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1. Introduction

The world energy crisis has recently become a more crucial issue because energy demand outstrips energy supply. Alternative energy sources and fuels have therefore been investigated as a means to indemnify the higher demand for natural fuels, which require many years of formation. Over the last 40 years, several renewable energy sources have been developed. Biodiesel can play an important role here because its high heating values are nearly equivalent to diesel fuels and it presents low environmental impact. It can be produced from many types of feedstock including waste cooking oil [1-3]. Data on monthly biodiesel production from 2011 to 2013 provided by the U.S. Energy Information Administration (EIA) (Fig. 1) show that production has steadily increased [4].

Fig.1

A concerned effort has been made to search out new highly efficient reactors that produce biodiesel as well as saving time and energy. Inefficient mass transfer is one of the main limitations in biphasic heterogeneous reactions, such as transesterification. Although many types of vigorous mixing have been investigated to address this requirement, most of them suffer from high energy demands [5-7]. Optimal mass/heat transfer is doubtless the key to enhancing biodiesel production. Dielectric heating has been proved to dramatically enhance transesterification reactions because it provides the improved heat transfer over the conventional methods [8]. Microwave (MW) as a volumetric heating and the selective overheating of polar catalysts/reagents has been widely exploited [9-10]. Besides avoiding the wall effect, flow-MW reactors also reduce energy consumption because energy is directly transferred through the reaction mixture [11]. For

example, the total energy consumption for biodiesel production from palm oil in a batch reactor using MW heating is less than that of the conventional as presented in Table 1.

Table 1

In conventional heating, heat transfer occurs by conduction and/or radiation. Moreover, the efficiency of heat transfer depends on material properties such as thermal conductivity, specific heat capacity and density, resulting in non-uniform heating in a reactor. However, MW irradiation can instantly interact with a sample matrix and does so via two mechanisms, dipolar rotation and ionic conduction. Dipolar rotation generates heat when sample dipoles try to align themselves after an oscillation in the electric field, while ionic conduction generates heat when the electric field direction is changed via friction at the molecular level and larger ions slow down. Both mechanisms lead to the localized superheating of material in a very short time [12, 13].

As mentioned above, industry level scale up and energy consumption are necessary issues in economical biodiesel production. Moreover, most procedures use the conventional mechanical stirring which requires high energy consumption, before applied the MW irradiation.

Therefore, we herein report a more efficient set up which uses the combination of two commercial reactors: a High-Shear Mixer (HSM, Magic-Lab - IKA) and a multimode MW reactor (MicroSynth, Milestone). Such a combination dramatically enhances both mass and heat transfer during the NaOH-catalyzed transesterification of refined palm oil and methanol. Energy consumption for biodiesel production and the analytical properties of biodiesel produced by each single system and their combinations are treated as the main criteria in process optimization.

2. Experimental method

2.1 Equipment

The HSM (Magic Lab, by IKA Germany) is a new modular laboratory system which is especially designed for mixing, dispersing, wet milling and incorporation of powders into liquids. It can produce homogeneity and stability in emulsions and suspensions using its three rotors, high-shear dispersing module. The system configuration is illustrated in Fig. 2(a). There are three rotors that differ according to orifice shape and slot width, as shown in Fig. 2(b), which are used to provide varying dispersion levels. The rotors are arranged in series including coarse, medium and fine, respectively for optimization of performance and functionality. The configuration also includes a cooling system which disperses heat, generated by the rotors and the operating unit, and controls the operating parameters such as temperature, rotor speed and rotation time.

Fig. 2(a) and (b)

MW irradiation was performed in a MicroSynth MW oven (by Milestone, Italy), with a maximum power setting of 800W and equipped with an IR pyrometer. The MW cavity is 35 x 37 x 35 cm^3. The precise reaction monitoring and parameters have been controlled by the software interface.

2.2 Chemicals

Commercial refined palm oil was kindly provided by Embouteille Company, Italy. Methanol reactant, of 99.9% purity, and methyl heptadecanoate, used as an internal standard for GC analysis, were purchased from Sigma-Aldrich. The NaOH catalyst, of 97.5% purity, and the heptane solvent, of 99.7% purity, were obtained from Carlo Erba Reagenti.

2.3 Experimental setup

The experimental set up was divided into 3 systems as follows:

System 1: A combination of the HSM (Magic Lab) and the MW reactor (HSM+MW). This combination is shown in Fig. 3. The catalyst was first mixed with methanol and then, all reaction mixtures were fed from the HSM and continually passed through the glass coil reactor, placed in the MW reactor. The outlet stream (reactants and products) was circulated to the HSM and fed through MW depending on the pre-decided circulation cycles.

Fig. 3

System 2: The HSM was used alone. The configuration of the system is illustrated in Fig. 4.

Fig. 4

System 3: A combination of a turbo mixer and MW reactor (TB+MW) was used to enhance mass and heat transfer of the reaction (Fig. 5). The procedure was the same as system 1. However, TB was used as a conventional means to mix reactants before they were fed into the MW. The aim of this set up is to emphasise the heat transfer effect of the MW.

Fig. 5

Feed flow rate was measured by a specific flow meter ASA (model G6-2600/39 for biodiesel, – Sesto S. Giovanni, Italy) and fixed at 250 cm^3 min^{-1} for all experiments. The effect of MW power (300, 400, 500 and 600W), methanol/oil molar ratio (6, 9 and 12), circulation cycle (5, 7, 10, 15 and 30) and different systems for biodiesel production (system 1, 2 and 3) on biodiesel yield have been tested. All experiments were repeated for 3 times.

2.4 Analytical method

After transesterification, glycerol product has been removed by centrifuge. Therefore, biodiesel sample (top layer) was washed 3 times using distilled water with a water/biodiesel volume ratio of 0.5 to 1 and a stirrer speed of 3.33 Hz at an ambient temperature [14]. After that the moisture and remaining methanol was removed under vacuum in a rotary evaporator for 1 h before analysis. Biodiesel yield was then analyzed according to the EN 14103 standard method using an Agilent Technologies 7820A GC system. This GC system is equipped with a flame ionization detector and a capillary column MEGA-WAX (0.25µm x 0.25mm x 30m). Helium and nitrogen were used as carrier gas and makeup gas, respectively. The oven temperature ramp program was started at 150°C and held for 5 min, then heated up to 190°C at a rate of 3°C min^{-1} and held for 5 min, then heated up again to 220°C at a rate of 3°C min^{-1} and held for 5 min. Injector and detector temperatures were 250°C. Biodiesel yield was calculated using the following equation

$$\%Yield = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\% \quad (2.1)$$

where $\sum A$ is total peak area, A_{EI} is the peak area that corresponds to methyl heptadecanoate, C_{EI} is the concentration of the methyl heptadecanoate solution (mg cm^{-3}), V_{EI} is the volume of methyl heptadecanoate (cm^3) and *m* is the biodiesel sample mass (mg). The properties of the purified biodiesel were then analyzed according to the EN and ASTM standards.

3. Results and discussion

3.1 Effect of MW power on biodiesel yield at various circulation cycle

Table 2 illustrates the obtained biodiesel yields at various MW power settings and circulation cycles when the methanol/oil molar ratio was fixed at 6. At a MW power of 300W, the obtained biodiesel yield was only 96.37% even when a high circulation cycle rate of 30 cycles was applied (~40 min of total reaction period). This value was not in accordance with the ASTM standard (96.5%). Therefore, the highest MW power setting was employed. The results indicated that the minimum biodiesel yield requirement can be archived at MW power settings of 400, 500 and 600W and with the circulation cycles of 30, 10 and 10, respectively.

Table 2

A high biodiesel yield was obtained in a short reaction time (related to the circulation cycles) at high MW power. This was because the rapid dipole moment reorientation of methanol occurred at the high MW power setting. This phenomenon destroys the boundary layer between methanol and oil and reduces the dielectric constant and the polarity of methanol and thus resulted in the homogenization of methanol and oil [15]. Therefore, a high biodiesel yield can be achieved.

In addition, MW irradiation can also enhance a reaction rate. The reaction rate can be described by the Arrhenius equation, which is shown below

$$K = A\, e^{-E_a/RT} \tag{3.1}$$

where K is the rate constant, A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the temperature. MW irradiation can increase the pre-exponential factor (A) by increasing molecular vibration from the mutual orientation of the polar molecule involved in the reaction [9, 16, 17]. A high reaction rate can therefore be obtained and

completed oil conversion was also achieved. It can be seen that temperature increased at high power and this also provided the positive influence on reaction rate and yields [18]. Encinar *et al.* [19] also proposed 65 to 90°C as the optimal temperature range under MW. The evaporated methanol fraction was finely dispersed in the oil causing high conversion in a relatively short reaction time. Moreover, the MW superheating of boiling methanol may also drive the kinetics of the transesterification.

3.2 Effect of methanol/oil molar ratio on biodiesel yield

The effect of the methanol/oil molar ratio may be a key parameter due to the high MW-absorption of methanol [19]. Owing to its high dielectric constant ($\varepsilon = 33$) as compared to palm oil ($\varepsilon = 3$), methanol strongly absorb MW energy. The effect of the methanol/oil molar ratio on biodiesel yield is shown in Table 3 (System 1). It was found that the optimal methanol/oil molar ratio was 9. This was because transesterification is the reversible reaction and hence requires a higher amount of methanol to shift the reaction [11, 18, 20, 21, 22]. However, an excessive amount of methanol will also hinder the reaction rate because it would increase the solubility of the by-product glycerol, for the reverse reaction [23, 24]. The methanol/oil molar ratio does not significantly affect the outlet temperature, perhaps because of the boiling of methanol. At a high molar ratio, the amount of methanol is greater and more energy is needed to turn methanol into vapour and thus the temperature increase is lower [19].

Table 3

3.3 Effect of MW power on biodiesel yield at the optimal circulation cycle

Biodiesel yield and required circulation cycles, at the optimal methanol/oil molar ratio of 9 and at any MW power setting, are summarized in Table 4. It was found that high biodiesel yield can be obtained with a lower number of cycles at this ratio than that of a methanol/oil molar ratio of 6. This confirms the effect of the optimal methanol/oil molar ratio for transesterification used in this work. It can be seen that the biodiesel yield for system 1, at MW power settings of 400, 500 and 600 W, were 96.90, 96.87 and 99.80% at circulation cycle numbers of only 10, 7 and 5 cycles, respectively. These results were obtained at a residence time of 30 s in MW reactor for each cycle.

Table 4

3.4 Effect of different systems for biodiesel production

The optimal condition from previous section was applied in order to compare the performance of each system. The results of all systems are summarized in Table 5. The best results were achieved with system 1 (HSM+MW), however system 3 (TB+MW) can also reach the minimum ASTM standard yield requirement (96.50%). Moreover, high biodiesel yield can be obtained in only 5 circulation cycles (~5 min of total reaction period and 30 s of residence time in MW reactor) at a MW power setting of 600 W. This clearly emphasizes the efficient mass transfer enhancement caused by applying HSM over conventional TB.

Table 5

To emphasise the effect of heat and mass transfer in this experimental set up, it was found that the biodiesel yield of system 2 was under the standard limit (<96.5%). This indicated that mass transfer enhancement alone could not shift the reaction equilibrium. It was more likely involved in the first stage of reaction (diffusion stage) [25], while MW irradiation probably dominated the

second stage of reaction (kinetic stage). Indeed, it facilitated the reduction in activation energy and raised the pre-exponential factor [9, 16, 17]. Therefore, the integration of HSM and MW reactor is the booster process for the continuous transesterification process.

3.5 The energy consumption for biodiesel production from each system

As mentioned above, energy consumption is another crucial aspect in this study, as illustrated in Table 6. Overall energy consumption was measured using a plug-in power meter and is therefore a measure of total actual energy. This is made up of the energy use of the MW reactor, HSM and cooling pump for system 1, the energy use of the HSM and cooling system for system 2 and of the MW reactor, TB and cooling pump for system 3. The results show that system 1 not only gave the highest biodiesel yield, in accordance with the ASTM standard, but it also only used around half the energy of system 3. This is because conventional TB operates (system 3) for the whole reaction mixture at the same time, while HSM (system 1) operates for the specific amount of reaction mixture that is required for the specific space to obtain the high shear rate [26]. This result obviously confirms the advantages of using HSM to enhance mass transfer and the MW reactor to increase the heat transfer for transesterification. Although, system 2 required less energy than systems 1 and 3, after 60 min the biodiesel yield was only 92%. The transesterification using HSM could not meet the ASTM conformance (<96.50%).

Table 6

Moreover, the theoretical energy consumption for the MW reactor has also been calculated. It was found that the theoretical energy consumption was 392.4 kJ dm^{-3} of biodiesel. This value corresponds with the result from Lertsathapornsuk *et al*. [27] that mentioned an energy

consumption value for biodiesel production in a continuous flow through MW reactor of 269.3 kJ dm^{-3} of biodiesel.

3.6 Biodiesel analysis

To ensure the quality of the biodiesel, its properties were compared to those of the ASTM standard. Table 7 highlights that all the main physical properties of the biodiesel obtained with systems 1 and 3 fully address ASTM standard requirements [13, 16, 28]. As you can see that, the remaining amount of monoglyceride, diglyceride, triglyceride, free and total glycerol after purification were under the standard limit. Density is one of the most important properties as it is related to other fuel properties such as viscosity, calorific value and cetane number. This parameter also effects fuel storage and transportation [29].

Table 7

4. Conclusion

This work proposes a new flow system for oil transesterification that combines a commercial HSM and a MW oven to simultaneously enhance mass and heat transfer. A high biodiesel yield of 99.80% was obtained in 5 circulation cycles (corresponding to 5 min of reaction time). The HSM provided excellent mixing (for the diffusion stage) with clearly less required energy than conventional TB. The heat transfer from MW irradiation (for the kinetic stage) has been proved to effectively enhance transesterification in a relatively short time. Moreover, the total energy consumption required for this hybrid reactor was noticeably lower than a conventional process affording biodiesel in the range of standard limits. The combination of these two energy souces provides a valuable guideline for further application in industry in terms of repeatability, scaling up and energy consumption.

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315 **Table 1**. Biodiesel yield in system 1 at various MW power settings and circulation cycles
316 (methanol to oil mole ratio of 6).

Power (W)	Cycles	$T_{out\ of\ MW}$ (K)	Yield* (%)
300	15	326.5	95.33
	30	336.8	96.37
400	10	339.3	94.51
	15	341.0	96.16
	30	339.7	98.01
500	5	348.0	95.56
	10	349.7	96.84
	15	350.0	98.37
600	5	353.1	95.94
	10	353.8	96.90

* Yield refers to mass yield of FAME

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320 **Table 2.** Biodiesel yield at various methanol to oil mole ratios (MW power of 400W, circulation
321 cycles of 15).

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Methanol/Oil Mole Ratio	$T_{out\ of\ MW}$ (K)	Yield* (%)
6	341.0	96.16
9	343.0	97.44
12	342.3	97.18

* Yield refers to mass yield of FAME

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324 **Table 3.** Biodiesel yield at various MW power settings and circulation cycles (methanol to oil
325 mole ratio of 9).

Power (W)	Cycles	$T_{out\ of\ MW}$ (K)	Yield* [a], (%)
400	10	342.30	96.90
500	7	349.40	96.87
600	5	352.20	99.80

* Yield refers to mass yield of FAME

[a] The standard deviation (S.D.) is less than 0.24

326 **Table 4**. Biodiesel yield at various MW power settings and circulation cycles from each system
327 (methanol to oil mole ratio of 9).

Cycles	Yield* (%)		
	System 1[a] (MW Power)	System 2[b]	System 3[c] (MW Power)
10	96.90 (400W)	93.44	96.55 (400W)
7	96.87 (500W)	92.06	96.50 (500W)
5	99.80 (600W)	91.57	96.40 (600W)

* Yield refers to mass yield of FAME
[a] The standard deviation (S.D.) is less than 0.24
[b] The standard deviation (S.D.) is less than 0.41
[c] The standard deviation (S.D.) is less than 0.43

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331 **Table 5.** Energy consumption for biodiesel production by system (MW power = 600W, Circulation
332 cycles = 5 and Methanol to oil mole ratio = 9).

Type of reactor	Energy consumption (kJ $dm^{-3}$of biodiesel)	Yield* (%)
System 1	1,200	99.80
System 2	263	91.57
System 3	2,120	96.40

* Yield refers to mass yield of FAME

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336 **Table 6.** Biodiesel physico-chemical properties (System 1).

Properties	Values		Units
	EN 14105/ASTM 6751	This work	
Monoglyceride	≤ 0.80	0.28	mass fraction (%)
Diglyceride	≤ 0.20	0.07	mass fraction (%)
Triglyceride	≤ 0.20	0.07	mass fraction (%)
Free glycerine	≤ 0.02	0.002	mass fraction (%)
Total glycerine	≤ 0.25	0.091	mass fraction (%)
Flash point	≥ 403	448	K
Pour point	263 - 285	271	K
Viscosity at 313 K	1.9 - 6.0	4.61	$mm^2 s^{-1}$
Density at 293 K	860 - 890	870	$kg m^{-3}$

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(a)

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(b)

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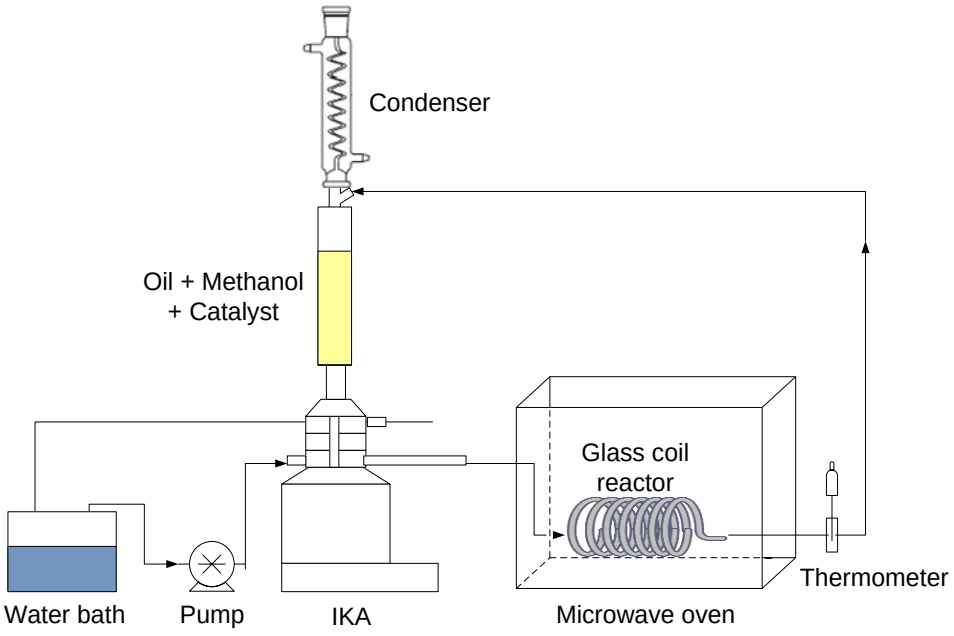
349 **Figure 1.** (a) HSM (Magic-Lab, IKA) and (b) Three types of rotor; coarse, medium and fine
350 rotor, respectively.



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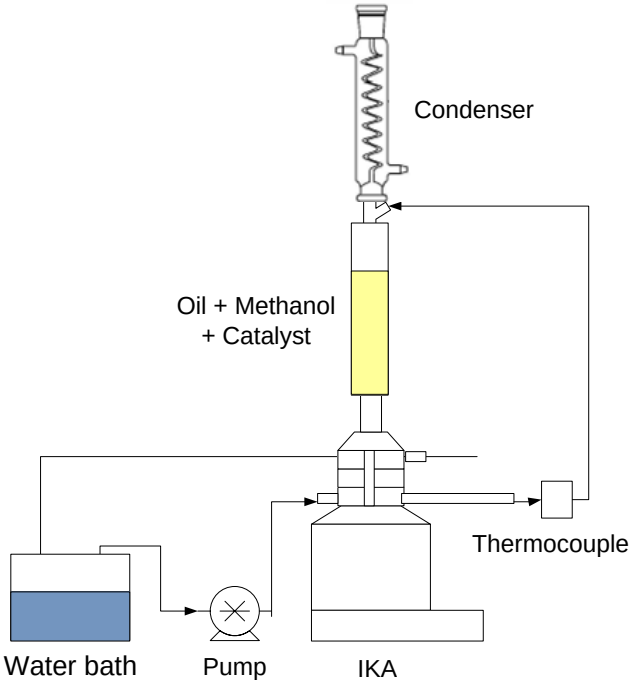
352 **Figure 2.** System 1: a combination of HSM and MW



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354 **Figure 3.** System 2: HSM alone

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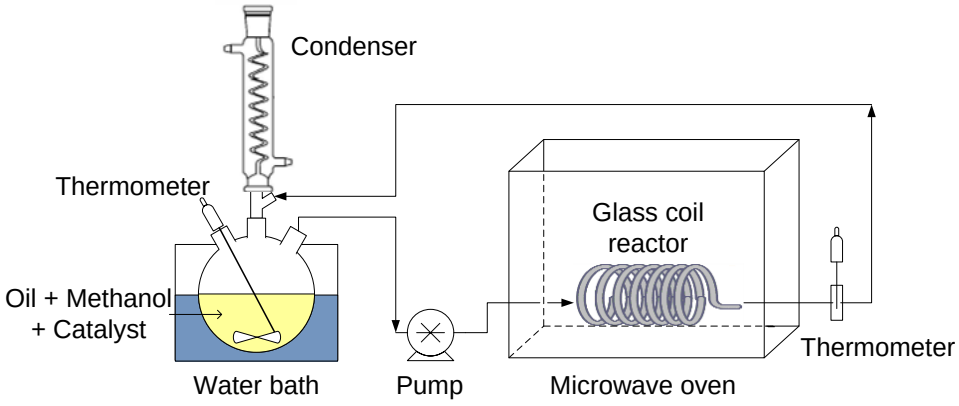

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358 **Figure 4.** System 3: a combination of TB and MW

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