ULTRASONIC ASSISTED BIODIESEL PRODUCTION

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ABSTRACT: One of the biggest hurdles in the production of biodiesel is the high production cost compared to petroleum-derived diesel. Even though the mechanical agitation utilised during biodiesel production is effective, it is energy intensive and costly. In this study ultrasonic assisted biodiesel production has been considered as a more economical alternative. The optimum transesterification reaction conditions were investigated using sunflower oil as a feedstock, methanol (MeOH) as the alcohol, along with potassium hydroxide (KOH) as catalyst. The transesterification reactions were carried out in an ELMA® ultrasonic bath. The reactions were completed at different ultrasonic frequencies, reaction times, alcohol to oil molar ratios and catalyst loading weights. Both Gas Chromatography (GC-MS) and FT-IR Spectroscopy analyses were used to determine the fatty acid methyl esters (FAME) content of the resulting biodiesel. The optimum ultrasonic assisted biodiesel production reactions were found to be 60ºC, 35 kHz, an alcohol to oil ratio of 9:1, a catalyst loading of 0.5 wt%, with a reaction time of 50 minutes. The resulting biodiesel FAME yields at these conditions were higher than 96.5 wt%. The reduction in reaction time due to the ultrasonic effect reduced the production cost by about 7% if compared to the traditional mechanical agitation.
Keywords: biodiesel, efficiency, energy, transesterification

1 INTRODUCTION

Fossil fuels are being depleted at a rapid rate and most studies estimate only a few decades of fossil fuel resources left. Biodiesel can reduce the dependency on petroleum based diesel for diesel engines. Biodiesel can be run in normal diesel engines with little to no needed changes to the engines [1]. Biodiesel is furthermore produced from renewable sources, such as sunflower oil, and is a cleaner burning fuel when compared to carbon based fuels, which produce more carbon dioxide and sulphur dioxide [2]. Biodiesel is thus a very attractive energy source for an environmentally friendly focused world.

Raw refined vegetable oils are the best feedstock for biodiesel production. These are the same oils which are used for human consumption and present problems for the market and availability of these oils [3]. Currently biodiesel feedstock prices favour the utilisation of crude fossil petroleum. With fossil fuel prices rising and the need for more environmentally friendly fuels the biofuels sector is growing with government funding. Furthermore, the taxation of petroleum diesel makes the production of biodiesel in the private sector viable if a cheap feedstock is used [3].

There are numerous methods for producing biodiesel, such as blending with petroleum diesel, pyrolysis, micro-emulsions (co-solvent blending) and transesterification [4]. The most widely used production method, transesterification, is the process where methyl esters, also known as fatty acid methyl esters (FAME), are derived from raw and renewable biological sources such as vegetable oils by using a short chained alcohol such as methanol.

The alcohol removes the glycerol structure part of the oil and replaces it with the smaller methyl group [4]. This reaction lowers the viscosity of the biodiesel and raises the heat content, raising the flow and volatility of the oil to the point comparable to a petroleum diesel fuel [5]. The biodiesel produced by the transesterification reaction is influenced by factors [6] such as moisture and free fatty acid (FFA) content of feedstock, the type and amount of catalyst, the type of alcohol and molar ratio of alcohol to oil, as well as the reaction temperature.

The transesterification reaction requires the thorough mixing of the reactants involved to ensure that the product can form. Therefore tanks with sufficient agitation have been employed in the past to ensure a successful reaction. However, new ways of effectively mixing the reaction mixture such as ultrasonic irradiation have been tested [4].

Research on ultrasonic assisted biodiesel production has produced favourable results in comparison to agitation-assisted reactions. Studies show that ultrasound can reduce treatment times and increase the FAME yields when compared to normal mechanically agitated reactions [4], [7]. Along with the aforementioned factors that influence biodiesel production, the use of ultrasonic irradiation adds the need to find an optimum ultrasonic frequency that promotes the cavitation effect by which the ultrasound influences the mixing of the reactants.

1.1 Catalyst

Different types of catalysts are used for transesterification including acidic, alkaline, enzymatic and heterogeneous catalysts [8]. A catalyst is unnecessary if the reaction takes place at the supercritical state of methanol [8]. The supercritical state of methanol requires a more complex reactor that raises operating costs. A chemical catalyst is therefore a more practical solution [6].

Alkaline-catalysed transesterification is much faster than the acidic-catalysed reaction. The two main factors that influence the choice of a catalyst are the free fatty acid content (FFA) and the moisture content [4]. These variables are monitored to prevent soap formation, which will not only contaminate the biodiesel, but also make the separation of glycerol and biodiesel very difficult [4].

If the FFA and moisture content is higher than the specifications for alkaline-catalysts then acidic catalysts can be used, but these catalysts have to be used at higher concentrations and require longer reaction times [4].

1.2 Alcohol to oil ratio

In order to maximise the conversion of triglycerides to biodiesel, an excess of alcohol is used to favour the forward reaction. The minimum stoichiometric ratio that should be utilised is 3 moles of alcohol to 1 mole of oil,

with many studies siting a ratio of 6:1 as being very effective [4].

If the FFA and moisture content of the feedstock is too high and acidic catalysts have to be used then the alcohol to oil molar ratio has to be increased drastically to compensate for the slower reaction rate compared to alkaline catalyst [9]. The optimum alcohol to oil molar ratio in the case of acidic-catalysed biodiesel production by transesterification is 15:1 [6].

1.3 Reaction temperature

The influence of temperature on ultrasonic assisted biodiesel production has a larger influence on the conversion when compared to normal agitated reactions. As the temperature has a direct correlation to the vapour pressure, an increase in ambient temperature leads to an increase in the vapour pressure of the solvent. This leads to easier cavitation, but less violent "cushioned" bubble collapses, explained further in Section 1.5.

As the temperature of the solvent approaches its boiling point, more and more cavitation occurs, but this acts as a sound barrier and dampens the ultrasonic energy from the source through the solvent. Therefore an optimum temperature must be found using methanol as the solvent. Favourable results have been reported using a reaction temperature of 60 °C, using methanol as reagent [7].

1.4 Ultrasonic frequency and the cavitation effect

Most biodiesel production experiments using sonochemistry are done at frequencies ranging from 20-50 kHz, due to the availability of commercial equipment in this range. Further studies have shown that higher frequencies decrease the cavitation effect, showing no benefit in conducting experiments at higher frequencies. The higher the frequency the higher the power requirement has to be to ensure cavitation inside the mixture [10].

The ultrasound waves on their own do not raise the sonochemical effects or chemical reactivity of the reaction due to the low frequency (20 to 100 kHz). The raised reactivity is caused by the phenomenon known as cavitation. The pressure wave from the ultrasound causes negative pressure areas which "tear up" the liquid resulting in the formation of micro bubbles or voids in the liquid [10], [11]. In short, these bubbles or voids expand and collapse, causing the triglycerides and methanol to mix on a micro scale. The mixing assists biodiesel production by speeding up the transesterification reaction.

Two forms of cavitation exist, namely stable and transient cavitation. Stable cavitation occurs when cavities oscillate and resonate with the applied ultrasonic field. Rectified diffusion results from these effects and causes the cavities to grow significantly before they collapse, thereby increasing the cavitation effect [10], [11]. Some of the stable cavities, however, oscillate nonlinearly, which cause them to reach equilibrium. When cavities reach equilibrium they do not collapse and last longer than one cavitation cycle.

Transient cavities, on the other hand, exist for one cycle only. During a cycle these cavities expand to about double their size (around 150-250 µm) depending on certain variables. Factors that influence cavitation are [10], [11]. The power and frequency of the ultrasonic irradiation, the reactant or solvent viscosity, surface tension and vapour pressure, as well as the temperature (influences the vapour pressure). After the initial expansion the voids collapse rapidly to a size smaller than 10 µm [11].

2 MATERIALS AND METHODS

2.1 Materials

The feedstock chosen for this study was sunflower oil, because it is an abundant vegetable oil in South Africa and the results from this study will be compared to other studies that used similar feedstocks. Sunflower oil has a low free fatty acid content (lower than 1 wt% on average) and is not contaminated with large amounts of water (below 0.5 wt% moisture). These values meet the specifications for alkaline catalysed reactions [4].

2.2 Chemicals

Methanol is the alcohol of choice for transesterification reactions catalysed by an alkali. The yields methanol provides are higher when compared to other short chained alcohols such as ethanol, even though ethanol is more soluble in vegetable oils than the methanol [14], [15].

Potassium hydroxide (KOH) was used as catalyst throughout all the experiments, as KOH gives the highest yields for a wide range of feedstocks, including sunflower oil [12], [13]. Another advantage of KOH is that less soap forms when compared to other alkaline catalysts such as NaOH [4].

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 (0.5, 1.0 and 1.5 wt% KOH/wt% oil) and added to the reaction mixture in a 250 ml Schott Duran® bottle. The required methanol was added according to the alcohol to oil molar ratios of 3:1, 6:1 and 9:1, bringing the total weight of the reactants to 60 g [17].

The ELMA® ultrasonic bath was filled with water and heated to 60 °C, which was found to be the optimum operating temperature [4], [7]. A frequency of either 35 kHz or 130 kHz was used, while the treatment times were set to 40, 50 and 60 minutes. The ultrasonic bath allows three modes of operation namely sweep, degas and normal, of which only normal and sweep were tested.

After the completion of the reaction a small amount of 10% sulphuric acid (H2SO4) was added to the reaction vessel to neutralize the reaction. The mixture was then poured into a separating funnel and left to stand for 2 hours. The biodiesel and glycerol layers were separated and the glycerol weighed and stored.

The biodiesel product was washed three times with 50 ml distilled water at 80 ºC and thereafter dried at 105 ºC for 2 hours. The dried biodiesel was weighed and stored for analytical analysis.

2.4 Analytical method

The FAME content of the biodiesel was measured by gas chromatography (GC). Fourier Transform Infrared spectroscopy (FTIR) was also used to determine which esters were present in the biodiesel. The SANS 1953 biodiesel standard was used to determine the quality of the biodiesel.

3 RESULTS AND DISCUSSION

3.1 Ultrasonic frequency

The effect of the alcohol to oil molar ratios on the FAME yield for different ultrasonic frequencies is shown in Figure 1. A higher ultrasonic frequency resulted in a decrease in the biodiesel yield. On average the biodiesel yield at 35 kHz was 81.56±2.03 wt% and at 130 kHz the average yield was 70.62±2.03 wt%.

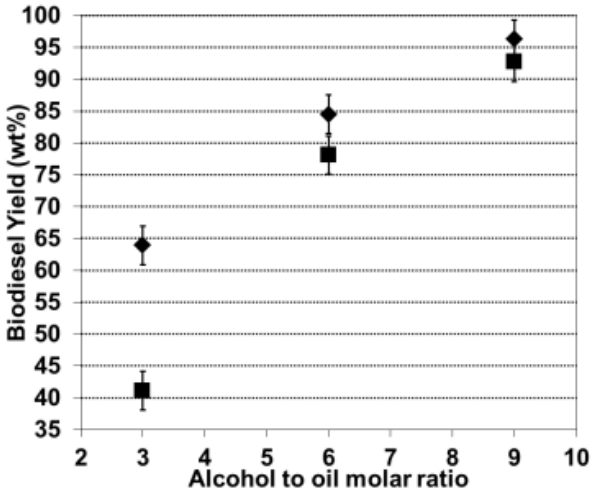

Figure 1: Effect of alcohol to oil molar ratio on biodiesel FAME yield during alkali catalysed transesterification of sunflower oil at different ultrasonic frequencies (◆ 35 kHz ■ 130 kHz)

It is therefore beneficial for ultrasonic assisted biodiesel production to be operated at lower frequencies. The 35 kHz frequency used falls between the optimum reported ultrasonic frequency for biodiesel transesterification ranges between 20 and 50 kHz [10].

The decline in yield can be attributed to the decrease of the cavitation effect. The increase in frequency decreases the cavitation bubble size [10]. This can be overcome by raising the ultrasonic power of the bath or the alcohol to oil molar ratio, but these changes results in higher operating costs are not recommended.

3.2 Alcohol to oil ratio

The average effect of the alcohol to oil ratio on the biodiesel is shown in Figure 2. An increase in alcohol to oil ratio led to an average increase in biodiesel yield. The average yield at 3:1 was 52.51±3.05 wt%, at 6:1 it was 81.30±3.05 wt% and at 9:1 the average was 94.46±3.05 wt%.

The increase of the FAME yield of the biodiesel can be attributed to the fact that the transesterification reaction is reversible and that an increase in the alcohol ratio will shift the reaction to FAME. On average the 9:1 ratio resulted in higher yields.

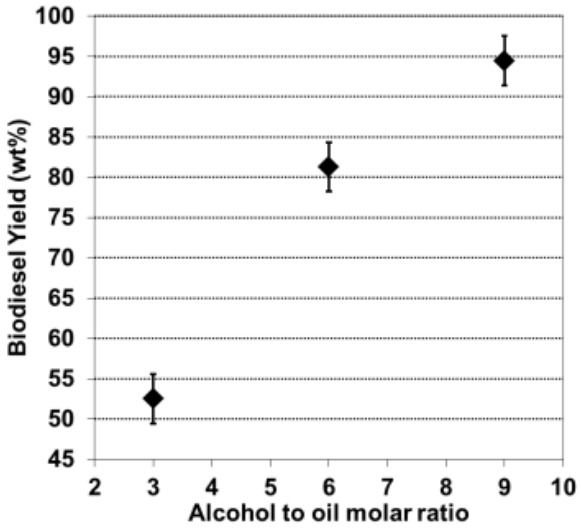

Figure 2: Effect of alcohol to oil ratio on biodiesel FAME yield during alkali catalysed transesterification of sunflower oil

3.3 Catalyst loading

The average effect of catalyst loading on the biodiesel is represented in Figure 3.

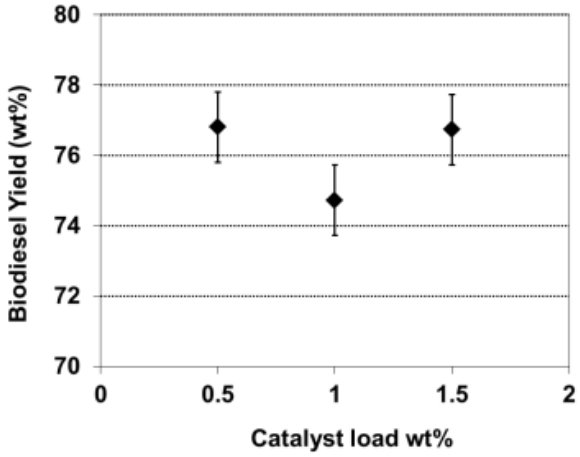

Figure 3: Effect of catalyst loading (wt%) on biodiesel yield during alkali catalysed transesterification of sunflower oil

The increase of catalyst load on ultrasonic assisted production of biodiesel had a negligible effect on the FAME yields. The influence of the catalyst load is observed when the layer yields (the bulk conversion of the sample to biodiesel) are weighed and measured and not the GC yields, which represent the purity of the product formed. Figure 4 shows the influence of the catalyst load on the layer yields which were weighed after the biodiesel was dried.

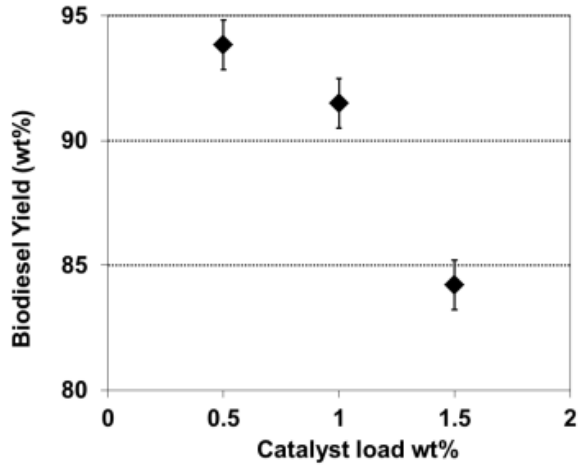

Figure 4: Effect of catalyst loading (wt%) on biodiesel layer yield during alkali catalysed transesterification of sunflower oil

From Figure 4 it is clear that higher catalyst weights have a negative effect on ultrasonic assisted biodiesel production. A load of more than 1.2 wt% catalyst decreases the biodiesel yield, because of an increase in soap formation [4], [7], [16]. For ultrasonic assisted transesterification lower catalyst weights are more beneficial to overall yield.

The best reaction conditions were found to be 0.5 wt% catalyst and 50 minutes reaction time, at a frequency of 35 kHz, yielding 96.84±4.56 wt% biodiesel. This sample met the SANS biodiesel specifications at the lowest possible cost.

3.4 Treatment time

Figure 5 shows the effect of the treatment time on the reaction. The increase in treatment time leads to an increase in biodiesel yields. After 50 minutes, however, the yield increased only by 1.69±1.02 wt%, while the yield increased between the time interval of 40 to 50 minutes by 11.03±1.02 wt%. An optimum reaction time of 40 minutes was also found in other studies [7].

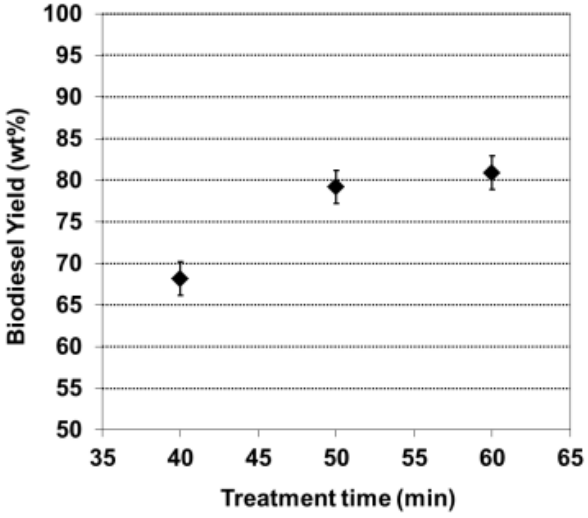

Figure 5: Effect of treatment time on the biodiesel yield during ultrasonic assisted biodiesel production

3.5 Cost comparison

The economic considerations were assessed by comparing the optimal conditions of mechanical and ultrasonic biodiesel production. The costs related to mechanical agitation were taken from literature [4], [7]. The comparison is shown in Table I.

Table I: Comparison between ultrasonic biodiesel production and mechanical agitation biodiesel production

Parameter	Ultrasonication (35 kHz)	Mechanical agitation (600 rpm)
Ester content of sample	96.84 wt%	97 wt%
Alcohol to oil molar ratio	9:1	7:1
Catalyst load	0.5 wt%	1.5 wt%
Treatment time	50 min	120 min
Power requirement	95 W	110 W

The use of ultrasonification decreases the reaction time required. Furthermore, ultrasonic assisted production reduces the energy requirement by 65%, resulting in an overall reduction in production cost of 7% when compared to mechanically agitated transesterification.

4 CONCLUSIONS

An optimum biodiesel yield of 96.84±4.56 wt% was obtained using a catalyst load of 0.5 wt%, a reaction time of 50 minutes and a frequency of 35 kHz. This was achieved at a reaction temperature of 60 °C. Lower frequencies (35 kHz) resulted in higher biodiesel yields. Even though higher catalyst loadings beyond the optimum point resulted in higher FAME yields, this also resulted in an increase in soap formation.

Ultrasonic assisted biodiesel production is a viable option for producing biodiesel as it reduces production time and energy input, while still meeting SANS specifications for biodiesel. The cost of producing biodiesel when compared to mechanical agitation can be lowered by about 7%.

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