



Continuous flow through a microwave oven for the large-scale production of biodiesel from waste cooking oil



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HIGHLIGHTS

- Fixed bed continuous flow microwave irradiation process is reported.
- SrO/SiO₂ is a promising heterogeneous catalyst for biodiesel production.
- Waste cooking oil conversion as high as 99.2 wt% is achieved.
- Sustainable catalytic activity is observed for 24.6 min of irradiation.

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ABSTRACT

This report presents a method for producing large quantities of biodiesel from waste cooking oil (WCO). Preliminary studies on optimization of the WCO transesterification process in a continuous-flow microwave reactor are carried out using commercial SrO as a catalyst. The SrO catalyst can be separated and reused for five reaction cycles without loss in activity. Challenges like mass flow and pressure drop constraints need to be surmounted. SrO nanoparticles deposited on millimeter-sized (3–6 mm) silica beads (41 wt% SrO/SiO₂) are prepared and evaluated as a substitute for the SrO catalyst. A WCO conversion value to biodiesel as high as 99.2 wt% was achieved with the reactor packed with 15 g of 41 wt% SrO/SiO₂ catalyst in 8.2 min with 820 mL of feed. Excellent performance of the fixed-bed catalyst without loss in activity for a lifetime of 24.6 min converting a feed of 2.46 L to FAME was observed.

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1. Introduction

Science is appreciated if it is used to create technology that can be handled by the common man. Energy demand and the need for a clean environment concern everyone. Conventional energy sources are nonrenewable. Energy extraction from such sources as well as their usage cause pollution and have detrimental impact on the environment. Moreover, the increasing population and rapid urbanization of the world create a huge demand for alternative and efficient energy sources. Thus, it is crucial to develop energy production processes that are demand-based, renewable, sustainable, and environmentally benign. Renewable energy sources must be economical and cost-competitive to be sustainable in meeting the growing demand. The transportation sector plays a major role in the production of greenhouse gas (GHG) emissions and consumes almost two thirds of the total crude oil. Fuel

demand in the transportation sector is expected to increase by 40% over the period of 2010–2040 (Leite et al., 2013). This prompts intense research for developing alternatives to fossil fuels. An immediately applicable and readily available option is the replacement of diesel fuel by biodiesel, consisting of fatty acid alkyl esters.

Biodiesel is considered to be one of the best sustainable energy sources to replace petroleum-based transportation fuels. With little modification, diesel engine vehicles can use biodiesel or blended biodiesel with fossil diesel at any ratio (Manh et al., 2012). Biodiesel is biodegradable and nontoxic and emits less CO and hydrocarbons than petroleum-based diesel when combusted. However, it does present other technical problems, such as low cloud point and elevated NO_x emissions. Biodiesel is commonly made from vegetable oils, waste oils, algae and animal fats by transesterification with an alcohol such as methanol and an acid or base catalyst. The products of the reaction are fatty acid methyl esters (FAMES), which constitute the biodiesel, and glycerol.

Among the well-known processes to produce biodiesel, transesterification has been proved to be the simplest, allowing significant

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reduction in the feedstock viscosity. Waste cooking oil (WCO) is of particular interest for biodiesel production for two reasons. First, WCOs are two to three times cheaper than virgin oils. Second, reusing and transforming WCO, instead of discarding it into the sewer, significantly decreases the water-treatment costs. This double effect makes WCO a very good environment-friendly feedstock (Mazubert et al., 2014). A summary of the recent developments in the catalytic processes for the conversion of waste cooking oil into biodiesel is presented in Table 1.

As suggested in Table 1, the catalysts play a crucial role in the transesterification reaction. Experimental conditions and optimization of the parameters depend directly on the choice of the catalyst. Homogeneous catalysts are commonly used, leading to high catalytic activity. Contrary to acid-catalyzed reactions that require extreme experimental conditions, such as longer time, high temperature and pressure (Tran et al., 2016), homogeneous-base catalysts result in almost complete conversion of the feedstock to biodiesel under modest reaction conditions (Al-Hamamre and Yamin, 2014).

The strontium oxide (SrO), despite its lower surface area and the partial solubility of the metal ion in the reaction medium, is a strong base used in several chemical reactions, such as oxidative coupling of methane, selective oxidation of propane, and mixed Tishchenko reactions. Liu et al. reported excellent catalytic performance for the transesterification process between soybean oil, methanol and SrO, leading to a biodiesel conversion of 95 wt% after 30 min of reaction performed at 65 °C, using methanol-to-oil molar ratio of 12:1 and 3 wt% catalyst amount, maintaining a sustainable activity even after 10 cycles (Liu et al., 2007). Chen et al. (2012) reported that SrO/SiO₂ catalyst displayed high catalytic performance, exhibiting 95% biodiesel yield within 10 min of the methanolysis reaction.

A transesterification reaction is commonly achieved under conventional heating. The required energy of the reaction in conventional heating is provided by convection, conduction and radiation of heat energy from the surfaces of the reactor to the reactants. Such heat transfer is energetically inefficient (Encinar et al., 2012). Recently, several technologies have been introduced to obtain precise mixing and mass transfer in the reaction system to decrease the input energy. These new technologies are based on the use of alternative energy sources in a special wavelength such as microwave or ultrasonic irradiation.

Microwave irradiation is a well-known strategy to accelerate several chemical reactions involved in biomass conversion (Mai and Koo, 2014). Gedanken et al. reported the use of microwave heating as a fast and simple way to prepare biodiesel from a variety of renewable feedstock in batch mode (Koberg and Gedanken, 2013; Tangy et al., 2016). Using microwave heating accelerates the rate of reactions and increases selectivity. The reduction of reaction time is mainly due to the interaction of the electromagnetic field with the molecules in the reaction medium. In the transesterification reaction, microwave efficiency is increased by the high polarity and high dielectric loss of methanol. The microwave effect on the transesterification reaction can be two-fold: 1) enhancement of reaction by a thermal effect, and 2) evaporation of methanol due to the strong microwave interaction of the material (Gude et al., 2013). The microwave interaction with the reagents (triglycerides and methanol) results in a large reduction in activation energy due to increased dipolar polarization. The potential of microwave irradiation to accelerate the transesterification reaction was exploited in a continuous-flow process. Using a homogenous base-catalyst for the transesterification reactions under microwave irradiation in continuous reactor conditions, high conversions or yields are obtained at very short reaction

Table 1
Catalytic processes for the conversion of waste cooking oil (WCO) to biodiesel.

Catalyst	Reaction conditions	Batch/continuous	Conversion of WCO to biodiesel (wt%)	References
KOH	Conventional heating; T = 50 °C; 30 min; MeOH:oil molar ratio = 9:1; 1 wt% catalyst amount	Batch	99.46	Al-Hamamre and Yamin (2014)
Chicken bone	Conventional heating; T = 65 °C; 4 h; MeOH:oil molar ratio = 15:1; 5 wt% catalyst; agitation speed of 500 rpm	Batch	89.33	Farooq and Ramli (2015)
Cu-doped ZnO nanocomposite	Conventional heating; T = 55 °C; 50 min; MeOH:oil molar ratio = 8:1; 12 wt% catalyst	Batch	97.71	Gurunathan and Ravi (2015)
Egg shell	RT; 11 h; MeOH:oil molar ratio = 6:1; 5.8 wt% catalyst amount	Batch	94.52	Piker et al. (2016)
FeCl ₃ -modified resin	Conventional heating; T = 78 °C; 3 h; EtOH:oil molar ratio = 4:1; 10.97 wt% catalyst	Batch	92.13	Ma et al. (2016)
KF supported Mg ₃ Al _{0.6} La _{0.4}	Conventional heating; T = 65 °C; 8 h; MeOH:oil molar ratio = 12:1; 3 wt% catalyst amount	Batch	98.9	Sun et al. (2015)
Modified coal fly ash	Ultrasound heating; 1.41 min; MeOH:oil molar ratio = 10.71:1; 4.97 wt% catalyst amount	Batch	95.57	Xiang et al. (2016)
Na-silica waste sponge	Ultrasound heating; T = 55 °C; 30 min; MeOH:oil molar ratio = 9:1; 3 wt% catalyst amount	Batch	98.4	Hindryawati and Maniam (2015)
SrO	Microwave irradiation; T = 60 °C; 10 s; MeOH:oil molar ratio = 6:1; 1.8 wt% catalyst amount	Batch	99.8	Koberg et al. (2011)
β-K ₂ Zr ₂ O ₅	Conventional heating; T = 65 °C; 2 h; MeOH:oil molar ratio = 10:1; 4 wt% catalyst amount	Batch	96.85	Singh et al. (2016)
CaO	Conventional heating; T = 65 °C; 3 h; MeOH:oil molar ratio = 6:1; 5 wt% catalyst amount	Catalytic bed system	92	Viola et al. (2012)
NaOH	Microwave irradiation; T = 78 °C; 30 s; EtOH:oil molar ratio = 12:1; 3 wt% catalyst amount	Continuous	97	Lertsathapornsuk et al. (2008)
NaOH	Ultrasound heating; 150 s; MeOH:oil molar ratio = 8.6:1; 0.5 wt% catalyst amount; 1 L/min	Continuous	90	Delavari et al. (2014)
Waste egg shell	Reactive distillation system; T = 65 °C; 7 h; MeOH:oil molar ratio = 4:1	Continuous	93.48	Niju et al. (2014))
Zr-SBA-15/bentonite	Packed bed reactor; T = 210 °C; 30 min; MeOH:oil molar ratio = 50:1; 28 g catalyst amount	Continuous	96	Melero et al. (2014)
Anion-exchange resin	Conventional heating; T = 50 °C; MeOH:oil molar ratio = 3.5:1; 600 g (wet); flow rate: 120 cm ³ /h	Expanded-bed reactor packed with the resin	92.3	Shibasaki-Kitakawa et al. (2011)
CaO supported on activated carbon	Conventional heating; T = 60 °C; 8 h; MeOH:oil molar ratio = 25:1; 295 mm packed bed height	Fixed-bed reactor	94	Buasri et al. (2012)

times. The application of this knowledge to the production of biodiesel is innovative and can yield large quantities of the fuel in a short reaction time. Upscaling microwave technology to higher production scales, from the multi-gram to the kilogram scale, has become a major topic for industrial chemists (Benaskar et al., 2011). Owing to the limited penetration depth of the microwave field, uniform heating at larger scales cannot be achieved without internal mixing. Depending on the dielectric properties of the liquid reaction mixture, the penetration depth is on the order of 10^{-2} to 10^{-3} m and, therefore, the heating is dominated by convective heat-transfer at larger liquid volumes.

The physical limitation of microwave reactors can be avoided using the continuous flow approach as a feasible upscale strategy. Continuous-flow microwave reactors are a synthetic platform technique resulting from the combination of microwave and continuous-flow enabling techniques. These reactors operate by passing the reagents through a flow cell inserted into the microwave cavity. The drawbacks of a continuous-flow microwave apparatus are that it can be difficult to process solids, highly viscous liquids, or heterogeneous reaction mixtures. Also, the adaptation of conditions from simple small-scale reactions to the continuous-flow cell may end up being time-consuming (Bowman et al., 2008).

The potential of SrO nanoparticles deposited on millimetric (3–6 mm) silica beads (SrO/SiO₂) was demonstrated for the conversion of WCO to FAME in just 10 s in a batch process in a domestic microwave oven. Moreover, the catalyst reusability was demonstrated for 10 reaction runs without loss in activity (Tangy et al., 2016). The present research aim to exploit SrO/SiO₂ as a fixed-bed catalyst for the continuous-flow production of FAME from WCO. The objective of the present work is to design an optimized continuous-flow biodiesel production process, using microwave heating as the methodology for biodiesel production with SrO/SiO₂ as the catalyst. This strategy can make the microwave-based biodiesel production process from waste cooking oil industrially feasible. The continuous-flow transesterification process currently developed is environmentally friendly because the waste cooked oil is effectively used as a fuel precursor by a fast methodology based on microwave irradiation and SrO/SiO₂ is used as a catalyst, thereby circumventing the challenges of mass flow and pressure drop which are usually encountered in continuous-flow processes.

2. Experimental details

2.1. Materials and methods

Waste cooking oil (WCO) was obtained free of charge from a restaurant near Bar-Ilan University. Ethanol and methanol were purchased from Bio-Lab Ltd., Israel. SrO (99.5%) was procured from Alfa Aesar. Sr(NO₃)₂ (≥99.0%), Na₂CO₃, KOH, SiO₂ gel beads (particles with sizes ranging from 3 to 6 mm) were purchased from Sigma-Aldrich. Ethylene diamine, EDA (+99%) was procured from Acros Organics. All the materials were used as received for catalyst preparation (SrO/SiO₂) and for the transesterification reaction for the continuous flow through production of biodiesel using WCO as feedstock under microwave irradiation.

2.2. WCO pretreatment

The acid value of the cooking oil determined by titrimetric method was found to be 3.6 mg KOH/g (Tangy et al., 2016). Briefly, pretreatment of WCO was performed by mixing the WCO with KOH solution followed by centrifugation for the removal of FFA as soap. WCO devoid of FFA is subsequently heated at 110 °C in an air oven to evaporate the water. The pretreated WCO was used

as feedstock for biodiesel production in a continuous-flow microwave irradiation process using either a commercial SrO catalyst or SrO/SiO₂ as a fixed-bed catalyst.

2.3. Aqueous-phase microwave assisted synthesis of SrO/SiO₂ catalyst

The preparation of the SrO/SiO₂ catalyst is described in detail in a previous paper (Tangy et al., 2016). In brief, the deposition of SrO on SiO₂ millimeter (3–6 mm) sized beads involves dissolving equimolar amounts of Sr(NO₃)₂ (4.23 g) and Na₂CO₃ (2.11 g) in 100 mL water under vigorous stirring in a 250-mL round bottom flask. 10 mL of ethylene diamine (EDA) are then added. Subsequently, 6 g SiO₂ gel beads (3–6 mm particle size) are added. The slurry is irradiated for 30 s. The residual solid mass obtained after cooling the contents is separated from the supernatant by centrifugation, washed with ethanol thrice and vacuum dried overnight. The material SrCO₃/SiO₂ is calcined at 900 °C for 4 h in air, yielding SrO/SiO₂. ICP-OES (Ultima 2, Jobin Yvon Horiba) analysis was carried out to estimate the amount of SrO deposited on the SiO₂ beads and the loading was found to be 41 wt%.

2.4. Biodiesel production in a continuous-flow microwave reactor

The transesterification reaction of waste cooking oil to biodiesel is carried out as a continuous-flow process on a FlowSYNTH microwave system (Milestone FlowSYNTH ATC-F0 300 continuous-flow microwave reactor, Fig. S1 in the Supplementary Material). The configuration of the system is similar to that described by Choedkiatsakul et al. (2015). The FlowSYNTH system is a continuous-flow microwave reactor with 1000 W available power, heating a vertically mounted 200-mL flow-through reactor. The reaction mixture is pumped by a high-pressure membrane pump from the base upwards through the column to the top. In-line sensors allow continuous monitoring of the reaction temperature. Homogeneity of the temperature along the entire length of the reactor is ensured by a magnetically-driven paddle-stirrer. An Archimedean screw provides agitation and helps maintain plug-flow characteristics, while reducing back-mixing. The reaction mixture is stirred mechanically inside the microwave cavity by means of a stir shaft equipped with three paddles. These paddles fit the agitator aid heating through conduction. The reactor is also equipped with a pump, to enable flow of the reaction solution through the reactor. The temperature of the reaction mixture is measured both in the microwave cavity and after exiting the cooler by means of thermocouples. The FlowSYNTH is controlled by an external touch-screen terminal, controlling process conditions such as temperature, power, and feed flow rate via software process control. The reaction chamber, with 190 mL working volume, is mounted vertically in the microwave cavity. The maximum working conditions for the reactor are 200 °C, 30 bar and 1000 W. The reaction mixture is pumped continuously through the reaction vessel under microwave heating. The peristaltic pump enables flow rates from 0.06 to 3400 mL/min. The continuous-flow process facilitates the large-scale production of biodiesel in a shorter time than the conventional biodiesel production process. A typical transesterification process in the flow system consists of feeding a mixture of waste cooking oil and methanol (different mole ratios, 1:6–1:12) and a SrO catalyst (5–8.75 g) at different flow rates (100–300 mL/min). The effect of various reaction parameters such as the stirring shaft rotation velocity, mole ratio of waste cooking oil to methanol, amount of catalyst, reaction time, reaction temperature, flow rate of the feed and microwave power on the conversion of waste cooking oil into biodiesel are evaluated. In the case of SrO supported on millimetric beads (41 wt% SrO/SiO₂), 15 g of the catalyst is packed in the microwave reactor system using a permeable membrane at its bottom that only enables

the liquid product, but not the solid catalyst, to pass through. The feed (WCO and methanol) flows from the top of the fixed bed of the catalyst packed in the reactor, under the optimized process parameters, using SrO (commercial) as the catalyst.

2.5. FAME analysis

Two flow processes are compared in this study. In the first, the commercial SrO is mixed with the feedstock and flows together with the product for the analysis. In the second, the SrO/SiO₂ catalyst is packed in the microwave reactor and stays intact for further flow of new feedstock. The analysis of the product and estimation of yield in the first process is performed as follows: the obtained reaction product from the transesterification of WCO is evaporated using a rotary evaporator to remove the unreacted methanol. Subsequently, the product is centrifuged and three layers are observed in the centrifugation tube: the top one is the biodiesel phase as well as the unreacted oil, if there is any, the middle one is the catalyst and the bottom one is the glycerol (Fig. S2). The top layer is collected and analyzed using ¹H NMR to determine the wt% conversion of waste cooking oil into biodiesel. The product analysis for the fixed-bed experiments is performed in the same way as described above, except for the catalyst in the reaction product, which is not used because the catalyst (SrO/SiO₂) is incorporated in the microwave reactor bed. ¹H NMR spectra are recorded on a Bruker Avance DPX 300 instrument and the chemical shift values are referenced to CDCl₃. The conversion percentage is calculated from the integrated areas of the triglyceride and FAME signals. The values of conversion (wt%) of the waste cooking oil to FAME are estimated according to

$$\text{Conversion(\%)} = \frac{2I_{\text{Me}}}{3I_{\text{CH}_2}} \times 100. \quad (1)$$

The signals chosen for integration were those of the methoxy groups in the FAME (3.64 ppm, singlet) and those of the α -methylene protons present in all the triglyceride derivatives (triplet centered at 2.28 ppm) of the oil. Factors 2 and 3 represent the two protons of the methylene carbon and the three protons attached to the methyl carbon. ¹H NMR spectroscopy is known as a fast and accurate method for analyzing the degree to which oil is converted to biodiesel, compared to GC–MS, which is the official method for biodiesel analysis (Mambrini et al., 2012).

In addition, the chemical composition of the FAME produced from WCO is analyzed by GC–MS (Varian 431-GC, 220-MS) using a VF-5 ms column. Various components present in FAME were identified by comparison of the retention time and mass spectra with library data of mass spectra compounds. The GC–MS conditions used are detailed in Table S1. A study of leaching of SrO from the SiO₂ surface after the continuous flow transesterification process was also made. Typical process of evaluation of the amount of SrO on SiO₂ in the spent catalyst comprise of dispersing known amount of SrO/SiO₂ (spent catalyst) in conc. HNO₃ and stirring the contents for 1 h at 50 °C leading to the dissolution of SrO. The silica beads were separated from the filtrate containing the Sr²⁺ ions by filtration using Whatman (150 MM Φ) filter paper. The filtrate was analyzed for Sr²⁺ ions by using an inductively coupled plasma (ICP) spectrometer (Ultima 2, Jobin Yvon Horiba). The amount of SrO content deduced from ICP analysis was subtracted from the initial amount of SrO (41.1 wt%) resulting in the amount of SrO leached out during the reaction.

3. Results and discussion

Preliminary studies on the optimization of continuous-flow biodiesel production are carried out using a SrO (commercial) catalyst.

The optimized process parameters, namely, the amount of catalyst, mole ratio of WCO to methanol, reaction temperature, and flow rate of the feed are used to produce biodiesel using the fixed-bed SrO/SiO₂ catalyst.

3.1. Transesterification of WCO under continuous-flow microwave irradiation using commercial SrO as a catalyst

3.1.1. Effect of the stirring-shaft rotation velocity on the conversion of WCO

The aim of the current study is to demonstrate that the batch process for the conversion of WCO to biodiesel using a SrO/SiO₂ catalyst in a domestic microwave oven⁶⁰ can be successfully transformed to a continuous-flow microwave irradiation process. Conversion of a batch process to a flow process has immediate implications relating to industrial applications. The flow system is provided with an in-built parameter, namely, the speed of rotation (%) of the stirring shaft of the microwave system through which the reaction mixture flows. The speed of rotation (%) varies between 20, 40, 60 and 80%. Preliminary process optimization studies are carried out using a commercial SrO catalyst. The catalyst (5 g) is mixed in a glass beaker with the required amount of methanol (200 mL) and an appropriate amount of WCO (800 mL), corresponding to a methanol-to-oil mole ratio of 1:6. The contents in the beaker are stirred on a magnetic stirrer using a stirring bar. The reaction mixture along with the catalyst is then caused to flow at a constant flow rate (100 mL/min) and at a reaction temperature of 65 °C. The amount of catalyst (5 g) used for 1 L of feed (oil and methanol) in this continuous-flow process is three times lower than that used by Koberg et al. in a typical batch process accelerated by microwave irradiation (Koberg et al., 2011). The speed of rotation (%) of the stirring shaft was found to have a significant impact on the conversion of the waste cooked oil, as depicted in Fig. 1.

After a single cycle at a rotation velocity of 20% in the microwave flow, a WCO conversion value as high as 84% that of oil is observed. With an increase in the rotation velocity from 20 to 80%, the conversion of oil is reduced from 84 to 42% (Fig. 1). Thus, the rotation velocity of the reactor (%) in the flow system has a profound impact on the conversion of the oil, leading to higher conversion of WCO at a lower speed of rotation of the stirring shaft. With an increase in the speed of rotation, phase separation of the oil and methanol in the feed occurs and the effect is similar to that of centrifugation. This leads to less interaction between the two reactants, namely, the WCO and methanol, thereby reducing the conversion of WCO to the desired product, FAME. The conversion

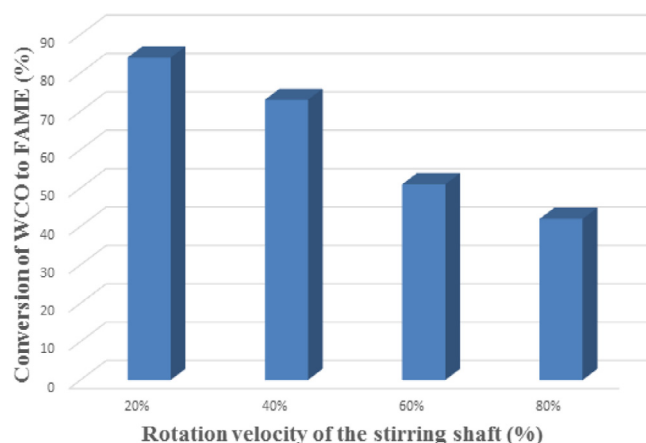


Fig. 1. Conversion of cooked oil to biodiesel as a function of the rotation velocity of the reactor (expressed in%) after a single cycle.

values of WCO at the rotation values of 60 and 80% are 51 and 42 wt%, respectively. To evaluate if cycling the feed once again into the reactor improves the conversion, the product collected at the outlet (as described above) is refed into the flow system. The reaction products obtained in the second cycle at the rotation velocities of 60 and 80% show WCO conversion values of 90 and 78 wt%, respectively. A comparison of the effect of the cycle number on the conversion of WCO is depicted in Fig. S3.

Even at a rotation velocity as high at 80%, 78 wt% conversion of the WCO is observed in the second cycle. The enhancement in biodiesel yield in the second cycle may be due to the presence of FAME formed in the first cycle that facilitates interaction between the unreacted oil and methanol. Moreover, the relative amounts of oil and methanol in the second cycle are lower than in the first cycle, which can result in increased conversion.

3.1.2. Effect of methanol-to-WCO ratio (mol/mol) on biodiesel yield

One of the important variables affecting the ester yield is the molar ratio of alcohol to triglyceride. According to the stoichiometric ratio of the transesterification reaction, 3 mol of alcohol and 1 mol of triglyceride are required to yield 3 mol of fatty acid methyl esters (FAME) and 1 mol of glycerol. However, transesterification is an equilibrium reaction in which increasing the alcohol may accelerate the reaction by shifting the reversible reaction forward. Furthermore, alcohol (especially methanol) absorbs microwave energy very well, so using a greater amount of alcohol results in more energy absorbance and decreasing consumption of microwave energy. This can influence the final temperature of the alcohol, affecting the conversion of triglyceride. In addition, excess alcohol results in better solubility of the biodiesel and glycerol. Because of its significance, this parameter was studied in detail. The effect of the mole ratio of oil to methanol on the conversion of WCO is represented in the histogram in Fig. 2. When the ratio of oil to methanol (mol/mol) was varied between 1:6, 1:7, 1:9 and 1:12, the conversion of waste cooking oil to FAME was found to be 86.5, 95.5, 94.4 and 97.8 wt%, respectively. A systematic increase in the conversion of WCO from 86.5 to 97.8 wt% was achieved with an increase in the oil to methanol ratio from 1:6 to 1:12. Thus, the oil to methanol ratio of 1:12 is the optimum value for the higher conversion (97.8%) of WCO. Increased conversion of WCO to FAME at a higher molar ratio of methanol to oil is due to the increase in the contact area between the alcohol and triglyceride moieties, leading to acceleration in the rate of the transesterification reaction.

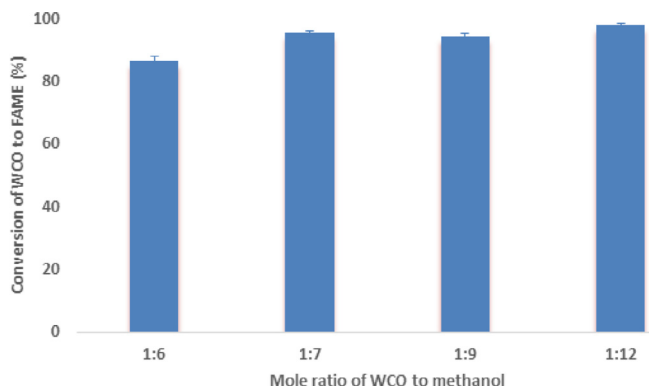


Fig. 2. Effect of mole ratio of WCO to methanol (mol/mol) on the wt% conversion of WCO to FAME with catalyst amount of 1.25 wt%, temperature reaction of 65 °C and 10 min reaction time.

3.1.3. Effect of microwave irradiation (reaction) time on the conversion of WCO to FAME

Since the transesterification reaction is a consecutive and reversible reaction in which di- and monoglycerides are formed as intermediates, yielding one ester molecule in each step, the selection of the proper transesterification time is required to guarantee the completion of the reaction. The reaction time enables adequate interaction between the microwave radiation and the reactants. Moreover, microwave heating over a period of time promotes interaction between the glyceride moieties of oil and methanol, leading to higher yields of FAME. This interaction of microwave radiation with the components of the reaction mixture is also influenced by the homogeneity or heterogeneity of the catalyst. Usually, microwaves have poor ability to penetrate through solid materials. Homogeneous catalysts, however, are completely dissolved in the solvent and the microwave effect is higher in liquid solvents, resulting in higher biodiesel yield. Unlike several other solid heterogeneous catalysts, in the case of SrO, the microwave irradiation has a pronounced accelerating effect on the transesterification reaction (Koberg and Gedanken, 2013). This is one of the reasons for using the SrO and SrO supported on millimetric silica beads as catalysts for the conversion of WCO to biodiesel in the current continuous-flow microwave irradiation process. The effect of the microwave irradiation time on the conversion of WCO to biodiesel is depicted in Fig. 3.

Conversion of WCO into biodiesel as high as 94.5% is achieved by irradiating the reaction mixture (oil:methanol = 1:12 mol/mol) for a short duration of 2 min using the SrO catalyst. The temperature of the reaction is 65 °C and the amount of pristine SrO (6.25 g) is 1.25 wt% relative to the amount of WCO. The power consumed in carrying out the flow process for 2 min is 242 W. The unit power is defined as the integral of energy consumed per time. Prolonging the irradiation time from 2 to 10 min increases the conversion of WCO from 94.5 to 97.8 wt%, after which no further improvement is observed. Thus, the optimal duration of microwave irradiation for the conversion of WCO to biodiesel is 10 min.

3.1.4. Effect of the amount of catalyst on the conversion of WCO to FAME

Koberg et al. reported an amount of 0.276 g of the SrO catalyst as the optimum value for 96 wt% conversion of WCO (15 g) to biodiesel in a batch transesterification process accelerated by microwave irradiation (Koberg et al., 2011). This loading corresponds to 1.84 wt% of the SrO catalyst relative to the amount of oil. Based on this result, in the current continuous-flow biodiesel production process, the optimization studies on the amount of catalyst are carried out by taking SrO amounts closer to 1.84 wt% but lower than the value mentioned above, with the objective of reducing the con-

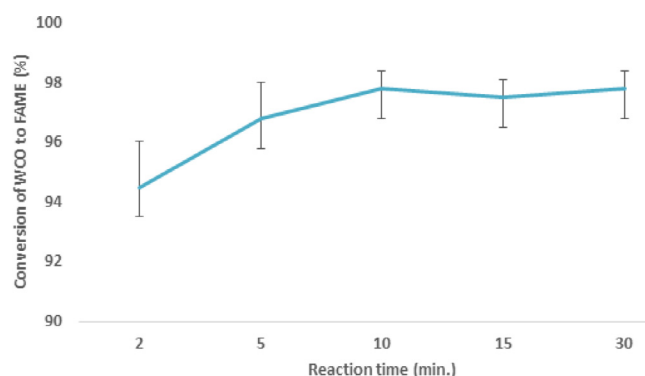


Fig. 3. Effect of microwave irradiation time and power consumption on the conversion of WCO to biodiesel.

sumption of the catalyst. The loading of the catalyst (SrO) relative to the amount of WCO is varied from 1.0 to 1.75 wt% and the conversion value of the WCO is monitored after an irradiation time of 10 min. The variation in the conversion of WCO to biodiesel as a function of the amount of SrO catalyst is depicted in Fig. S4. The reaction temperature is 65 °C and the ratio of WCO to methanol is 1:12 mol/mol. The reaction mixture is fed into the reactor at a flow rate of 200 mL/min. An increase in the catalyst amount from 1.0 (5.0 g) to 1.25 (6.25 g) wt% results in a sharp rise in the WCO conversion value from 90.7 to 97.8 wt%. No further improvement in the conversion value is observed even after increasing the amount of SrO catalyst from 1.5 (7.25 g) to 1.75 (8.75 g) wt%. Thus, 1.25 wt% (6.25 g) of SrO is the optimum value for the efficient conversion of WCO to biodiesel. Moreover, the amount of 1.25 wt% SrO catalyst is relatively lower than that required in a batch process.

3.1.5. Reusability of the catalyst

After completion of the transesterification reaction under optimal reaction conditions using SrO (commercial) as the catalyst, the product is subjected to rotary evaporation to remove and regenerate the unreacted methanol, followed by filtration under vacuum using Whatman (150 MM Φ) filter paper to separate the SrO catalyst from the product biodiesel and the byproduct glycerol.

The catalyst is reused as is without any further activation or regeneration. The SrO catalyst is reused for at least 5 consecutive reaction cycles without appreciable loss in catalytic activity. The conversion value of WCO decreases from 97.3 to only 95.3 wt% when the catalyst is used for five reaction runs. Beyond five repeated uses, significant decrease is observed in catalytic activity from 92.7 to 78.1 wt% for 6–10 cycles (Fig. 4). There are several reports in the literature relating to the use of the continuous-flow microwave irradiation technique for large-scale production of biodiesel from vegetable oil using conventional homogeneous catalysts such as KOH and NaOH (Barnard et al., 2007; Choedkiatsakul et al., 2015; Encinar et al., 2012; Kim et al., 2016; Lertsathapornsuk et al., 2008). The unique advantage of the process reported here is the use of an environmentally friendly, active and selective SrO catalyst that can be easily separated from the reaction product and reused for several reaction cycles (Fig. 4).

Catalyst reusability and soap formation cause problems during the separation of esters from glycerol (Čapek et al., 2014). It is more convenient to use heterogeneous catalysts that facilitate easy separation from the product mixture, improved catalytic performance in terms of activity and selectivity, and reusability for several reaction runs. Generally, the decrease in the activity of the catalyst may

be caused by the deactivation of the active species or by their loss to the liquid phase. It is also possible that the product is strongly attached to the catalyst active sites, blocking its activity when new molecules approach.

3.1.6. Effect of reaction temperature and feed flow rate on the conversion of WCO to FAME

The transesterification reaction of WCO is carried out at different reaction temperatures in the vicinity of the boiling temperature of methanol (74.5 °C). A higher amount of alcohol may lead to mass transfer obstacles during the transesterification process at low temperatures as alcohol is not soluble in triglycerides at methanol to oil molar ratios larger than 3:1. Generally, the speed of the reaction at the initial time is controlled by the diffusion of reagents between the phases. Increasing the alcohol:oil molar ratio decreases the contact between the phases, leading to diffusion problems. These problems are diminished at a higher reaction temperature when alcohol is evaporated and the contact between the phases increases (Encinar et al., 2012). Cravotto et al. (Choedkiatsakul et al., 2015) reported 70 °C as the optimal temperature for the conversion of palm oil to biodiesel in a continuous-flow microwave reaction using NaOH as the catalyst. In the current investigation, as the reaction temperature varies between 60, 65 and 70 °C, the WCO conversion (wt%) values vary between 97.4, 97.8 and 96.6%, respectively. In other words, the temperature does not affect the yield of products in the range 60–70 °C. The effect of feed flow rate (mL/min) on the conversion of WCO is evaluated and depicted in Fig. 5. When the flow rate of the feed is changed from 100 to 200 and 300 mL/min, the observed conversion of WCO becomes 97.3, 97.8 and 97.6 wt%, respectively. The transesterification reaction reaches a steady state after 10 min of microwave irradiation in the flow reactor and, consequently, no appreciable change in conversion of WCO is noticed when the flow rate is varied between 100 and 300 mL/min.

As the optimal reaction time was found to be 10 min (Fig. 3), the optimal flow rate may be in the range of 100–300 mL/min, depending on the type of catalyst. In the fixed-bed microwave reactor, highest biodiesel conversion values could be achieved when the feed (WCO + methanol) stay in contact with the catalyst as longer as possible as well as by minimizing the pressure encountered by the feed in contact with the catalyst. That is the reason that in the fixed-bed microwave reactor packed with a solid-base catalyst comprising of SrO deposited on millimetric silica beads (SrO/SiO₂), a lower flow rate of 100 mL/min is preferred for the smooth running of the transesterification reaction without a drop in pressure.

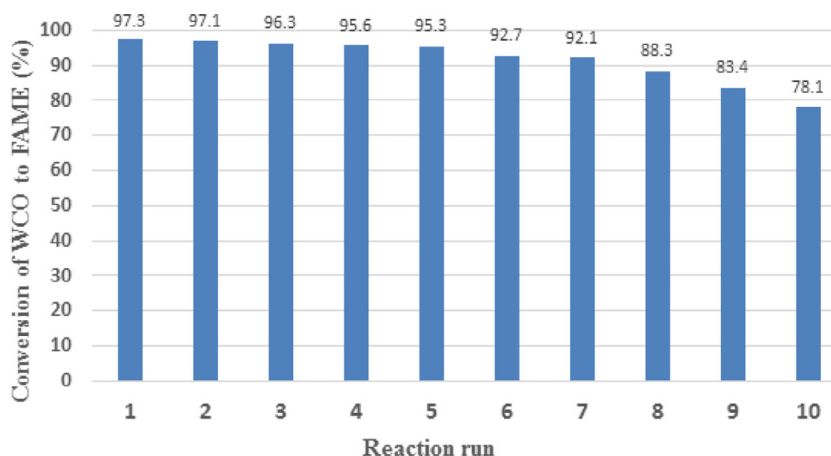


Fig. 4. Effect of reusability of the SrO catalyst on the conversion of WCO in a continuous-flow microwave irradiation system.

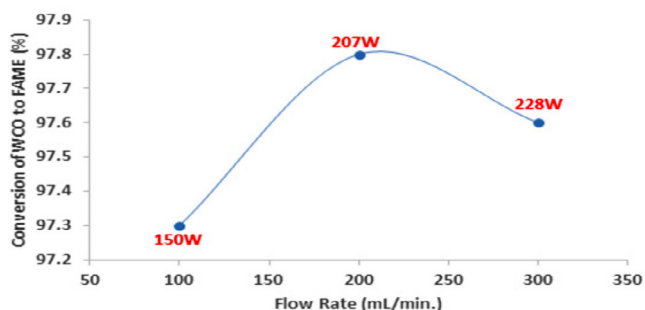


Fig. 5. Effect of flow rate of the feed on the conversion of WCO to biodiesel.

3.1.7. Biodiesel composition

The biodiesel composition is analyzed by the GC–MS method. The typical composition of biodiesel produced from waste cooking oil using the SrO (commercial) catalyst under optimized process parameters in a microwave-flow system is shown in Table S2.

The obtained ratio of saturated, monounsaturated, and polyunsaturated FAMES in biodiesel obtained from WCO is close to that reported in similar studies: 15–20% saturated FAMES, 20–25% monosaturated FAMES, and 40–60% polyunsaturated FAMES (Ramírez-Verduzco et al., 2012).

3.2. Evaluation of the catalytic activity of the SrO/SiO₂ catalyst for continuous-flow biodiesel production from WCO

3.2.1. Studies on the lifetime of the fixed-bed catalyst SrO/SiO₂

Using the optimized process parameters, namely, the velocity of rotation of the stirring shaft (20%), the mole ratio of WCO to methanol (1:12), the reaction temperature (65 °C) and the feed flow rate (100 mL/min), the transesterification reaction of WCO and methanol is carried out using the SrO catalyst deposited on millimetric-sized silica beads (41.3 wt% SrO/SiO₂) (Tangy et al., 2016). The diameter of the silica beads is 3–6 mm. Unlike the commercial SrO catalyst with micrometer particle size, which cannot in itself be used for packing the microwave reactor owing to problems such as hindrance to the feed flow, SrO/SiO₂ (15 g) can be successfully packed into the microwave reactor, and a mixture of oil and methanol (1:12 mol ratio, 820 mL) can be fed through the catalyst bed at a flow rate of 100 mL/min without any flow constraints. The actual amount of active SrO component in 15 g of supported catalyst (SrO/SiO₂) is only 6.195 g. This amount is similar to the optimal amount of commercial SrO catalyst (6.25 g) for the conversion of WCO to biodiesel through the flow reaction (Fig. S4). At this modest amount of catalyst loading, WCO conversion as high as 99.2 wt% is achieved in the first 8 min of flow. A plot of the variation in the conversion of WCO as a function of the reaction run using the SrO catalyst supported on millimetric-sized silica beads is depicted in Fig. 6.

The catalyst can be used for 24.6 min in the fixed bed without appreciable loss in activity. Even after converting nearly 2.46 L of feed (waste cooking oil and methanol mixture) into biodiesel, the activity of the catalyst is retained, as evident from the high conversion value of 93.3 wt% at 25.6 min. Beyond this point there is a steady decrease in the conversion values from 89.5 to 77.6 wt% when the volume of the reactants fed is increased from 3.28 to 4.92 L.

Such loss in the catalytic activity result from the partial dissolution of SrO in FAME and glycerol in the presence of methanol as well as leaching out of the active component from the surface of the SiO₂ support. The amount of SrO in the spent catalyst (SrO/SiO₂) used for 49.2 min. in the continuous flow microwave reacted

was analyzed by ICP analysis and was found to be 24.7 wt% indicating leaching of nearly 16.4 wt%. A non-negligible part of the SrO leaching is due to the friction of the catalyst with the paddle stirrer inside the reactor (Fig. S1). The loss in activity could also be due to structural change (Kaur and Ali, 2014) of the active component from the surface of the SiO₂ support, directly affecting catalyst deactivation characteristics (Dias et al., 2012). The lower accessibility of basic sites at catalyst surface, the loss of active metal precursor as well as the adsorption of other species and blockage of active sites by impurities from reaction medium (mainly by glycerol) are other reasons of activity decrease during reusability of the catalyst (Kaur and Ali, 2014). To prevent the leaching of SrO/SiO₂ during the transesterification reaction, Chen et al. have proposed to decrease the reaction temperature to 45 °C and to add hexane as cosolvent, enhancing the miscibility between vegetable oil and methanol (Chen et al., 2012). Regeneration of the catalyst can also improve its reusability.

Even though the transesterification reaction temperature is only 65 °C, the possibility of coke formation on the catalyst surface from WCO cannot be ruled out because of the formation of hot spots and superheating prevailing during microwave irradiation. Polar materials such as alcohol and triglycerides can absorb microwave irradiation, while non-polar molecules are inert in the microwave electric fields (Koberg and Gedanken, 2013). Selective heating of certain compounds leads to the formation of “hot spots” with a temperature much higher than the overall temperature of the reaction bulk mixture, increasing the acceleration of the chemical reaction rate (Manco et al., 2012). Localized superheating also leads to high temperature gradients. Both hot-spot formation and superheating can occur simultaneously in transesterification (Mazubert et al., 2014). Even though these phenomena can contribute to the acceleration of the biodiesel production process, they may contribute to loss in the catalytic activity over repeated use because of coke deposition.

Even though the catalyst can be used for converting 2.46 L of feed without significant loss in catalytic activity, yielding high values of WCO conversion to biodiesel, the use of SrO/SiO₂ has several advantages that facilitate its industrial adoptability in fixed-bed flow reactors for handling large quantities of feedstock. Typical challenges encountered when using micrometer-sized solid catalysts, such as mass flow constraints, pressure build-up, diffusion constraints and temperature gradients can be surmounted using the current SrO/SiO₂ catalyst, as demonstrated in a fixed-bed flow process for the conversion of waste cooking oil to biodiesel.

As summarized in Table 1, there have been several attempts by various research groups for designing a sustainable continuous flow biodiesel production process. But none of them could reach the state of commercialization yet. Shibasaki-Kitakawa et al., successfully demonstrated continuous flow transesterification of triolein with ethanol in expandable bed reactor using an acidic ion exchange resin as catalyst. A residence time of 60 min. is required for the reaction to reach equilibrium state resulting in equilibrium conversion values in the range of 1–1.2. The equilibrium conversion values above 1 were attributed to the reaction of impurities in the crude triolein (di and monoglycerides bonded linoleic acid group as well as oleic acid group with ethanol forming fatty acid esters). The continuous flow process driven by conventional heating source (thermal bath) on the resin bed catalyst was demonstrated for 120 min. without loss in activity of the catalyst. But details of the total volume of the feed flown or biodiesel obtained in the 2 h continuous flow process are not provided (Shibasaki-Kitakawa et al., 2007). The authors have further extended this methodology for the direct conversion of crude rice bran oil (with high content, 14 wt% of FFA and alcohol) to biodiesel (98.6 wt% conv.) using a cation exchange resin as a catalyst. Moreover, no extra operations like, dewaxing, byproduct removal and alcohol

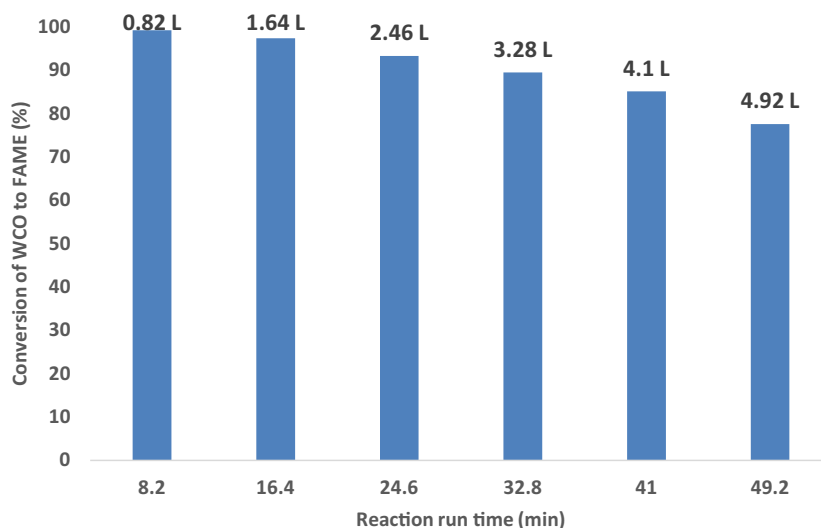


Fig. 6. Demonstration of the reusability of 41 wt% SrO/SiO₂ catalyst for the conversion of WCO to biodiesel (Reaction conditions: Flow rate of the feed: 100 mL/min; Reaction temperature – 65 °C; mole ratio of oil to methanol = 1:12; amount of catalyst – 15 g).

addition were done reducing the number of process steps in biodiesel production (Shibasaki-Kitakawa et al., 2010). Further, Shibasaki-Kitakawa et al., have designed a bench-scale continuous flow expandable reactor for the simultaneous production of biodiesel and glycerin using cation and anion exchange catalysts from *Jatropha* oil as feedstock (Shibasaki-Kitakawa et al., 2013).

The successful demonstration of the use of the heterogeneous-base catalyst SrO/SiO₂ in a fixed-bed microwave reactor is a significant step towards large-scale demand-based biodiesel production from waste cooking oil in an environmentally benign way, completely replacing the use of the homogeneous-base catalysts. This is an advancement compared to the state-of-the-art microwave-based flow process reported in the literature (Table 1), and it is also environmentally friendly compared to the flow process reported by Cravotto, which is based on the use of the NaOH catalyst (Choedkiatsakul et al., 2015). There is still scope for further improvement of the functionality of the SrO/SiO₂ catalyst, like in-situ conversion of the FFA to respective esters as proposed by Shibasaki-Kitakawa et al. (2015, 2007) to simultaneously utilize the impurities of the crude as well for biodiesel production.

3.3. Energy consumption in the biodiesel production process

In the current continuous-flow microwave-irradiation process, using SrO as a heterogeneous catalyst under optimal reaction conditions, the energy consumption was found to be 0.1132 kW h/L (liter of biodiesel). The microwave energy consumption was calculated from the time integral of the absorbed microwave power. It is assumed that most of the microwave energy is used for heating the reactor until it reaches the optimal temperature (Kim et al., 2011). The microwave power for maintaining the temperature was averaged over the absorbed microwave power during the reaction. The calculated energy consumption value is similar to the value reported by Cravotto et al. (0.1167 kW h/L) (Choedkiatsakul et al., 2015). This energy is about half of that consumed in typical biodiesel production using conventional heating (0.222 kW h/L). When microwave heating is applied, the heat is generated from inside the material. Thus, the sample is directly heated, resulting in much greater efficiency compared to conventional heating. Patil et al. (2010) have shown that the energy required for the conventional method is about 23 times greater than that required for microwave heating. This clearly points out the higher heat transfer efficiency

that MW heating provides over conventional heating, leading to reduction in energy consumption. Energy consumption profile for the biodiesel production process is provided in Fig. S5.

4. Conclusion

Waste cooking oil (WCO) is a sustainable and preferred feedstock relative to vegetable oils or lipid rich micro-algae or non-edible terrestrial biomass for biodiesel production. The suitability of SrO/SiO₂ as the fixed-bed catalyst in a continuous-flow microwave reactor for the conversion of WCO to biodiesel is demonstrated. At a modest loading of 41 wt% SrO on millimetric silica beads, the catalyst exhibited a lifetime of 24.6 min with sustainable activity converting 2.46 L of feed to biodiesel. The novel solid base catalyst developed (SrO/SiO₂) could be a substitute to either conventional homogeneous (NaOH and KOH) or the commercial SrO catalyst. However, efforts should be made to improve the process efficiency by increasing the life time of the catalyst (preventing SrO leaching) and also effectively utilizing the FFA component of the feed for biodiesel production.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2016.10.068>.

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