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Original Research Article

Utilization of Waste Eggshell as Catalyst in Biodiesel Production and Investigation of Efficiency, Density and Viscosity Parameters of Biodiesel Obtained in Different Reaction Times



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ABSTRACT

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Rise in the global population, industrialization and urbanization together with increasing global trade and production facilities increase the demand for energy and natural resources every other year. Meeting the energy need arising from increasing industrialization, population growth and urbanization is reasonably the initial requirement of a sustainable development. Due to the start of rapid depletion of fossil fuels, alternative energy sources have undertaken a crucial role in producing energy. One of them is biodiesel. In production process of biodiesel via transesterification, one of the most vital parameters affecting the production efficiency is the catalyst that is used. Homogeneous and heterogeneous catalysts are utilized in biodiesel production. A number of factors such as saponification, spending great amount of reactive and extra dissociation cost have negative influences on production cost. Because of these reasons, efforts to develop high heterogeneous catalysts to hinder saponification, and the ones with high efficiency and possessing reusability have gained great acceleration and significance nowadays. In this study, using cheap and local waste eggshell as catalyst and the efficiency of biodiesel obtained in different reaction times and the effect of density and viscosity parameters were investigated. In the optimization studies (3-hour reaction time), the efficiency of the biodiesel obtained as a result of the first use of the catalyst was 94,82%, the density was 887kg / m³ and the viscosity was 4,965mm² / s. The results obtained in the second and third uses of the catalyst were 93.43%, 890 kg / m³, 4.962 mm² / s and 91.96, 889 kg / m³, 4.968 mm² / s, respectively. The study was detailed by means of analysis methods such as XRD and P-XRF. The results obtained suggest that waste eggshell can be used as catalyst, and that this can have great effect on biodiesel efficiency and that waste eggshell catalyst can be reused and that it can particularly reduce the biodiesel cost significantly.

Keywords: Biodiesel, Catalyst, Waste Egg Shell, Yield, Density, Viscosity

1. Introduction

Most of the countries in the world meet great amount of their energy requirements out of oil, hence they import great majority of this oil; and

this creates a very critical problem called as energy dependency. The energy input of today's industry societies is based on fossil fuels to a great extent. Alternative energy resources

produced from domestic means are of vital importance for countries, such as our country, importing great amount of their fossil origin fuels. Of alternative energy sources, renewable energy sources, which have gradually gained significance throughout the world, have directed attentions about energy towards this point in order that they can be used as energy sources alternative to fossil fuels. It is essential that the alternative energy sources should be the ones which can be obtained from local facilities for a sustainable economic development and a cleaner environment, people oriented, renewable, applicable and easily obtainable. The fact that biodiesel, occupying a significant place among alternative energy sources, can be used as an alternative fuel to fossil fuels attracts all the attentions to the energy issue. By the year 2017, the biodiesel amount consumed throughout the globe is about 30 billion liters [1]. Though the dependency on the fossil fuels is very high in the current situation, the biodiesel usage is gradually increasing by years [2,3]. The most important property differing biodiesel energy from the other types of energy sources is that biodiesel renews itself naturally and dissolves in the nature. Besides, biodiesel is very crucial in such terms as decreasing carbon emissions, which are harmful for the environment, and not needing to be imported since they are of domestic source and thanks to these, decreasing the dependency to abroad. The most commonly used method in production of biodiesel is transesterification method, though there are several methods [4]. Transesterification method is browning reaction of oil acids (vegetable oils, domestic waste oils, and animal fats) with alcohol (methanol, ethanol etc.) in company with catalyst [5]. In the processes where transesterification procedure is realized, catalysts are the most important parameters influencing biodiesel yield efficiency. Today, the catalysts mostly used in biodiesel production are homogenous structured basic and acidic catalysts [6]. Basic catalysts are preferred in commercial procedures due to their high transformation efficiencies and their short reaction times [7]. Sodium hydroxide, sodium methoxide and potassium hydroxide can be given as examples of the mostly used catalysts [8]. Acidic homogenous catalysts are used instead of basic homogenous catalysts in

transesterification of oils which have higher free oil acid (FOA) rate and water content like animal fats. Also, pre-neutralization process is conducted by means of acidic catalyst using two processes, thus, basic homogenous catalyst is used in the second process. The most significant disadvantages of basic homogenous catalysts preferred due to their high efficiency are saponification reactions stemming from high FOA and water content during biodiesel production and product purification processes with high cost. Saponification reaction not only lowers the biodiesel efficiency but also aggravates post-reaction separation processes. Taking these factors into consideration, efforts to enhance heterogeneous catalysts which prevent saponification, with high efficiency and high reusability have become the subject of scientific researches [9]. In recent years, the efforts to develop heterogeneous catalysts for biodiesel attainment have gained quite a high momentum. The most important reasons for this rise are that there is separation after synthesis, and there is no purification process; and neutralization phase of free oil acids is eliminated, and no saponification of triglycerides is seen, and no catalytic waste is left in methyl esters and glyceride, and it makes the yield more economical. At the same time, heterogeneous catalysts are environment friendly catalysts that can be obtained by product conversion [10]. Therefore, these kinds of studies are investigations which provide facility for making use of eggshells, an important waste in egg industry, and usage of an environment friendly catalyst [11]. Chakraborty et al. used fly ash and eggshell derivatives as solid catalyst in transesterification of soya oil. In their study, a novel catalyst was developed by using waste eggshells in order to increase CaO and supported fly ash catalysts in transesterification use. The waste eggshells were used after they were calcined. Catalysts exhibiting tiny pores and high basic activity were prepared. 96% methyl ester efficiency was obtained from the prepared catalyst under optimum experimental conditions. Moreover, the catalyst displayed high reusability feature [12]. Wei et al. studied eggshells by means of triglyceride transesterification with a view to determine its viability as a solid catalyst to use in biodiesel synthesis. They also investigated

the effects of calcination temperature on structure and activity of eggshell catalysts [13]. Khemthong et al. used eggshell wastes in their studies as heterogeneous catalysts for microwave assisted biodiesel production [14]. Ayodeji et al., in their study where CaO and eggshells were used as catalysts for biodiesel production, were witnessed to have reached 89% biodiesel efficiency when they used methanol/oil: 8/1 rate and 4% catalyst (wt/wt%) within 3-hour reaction period [15]. Tan et al. "Waste ostrich- and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: Catalyst characterization and biodiesel yield performance" in their studies the experimental result showed that 1.5 wt.% catalyst, 12:1 M ratio of methanol to oil, 65 C reaction temperature, 2 h reaction time with speed of 250 rpm gave the best results. It was found that the ostrich-eggshell derived CaO catalyst shows higher surface area, higher basicity and smaller particle size. The maximum biodiesel yield is 96% and 94% for calcined ostrich-eggshell and chicken-eggshell, respectively [16]. Shan et al. "Catalytic applications of calcium rich waste materials for biodiesel: Current state and perspectives" in their studies the CaO catalyst was easily obtained by calcining eggshell at 1000 C. The prepared catalyst exhibited high activity and over 95% biodiesel yield was obtained under the suitable conditions [17]. Laca et al. "Eggshell waste as catalyst: A review" in their studies the effect of these factors on catalyst activity for biodiesel production has been widely studied and it is clear that in the development of eggshell catalyst to obtain biodiesel the calcination conditions are determinant on catalyst performance. Temperatures given as optimal for calcinations vary between 600 and 1000 C, depending on the authors. In addition, catalyst deactivation after several cycles of use was related to a reduction of the surface area due to structure modifications and/or deposits of intermediates on catalysts surface that leads to a decrease of catalytic activity [18]. In this study, using heterogeneous catalyst obtained by calcining waste eggshells, they investigated reaction parameters of biodiesel production out of sun-flower seeds and methanol; and they studied the effects of efficiency, density and

viscosity parameters of biodiesel obtained in different reaction periods.

2. Experimental

2.1. Materials and Catalyst Preparation

Sun-flower seed oil used in the experiments was purchased from a local market. Methyl alcohol of 99.7% purity of Sigma Aldrich firm was bought from a commercial company to realize fuel production in accordance with standards. Waste eggshells, after being washed with clean water, were disposed of membrane and other wastes. The cleaned eggshells were dried in the oven for one hour at 115°C. The dried eggshells were ground in the electrical grinder approximately 80 mm sized pieces after they were cleared of inside coat and other dirt. The obtained eggshell dust calcined in an oven at 900°C for 24 hours for conversion of CaCO₃ into CaO. The product obtained was used as heterogeneous basic catalyst in production methyl ester.

2.2. Catalyst Characterization

XRD examinations were performed on the product obtained as a result of calcination of organic material (egg shell) at 900°C for 24 hours. XRD analyses were carried out by Rigaku brand, Miniflex-II model X-beams diffractometers at Geology Engineering Department Research Laboratory in Batman University (Anode = Cu (CuK_α=1.541871 Å), Filter = Ni, Voltage = 35 kV, Current = 15 mA, Goniometer speed = 2°/min., Paper speed = 2cm/min., Time constant = 1 s, Crack = 1° 0.15 mm 1° 0.30 mm, Paper clearance = 2θ = 20-80°). Despite the calcination of calcite crystal phase, it shows that the peaks observed in 3.03 Å and in 3.78 Å facing calcite minerals surface (104) still continue. In Figure 1, it is observed that the best catalytic conversion performance was obtained at 900°C. The best conversion efficiencies in similar studies were witnessed between the clearances of 800-900°C. Wei et al. found out that the best efficiency was obtained at 900°C in biodiesel production by means of application of waste eggshell as low-cost solid catalyst [13]. Viriya-empikul et al. uttered that they attained optimum efficiency at 800°C during the 4-hour calcination in their investigations for biodiesel production derived from industrial wastes by Ca-based solid

catalysts [19]. Niju et al. examined calcination times at 600-900°C in their studies in biodiesel production by modification of eggshell and its application, and stated that they reached the best conversion efficiency between these clearances [20].

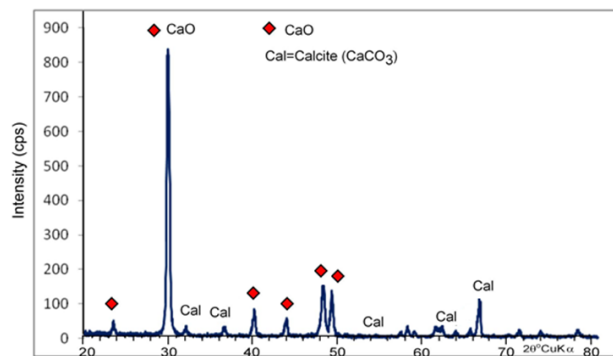


Figure 1. XRD patterns belonging to calcination of eggshell at 900°C

The chemical analyses of calcined and uncalcined eggshells were carried out with the help of Portable X-ray Fluorescent Spectrometry (P-XRF). According to the analyses results, it is observed that nearly all of

eggshell is composed of CaO. It can clearly be seen that in similar studies, results very close to our values were obtained [20,21]. In Table 1, the P-XRF analysis results of calcined and uncalcined eggshells are given.

The experiments were planned so as to find out the effects of reaction time on the efficiency of biodiesel, density and kinematic viscosity. According to results obtained, the most convenient conditions were decided, and biodiesel, produced under optimized conditions, was studied in terms of fuel properties to evaluate its consistency as diesel fuel. Afterwards, the catalyst used in the experiments was washed with ionized water and dried at about 100°C; and then reused in production of biodiesel under the same conditions and the parameters mentioned above (efficiency of product, viscosity and density) were measured. The same catalysts were washed for the second time and the same procedures were repeated, and thus the values of parameters were fixed at the end of the reaction.

Table 1. P-XRF analysis results of calcined and uncalcined eggshells
Chemical Composition of the Catalyst (wt%)

Compound	Uncalcined Eggshell	Calcined Eggshell
SiO ₂	0.0566	0.0601
P ₂ O ₅	0.3074	0.3806
SO ₃	0.9822	0.7353
ZnO	0.0012	0.0014
CaO	97.9459	98.81
Fe ₂ O ₃	--	--
SrO	0.04678	0.0189
ZrO ₂	--	--
BaO	--	--
La ₂ O ₄	--	--
CeO ₂	--	--
Pr ₂ O ₃	--	--
Yb ₂ O ₃	--	--

3. Results and Discussion

3.1. Effect of Reaction Time

The reaction time affects the conversion efficiency of the transesterification process of converting oil into biodiesel [22]. According to a number of researches conducted, biodiesel production has always been proportional to reaction time. In other words, the yield of biodiesel increases when reaction time increases [23]. The completion of the basic-catalyzed transesterification process depends on reaction time. It is suggested that excess reaction time does not increase the conversion but favours the

backward reaction (hydrolysis of esters) which results in a reduction of product yield [24]. The results of present study clearly demonstrate that the conversion rate increases with reaction time [25–26].

It is important to determine adequate reaction time since this is directly related to energy consumption during biodiesel production. In this study, reaction time is evaluated until four hours with one hour intervals. The effect of reaction time is examined maintaining reaction conditions with methanol/oil mole ratio: 6/1, amount of catalyst 3% (weight) at 60°C.

Production efficiency, density and viscosity parameters obtained at the end of these studies are recorded. Then, the catalyst used in the experiments was washed with ionized water and dried at about 100°C; and then reused in production of biodiesel under the same conditions and the parameters mentioned above (efficiency of product, viscosity and density)

were measured. The same catalysts that we used in the experiments were washed for the second time and the same procedures were repeated, and thus the values of parameters were fixed at the end of the reaction. In Table 2, examination of biodiesel efficiency, density and viscosity parameters obtained different reaction times as a result of optimization activities can be seen.

Table 2. The effect of reaction time on production yield, viscosity and density
Using egg Shell catalyst

Use of Catalyst	Rxn time (h)	Biodiesel yield (%)	Density (kg/m ³)	Viscosity (mm ² /s)
	1	93.60	889	4.956
1. Use of Catalyst	2	94.65	888	4.968
	3	94.82	887	4.962
	4	93.25	888	4.965
	1	92.93	892	4.958
2. Use of Catalyst	2	93.12	891	4.970
	3	93.43	890	4.965
	4	92.32	892	4.968
	1	92.40	894	4.966
3. Use of Catalyst	2	92.40	890	4.972
	3	91.96	889	4.968
	4	91.32	891	4.970

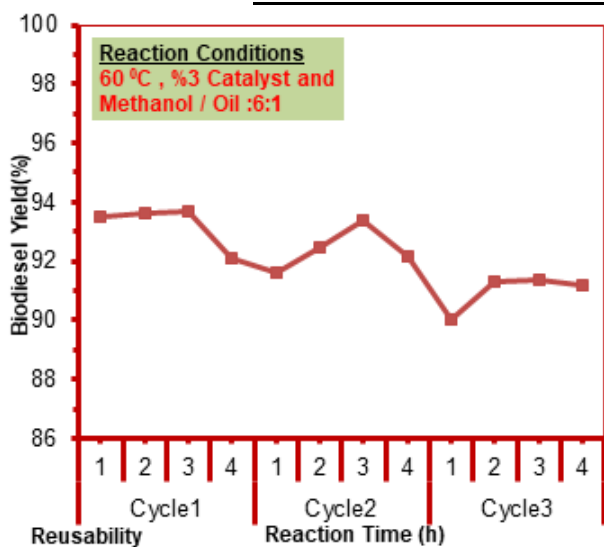


Figure 2. Change in Biodiesel yield with reaction time

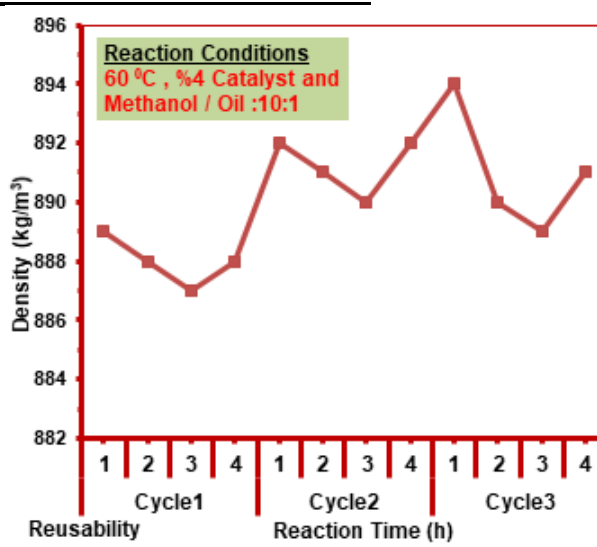


Figure 3. Change in Biodiesel density with reaction time

The effect of reaction time is examined by keeping the reaction conditions constant with 3% catalyst, 6:1 methanol/oil molar ratio and at 60°C temperature. As can be seen in Figure 2, when the reaction time is increased gradually, it is seen that biodiesel yield has also gradually increased at first three hour periods; however, when we increased reaction time up to 4 hours, the yield has partially decreased. It has been found out that expected partial decrease in biodiesel yield has occurred when catalysts have been used for the second and third times. When

reaction time has been increased over 4 hours for all three usages, this has affected the result in direction to decrease the reaction efficiency. As can be seen in Figure 2, when reaction time has been gradually increased at the first three hour periods, it has been witnessed that biodiesel yield has increased in parallel way, whereas when we increased the reaction time to 4 hours, the yield has partially decreased. The expected partial decrease in biodiesel yield has been fixed to be 1.46% and 3,0% after the catalysts have been used for the second and the

third time. When the reaction time has increased over 4 hours for all three usages, it has been seen that they act in direction to decrease reaction efficiency.

When looked at Figure 3, it can be seen that the density of the biodiesel obtained with the first three hour slots decreases step by step when reaction time is gradually increased. On the other hand, when we increase the reaction time to four hours, it is observed that the density increases one unit. Likewise, when the catalysts are used for the second and third times, it is determined that biodiesel densities increase incrementally. In all three usages of catalyst use, when the reaction time is increased over 4 hours, it can clearly be seen that there is a partly increase in the density of biodiesel.

When Figure 4 is examined, it can be seen that though a little, the density and together with viscosity of the biodiesel obtained with the first three hour slots have decreased step by step when reaction time is gradually increased. On the other hand, when we increase the reaction time to four hours, it is observed that though very little, the viscosity has increased. Likewise, when the catalysts are used for the second and third times, it is determined that biodiesel viscosities have increased incrementally. In all three catalyst use, when the reaction time is increased over 4 hours, it can clearly be seen that there has been a little increase in the viscosity of biodiesel.

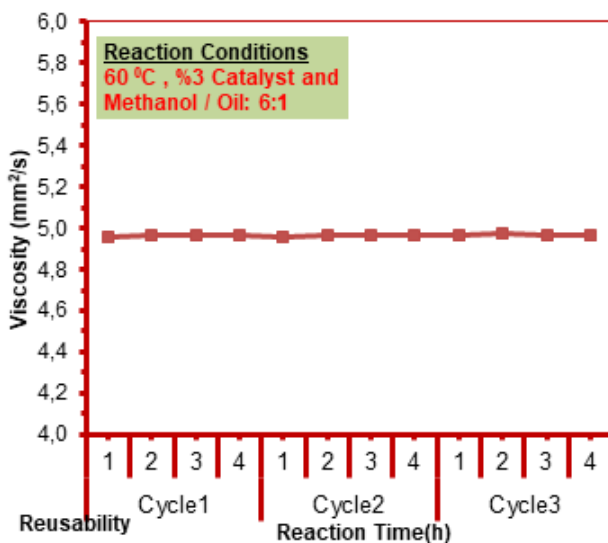


Figure 4. Change in biodiesel viscosity with reaction time

4. Conclusion

We found out that waste eggshell catalyst that we used in the experiments can be reused if

necessary processes are applied. We are of the opinion that using the obtained catalyst in biodiesel yield has a significant advantage not only in terms of environment but also in terms of cost. The fact that efficiency of first phase biodiesel that we attained was quite high (94,82%) was an indicator that the used catalyst and other parameters were optimum. It is considered that in the second and the third phase, the efficiency decreased partly (1,46% and 3,0%), and that this can be tolerated. In all these phases, it is determined that the density and viscosity values of yielded biodiesel were within EN950 standard values. As a result, it is seen that eggshell, a waste product in terms of environment, can be used as a catalyst in biodiesel production after a few simple and cheap processes.

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