium, barium, magnesium, or lanthanum as catalysts. The catalysts activities were examined for esterification at 60°C with a molar ratio of methanol to oil 6:1 and reaction time of 10 h. The catalysts consist of calcium ($CaTiO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$ and $CaO–CeO_2$) have shown high activities and yield of methyl ester production (approximately 90%). Georgogianni and his coworkers have compared the transesterification of rapeseed oil for production of biodiesel using homogeneous and heterogeneous catalysts [22]. They have discovered that homogeneous catalyst significantly accelerated the transesterification reaction, as compared to all heterogeneous catalysts, using both mechanical stirrer and ultrasonication. Park *et al.* have studied esterification process of waste cooking oils (WCO) using heterogeneous Tungsten and zirconium oxides, sulfated zirconium and Amberlyst-15 catalysts for biodiesel production [8]. Among all of these catalysts, tungsten oxide zirconium had the highest activity and reaction conversion (93%). In an investigation Kansedo *et al.* have used palm oil to produce biodiesel via montmorillonite KSF heterogeneous catalyst [23]. It was found that with 3% catalyst the yield of palm oil fatty acid methyl esters had reached to 79.6% at reaction temperature of 190°C and methanol/oil molar ratio of 8:1. Arzamendi *et al*. have synthesized biodiesel with heterogeneous NaOH/alumina catalysts and homogeneous NaOH catalyst [24]. The results have shown that the transesterification rate largely depends on weight of catalyst and molar ratio of methanol/FFA. The selectivity of catalyst was affected by the feed molar ratio of methanol/oil. Furthermore, they have found that at 393 K with the use of homogeneous and heterogeneous catalysts (NaOH and NaOH/alumina) the reaction yields were about the same level.

The purpose of present research paper was to focus on two important parameters in esterification reaction. Mass ratios of free fatty acid/ethanol and reaction temperature in a short retention time were investigated. These parameters were very essential. The reaction at high temperature was quite fast so, as the reactants reached to catalysts active sites, the product was formed. Esterification was carried out with variable mass ratios in the range of 1:5 to 3:5. Optimal molar ratio was obtained and the effect of temperature on the yield of process was evaluated.

MATERIALS AND METHODS

Materials: Free fatty acid (FFA) was analyzed using Mass Spectroscopy – Gas Chromatography system (AGILENT model 6890 N). The composition of the FFA mixture is summarized in Table 1.

Table 1: Analysis of free fatty acid

Free fatty acids	Composition (wt. %)
Myristic acid (C14:0)[a]	0.23
Decanoic acid (C10:0)	1.15
Lauric acid (C12:0)	7.14
Palmitic acid (C16:0)	12.00
Oleic acid (C18:1)	78.17
Others/unknown	1.31

[a]Numbers in parenthesis signify the number of carbon atoms and the Unsaturated centers (double bonds)

Table 2: Physical Characteristics of Oleic acid

Physical properties	Value
Boiling point	286°C
Density (d 20°/4°)	0.854
Melting point	14.3°C
Assay (GC)	65-88%
Acid value	196-204
Iodine value	87-95
Peroxide value	10
Sulfated ash (800°C)	0.1%

Table 3: Physical Characteristics of Ethanol

Physical properties	Value
Boiling point	78.32°C
Freezing point	-114.15°C
Density (d 20°/4°)	0.78942
Specific heat (16-21 °C, 289-294 K)	2415 $J.g^{-1}.K^{-1}$
Thermal conductivity (20 °C, 293 K)	1.8 $\mu w.m^{-1}.K^{-1}$
Heat of combustion (constant volume)	1,379.82 $kJ.mol^{-1}$
Flash point	13°C

Since the major composition of the FFA mixture is oleic acid, physical properties of oleic acid are shown in Table 2. FFA was obtained from Applichem Company (Germany).

The ethanol (industrial grade) with purity of 96% was used in the experimental runs because of it is not considered as toxic compound. Also it burns better and provides greater heat of combustion than methanol [25]. The physical properties of ethanol are summarized in Table 3.

Catalyst Preparation and Characterization: The heterogeneous nanopowder catalysts γ-Al_2O_3/ZrO_2 were prepared with sol-gel method. Catalyst was composed of Alumina chloride ($AlCl_3.6H_2O$, Merck), Zirconium chloride ($ZrCl_4$, Merck), Yttrium nitrate ($Y(NO_3)_3.6H_2O$, Merck), Citric acid ($C_6H_8O_7$, Merck) and Ethylene glycol ($HOCH_2CH_2OH$, Merck). The synthesized catalyst was ã-Al_2O_3/ZrO_2 nanopowders and clay plates coated against title catalyst, then gel and coated clay plates left in a dry oven at 70°C for 12 h. The dried gel and coated clay plates was calcined at approximately 700°C with a heating rate of 5°C/min and maintained for 5 h. the size of cylindrical shape pelletized catalyst was 2-2.5 mm diameter and 1.5-2 mm length. The morphology of calcinated catalysts particles were investigated by Philips EM208S transmission electron microscope (TEM).

Experimental Setup: The esterification process was carried out in a continuous packed bed reactor. The column was made from galvanized cast iron pipe (Sepahan, Isfahan, Iran). The galvanized reactor height, inner and outer diameters were 120, 3 and 3.5 cm, respectively. The column was packed and loaded with pelletized catalysts (600 g, γ-Al_2O_3/ZrO_2). Metal wire gaze was used as a support to hold the catalyst. About 82% of the reactor volume was occupied by the pelletized catalysts. The schematic diagram for the experimental setup is shown in Fig. 2.

Fatty acids mixture, ethanol were primarily heated to 50°C in a mixing tank. The mixture was agitated in a hot plate magnetic stirrer (VELP company, model ARE, Europe) with temperature controller (Zentai company, model TEL96-2301, Iran). The column was surrounded with a heating element (1500W) to heat the catalyst bed. In order to preheat the packed bed column, it was gradually heated up to 250°C for 40-45 min. The column temperature was controlled by means of a thermocouple installed inside the bed. The feed mixture was pumped (peristaltic pump series B, Italy) into the top of the reactor with a fixed flow rate of 25 ml/min. The vaporized ethanol at high temperature was present in the packed bed reactor with sufficient contact with active sites of the catalysts. As the fatty acids were pumped to the top of the column, met and interacted with ethanol on the active site and the ester product was instantaneously formed. That was the greatest ability of the fabricated heterogeneous catalytic reactor used in this work. The esterification process was carried out in a packed bed reactor filled with γ-Al_2O_3/ZrO_2 catalysts. The defined amount of ethanol (150 g) added to FFA. The operational variables were free fatty acid/ethanol mass ratio (1: 5, 1.5: 5, 2:5, 2.5:5 and 3:5) and temperature range (150-250°C). The reaction time was set at 6 min and the feed flow rate was fixed. The product was led to a flash drum separator.

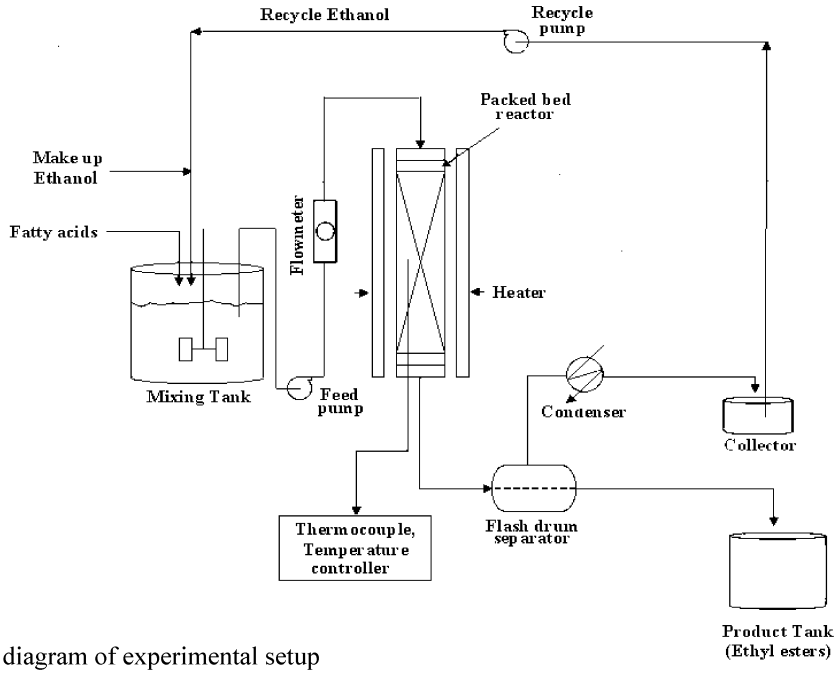

Fig. 2: Schematic diagram of experimental setup

RESULTS AND DISCUSSION

The catalyst particle size and the porosity were investigated. The particles were calcinated at high temperature (700°C). A transmission electron microscope (TEM) was used to analyze the morphology of catalyst particles. The details of catalyst characterization are discussed elsewhere. Fig. 3 shows the micrograph of γ-alumina–zirconia particles synthesized by sol gel method. Most of the particles were in the range of 10-15nm. The meso-porosity of the catalyst particles were confirmed by TEM image and most of the particles were in spherical shape.

The esterification reaction with ethanol, FFA was carried out with the aim of maximizing ethyl ester production. The experiments were conducted with variable temperatures and mass ratios of FFA/ethanol. In the following sections the effect of each operational parameters are discussed.

Free Fatty Acid/ethanol Mass Ratio Optimization: The rate of esterification is strongly influenced by the mass ratio of fatty acid to ethanol. Since the esterification process is reversible, the yield of ethyl esters produced is favored with the excess amount of ethanol. In order to obtain an optimal mass ratio for this process, six experiments were carried out with variable free fatty acid/ethanol mass ratio between 1:5 and 4:5 as discussed in material and methods. Fig. 4 shows the ethyl ester formation as a function of mass ratio of fatty acid/ethanol. For the stoichiometric esterification process the theoretical molar ratio of fatty acid to ethanol is expected to be 1:1. However, the presented data demonstrate that at a mass ratio of 3:5, maximum ester yield was obtained. For the higher mass ratio than the theoretical value, complete reaction and therefore high esterification of FFA is expected. As the mass ratio of FFA/ethanol increased, gradually soap formation appeared. For the mass ratio of 4:5, the reaction leads to soap formation and the product mixture was solidified. Increasing the mass ratio from 1:1 to 3:5 raised the ester formation from 25 to 90%.

Fig. 5 depicts the esterification of individual free fatty acids with respect to mass ratio. At low mass ratios there were significant differences in ethyl ester formation. That was probably due to the molecular structure of free fatty acids and interaction with ethanol at the active sites of catalyst. The low molecular weight fatty acids may yield high esterification while the lowest yield was related to oleic acid with high molecular weight. As the amount of ethanol and the mass ratio increased the reaction yield for all of the individual free fatty acids were also increased. However, the increasing rate of lauric acid and oleic acid were slightly lower than other free fatty acids. At high mass ratio (3:5) the esterification yield of individual free fatty acids was in the range of 81-95%.

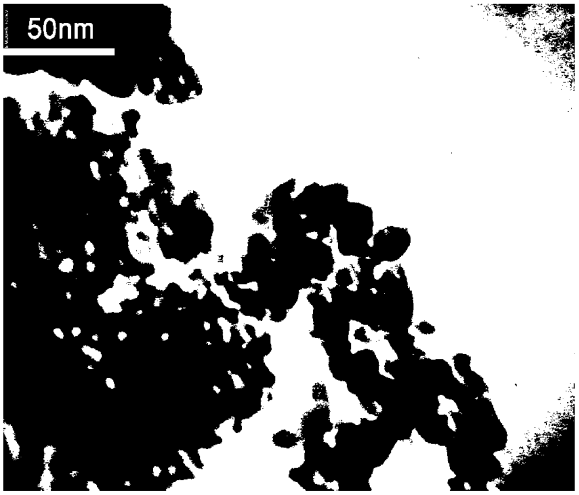

Fig. 3: Transmission electron micrographs of the γ-alumina-zirconia particles calcinated at 700°C for 5 h

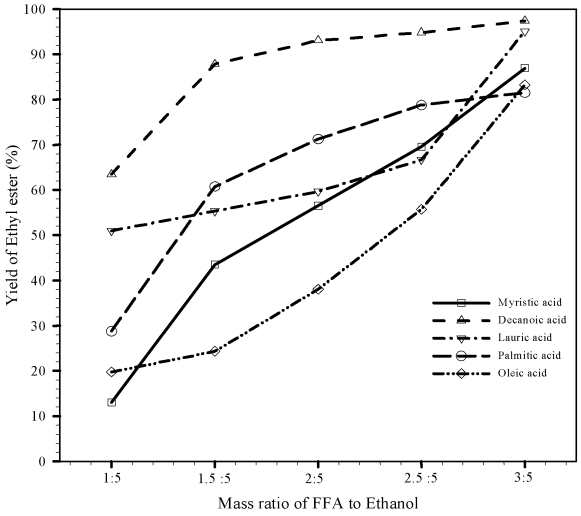

Fig. 5: Effect of mass ratio of FFA/ETOH on yield of ethyl ester

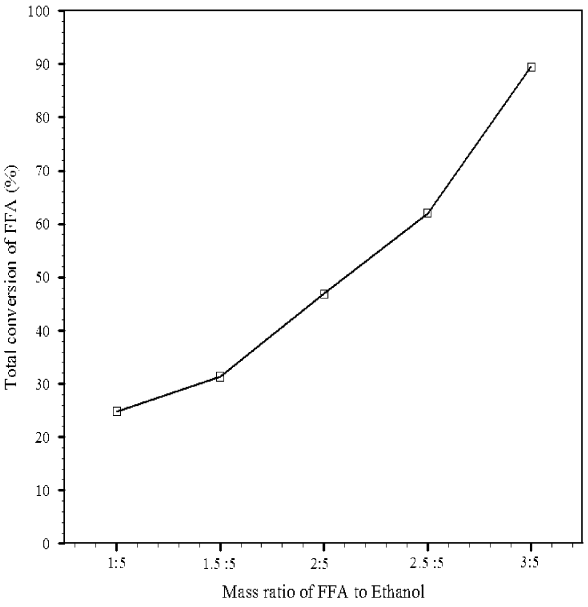

Fig. 4: Conversion of FFA to ethyl ester as a function of mass ratio of FFA/ETOH

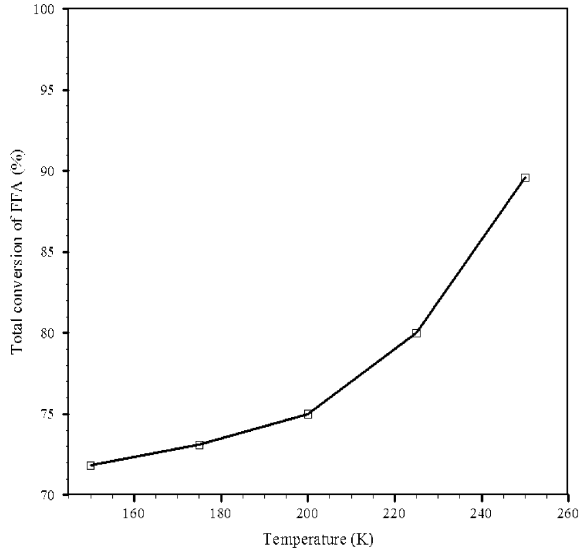

Fig. 6: Conversion of FFA to ethyl ester as a function of reaction temperature

Effects of Reaction Temperature: Ethyl ester formation was strongly depended on reaction temperature. To evaluate the effect of reaction temperature on production of ethyl esters, the esterification process was carried out under optimal conditions (fatty acid/ethanol mass ratio of 3:5). Esterification can be conducted at various temperatures. In most of the cases the temperature is kept close to the boiling point of alcohol used in the process [26] However, high temperatures reduce the reaction time. In this research temperature was varied between 150 and 250°C. Fig. 6 represents the effect of temperature on esterification of FFA. As the reaction temperature increased, the formation of total ethyl esters was progressively increased. The results indicated that increasing the reaction temperature had a favorable influence on the yield of ethyl ester formation.

Fig. 7 shows the effect of temperature on the yield of individual FFA. Temperature significantly affected decanoic acid yield and the yield was raised from 58.26 to 87.82%. However, some of the free fatty acids yield was not strongly temperature dependent,

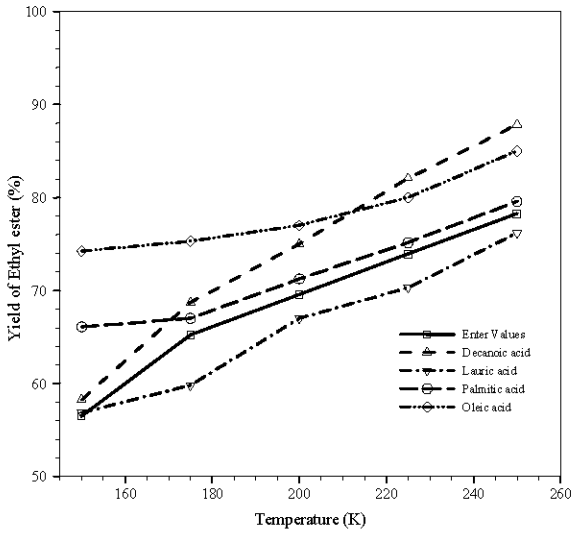

Fig. 7: Effect of temperature on yield of ethyl ester

which was most probably due to the nature and chemical structure of the specific free fatty acid. Effect of temperature is directly related to viscosity of the fatty acids. As the temperature increases the diffusion coefficients and also the rate of penetration of the fatty acids into pore of the catalyst may increase. These parameters may enhance the yield of product formation.

CONCLUSION

The heterogeneous catalytic reactor had great ability to produce biodiesel fuel in a short reaction time. It was concluded that as the mass ratio of FFA/ethanol increased the reaction yield and conversion of free fatty acid were increased. Maximum reaction yield at mass ratio of 3:5 was 95%. The reaction temperature had positive impact on most of the free fatty acids. At high temperature (250°C) high reaction conversion has reached. As expected, at low temperature the conversion was low. With implementation of optimal operational condition the maximum yield of approximately 95% was achieved.

ACKNOWLEDGMENT

The authors gratefully acknowledged Material and Energy Research Center (Karaj, Iran) and Babol Noshirvani University of Technology for technical support. Special thanks go to Iranian Nanotechnology Innovative Council for their financial support.

REFERENCES

1. Georgogianni, K., A. Katsoulidis, P. Pomonis and M. Kontominas, 2009. Transesterification of soybean frying oil to biodiesel using heterogeneous catalysts. Fuel Processing Technol., 90(5): 671-676.
2. Sharma, P. and N. Kumar, 2009. Life cycle assessment (LCA) of biodiesel: A tool for sustainability, in New Frontiers in Biofuels, S.P. A Singla , N Kumar, PB Sharma Editor. Scitech Publications: New Delhi, pp: 80-88.
3. Singla, A., S. Pande and N. Kumar, 2009. Life cycle assessment (LCA) of biodiesel: A tool for sustainability. ed. P. Sharma and N. Kumar, Scitech Publications: New Delhi, pp: 80-88.
4. Bhake, A., S. Bankar, S. Shastri and L. NM, 2009. Aspects of ultrasonically assisted transesterification of vegetable oils. New Frontiers in Biofuels, eds. P. Sharma and N. Kumar. 2009, Scitech Publications: New Delhi, pp: 62-69.
5. Enweremadu, C. and M. Mbarawa, 2009. Technical aspects of production and analysis of biodiesel from used cooking oil--A review. Renewable and Sustainable Energy Reviews.
6. Demirbas, A., 2008. Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. Energy Conversion and Management, 49(1): 125-130.
7. Vicente, G., M. Martinez and J. Aracil, 2007. Optimisation of integrated biodiesel production. Part I. A study of the biodiesel purity and yield. Bioresource Technol., 98(9): 1724-1733.
8. Park, Y., J. Lee, S. Chung, I. Park, S. Lee, D. Kim, J. Lee and K. Lee, 2010. Esterification of used vegetable oils using the heterogeneous WO3/ZrO2 catalyst for production of biodiesel. Bioresource Technol., 101(1): S59-S61.
9. Freedman, B., R. Butterfield and E. Pryde, 1986. Transesterification kinetics of soybean oil 1. J. the American Oil Chemists' Society, 63(10): 1375-1380.
10. Gryglewicz, S., 2000. Alkaline-earth metal compounds as alcoholysis catalysts for ester oils synthesis. Applied Catalysis A: General, 192(1): 23-28.
11. Schmidt, J., D. Reusch, K. Elgeti and R. Schomäcker, 1999. Kinetics of transesterification of ethanol and butyl acetate-A model system for reactive rectification. Chemie Ingenieur Technik, 71: 704-707.

12. Davies, B. and G. Jeffreys, 1973. The continuous trans-esterification of ethyl alcohol and butyl acetate in a sieve plate column-part II: batch reaction kinetics studies. Chemical Engineering Research and Design, 51(a): 271-274.
13. Otera, J., 1993. Transesterification. Chemical Reviews, 93(4): 1449-1470.
14. Ognjanovic, N., D. Bezbradica and Z. Knezevic-Jugovic, 2009. Enzymatic conversion of sunflower oil to biodiesel in a solvent-free system: Process optimization and the immobilized system stability. Bioresource Technology.
15. Shah, S. and M. Gupta, 2007. Lipase catalyzed preparation of biodiesel from Jatropha oil in a solvent free system. Process Biochemistry, 42(3): 409-414.
16. Kim, H., B. Kang, M. Kim, Y. Park, D. Kim, J. Lee and K. Lee, 2004. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. Catalysis Today, 93: 315-320.
17. Xie, W. and H. Li, 2006. Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil. J. Molecular Catalysis A: Chemical, 255(1-2): 1-9.
18. Glisic, S. and D. Skala, 2009. The problems in design and detailed analyses of energy consumption for biodiesel synthesis at supercritical conditions. The J. Supercritical Fluids, 49(2): 293-301.
19. Zabeti, M., W. Daud, W. Ashri and M. Aroua, 2009. Activity of solid catalysts for biodiesel production: A review. Fuel Processing Technol., 90(6): 770-777.
20. Vujicic, D., D. Comic, A. Zarubica, R. Micic and G. Boskovic, 2009. Kinetics of biodiesel synthesis from sunflower oil over CaO Heterogeneous Catalyst. Fuel.
21. Kawashima, A., K. Matsubara and K. Honda, 2008. Development of heterogeneous base catalysts for biodiesel production. Bioresource Technol., 99(9): 3439-3443.
22. Georgogianni, K., A. Katsoulidis, P. Pomonis, G. Manos and M. Kontominas, 2009. Transesterification of rapeseed oil for the production of biodiesel using homogeneous and heterogeneous catalysis. Fuel Processing Technol., 90(7-8): 1016-1022.
23. Kansedo, J., K. Lee and S. Bhatia, 2009. Biodiesel production from palm oil via heterogeneous transesterification. Biomass and Bioenergy, 33(2): 271-276.
24. Arzamendi, G., I. Campo, E. Arguinarena, M. Sanchez, M. Montes and L. Gandia, 2007. Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts: comparison with homogeneous NaOH. Chemical Engineering J., 134(1-3): 123-130.
25. Felder, R.M. and R.W. Rousseau, 1986. Elementary princoples of chemical processes. 2nd Ed. John Wiley & Sons, New York.
26. Fernando, S., P. Karra, R. Hernandez and S. Jha, 2007. Effect of incompletely converted soybean oil on biodiesel quality. Energy, 32(5): 844-851.