

Biodiesel Production by Alkali Catalyzed Transesterification of Chicken and Beef Fats

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Abstract

Biodiesel is renewable, biodegradable and environment friendly fuel. Actually biodiesel is mono alkyl esters of animal fats oil and vegetable oils. Biodiesel from animal fat oils produced through transesterification in presence of methanol and alkaline catalyst. In this study alkaline base catalyst KOH was used. The response surface methodology (RSM) was used to determine the optimum conditions for the production of biodiesel through alkaline-catalyzed transesterification of chicken and beef tallow. From the results of the present study the optimum reaction conditions for methanolysis of chicken and beef tallow i.e., 0.50% KOH as catalyst, methanol/ oil molar ratio 2.1:1, reaction temperature 60°C, rate of mixing 600 rpm and a reaction time of 60 min, provided 88% of biodiesel yield. The influence of the catalyst concentration was very important because at higher catalyst concentrations the % age yield of biodiesel was decreased and also if moisture content is greater in environment then conversion lead to the soap formation. The oil/methanol molar ratio was one of the variables that had the most prevalent influence on the transesterification process. Fuel properties were determined such as the flash, pour points of biodiesel produced are found to be somewhat higher, which may point to potential difficulties in cold starts. Thus, biodiesel derived from chicken and beef tallow is an acceptable substitute for petrodiesel. Physical and chemical analysis of biodiesel showed that it is more economical and contributes less to global warming as compared to fossil fuels burning. Biodiesel seems to be realistic fuel for future. It has become more attractive recently because of its environmental benefits.

Keywords: Biodiesel, biodegradable, global warming, environmental benefits.

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INTRODUCTION

If there is increase in number of automobiles, vehicles and transport, then obviously there will be increase in demand for fuel oils (Jaichandar and Annamalai, 2011). Day by day increasing demand of fuels will result in rapidly dwindling of fossil fuels. US department of energy estimate that world oil supplies around the year 2020 will reach its maximum production and midpoint of depletion (Liaquat *et al.*, 2013). Burning of fossil fuels cause global warming, health problems and environmental hazards. So there is needed to develop environment friendly fuel that must be safe for human health (Liaquat *et al.*, 2013). Also the day by day increase in prices of petroleum products forces the development of such fuels that will be economical, cheap and beneficial (Bhattarai *et al.*, 2013).

Because of following problems discussed above one of the most important areas in technology and science today is the production and use of beneficial fuels. The Fuels that must be renewable unlike fossil fuels which are non-

renewable. Such renewable fuels are produced from vegetable oils and animal fats (Batista *et al.*, 2012). Vegetable oils and animal fats are triglycerides produced through intracellular metabolism, are hydrophobic substances (Batista *et al.*, 2012).

From vegetable oils and animal fats, biodiesel is produced through the process of transesterification. Transesterification is carried out in presence of suitable catalyst and methanol (Batista *et al.*, 2012; Abdullah *et al.*, 2007).

There are four major reasons for the production of biodiesel i.e. higher costs of fossil fuels, climate change policy, reduction of fossil fuel resources and production from renewable resources (Gerpen, 2004).

The biggest difference why we need to develop biofuels or biodiesel is its environment friendly chemical properties. Biodiesel is more promising, beneficial alternative fuel unlike petroleum products due to following reasons, It is accessible, reliable and renewable fuel; Free

of sulfur and aromatics (Demiras, 2010; Batista *et al.*, 2012; Vieitez *et al.*, 2014); It is biodegradable than any other petroleum product; It reduces CO emission so contribute much less to global warming (Batista *et al.*, 2012; Vieitez *et al.*, 2014; Jaichandar and Annamalai, 2011); Biodiesel can be used without modification of engines (Demiras, 2010; Jaichandar and Annamalai 2011; Ahmad *et al.*, 2013); It is more lubricating (Jaichandar and Annamalai 2011).

In Pakistan as it is developing country where the petroleum prices are soaring and the numbers of fossil fuels are much more less so it's the need of hour to develop cheap, economical fuel sources that will easily accessible to every citizen of Pakistan. The only solution to this problem is production of biodiesel from waste animal tallow (beef fat, mutton fat), poultry fats, vegetable oils and waste frying oils (Ahmad *et al.*, 2013). The purpose of current research work was the optimization of alkaline catalyzed transesterification reaction used for biodiesel production using chicken and beef fats oil as feedstock.

MATERIALS AND METHODS

This study was conducted to evaluate the effects of various reaction parameters *i.e.* reaction temperature, catalyst concentration, reaction time and methanol to oil molar ratio on biodiesel yield. All the experiments were performed thrice and results were presented as Mean \pm standard deviation.

Fats:

- Chicken Fats
- Beef Fats

Chemicals:

Isopropanol, KOH, Phenolphthalein, Toluene, Methanol, Chloroform, Acetic acid, Starch, Sodium thiosulfate, Hydrochloric acid, Potassium iodide, Iodine trichloride, Carbon tetrachloride.

Procurement of raw materials

Fats were purchased from butchers shop: beef fats and poultry (chicken) fats. 250 g of each animal fat was heated for about one hour, for the purpose of oil extraction. Extracted oil was sealed in container, jar or bottle and the solid waste of fats thrown into dustbin.

Preliminary tests for raw chicken and beef fat oil

Methods given in American Oil Chemists Society (AOCS) were used to perform all the tests for physico-chemical characterization of chicken and beef fats oil feedstock.

PHYSICAL CHARACTERISTICS

Different physical characteristics of feedstock oil were determined. These were given as follows:

Specific gravity (AOCS method Cc10a-25):

Specific gravity of feedstock oil was determined by using specific gravity bottles. For this purpose specific

gravity bottle of 25 ml capacity was firstly weighed. Then it was filled with water and the weight was noted again. It was mandatory that there must be no air bubble in the liquid. From the initial and final readings, the density of water was calculated according to formula:

$$\text{Density} = \text{weight} / \text{volume}$$

For determining specific gravity of feedstock oil, same procedure was adopted to calculate density of sample as used in density calculation of water. Then specific gravity was calculated according to formula:

$$\text{Specific gravity: density of oil/ density of water.}$$

Refractive index (AOCS method Cc 7-25):

Refractive index of feedstock oil was determined by using Abbes refractometer. Firstly all prisms of Abbes refractometer were sterilized with the help of toluene then dried completely. Calibration was carried out by running water firstly in refractometer. After calibration prisms were again cleaned with toluene and dried. Abbes refractometer was then adjusted to 60°C. Then a drop of sample oil was placed using glass rod making a thin film between prisms and close in tightly. Then the refractometer was allowed to stand for 2-3 minutes or until the temperature of sample oil became equal to temperature of refractometer. Then telescope was rotated in such a manner that field of view appeared to be divided into half equal dark and light portions. When the end of bright portion coincided with telescope wire, readings were noted from the scale of refractometer at room temperature. Average of three readings was taken as final reading.

CHEMICAL CHARACTERISTICS:

Different chemical characteristics of raw chicken and beef fat oil were determined. These were given as follows:

Acid value: (AOCS method Cd 3d-63)

Firstly burette was filled with freshly prepared KOH titrant. In titration flask accurately weighed 2 g of sample oil was taken then 25 ml of solvent was added following the addition of 0.4 ml indicator into it and mixed it until completely dissolved. The volume / initial readings were noted on burette. Then titrated it against KOH by drop wise addition with stirring until light pink color remains persistent. The final reading was noted from the burette. Then the difference between initial and final reading was calculated. This was reading for sample. Then same procedure was adopted for blank without addition of sample oil. Then titrant was added again drop wise until faint pink color remains persistent. Then final reading was calculated.

Acid value was determining by using following formula

$$[(A-B) N \times 56.11] / W$$

A=volume of titrant for sample

B= volume of titrant for blank

N= KOH normality=0.02

W=sample weight ~ 2 g

Peroxide value: (AOCS method cd 8-53)

Accurately weighed 5 g sample oil was added in conical flask then 30 ml of PV solution was added following addition of 1 ml KI solution. Then conical flask was allowed to stay for one minute, added 30 ml distilled water into it and added starch solution sequentially. Titrate resulting solution with $\text{Na}_2\text{S}_2\text{O}_3$ (0.1N) till the end point appeared which was colorless. Then the peroxide value was evaluated by following formula:

Peroxide value: $\text{vol. of Na}_2\text{S}_2\text{O}_3 \times 0.1\text{N} \times 1000 / \text{wt. of sample (g)}$.

Iodine value: (AOCS method Cd 1-25)

In a conical flask, 0.25 g of sample oil was taken and then 5 ml of CCl_4 was added along with addition of Wijs solution (5ml). After shaking conical flask, it was kept in the dark for half an hour. After removal from dark add 5 ml of 15% KI solution added following 25 ml of water. Titrated it with sodium thiosulfate solution (0.1N) till the colorless point appeared. Then freshly prepared starch solution was added in small quantity of 2-3 drops and titrated resultant solution again with sodium thiosulfate until equivalence point appeared. Final readings were calculated. For blank solution reading same procedure was applied without addition of oil. Finally calculated iodine value by using formula given below:

Iodine value = $\text{blank reading} - \text{sample reading} \times 0.1\text{N} \times 12.69 / \text{wt. of sample (g)}$.

Saponification value: (AOCS method Cd 3-25)

KOH alcoholic 0.5 N: KOH (0.5) was obtained by mixing the 28.05 g KOH in 95% ethanol and made the volume up to 11. The standardization is done by titrating it with standard solution of 0.5 N HCl. Phenolphthalein (1%) was used as indicator.

HCl 0.5 N: Normality of conc. HCl is about 10. 0.5 N HCl is prepared by diluting 5 ml conc. HCl with 95 ml distilled water. The standardization of this dilute HCl was done with Na_2CO_3 solution to get accurate normality.

In a conical flask accurately weighed 1 g of sample oil was added and refluxed it with 25 ml KOH for half an hour on water bath, then allowed it to stay for some time till its temperature became equal to room temperature. Titrated the resulting solution with HCl and indicator used for phenolphthalein. Then using the same procedure reading for blank was determined in the absence of oil. Finally given formula was used to find saponification value:

Saponification value = $28.5 \times (X - Y) / \text{sample oil weight (g)}$

X = Reading of blank

Y = Reading of sample

EXPERIMENTAL DESIGN

For this purpose, 250 ml flat bottom three neck flask was used with thermometer, magnet bar or magnetic

stirrer, a condenser, and placed on hot plate, set at 600 rpm stirring rate to produce biodiesel.

EXTRACTED OIL

Oil extracted from sample fats taken into flat bottom three neck flask 25 g by weight. Then the sample was slightly heated to given temperature on hot plate.

MIXING OF CATALYST AND METHANOL:

Add 12 g of methanol by weight by using digital weighing balance in separate beaker. Next add 0.5% catalyst KOH in beaker. Take great care while handling the mixture, as methanol is highly evaporative, cover the beaker immediately with aluminum foil after pouring methanol from bottle to beaker. Shake it and wait for a while until they get completely dissolve.

ADDING METH OXIDE IN OIL

The mixture when KOH completely dissolve in methanol called methoxide. Add this to sample oil in flat bottom three neck flask.

TRANSESTERIFICATION

Transesterification of sample fat oil was carried out by placing sample oils one by one in flat bottom three neck flasks. Methoxide was poured in flask having sample oil. Flask with mixture was placed on hot plate set the temperature at 60°C and stirred at 600 rpm. This reaction was run for 1 hour at constant temperature.

After completion of one hour, the resultant mixture was poured into separating funnel. After 24 hours two layers were formed one upper with methyl esters and the other lower with glycerol.

SEPARATION OF GLYCEROL

After the transesterification reaction, one must wait for the glycerol to settle to the bottom of the container. This happens because Glycerol is heavier than biodiesel. The settling will begin immediately, but the mixture should be left a minimum of eight hours to make sure all of the Glycerol has settled out. The Glycerol volume should be approximately 20% of the original oil volume.

WASHING OF METHYL ESTERS

After separation of glycerol from separating funnel, heated the methylester layer on Bunsen burner flame. In separating funnel warm distilled water was slightly added, shakeed well, after some time two layers were formed somewhat milky. Released the lower layer, and this process was repeated three times to purify diesel from catalyst and any remain of methanol.

Response surface plots were employed to obtain appropriate combination of variables for optimum biodiesel yield.

OPTIMIZATION OF REACTION VARIABLES

Optimization of various reaction variables *i.e.* reaction temperature, catalyst concentration, time of reaction and molar ratio was done by using central composite response surface design to obtain maximum % yield and of good quality biodiesel.

FUEL CHARACTERISTICS OF RESULTING BIODIESEL

Different fuel characteristics of resulting biodiesel were determined including kinematic viscosity, specific gravity, flash point, density, sulfur content, pour point, cetane number, cloud point, acid value and water content using ASTM standard method.

RESULTS AND DISCUSSION

The response surface methodology (RSM) was used to determine the optimum conditions for the production of biodiesel through alkaline-catalyzed transesterification of chicken and beef tallow. From the results of the present study the optimum reaction conditions for methanolysis of chicken and beef tallow *i.e.*, 0.50% KOH as catalyst, methanol/ oil molar ratio 2.1:1, reaction temperature 60°C, rate of mixing 600 rpm and a reaction time of 60 min, provided 88% of biodiesel yield (Table 1).

Table 1. Optimum conditions for the production of biodiesel through alkaline-catalyzed transesterification of chicken and beef tallow.

Factors	Optimum values	Yield
KOH	0.50%	
Methanol/ oil molar ratio	2.1:1	
Reaction temperature	60°C	88%
Rate of mixing	600 rpm	
Reaction time	60 min	

Acid values are used to measure the extent to which glycerides in the oil have been decomposed by catalyst and other actions such as light and heat. The acid value indicates the amount of free fatty acids present in the oil/fat, which in turn indicates the degree to which the fat can rancidify. As fats undergo rancidity, triglycerides are converted to fatty acids and glycerol, causing an increase in acid value. The calculated Acid value of beef tallow was 1.07 mg KOH/g which was lesser than the Fadhil (2013) calculated acid value that was 4.66 mg KOH/ g and of chicken tallow was 0.56 mg KOH/g that was similar to calculated acid value by Mata et al. (2010).

Iodine value of the beef tallow and chicken tallow was 44 g I₂/100 g and 73 g I₂/100 g respectively, beef tallow iodine number was higher than the iodine value of Fadhil (2013) calculated that was 33 g I₂/100 g. While Mata et al. (2010) calculated iodine value was 76.7 g I₂/100 g higher than our calculated. The density of beef tallow was 0.971 g/ ml at (16°C) lesser than the density of beef tallow calculated by Fadhil (2013) that was 0.9216 g/ ml at (16°C)

and density of chicken tallow was 0.962 g/ ml at (16°C) while according to Alptekin et al. (2011) was 4.35 mm²s⁻¹. Calculated value of kine viscosity for beef tallow was 36.39 at 40°C (KV, mm²/s) lesser than Fadhil (2013) 37.39 at 40°C (KV, mm²/s). And value for chicken tallow was 56.2 at 40°C (KV, mm²/s) higher than Alptekin et al. (2011) 4.35at 40°C (KV, mm²/s). Refractive index for beef tallow was 1.478 at 20 °C similar to Fadhil (2013).

The carbon residue value is considered to give an approximate indication of the combustibility and deposit forming tendencies of the fuel. The calculated condradson carbon residue for beef tallow was 0.28 % which according to Fadhil (2013) was 0.23%.

The higher heating value of beef tallow was 38.6 MJ/kg fat lesser than Fadhil (2013) that was 39.23 MJ/kg fat. The HHV of chicken tallow was 39.8 MJ/kg fat lesser than the value calculated by Mata et al. (2010) that was 44.71 MJ/kg fat (Table 2).

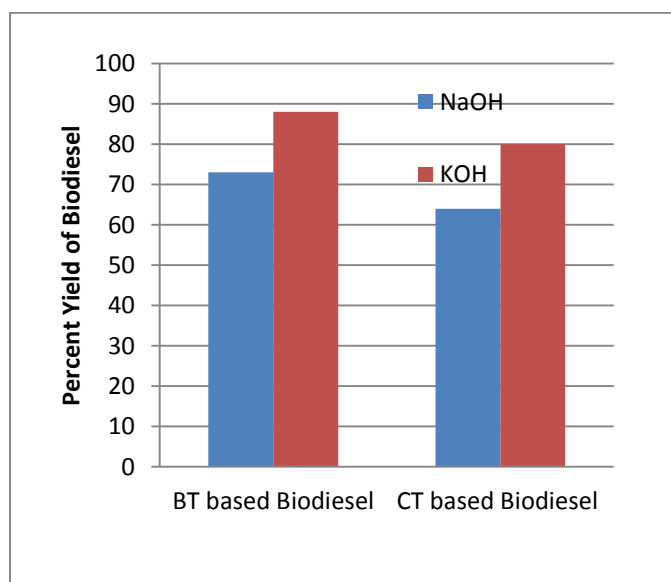
Figure 1 showed the % yield of biodiesel based on beef tallow and chicken tallow. By using KOH the %yield of biodiesel from beef tallow and chicken tallow was 88% and 80% respectively. Mata et al. (2011) concluded that the % yield of biodiesel from beef and chicken tallow was 90.8% and 76.8% respectively. If NaOH used as catalyst then the % yield will be 73% and 62% for beef and chicken tallow respectively, which was lesser than KOH based biodiesel.

Analysis of BT and CT based biodiesel was performed with the help of FTIR. FTIR spectrum gives a lot of information about simple BT and CT based biodiesel (Table 3). FTIR spectrums showed that IR bands are in the region 1425-1447 cm⁻¹ for CH₃ asymmetric bending and 1188-1200 for O-CH₃ stretching, these both CH₃ asymmetric bends and O-CH₃ stretching were present in BT and CT based biodiesel IR spectrum. Further interpretation of BT and CT based biodiesel spectrum showed that the region 1370-1400 cm⁻¹ for O-CH₂ groups in glycerol (moiety of TG, DG, and MG) and 1075-1111 cm⁻¹ for O-CH₂-C asymmetric axial stretching were absent. The FTIR spectrum of BT and CT based biodiesel showed the presence of the region 1700-1800cm⁻¹ for C=O stretch and 2800-3000cm⁻¹ for symmetric CH₂ stretching and the asymmetric CH₃ and CH₂ (Table 3).

Fatty acid composition of biodiesel derived from beef oil was determined by Gas Chromatography which showed different carbon chain compound was present in this sample. It was found that beef biodiesel contained 1.43 wt. % lauric acid, 6.31 wt. % Myristic acid, 28 wt. % Palmitic acid, 4.7 wt. % Palmitoleic acid, 18 wt. % Stearic acid, 41 wt. % Oleic acid, 3.3 wt. % Linoleic acid, 0.8 wt. % Linolenic acid (Table 4). Encinar et al. (2011) reported the percentage of different faty acid which was 1.5 wt. % Myristic acid, 28.1 wt. % Palmitic acid, 4.0 wt. % Palmitoleic acid, 12.0 wt. % Stearic acid, 44.6 % Oleic acid, 9.4 wt. % Linoleic acid and 0.5 wt. % Linolenic acid.

Table 2. Physicochemical properties of beef tallow (BT) and chicken tallow (CT)

Property	Test Procedure	BT Value	CT Value
Density at 16°C g/ml (D)	ASTM D4052-91	0.971	0.962
Kine Viscosity at 40°C (KV, mm ² /s)	ASTM D445	36.39	56.2
Acid Value (AV, mg KOH/g)	ASTM D664	1.07	0.56
Iodine number (g iodine/100 g fat)	ISO 3961	44	73
Refractive index at 20 °C (RI)	D1747-09	1.478	1.491
Conradson Carbon Residue (CCR, %)	ASTM D4530	0.28	0.31
Higher heating value (MJ/kg fat)	Oxygen bomb calorimeter	38.6	39.8

**Fig. 1. Percent yield of BT and CT based biodiesel**

Fatty acid composition of biodiesel derived from chicken oil was determined by Gas Chromatography which showed different carbon chain compound was present in this

sample. It was found that chicken biodiesel contained 1.32 wt. % Myristic acid, 23 wt. % Palmitic acid, 5.4 wt. % Palmitoleic acid, 7 wt. % Stearic acid, 38 wt. % Oleic acid, 27.6 wt. % Linoleic acid, 1.72 wt. % Linolenic acid (Table 4). Mata et al. (2011) reported the percentage of different fatty acid which was 30.08 wt. % Palmitic acid, 5.95 wt. % Stearic acid, 47.03 % Oleic acid, 15.55 wt. % Linoleic acid and 1.39 wt. % Linolenic acid.

Fuel properties of biodiesel based on beef tallow and chicken tallow i.e. higher heating value, (the amount of heat released when a specified substance is combusted), viscosity, density, cetane number, (is a measurement of the combustion quality of diesel fuel during compression ignition), flash point (The flash point of a volatile material is the lowest temperature at which it can vaporize), pour point (pour point of a liquid is the temperature at which it becomes semi solid and loses its flow characteristics), acid value and iodine values listed in table 5, it explained that biodiesel based on beef and chicken tallow is more accessible, reliable, and have positive effects on engine. Biodiesel fuels from animal fats are more accessible, less costly; everyone can afford it and can easily be used without modification of engines. Bioethanol and Biogas can also act as an alternative, sustainable and renewable energy resource (Shaukat *et al.*, 2016; Afshan *et al.*, 2017).

Table 3. Characteristics regions of BT and CT based biodiesel

Sr.No.	Region (cm-1)	Assignment	BT based biodiesel	CT based biodiesel
1	1425- 1447	CH ₃ asymmetric bending	present	present
2	1188-1200	O-CH ₃ stretching	present	present
3	1370-1400	O-CH ₂ groups in glycerol moiety of TG, DG, and MG	absent	absent
4	1075-1111	O-CH ₂ -C asymmetric axial stretching	absent	absent
5	1700-1800	C=O stretch	present	present

Table 4. Major fatty acid composition of BT and CT based Biodiesel

Fatty acid	BT	CT
Lauric acid (C 12:0)	1.43	-
Myristic acid (C 14:0)	6.31	1.32
Palmitic acid (C 16:0)	28	23
Palmitoleic (C 16:1)	4.7	5.4
Stearic acid (C 18:0)	18	7
Oleic acid (C 18:1)	41	38
Linoleic acid (C 18:2)	3.3	27.6
Linolenic acid (C 18:3)	0.8	1.72

Table 5. Fuel properties of BT and CT based biodiesel

Property	BT based biodiesel	CT based biodiesel
Higher Heating Value KJ/kg	41	41.5
Viscosity (mm ² /s) at 40 °C	5.29	5.56
Density (kg/m ³) at 15 °C	859	887
Cetane number	58.2	57.4
Flash point (°C)	161	176
Pour point (°C)	14	12
Acid value (mg KOH/g)	0.2	0.8
Iodine value (g I ₂ /100g)	44	38

CONCLUSION

It is recommended that people must use waste materials like waste frying oil, plants oil, and also animal fats to meet the day by day increasing demand for fuels. As we know natural fossil fuels are dwindling very rapidly. If we do not properly discard fats than they will produce smell and pollute the environment. And if we produce biodiesel from those waste fats the problem of discarding will also solve.

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CONFLICT OF INTEREST

There is no conflict of interest.

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