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Optimization of biodiesel synthesis under simultaneous ultrasound-microwave irradiation using response surface methodology (RSM)

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Abstract: This work investigates the effect of simultaneous ultrasound-microwave irradiation on palm oil transesterification and uncovers optimal operating conditions. Response surface methodology (RSM) has been used to analyze the influence of reaction conditions, including methanol/palm oil molar ratio, catalyst concentration, reaction temperature and irradiation time on biodiesel yield. RSM analyses indicate 136 s and 129 s as the optimal sonication and microwave irradiation times, respectively. Optimized parameters for full conversion (97.53%) are 1.09% catalyst concentration and a 7:3.1 methanol/oil molar ratio at 58.4°C. Simultaneous ultrasound-microwave irradiation dramatically accelerates the palm oil transesterification reaction. Pure biodiesel was obtained after only 2.2 min while the conventional method requires about 1 h.

Keywords: biodiesel; microwaves; palm oil; transesterification; ultrasound.

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1 Introduction

The production of biofuel, a sustainable alternative to mineral oil, from renewable sources is steadily growing. The driving forces for this development can be found in its lower environmental impact [1–6] and the availability of new technologies which reduce production costs [7, 8]. Currently, the main sources for biodiesel production in the market are oil seeds [9, 10] and, in particular, palm oil (*Elaeis guineensis*) because of its high farm yields (3.5–5 ton/ha/year) [11, 12].

Transesterification, the most common biodiesel production method [13], is usually a slow reaction which can take more than 1 h and requires about 3–5 h for workup and phase separation. As it is a reversible reaction, prediction of a final equation is complicated [14], and difficult energy/mass transfer hinders the reaction rate and yield. Several studies have dealt with methods that act upon the interface between the two insoluble layers [15].

A combination of microwaves and ultrasound, used in sequential or simultaneous mode, has recently been the focus of great attention in the scientific community as it can boast of preliminary application in biodiesel production [16–20], among other uses. Heat and mass transfer limitations can be easily overcome when combining these two techniques [21]. Ultrasound and cavitation phenomena cause a reduction in transesterification reaction time and higher yields in typical liquid-liquid heterogeneous reaction systems [22–27]. It is clear to see that this technique is effective in providing mixing and activation energy, as the application of ultrasonic energy to biodiesel production increases the yield, up to 99%, in few minutes [16]. Several authors have reported on the effectiveness of power ultrasound and have suggested a host of advantages which include shorter reaction times, improved mass transfer, reduced costs and energy consumption over mechanical agitators [28–31]. In recent years, researchers have widely used microwaves in biodiesel production because of its unique acceleration, lower alcohol to oil ratio and effectively-reduced byproduct amounts [32–38].

We also reported the advantages of integrated flow reactors combining high-shear mixing and microwave irradiation for biodiesel production [39].

The optimal conditions for the microwave-assisted transesterification of dry algae biomass have been elucidated via the use of response surface methodology (RSM) [40]. These conditions were found to be a 12:1 methanol/dried algae ratio, 2% (w/w) catalyst concentration and 4 min reaction time.

The ultrasonic-microwave combination has been compared with a simple sonochemical process. Transesterification and esterification reaction times were decreased from 60 min to 15 min and from 20 min to 6 min, respectively. Another study has indicated conditions of 1 min ultrasonic mixing, 2 min of microwave irradiation, 1% catalyst and 6:1 molar ratio at 59.8°C [20].

In another work on castor oil, RSM was used to obtain optimal conditions for microwave and ultrasound based methyl ester production. Around 95% conversion was achieved after 126 s microwave irradiation (500 W) and 240 s ultrasonic mixing (80 W) [16].

The main technical solutions for the difficulties faced in simultaneous ultrasound/microwave irradiation have been described by Cravotto and Cintas [19] and applied even for critical mixing involving metallic turnings [41].

We herein report the efficient application of simultaneous ultrasound/microwave irradiation to the production of biodiesel from palm oil and present the accurate elucidation of optimal operation conditions.

2 Materials and methods

2.1 Materials

Crude palm oil was supplied by Olitalia Srl (Forlì, Italy) and used as the raw material for transesterification. Table 1 shows some characterization data of crude palm oil. Methanol 99.9%, potassium hydroxide pellets (KOH, purity 85%) and *n*-heptane (standard grade for gas chromatography [GC] analysis) were provided by Sigma-Aldrich (Milan, Italy).

Table 1: Composition and properties of palm oil.

FA composition (wt%)	Value
C16,0	1.1
C16,0	44.9
C18,0	4.5
C18,1	38.8
C18,2	9.8
C18,3	0.2
Iodine value (g I2/100 g)	50.4
Saponification value (mg KOH/g)	196

2.2 Equipment

As depicted in Figure 1, simultaneous ultrasound/microwave irradiation was performed by means of a Pyrex horn (Danacamerini sas, Turin, Italy) inserted into a professional multimode oven (MicroSYNTH, Milestone srl, Bergamo, Italy). Microwave irradiation at 2.45 GHz was performed with a power of 900 W, and ultrasound at 25 kHz with a power of 100 W.

The reaction was performed in a two-neck round-bottomed flask (250 ml) inside which the horn was tightly fixed using elastomeric connections. Palm oil (200 g) was added to the premixed homogeneous solution of methanol and KOH catalyst. The temperature was measured using an optical-fiber thermometer. A watt meter (FAPI 30073) was used for measuring power consumption.

Once irradiated, the reaction flask was rapidly cooled down in ice. Samples were then centrifuged (5 min at 6000 rpm) to separate the methyl ester phase from glycerin. The upper phase was isolated, leached three times and dried at 105°C. Finally, 50 mg of biodiesel phase was transferred into a microtube, adding 1 ml of an internal standard solution (C17, concentration 7 mg/ml).

Following EN 14103 recommendations, GC analyses were performed in an Agilent Technologies 7820A Network GC System equipped with a flame ionization detector detector and using a capillary column (Mega WAX, length 30 m; i.d. 0.25 mm; film thickness 0.25 µm). A starting temperature of 60°C was held for 2 min and then raised to 210°C on a 10°C/min slope, and then to 230°C on a 5°C/min slope. It was kept at this final temperature for 10 min. The palm oil fatty acid profile was used to calculate molar mass. The average molar mass of the studied palm oil was 861.1 g/mol. Methyl ester percentage in biodiesel was measured using Eq. (1). The free fatty acid content of samples was determined using a methyl heptadecanoate and a normal heptane solution [42]:

$$\%\ of\ ME = \frac{\sum A\text{-}A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100 \quad (1)$$

where ΣA=total peak area from the methyl ester on C14 to the one on C24, A_{EI}=methyl heptadecanoate peak area, C_{EI}=methyl

Figure 1: Set up of simultaneous ultrasound-microwave irradiation apparatus.

heptadecanoate solution concentration (mg/ml), V_{EI}=methyl heptadecanoate solution volume (ml) and m=mass of the sample (mg)

3 Experimental design

The objective of this study was to examine the effect of simultaneous ultrasound/microwave irradiation on the transesterification reaction. The experiment was made up of two steps. Firstly, design factors for the transesterification reaction, including ultrasonic mixing time (x_1=60–180 s) and microwave irradiation time (x_2=60–180 s) were studied in five levels. A molar ratio of 6:1 and 1% catalyst were included. Central composite design was selected, as it is one of the best all-round RSM designs, to study the effect of biodiesel process parameters [14]. Table 2 presents the coded and un-coded study parameters.

Once the optimal conditions for simultaneous ultrasonic mixing and microwave irradiation were found, the effective transesterification reaction parameters were assessed under these conditions. The reaction parameters included molar ratio (x_1=6–12), catalyst concentration (x_2=0.5–1.5), and reaction temperature (x_3=50–65). In this step, the Box-Behnken method was applied in three levels in order to facilitate the determination of catalyst percentage. The biodiesel percentage produced was selected as the study's response. Table 3 shows the range of experimental parameters. Minitab 16.1 was used for the graphical and regression analysis of study data.

By calculating the reaction efficiency at the end of experiments, the optimal points of the process were determined by selecting suitable input weights and an appropriate range of variations for the experimental design. The experiment was repeated at the optimal point to assess its value.

The second-order model was fitted in both steps in order to study the relationship between the response variable (biodiesel efficiency) and independent variables. The general form of the multinomial second-order equation can be found below [Eq. (2)] [43]:

$$Y=\beta_0+\sum_{i=1}^{k}\beta_i X_i+\sum_{i=1}^{k}\beta_{ii}X_i^2+\sum_{i=1}^{k}\sum_{j=i+1}^{k}\beta_{ij}X_iX_j+\varepsilon \quad (2)$$

where, Y is the response (dependent variable) which is the biodiesel conversion percentage in this case, β_0 is a constant, β_i, β_{ji} and β_{ij} are the linear and square coefficients and the mutual effect of parameters, respectively, while ε denotes the prediction error. X_i and X_j are the independent variables, which are the reaction temperature, catalyst amount, and molar ratio in this case. The amount of α was selected in order to determine correct parameter values and to access the correct power range for better accuracy and improved convenience [19].

4 Results and discussion

All of the main parameters for the transesterification reaction under simultaneous ultrasound/microwave irradiation (e.g. catalyst concentration, methanol/oil molar ratio, reaction temperature) were studied. RSM was applied, with the aim of optimizing ultrasonic mixing and dielectric heating, and 13 experiments (3 replications) were performed. Table 4 presents the results.

At a molar ratio of 6:1 and a 1% catalyst concentration, the conversion rate ranged from 89.3% to 97.8%. ANOVA results showed that the effects of treatment time (acoustic cavitation and dielectric heating) were significant at the 5% level. These significant effects indicate the importance and effectiveness of the selected independent variables for the experiments.

The study results are in agreement with those reported in the literature. ANOVA was used to explore the significant effects of process variables on the response. As shown in the ANOVA table, Table 5, the lack-of-fit-test was nonsignificant for the study data. This indicates a good data trends prediction by the model [44].

Table 2: Independent variables for central composite design CCD.

Independent variable	X_i	Codes factor levels				
		+α	+1	0	-1	-α
Ultrasonic mixing time (s)	X_1	180	150	120	90	60
Microwave irradation time (s)	X_2	180	150	120	90	60

Table 3: Experimental range and levels of the independent variables.

Independent variable	X_i	Range and levels		
		-1	0	+1
Reaction temperature (min)	X_1	50	57.5	65
Catalyst concentration (w%)	X_2	6,1	9,1	12,1
Methanol/oil molar ratio	X_3	0.5	1	1.5

Table 4: Central composite design for four variables and the response.

Run	Microwave irritation time (s)	Ultrasonic mixing time (s)	Conversion rate (%)
1	110	180	86.92
2	190	180	97.11
3	150	120	95.92
4	70	240	89.35
5	150	240	96.8
6	150	120	89.75
7	110	180	93.12
8	70	240	92.85
9	110	180	97.8
10	110	180	94.01
11	70	120	92.3
12	150	120	97.75
13	70	120	95.87

Table 5: Analysis of variance table.

Source	df	Sum of square	Mean square	F-value	p-Value
Model	5	133.83	26.77	13.67	0.0017
X_1	1	23.91	23.91	12.21	0.0101
X_2	1	22.63	22.63	11.56	0.0114
$X_2 \times X_1$	1	0.69	0.69	0.35	0.5717
X_1^2	1	76.73	76.73	39.19	0.0004
X_2^2	1	30.23	30.23	15.44	0.0057
Residual	7	13.71	1.96		
Lack of fit	3	11.31	3.77	6.31	0.0537
Pure error	4	2.39	0.60		
Total	12	147.53			

Multivariate regression analysis resulted in a multinomial second-order model for predicting the response. The second-order polynomial equation obtained using multiple regression analysis of the experimental data is presented as Eq. (3):

$$\text{Conversion rate (\%)} = 31.123X_1 + 0.5903X_2 - 1.276X_1^2 - 2.0332X_2^2 \quad (3)$$

Figure 2 is a 3D representation of the simultaneous effect of ultrasound and microwave irradiation. As shown in the figure, conversion increases over irradiation time however, longer treatments became deleterious as transesterification is a reversible reaction. Results suggest that the range of conditions within which it is possible to reach a conversion of over 96% is quite broad. The optimal irradiation times were 129 s for microwaves and 136 s for ultrasound, which gave a conversion rate of 97.16%. Optimal conditions from model assessment gave a slightly lower conversion (96.08) which is somewhat smaller than the obtained value.

The Box-Behnken experimental design was utilized in the search for the best parameters and conditions for biodiesel production and methyl ester percentage (i.e. reaction temperature, molar ratio and catalyst amount). A total of 17 experiments (3 replications) were performed for the RSM optimization of three parameters at three levels [44]. The results of these experiments are presented in Table 6, with the highest conversion efficiency achieved at the molar ratio of 9:1, catalyst concentration of 1% and reaction temperature of 57.5°C.

ANOVA investigated the significant effect of each independent variable on the dependent variable and also the mutual effect of independent variables. ANOVA results for the effect of the various variables on oil-to-biofuel conversion percentage are presented in Table 7.

As shown in the ANOVA results table, the lack-of-fit-test was nonsignificant. This indicates that the model can be well fitted to the study data. By contrast, the response with a 95% coefficient of determination was significant, showing that the model can properly predict data variation trends with a maximum error of 5%. The coefficient of determination, R^2, is expressed as the ratio of model-explained variance to the total variance, which is an indication of goodness of fit.

Multivariate regression analysis resulted in a second-order multinomial model for response prediction. Eq. (4) is a second-order multinomial relation based on the variables derived from multivariate regression analysis of empirical data:

$$\text{Conversion rate (\%)} = -249.11 + 12.304X_2 + 73.92X_3 + 0.208X_2X_3 - 0.071X_2^1 - 0.66X_2^2 - 27.839X_3^2 \quad (4)$$

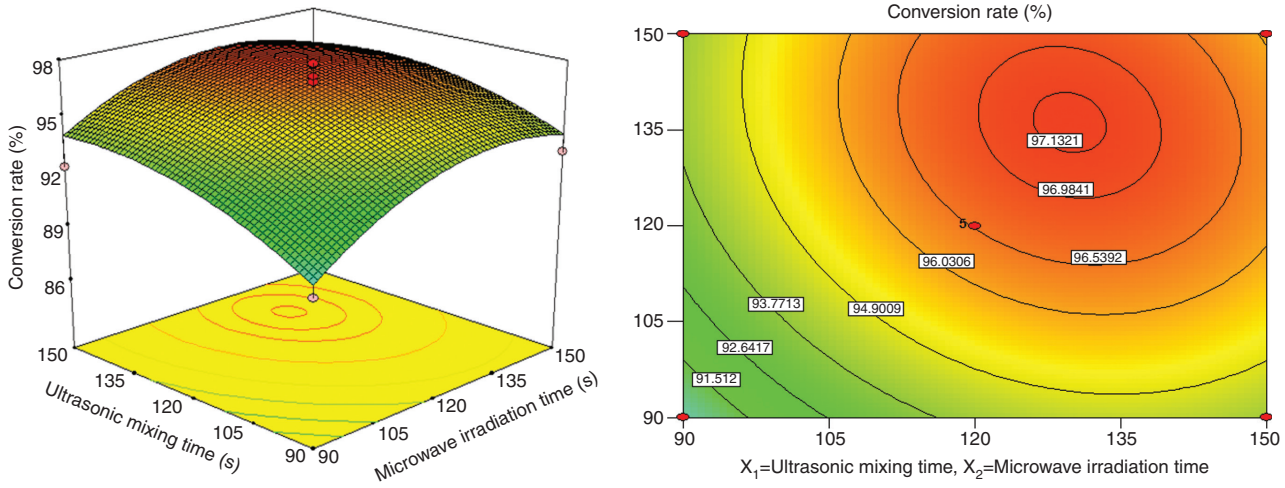

Figure 2: Interaction effect of ultrasound and microwave irradiation on fatty acid methyl ester (FAME) conversion rate.

Table 6: Box-Behnken design for three-level-three-factor response surface analysis.

Run	Std	Reaction temperature	Catalyst amount	Methanol/oil molar ratio	Conversion rate (%)
1	3	-1 (50)	0 (1)	1 (12)	78.86
2	5	-1 (50)	-1 (0.5)	0 (9)	83.48
3	17	0 (57.5)	0 (1)	0 (9)	94.17
4	1	-1 (50)	0 (1)	-1(6)	90.07
5	10	0 (57.5)	-1 (0.5)	1(12)	73.02
6	13	0 (57.5)	0 (1)	0 (9)	96.46
7	11	0 (57.5)	1(1.5)	-1 (6)	92.07
8	2	1 (65)	0 (1)	-1 (6)	94.79
9	12	0 (57.5)	1 (1.5)	1 (12)	81.64
10	16	0 (57.5)	0 (1)	0 (9)	96.78
11	14	0 (57.5)	0 (1)	0 (9)	94.05
12	6	1 (65)	-1 (0.5)	0 (9)	85.2
13	15	0 (57.5)	0 (1)	0(9)	97.5
14	8	1 (65)	1 (1.5)	0 (9)	84.13
15	7	-1 (50)	1 (1.5)	0 (9)	86.5
16	9	0 (57.5)	-1 (0.5)	-1 (6)	84.7
17	4	1 (65)	0 (1)	1 (12)	79.53

Table 7: Analysis of variance table.

Source	df	Sum of square	Mean square	F-value	p-Value
Model	9	90.55	90.55	15.24	0.0008
X_1	1	2.81	2.81	0.49	0.5138
X_2	1	295.00	295.00	49.66	0.0002
X_3	1	40.23	40.23	6.77	0.0353
$X_1 \times X_2$	1	4.10	4.10	0.69	0.4335
$X_2 \times X_1$	1	4.18	4.18	0.70	0.4292
$X_2 \times X_3$	1	0.39	0.39	0.066	0.0050
X_1^2	1	67.53	67.53	11.37	0.0119
X_2^2	1	150.31	150.31	25.30	0.0015
X_2^2	1	203.95	203.95	34.33	0.0006
Residual	7	41.58	5.94		
Lack of fit	3	31.58	10.53	4.21	0.0994
Pure error	4	10.01	2.50		
Total	16	856.56			

Eq. (4) suggests that palm oil conversion percentage has a linear and second-order relationship with the selected parameters. A positive sign indicates a synergic effect and a negative sign denotes an antagonistic one (i.e. a negative impact on the conversion percent).

ANOVA results showed that effects from alcohol/oil molar ratio and catalyst amount are significant at the 1% and 5% levels, respectively. The temperature factor, however, had no significant effect on the reaction efficiency within the study temperature range. The significance of these effects indicates the importance and effectiveness of the study's independent variables. The F-statistic value suggests that the alcohol/oil molar ratio had a larger effect than other parameters. The interaction between temperature and molar ratio and also between temperature and catalyst amount were nonsignificant. The interaction between catalyst amount and molar ratio was, however, significant. The 3D response surface and the 2D contour plots are generally the graphical representations of the regression equation, and the 2D contour plots are presented in Figures 3–5.

Figures 3 and 4 show that an increase in temperature can enhance FAME conversion because the transesterification reaction is both endothermic and reversible. The increasing trend continues until the optimal set up is reached (at 58°C, according to the figure). Further temperature increases negatively affected the equilibrium and promoted saponification. Other parameters were at the center point in the figure. Acoustic cavitation is much weaker at higher temperatures and methanol evaporation is higher, causing poor mass transfer and lower FAME conversion.

According to Figure 4, increasing catalyst loading from 0.5% to 1% improved the reaction yield. Further concentration increase was not effective. This is due to the saponification side-reaction between the excess catalyst and fatty acids derived from the triglyceride branch, which impedes the transesterification reaction and thus reduces yields.

The reaction stoichiometry gave a 3:1 molar ratio for alcohol/oil and three different ratios were used (6:1, 9:1 and 12:1) [45]. It was found that molar ratios higher than 6:1 were ineffective. Once the initial point was passed, the yield slightly increased and then took a mild decreasing trend to the middle point from where it followed a much steeper decreasing slope. Figure 5.

The reason behind the decrease in yield after optimal conditions is that the excess alcohol, in molar ratios higher than 7:1, makes it more soluble in the produced glycerin which, in turn, causes reversibility in the reaction. Moreover, its yield first increased and then decreased with increasing time. Glycerin and methanol are both polar and dissolve in each other. Therefore, more glycerin is produced in longer reaction times which dissolves more methanol and makes it less accessible to the reaction; a typical equilibrium plateau in which the reaction does not reach completion [45].

Under optimized conditions (58.4°C, molar ratio 7:3, and catalyst amount 1.09) the conversion rate was 97.53%. The study results are in agreement with those reported in other papers [19, 23]. Moreover, the reaction time was shorter than all previous studies which use consecutive and single microwave or ultrasound irradiation

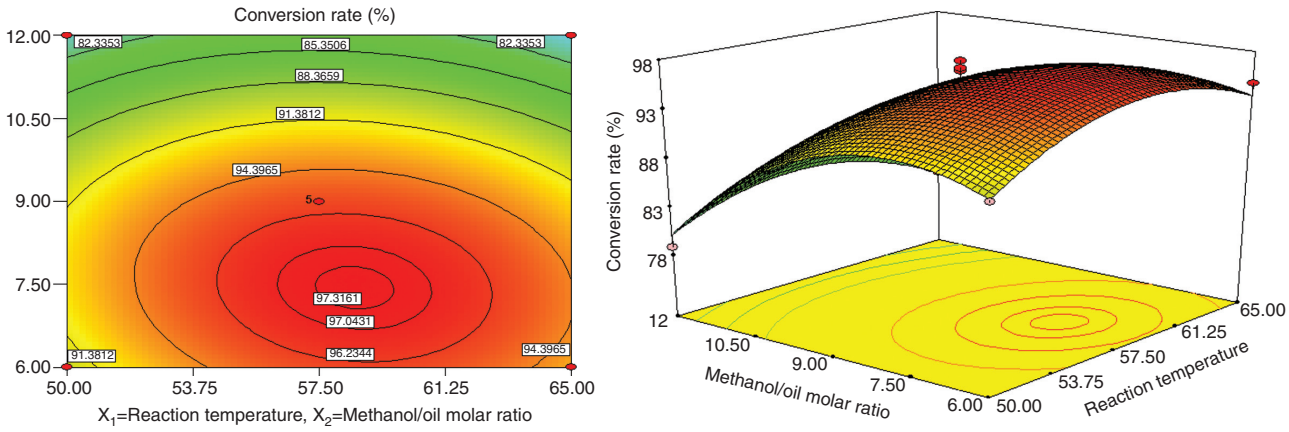

Figure 3: Interaction effect between reaction temperature and methanol/oil molar ratio on FAME Conversion rate.

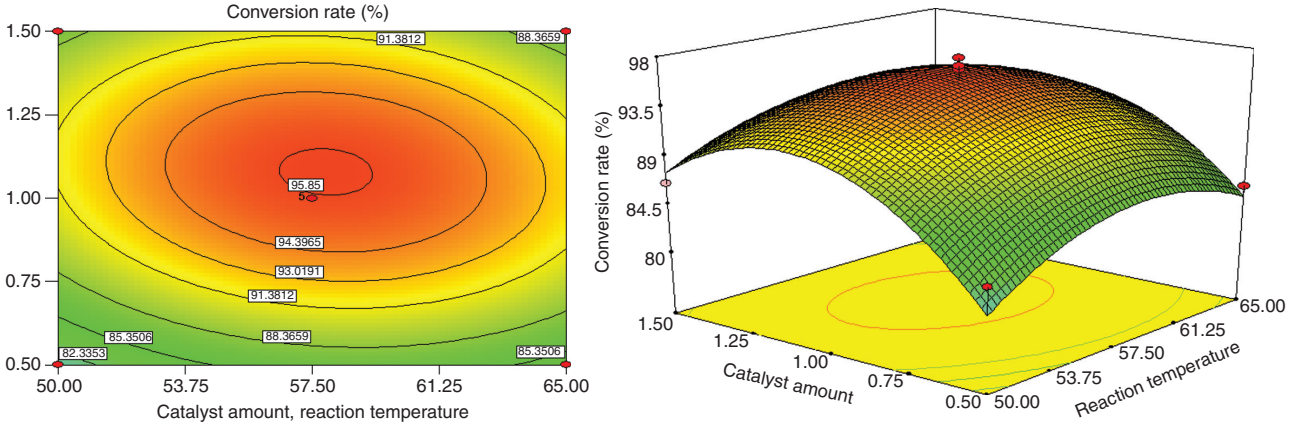

Figure 4: Interaction effect between reaction temperature and catalyst amount on FAME conversion rate.

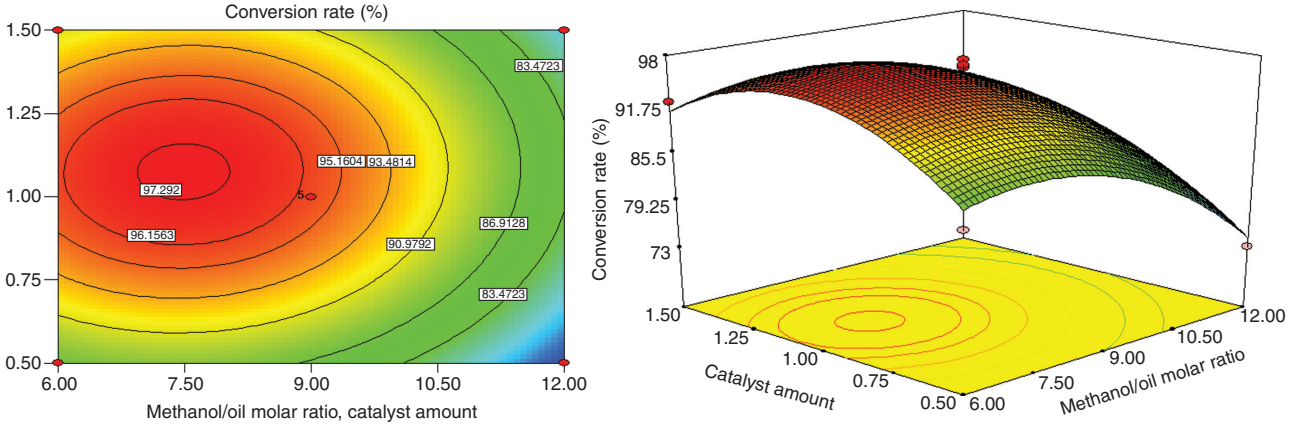

Figure 5: Interaction effect between catalyst amount and methanol/oil on FAME conversion rate.

[19, 33]. In a previous study under microwave irradiation a biodiesel yield of 93.5% was reported (methanol/waste cooking oil molar ratio 6:1, irradiation 5 min) [38] and under sonochemical conditions 90% yield was achieved (methanol/oil molar ratio 12:1, sonication 30 min) [2]. In our optimized conditions of simultaneous ultrasonic/microwave irradiation, all the tests afforded higher yields in only 2 min.

Table 8: Biodiesel physicochemical properties.

Parameter	Unit	Palm biodiesel	EN 14105/ ASTM 6751
Methyl ester content	% Mass	98	≥96.5
Viscosity (40°C)	(mm^2/s)	4.62	1.9–6.0
Density	Kg/m^3	860	860–890
Flash point	°C	175	≥130
Pour point	°C	-2	-10 to 12
Total glycerol	Mass%	0.097	≤0.25
Free glycerol	Mass%	<0.001	≤0.02
Monoglyceride	Mass%	0.34	≤0.80
Diglyceride	Mass%	0.08	≤0.20
Water content	wt.%	0.05	–

In this study, the chemical composition and the main physical properties of the biodiesel obtained are summarized in Table 8.

5 Validation experiments

The optimized reaction conditions for fast transesterification under ultrasound/microwave irradiation have been defined in this study. The response surface analysis predicted the optimum points for a 97.53% yield. These are: a temperature of 58.4°C, a molar ratio of 7:3 and a relative catalyst amount of 1.09. The experiment was then performed at the RSM-predicted optimum point. The experimental reaction yield was just slightly lower than the predicted value (96.71 vs. 97.53). This difference was assessed as acceptable according to the ANOVA results and significance table at the 5% level, which is in practice a random noise caused by instruments or operators.

6 Conclusions

RSM has been used to optimize the reaction conditions of palm oil transesterification under simultaneous ultrasound/microwave irradiation. Findings suggest that study parameters (i.e. sonication time, microwave irradiation time, catalyst amount and molar ratio) have significant effects on methyl ester production rate. The simultaneous application of ultrasound and microwaves can dramatically improve reaction outcome and yield. This hybrid technique has reduced reaction times compared to traditional methods and even compared to previous works where ultrasound and microwaves have been applied in a sequential mode. Several studies have reported that microwaves are effective due to selective volumetric heating. This work has proven that simultaneous irradiation provokes an additive effect on the reaction rate, via an increase in contact area between oil and alcohol, leading to faster reaction. Simultaneous application can also address the issues facing consecutive application. In this experiment, all samples of the biodiesel produced complied with ASTM regulations. The total energy consumption for the transesterification reaction under simultaneous ultrasound/microwave irradiation was much lower than conventional method (0.36 MJ/l vs. 1.92 MJ/l (heating+stirring 400 W for 40 min). The simultaneous irradiation can reduce transesterification time by 26.4 times over the traditional method.

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References

[1] Shafiee S, Topal E. *Energy Policy* 2008, 36, 775–786.
[2] Talebian-Kiakalaieh A, Amin NAS, Mazaheri H. *Appl. Energy* 2013, 104, 683–610.
[3] Safieddin Ardebili M, Ghobadian B, Najafi G, Chegeni A. *Renewable Sustainable Energy Rev.* 2011, 15, 3041–3044.
[4] Najafi G, Ghobadian B, Yusaf TF. *Renewable Sustainable Energy Rev.* 2011, 15, 3870–3876.
[5] Shahriar S, Erkan T. *Energy Policy* 2009, 37, 181–189.
[6] Murugesan A, Umarani C, Chinnusamy TR, Krishnan M, Subramanian R, Neduzchezhain, N. *Renewable Sustainable Energy Rev.* 2009, 13, 825–834.
[7] Morschhäuser R, Krull M, Kayser C, Boberski C, Bierbaum R, Püschner PA, Glasnov TN, Kappe CO. *Green Process Synth.* 2010, 1, 281–290.
[8] Cintas P, Mantegna S, Calcio Gaudino E, Cravotto G. *Ultrason. Sonochem*. 2010, 17, 985–989.
[9] Kocar G, Civas N. *Renewable Sustainable Energy Rev.* 2013, 28, 900–916.
[10] Basumatary S. *Res. J. Chem. Sci.* 2013, 3, 99–93.
[11] Khalzani K, Khalisanni K. *J. Appl. Sci.* 2011, 8, 804–809.
[12] Aqeel AB, Gholamreza Z, Haslenda H. *Renewable Sustainable Energy Rev.* 2011, 15, 574–583.
[13] Kapilan N, Baykov BD. *Pet. Coal* 2014, 56, 62–73.
[14] Martinez M, Vicente G, Aracil J. *Bioresour. Technol.* 2007, 98, 1724–1733.
[15] El-Amin M. *Mass Transfer in Multiphase Systems and its Applications*. India, In tech, 2011.
[16] Safieddin Ardebili M, Tavakoli Hashjin T, Ghobadian B, Najafi GH. *J. Middle East Appl. Sci. Technol.* 2014, 6, 149–155.
[17] Gole VL, Gogate PR. *Fuel Process Technol.* 2012, 16, 62–69.
[18] Leonelli C, Mason TJ. *Chem. Eng. Process. Int.* 2010, 49, 885–900.

[19] Cravotto G, Cintas P. *Chemistry* 2007, 13, 1902–1909.
[20] Hsiao MC, Lin CC, Chang YH, Chen LC. *Fuel* 2010, 89, 3618–3622.
[21] Cravotto G, Cintas P. *The Combined Use of Microwaves and Ultrasound. Methods and Practice in Microwaves in Organic Synthesis*, 3rd ed., Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2012.
[22] Qiu Z, Zhao L, Weatherley L. *Chem. Eng. Process. Int.* 2010, 49, 323–330.
[23] Choedkiatsakul I, Ngaosuwan K, Cravotto G, Assabumrungrat S. *Ultrason. Sonochem*. 2014, 21, 1585–1591.
[24] Lee SB, Lee JD, Hong IK. *J. Ind. Eng. Chem.* 2011, 17, 138–143.
[25] Thanh LT, Okitsu K, Sadanaja Y, Takenaka N, Maea Y, Bandow H. *Bioresour. Technol.* 2010, 101, 639–645.
[26] Deshmane VG, Gogate PR, Pandit AB. *Ultrason. Sonochem.* 2009, 16, 345–350.
[27] Stavarache C, Vinatoru M, Nishimura R, Maeda Y. *Ultrason. Sonochem*. 2005, 12, 367–372.
[28] Hanh HD, Okitsu K, Nishimura R, Maeda Y. *Renew. Energ.* 2009, 34, 766–768.
[29] Santos FFP, Rodrigues S, Fernandes FAN. *Fuel Process Technol.* 2009, 90, 312–316.
[30] Kelkar MA, Gogate PR, Pandit AB, *Ultrason. Sonochem.* 2008, 15, 188–194.
[31] Singh AK, Fernando SD, Hernandez R. *Energ. Fuels* 2007, 21, 1161–1164.
[32] Encinar J, González J, Martínez G, Sánchez N, Pardal A. *Fuel* 2012, 95, 386–393.
[33] Motasemi FN, Ani FN. *Renewable Sustainable Energy Rev.* 2012, 16, 4719–4733.
[34] Gude VG, Patil P, Martinez-Guerra E, Deng S, Nirmalakhandan N. *Sustainable Chem. Process.* 2013, 1, 1–31.
[35] Hernando J, Leton P, Matia MP, Novella JL, Alvarez-Builla J. *Fuel* 2006, 86, 1641–1644.
[36] Perin C, Álvaro G, Westphal E, Viana LH, Jacob RG, Lenardão EJ. *Fuel* 2008, 87, 2830–2841.
[37] Azcan N, Danisman A. *Fuel* 2008, 87, 1781–1788.
[38] Azcan N, Yilmaz O. *Fuel* 2013, 104, 614–419.
[39] Choedkiatsakul I, Ngaosuwan K, Assabumrungrat S, Tabasso S, Cravotto G. *Biomass Bioenerg.* 2015, 77, 186–191.
[40] Patil PD, Gude VG, Mannarswamy A, Cooke P, Munson-McGee S, Nirmalakhandan N, Lammers P, Deng S. *Bioresour. Technol.* 2011, 102, 1399–1305.
[41] Cintas P, Barge A, Tagliapietra T, Boffa L, Cravotto G. *Nature Prot.* 2010, 5, 607–616.
[42] Sharma Siddharth Jain MP, Rajvanshi S. *Fuel Process Technol.* 2011, 92, 32–38.
[43] Yuan JLX, Zeng G, Shi J, Tong J, Huang G. *Renew. Energ.* 2008, 33, 1678–1684.
[44] Montgomery DC. *Design and Analysis of Experiments*. 8th ed., John Wiley & Sons: New York, 2012.
[44] Gerpen JV. *Fuel Process Technol.* 2005, 86, 1097–1007.

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