WASTE BUTTER AND MARGARINE AS FEEDSTOCK FOR BIODIESEL PRODUCTION

CJ Schabort, HP Visser, A Hartzenberg, R Venter, S Marx
School of Chemical and Minerals Engineering, North-West University, Potchefstroom, South Africa
Tel.: +27 18 299 1760 Fax: +27 18 299 1535 E-mail: corneels.schabort@nwu.ac.za

ABSTRACT: The resulting bio-waste from butter and margarine factories should be disposed of in an environmentally friendly manner. Currently the bio-waste is either flushed into the municipal sewerage system or moved to landfill sites. The bio-waste from butter and margarine factories provides a potential alternative feedstock for biodiesel production, being both non-edible and non-competitive with edible oils. A butter factory (Clover) near Frankfort, South Africa, has been identified as a source of bio-waste for biodiesel production. This facility produces 60 tons of fatty bio-waste per annum. In this study fatty acid methyl esters (FAME) were produced using cow's milk butter, margarine, as well as the actual butter factory's bio-waste as feedstock. Even though yields in excess of 90% were obtained, the biodiesel produced from the butter factory's bio-waste failed to meet the specifications for sulphur (18 wt ppm) and oxidation stability. Unless further purification methods are considered, the resulting biodiesel cannot meet the 10 wt ppm specification. The problem with regards to oxidation stability and sulphur content can be addressed by blending with ultra-low sulphur biodiesel. The oxidation stability can also be improved by the addition of a commercial antioxidant formulation.

Keywords: biodiesel, biofuels, transesterification, waste disposal.

1 INTRODUCTION

Due to the depletion of fossil fuels the world is constantly searching for alternative, renewable energy sources. The energy obtainable from biomass is one possibility that shows a lot of promise and has enjoyed an equal amount of interest and research.

The production of biodiesel from vegetable oils and fats is one of the ways in which energy can be obtained from biomass. The biodiesel product formed during transesterification can be used in a diesel engine without any adaptations made to the engine and thus the production of biodiesel is very feasible from a technical point of view [1].

Apart from the fact that biodiesel can be produced from renewable sources, the biodiesel product is a cleaner burning fuel and shows increased engine performance than its petroleum derived counterpart [2].

The best feedstock for biodiesel production, from a production and process point of view, is refined vegetable oils and animal fats. However, these are normally used for human consumption, and competition between these two markets causes increases in feedstock prices which, in turn, cause high production costs [3]. Due to the high production costs, biodiesel cannot economically compete with its petroleum derived counterpart. There is a need for a cheap source of feedstock which can be used for biodiesel production. Using waste feedstock from a butter factory might be viable due to the low costs associated with waste oils and fats as well as the added benefit of consuming waste products which might have a negative effect on the environment [4].

The disadvantage of waste oils and fats is the large amounts of free fatty acids and moisture normally present in these feedstock which might influence the alkali catalyzed transesterification reaction [5]. There are, however, methods to reduce these impurities and make the feedstock suitable for alkali catalyzed transesterification [6].

According to Cheng [1] transesterification is the preferred method for biodiesel production from triglycerides as this method shows the highest yield of biodiesel product that has a low enough viscosity to prevent carbon deposits in engines. There are a few important factors that influence the final yield of biodiesel [1]:

- Moisture and free fatty acid (FFA) content of feedstock
- Type and amount of catalyst
- Type of alcohol and molar ratio of alcohol to oil
- Reaction temperature

It is important to obtain the FFA and moisture contents of the feedstock used during transesterification as these two parameters affect the choice and concentrations of alcohol and catalyst used during the reaction step [6].

1.1 Type and amount of catalyst

Catalysts used during transesterification include alkaline, acidic, enzymatic and heterogeneous catalysts [7]. It is possible to convert triglycerides without catalyst using methanol in its supercritical state [8]. When methanol enters its supercritical state the dielectric constant lowers which makes it soluble in the oil, therefore excluding the necessity of a catalyst to speed up the reaction rate.

The use of chemical catalysts is, however, most often used due to the availability and the high operating costs when using other catalysts/non-catalytic processes [1]. Alkaline catalysts such as KOH and NaOH are normally used. The use of these catalysts result in fast reaction rates, and the optimum concentrations in terms of biodiesel yield is 1 wt% of oil [4]. As mentioned before the quality of the feedstock determines the type of catalyst used during transesterification. According to Yuan *et al.* [4] alkaline catalysts will form soap in the presence of FFA and moisture. FFA and moisture contents should be lower than 1% and 0.5% respectively to permit the use of alkaline catalysts [9].

Acidic catalysts can be used when the FFA and moisture content excludes the use of alkaline catalysts. However, acidic catalysts are not as effective as their alkaline counterparts [6]. Acids normally used during transesterification include sulphuric acid, hydrochloric acid and phosphoric acid [1]. According to Al-Widyan and Al-Shyoukh [10] sulphuric acid is the most effective at concentrations of 2.25 M.

1.2 Alcohol to oil molar ratio

An excess of alcohol is added to the reaction mixture to shift the equilibrium to the right. The amount of excess alcohol used during transesterification depends on the quality of feedstock used. As mentioned before alkaline catalysts are the most effective. During transesterification using alkaline catalysts, the optimum alcohol to oil molar ratio was found to be 6:1 [5,6].

Given a feedstock with a high FFA and moisture content necessitates the use of an acidic catalyst. The disadvantage of using acidic catalysts is the decrease in reaction rate associated with these catalysts and therefore higher alcohol to oil ratios needed to obtain the same conversion when compared to alkaline catalyzed transesterification [6]. According to Cheng [1] the optimum alcohol to oil molar ratio for acidic catalyzed transesterification is 15:1.

1.3 Reaction temperature

Normally transesterification reactions are carried out close to the boiling point of the specific alcohol used during reaction [1]. This might be to increase the reaction rate without boiling of the alcohol. There is however optimum temperatures at which transesterification can be carried out. According to Banerjee and Chakraborty [6] these temperatures depend on the quality of the feedstock used during transesterification.

Although the optimum temperature for transesterification of refined oils and fats is close to 60 °C (the boiling point of methanol), various researchers have found that the optimum temperature for transesterification of waste cooking oils and fats are lower than 60 °C, close to 50 °C [4,5,8].

2 MATERIALS AND METHODS

2.1 Materials

Two butter brands (Kerrygold and Clover butro), two margarine brands (House Brand and Sunshine D), as well as an oil effluent from a butter factory were used as feedstock. The feedstock was boiled under continuous agitation on a hot plate equipped with a magnetic stirrer. When a temperature of 110 ºC was reached the feedstock was removed from the hot plate and placed in an oven at 105 ºC for 1 hour. The dried feedstock was analysed for water and FFA content, as shown in Table I.

Table I: Water and FFA content of the feedstock

Feedstock	Water (ppm)	FFA (wt%)
Kerrygold Butter	464	0.46
Clover Butro Butter	522	0.34
House Brand Margarine	226	0.28
Sunshine D Margarine	240	0.36
Butter factory waste	490	0.20

From Table I it can be seen that all the feedstocks had a low enough water and FFA content to allow alkali catalyzed transesterification.

As this study specifically focuses on the possibility of using bio-waste as feedstock the butter factory waste was further characterised and it was found that the feedstock had a sulphur content of 18 ppm, a density of 914 kg/m^3, and a viscosity of 46.9 cSt at 40 ºC.

2.2 Chemicals

Methanol was used as the alcohol during the alkali transesterification. This is due to the lower cost when compared to other alcohols. Methanol is not as soluble in oil as ethanol but according to Issariyakul *et al.* (2007) and Demirbas (2009) the yield obtained from methanol is higher than that of ethanol [11,12].

The alkali catalyst used was KOH, as potassium hydroxide gives the highest yield for the largest range of feedstock [13,14]. During the treatment of biodiesel samples sulphuric acid was used to remove any unreacted reagents and neutralize the alkali catalyst.

2.3 Experimental procedure

The experimental procedure for all five feedstocks was identical. 300 g of dried feedstock was heated to the reaction temperature in a three neck round bottom flask, fitted with a condenser, a thermometer and a rubber seal using a hot plate with magnetic stirrer. The KOH was dissolved in the methanol (1 wt% KOH/wt% oil) and added to the reaction mixture.

The temperature dependant experiments for the butter and margarine were conducted at four specific temperatures, ranging from 40 ºC to 70 ºC. In the case of the butter factory waste the temperatures were varied from 50 ºC to 65 ºC, in order to determine the optimum temperature.

The molar ratio dependent experiments for the butter and the margarine were conducted at four specific alcohol to oil molar ratios, ranging from 5:1 to 8:1. The molar ratio was varied from 3:1 to 8:1 in the case of the butter factory waste.

The reaction was left at the set conditions for 1 hour, after which the biodiesel was separated from the glycerol. The biodiesel product was washed with distilled water and dried at 100 ºC for 2 hours.

2.4 Analytical method

The individual ester content of the biodiesel was measured by gas chromatography (GC). The GC was set up as follows:

A HP-88 100m column with a split ratio of 1:50 and helium as carrier gas was used. The oven was set at 100 °C for 5 minutes and then ramped at 10 °C/min up to 120 °C, which was then kept constant for 1 minute. The oven was then heated 10 °C/min to 175 °C and held constant for 10 minutes. The next ramp was 5 °C/min up to 210 °C and held for 5 minutes. The final ramp was 5 °C/min to 230 °C and held constant for 5 minutes. The FID was set at 350 °C.

Fourier Transform Infrared spectroscopy (FTIR) was also used to determine the total ester content. The mid-infrared range was used. The Eraspec by Eralytics was used for analysis.

The biodiesel quality was determined according to SANS 1953 standards.

3 RESULTS AND DISCUSSION

3.1 Temperature

The effect of temperature on the FAME yield for the butter and margarine is shown in Figure 1.

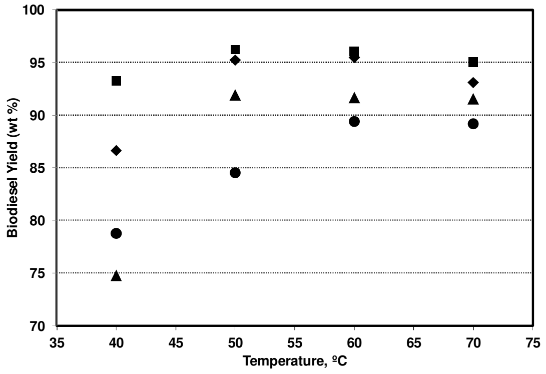

Figure 1: Effect of temperature on biodiesel yield during alkali catalyzed transesterification (■ Sunshine D ◆ Housebrand ● Kerrygold ▲ Clover)

With an increase in temperature, there was an increase in biodiesel yield for both the butter and the margarine. The maximum biodiesel yield obtained at an alcohol to oil molar ratio of 6:1 using Kerrygold was 89.4±0.7 wt% at 60 ºC. There is no significant change in biodiesel yield for the Clover Butro between 50 ºC and 70 ºC, with a maximum yield of 91.9±0.5 wt% at 50 ºC.

The optimum temperature in the case of the margarine was also found to be 60 ºC. The steady decline in yield above 60 ºC can be attributed to the boiling point of methanol, which is 64.7 ºC. A maximum yield of 96.2±0.6 wt% and 95.5±1.4 wt% were reported for the Sunshine D and Housebrand respectively.

The optimum temperature for transesterification found for both the butter and margarine is similar to the optimum temperatures reported by researches using refined vegetable oils with low FFA and water contents as feedstocks [15].

The experiment was repeated with an alcohol to oil ratio of 6:1 using the butter factory waste as feedstock. The effect of temperature on the FAME yield for the butter factory waste is shown in Figure 2.

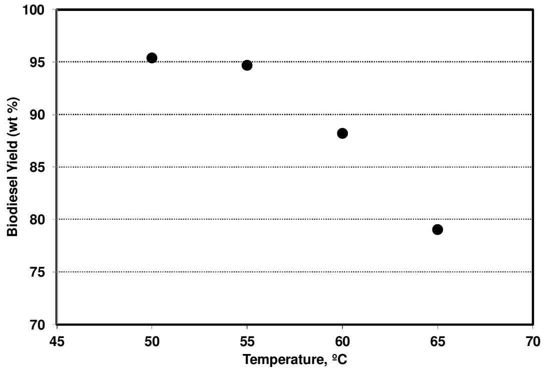

Figure 2: Effect of temperature on biodiesel yield during alkali catalyzed transesterification of butter factory waste

The optimal temperature for the butter factory waste was 50 °C. A further increase in temperature decreases the biodiesel yield. As previously mentioned, the decrease in yield is due to the increase of methanol in the vapour phase. A maximum yield of 95.37±1.67wt% was obtained at 50 °C for a 6:1 alcohol to oil molar ratio and 1.2 wt% (with respect to the oil) catalyst load.

3.2 Alcohol to oil molar ratio

The effect of the alcohol to oil ratio on the biodiesel yield at a reaction temperature of 60 ºC is shown in Figure 3.

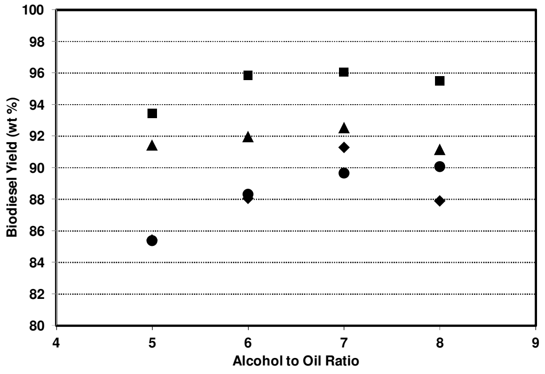

Figure 3: Effect of alcohol to oil ratio on biodiesel yield during alkali catalyzed transesterification (■ Sunshine D ◆ Housebrand ● Kerrygold ▲ Clover)

With an increase in alcohol to oil ratio, there was an increase in biodiesel yield for all of the feedstocks. With the exception of the Kerrygold butter, all the feedstocks showed an optimum alcohol to oil ratio of 7:1. There was a decrease in biodiesel yield at higher alcohol to oil ratios. The optimum biodiesel yields of 96.0±0.5 wt%, 92.5±0.5 wt% and 91.3±0.4 wt% were reported for the Sunshine D, Clover Butro and Housebrand respectively. The optimum biodiesel yield for the Kerrygold was found to be 90.1±0.7 wt% at an alcohol to oil ratio of 8:1.

The experiment was repeated at a temperature of 50 ºC using the butter factory waste as feedstock. The effect of a change in alcohol to oil ratio on the FAME yield for the butter factory waste is shown in Figure 4.

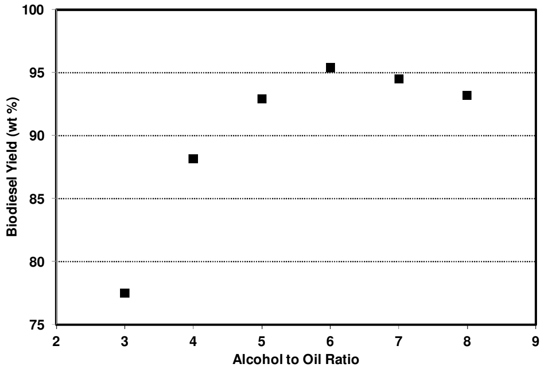

Figure 4: Effect of alcohol to oil ratio on biodiesel yield during alkali catalyzed transesterification of butter factory waste

As with the butter and margarine, an increase in alcohol to oil ratio, led to an increase in yield. The maximum yield of 95.37±1.67 wt% was obtained at an alcohol to oil molar ratio of 6:1.

The increase in yield with an increase in alcohol to oil ratio can be attributed to the fact that the biodiesel transesterification reaction is a reversible reaction. An increase in excess methanol will generally push the reaction to the right. The decrease in yield at a higher ratio of 8:1 can be ascribed to the excess methanol causing an increase in solubility of the glycerol in the biodiesel layer [16].

The 7:1 ratio (margarine and butter) is, however, in line with similar studies done using refined or waste oils and fats, *i.e.* 6.5:1 and 7:1 [4,5,15].

3.3 Catalyst loading

The effect of the catalyst load on the biodiesel yield of the butter factory waste, is represented in Figure 5. The effect of the catalyst was evaluated with a constant reaction temperature of 50 °C and an alcohol to oil ratio of 6:1.

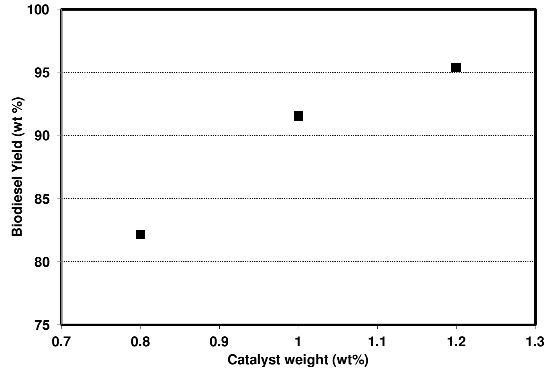

Figure 5: Effect of catalyst loading (wt%) on biodiesel yield during alkali catalyzed transesterification of butter factory waste

An increase of biodiesel yield was observed with an increase of catalyst. The optimal biodiesel yield, 95.37±1.67 wt%, was at a catalyst load of 1.2 wt%. According to Agarwal *et al.* [17], a catalyst load of more than 1 wt% leads to a decrease in yield due to soap formation. The waste oil used by Agarwal *et al.* [17], has an acid value of 1.95 mg KOH/g while the butter factory waste has an acid value of 0.04 mg KOH/g. Thus an increase in catalyst will not lead to an increase of soap formation for this feedstock, but will lead to higher yields. The optimal catalyst load for this study is in line with literature on low acid value feedstock [18].

3.4 Biodiesel quality

A batch of biodiesel was produced from the butter factory waste at the optimum conditions, *i.e.* a temperature of 50 °C, an alcohol to oil ratio of 6:1, and a catalyst loading of 1.2 wt%. This biodiesel batch was analysed to determine whether the biodiesel conforms to the SANS 1935 standard. The results are shown in Table II.

Table II: Results of the analysis of waste butter FAME

Parameter	Waste butter biodiesel	SANS 1935
Ester content	96.5 vol%	95.37±1.67 vol%
Density	803 g/cm^3	860 - 900 g/cm^3
Kinematic viscosity @ 40°C	4.5 cSt	3.5 – 5.0 cSt
Sulphur content (max)	18 ppm	10 ppm
Cetane number (min)	57.95	51.0
Water content (max)	0.03 wt%	0.05 wt%
Copper strip corrosion (max)	Class 1	Class 1
Oxidation stability (min)	0.395 h	6 h
Acid value (max)	0.03 mg KOH/g	0.5 mg KOH/g
Iodine value (max)	26 g/100 g	140 g/100 g
Linolenic acid methyl ester (max)	0.266 wt%	12 wt%
Polyunsaturated methyl ester (max)	N/D	1 wt%
Methanol content (max)	N/D	0.2 wt%
Group I metals (Na and K) (max)	N/D	5.0 ppm
Group II metals (Ca and Mg) (max)	1 ppm	5.0 ppm
Phosphorous content (max)	2 ppm	4 ppm

The parameters that do not meet the standards (density, sulphur content and oxidative stability) can be improved to meet the requirements of both biodiesel and diesel standards. A 40 vol% blend of biodiesel in diesel increases the oxidative stability to over 20 hours.

4 CONCLUSIONS

The optimum temperature and alcohol to oil ratio for biodiesel production from butter and margarine were found to be 60 °C and 7:1 respectively. Biodiesel yields greater than 90 wt% was obtained at these conditions, showing that butter and margarine are suitable feedstocks in the production of biodiesel. These parameters were used as guidelines in the production of biodiesel from butter factory waste.

The highest biodiesel yield of 95.37±1.67 wt% was achieved with the butter factory waste at a temperature of 50 °C, an alcohol to oil ratio of 6:1, as well as a catalyst loading of 1.2 wt%.

Waste butter is a viable option for biodiesel production. The biodiesel should, however, be blended with ultra-low fossil diesel to meet the specifications for density, sulphur content and oxidative stability.

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