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Production of biodiesel from animal waste using eggshell catalyst

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ABSTRACT

Biodiesel is a clean fuel produced from recyclable materials such as plant and animal fats used as catalyst. This present study is intended to use animal waste as feedstocks (raw material) to produce biodiesel. The biodiesel production reaction is an esterification reaction in which variables such as reaction time, used solvent. Also, catalysts play a significant role in the intrinsic properties of fuel and the efficiency of the product. In this research study, calcinated eggshell was selected as a catalyst and ethanol as solvent. Biodiesel has been extracted using the substances mentioned above in one phase. The given optimal conditions include 5 h period, the amount of catalyst (4.5 g), and the quantity of solvent (13.91 mL). The produced sample was derived under conditions with the maximum quantity and physical properties, including cloud point and pour point, viscosity, and density in respective of producing biodiesel fuels from other materials. The results revealed reduction of properties at cloud point and pour point.

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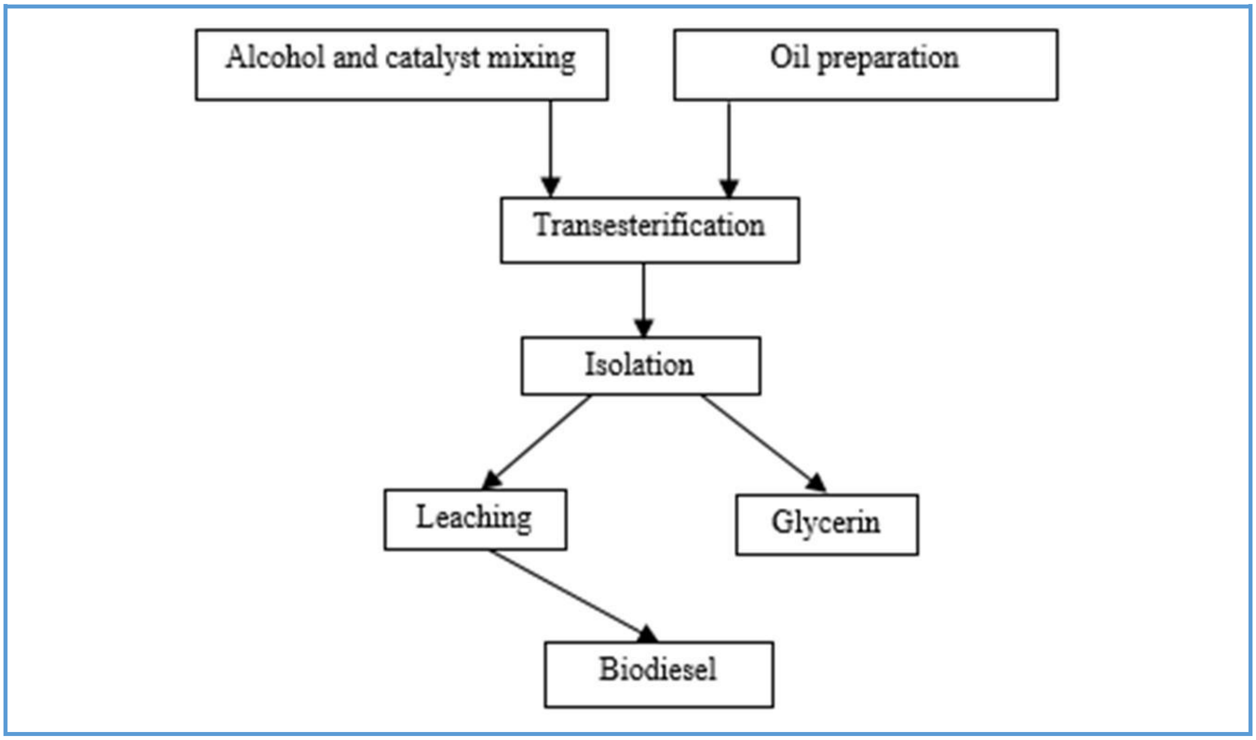
Graphical Abstract



Introduction

The ever-increasing use of fossil fuels, a rise of prices of oil products, and decrease of the existing oil deposits have compelled researchers to find new non-oil resources. At present, the approximate quantity of world oil reserves is, to the extent that if the trend of reliance on fossil fuels is continued, the world will be exposed to a lot of problems regarding the environment and shortage of raw materials in the near future [1, 2]. Fuel and environmental pollution are two subjects that have been the most significant challenge to which humans were exposed during recent years. The invention of internal- combustion engines such as diesel engines and the given advancements in the technology of manufacturing of engines have been led to the comprehensive, advanced technology of internal- combustion engines in the sector of railway and road transportation and agricultural industry, and other industries that have been followed by rising consumption of fuel sources in the world [3, 4].

Biodiesel is one of the alternative clean fuels with plant and animal sources composed of mono mono-alkyl esters derived from the esterified exchange of triglycerides (triple esters of fatty acids) esterification of free fatty acids with short-chain alcohol [5–7]. One can refer to better lubrication, propagation of lesser pollutants such as carbon monoxide and sulfur dioxide, gradability, biodegradability, reduced accumulation of greenhouse gases in the atmosphere, complete combustion because of having 21% of the weight of oxygen in the given structure, and a reduction of the problem of global health as some of the advantages of biodiesel [8–10]. A comparison between biodiesel and fossil diesel is presented in Table 1 in terms of physical and chemical properties [11].

Table 1. Comparison of intrinsic properties of biodiesel and fossil diesel fuel

Characteristic	Biodiesel	Fossil diesel
Density at temperature 15 °C (kg.m^3)	870-895	810-860
Kinematic viscosity at 40 °C (cst)	3.5-5.5	2-3.5
Cetane index	45-65	40-55
Filter block point (°C)	5-10	0-25
Cloud point (°C)	5-10	0-20
Pour point (°C)	10-15	0-35
Minimum thermal value (MJ. Kg)	36.5-38	42.5-44
Water content (mg.kg^{-1})	0-500	-
Acidity index (mg KOH/g oil)	0-0.6	-
Ester content (wt.%)	More than 96%	-
Glycerin content (wt.%)	0-0.25	-
Sulfur content (mg.kg^{-1})	-	15-500

Fat-tail sheep has been used to produce biodiesel fuel in this investigation in which the tail and rump contain a noticeable amount of types of saturated fatty acids. Their weight in sheep is about 15-20% of the total weight of the sheep's body. Features of tail-rump fat vary with fat in the sheep's body, and it possesses a lower melting point and higher Iodine index than the rump. The tail-rump constituent saturated fatty acids mainly include palmitic acid and stearic acid, ranging from 42 to 72%. Concerning the high percentage of saturated fatty acids existing in the tail-rump, use of them is not recommended in food preparation. Sheep rump has a more significant amount of stearic acid, and as a result, its melting point is higher than cattle rump, and thus it is more solid and brittle than this rump [12].

Production of biodiesel fuel extracted from animal waste oil (sheep) has been assessed in this study using an eggshell catalyst for the first time. Structural properties of producing fuel were evaluated using various tests. It is hoped to replace it as a substitute for fossil fuels.

Experimental

Materials and methods

The materials used in this study include animal waste oil according to Figure 1, pure ethanol (prepared by Qom Qadirshahr city), eggshell, KOH, and acetone from Merk a German Company.

Figure 1. Animal waste oil, sheep rump

Preparation of sheep rump

The sheep rump was prepared from sale ers in Lorestan Province in Iran, and it was sliced into small pieces and melted using indirect heat at 32 °C. Solid impurities were isolated from the rump, and it was kept at 4 °C during the execution of reactions. It was stored in a closed, tight vessel to prevent possible perishing and the creation of molds.

Measurement of saponification index and acidity index of sheep rump

To acquire saponification index, 2 g animal waste was initially mixed with 25 mL of alcohol potash (0.5 N) and poured into the balloon using reflex for 2 h. The 26 mL alcohol potash was titrated using HCl (0.5 N) standard. The given volume is assumed as V_a. After the reaction for 2 h, the given solution, including animal waste and potash, is poured into Erlenmeyer, and it is titrated using 0.5 N HCl. Then the resulting volume is considered as V_b. At the end, quantities of soap index and its molecular mass are obtained using the following formulae according to Iranian national standard (10495):

$$\text{Soap Index}=[56.11\times N_{acid}\times(Va - Va)]/W_{oil} \quad (1)$$

$$M_{Woi}=(3\times 56100)/\text{Soap Index} \quad (2)$$

Now, this solution's soap index and molecular mass are 211.82 and 794.56, respectively, for the extracted animal waste oil in this study. 28.02 g of animal waste is currently mixed with 50 mL of ethanol by pouring them into an Erlenmeyer to acquire acidity index. Then, titration is done using 0.1 N KOH, and the consumed volume of potash is measured from a burette. At last, the acidity index is derived from the following formulae for an acidity index of animal waste:

$$V_{KOH} \times N_{KOH} \times 56.11 / W_{oil} = [\text{ Acid Index}] \quad (3)$$

$$FFA\% = (100 \times \text{Acid Index} \times M_{Woi}) / (3\times 56100) \quad (4)$$

Whereas acidity index may contribute to the selection of a type of catalyst. Thus the calculated number is for animal waste as follows: FFA% = 0.923

Synthesis of biodiesel

A magnetic mixer heater was used to supply and control the heat. 80 g of solid oil of animal waste was poured into a Balloon 250 mL (as reaction reactor) along with a spiral refrigerant connected to the urban water grid to prevent from exiting of ethanol from the given ambiance at temperature 80 °C within specific periods and with 800 rpm speed according to Figure 2.

Figure 2. The equipment to produce biodiesel from animal waste

At this step, 1, 4.5, and 8 g of catalyst (eggshell) are ground using a pounder and poured into Chinese crucible and is being heat them in an oven at 1200 °C for 4 h to execute calcination operation, then, exit catalyst from the furnace and weighed it in amounts of 1, 4.5, and 8 g and with ethanol at the same time are added to oil at 80 °C and condenser put on the balloon and open water tap. Afterwards, we adjust the heater timer at specific intervals (1, 3, and 5 h) and let the reaction occur. After the reaction time, we turn off the heater and let it become cool. Then we pass it from filtration paper, and after the end of reaction time, the contents inside the balloon are transferred into the decanter funnel.

The needed time is devoted to forming two phases, and this may take from 4-24 h in which biodiesel is placed on the top and glycerol at the bottom based on a difference of density. Glycerol exists from the end of the decanter funnel. To purify biodiesel from glycerol, we wash the catalyst and methanol with distilled water at temperature 60 °C (to reduce the time and number of washing by water) to approach the pH of output water from a decanter funnel to distilled water by repeating of washing phases. Number of washing is noted down to remove the acidity of biodiesel. One can add 1 or 2 drops to water from washing using phenolphthalein. We repeated this operation every time of washing until it became colorless. Figure 3 shows the schemata of this phase.

Figure 3. Isolation of biodiesel and washing it until removal of acidity state

After washing and exiting the water from the bottom of the decanter, the contents of the decanter funnel are conveyed to a beaker. To isolate the existing water in the given product that may not be extracted by decanter, the beaker is put on the heater, and the gradual temperature of the product is increased to reach 115 °C and kept at this temperature until the isolation of water from the product (approximately for 23 min). To prevent possible dissemination of oil due to a sooner tendency of water drops to change of phase and resistance of oil placed at the top of the vessel because of lower density, a magnet (3 cm) is utilized for which 533 rpm speed is designated for it. The produced fuel becomes more transparent. After cooling, the sample was considered to execute analyses and determine chemical and physical properties.

Results and Discussion

Biodiesel is prepared from an esterified exchange between plant and animal oils (triglycerides) with alcohol (base, acid, and enzyme). In this reaction, the connected chain for the factor group of hydroxyl in alcohol is replaced with glycerol in the triglyceride molecule. The alcohol factor will be substituted with the corresponding ester to glycerol. Three-factor ester (triglyceride) is converted into three esters of a factor for which that alkyl is called esters of fatty acid or biodiesel [13].

$$\text{Triglycerides} + C_2H_5OH \xleftrightarrow{\text{Catalyst}} \text{Diglycerides} + R_1COOC_2H_5$$

$$\text{Diglycerides} + C_2H_5OH \xleftrightarrow{\text{Catalyst}} \text{Monoglycerides} + R_2COOC_2H_5$$

$$\text{monoglycerides} + C_2H_5OH \xleftrightarrow{\text{Catalyst}} \text{Glycerol} + R_3COOC_2H_5$$

The quantity of water and free fatty acids is vital in catalytic processes, and their presence may reduce efficiency. Homogeneous and heterogeneous (basic and acid) catalysts are utilized in the trans-esterification technique. In most cases, reaction with primary catalysts is executed with more incredible speed with acid catalysts, and they are more prevalent [14]. Similarly, the use of homogeneous catalysts in the reaction will be followed by difficulty in isolation of catalyst and cost rise. It needs significant amounts of water for its isolation [15]. The production of biofuel's structural and intrinsic properties depend on different parameters, including the molecular ratio of alcohol/waste oil, a quantity of catalyst, and reflection. In Table 2, are examined 17 samples with different conditions.

Table 2. Samples of producing biodiesel in laboratory conditions

Samples	Time (h)	Oil/ethanol	Catalyst (g)
1	3	3	8
2	3	12	8
3	5	3	4.5
4	5	12	4.5
5	1	7.5	1
6	1	12	4.5
7	1	3	4.5
8	3	7.5	4.5
9	3	12	1
10	5	7.5	8
11	3	1	12
12	1	7.5	8
13	1	3	1
14	1	12	1
15	3	7.5	1
16	3	12	4.5
17	5	7.5	4.5

Rise of temperature due to reduction of viscosity causes more straightforward mixture and loosing of bonds and ease of producing esterified ethyl and increase in reaction efficiency. Due to the high rate of evaporation of ethanol and the lesser presence of this factor in reaction, higher temperatures cause saponification and e the efficiency of biodiesel production that its impact will also be tangible in the number of washing [16]. The optimal temperature varies from 70 to 75 °C in the use of ethanol, while in this study, it was considered 72 °C in this reaction at ambient conditions. It is noteworthy that the rise of temperature may be followed by negative and positive effects on reaction efficiency. The fixed temperature has been designated in all of the samples. According to the given data, this study's optimal time is 5 h. The rate of alcohol use depends on selecting the suitable catalyst to a great extent. Molecular ratios of alcohol to animal waste oil have acquired 3 as optimal values that are sampled No.3 in which catalysts play an essential role in determining reaction time. The value of optimized catalyst is 4.5, where the highest volume of biodiesel is 68.3 mL with 73.1 g. All of the samples have been evaluated in terms of physical and chemical properties, so the analytical data of the sample are visible in Table 3.

Analysis of effects of molecular ratio of ethanol to oil in production of biodiesel

Concerning the given results of laboratory samples, the amount of produced fuel was considered as a criterion for assessment. The fixed 4.5 g of catalyst and at fixed and different time intervals along with the effect if the value of the molecular ratio of alcohol to oil is examined in production of fuel in which as the amount of produced ethanol is increased at a

Table 3. Physical properties of producing biodiesel under different laboratory conditions (in laboratory conditions)

Samples	Melting point °C	Cloud point °C	Freeze point °C	Pour point °C	Biodiesel volume mL	Biodiesel weight g
1	57.8	37.9	22.3	27.3	67.8	72.2
2	59.2	38.8	23.2	28.1	65.2	70.3
3	56.7	37.1	21.9	26.7	68.3	73.1
4	58.3	38.7	22.7	27.4	65.3	70.4
5	56.2	37.7	21.8	26.6	66.4	71.6
6	58.4	38.4	23.2	28.2	67.4	72.3
7	59.4	39.2	23.5	27.4	65.9	70.2
8	55.9	36.8	21.7	26.8	66.3	71.6
9	56.8	37.2	22.4	27.5	66.7	71.8
10	56.1	37.3	22.4	27.8	67.9	72.5
11	55.8	36.5	21.4	26.9	66.7	61.8
12	59.3	39.1	23.6	28.4	67.4	72.6
13	58.5	38.2	22.9	27.3	65.8	70.7
14	56.7	36.6	22.1	26.9	67.6	72.8
15	57.1	37.9	22.7	27.4	66.5	71.7
16	58.6	38.6	23.1	28.1	65.9	72.1
17	57.2	37.6	22.5	27.6	67.4	72.9

fixed time (1 h), production of fuel is increased. Its physical and chemical properties are improved. The above result increases by an increase of time to 3 h, and the maximum amount of produced fuel is acquired at a molecular ratio of ethanol/oil at 12 (Table 4).

However, the acceptable point is related to the comparison of samples Nos. 6 and 16 in which to rise over time, a quantity of fuel has been reduced Comparing samples 6 and 16, conclude that has decreased over time, the amount of fuel. In contrast, if this time has been kept fixed at 5 h, the maximum amount of produced fuel has been acquired in the third laboratory sample with a molecular ratio of 3 i.e., 73.1 g. This indicates lesser solvents can be used for fuel production with the rise of extraction time.

Analysis of effect of catalyst value in production of biodiesel from animal waste oil

To examine the effects of the quantity of catalyst on the esterification reaction of animal waste oil to produce fuel, reaction time was considered fixed at three hours and value of ethanol/oil molecular ratio as 12, and quantities of catalyst is added. Initially, the amount of catalyst is increased from one gram to 4.5 g of producing biodiesel quantity. However, it has reversed and inhibiting effect by increasing this weight to 8 g, and it causes a reduction in the amount of producing a fuel amount. The results are shown in Table 5.

Analysis of effect of time in production of biodiesel from animal waste oil

According to Table 6, the effects of time are examined by fixing the quantity of catalyst and ethanol/oil ratio. Under these conditions and by analysis on the amount of giving fuel amount for which amount of catalyst is 4.5 g and ethanol/oil molecular ratio 12, as time is reduced percent of the fuel production increase. These results show that one can improve production efficiency in a shorter time by increasing the ethanol/oil molecular ratio.

Table 4. Effect of ethanol/oil molecular ratio in the efficiency of producing fuel

Test	Time/h	Catalyst/g	Ethanol/oil	Biodiesel weight/g
7	1	4.5	3	70.2
6	1	4.5	12	72.3
8	3	4.5	7.5	71.6
16	3	4.5	12	72.1
3	5	4.5	3	73.1
17	5	4.5	7.5	72.9
4	5	4.5	12	70.4

Table 5. Effect of amount of catalyst in the efficiency of producing fuel

Test	Time/h	Catalyst/g	Ethanol/Oil	Biodiesel weight/g
9	3	1	12	71.8
16	3	4.5	12	72.1
2	3	8	12	70.3

Table 6. Effect of reaction time on the efficiency of producing fuel

Test	Time/h	Catalyst/g	Ethanol/oil	Biodiesel weight/g
6	1	4.5	12	72.3
16	3	4.2	12	72.1
4	5	4.5	12	70.4

Table 7. The physical properties of laboratory sample of No 3

Physical properties	Unit	Results
dynamic viscosity (T=343K)	Pa.s	0.0179
Kinematic viscosity	mm^2/s	1.68
Boiling point	°C	223
Flash point	°C	92.3
Cetane index	-	52

Conclusions

Due to having 21-31 wt.% of oxygen in its structure, biodiesel causes complete combustion, preventing the propagation of carbon particulates through the air. So that in average, it propagates carbon monoxide 44% less than diesel fuel. In other words, it lacks sulfur and aromatic compounds [17, 18]. The efficient parameters in reaction will impact the production rate of biodiesel as the main product and glycerine as a side-product. In this study, optimal values of efficient parameters were determined in reaction, and the physical properties of methyl ester were examined. To determine the optimal values of efficient reaction parameters, the amount of eggshell catalyst, ethanol/oil molecular ratio, and reaction time were evaluated at temperature 80 °C with mixer speed 800 rpm. Animal waste oil was used for the production of biodiesel, and physical parameters of all product samples are visible in Table 3. Concerning the best-given laboratory sample, the quantity of catalyst was derived as 4.5 g, ethanol/oil molecular ratio 3, and time as 5 h. Table 7 shows intrinsic properties and given physical parameters in this sample.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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