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Comparative study of ultrasonic and conventional method for biodiesel production using different heterogeneous catalyst

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The application of heterogeneous catalyst has recently attracted a substantial interest in production of biodiesel compared to homogeneous catalyst due to its repeatability in successive reactions and its easier separation from the reaction mixture. Detailed methods by which biodiesel is produced using the low-frequency ultrasonic energy (20 kHz) and the conventional mechanical stirrer are described. Waste cooking soybean oil (WCSO) will be used as a feedstock for this purpose. The experiments were conducted at oil/alcohol molar ratio (1:6), reaction time (60 min), reaction temperature (65°C) with three different catalysts aluminium oxide (Al_2O_3), calcium oxide (CaO) and magnesium oxide (MgO) at three different percentages (0.5 wt.%, 0.75 wt.%, 1 wt.%). WCSO biodiesel has been determined for its significant chemical and physical properties. The result shows that biodiesel production through the ultrasound process is relatively simple and more efficient than that produced by the conventional method.

Keywords: Biodiesel, waste cooking soybean oil, Al_2O_3, CaO, MgO.

Introduction

Owing to the decline of fossil fuel, the prices of fossil fuels grew steeply and it drives researchers and scientists to search the energy needs of the planet by seeking alternative fuel in an efficient way, so as to satisfy their environmental concerns[1]. To fulfil the world energy demand the best available source is biodiesel. Biodiesel, an organic compound that can be made from different triglycerides, alcohols and a catalyst, is extremely energy-intensive[2–4]. Currently, a number of methods are available for biodiesel production from different feedstocks such as the blending of raw oils and direct use, transesterification, thermal cracking, and microemulsions[5–7]. The main source of decreased carbon chains are the fatty acids and this response has been promoted. During this reaction, the oil is directly transesterified by alcohol and results in a biodiesel molecule[8]. Using waste cooking oil is a key component to reduce biodiesel production costs by up to 60–90%. The most common method of processing biodiesel is by catalyzed transesterification. Soybeans, sunflower, palm, rapeseed canola, cotton seeds are the most widely used oils in biodiesel production[8–10]. The possible low-priced biodiesel sources of waste plant oils and non-edible raw vegetable oils are chosen because the prices of edible vegetable oils are higher than those of diesel[11,12].

Waste cooking oil is cheaper than other oils (refine oils) and simple to gather from other sectors, including restaurant and household use. Such oils may be used for raw materials to reduce the costs of production of biodiesel[13,14]. A low cost and environmental emission reduction are the benefits of using waste cooking oils to manufacture biodiesel. In order to prevent pollution before environment disposal these oils must be treated. Because of it expensive disposal costs, many individuals chose to dispose of cooking oils in areas outside of towns, polluting the environment. It concludes that the use of waste-cooking oils as the basis for biodiesel production is an effective way[15,16].

A non-conventional (ultrasonic) process technique has been employed for direct transformation of waste cooking oil

into biodiesel in one single stage. As a result, the process of ultrasound transesterification waste-to-cooking oils to biodiesel with low energy and chemical use is significantly reduced as compared with traditional biodiesel processes by rising mass/heat transfer phenomena and the precise thermal effects at molecular levels. Catalysts are compounds that accelerate reactions without participating in the reaction by reducing activation energy[17,18]. Catalysts play a major role in biodiesel production, especially homogeneous and heterogeneous catalysts. High levels of soap production with homogeneous catalysts have been observed in biodiesel production, reducing biodiesel yields and causing problems during product purification. Heterogeneous catalysts have major advantages in the presence of heterogeneous catalysts, for instance the easy product separation; reusable and reactive conditions under minor reaction conditions[19,20]. Thus, because of its high activity, availability, low price, and heterogeneous catalysts selected for biodiesel from WCSO.

In this work, the WCSO biodiesel production experiments were carried out using ultrasonic and conventional transesterification processes. Comparative descriptions of biodiesel processing using the low-frequency ultrasonic energy (20 kHz) and the traditional mechanical stirrer methods are presented in the research work. The experiments have been performed for molar ratio (oil/alcohol) 1:6, reaction time (60 min), reaction temperature (65°C) with three different catalysts Al_2O_3, CaO and MgO at three different percentages (0.5 wt.%, 0.75 wt.%, 1 wt.%) and the objective is to test the effect on yield of methyl ester of a different heterogeneous catalyst.

Materials and methods

Materials:

Raw WCSO, have been used for biodiesel production and it is collected from the local area hotels. Analytical (AR) grade Al_2O_3, CaO, MgO, and methanol (99.5%) were used for experimentation. In biodiesel production reactors that require mechanical mixing and ultrasonication. The heating mantle with a traditional mechanical stirrer system was used with two liters of round-bottom flask with water-cooled reflux condenser to heat the mixture in the flask and the mixtures were mixed at a constant speed with the conventional mechanical stirrer method of transesterification. The properties of WCSO are shown in Table 1.

Table 1. Properties of waste cooking soybean oil (WCSO)

Property	Value
Acid value (mg KOH/g)	0.48
Saponification value (mg/g)	198.3
Iodine value (mg iodine/g)	228
FFA content (%)	0.38
Density (g/cm^3)	0.860

Systems requirements (specifications):

Experimental setups:

Ultrasonic method experimental setup:

A 1.5 liter reactor in which the ultrasound probe is submerged constitutes the fundamental configuration. A feed inlet and outlet for the product are given to the reactor. The probe is connected to the transducer which is operated in turn by the ultrasound generator, with a frequency of 20 kHz. To measure the inner temperature shown on the generator, a thermocouple is placed in the reactor. The reactor is supplied with an overhead condenser to condense methanol vapors that are produced if necessary. The temperature on the generator can be set for all parameters, including reaction time. The entire system is held in a wood box functioning as a sound shield. Fig. 1 shows the schematic representation of the ultrasonic method experimental set-up.

Conventional method experimental setup:

Three-necked 1.5 liter round bottom batch reactor is used

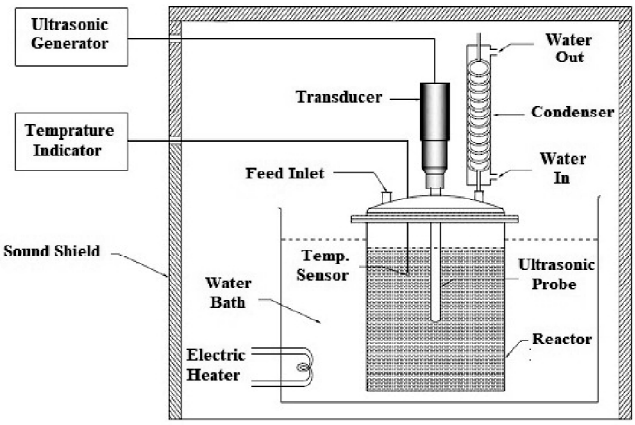

Fig. 1. Schematic diagram of the experimental setup (ultrasonic process).

for transesterification experiments with a standardized mechanical stirrer with a thermocouple and two necks attached to a heater plate, one is a sample removal stopper and for feeding raw materials (cooking oil, catalyst, thermometer) and one for the thermometer. Fig. 2 shows the schematic representation of a conventional method experimental setup.

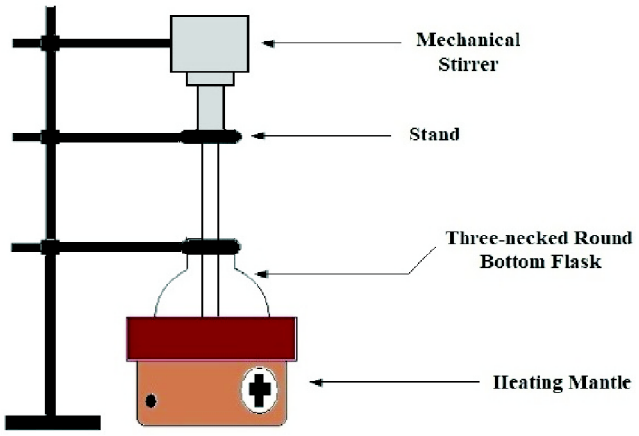

Fig. 2. Schematic representation of conventional method experimental setup.

Methods:

Ultrasonic method for transesterification of WCSO:

In an ultrasonic reactor horn type assembly, transesterification reactions were performed. The horn is fixed to a transducer in a horn-type reactor that creates ultrasonic irradiation in the mixture. At a constant time of 60 min, ultrasonic processor frequency is between 20 kHz and the transducer horn should then be immersed in the separating boundary of two immiscible fluids. There is an integrated arrangement to support the beaker (1.5 liter). The transducer's horn was approximately submerged methanol and fatty acid oil 2 cm in reactive blending. A water bath controlled the temperature of the reaction mixture. Heated fatty acid oil (500 g, 60°C) was poured into the reactor at the beginning. The reaction started when a mixture consisting of the desired amount (0.5 wt.% , 0.75 wt.%, 1 wt.%) of Al_2O_3, CaO, and MgO was dissolved in methanol, it was poured into the heated reactor. The reaction is performed through the acoustic rod horn ultrasonic irradiation integrated with the transducer. The cavities are produced by the irradiation of ultrasonic power in immiscible liquid with sufficient energy (oil and alcohol do not miscible) as a result of which microfine bubbles are formed that collapse at different locations of the reactor and disturb the phase limit between two immiscible liquids that leads to mix-emulsion.

Conventional method for transesterification of WCSO:

The transesterification reaction was carried out three-necked 1.5 liter round bottom batch reactor with a mechanical stirrer, thermometer, stopper, and heating mantle. Raw WCSO as a feed has freed of water as certain catalysts are absorbed by any water or moisture in the system and the transesterification reaction slow. The transesterification process was studied for catalyst (0.5 wt.%, 0.75 wt.%, 1 wt.%) of Al_2O_3, CaO, and MgO at a reaction time (60 min) at 65°C and at atmospheric pressure. On the weighing machine, the WCSO sample was carefully measured. The sample was agitated for 60 min continuously and it was a feculent or turbid reaction combination. The product was placed overnight in the separating funnel. As a result of transesterification, two phases of a different density were formed. The top layer was biodiesel, alcohol, soap, and the lower was glycerin,

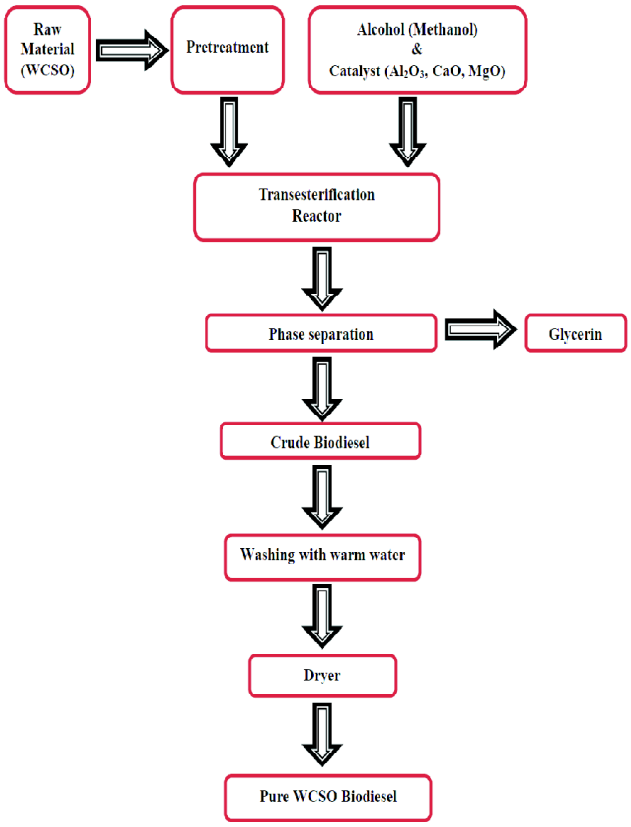

Fig. 3. Flow diagram for biodiesel production from WCSO.

unreacted catalyst and excess alcohol. Two layers were separated and measured. Fig. 3 shows the flow diagram for biodiesel production from WCSO.

Results and discussion

In a 1.5 liter beaker, WCSO (500 g) is taken and filtered to eliminate impurities and heated up to 120°C, with the intention of removing the water content of oil in order to prevent soap formation. The oil will cool down to a temperature of 60°C. Methanol (CH_3OH) with a molar ratio of (1:6) and catalysts Al_2O_3, CaO, MgO is taken as (0.5 wt.%, 0.75 wt.%, and 1 wt.%) by the weight of oil. The methyl alcohol and Al_2O_3, CaO, MgO then mixed until it was dissolved in methyl alcohol and mixed with SWCO. The oil, methanol and catalyst mixture comes into contact with the ultrasonic transducer, which operates at a frequency of 20 kHz in the ultrasonic phase. The mixture temperature is kept at a constant time of 60–65°C throughout the reaction. The beaker is kept for separation when the reaction is complete. The fatty acid has a higher weight, so it lies down on the bottom. It will take 2 to 3 hours to separate methyl ester and glycerol. Biodiesel (methyl ester) is visible in the top and bottom layers as glycerol after complete separation and for the purification process; it is separated from the beaker. Water is mixed with a methyl ester to remove the catalyst and left to settle and because of the higher specific gravity collected at the bottom. The distillation technique has removed excess methanol present in biodiesel.

Experimental data are collected by performing ultrasonic and conventional method on the sample which is a mixture of WCSO, methanol (CH_3OH) and catalyst (Al_2O_3, CaO, MgO). The development of biodiesel and the performance of methyl ester for each sample reaction time are measured continuously. Figs. 4, 5 and 6 shows the yield (%) of WCSO at 0.5 wt.%, 0.75 wt.% and 1 wt.% catalysts concentration by ultrasonic method respectively and Figs. 7, 8 and 9 shows yield (%) of WCSO at 0.5 wt.%, 0.75 wt.%, and 1 wt.% catalysts concentration by conventional method respectively. It was the highest when catalyst Al_2O_3 was used in both the

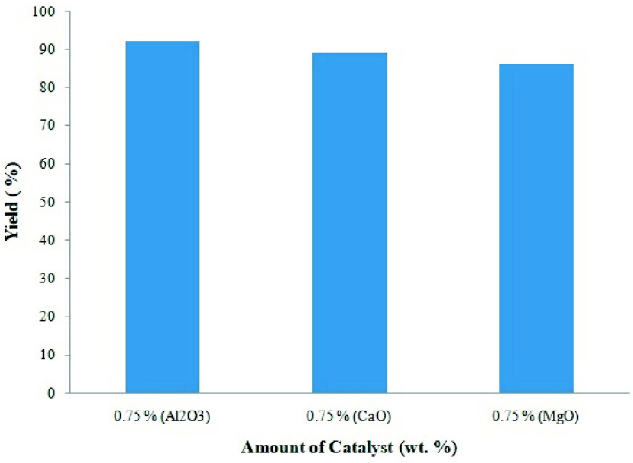

Fig. 5. Yield (%) of WCSO at 0.75 wt.% catalysts concentration by ultrasonic method.

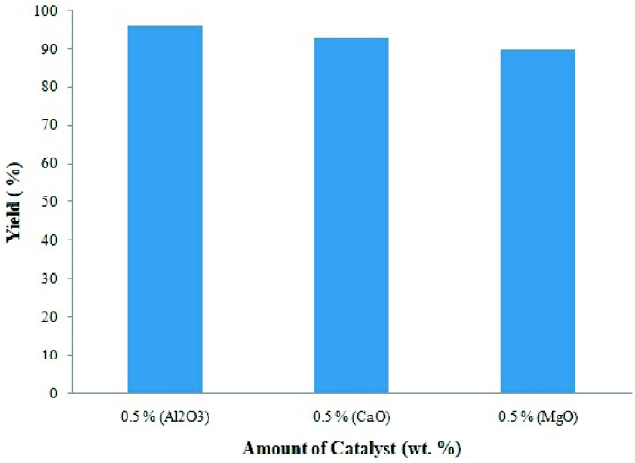

Fig. 4. Yield (%) of WCSO at 0.5 wt.% catalysts concentration by ultrasonic method.

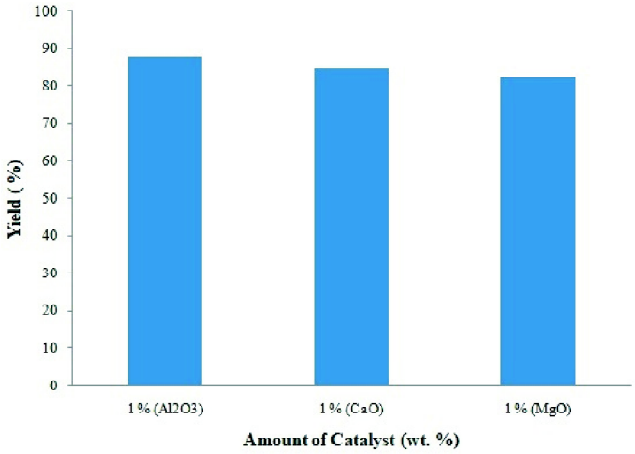

Fig. 6. Yield (%) of WCSO at 1 wt.% catalysts concentration by ultrasonic method.

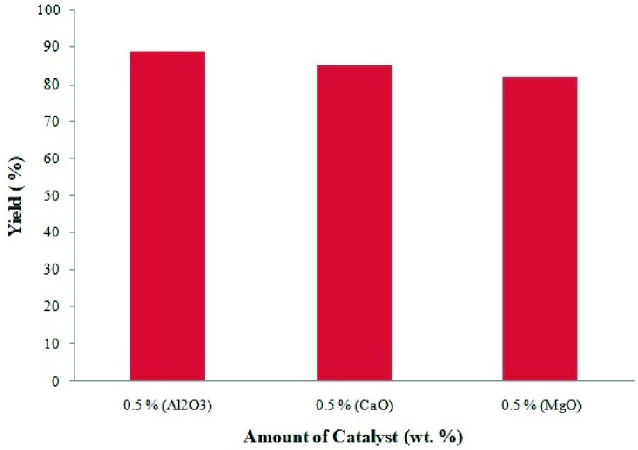

Fig. 7. Yield (%) of WCSO at 0.5 wt.% catalysts concentration by conventional method.

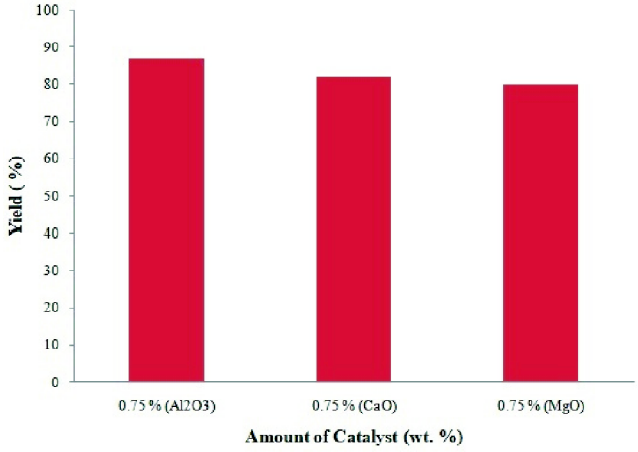

Fig. 8. Yield (%) of WCSO at 0.75 wt.% catalysts concentration by conventional method.

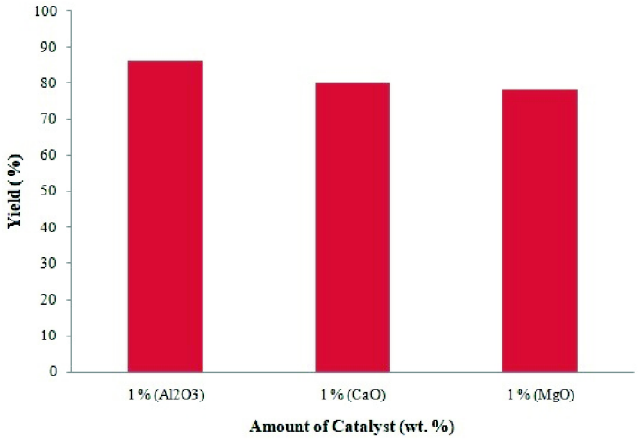

Fig. 9. Yield (%) of WCSO at 1 wt.% catalysts concentration by conventional method.

processes i.e. 96% yield from the ultrasonic process and 89% yield from the conventional process. The biodiesel produced using catalyst MgO yielded the least compared to the other two catalysts with both the production processes. The yield obtained for the ultrasonic process and the conventional process was 90% and 84% respectively using MgO. Similarly, the biodiesel yield obtained by using catalyst CaO was 93% and 84% for the ultrasonic process and the conventional process respectively. Fig. 10 shows the comparison of results i.e. yield (%) for the ultrasonic and conventional methods. The sample of biodiesel obtained from the ultrasonic process using catalyst Al_2O_3 was analyzed and Table 2 shows the biodiesel properties produced by WCSO.

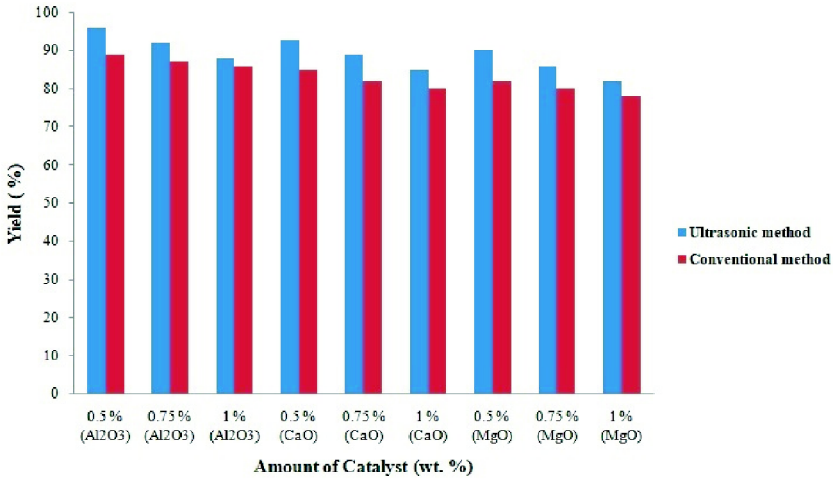

Fig. 10. Comparison of results i.e. yield (%) for the ultrasonic and conventional methods.

Table 2. Biodiesel properties produced from WCSO

Property	WCSO biodiesel
Appearance	Clear
Color	Brownish
Density at 15°C	0.886
Specific gravity (g/ml)	0.88
Flash point (°C)	162
Cloud point (°C)	–3
Pour point (°C)	–8
Cetane number	55
Viscosity (cP)	4.92
Water content (w/w%)	0.043
Sulphur contents (w/w%)	0.0135

Conclusion

Ultrasonic as well as the conventional method for production of biodiesel from WCSO using three different catalysts i.e. Al_2O_3, CaO and MgO at percentages (0.5 wt.%, 0.75 wt.%, 1 wt.%) was performed. The result shows the percentage yield was the highest when catalyst Al_2O_3 was used in both the processes i.e. 96%, 92%, 88% yield from ultrasonic process at 0.5 wt.%, 0.75 wt.%, 1 wt.% respectively and 89%, 87%, 85% yield from conventional process at 0.5 wt.%, 0.75 wt.%, 1 wt.% respectively. The biodiesel produced using catalyst MgO yielded the least compared to the other two catalysts with both the production processes. The yield obtained for the ultrasonic process was 90%, 86%, 82% at 0.5 wt.%, 0.75 wt.%, 1 wt.% respectively and the conventional process 82%, 80% 78 at 0.5 wt.%, 0.75 wt.%, 1 wt.% respectively using MgO. Similarly, the biodiesel yield obtained by using catalyst CaO was 93%, 89%, 85% for the ultrasonic process at 0.5 wt.%, 0.75 wt.%, 1 wt.% respectively and 85%, 82%, 80% for the conventional process at 0.5 wt.%, 0.75 wt.%, 1 wt.% respectively. Therefore it is concluded that the ultrasonic method is an effective way of converting crude WCSO into biodiesel by using Al_2O_3 at 0.5 wt.%.

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Abbreviations

Al_2O_3	Aluminium oxide
CaO	Calcium oxide
MgO	Magnesium oxide
WCSO	Waste cooking soybean oil
CH_3OH	Methanol
ASTM	American Society for Testing and Materials
ppm	Parts per million
FFA	Free fatty acid

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