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Article

Low-Cost Feedstock Conversion to Biodiesel via Ultrasound Technology

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Abstract: Biodiesel has attracted increasing interest and has proved to be a good substitute for fossil-based fuels due to its environmental advantages and availability from renewable resources such as refined and waste vegetable oils. Several studies have shown that biodiesel is a better fuel than the fossil-derived diesel in terms of engine performance, emissions reduction, lubricity and environmental benefits. The increasing popularity of biodiesel has generated great demand for its commercial production methods, which in turn calls for the development of technically and economically sound process technologies. This paper explores the applicability of ultrasound in the optimization of low-cost feedstock – in this case waste cooking oil – in the transesterification conversion to biodiesel. It was found that the conversion efficiency of the waste oil using ultrasound was higher than with the mechanical stirring method. The optimized variables of 6:1 methanol/oil ratio at a reaction temperature of 30 °C and a reaction time of 30 min and 0.75% KOH (wt/wt) catalyst concentration was obtained for the transesterification of the waste oil via the use of ultrasound.

Keywords: biodiesel; conversion efficiency; glycerol; transesterification; ultrasound

1. Introduction

Petroleum oil is the World's primary source of energy and chemicals, with a current demand of about 12 million tonnes (84 million barrels) per day, with a projection to increase to 16 million tons (116 million barrels) per day by 2030 [1]. A short and medium term alternative is needed. Crop-based fuels denoted as biofuels and including biodiesel and bioethanol, have emerged as a real alternative to the use of gasoline and conventional diesel in transportation and ideally, such oil alternatives should reduce (or even remove) the dependence of oil as well as contributing as much as possible to meet the greenhouse gases emissions (GHG) emissions target with joint efforts from politicians, regulators, scientists and consumers needed to support an independent oil/ GHG controlled scenario in the future [2].

An exponential increase in the consumption of such biofuels has taken place in the last few years as it is currently being developed as an alternative to fossil fuels due to its numerous advantages, which include renewability, energy efficiency, greenhouse effect and therefore reduction of global warming, reduction of tailpipe emissions, non toxicity, less air pollution, less water and soil pollution and less health risks [2,3]; its cetane number, energy content, viscosity and phase changes are similar to those of petroleum based diesel fuel. It comprises mainly monoalkyl esters of long chain fatty acids derived from vegetable oils, waste oils, and animal fats [4] and more recently, algae [2,3]. Biodiesel is a renewable and biodegradable form and source of energy due to the fact that vegetable oils are produced from agricultural resources and is produced by the transesterification of the feedstock with short chain alcohols (methanol or ethanol). This process takes place in the presence of acidic [6], basic [7,8] or enzymatic catalysis [9], each of which have advantages and disadvantages. The current standard method of production of biodiesel (under alkaline chemical conditions) is considered to be the most technically simple way to reduce the viscosity of vegetable oils from a range of 11–17 to about 2 times to that of petroleum diesel [10–13]. The main disadvantage of using alkaline catalyst is the side reaction formation of soaps that consumes the catalysts, thus decreasing the biodiesel yield, especially when the oil has a high content of free fatty acids [14].

The different applications of sonochemistry, the chemical reaction during ultrasound homogenization has developed as an expanding research area for the past two decades [15–18]. The use of sonochemistry is also applied in biodiesel production as the ultrasonic field is known to produce chemical and physical effects that arise from the collapse of cavitation bubbles [19]. Low frequency sonication can be used to produce emulsions from immiscible liquids [20] and since oil and alcohol are immiscible, this effect could be employed for biodiesel preparation. Production of biodiesel under ultrasonic processing possesses the following advantages: reduction in processing time, amount of alcohol and catalyst required, separation time and reaction temperature.

Biodiesel production from seed oils and waste oils has been improved with the application of the ultrasound. Stavarache *et al.* [15] reported that with high frequency ultrasound (40 kHz), the transesterification process proceeds quickly with an increased biodiesel yield. Colucci [21] also showed that in his experiments the use of ultrasonication increased the apparent rate constants of alkaline transesterification. Studies done by Georgogianni *et al.* [22,23] emphasized that the use of ultrasound significantly accelerated the transesterification soybean frying oil as compared to mechanical stirring (10 min vs. 5 h) and (5 h vs. 24 h) via the use of an homogeneous catalyst and various heterogeneous catalysts, respectively.

Recent studies by Thanh *et al.* [24,25] reported a maximum FAME yield of more than 99% with a methanol/oil molar ratio of 5:1, 0.7 wt.% potassium hydroxide catalyst and 50 min reaction time via the ultrasound-assisted transesterification reaction of canola oil and methanol. They also reported the use of a continuous ultrasonic reactor with a two-step process as a beneficial technique for the production of biodiesel from waste cooking oil as the use of waste cooking oil reduces the cost of the raw material needed in biodiesel production and the properties of the products in both studies meet Industrial Standards.

Since the use of mechanical agitation is predominant in biodiesel production, the importance of stirring conditions in methanolysis has motivated the proposal of other types of stirred reactors such as high shear mixers, oscillatory flow reactors and ultrasound reactors in order to improve the yield of biodiesel or to shorten the time of the process. This study was therefore a preliminary study aimed to compare the transesterification reaction rate and the conversion efficiency of refined vegetable oils (sunflower and soybean) and waste vegetable oil (WCO) in the presence of a low frequency ultrasonic homogenizer to the conventional mechanical agitation process as part of ongoing studies that are underway using a jet reactor to improve the biodiesel production process.

2. Experimental Section

Biodiesels with good properties have been obtained in many studies using KOH [14,24], hence the use of KOH in this study too. The KOH pellets were supplied by Kimix Chemicals Limited and methanol (>99:5%) was purchased from Merck Chemicals and used without purification. The alcohol of choice, methanol, dominates most of the literature reviewed as it is considerably cheaper than ethanol and the downstream recovery of the unreacted alcohol is much easier. The vegetable oils (sunflower and soybean) were of commercial edible grade purchased from Pick and Pay stores while the waste cooking oil was obtained from a french fry restaurant in Stellenbosch, Cape Town. The waste oil contained some food particles, phospholipids and grease, thus it had to be pre-treated by filtering under vacuum, after being dehydrated overnight using anhydrous sodium sulphate (Merck Chemicals) and finally again filtered under vacuum, prior to use.

The chemical properties and fatty acid compositions of the waste oil are summarized and compared with some pure vegetable oils used in previous works in Table 1. Fatty acid composition and the average molecular mass were calculated based on the fatty acid methyl ester composition of the waste oil as identified by Gas Chromatography. The free fatty acid content was calculated by titration using the acidity of the oil samples is quantified by the measurement of its acid value according to ISO 1242:1999. The value is defined as Equation 1:

$$Y = \frac{C \times V \times 56.1}{m} \quad [1]$$

where Y is the acid value, V is the consumed volume of KOH (mL), C is the concentration of KOH (mol/L), and the m is the mass of the tested sample (g). Viscosity is closely related to the fatty acid composition of a given biodiesel sample [26]. It increases with increasing length of both the fatty acid chain and the alcohol group, thus explaining the high viscosity value for the waste oil. The viscosity of the oil samples and the produced FAME were determined using Anton Parr Physica MCR 501 Rheometer.

Table 1. Shows the chemical properties and fatty acid composition of the oil.

Property	Waste Oil	Soybean Oil	Sunflower Oil
Fatty Acid Composition (%)			
Palmitic Acid C16:0	14	11.75	6.08
Stearic acid C18:0	6.02	3.15	3.26
Oleic Acid C18:1	35.60	23.26	16.93
Linoleic Acid C18:2	44.78	55.53	73.73
Linolenic Acid C18:3	0.6	6.31	0.00
Mean Molecular weight	884.16		
Viscosity (m Pas) at 40°C	37	29.3	29.4
Fatty Acid Value	1.73	0.021	0.03

A column injection Gas Chromatograph (DANI Instruments, USA) was used for the determination of mono-, di- and triglycerides in accordance with the ASTM D 6584 standard method. A capillary GC column was used in the apparatus with an internal diameter of 0.32 mm and length of 30 m. The temperature of the flame ionization detector was 250 °C and the carrier gas pressure was 80 Kpa. The analysis of FAME for each sample was carried out by dissolving 100 mg of the sample in 8 mL of heptane and injecting 1 µL of the solution into the GC. Two internal standards are used; one for glycerol and one for the triglycerides and the free glycerol are expressed as weight percent (%w/w). The instrument was calibrated using glycerol, monoolein, diolein and triolein in *n*-heptane solutions.

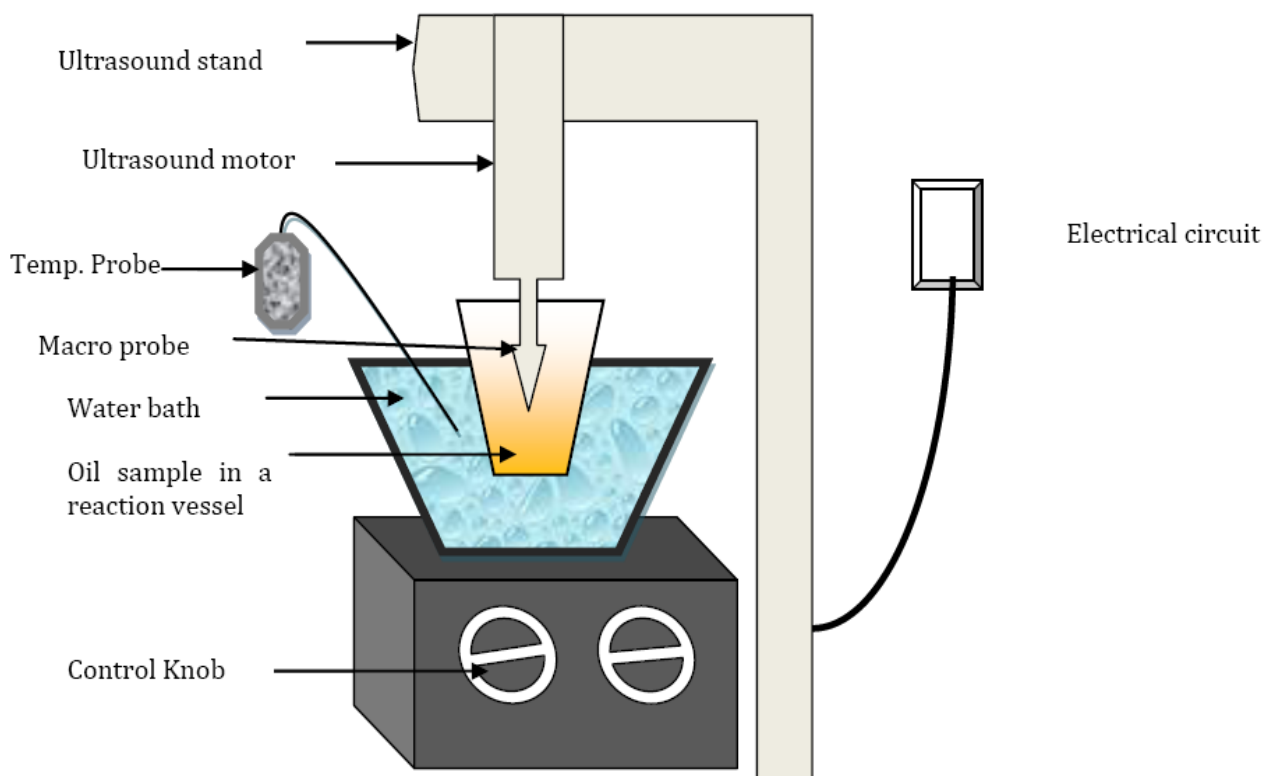
The optimized parameter from a previous study by the authors stirred mechanically was obtained at a temperature of 60 °C, catalyst amount of 1.0 wt% of waste oil, reaction time of 90 min and a stirring speed of 500 rpm. The mechanical stirrer used for this batch of experiments was a Heidolph MR 3001K, with an adjustable speed up to 700 rpm.

The sonication was carried out using an Omni ultrasound homogenizer with 20 kHz frequency and power output of 400 Watts. The sonication was performed at the controlled temperature of 30 °C using a water bath. The pre-treated waste oil sample and the appropriate volume of methanol and KOH were placed under the ultrasonic homogenizer with the ultrasound macro tip placed inside the reaction vessel. The alcohol to oil molar ratio used was 6:1 and based on the extensive literature that verifies this ratio as being most suitable for maximum conversion to the ester in the transesterification process [27–30].

The reaction mixture consisted of 100 g oil and 21.70 g of methanol. In order to determine the effect of the amount of catalyst needed to convert the waste oil triglycerides to its respective FAMES via the ultrasound technology, reactions were conducted with catalyst amounts of 0.5 wt%, 0.75 wt%, 1.0 wt%, 1.3 wt%, 1.5% wt based on pre weighed sample of waste oil. The reaction time was varied from 10 min to 50 min at an interval of 10 mins. After a complete conversion, the reaction mixture was allowed to stand for at least 8 hrs for phase separation. The esters mixture formed the upper layer and the glycerin, the lower layer. After the separation of the phases, the upper layer (methyl esters, some methanol and traces of the catalyst) was placed under the rotary evaporator to distill off the excess methanol as the case may be and then cleaned in a column packed with macroporous polymer resins (GF 202). These resins were obtained from Chemical and Water Engineering Associates Limited. It was however impossible to obtain any information on the chemical composition of the resins for commercial confidentiality reasons. The use of resins is proposed to eliminate the use of a large

amount of water needed for water-washing, the generation of high polluting liquid effluent, the removal of alkali metals and water from the final product and reduction in significant product loss retained in the water phase. The experimental set up for the transesterification reaction via the use of the ultrasound is illustrated in Figure 1.

Figure 1. Experimental set up of the ultrasonic homogenizer.



3. Results and Discussion

To accurately compare the conversion efficiency of the ultrasound process to the mechanical stirring method, the results achieved using the waste oil feedstock were studied and compared with those produced from a virgin vegetable oil (sunflower oil). The optimum conditions derived using the mechanical stirring method are also highlighted.

3.1. Effect of Catalyst Concentration

The concentration of the catalyst is an important parameter of the transesterification reaction and a strong influence on the yield of the isolated methyl esters. Table 2 highlights the results and shows that the addition of a large amount of catalyst did not lead to an increase in the biodiesel yield in either the ultrasonication or mechanical stirring methods. Excess catalyst reacted with the oil, leading to the formation of soap, thus as the catalyst concentration increased, the separation of esters became difficult. A minimal amount of 0.5% wt/wt catalyst was adequate in propelling the transesterification reaction using the ultrasonic homogenizer, however a concentration of 0.75% wt/wt gave the best yields and when compared to the percentage required for the conventional stirring method, there was a reduction of about 25% in the amount of catalyst needed for the transesterification reaction. As

mentioned previously, high concentrations of alkaline catalyst form soaps in the presence of large residues of fatty acids resulting in emulsion formation between soaps and water molecules, thus leading to low yields of methyl esters. Lifka and Ondruscka [31] studied the effect of ultrasonication *versus* mechanical stirring on the alkaline transesterification of rapeseed using NaOH at a concentration of 0.5% w/w at 45 °C and reported a conversion of 80–85% obtained for both the ultrasonicated and mechanically stirred reactions after 30 mins. Georgogianni *et al.* [32] also reported a yield of 81% with regards to using a catalyst concentration of 1.5% w/w NaOH on sunflower seed oil which slightly corresponds to the value reported above in Table 2. In a report by Thanh *et al.* [33] the optimal amount of potassium hydroxide recorded in the pilot studies conducted, although with a two step continuous ultrasound process, was 1.0 wt.%.

Table 2. Effect of catalyst concentration on FAME yield via the mechanical and ultrasonic process.

Catalyst Concentration KOH (%wt/wt)	Mechanical Stirring (600 rpm) Yield (%)			Ultrasonication (24 kHz) Yield (%)		
	WCO	Sunflower	Soybean	WCO	Sunflower	Soybean
0.5	71.3 ± 0.2	92.2 ± 0.12	90 ± 0.67	78.2 ± 0.06	95.30 ± 0.8	98.23 ± 0.2
0.75				96.8 ± 0.08	94.32 ± 0.4	97.65 ± 0.04
1.0	87.33 ± 0.3	93.32 ± 0.2	92 ± 1.2	95.98 ± 0.7	91.78 ± 0.3	93.67 ± 0.56
1.25				93.4 ± 0.67	90.64 ± 0.5	90.03 ± 0.78
1.5	91.2 ± 0.1	90.12 ± 1.1	88.2 ± 0.7	94.8 ± 0.03	88.78 ± 0.3	86.4 ± 0.45

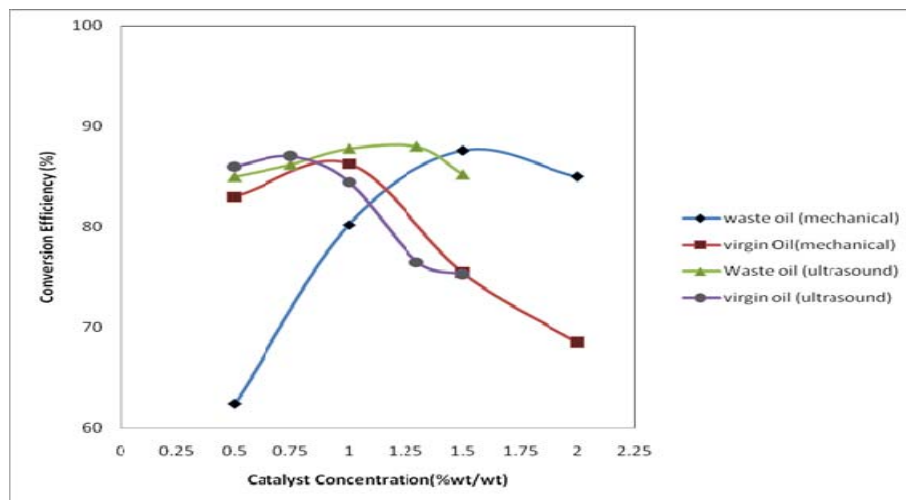
This experimental result represents the best performance for the biodiesel production via the different processes; experiments were carried out three times at the same conditions to ascertain reproducibility.

A study carried out with low concentrations of catalyst from 0.2 to 0.6% wt/wt on soybean oil done by Santos *et al.* to verify the efficiency of the ultrasonic process also showed that the yield of biodiesel decreased when high concentrations of catalyst were applied due to soap formation [34].

A plot of the catalyst concentration *versus* the conversion efficiency for the reactions conducted under ultrasonication and the mechanical stirring is illustrated in Figure 2, under the following reaction conditions: a reaction time of 90 min, temperature of 30 °C and a reaction time of 30 mins, temperature of 60 °C, respectively. The conversion efficiency of the waste oil was maximal at a catalyst concentration of 1% wt/wt, slightly higher than at a catalyst concentration of 0.75% during the ultrasonication, while the maximum conversion efficiency for the waste oil under the mechanical stirring was observed at a catalyst concentration of 1.5% wt/wt. The high value observed can be attributed to the acid value of the waste oil.

This trend is also corroborated by results of analysis of biodiesel samples done over a period of time by a South African analytical company, it was concluded that the presence of polymerized and oxidized material in waste oil is thought to affect the efficiency of catalysts in the transesterification reaction causing the difference between the conversion efficiencies of the waste and virgin oil [35].

Figure 2. Effect of catalyst concentration on conversion efficiency of the oil samples under a 6:1 methanol/oil ratio at 30 °C and reaction time of 30 mins.



3.2. Effect of Reaction Time

Figures 3 and Figures 4 illustrate the relationship between the methyl ester yield and exposure of reactants during the ultrasonication and the conventional mechanical stirring conditions respectively. It should be noted that the reaction conditions vary under both processes. The reaction conditions were kept constant at a catalyst amount of 0.75% wt/wt and 1% wt/wt, a molar ratio of 6:1 (alcohol:oil) and at temperatures of 30 °C and 60 °C, respectively. A FAME yield of 96.78% was recorded from the waste cooking oil under the ultrasonic condition which was higher than a value of 87.30 % recorded under the conventional stirring method at lower temperature (30 °C) and shorter time (30 mins) this can be attributed to the fact that sonochemical effect induced by the acoustic cavitations was stimulated by the ultrasonic irradiation on the oil and methanol molecules to form microscale fine emulsions causing them to suspend each other easily. It is also postulated that an increase in the interfacial area of droplets strongly accelerates the reaction rate, which agrees with studies done by Ramachandran *et al.* [36]. FAME yields of 94.32% and 89.70% were observed from the virgin oil under the ultrasonic and mechanical stirring processes, respectively. These values agree with reports from studies done on a comparison of ultrasonic irradiation with mechanical stirring for transesterification of neat vegetable oil and methanol with base-catalyst was made by Georgogianni *et al.* [22,32]

In a recent work by Thanh *et al.* [25] the transesterification of canola oil containing 0.4 wt% of FFA with methanol was assisted by ultrasound irradiation in a circulation process, the optimal FAME yield was observed at a KOH concentration of 0.7 wt% at a reaction time of 50 mins, although at a reduced molar ratio, while also conducting a similar system during the transesterification of waste cooking oil containing 1.7 wt% of FFA, the best yield of FAME was attained when the amount of KOH catalyst was 1.0 wt.% at same reaction time [24]. As conversion rate increases with time, it was observed that the initial rate of transesterification reaction of the sunflower oil was slow, so that its yield was lower than WCO before 20 min reaction time, the WCO gave a higher yield than sunflower oil up to 40 mins into the reactants exposure to the ultrasonic irradiation and afterwards yield values became identical.

Although natural oils contain different amounts of triglyceride mixture, their transesterifications are, by and large, similar to a single compound, triolein. The waste cooking oil used had the highest amount of short carbon chains of fatty acids (C16:0) in comparison to sunflower oil. These short carbon chains of fatty acids have less steric hindrance in comparison to long carbon chains of fatty acids and, therefore, having more possibility of contact with catalyst [37] consequently attributing largely to the reduced conversion time and corresponding increased biodiesel yield.

Figure 3. Effect of reaction time on FAME yield via the ultrasound under a 6:1methanol/oil ratio, at 30 °C and catalyst concentration of 0.75%wt of oil.

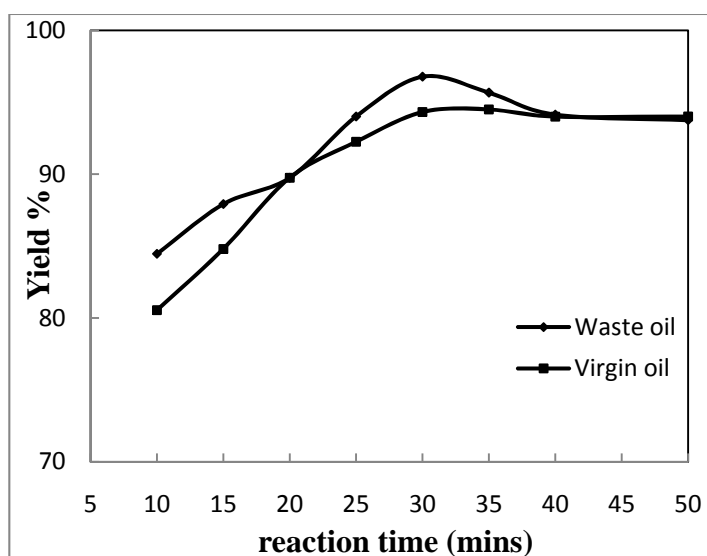
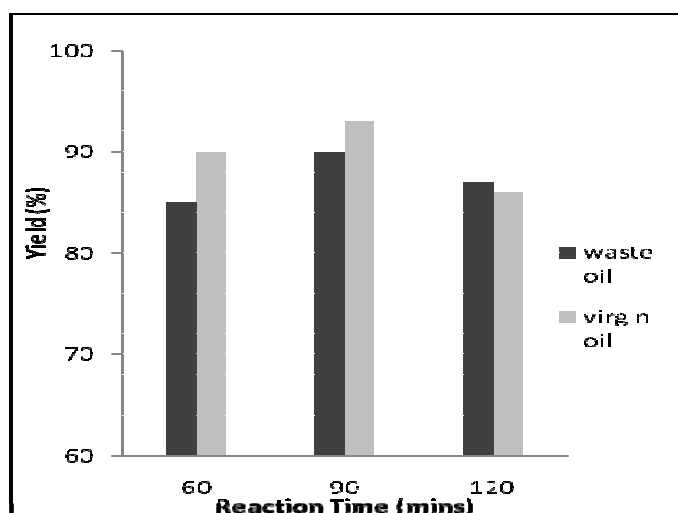


Figure 4. Effect of reaction time on FAME yield via the mechanical stirring under a 6:1methanol/oil ratio, at 60 °C and catalyst concentration of 1%wt of oil.

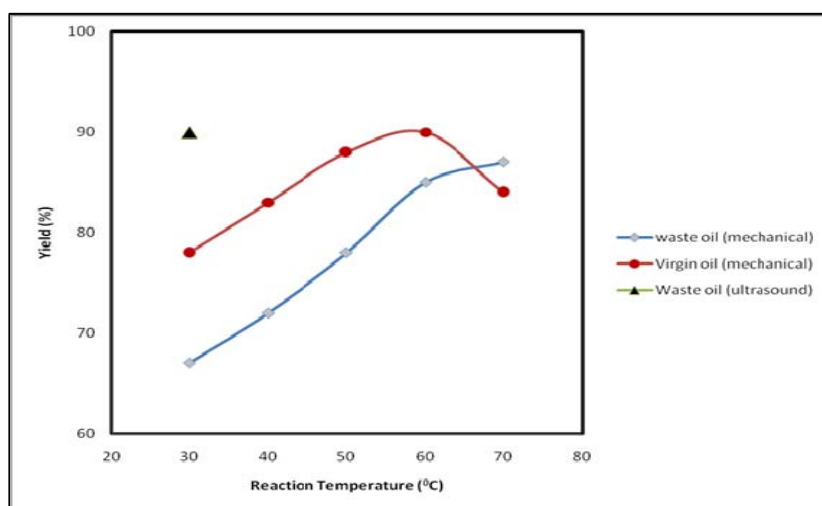


3.3. Effect of Reaction Temperature

The effect of reaction temperature on the ester yield is shown in Figure 5. The maximum ester yield of 87% for the waste oil was obtained at a temperature of 70 °C using the mechanical stirring method although previous studies have reported lower temperatures [7,12]. Transesterification can proceed at

ambient temperature depending on the feedstock used as an ultrasonic field causes cavitation bubbles near the phase boundary between the alcohol and oil phases, and this result in microfine bubbles being formed. The cavitations may also lead to a localized increase in temperature at the phase boundary enhancing the transesterification reaction and due to this formation of micro jets and localized temperature increase neither agitation nor heating is required to produce biodiesel via the ultrasound technology [34]. It is noteworthy to mention that the transesterification under the ultrasonication conducted at 30 °C temperature was controlled with a water bath, and a yield of 90% was obtained. This result corresponds to similar studies done by Ji *et al.*, [38], where a similar result was reported (biodiesel yields from 90% to 97%). In this work, the conversion efficiency of the waste oil under the ultrasonication was as high as 98% even at low temperature when compared to the conversion efficiency under the mechanical stirring process, reason for this is due to a high viscosity value obtained most probably due to the evaporation of methanol when the reaction temperature exceeds its boiling point consequently resulting in an incomplete reaction.

Figure 5. Effect of reaction temp. on FAME yield via the ultrasound and mechanical stirring under a 6:1 methanol/oil ratio at 30 °C and catalyst concentration of 0.75% wt/wt and 1% wt/wt, respectively.



It was found that the optimized variables of 6:1 methanol/oil ratio at reaction temperature of 30 °C for 30 min and 0.75% KOH (wt/wt) catalyst concentration was obtained for the transesterification of the waste oil via the ultrasound technology since theoretically, it is considered that the emulsion between triglycerides and alcohols occurs more rapidly compared to the stirring condition because the smaller size of emulsion droplets would be formed with the use of the ultrasound and when they are formed the contact surface area of immiscible solution increases, resulting in the higher rate of the transesterification reaction. In other words, the effective mass transfer in the ultrasonic field would affect the higher rate of transesterification reaction.

The chemical compositions and physical properties of the product obtained in this study are given in Table 3. The quality of the final product obtained from the optimal conditions was tested by Bioservices Company, Randburg, South Africa. In South Africa, the national standard for automotive fuel for diesel engines is SANS 1935:2004. This standard specifies the requirements and test methods

to be used for marketed and delivered biodiesel either as automotive fuel for diesel engines at 100% concentration or as an extender for automotive fuel for diesel engines. However this standard still has to be accepted internationally. The testing results presented are comparative with the South African National Standard and American Standards.

Table 3. Properties of FAME obtained from waste oil.

Test parameter	Unit	Result	SANS 1935:2004	Test method
Total ester	Mass%	96.78	96.5 min	ASTM 6584
Total glycerol	Mass%	0.25	0.25 max	ASTM 6584
Free glycerol	Mass%	0.01	0.02 max	AOCS Ca14-56
Monoglyceride	Mass%	0.65	0.8 max	AOCS Ca14-56
Diglyceride	Mass%	0.17	0.2 max	ASTM 6584
Triglyceride	Mass%	0.18	0.2 max	ASTM 6584
Methanol	Mass%	0.14	0.2 max	EN 14110
Viscosity (40 °C)	(mm ² /s)	4.08	1.9–6.0	
Flash point	°C	150	min 120	ISO 3679
Density	Kg/m ⁻³	891.1	860-900	ISO 3675

4. Conclusions

In the present study the transesterification reaction of waste sunflower frying oil with base catalysts (KOH) using both mechanical stirring and ultrasonication was investigated. Ultrasonic homogenization proved suitable for large scale processing of both virgin oils and waste oils resulting in a better yield and higher conversion efficiency. The effective mass transfer in the ultrasonic field enhanced the higher rate of transesterification reaction compared to mechanical mixing (stirring conditions). Reduction in the reaction conditions (time, temp.) and catalyst used for biodiesel production could help improve the economics of biodiesel production. The biodiesel purification operations also performed at significantly improved levels due to better glycerin removal, and less excess catalyst in the biodiesel. Yields of soap by-products at the resin purification stage were greatly reduced as a result of better reaction conversion. The properties of the products met the South African National Standard (SANS 1935:2004) which is almost the same as EN14214 and ASTM D6751 standards.

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