



Green chemistry with process intensification for sustainable biodiesel production

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Received: 1 August 2017 / Accepted: 11 November 2017 / Published online: 22 November 2017
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Abstract

Biodiesel as a renewable fuel has the potential to replace non-renewable fossil fuels and associated environmental pollution. The most commonly used method in biodiesel production is transesterification of virgin and used oil feedstock. However, the chemical reaction (transesterification) does not proceed spontaneously, which means excess reactants are required to move the reaction to completion. The biodiesel reaction efficiency can be improved by incorporating green chemistry principles and process intensification effects. Green chemistry principles can be used to design chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Microwave- and ultrasound-enhanced biodiesel synthesis can improve the reaction efficiency due to higher product recovery, low by-product formation, and reduced energy consumption. In addition, utilization of green metrics such as E-factor, atom economy (utilization), mass intensity or mass productivity, and reaction mass efficiency can help design safer and highly efficient biodiesel synthesis. Green chemistry principles have been analyzed for other processes in greater details, but they are rarely discussed in the context of biodiesel production. Process intensification by microwave- and ultrasound-mediated biodiesel production was never discussed from the perspective of green chemistry and sustainable process development. This research review article discusses the role of green chemistry and process intensification in biodiesel production followed by specific examples and illustrations on green metrics of microwave- and ultrasound-enhanced biodiesel synthesis and the effect of catalysts and solvents including discussions on reaction kinetics and activation energy in detail for the first time in the literature.

Keywords Green chemistry · Biodiesel · Microwaves · Ultrasound · Atom economy · E-factor · Process intensification

Green chemistry

Green chemistry is a chemical approach founded on environmental consciousness when accomplishing the science already being performed regardless of the scientific discipline or the applied techniques (Tucker 2006). Green chemistry is a concept driven by efficiency coupled with environmental responsibility. It offers a protocol when developing chemical processes and plays a major role in the production of most essential chemicals, reduction of energy demands, creation of safer processes, and avoidance of hazardous chemical use and production (Cherubini 2010).

Anastas and Warner (1998) introduced twelve green chemistry principles for safe and environmentally responsible chemistry. The principles are listed as: (1) prevention; (2) atom economy; (3) less hazardous chemical synthesis; (4) designing safer chemicals; (5) safer solvents and auxiliaries; (6) design for efficiency; (7) use of renewable feedstock; (8) reductive derivatives; (9) catalysis; (10) design for degradation; (11) real-time analysis for pollution prevention; and (12) inherently safer chemistry for accident prevention. These principles can be implemented in any process that involves a chemical transformation of one compound to another compound. Green chemistry is highly pronounced in industries such as pharmaceuticals, petrochemicals, food, and other chemistry-based industrial processes (Beach et al. 2009; Lancaster 2016). However, considering the present energy and environmental crises worldwide, green synthesis of renewable fuels such as biodiesel and bioethanol has become a major environmental priority. Efficient synthesis of renewable fuels remains a challenging and important area

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of research. Embracing the principles of green chemistry might result in a sustainable route for renewable fuel production. Green chemistry provides unique opportunities for innovation via product substitution, new feedstock generation, catalysis in aqueous media, utilization of microwaves and ultrasound, waste minimization, and scope for alternative or natural solvents (Loupy et al. 2001; Moseley and Kappe 2011; Martinez-Guerra et al. 2014a, b; Martinez-Guerra and Gude 2014a, b, c). The potential of utilizing waste as a new resource and the development of integrated processes producing multiple products from biomass are highly desirable to improve the economics of the renewable fuels (Gude et al. 2013a).

Green chemistry principles have been analyzed for other processes in greater details (Sheldon 2008) including ethanol production, but they are rarely discussed in the context of biodiesel production. Process intensification by microwave- and ultrasound-mediated biodiesel production was never discussed from the perspective of green chemistry and sustainable process development. Therefore, in this research review article, first the role of green chemistry and process intensification in biodiesel production will be discussed, followed by specific examples and illustrations on the green metrics of microwave- and ultrasound-enhanced biodiesel synthesis and the effect of catalysts and solvents including discussions on reaction kinetics and activation energy.

Basics of biodiesel production

There are several methods to obtain biodiesel from various feedstocks which include direct use, blending with petro-fuels, microemulsions, thermal cracking (pyrolysis), and transesterification (Ma and Hanna 1999; Gude et al. 2013b). The most commonly used method for biodiesel production is by transesterification of oil using an alcohol. Transesterification is defined as a process where esters of saturated and unsaturated carboxylic acid (also known as triglyceride) react with alcohol in the presence of catalyst to produce mixtures of fatty acid esters as the main product

and glycerol as by-product (Leung et al. 2010) as shown in Scheme 1 (Marchetti et al. 2007). The reaction is considered as a replacement of one ester group with an alkyl group. The overall process is normally a sequence of three consecutive steps, which are reversible reactions. In the first step, from triglycerides diglyceride is obtained, from diglyceride, monoglyceride is produced, and in the last step, from monoglycerides, glycerol is obtained. In all these reactions, esters are produced. The stoichiometric relation between alcohol and the oil is 3:1. However, excess alcohol is usually more appropriate to drive the reaction toward the desired product formation. This process is mainly carried out to reduce the viscosity of the feedstock, which can sometimes have high viscosity and not suitable for direct use in diesel engine. Transesterification process can be influenced by various parameters, including free fatty acids and water content, molar ratio of alcohol to oil, catalyst type and loading, reaction temperature, and stirring rate (Sharma and Singh 2009).

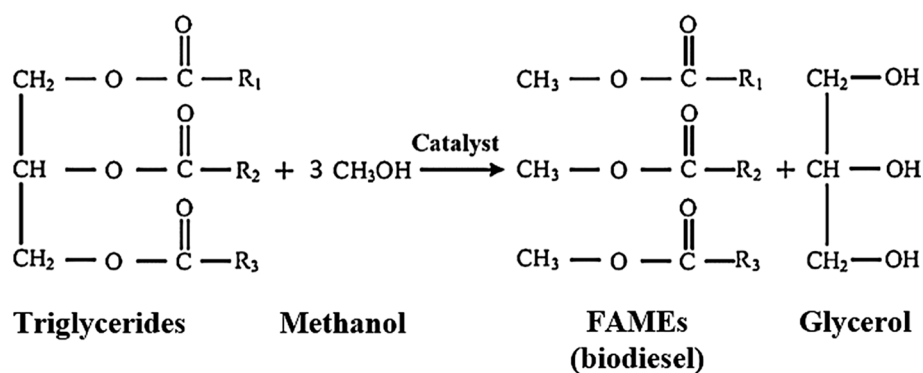
Process intensification

Biodiesel production via transesterification reaction can be performed under conventional heating methods, which usually employ heated plates (laboratory scale), oil, or sand baths, and water heated jacketed reactors combined with mechanical mixing. This process usually takes longer times to complete the reaction. Novel heating techniques like microwaves and ultrasound are known to drastically reduce the reaction time while improving the biodiesel yields simultaneously through an effect called “process intensification.”

Use of microwave irradiation

The use of microwave irradiation in organic synthesis has become increasingly popular among all the chemistry-based industries. Thermally driven chemical transformations were promoted by two methods: either conventional heating or microwave-accelerated heating (Hayes 2004). In the first

Scheme 1 Basic transesterification reaction converting triglycerides (oil) into fatty acid alkyl esters (biodiesel) with methanol as an example



method, reactants are slowly activated by a conventional external heat source. Heat is driven into the substance, passing first through the walls of the vessel in order to reach the solvent and reactants. This is a slow and inefficient method for transferring energy into the reaction system. In the second method, microwaves couple directly with the molecules of the entire reaction mixture, leading to a rapid rise in temperature. Since the process is not limited by the thermal conductivity of the vessel, the result is an instantaneous localized superheating of any substance that will respond to either dipole rotation or ionic conduction—the two fundamental mechanisms for transferring energy from microwaves to the substance(s) being heated.

Microwave irradiation is the electromagnetic irradiation having a frequency between 0.3 and 300 GHz with wavelengths between 0.01 and 1 m. Commercial microwave ovens approved for domestic applications operate at a frequency of 2.45 GHz, and most of the reported microwave chemistry experiments were conducted at this frequency (the corresponding wavelength is 12.24 cm) (Lidstrom et al. 2001). The highest absorption of microwave energy by the reaction materials (e.g., water) is reported at this frequency. Microwaves produce dielectric heating in substances that possess dipole momentum and ionic polarization (Stuerga and Delmotte 2002; Mingos 2004; Gabriel et al. 1998; Baghurst and Mingos 1991). There are several mechanisms which are responsible for this, including ionic conduction, molecular (dipole), and interfacial (space charge) polarization, which is a combination of ionic conduction and dipole momentum (Taylor et al. 2005). The energy associated with microwaves itself is very low which does not have the capability to break the chemical bonding, but it produces certain thermal and non-thermal effects induced by above-mentioned mechanisms (Metaxas and Meredith 1993; Peterson 1994; Chemat-Djenni et al. 2007).

Microwaves, as an energy source, produce heat by their interaction with the materials at molecular level without altering the molecular structure (Varma 2001; Refaat 2010).

Microwave heating offers several advantages over conventional heating such as non-contact heating (reduction in overheating of material surfaces), energy transfer instead of heat transfer (penetrative radiation), reduced thermal gradients, material selective and volumetric heating, fast start-up and stopping and reverse thermal effect, i.e., heat starts from the interior of reaction mixture. Relevant benefits in biodiesel production could include more effective heating, fast heating of catalysts, reduced equipment size, faster response to process heating control, faster start-up, increased production, and elimination of trivial process steps (Chemat-Djenni et al. 2007).

Use of ultrasound irradiation

Ultrasound activation is entirely different from the microwave mechanism. Ultrasound induces cavitations that produce microbubbles to increase the mass transfer rates and generate heat at microscopic levels due to continuous rarefaction and compression cycles of acoustic waves (Suslick 1990; Kasaaï 2013; Parkar et al. 2012a, b). Ultrasonic irradiation is unique from other conventional energy sources in exposure, pressure, and energy per molecule and the duration. The immense local temperatures and pressures, and the extraordinary heating and cooling rates generated by collapse of cavitation bubbles provide an unusual mechanism for generating high-energy chemistry. In ultrasound activation, very large amounts of energy are introduced in a short period of time leading to high temperatures, but the duration is very short (by $> 10^4$) and the temperatures are even higher (by fivefold to tenfold) when compared to pyrolysis (Suslick and Crum 1997; Gude and Grant 2013).

Comparison of process intensification

A comparison of the different heating methods is provided in Table 1. For biodiesel reactions, the notable differences would be reaction times, solvent requirements, yields,

Table 1 Comparison between conventional, microwave, and ultrasonic heating methods for biodiesel production

Conventional heating	Microwave heating	Ultrasonic heating
Thermal gradient (outside to inside) Conduction and convection currents	Inverse thermal gradient (inside to outside) Molecular-level hot spots	Limited thermal gradient due to mixing Microbubble formation and collapse (compression and rarefaction cycles)
Longer processing times	Very short and instant heating	Relatively very short reaction times, not as quick as microwaves
No or low solvent savings	No or low solvent reactions possible	Solvent savings possible
Product quality and quantity can be affected	Higher product quality and quantity possible	Same as conventional heating
Separation times are long	Very short separation times	Less than conventional heating
High energy consumption	Moderate to low energy consumption	Moderate to low energy consumption
Simple process configuration	Very simple process	Moderate complexity

separation times, and specific energy consumption. Shorter reaction times result in significant energy savings, which are attributed to the special effects of microwaves and ultrasound. A comparison of laboratory-scale biodiesel production metrics is shown in Fig. 1. Transesterification of waste cooking oil was performed using conventional (laboratory hot plate), microwave, and ultrasound methods. The conventional heating method takes the longest reaction time (105 min). Microwaves reduce the reaction time significantly to as low as 6 min. The reasons for enhanced reaction rates for non-conventional heating are compared with conventional heating in Table 1 (Gude et al. 2012). When direct sonication was applied, the reaction temperature could increase without any external heat addition similar to microwave conditions. Reaction mixture temperatures as high as 85 °C were recorded under 2 min of reaction time. This depends on the catalyst ratio and reaction mixture volume (Gude and Grant 2013).

In the above experiments, the biodiesel yield and energy requirements were calculated according to the following equations:

$$\text{Biodiesel Yield (\%)} = \frac{\text{Biodiesel Produced (g)}}{\text{Waste cooking oil (g)}} \times 100 \quad (1)$$

$$\text{Energy Required (kJ)} = \text{Power supplied (W)} \times \text{reaction time (t)} \quad (2)$$

As shown in Fig. 1, increased reaction times result in increased energy expenditures. Conventional heating on a laboratory hot plate requires about 3150 kJ of energy, while microwave and ultrasonic processes required 288 and 60 kJ of energy. This shows that non-conventional heating and mixing (process intensification) techniques have the potential to reduce the process energy requirements significantly. Another important benefit with microwave process is that it provides high-quality biodiesel product compared to other two methods of biodiesel conversion. Conventional and ultrasonic-based transesterification involves intense mixing of reaction mixture, thus resulting in increased separation times and reduced product yield and quality (Patil et al. 2010; Gude et al. 2011).

Synergistic effect of process intensification (microwave and ultrasound)

Microwaves deliver an effect generated by the electromagnetic interaction with reaction materials often resulting in thermal enhancement that produces superior results in chemical synthesis (England 2003). Ultrasound effects are the acoustic cavitations generated by interaction of the sound waves with the reaction compounds resulting in intense mixing to increase the mass and heat transfer among the reaction mixtures leading to higher process efficiency (Gude and Grant 2013; Luo 2014). For example, process intensification by ultrasound can promote mass transfer among gas and liquid components by up to fivefold, while the liquid–solid mass transfer can be increased by 20–25-fold and increase product yields significantly (Fig. 2). The reaction times can be drastically reduced by microwave heating by up to 1250 times due to rapid heat enhancement (Stankiewicz 2006). These two irradiations can also improve the energy and material efficiencies due to higher product conversion and yields. Although microwaves provide for rapid heating of the reaction materials, mass transfer of the reaction medium is often compromised in these reactors (Martinez-Guerra and Gude 2014a). In addition, they interact with reaction materials at a higher rate which may cause hot spot formation and thermal runaway. This phenomenon clearly indicates the necessity for a mixing mechanism which can ensure uniform heating of reaction materials and mass transfer promoted by the unusual heating advantage of the microwaves. In a similar context, ultrasound is capable of promoting heat and mass transfer within the reaction medium due to the intense mixing as a result

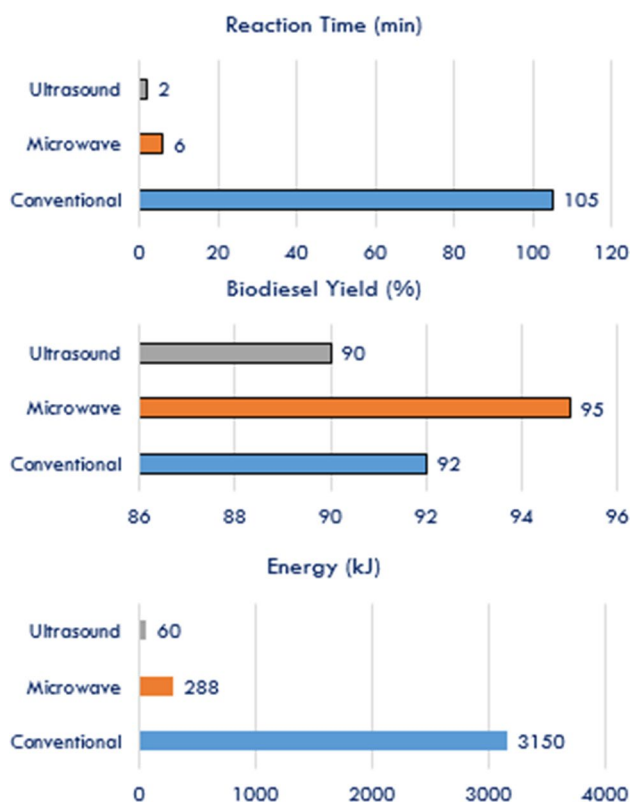
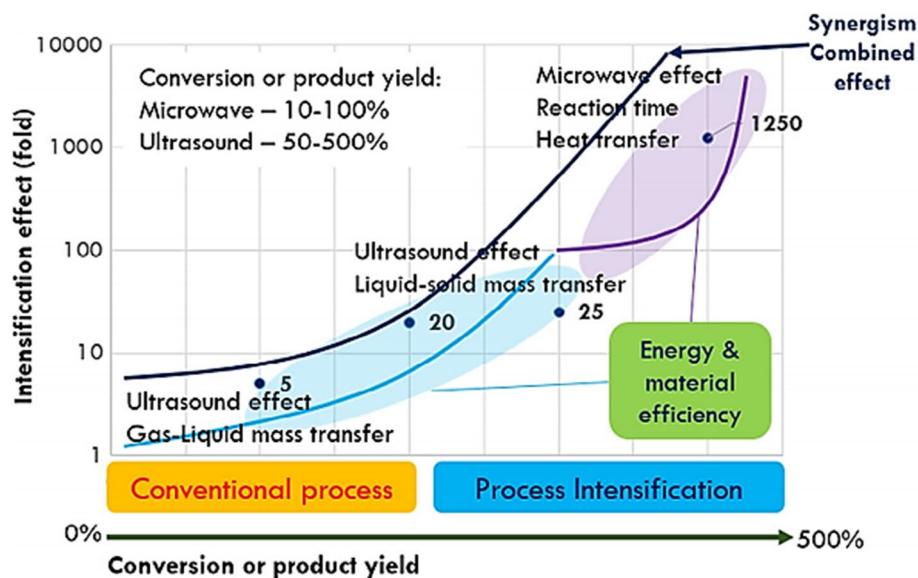


Fig. 1 Comparison of waste cooking oil conversion by conventional/non-conventional methods (note: conventional heating was conducted by using a hot plate at 500 W power, microwave irradiation was applied at 800 W, while ultrasound irradiation was applied at 500 W. Other conditions: 10 mL waste cooking oil, 9:1 methanol-to-oil ratio and 1% NaOH catalyst; (Gude et al. 2013a)

Fig. 2 Process intensification effects by MWs (electromagnetic field) and US (cavitation field): energy and material efficiency are the potential sustainability effects (Gude 2015)



of the acoustic cavitations. The formation–release–collapse of these microbubbles provides cooling and heating cycles at microscales accompanied by high thermal and pressure release. Since this energy release is at microlevels, this energy is not adequate to cause high temperature gains in the reaction medium which depends on the time of exposure, reactor volume/design, and the type of reaction. This clearly presents a limitation for US-mediated reactions (Martinez-Guerra and Gude 2014a). These reactions require external heating to enhance the process kinetics. Considering the aforementioned prospects and limitations for the individual process intensification mechanisms, it is convenient to design a hybrid system that incorporates both non-conventional heating and mixing effects that may provide enhanced process outcomes. This is considered a greener chemistry approach since efficient use of chemicals, energy, and materials can be anticipated (Cravotto and Cintas 2007). Superior benefits gained through the integrated process intensification effects might prove to be economical at large-scale applications. It is important to note that this hybrid technology will prove to be ideal for production of high-value bioproducts combined with biofuels at present.

Green chemistry metrics for biodiesel synthesis

Sustainable chemical process development should consider minimizing the negative environmental impacts of the chemical and industrial processes by adopting green chemistry performance metrics (Gude 2017). The chemical processes should be optimized to produce less waste and consume less energy sources. The following green metrics are useful when measuring or evaluating how “green” a chemical process is (Constable et al. 2002).

- E-factor (the environmental factor)
- Atom economy (utilization) or atomic efficiency
- Mass intensity and mass productivity
- Reaction mass efficiency

Other important factors that could be considered and not addressed by these metrics are energy concerns (process—internal and external); utilization of renewable feedstock (starting raw materials); reaction types; catalysts versus stoichiometric reagents; safety; life cycle analysis; and the environmental quotient. Here, a few illustrations are provided to understand how some of these metrics can be applied in sustainable biodiesel production.

E-factor

E-factor was proposed by Roger Sheldon (1997, 2010), which considers the amount of total waste generated by a process. It is expressed as:

$$\text{E-factor} = \frac{\text{Total waste (kg)}}{\text{kg product}} \quad (3)$$

The E-factor represents the actual amount of waste produced in the process, defined as everything but the desired product (Sheldon 2010). It takes the chemical yield into account and includes reagents, solvent losses, process aids, and fuel (energy input). Water is generally excluded from the E-factor as the inclusion of all process water could lead to exceptionally high E-factors in many cases and make meaningful comparisons of processes difficult. A higher E-factor means more waste and, consequently, a larger environmental footprint. The ideal E-factor is zero. In simple terms, it is the total mass of raw materials minus the total mass of product,

all divided by the total mass of product. For example, the oil refining process has an E-factor of less than 0.1, compared to fine chemical industry (E-factor between 5 and 50) and the pharmaceutical processes with E-factors between 25 and 100. These numbers suggest that the pharmaceutical chemical processes have the largest scope to implement green chemistry principles to reduce the waste generation (Sheldon 1997; Roger and Sheldon 2000).

For biodiesel production, the E-factor could be very small meaning that the process is environmentally friendly. For a typical transesterification reaction producing biodiesel from virgin oil, the following simple calculations can be made. Biodiesel production essentially requires feedstock such as virgin oils, an alcohol as a reactant, and a catalyst. The conversion efficiency of > 90% is commonly reported (Grant and Gude 2013). The E-factor for biodiesel reaction can be written as follows:

$$\text{Biodiesel E-factor} = \frac{\text{Glycerol (kg)} + \text{Unconverted oil} + \text{Excess methanol}}{\text{kg (Biodiesel)}} \quad (4)$$

In few cases, glycerol is considered as a useful product; therefore excluding glycerol, the E-factor can be expressed as:

$$\text{Biodiesel E-factor} = \frac{\text{Unconverted oil} + \text{Excess methanol}}{\text{kg (Biodiesel)}} \quad (5)$$

For example, in theory, at 100% conversion following stoichiometric ratios, for every 100 lb of oil reacting with 10 lb of alcohol, 100 lb of biodiesel (fatty acid alkyl esters, FAAEs) and 10 lb of glycerol can be produced. The E-factors following the above two equations would then be:

$$\text{Biodiesel E-factor} = \frac{10 \text{ (kg)} + 0 + 0}{100 \text{ kg (Biodiesel)}} = 0.1$$

$$\text{Biodiesel E-factor} = \frac{0 + 0}{110 \text{ kg (Biodiesel)}} = 0$$

Since the reactions do not proceed at chemical or thermodynamic equilibrium conditions, excess reactants are required to promote the reactions to completion. The

following data are obtained from our laboratory studies, for transesterification reaction of vegetable oil at different ethanol-to-oil ratios under microwave irradiation (Table 2). The first three columns represent the reactants (feedstock + alcohol + catalyst), and the next three columns show the products obtained for a microwave-mediated reaction for two minutes. Unreacted reactants are those that were lost during washing and drying processes. For example, the excess ethanol used in this reaction is lost through evaporation and the catalyst through water washing.

When glycerol was considered a useful product, the E-factors for the above experiments were between 0.16 and 0.72 for different alcohol ratios as shown in Fig. 3. When it is considered waste, the E-factors were between 0.52 and 1.1. The optimum ratio of ethanol is very important to reduce the solvent losses and waste generated. The E-factor can vary with size of the production process; smaller systems may

have higher values and vice versa. Water is required to grow the crops and clean the biodiesel produced through homogeneously catalyzed reactions. If water consumption in the entire life cycle process were to be considered, the E-factor

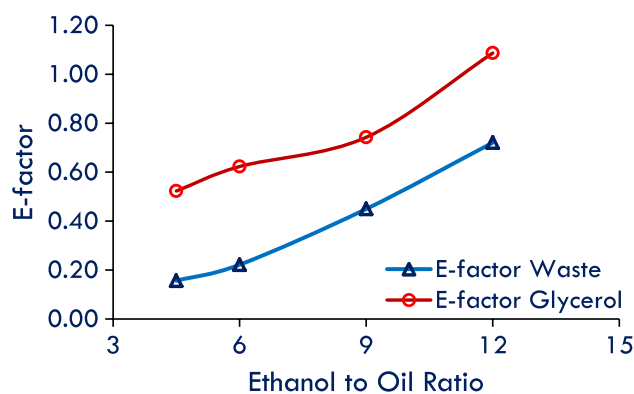


Fig. 3 Effect of reactant ratio on the E-factor of the transesterification reaction of waste cooking oil (reaction conditions are summarized in Table 3)

Table 2 Reactant and product data for E-factor calculations

Reactants			Products		
Oil (g)	Ethanol (g)	Catalyst (g)	Biodiesel (g)	Glycerol (g)	Unreacted reactants (g)
20	6.3	0.18	16.5	5.2	3.4
20	8.4	0.18	16.5	5.4	4.9
20	12.5	0.18	17.3	3.5	9.3
20	16.7	0.18	16.0	3.4	14.0

of the biodiesel production can be enormous. However, similar to all other processes, the E-factor considering the raw materials employed in the actual transesterification reaction would seem to provide a benchmark to compare different industrial processes. Biodiesel washing process requires 0.5:1 ratio of water to biodiesel to remove the unreacted methanol and catalyst. Since water is not used as reactant in the original transesterification reaction, this can be avoided. E-factor should also consider the amount of energy input required (energy footprint) in the process. Energy production involves significant use of resources including water. This can have significant environmental impact on the overall sustainability.

Atom economy

Conventionally, attaining the highest yield and product selectivity were the governing factors of chemical synthesis (Li et al. 2008). However, knowledge of the stoichiometric relationship allows to predict the theoretical minimum amount of waste that can be expected. This can be done theoretically prior to experimental studies. Atom economy or utilization concept provides a quick assessment of environmental friendliness of alternative processes to produce a particular product (Sheldon 1992; Trost 1991, 1995).

Atom economy is a measure of the proportion of reactant atoms which are incorporated into the desired product of a chemical reaction. Calculation of atom economy therefore also gives an indication of the proportion of reactant atoms forming waste products. Atom economy is defined as the ratio of molecular mass of the desired products divided by the molecular masses of the reactants. For example, the atom economy for the following reaction can be expressed as:



$$\text{Atom Economy} = \frac{\text{Molecular weight of (C + D)}}{\text{Molecular weight of (A + B)}} \quad (7)$$

For transesterification reaction, it can be expressed as:

$$\text{Atom Economy} = \frac{\text{Molecular weight of Biodiesel (FAMES)}}{\text{Molecular weight of (oil + alcohol)}} \quad (8)$$

In a case where glycerol is considered a useful product, the atom economy is defined as:

$$\text{Atom Economy} = \frac{\text{Molecular weight of Biodiesel and Glycerol}}{\text{Molecular weight of oil and alcohol}} \quad (9)$$

The atom economy of a reaction depends on the reagents used and the type of chemical reaction involved. Most chemical reactions can be classified as rearrangement (migration of an alkyl group), addition, substitution (e.g., chlorination of methane), or elimination (e.g., dehydration).

Rearrangement and addition reactions are atom economical by their very nature, since they simply involve reactant atoms being repositioned within the same molecule or incorporated within a second molecule. Substitution reactions, however, involve replacement of one group with another and therefore have intrinsically poor atom economy. Elimination reactions are also inherently atom uneconomical since eliminated atoms are always lost as waste. In developing an atom economical reaction pathway, therefore, the industrial chemist may well prefer rearrangement and addition reactions over less environmentally friendly substitution and elimination reactions. Since atom economy provides indicative and theoretical utilization of reactants, the real atom efficiency can be calculated using the following expression:

$$\text{Atom Efficiency} = \text{atom economy} \times \text{yield} \quad (10)$$

The atom efficiency of the transesterification reaction was calculated using the data from Table 2. The actual yield of the reaction varied between 89 and 96%, while the atom economy reduced with increasing use of reactants (from 88 to 83%), in this case alcohol (Fig. 4). The atom efficiency was calculated using the actual yield and atom economy, which represents actual efficiency of the transesterification reaction, which varied between 73.7 and 81.2%.

Mass intensity

Another important metric discussed in these reactions is mass intensity. Mass intensity is expressed as follows (Cuzzons et al. 2001):

$$\text{Mass Intensity} = \frac{\text{Total mass used in a process (kg)}}{\text{Mass of product}} \quad (11)$$

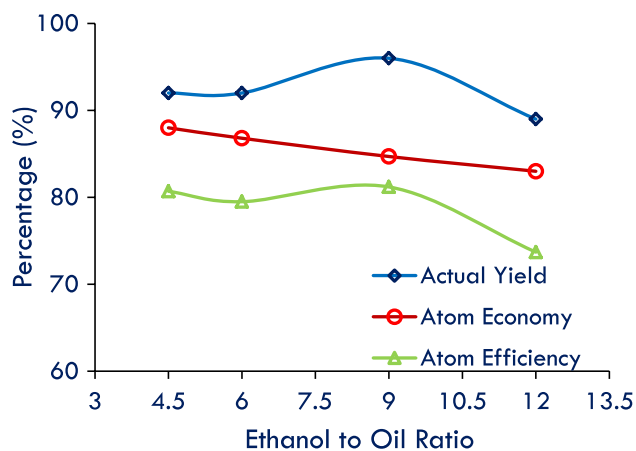


Fig. 4 Effect of reactant ratio on atom economy and atom efficiency of the transesterification reaction of waste cooking oil (reaction conditions are summarized in Table 2)

Mass intensity (MI) takes into account the yield, stoichiometry, the solvent, and the reagent used in the reaction mixture and expresses this on a weight/weight basis rather than a percentage. In the ideal situation, MI would approach 1. Total mass includes everything that is used in a process or process step with the exception of water, i.e., reactants, reagents, solvents, catalysts, etc. Total mass also includes all mass used in acid, base, salt and organic solvent washes, and organic solvents used for extractions. Similar to E-factor, water is excluded from mass calculations since it skews mass data in many processes.

It may also be useful to compare MI with E-factor where:

$$\text{E-Factor} = \text{MI} - 1 \quad (12)$$

By expressing mass intensity as its reciprocal and making it a percentage, it is in a form similar to effective mass yield and atom economy. This metric can be called mass productivity.

$$\begin{aligned} \text{Mass Productivity} &= \frac{1}{\text{MI}} \times 100 \\ &= \frac{\text{Mass of product}}{\text{Total mass in process}} \times 100 \end{aligned} \quad (13)$$

The results for MI and MP using different solvents (methanol or ethanol) are shown in Figs. 5 and 6, respectively (Martinez-Guerra 2016) for various reaction conditions. The process mass intensity is much higher when using ethanol,

which means that the total mass used in the process is not recovered, and the mass of the final product is low. Despite the fact, the results revealed that the ideal MI (1 kg/kg) was almost achieved by methanol; the MI when using ethanol was also close to unity. Therefore, both of these alcohols are green solutions or solvents to produce biodiesel being methanol better than ethanol. It should be noted that with higher alcohol ratios, the mass productivity decreases for ethanol which mainly depends on the experimental yields achieved in this study.

Reaction mass efficiency

When calculating reaction mass efficiency, atom economy (AE), yield, and the stoichiometry of reactants are included. RME is the percentage of the mass of the reactants that remain in the product.

For a generic reaction, $A + B \rightarrow C + D$, RME is expressed as:

$$\text{Reaction Mass Efficiency} = \frac{\text{mass of product (C + D)}}{\text{mass of (A + B)}} \times 100 \quad (14)$$

As shown in Fig. 7, the reaction mass efficiency percentages were higher for methanol as a reactant or solvent. These can be calculated based on E-factor which is solely based on the amount of waste produced. Therefore, more than one alternative is available to calculate RME. Transesterification

Fig. 5 Mass intensity results for simultaneous effect of MW/US in WCO transesterification for different reaction times, alcohol-to-oil molar ratios, catalyst concentrations, and oil volumes

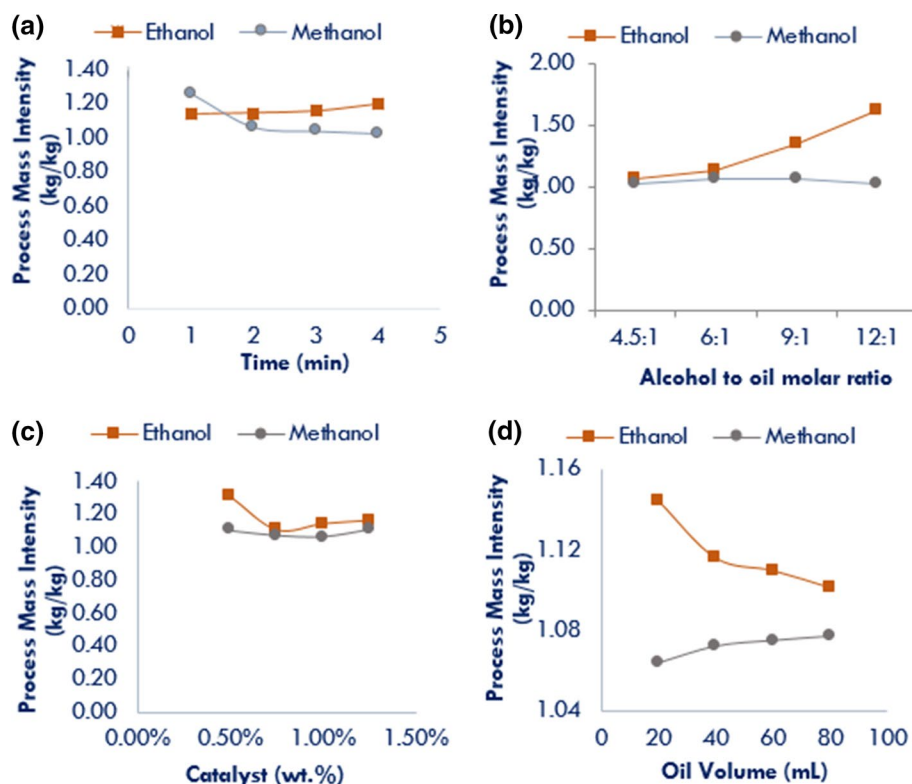


Fig. 6 Mass productivity for simultaneous effect of MW/US in WCO transesterification for different reaction times, alcohol-to-oil molar ratios, catalyst concentrations, and oil volumes

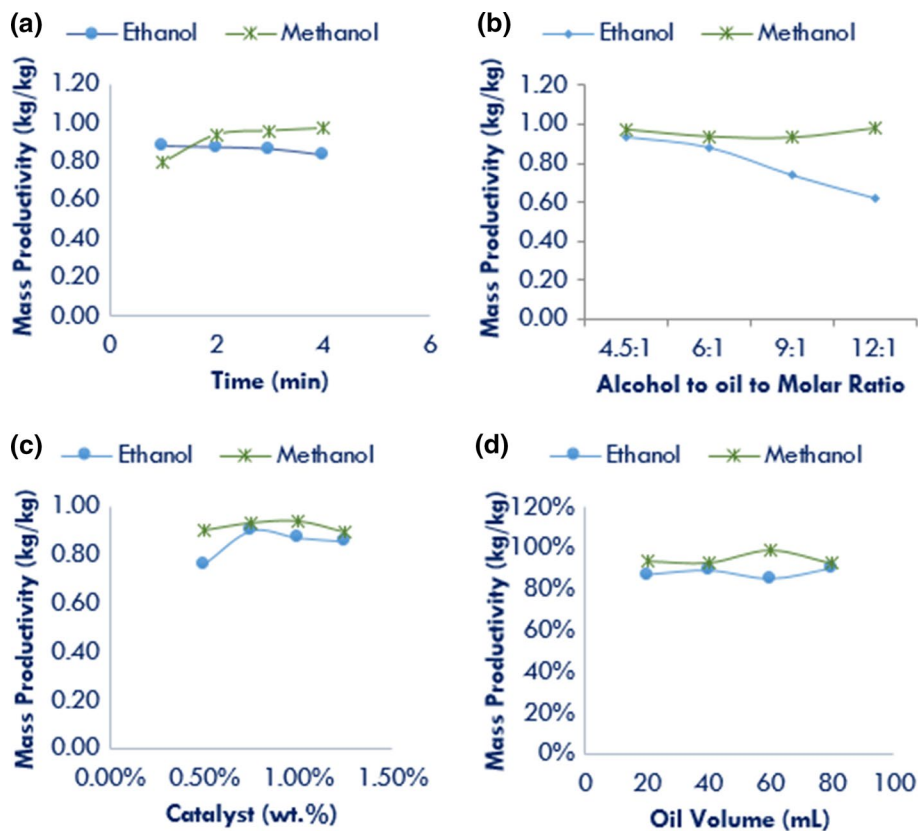
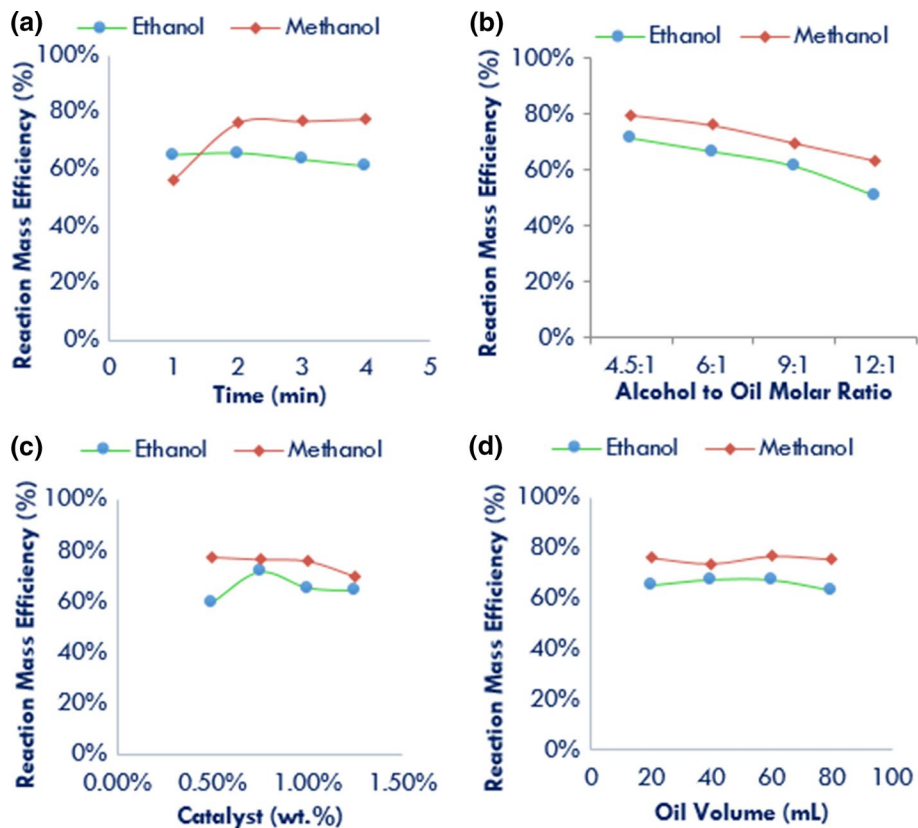


Fig. 7 Reaction mass efficiency for simultaneous effect of MW/US in WCO transesterification for different reaction times, alcohol-to-oil molar ratios, catalyst concentrations, and oil volume



reaction using methanol is favored for various reasons which include molecular weight, boiling point and reactivity with triglycerides and catalyst and interaction with process intensification effects of microwave and ultrasound irradiation.

Among the four metrics discussed above, atom economy provides the actual reaction efficiency and utilization of atoms to produce useful products. E-factor allows one to quantify the waste that could be generated from an anticipated process scheme which is another useful metric. Reaction mass efficiency combines key elements of chemistry and process and represents a simple metric which is very similar to E-factor. Mass intensity may be usefully expressed as mass productivity to understand the efficiency of the overall process schemes. These metrics assist the chemists, process and chemical engineers, and business managers to make meaningful decisions when considering new chemical reaction schemes and processes by providing simple and objective tools for analysis.

Role of catalysts

Non-catalytic reaction

A variety of catalysts of homogenous and heterogeneous nature is employed in transesterification reactions. Among these, homogeneous catalysts have shown superior results. However, despite its advantages, such as high activities and selectivity, compared to heterogeneous counterparts, homogeneous catalysis suffers from serious shortcomings. Recovery of the catalyst in an active form suitable for recycling is often cumbersome, and the product can be contaminated with catalyst residues (Tang et al. 2005; Sheldon 2008). On the other hand, heterogeneous catalysts provide cleaner end products but require severe process conditions to overcome the mass transfer-related limitations.

Transesterification reaction without use of catalyst (i.e., catalyst-free) would seem ideal and may result in higher product recovery. Catalyst-free reactions, however, may require excess reactant ratios combined with extreme process reaction conditions to promote the desired transesterification reaction in the non-catalytic environment. For example, He et al. (2007) studied continuous biodiesel production from vegetable oil under supercritical conditions. The optimal reaction conditions under constant reaction temperature process were 40:1 of the molar ratio of alcohol to oil, 25 min of residence time, 35 MPa and 310 °C with a maximum production yield of 96% under gradual heating. At constant reaction temperature, the process yield was only 77% due to the losses caused by the side reactions of unsaturated FAME at high reaction temperature (He et al. 2007). Due to many advantages associated with this method such as shorter reaction times, insensitive to water content

and acid value, this method was very well studied by the researchers recently (Saka and Kusdiana 2001; Fangrui and Hanna 1999; Demirbas 2002). The C18 fatty acids esterification under microwave irradiation was studied (Melo-Junior et al. 2009a, b). The effects of alcohol used (methanol or ethanol), temperature (150–225 °C), molar ratio of alcohol/fatty acid (3.5–20), and total microwave irradiation power on the non-catalytic reaction conversion were evaluated. The results showed conversion up to 60% in 60 min of reaction.

The E-factor for the supercritical methods (where mediated by the microwaves or not) can be higher since they require excess solvents to promote non-catalytic reactions. Severe process conditions are essential to conduct this method. Table 3 compares the energy requirements for conventional, microwave-mediated catalytic and microwave-mediated non-catalytic transesterification reaction. This table presents the energy consumption per unit product (kJ/L, specific energy consumption) in conventional and microwave-based biodiesel processes. It should be noted that the energy consumption patterns depend largely on the scale of production process. Supercritical conditions in both conventional and microwave-mediated processes demand higher energy inputs due to severity of the process conditions. It may be possible that the specific energy consumption for the conventional and microwave-mediated processes may match at large-scale biodiesel production, but the other distinguished advantages of the microwave-mediated process should be carefully considered.

When the feedstock is microalgae biomass, the supercritical method provides for a simple and single-step process for simultaneous extraction and transesterification of oils (Patil et al. 2011a). Alternatively, microwaves can be used to extract the lipids and transesterify them simultaneously (Patil et al. 2011b). A single-step microwave-mediated transesterification of dry algal biomass to biodiesel under supercritical ethanol conditions was demonstrated. This microwave-mediated catalyst-free approach improved extraction of algae significantly, with higher energy efficiency, reduced extractive-transesterification time, and increased FAEE yield. In addition, this process produced highly purified extracts that are free of harmful residues and may reduce the energy consumption and cost of the process due to easier separation and purification steps. The maximum fatty acid ethyl ester (FAEE) was obtained employing supercritical conditions (265 °C, ca. 80 bar) for dry algal biomass at 1:12 algae to ethanol (wt./vol.) ratio and 20 min of reaction time under controlled power dissipation. The continuous-flow model using this existing process for the algal biodiesel production could solve the scale-up difficulties to some measurable extent (Patil et al. 2013; Tan et al. 2010). Ultrasound can also be used to extract lipids from microalgal biomass as reported in other studies (Araujo et al. 2013; Martinez-Guerra et al. 2014b; Lee et al. 2010).

Table 3 Comparison of energy consumption per unit biodiesel production under different heating methods

Type of heating	Conditions	Energy consumption (kJ/L)	Ref
Conventional	Continuous (industrial scale)	94.3	Chand et al. (2010)
Microwave	Continuous, 7.2 L/min	26	Barnard et al. (2007)
Microwave	Continuous, 2 L/min (a power consumption of 1700 W and a microwave input of 1045 W)	60.3	
Microwave	Continuous, 2 L/min (a power consumption of 2600 W and a microwave input of 1600 W)	92.3	
Microwave	Batch, 4.6 L (a power consumption of 1300 W, a microwave input of 800 W, a time to reach 50 °C of 3.5 min, and a hold time at 50 °C of 1 min.)	90.1	
Microwave	Supercritical, 10 ethanol/oleic acid molar ratio, 150 °C, 3.6 min (milliliter scale)	265	Melo-Junior et al. (2009a, b)
Microwave	Supercritical, 10 ethanol/oleic acid molar ratio, 200 °C, 5.7 min (milliliter scale)	762	
Microwave	Supercritical, 10 methanol/oleic acid molar ratio, 150 °C, 3.7 min (milliliter scale)	251	
Microwave	Supercritical, 20 methanol/oleic acid (milliliter scale) molar ratio, 200 °C, 3.7 min	609	
Microwave	Supercritical, 10 methanol/oleic acid molar ratio, 200 °C, 5.5 min	753	
Microwave	Supercritical, 5 methanol/oleic acid molar ratio, 200 °C, 5.1 min	804	
Ultrasound		137.5	Chand et al. (2010)

Heterogeneous catalysts offer several benefits for reuse and recycling of materials and higher product recoveries. Many inorganic catalysts including those derived from waste materials were utilized in biodiesel production in combination with microwaves and ultrasound. Alkaline earth metal oxides, heteropolyacids, and zeolites have been investigated for biodiesel production, among which alkaline earth metal oxides, and in particular CaO, have shown good performance (Khemthong et al. 2012). Utilization of natural calcium sources from waste materials such as waste shells of freshwater mussel, cockle (*Anadara granosa*), mollusk, egg, *Turbonilla striatula*, oyster, and Rohu fish (*Labeo rohita*) scale exhibited high catalytic activities at very low costs of production (Boro et al. 2012). Impregnation methods were used to develop novel heterogeneous catalysts such as CaO-SnO₂ catalysts which were shown to be stable and durable for transesterification reaction (Xie and Zhao 2013). Stable solid base catalysts with tetraalkylammonium hydroxide-functionalized SBA-15 materials (SBA-15-pr-NR₃OH) by anchoring dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium hydroxides onto the surface of mesoporous SBA-15 silica have shown over 99.4% yields in transesterification reaction (Xie and Fan 2014).

Enzyme-catalyzed transesterification can be performed at ambient or moderate temperatures with high yields. High enzyme costs and the problems related to its deactivation caused by feed impurities cause barriers for their practical implementation (Di Serio et al. 2007). The enzyme can be immobilized on a support to obtain a heterogeneous catalyst, only if the enzyme costs are reduced as in the case of

enzyme use in detergents, dairy products, textile, and leather processing. Several types of support materials are used for the immobilization of enzymes which include natural macromolecules, inorganic materials, and some synthetic polymers (Salis et al. 2008). One of the approaches taken to immobilize the enzyme is by using covalent bonding with magnetic microsphere which provided a decent conversion of 86% without much loss of activity after the use of four cycles (Xie and Wang 2014). Efficient use of enzymes, increasing its reactivities, immobilization and process optimization and reuse and recycle stabilities are important factors which need further research and development to make this option practically feasible and economically affordable.

Process intensification and catalyst effects on reaction kinetics

The reaction kinetics of transesterification under microwave or ultrasound irradiation could be very different from conventional heating. Reactants respond to microwave heating depending on their polarity, dipole momentum, and microwave absorption capacity. Therefore, each of the reactants in a microwave-enhanced reaction may have a different reaction rate. The reaction rates with respect to individual reactants such as oil and methanol are not reported in many studies. This is important because the kinetics of transesterification reaction depends on both the reactants and their individual interaction with microwaves. Ultrasound activation has entirely different effects on the reaction kinetics. It creates microbubbles and microenvironments with elevated

pressures and temperatures with intense mixing allowing for faster diffusion and disruption.

Microwave kinetics

The effect of process intensification depends on the reaction conditions including the reactants and catalysts. Kinetics of the transesterification of *Camelina Sativa* oil were reported recently using four different heterogeneous catalysts (BaO, CaO, MgO, and SrO) with varying strengths (Patil et al. 2011a, b, c). Eight different cases were evaluated with respect to reaction order of individual reactants, i.e., oil and methanol. It was reported that both BaO and SrO fit second order with respect to triglycerides and first order with respect to methanol. The reaction rate constants were 0.0526 and 0.0493 $\text{g}^2 \text{mol}^{-2} \text{min}^{-1}$, respectively. For CaO, the reaction rate constant observed was the minimum which is about two orders of magnitude (87 times) smaller than that for BaO with overall first-order reaction. The reaction order for BaO with respect to triglycerides and methanol is similar to conventional heating method except that the reaction rate constant is two orders of magnitude (98.7 times) higher for microwave-assisted heating method. This is reflected by the short reaction times required for microwave heating and efficient heating of the reaction compounds. Similarly, for SrO, the reaction rate constant for microwave-assisted heating is one order of magnitude higher than conventional heating method.

Ultrasound kinetics

Colucci et al. (2005) reported a pseudo-second-order kinetic model for the ultrasonic hydrolysis of DG and TG and reaction rate constants were three to five times higher than those for mechanical agitation. Parkar et al. (2012a, b) compared the ultrasonic transesterification of soybean oil with conventional alkali-catalyzed reaction with mechanical stirring and reported similar effects. Use of homogeneous catalysts can have significant effect on the reaction rates and order of reactions. The reaction rate constants determined in homogeneously catalyzed reactions are higher than those observed in heterogeneous catalyst studies. In addition, the effect depends on the type of catalyst whether acidic or basic. The reaction rate enhancements can be attributed to the increase in interfacial area and activity of the microscopic and macroscopic bubbles formed when ultrasonic waves of 20 kHz were applied to a two-phase reaction system. The major physical effect of sonication of reaction mixture is very fine emulsification that generates enormous interfacial area for reaction that overwhelms the effect of specific rate constant, which in turn is a function of activation energy and reaction temperature.

Activation energy

The activation energy reported in studies using microwave or ultrasound process intensification is usually in the lower range of reported values in the literature. For ultrasound-mediated reactions, a wide variation of activation energies is reported. Deshmane and Adewuyi (2013) reported an activation energy value of $64,000 \text{ J mol}^{-1} \text{ K}^{-1}$, and Colucci et al. (2005) reported in the similar range. Vyas et al. (2011) reported the activation energy of ultrasonic transesterification of *jatropha curcas* oils as $16,691 \text{ J mol}^{-1} \text{ K}^{-1}$. These studies reported kinetics on pure vegetable or seed oils. Lee et al. (2007) reported the activated energy for used soybean frying oil of $29,000 \text{ J mol}^{-1} \text{ K}^{-1}$. Krishnan and Dass (2012) reported very low activation energy values of $5400\text{--}10,600 \text{ J mol}^{-1} \text{ K}^{-1}$ for transesterification of waste cooking oil using conventional heating method (heating mantle) between 50 and 65 °C. However, it should be noted that the activation energy depends on the reaction mixture (quality of oil, alcohol–catalyst) and the reaction conditions. In general, lower activation energies are desired as this is the minimum energy required to initiate a chemical reaction (or the energy that must be overcome in order for a reaction to occur).

Role of solvents

Safer solvents or solvent-free reactions

Solvents are often used to extract the oils from the feedstock. They are also used as co-reactant to improve the reaction efficiencies (Tan et al. 2010). Hexane is a commonly used reactant, while heptane is considered safer solvent. In a non-catalytic supercritical methanol reaction, heptane as solvent improved the reaction yields due to high tolerance to water content and free fatty acid content (Tan et al. 2010). Transesterification of *Camelina Sativa* oil under supercritical methanol conditions with hexane as a co-solvent and subcritical methanol along with potassium hydroxide as a co-solvent/catalyst was investigated (Patil et al. 2009). It was found that co-solvents play a vital role in reducing the severity of critical operational parameters and maximize the biodiesel yield.

Hexane as solvent and its effects

Alcohols in excess quantities can be used as a reactant and a solvent. In single-step extractive-transesterification of microalgal lipids, methanol can act as both reactant and solvent. The solvent properties of methanol would help extract the oils under microwave and convert them simultaneously into biodiesel via transesterification reaction.

Microalgae lipids have higher selectivity toward chloroform–methanol–water system, due to their polar nature and excellent solvent characteristics of chloroform (Araujo et al. 2013). Solvents used in conventional Bligh and dyer (BD) method (especially chloroform) may cause cell wall disruption, thus contributing toward extraction of oil/lipids from the microalgae cells. Microwave irradiation can contribute via diffusive and disruptive extraction of microalgal lipids in the solvent (Patil et al. 2011a, b; Martinez-Guerra et al. 2014a, b). Microwave-enhanced extraction process has performed consistently better than the BD method and the method using hexane as co-solvent in terms of both the lipid extraction (yields) and the fatty acid ethyl ester conversion (Martinez-Guerra et al. 2014a). Hexane addition reduced the requirement for higher ethanol concentrations and assisted further in extraction of lipids while resulting in higher conversion than BD method. Lee et al. (2010) reported that lipid extraction yield was higher for microwave method compared to autoclaving, bead-beating, sonication, and a 10% NaCl solution extraction methods.

Supercritical reactions allow for extraction without solvents at severe process conditions possibly with higher energy inputs. This also indicates higher capital costs and safety requirements. The same reactions can be performed with microwave-based supercritical reactions requiring much less reaction times, but the same limitations as conventional supercritical reactors may apply (Patil et al. 2013). The inherent advantage with the microwave reactors is that they are able to produce superior results at ambient pressures due to the special thermal and non-thermal mechanisms associated with them.

Concluding remarks

In order to establish a sustainable route for biodiesel production, the integration of green chemistry, along with the use of high performance process intensification and low environmental impact technologies such as microwaves and/or ultrasound, is mandatory. Green chemistry can be considered as a set of principles for the manufacture and application of products that aim at eliminating the use, or generation, of environmentally harmful and hazardous chemicals (Clark et al. 2009). It offers a simple tool kit of techniques, underlying principles, and metrics that any chemist, engineer, and scientist could apply when designing new chemical reactions for biodiesel production.

Green metrics discussed in this research review article shed light on evaluation of various options for determining the suitability of various chemical reactions, and reaction designs for sustainable biodiesel production. These metrics can be used to evaluate the potential “greenness” of the process prior to its implementation. Further, some other

metrics such as E-factor and mass reaction efficiency provide an insight into the performance of the process and indicate the alternative pathways to improve the sustainability of biodiesel production. Green metrics discussed in this article can be applied to any process and chemical reaction design and research involving fuel and chemical production.

In conclusion, for microwave- or ultrasound-enhanced biodiesel production, the green chemistry principles can be further simplified and summarized as: (1) safe (yes, microwaves are safe); (2) atom efficient (biodiesel reaction is atom efficient); (3) environmentally acceptable (less by-product formation); (4) high yield (nearly 100%); (5) simple operation; (6) one step (single-step extractive-transesterification); (7) no waste reagents (non-catalytic and solvent-free reactions); and (8) available materials (renewable feedstock). By following these simple principles, microwave- or ultrasound-enhanced synthesis will contribute to green and sustainable biodiesel production.

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