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Research Article

The effect of changing the concentration of loaded KOH to a zeolite heterogeneous catalyst activity in biodiesel production by electrolysis

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ABSTRACT

Biodiesel is a renewable energy sources which is produced from transesterification reaction of vegetable oils, animal fats and cooking oil. This makes it non-toxic, environmentally friendly and alternative for diesel fuels. In this study, the electrolysis method of cooking oil to biodiesel transesterification reaction (alkyl esters of fatty acids) using heterogeneous catalyst clinoptilolite was used. First, KOH concentration load (1, 2, 3, 4 M) was studied and the best efficiency of biodiesel were selected for further testing. Many parameters such as percent of the catalyst, the ratio of alcohol to oil, time, solvent and voltage were measured. Finally, using GC-MS the ratio of methyl ester to fatty acid was measured, the results indicate the efficiency of biodiesel in the presence 2wt% catalyst at a concentration of potassium hydroxide, 10wt%, 3 of the solvent THF, the 10 V and 4 houres, was 90%. At the end, properties of the catalyst were studied using XRD method.

Keywords: electrolysis, biodiesel, transesterification, heterogeneous catalysts, zeolite

1. INTRODUCTION

One of the most basic needs of the economic sectors in developed and developing countries is energy. The growing human population and increasing industrial activity has led to energy consumption is steadily rising [1]. Common sources of energy, crude oil, natural gas and coal, which the fossil fuels are non-renewable sources of energy quickly reduce excessive consumption. The rising cost of fossil fuels, reduction of Refinement's capacity, the viability and the pollution caused by them, makes human to alternative fuels that they are renewable and non-polluting [2]. The biodiesel can be replaced as a renewable source.

Biodiesel is produced from the reaction of lipid biodegradable materials from natural resources such as fresh or second-hand vegetable oil, animal fats, waste oils or seaweed. This type of raw material and reacts with alcohol and OH's alcohol, replace with the oil in the hydrocarbon chain, and as a result of stress by building new molecular alkyl esters of fatty acids are produced. In this reaction, the alcohol ester replace with an alcohol (methanol or ethanol) in the process. This process is similar to hydrolysis, except that instead of water, alcohol is replaced, also, this method use to produce methyl esters in industrial cleaners and cosmetics applications [3].

Transesterification reaction will be done with suitable catalysts more rapidly. If during the process, the catalyst is in a similar phase to liquid biodiesel is called homogeneous catalysts that are

divided to groups, acid (sulfuric acid and chloric acid) and alkaline (sodium hydroxide and potassium hydroxide). On the contrary [4], if at the end of the reaction the trans - esterified catalyst be in other phase than the reactants phase such as gas, solid and liquid phase mixture is allowed to say a heterogeneous catalyst [5].

Heterogeneous catalysts have specific features, such as reusability, perfect alkalinity and low corrosion properties than the homogeneous catalyst. Glycerol obtained from the homogeneous catalyst transesterification reaction has low quality and requires a long process of purification [6]. All the above processes will increase the final price of biodiesel and glycerin; in addition, homogeneous catalysts during the reaction face the problem of multi-phase raw material. On the other hand, a heterogeneous catalyst in the process of transesterification does not mix with methanol and ethanol, and after the reaction easily will be removed of biodiesel and glycerol [7].

These days, using heterogenous catalysts increased. Solid catalysts have been studied for the transesterification reaction oil, include alkali and alkaline metals, Al_2O_3 [8], calcium oxide [9], magnesium oxide, activated carbon [10], etc. However, several issues must be considered for the selection of solid catalysts. It should be plenty of resources, access to those resources is convenient and the price is cheap. Zeolites are group of aluminosilicate and has small pores that contain a balance of alkali metal cations and alkali and alkaline metals, (Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}) [11]. Zeolites are generally divided into two categories of natural and synthetic. Physical and chemical properties of zeolites function of their crystal structure and chemical composition, which in turn determines the consumption [12].

Biodiesel synthesis using electrolysis method, first reported by Goran and colleagues [13]. This method has several advantages compared to other available methods, including: The amount of water contained in the raw material has a direct effect on the electrolysis process; the process is done without heating at room temperature, cheaper method compared with other methods while it is new and applicable .

In this study, the electrolysis method was used to produce biodiesel at room temperature, the catalyst was clinoptilolite; also, the catalyst concentration, the ratio of alcohol to oil, time, different solvents and voltage on the output of biodiesel were investigated.

2. MATERIALS AND METHODS

2.1 materials and devices

Clinoptilolite prepared from the Negin Poodre Semnan company, potassium hydroxide (99%), sodium sulfate (99%) were obtained from Merck company, and waste oil were collected from a buffet of Department of Chemistry, University of Islamic North Tehran.

Instruments used include: Furnace model BATE pc 21 made in Iran, heater stirrer Robin Com-81 made in Germany, Avon Model Lab tech made in Iran, Spectrometer infrared model Nicolet 8700 construction Netherlands, power supply model deck power supply 8303 made in Iran, graphite electrode and XRD system Stidy-mp manufacturing Co. STOE Germany.

2.2 Preparation of Catalyst

Initially, 7.5 grams of clinoptilolite powder mixed with 15 g of KOH and was calcined for 2 hours at 550ºC in the oven, then, the product was refluxed for 16 hours with a solution (1, 2, 3, 4 M) potassium hydroxide, then dried at the room temperature.

3.2 electrolysis

In an electrolysis cell to a volume of 100 ml, two graphite electrodes with 2.2 * 2.2 surface and a distance of 1 cm from each other, 50 g of oil were used. Catalyst were added to the oil in ratios (1, 2, 3, 5 wt%) and alcohol to oil ratios (1: 4, 1: 6, 1:9, 1: 11), Then, 1.3 g of water (2% by weight based on the total weight of the mixture) was added to the reaction mixture, different solvents was used for making single-phase mixture (tetrahydrofuran, acetone, methyl ether tree butyl

ether without solvent). Then, the mixture react at room temperature by applying currents 10V, the stirrer speed was 100 rpm under reaction. In test after half an hour glycerin separates from biodiesel, but for completing the process, different periods was allocated to it.

4.2 Analysis of Biodiesel

Methyl ester production phase was washed with deionized water to remove the catalyst and the excess alcohol. The concentration of produced biodiesel and unreacted oils by chromatography (HPLC, Varian, Australia) was measured. Total methyl esters and unreacted glycerides were displayed by separate chromatogram peaks. Methyl ester yield was calculated by the following formula.

3. RESULTS & DISCUSSION

3.1 XRD spectrum

XRD analysis shows the inner structure, size and crystallization phase of catalyst. XRD pattern for zeolite shows different peaks at Bragg angle (2□), the angles are 44/09°, 37/01°, 29/91°, 19/06°, 11/17°, which confirms this topic. Raw zeolite is used in this research in inorganic compounds.

Figure 2 shows the XRD pattern of catalyst loading. Bragg angle (2□) as follows: 55°, 51°, 39/34°, 31/78° shows the new phase of K_2O. In the calcination process, potassium hydroxide molecules on the surface of zeolite were converted to K_2O. K_2O has an important role in the transesterification process.

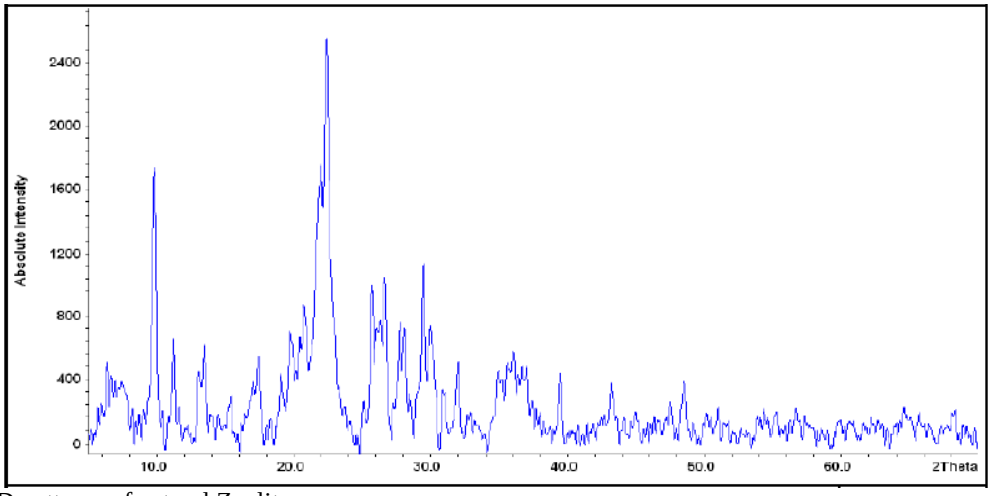

Fig 1. XRD patterns of natural Zeolite

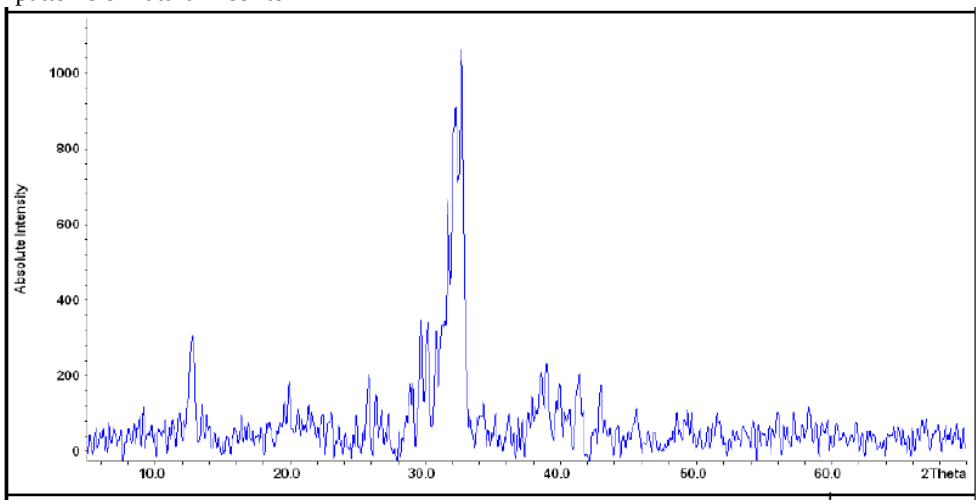

Fig 2. XRD patterns of Catalyst

3.2 Electrolysis

Electrolytic cells include two graphite electrodes which separated by a certain distance. Electrolysis cells in the reaction mixture include: methanol, oil, solvents, catalysts and water are covered with electrolyte solution. Methanol-to-oil molar ratio is 4.11. Zeolite concentration / potassium hydroxide 1-5% by weight based on the weight of the oil and water concentration is 1.2% by weight based on the weight of the reaction mixture. Electrolysis is performed at room temperature according to the method (constant voltage). Electrolysis voltage is set in the range of 10V.

When the reaction mixture contains water and catalyst zeolite / KOH goes into the electrolysis cells, may form hydroxide or oxygen at the anode (reaction 1,2). On the other hand, the hydroxyl ions or hydrogen is formed at the cathode (reaction 3).

Transesterification of triglycerides with methanol requires an active species of ions methoxide (reaction 4). Monoxide inos obtained from the reaction of methanol and hydroxide which are strongly nucleophilic and they attack to carbon in triglyceride molecules to produce methyl esters (reaction 5).

Anodic Reaction

$$2KOH \longrightarrow 2OH^- + 2K$$

$$2OH^- \longrightarrow H_2O + 2e^- \quad (1)$$

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \quad (2)$$

Cathodic Reaction

$$2H_2O + 4e^- \longrightarrow H_2 + 2OH^- \quad (3)$$

Proton transfer reaction

$$CH_3OH + OH^- \rightleftharpoons CH_3O^- + H_2O \quad (4)$$

Transesterification

$$TG + 9CH_3OH \rightleftharpoons FAME + Glycerol \quad (5)$$

Fig 3. Electrolysis reaction

3.3 Effect of KOH loaded on biodiesel yield

The effects of potassium hydroxide loaded on biodiesel yields were studied. Clinoptilolite catalyst in potassium hydroxide solution with different concentrations (1, 2, 3, 4 M) was placed under reflux and stirring. Based on the figure 4 biodiesel yield, when the reaction solution is 3 M, reaches its maximum value and by increasing the concentration to 4 M, biodiesel output is fixed and does not change.

During the transesterification reaction KOH was changed to K_2O which its pikes are identified in XDR charts. K_2O has a high catalyst reaction during transesterification, while increase the Methoxid ion. So, increasing K_2O makes biodiesel yield increase (Fig.4).

4.3 effect of catalyst concetration and the ratio of alcohol to oil

Figure 5 shows the methyl ester yield by increasing the catalyst of 0.5 wt% to 1 gram increase is equal to 87%, but with a catalyst weight gain of 1 to 1.5 grams of biodiesel yields fell (from 87% to 76%).

Because the progress of saponification reaction in competition with the main reaction by an excess of an alkaline catalyst leads to lower yields and a lack of proper separation of emulsion and soap is in effect. Figure 6 shows the effect of the oil with methanol in the presence of 1 g of catalyst and% 2wt water. By increasing the methanol molar ratio of 1: 4 ratio of oil to 1: 9, efficiency increases. But when the amount of methanol used is more than 11 times than oil, because alcohol has a biodiesel emulsifier, therefore, some of the biodiesel emulsify methanol with water and the time of glycerin separation, the possibility of phase separation is not possible and the amount of product in the process of leaching will be wasted.

5.3 Reaction Time

Biodiesel yields with increased electrolysis time of 1 to 4 hours in the presence of 1 g of catalyst, 2wt% water was 92.5. Increasing electrolysis

time up to 5 hours, was decreased 3% ester conversion (Figure 7).

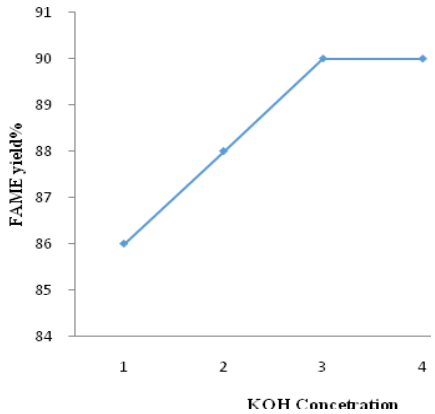

Fig 4. Yield of biodiesel as a KOH loaded on biodiesel.

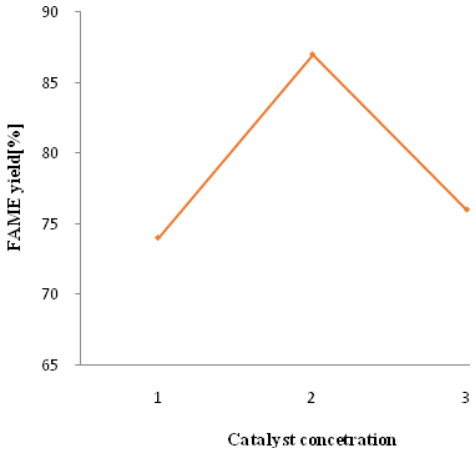

Fig 5. Yield of biodiesel as a Catalyst concentration.

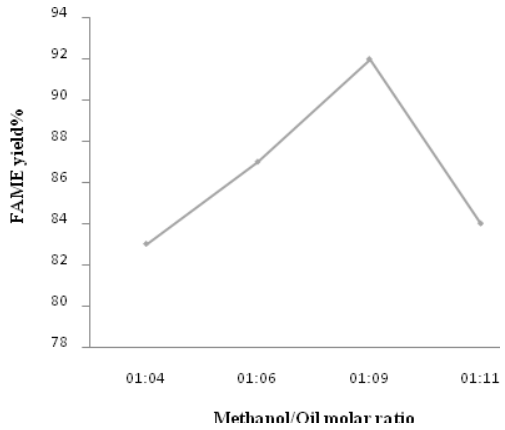

Fig 6. Yield of biodiesel as a Methanol/Oil ratio.

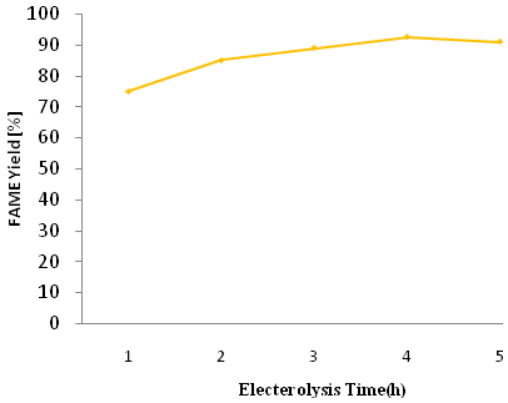

Fig 7. Yield of biodiesel as a function of reaction time.

6.3 Effect of solvent

Figure 8 shows the effect of solvents on the reaction yield with % 2wt in the presence of water, 1 gram of catalyst clinoptilolite / KOH, a ratio of 1: 9 alcohol and oil within 4 hours. When the solvent dose not used in the reaction, mixture will be two-phase, so in this part of the testing, various solvents were used. Changing the solvent does not have an effect on increasing or decreasing efficiency, which one of the advantages of this method is using different solvents with similar efficiency, but because tetrahydrofuran (polar solvent) that heterogeneous catalysts absorb the polar regions. The highest efficiency and lowest viscosity of 90% was achieved with this type of solvent, solvent was selected to continue the tests.

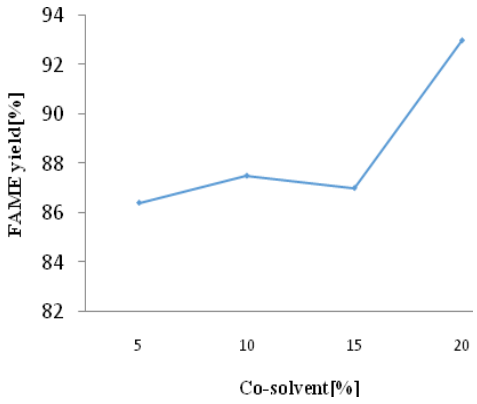

Fig 8. Yield of biodiesel as a type of Co-solvent

4. CONCLUSION

In tise study, natural zeolite clinoptilolite was used as the base catalyst for biodiesel production. Frist, the zeolite with KOH was calcined at 550 ^{o}C; during calcination process KOH conversed to K_2O. The following, composition was refluxed with KOH, 1, 2, 3, 4 M until Feldspar and all impurities are removed during the process of alkaline hydrothermal. Most biodiesel yield observed in 3M solution which was selected to continue the research. First biodiesel production by electrolysis in the presence of a homogeneous catalyst NaCl with efficiency of 97% was reported by Guan [13] and et al. Putra and et al [14] used this method for transtrification of cooking oil in the presence of heterogeneous catalytic reactions alkali chitosan and during the 4 hours was reached to yield 59/1% was reached. In this work, the electrolysis method was loaded for transesterification reaction in the presence of natural zeolite. KOH parameters amount loaded on the zeolite catalyst concentration, ratio of alcohol to oil, time, solvent and voltage on the output of biodiesel were investigated. Finally biodiesel in the presence of 2 wt% catalyst, the ratio of 1: 9 alcohols to oil, during 4 hours, 10 wt% solvent tetrahydrofuran and 10 V with a current efficiency of 90% was produced.

Finally, it is suggested to:

1. Apart from cooking oil (oil used in this study) other triglyceride oils can be used.
2. Other heterogeneous catalysts should be studied to obtain better and higher efficiency.
3. Different alcohol instead of methanol to be used.

5. REFERENCES

1. Sankaranarayanan, S., Antonyraj, C. A., & Kannan, S. (2012). Transesterification of edible, non-edible and used cooking oils for biodiesel production using calcined layered double hydroxides as reusable base catalysts. *Bioresource technology*, *109*, 57-62.
2. Supamathanon, N., Wittayakun, J., & Prayoonpokarach, S. (2011). Properties of Jatropha seed oil from Northeastern Thailand and its transesterification catalyzed by potassium supported on NaY zeolite. *Journal of Industrial and Engineering Chemistry*, *17*(2), 182-185.
3. Chouhan, A. S., & Sarma, A. K. (2011). Modern heterogeneous catalysts for biodiesel production: a comprehensive review. *Renewable and Sustainable Energy Reviews*, *15*(9), 4378-4399.
4. de Vasconcellos, A., Paula, A. S., Luizon Filho, R. A., Farias, L. A., Gomes, E., Aranda, D. A., & Nery, J. G. (2012). Synergistic effect in the catalytic activity of lipase Rhizomucor miehei immobilized on zeolites for the production of biodiesel. *Microporous and Mesoporous Materials*, *163*, 343-355.
5. Kay, K. H., & Yasir, S. M. (2012). Biodiesel production from low quality crude Jatropha oil using heterogeneous catalyst. *APCBEE Procedia*, *3*, 23-27.
6. Borges, L. D., Moura, N. N., Costa, A. A., Braga, P. R., Dias, J. A., Dias, S. C., ... & Ghesti, G. F. (2013). Investigation of biodiesel production by HUSY and Ce/HUSY zeolites: Influence of structural and acidity parameters. *Applied Catalysis A: General*, *450*, 114-119.
7. Ramos, M. J., Casas, A., Rodríguez, L., Romero, R., & Pérez, Á. (2008). Transesterification of sunflower oil over zeolites using different metal loading: a case of leaching and agglomeration studies. *Applied Catalysis A: General*, *346*(1), 79-85.
8. Kusuma, R. I., Hadinoto, J. P., Ayucitra, A., Soetaredjo, F. E., & Ismadji, S. (2013). Natural zeolite from Pacitan Indonesia, as catalyst support for transesterification of palm oil. *Applied Clay Science*, *74*, 121-126.
9. Teo, S. H., Islam, A., Yusaf, T., & Taufiq-Yap, Y. H. (2014). Transesterification of Nannochloropsis oculata microalga's oil to biodiesel using calcium methoxide catalyst. *Energy*, *78*, 63-71.
10. Kesica, Z., Lukic, I., Zdujic, M., Liu, H., & Skala, D. (2012). Mechanochemically Synthesized CaO ZnO Catalyst For

Biodiesel Production. *Procedia Engineering*, *42*, 1169-1178.

11. Tahvildari, K., Anaraki, Y. N., Fazaeli, R., Mirpanji, S., & Delrish, E. (2015). The study of CaO and MgO heterogenic nano-catalyst coupling on transesterification reaction efficacy in the production of biodiesel from recycled cooking oil. *Journal of Environmental Health Science and Engineering*, *13*(1), 1.
12. Helmi, M. Fereidooni,L. Tahvildari, K. (2015) The international conference on new research in Chemistry and chemical engineering, Iran.
13. Guan, G., & Kusakabe, K. (2009). Synthesis of biodiesel fuel using an electrolysis method. *Chemical Engineering Journal*, *153*(1), 159-163.
14. Putra, R. S., Hartono, P., & Julianto, T. S. (2015). Conversion of Methyl Ester from Used Cooking Oil: The Combined Use of Electrolysis Process and Chitosan. *Energy Procedia*, *65*, 309-316.