ANNALS of the ORADEA UNIVERSITY.
Fascicle of Management and Technological Engineering, Volume XI (XXI), 2012, NR2

THE INFLUENCE OF REACTION CONDITIONS ON THE TRANSESTERIFICATION OF SUNFLOWER OIL WITH METHANOL

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Keywords: biodiesel, transesterification, renewable energy.

Abstract: The rising price of petroleum in the world, combined with the increase of the fuel taxes in Romania has created a great demand for environmentally renewable energy resources. This paper presents a series of experimental research done on an experimental biodiesel installation. The author builds a small biodiesel installation in the Laboratory of Thermodynamics and Thermal Machines to investigate the reaction condition for biodiesel production. Transesterification reaction is the most common process to produce biodiesel from variety of vegetable oils and animal fat. In this paper, the transesterification reaction for production of sunflower oil methyl ester has been analyzed and the various process variables like working temperature, catalyst concentration, amount of methanol and reaction time have been optimized. The optimum conditions for transesterification of sunflower oil with methanol and NaOH as catalyst on the experimental biodiesel installation were found to be 60°C reaction temperature, 6:1 molar ratio of sunflower oil to methanol, 2 % catalyst and 2 hours reaction time.

1. INTRODUCTION

Biodiesel is an environmentally friendly liquid fuel with similar combustion properties to petroleum diesel. Increasing environmental concern, diminishing petroleum reserves and the agriculture-based economy are the driving forces to promote biodiesel as an alternative fuel [10]. In the world are more than 350 oil-bearing crops identified, among which only sunflower, safflower, soybean, cottonseed, rapeseed, and peanut oils are considered as potential alternative fuels for diesel engines [5, 9]. The increase in petroleum prices and uncertainties concerning petroleum availability renewed the interest in vegetable oil fuels for diesel engines [4]. The high viscosity and poor volatility are the major limitations of vegetable oils and animal fats for their utilization as fuel in petroleum diesel engines. Converting to biodiesel is one of the options to reduce the viscosity of vegetable oils [8]. Biodiesel is mono-alkyl-esters of long chain fatty acids derived from vegetable oils or animal fats produced by process of transesterification in which, oil is reacted with a monohydric alcohol in presence of a catalyst [7]. The most studied process to obtain biodiesel from vegetable oil is transesterification of triglycerides with low molecular weight alcohols catalyzed by homogenous catalysts [3]. Several researchers studied optimization of conversion process parameters of waste rapeseed oil with high free fatty acids (FFA) into biodiesel by response surface methodology and found maximum conversion at methanol/oil molar ratio of 6.5:1, catalyst concentration of 1% (by the weight of the oil), reaction time of 65.4 min and temperature of 48.2°C [13]. Also [7] studied the combination of process parameters giving optimum biodiesel yield at 6:1 molar ratio of methanol to oil, 0.75% KOH (w/w), 60°C reaction, temperature and 1 hour reaction time. Under typical transesterification reaction conditions of 60^oC temperature, 100.0g PKO, 20.0g ethanol, 1.0% catalyst (KOH) concentration and 30-120 min. reaction time, biodiesel gave promising results as alternative diesel fuel with acceptable specific gravity, viscosity, cloud point, pour point and flash point values with a maximum biodiesel yield of 96% at a reaction time of 90 min [1]. Optimal values for conversion of triglycerides was found at a reaction temperature of 60^oC, reaction time of 60 min., agitation speed of 250 rpm and a dosage of KOH of 1.4 wt% [2]. In this paper the main objective is to study the reaction condition in biodiesel synthesis through base catalyzes of vegetable oil, to check quality of biodiesel produced and maximize the methyl ester yield.

2. MATERIAL AND METHODS

The research on the reaction condition for biodiesel production was performed using an installation with a capacity of 30 L per batch. In the Laboratories of Thermodynamics and Thermal Machines of the Faculty of Mechanical Engineering, University of Craiova, it was conceived and built a small experimental installation for biodiesel production [12] using sunflower oil as raw material (Fig.1). The installation presented in Fig. 3 is composed by a reactor (were the reaction take place), a command panel to establish the reaction condition, an electrical resistance to heat the blend, a system for methanol recovery and different barrels for the reactants. The reactant mixing is done in three different ways: by the electric mixer, through the mix of the blend with the pump and to the use in the same time of the electric mixer and the pump. In the experiments was used a base catalyst, NaOH with a purity of 99% purchased from S.C. Laborex Romania. The quantity of catalyst used was measured with a precision balance model PGW 153e.

For the experiments was used sunflower oil from IPROCON SRL Craiova. The conversion of sunflower oil into its metyl ester was determined using Gas Chromatograph on a HP-INNOWax (cross-linked PEG) capillary column, with flame ionization detection. The percentages of each peaks of methyl esters were calculated and based on these values, ester conversion was calculated. During the experimental researches [12] was used a quantity of 20 L of vegetable oil to familiarize with the whole process and to prevent any waste of fuel in case the experiments won’t work as planned. From the command panel the pump is turned on to add the sunflower oil and sodium methoxide solution in the reactor and then the digital thermostat is set to heat the electrical resistance until a temperature of 60^{o}C.

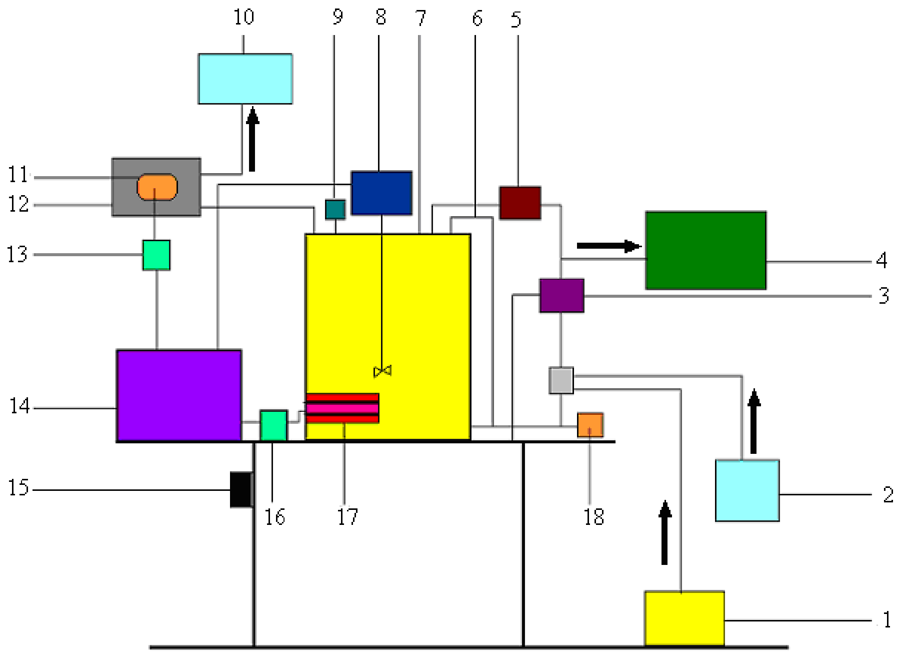

Figure 1. Scheme of principle for biodiesel installation

1- tank of vegetable oil; 2- methoxid barrel; 3- pump; 4- tank of biodiesel; 5- meter; 6- level pipe; 7- reactor; 8- electric mixer; 9- manometer; 10- methanol tank; 11- fan; 12- heat exchanger; 13- variable voltage control; 14- command panel; 15- meter electric power; 16- variable voltage control; 17- 2000W electrical resistance; 18- thermometer;

Figure 2. Front view of the experimental installation for biodiesel production

The mixture heating starts from a temperature of 22.5^{o}C (ambient temperature) and then the electric stirrer and mixing pump is turned on to blend the reactants. Electric stirrer facility is equipped with a variable voltage to change the speed of stirring in the reactor. Also the installation has a system to recover the methanol vapors resulted in the transesterification process. The system has a heat exchanger unit equipped with an electric fan to condensate the resulted alcohol vapors. At the base of the reactor, a thermometer indicate the inside temperature of the mixture.

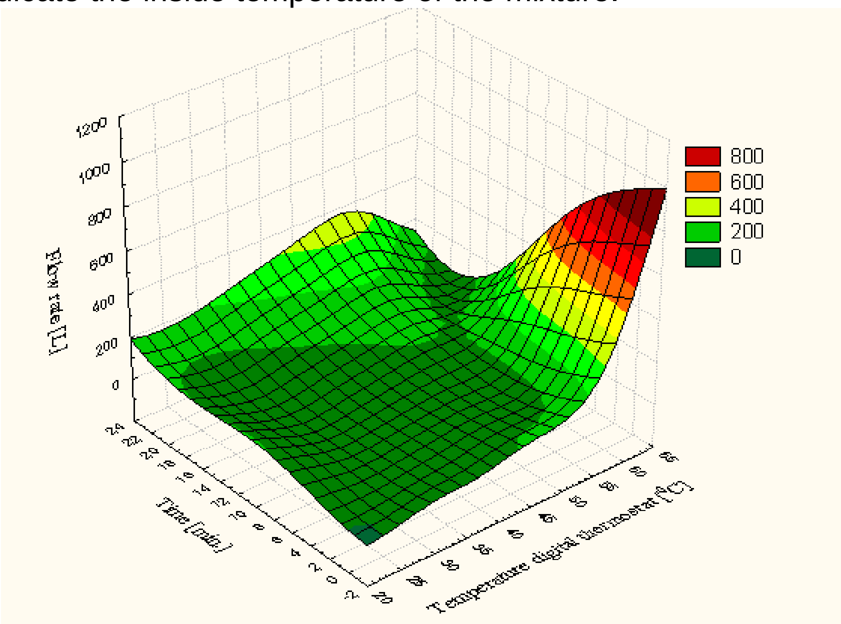

Figure 3. Technical parameters in biodiesel installation

According to the Fig. 3 the electric resistance controlled by the digital thermostat heat the mixture until 60^{o}C, after which the relay interrupts power supply to the resistance, the temperature increases up to 63^{o}C and then decreases. It is noticed a rise of the flow through the electric pump due to the decreases of the blend viscosity. In the experiments were measured the temperature of the digital thermostat, time, the thermometer temperature, energy consumption and flow rate of the blend. In the transesterification process is necessary to preheat the vegetable oil in the reactor up to a certain temperature and then to add the sodium methoxide solution. In the experiments is used a quantity 20 liters of sunflower oil, methanol (a molar ratio of 3:1) and sodium hydroxide. From the command panel the pump is turned on to add the sunflower oil in the reactor and then the digital thermostat is set to heat the electrical resistance until a temperature of 65^{o}C. When the oil reach the temperature the sodium methoxide solution is introduced into the reactor at ambient temperature.

3. RESULTS AND DISCUSSION

Molar ratio of alcohol to vegetable oil is an important parameter in biodiesel production affecting the final product. The stoichiometric ratio of transesterification reaction requires three moles of alcohol per mole of triglyceride to produce three moles of methyl esters and one mole of glycerol. Because it is a reversible reaction to obtain alkyl esters is necessary to work with excess alcohol. In this paper, the effect of methanol was investigated in the range of 3:1 to 8.5:1 (molar ratio), keeping other process parameters constant. Tests were performed on a volume of 20 liters of sunflower oil with a stirring speed of 250 rpm remaining constant throughout the experiments, a temperature of 60^oC and a catalyst concentration of 1.5% (w/w_{oil}). The conversion rate of the vegetable oil increases with molar rapport methanol: vegetable oil.

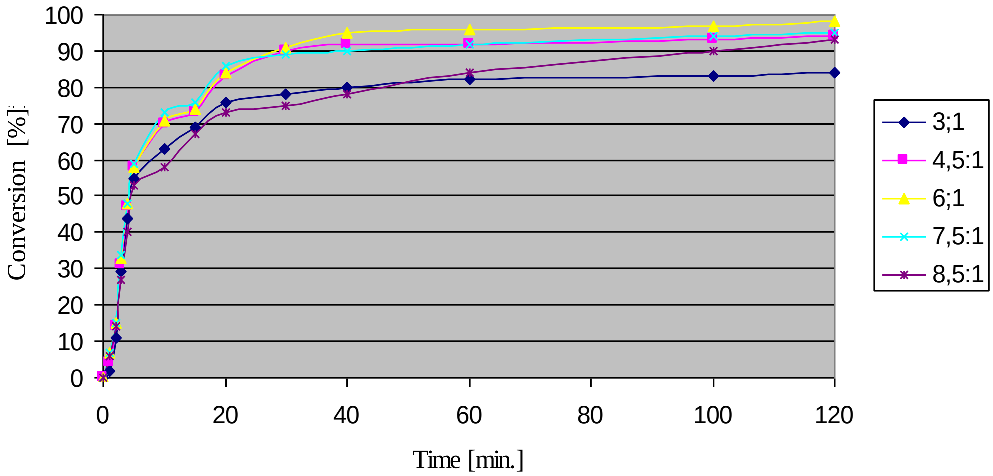

Figure 4. Effect of molar ratio of alcohol to vegetable oil on biodiesel conversion

According to the results obtained (Fig.4) the reaction is carried out at high reaction rate in the first 20 minutes, then evolves slowly approaching equilibrium which it will reach in about 2 hours depending on the molar ratio used. Optimal molar ratio was found at a value of 6:1 with a total conversion of 98% in biodiesel. In general the reaction products of the reaction are separated into two layers, the upper layer containing alkyl esters with mono and diglycerides, traces of methanol, catalyst and glycerin and lower layer composed by glycerin, alcohol excess, catalyst mono and diglycerides. However, the increase of molar ratio to higher values did not result in higher conversions. The improvement of conversion is due to the change of the transesterification reaction to the right. Superior molar conversion reports not increase the conversion, but only interfere in the separation of glycerol by decreasing density of the upper and lower layers (noticed in the experiments). This makes the separation of different layers to be more difficult in the end. If we use large rapports of methanol in biodiesel production in the reactor can form a third layer [6] formed only from excess methanol which leads to great difficulties in the separation process.

Effect of alkaline catalyst concentration was studied using sunflower oil and methanol with various amounts of NaOH varying from 0.25 to 5% (weight of NaOH/weight of oil).

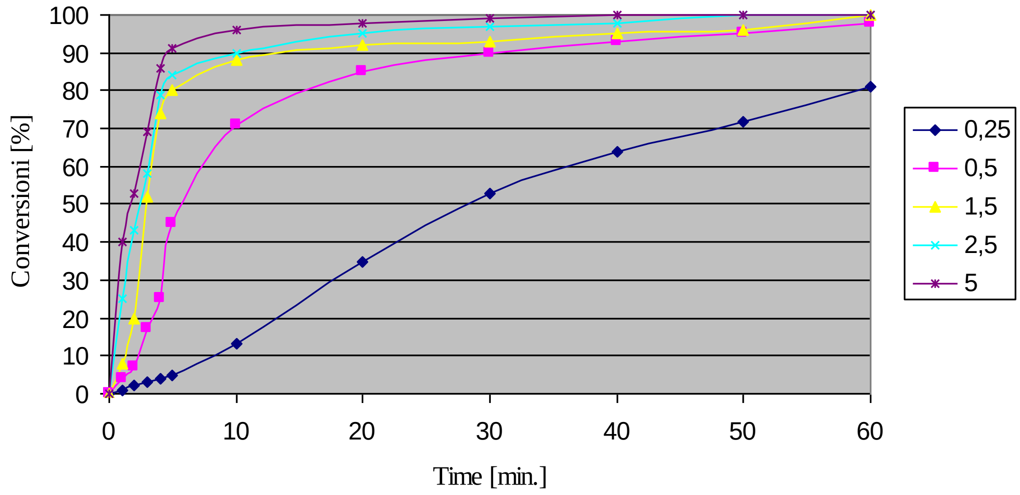

Figure 5. Effect of catalyst concentration on biodiesel conversion

The molar ratio of alcohol to vegetable oil 6:1, stirring speed, reaction temperature 60^0C and 1 hour time is kept constant during the experiments. The results for different catalyst concentration are shown in Fig. 5. An increasing amount of catalyst do not increase conversion rate but increase the cost of production due to the high soap formation and is necessary to remove the catalyst from the reaction products. It is noted that the reaction is carried out at high reaction rate in the first 10 minutes for the higher concentrations of NaOH, and then slowly evolves according to the proportion of catalyst used.

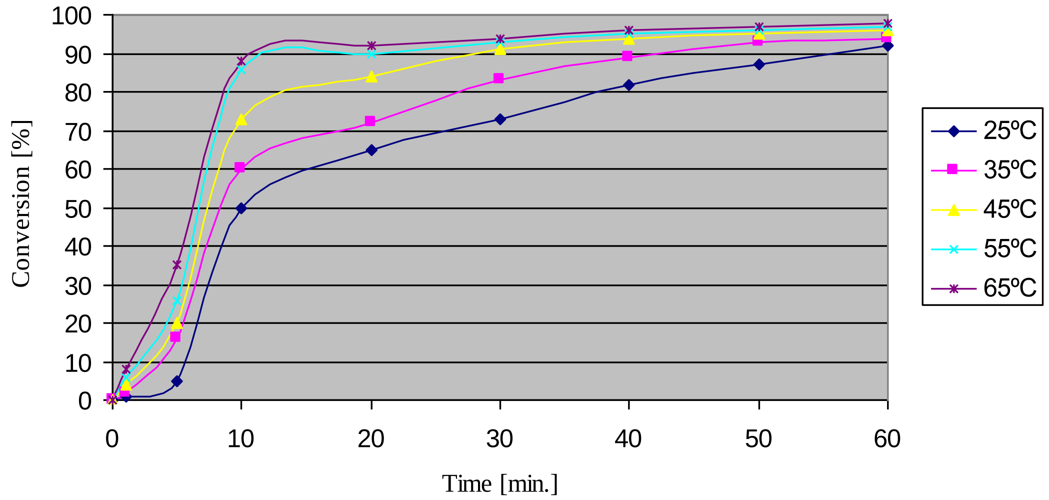

Figure 6. Effect of temperature on biodiesel conversion

Effect of reaction temperature was studied at 25, 35, 45, 55, 65^oC while all other parameters, molar ratio, catalyst concentration and time reaction were kept constant at 6:1, 1.5 % and 1 hour. The effect of reaction temperature on the ester conversion is shown in Fig. 6. It can be seen that the conversion rate increase with the rise of the temperature in the reactor. After 60 minutes, the transesterification reaction has reached equilibrium with a value of 98% to an average temperature of 65^oC. Since the transesterification reaction is a moderate exothermic reaction temperatures higher of 65….70^oC, can lead to a decrease in biodiesel conversion. The best results were obtained at temperatures of 45, 55 and 65 ^oC.

5. CONCLUSION

In this study, an experimental installation for biodiesel production was build and tested in different working condition. Biodiesel production from sunflower oil using NaOH as catalyst was analyzed and was found that NaOH can be utilized as a catalyst for biodiesel production without any difficulty. According to the data obtained in the tests, the formation of the methyl esters is affected by the molar ratio of glycerides to alcohol, catalyst, reaction temperature and reaction time. It is noticed that a high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because it is an increase in solubility of the mixture. Due to the fact that triglycerides and methanol are not miscible at ambient temperature the reactants needs to be blended through mechanical agitation to improve the mass transfer in the reaction. The rise of reaction temperature and base concentration lead to the increases of biodiesel conversion.

ACKNOWLEDGEMENTS

This work was supported by the strategic grant POSDRU/89/1.5/S/61968, Project ID61968 (2009), co-financed by the European Social Fund within the Sectorial Operational Program Human Resources Development 2007-2013.

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