Techno-economic conversion of Waste Fried Oil into Biodiesel through Transesterification

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Abstract. In India kitchen waste is the largest component of the waste stream by weight. A major constituent of kitchen waste is Waste Fried Oil (WFO). After repeatedly frying waste fried oil is not suitable for human consumption. Everyday several litres of WFO are drained and dumped untreated. To meet growing energy needs resulting from demand and diminishing supply, alternate energy source “Bio-fuel” are receiving more attention. In addition, the increasing global concern has caused to focus on oxygenated fuels because of the environmental pollution from diesel engines. High viscosity and poor volatility are the major limitations of WFO for direct utilization as a fuel in diesel engines. Direct synthesis via transesterification of WFO will yield biodiesel. The general aim of this paper is to evaluate the assumed sustainability of waste fried oil from kitchen for biodiesel production and use. Biodiesel was produced from WFO using transesterification process with KOH as catalyst. Various properties of the biodiesel thus developed are evaluated and compared in relation to that of mineral diesel. Cost of production of biodiesel (WFOME) from WFO is also presented. The transesterification process output included 85 % of methyl ester (biodiesel), 9 % of glycerine, and 6 % of recovered methanol. WFOME properties were as per the ASTM specifications. The cost of biodiesel produced from WFO has been 65 % of the cost of subsidized mineral diesel.

1. Introduction

Depletion of global petroleum reserves and increased environmental concerns has stimulated recent interest in alternative sources for petroleum-based fuels. Biomass, which is a rich source of energy, is readily available in the form of plant, animal, and human waste. Biodiesel produced from vegetable oil or animal fats by transesterification with alcohol like methanol and ethanol is recommended for use as a substitute for petroleum-based diesel mainly because biodiesel is an oxygenated, renewable, biodegradable and environmental friendly bio-fuel with similar flow and combustion properties to mineral diesel and low emission profile [1, 2]. The use of cooking oil more than once poses threats to humans [3]. A toxic compound – 4-hydroxy-trans-2-nonenal (HNE) accumulates over time in some vegetable oils (e.g. corn, soybean, canola, sunflower oils) and this will react with amino acids, DNA and other bio-molecules in the human body. HNE consumption can lead to diseases such as heart diseases, stroke, Parkinson’s disease, Alzheimer’s disease, and liver diseases [3]. Therefore people are advised to refrain from heating any oil to the point of smoking and should never reuse the same
cooking oil. When UCO is dumped into rivers, streams or ponds, it is difficult to remove them. One litre oil can easily contaminate 1 million litre of water [4]. After repeated frying, WFO is not suitable for human consumption as it is found to increase the blood cholesterol level. Americans throw away about 43.6 million tons of food each year [5]. Large quantities of waste or by-products are generated from kitchen of big hotels. Moreover, over 80 % of cooking oil is consumed at home; the control of this disposal behavior becomes a huge problem because of the large volumes involved [4].

Waste edible oils and fats pose significant disposal problems in many parts of the world. In India, edible oil consumption during 2007–08 was 14.3 million tons [6]. It is reported that nearly 10 % of edible oil that is being thrown out as waste cannot be reused [7]. If 10 % of the edible oil is assumed to be consumed in hotels and restaurants, then the total used cooking oil available in 2007–2008 would be about 0.14 million tons. Assuming that with adequate incentives, 70% of the used cooking oil could be recovered which would be approximately 0.1 million tons. If India plans a 10 % mix in the total diesel consumption (46.8 million tons during 2008–2009), 4.7 million tons of biodiesel will be required. With the available quantity of used cooking oil, nearly about 0.095 million tons of biodiesel can be generated. In India, nearly 0.2 % diesel oil can be replaced by using the biodiesel generated from used cooking oil. In India during 2007–08 biodiesel production was 0.104 million tons [8]. The available used cooking oil is thus comparable to the current biodiesel production. All these data indicate that the waste fried oil can be a potential source for biodiesel production. This study discusses suitability of WFO from kitchen for energy conversion.

2. Methodology

Biodiesel is an alternative fuel similar to conventional fossil diesel. Biodiesel can be produced from straight vegetable oil or animal oil/fats, tallow and waste cooking oil. The used cooking oil has been classified as waste, while its potential as a liquid fuel through physical and chemical conversion remains an area of research interest. It is increasingly gaining much interest because of its great potential to be used as a diesel substitute known as bio-diesel. Direct synthesis via transesterification of vegetable oils yields bio-diesel [9].

2.1. Transesterification Mechanism

Transesterification, also known as alcoholysis is the reaction of vegetable oil or fat with an alcohol to form esters and glycerol. To complete a transesterification reaction stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is needed. In practice, to have a maximum ester yield, this ratio needs to be higher than the stoichiometric ratio. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side. Transesterification or alcoholysis is the displacement of alcohol to from an ester by another in a process similar to hydrolysis, except that alcohol is used instead of water. This process has been widely used to reduce the high viscosity of triglycerides. Transesterification is one of the reversible reactions and proceeds essentially by mixing reactants. However, the presence of a catalyst (a strong acid or base) accelerates conversion. Transesterification of triglycerides produce fatty acid alkyl esters and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this process. The reaction can be catalyzed by alkalis, acids, or enzymes. Step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In the presence of excess alcohol, the foreword reaction is pseudo-first order and the reverse reaction is found to be second order. It was also observed that transesterification is faster when catalyzed by an alkali [10]. The reaction is shown in Figure 1.
The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and finally monoglycerides to glycerol, thereby yielding one ester molecule for each glyceride at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acids esters and glycerol. The mechanism of transesterification is described in Figure 2.

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\begin{align*}
\text{Triglyceride} + \text{ROH} & \rightleftharpoons \text{Diglyceride} + \text{R’COOR} \\
\text{Diglyceride} + \text{ROH} & \rightleftharpoons \text{Monoglyceride} + \text{R’COOR} \\
\text{Monoglyceride} + \text{ROH} & \rightleftharpoons \text{Glycerol} + \text{R’COOR}
\end{align*}
\]

Figure 2 Mechanism of Transesterification

2.2. Preparation of WFOME
The raw material (i.e. WFO) was collected from different hotels in Goa. The properties of raw WFO were measured at Sadekar Enviro. Labs, Panaji, Goa. This is testing laboratory approved by Government of Goa. The properties of waste fried oil are presented in the Table 1.

| Sr. No. | Property                        | Results |
|---------|--------------------------------|
| 1.      | Specific gravity                | 0.913   |
| 2.      | Viscosity at 40°C (cSt)         | 65.5    |
| 3.      | Cloud point (°C)                | -1.00   |
| 4.      | Pour point (°C)                 | -16.00  |
| 5.      | Flash point (°C)                | 181.00  |
| 6.      | Calorific value (kJ/kg)         | 31300   |

The procedure followed to produce biodiesel from WFO is shown in Figure 3.
The steps followed to produce biodiesel from WFO are as follows.

1. The waste fried oil was filtered to remove food residues and solid precipitate by using double layer of cheesecloth in a funnel.
2. The waste normally contains water, which can slow down the reaction and cause saponification (soap formation). To avoid soap formation due to water the filtered fried oil was dried by heating it at 100°C.
3. For the high yields, normally Potassium Hydroxide (KOH) is preferred as a catalyst in the transesterification reaction. The amount of KOH needed was calculated as 7.7 g for every litre of WFO by titration.
4. In the chemical process, for 1000 ml of waste fried oil (molar ratio 6:1), 200 ml of methanol was used. The solution (mixture of WFO, Methanol and KOH) was stirred at 600 rpm for 15 minutes and glycerin was allowed to settle for 24 hours.
5. The ester layer was separated from the glycerol layer in a separating funnel.
6. Crude ester layer consists of methyl ester, unreacted oil and methanol of glycerol, catalyst residue, and small amount of produced soap. In the separating funnel, layer was washed with hot water until the washings were neutral.
7. At the end ester was dried and filtered.

Transesterification process inputs and outputs are presented in the Table 2.

![Figure 3 Biodiesel Production Process](image-url)
Table 2 Mass balance of transesterification of WFO

| Input          | Out put          |
|----------------|------------------|
| WFO + KOH      | 1000 ml          |
| Methanol       | 200 ml           |
| -              | -                |
| Total          | 1200 ml          |
| 83.33 %        | 85 %             |
| 16.66 %        | 9 %              |
| -              | 6 %              |
| 100 %          | 100%             |

2.3. Properties of WFOME

The performance of a DI diesel engine is affected by the spray characteristics of the fuel emerging through the injector holes. Some researchers have reported that the most detrimental parameter in the use of vegetable oil as fuel is its high viscosity [11]. The high viscosity is the cause of blockage of fuel lines and filters, high nozzle valve opening pressures and poor atomization [12]. The problem of high fuel viscosity can be overcome by using esters, blending and heating [13]. The properties of biodiesel produced are very important and should be taken into consideration before testing it in the engine [14-15].

Redwood viscometer was used to determine viscosity of WFO, WFOME and diesel. The viscosity of pure WFOME was significantly lower (6.8 cSt) at 40 ºC. The calorific value was estimated with the help of bomb calorimeter. The calorific value of WFOME (39000 kJ/kg) was lower than that of mineral diesel by 9.3 %. The flash point temperature was determined using flash point apparatus. It was more than 93 ºC, which is minimum requirement for biodiesel based on ASTM D 6751-09. The various properties of WFOME are presented in Table 3.

Table 3 Properties of WFOME

| Sr. No. | Parameter                  | Results |
|---------|----------------------------|---------|
| 1.      | Specific gravity           | 0.870   |
| 2.      | Viscosity at 40 ºC (cSt)   | 6.8     |
| 3.      | Cloud point (º C)          | -7.7    |
| 4.      | Pour point (º C)           | -11.60  |
| 5.      | Flash point (º C)          | 140.00  |
| 6.      | Cetane Number              | 55      |
| 7.      | Calorific Value (kJ/kg)    | 39000   |
| 7.      | % of O₂ in Biodiesel       | 11      |

The properties of WFO, WFOME and mineral diesel with respect to ASTM are presented in Table 4. The properties of WFOME were within acceptable ranges.
Table 4 Properties Comparison

| Properties                  | WFOME  | Diesel | Method          | Equipment Used            |
|-----------------------------|--------|--------|-----------------|---------------------------|
| Viscosity @40°C (cSt)       | 6.8    | 4.32   | ASTM D445       | Redwood Viscometer        |
| Specific Gravity            | 0.87   | 0.83   | ASTM D941       | Hydrometer                 |
| Calorific Value (kJ/kg)     | 39000  | 43000  | ASTM D240       | Bomb calorimeter           |
| Flash point (°C)            | 140    | 70     | ASTM D93        | Flash point Apparatus      |

2.4. Economic Analysis of Conversion

Currently the cost of biodiesel is higher than petro diesel because most of the biodiesel is produced from refined edible oils. One way of reduce this cost is to use less expensive feedstock such as waste vegetable oils, used frying oils and animal fats. WFO which is otherwise left untreated is one of the most economical choices for producing biodiesel. Oil feedstock is the major cost involved in production of biodiesel which is accounts for 70 % of the total cost. Hence, if WFO is used as feedstock, the cost of production of biodiesel can be significantly improved. Moreover, the use of WFO also reduces the waste treatment cost.

For conversion of WFO, methanol and potassium hydroxide were available at a rate of 45 INR per litre and 600 INR per litre respectively. WFO is treated as discarded waste, harmful to the environment. The cost of WFO in this analysis was considered as 10 INR per litre. Biodiesel cost depends greatly on methanol prices and economy can be achieved by varying the grade of methanol. The by-product of transesterification is industrial grade glycerin and it is an important constituent in the chemical, pharmaceutical and cosmetic industry. Table 5 shows that the production cost of biodiesel is substantially lower than the market price of mineral diesel.

Table 5 Cost of biodiesel production

| Biodiesel from WFO          | Cost (Rs/lit.) | Cost (USD/lit.) |
|-----------------------------|----------------|-----------------|
| Waste fried oil             | 15.00          | -               |
| Methanol (200 ml)           | 11.00          | -               |
| Waste collection            | 4.00           | -               |
| Waste water treatment       | 1.00           | -               |
| KOH (7.7 gms)               | 4.80           | -               |
| Electricity                 | 1.00           | -               |
| Purification                | 0.80           | -               |
| Labour                      | 3.60           | -               |
| Sub total                   | 27.20          | -               |
| Revenue from utility of glycerine | 4.00            | -               |
| **Total (cost less revenue)** | **41.20**      | **0.64**        |
| **Cost of Diesel**          | **63**         | **0.99**        |
3. Conclusion

Enormous amount of waste, generated from hotels located in different parts of the world is illegally dumped into the environment. Energy from kitchen waste not only reduces waste treatment cost, but also helps in producing a useful source for energy. Waste fried oil from kitchen was selected for efficient and economical energy conversion. High viscosity and poor volatility are the major limitations of waste fried oil for utilization as a fuel in diesel engines. The transesterification process is the most effective and economical process in converting waste fried oil into biodiesel and KOH is the most commonly used catalyst. Following conclusions can be made from this investigation:

1. Transesterification process output was 85 % methyl ester (Biodiesel), glycerin 9 %, and recovered methanol 6 %.

2. The Cost of conversion of biodiesel from waste fried oil was 65 % lower than market price of diesel.

3. WFOME satisfies the ASTM standard. The caloric value of WFOME was 9.3 % lower than that of mineral diesel.

4. At 40 °C, the viscosity of the WFOME was 6.8 cSt which was lower by 89.6 % than that of WFO and higher by 57.4 % than that of mineral diesel.

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