Biodiesel Fuel Production From Residual Animal Fat as an Inedible And Inexpensive Feedstock

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ABSTRACT: In agricultural parts, the main consumers of fuel are diesel engines and agricultural machinery. Between agricultural Machineries Tractors and combines are the greatest consumers of diesel fuel. Bio-diesel is an alternative to petroleum-based fuels derived from vegetable oils, animal fats, and used waste cooking oil including triglycerides. Using low-cost feedstocks such as rendered animal fats in biodiesel production will cause biodiesel expenditures to be reduced. The aim of this study was to obtain a new and environmentally friendly process for developing biodiesel production technology from waste animal fats, as an inedible and inexpensive feedstock (as low cost sustainable potential feed stock for biodiesel production). Their main characteristic was high free fatty acid content. This is based on a study of the amounts of residual fat that is possible to recover from local animal butchery (Slaughterhouse). Waste animal fat is considered a promising cheap alternative feedstock for biodiesel production that does not compete with food stock. In addition, using waste animal fat as a feedstock is considered a waste management process. The data resulted from gas chromatography (GC) revealed these percentages for fatty acid compositions: myristic acid (3%), palmitic acid (27%), stearic acid (0.19%), oleic acid (59%), linoleic acid (3%) and gadoleic acid (5.5%). Animal fats were transesterified with acid catalyst and basic catalyst with and without pre-esterification. Pre-treatment was effective for fats with different FFA content. Alkali transesterification of esterified fats resulted in a product with 98 wt. % ester content. Biodiesel quality was evaluated and most of properties were well within EN 14214.

Keywords: Biofuel, Free Fatty Acid, renewable energy, Animal Fat, transesterification.

INTRODUCTION

Bio-diesel is an alternative to petroleum-based fuels derived from vegetable oils, animal fats, and used waste cooking oil including triglycerides. Since the petroleum crises in 1970s, the rapidly increasing prices and uncertainties concerning petroleum availability, a growing concern of the environment and the effect of greenhouse gases during the last decades, has revived more and more interests in the use of vegetable oils as a substitute of fossil fuel (Wang Y. D. et al, 2006). The use of biodiesel in internal combustion engines, especially in compression ignition engine, represents an excellent option on the ecological point of view. Most of CO₂ emissions are from renewable carbon stocks. Biodiesel is usually produced from high quality vegetable oils. These feed stocks have high cost, which currently accounts for over 85% of biodiesel production expenses (Moser, 2008). In recent years, a wide range of studies have been carried out on biodiesel production from feed stocks of low cost. Frying oils (Encinar et al., 2005, 2007; Tomasevic and Siler-Marinkovic, 2003; Zhang et al., 2003), new vegetable species (Encinar et al., 2002; Kulkarni et al., 2007; Meher et al., 2006) and animal fats (Canakci and Van Gerpen, 2001, 2003; Dias et al., 2008, 2009; Ngo et al., 2007) have been researched. The last kind of low cost feedstock has not been developed in depth (Berrios et al., 2009).

Fuels derived from biological sources, among them lipid materials such as fats and oils, have received increasing attention. Different production processes using fats and oils as feedstocks yield fuels with different compositions and properties. The most prominent of these fuels is biodiesel (Umdu et al, 2009), which is defined as the mono-alkyl esters of vegetable oils or animal fats, obtained by transesterifying an oil or fat with an alcohol. The major reason for not using a neat vegetable oil as fuel is its high viscosity (usually in the range of 28–40 mm²/s), which leads to operational problems in diesel engine including formation of deposits and injector coking due to poorer atomization upon injection into the combustion chamber. Transesterification of the oil reduces the viscosity of the oil to a range (usually 4–5 mm²/s) closer to that of petro diesel. However, a fuel
which can be termed “renewable diesel” and whose composition resembles that of petroleum-derived diesel fuel (petro diesel), has been gaining attention in recent years. Several processes (cracking or pyrolysis, hydride oxygenation) can be used to obtain fuels resembling petrodiesel (Takuya Ito et al, 2012). Figure 1 is a flow chart for fuels from triacylglycerol containing feeds tocks from production to engine combustion.

![Flowchart for transformation of lipid materials (biodiesel and renewable diesel by hydride oxygenation) to products of engine combustion.](image)

Biodiesel from animal fats compared with biodiesel from vegetable origin has the advantage a higher cetane number, the most significant indicator of diesel combustion behavior (Tong et al., 2011); nevertheless, the fuel produced from fats has higher cold filter plugging point because of this raw material has significant content of saturated fatty acids (Lebedevas et al., 2006). Furthermore, biodiesel from animal fats is less stable for oxidation, this fact being attributed to the absence of natural antioxidants as compared to biodiesel of vegetable origin (Sendzikiene et al., 2005). For these properties, the biodiesel produced from animal fats might not be adequate to use it 100% pure in vehicles during cold weather; however might be used 100% pure in boilers for heat generation. Alternatively, fats might be mixed with other raw materials to get a biodiesel obeying such quality specifications, being even possible to enhance some biodiesel properties by incorporation of fats in the raw material (Canoira et al., 2008; Dias et al., 2008).

In Iran, Fars province is one of the major meat producers. In 2012 its production corresponded to nearly 108 thousand tons of poultry and 70 thousand tons of beef. Thus, meat-processing and rendering industries produce annually a large amount of animal fats with different quality degrees. Part of this by-product of high quality is generally destined for food, pharmaceutical and chemical industry. On the other hand, there are often problems in management of fat residual fraction, leading to its inappropriate disposal. Also pharmaceutical and chemical industries extract glycerol from animal fat and then throw out the other parts. So animal fat as biodiesel production feedstock would be useful.

**MATERIALS AND METHODS**

In order to obtain waste animal fat for biodiesel production, the waste animal fat should be supplied from slaughterhouse. Test samples were selected from slaughterhouse around Shiraz (Shiraz is the capital city of Fars province, Iran, at 29°36′ N latitude and N 52°32′ E longitude) with three different type.

**Extraction and Purification of Fat from Animal Fats Samples**

For drawing oil and removing moisture from the samples they were cooked in a large boiler (pot) at about 110 °C and the dried fat was used directly in the esterification reaction. Chemical composition of oils and fats used in the biodiesel synthesis can influence processing and storage conditions, due to the percentage of unsaturated fatty acids (Ramalho et al, 2011). Therefore, the Metcalf method was used to metilize the extracted oil. Fatty acid profile was determined using a gas chromatography. Chromatogram of animal fat oil used in this research work is shown in Figure 2.
High free fatty acid content of the oil caused transesterification reaction to fail and led to soap production. For free fatty acid (FFA) content of more than 1%, the following equations (based on weight ratio) were used for titration and calculation of catalyst rates (Gerpen et al., 2004):

\[
\text{% FFA} = \frac{0.5 \times A \times N \times W_{\text{cat}}}{W} \tag{1}
\]

\[
KOH (\text{gr}) = \left[ \frac{\text{% FFA}}{0.197} \right] \times \frac{0.197}{0.86} + \text{% 1} \tag{2}
\]

Where:
- \( A \) = Catalyst volume for oil titration (ml)
- \( W \) = The sample value (g)
- \( N \) = Normality
- \( W_{\text{cat}} \) = Molecular mass of catalyst (g) which is 56.1 for KOH

The free fatty acid (FFA) level of the animal fat was determined 11% using titration method, which is not sufficient to complete the reaction with alkaline catalysts. The reduction of FFA esterification reaction was carried out using methanol and sulfuric acid. After reactions proceeded to completion, the level of FFA was reduced to less than 1%. The transesterification reaction started in the presence of methanol, alkaline catalyst and the animal fat with free fatty acid levels of less than 1%.

Methanol (99.7%) and KOH (99%) used in this study, were provided from Merck company products. The most preferred alcohol used in biodiesel production is methanol because of its low price, physical and chemical advantages (polar and the shortest chain alcohol). It can easily react with triglycerides and catalysts (Alptekin and Canakci, 2011). Potassium hydroxide (KOH, 99% assays) in the form of solid tablets was used as catalyst as it shown in Figure 3:
Gas chromatography (GC) set, Perkin Elmer clarus-580 based on BS-EN 14103 standards and equations (3 and 4) were used to determine biodiesel yield and percentage of methyl ester content in the produced biodiesel. Therefore:

\[
C = \frac{\sum A - A_{IS}}{A_{IS}} \times \frac{M_{IS}}{M} \times 100 \tag{3}
\]

Where:
- \(\sum A\) = Total area under pick for fatty acids \(C_6\) to \(C_{14}\), \(\mu V*sec\).
- \(A_{IS}\) = Area under thr internal standard (methyl heptadecanoate) pick, \(\mu V*sec\).
- \(M_{IS}\) = Mass of applied internal standard (mg).
- \(M\) = Mass of biodiesel sample (mg).

Conversion of percentage of oil to methyl ester (biodiesel) is obtained from following equation (4) (Thanh et al., 2010):

\[
\text{FAME} = \frac{W_{\text{FAME}}}{3W_{\text{WCO}}} \times \frac{M_{\text{FAME}}}{M_{\text{WCO}}} \times 100 \tag{4}
\]

Where:
- \(W_{\text{FAME}}\) = Produced biodiesel (mg)
- \(W_{\text{WCO}}\) = Mass of animal fat (mg)
- \(M_{\text{FAME}}\) = Mean molecular mass for biodiesel
- \(M_{\text{WCO}}\) = Mean molecular mass for animal fat oil

For the transesterification to give maximum yield, the alcohol should be free of moisture and the FFA content of the oil should be less than 0.5% (Geise, 2002). The absence of moisture in the transesterification reaction is important because according to the following equation (shown for methyl esters), hydrolysis of the formed alkyl esters to FFA can occur. Similarly, because triacylglycerols are also esters, the reaction of the triacylglycerols with water can form FFA. At 32°C, transesterification was 99% complete in 4 hours when using an alkaline catalyst (NaOH or NaOMe) (Gerpen and Knothe, 2005). Two phases could be identified after the pre-treatment. The upper phase consisted of methanol, catalyst, \(H_2O\), resulted soap and impurities. This layer should be separated to reach acceptable levels for fuel parameters. The lower phase mainly consisted of fats and the esterified fatty acids. For this purpose, the biodiesel was obtained by transesterification reaction, via methylic routes. Samples and reaction final mixture were placed in decantation funnels and allowed to stand overnight and centrifuged to ensure the complete phase separation (methyl esters and glycerol). After reaction, the glycerol phase (bottom phase) was separated by decantation and the biodiesel phase (upper phase) was heated at 85°C (with anhydrous sodium sulfate, before filtration) to eliminate methanol. The biodiesel was neutralized with KOH (20% KOH needed was to neutralize the added \(H_2SO_4\) as catalyst) and it was washed with distilled water to remove catalyst and reach neutral pH. The collected fat was mixed with a basic solution of potassium hydroxide (KOH) to remove the free fatty acids (FFA) in the form of soap. The soap was separated from the fat content by centrifugation. The purified fat was processed to the next step, transesterification.

Transesterification of Fat

Animal fats were transesterified with acid catalyst and basic catalyst with and without pre-esterification. Biodiesel of 89.0 wt.% ester content was obtained by acid-transesterification (9 wt.% \(H_2SO_4\), 6:1 methanol:fats molar ratio, 60 °C, 48 h). Pre-esterification conditions were studied for different fats and acid catalysts: 0.5 wt.% \(H_2SO_4\) or 1.0 wt.% p-TsOH, 6:1 methanol:fats molar ratio, 65 °C and 4 h made it possible to obtain fats with acid value less than 0.5% FFA. Pre-treatment was effective for fats with different FFA content. Alkali transesterification of esterified fats resulted in a product with 97.3 wt. % ester content. Biodiesel quality was evaluated and most of its properties were well within EN 14214 standard (Encinar et al, 2011).

Transesterification of the purified fat described above was conducted to convert the triglycerides to biodiesel. In this process, the recovered fat content was preheated to 100 °C and cooled to room temperature to remove the traces of water present. A solution of methanol and KOH (as a catalyst) were added to the fat. The reaction mixture was refluxed at 60 °C for 1 hour. Optimization of the transesterification reaction was achieved by varying the amounts of methanol and potassium hydroxide. After the transesterification process, the reaction mixture was allowed to cool to room temperature overnight. The glycerol layer, which contains un-reacted alcohol and catalyst, was separated from the biodiesel. The top layer was then washed twice with
warm water (40-45 °C) and with acidified water (0.5 wt% tannic acid) to remove the excess methanol and the traces of catalyst (Kondamudi et al., 2009). This two-step protocol typically gives high degrees of transesterification (>98%), with negligible amounts of remaining unreacted (complete or partial) acylglycerols. The final ester product separates readily from the polar liquid phase, which contains unreacted alcohol, the glycerol coproduct, and the catalyst. The water washing step is intended to remove any remaining catalyst, soap, salts, methanol, or free glycerol from the biodiesel Neutralization before washing reduces the amount of water required and minimizes the potential for emulsions to form when the wash water is added to the biodiesel. After the wash process, any remaining water is removed from the biodiesel by a vacuum flash process (Gerpen and Knothe, 2005). After drying, the produced animal fat methyl esters (biodiesel) were characterized by determining their viscosity, density, flash point and acid value and the purified biodiesel was characterized by Gas chromatography (GC) set (Perkin Elmer clarus-580) based on BS-EN 14103 standards (Figure 4).

![Image](https://example.com/image.png)

Figure 4. The Gas Chromatograph used for oil and produced biodiesel analysis.

RESULTS AND DISCUSSION

Raw Material

Raw material properties and its fatty acid profile are showed in Table 1. The main problem with processing these fats is that they contain large amounts of free fatty acids that could not be converted to biodiesel using an alkaline catalyst due to formation of fatty acids salts (soap). Soaps can prevent separation of the biodiesel from the glycerine fraction. In a study of transesterification of beef tallow with alkaline catalyst, fatty acids content needs to be kept below 0.5% (1 mgKOH g⁻¹) was stated; this means that fats and vegetable oils, as fats used in this study, must be refined to remove free fatty acids (Ma et al., 1998b).

The water content of the fats is relatively low; however conversion could be affected, according to Kusdiana and Saka (2004). For alkaline-catalyzed method, the conversion was slightly reduced when more water was added; nevertheless in the acid-catalyzed method, only as little as 0.1% of water added led to some reduction of the yield of methyl esters. For esterification reaction, using H₂SO₄ as catalyst, the conversion of oleic acid to methyl oleate was somewhat reduced when the water content was increased.

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>A (%)</th>
<th>B (%)</th>
<th>C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 12:0 Lauric</td>
<td>0.07%</td>
<td>0.09%</td>
<td>0.05%</td>
</tr>
<tr>
<td>C 14:0 Myristic</td>
<td>2.64%</td>
<td>1.5%</td>
<td>2.33%</td>
</tr>
<tr>
<td>C 16:0 Palmitic</td>
<td>26.50%</td>
<td>27.90%</td>
<td>27.0%</td>
</tr>
<tr>
<td>C 18:0 Stearic</td>
<td>0.19%</td>
<td>12.0%</td>
<td>3.50%</td>
</tr>
<tr>
<td>C 18:1 Oleic(c)</td>
<td>29.60%</td>
<td>20.00%</td>
<td>28.20%</td>
</tr>
<tr>
<td>C 18:1 Oleic(t)</td>
<td>32.01%</td>
<td>22.80%</td>
<td>26.50%</td>
</tr>
<tr>
<td>C 18:2 Linoleic</td>
<td>3.42%</td>
<td>10.50%</td>
<td>6.60%</td>
</tr>
<tr>
<td>C 18:3 Linolenic</td>
<td>0.50%</td>
<td>0.7%</td>
<td>0.7%</td>
</tr>
<tr>
<td>C 20:0 Arachidic acid</td>
<td>0.24%</td>
<td>0.01</td>
<td>0.5%</td>
</tr>
<tr>
<td>C 24:1 Gadoleic</td>
<td>5.30%</td>
<td>-----</td>
<td>2.80%</td>
</tr>
<tr>
<td>Other fatty acids</td>
<td>0.25%</td>
<td>4.5%</td>
<td>1.80%</td>
</tr>
</tbody>
</table>
They suggested that the methyl oleate formed may be hydrolyzed over a prolonged treatment and high temperature; but these results correspond to high water content. In our study, water content is very low (Table 1) so its effect could only be expected in acid transesterification reactions.

The major fatty acids of the feedstocks were palmitic (26–28%) and oleic (30–33%), acids with low degree of unsaturation. Most properties of biodiesel depend on the used feedstock. It has been reported that biodiesel viscosity and density can be predicted based on feedstock fatty acid profile. High viscosity is expected because the main fatty acids have long chain of carbon and low degree of unsaturation, as well as no high density is expected for the same reasons. Density increases with decreasing chain length and increasing number of double bonds (Refaat, 2009). Also percent of FFA content of the samples was 11% on average.

Figure 5, shows the raw material before esterification condition:

![Figure 5. Animal fat](image)

**Pre-esterification conditions**

To obtain high ester content by pre-esterification, with $\text{H}_2\text{SO}_4$ as catalyst, followed by basic transesterification, with KOH as catalyst, the main variables of both steps were studied. Firstly pre-esterification conditions were studied changing catalyst amount, methanol:fats molar ratio, and reaction temperature, whereas the transesterification conditions were kept constant (1.5 wt.% KOH, 6:1 methanol:esterified fats molar ratio, 65 ºC and 2 h of reaction time). This is a high catalyst amount to get the reaction of all tri-, di- and monoglycerides from esterified fats to methyl esters if the raw material does not have an excessive acid value.

The effect of $\text{H}_2\text{SO}_4$ amount as catalyst in esterification reaction was studied. The decrease of the acid value was high initially and then tended to stabilize. This behavior is according to previous research and the lack of acid decrease at later times may be due to accumulation of water, because the sulfuric acid tends to migrate into the water, out of the methanol, rendering it unavailable for the reaction (Diaz-Felix et al., 2009; Van Gerpen et al., 2004).

**Biodiesel specifications**

The main parameters of a generic biodiesel obtained by pre-esterification followed by basic transesterification were determined. The obtained results and the specifications of European Standard EN 14214 are summarized in Table 2. Methyl ester content, density and viscosity met European Standard. Although pure animal fats as feed stock usually have high viscosity, slightly out of the specification. This is due to viscosity increase with the number of CH$_2$ groups in the FAME chain characteristic of the most saturated animal fats (Canoira et al., 2008). However, the obtained biodiesel in this research is in the range of the standard, close to upper limit.

Water content and flash point are in the ranges of the specifications.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Standards EN 14214</th>
<th>Biodiesel Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl ester content</td>
<td>&gt;96.5</td>
<td>98.0 wt.%</td>
</tr>
<tr>
<td>Water content</td>
<td>&lt;0.05</td>
<td>0.06 wt.%</td>
</tr>
<tr>
<td>Density 15 ºC</td>
<td>860-900</td>
<td>874 kg m$^{-3}$</td>
</tr>
<tr>
<td>Density 40 ºC</td>
<td>875</td>
<td>4.95 mm s$^{-1}$</td>
</tr>
<tr>
<td>Viscosity 40 ºC</td>
<td>&gt;120</td>
<td>169.2 °C</td>
</tr>
</tbody>
</table>

**CONCLUSION**

Animal fats characterized by high free fatty acids were suitable feedstock to obtain biodiesel. By acid transesterification a biodiesel with 89.0 wt.% ester content was produced. By esterification with 0.5 wt.%
H$_2$SO$_4$or 1.0 wt.% p-TsOH and 6:1 methanol:fats molar ratio an acid value less than 1.0% FFA was achieved for fats with different FFA content, which were transesterified with only 0.5 wt.% KOH and 6:1 of methanol:fats molar ratio, reaching 98 wt.% ester content in the biodiesel. The main biodiesel parameters were compared with European Standard and most of the properties conformed with the standard specifications.

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REFERENCES


