

## Non-thermal effects of microwaves and kinetics on the transesterification of soybean oil

Ming-Chien Hsiao<sup>\*1</sup>, Pei-Hung Liao<sup>1</sup> and Li-Wen Chang<sup>2</sup>

<sup>1</sup>Department of Environmental Engineering, Kun Shan University, Tainan City, Taiwan

<sup>2</sup>Department of Materials Engineering, Kun Shan University, Tainan City, Taiwan

(Received June 25, 2012, Revised August 7, 2012, Accepted August 14, 2012)

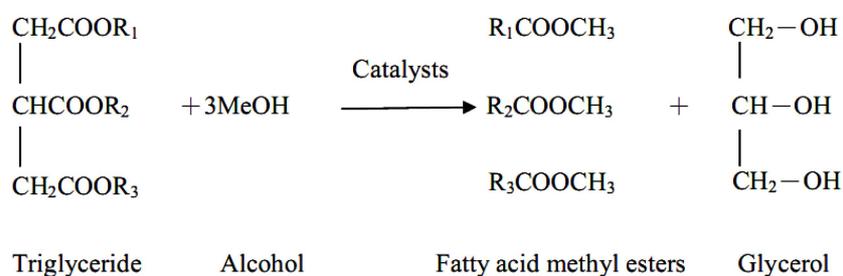
**Abstract.** A kinetic study of the transesterification of soybean oil was conducted using microwaves under various temperatures, power densities, and reaction times. Results show that power density affects the kinetics and yield. The biodiesel yield increased with increasing microwave power density. The non-thermal effects of microwave irradiation on transesterification reactions were evaluated at a constant reaction temperature (65°C) and power density (0.204 Wg<sup>-1</sup>). Microwave irradiation was found to increase the reaction rates by 3.52–7.06 fold.

**Keywords:** biodiesel; transesterification; microwave; non-thermal effects; kinetics

### 1. Introduction

The limited supply of fossil fuels and greenhouse gas emissions have motivated research into alternative renewable fuels. A promising approach is the conversion of vegetable oils (VOs) and other feedstocks, which primarily contain triglycerides (TG) and free fatty acids (FFA), into biodiesel (Lopez *et al.* 2005).

TG are esters derived from glycerol and three fatty acids. When TG react with an alcohol, three fatty acid chains are liberated from the glycerol skeleton and combine with the alcohol to yield biodiesel (fatty acid methyl esters, FAME). Glycerol is produced as a by-product, as shown in Scheme 1 (Bournay *et al.* 2005, Zhang *et al.* 2003).



Scheme 1 Transesterification of triglyceride with alcohol

\*Corresponding author, Professor, E-mail: [johnson@mail.ksu.edu.tw](mailto:johnson@mail.ksu.edu.tw)

The following processes are used for biodiesel production: (1) transesterification, (2) microemulsions, (3) blending, and (4) pyrolysis. Transesterification, the most commonly used method, is a catalyzed (based-catalyzed or acid-catalyzed) chemical reaction involving triglyceride and an alcohol that produces fatty acid alkyl esters (i.e., biodiesel) and glycerol. An alkali process can achieve high purity and yield of the biodiesel product for 30–60 min (Vicente *et al.* 2004, Ghadge and Raheman 2006, Wang *et al.* 2006).

Microwave irradiation activates the smallest degree of variance of polar molecules and ions in the mixture of vegetable oil, potassium hydroxide, and methanol. The polar and ionic components interact with molecular dipoles and charged ions, making the molecules and ions rotate rapidly. Heat is generated due to molecular friction. A rapid microwave-accelerated derivatization process for the GC–MS analysis of steroid estrogens, 60 s irradiation at 800W was found as efficient as the conventional heating in a sand bath at 80°C for 30 min (Zuo *et al.* 2007). Microwave irradiation thus enhances the chemical reaction and increases yield within a short time. When the reaction is carried out under microwave irradiation, the reaction time of transesterification decreases and high-purity biodiesel is obtained with reduced energy consumption (Leadbeater and Stencel 2006, Azcan and Danisman 2007, Barnard *et al.* 2007, Hernando *et al.* 2007, Wang *et al.* 2010, Fan *et al.* 2011).

In the present study, results show that the optimal conditions are 1 min of ultrasonic mixing and 2 min of closed microwave irradiation. The closed microwave irradiation has several advantages, for example, not only does closed microwave irradiation require no stirring and cooling facility, it also reduces volatilization of alcohol (Hsiao *et al.* 2010).

Although microwave irradiation is commonly used to enhance the reaction rates of chemical reactions, few studies have been conducted on the non-thermal effects of microwave irradiation and kinetics on transesterification reactions. In addition, the proposed mechanisms do not explain the reported high yields and rapid conversions. Most studies have used domestic ovens and the thermal and non-thermal effects have not been distinguished (Roy and Gupta 2003, Diasakou *et al.* 1998, Kusdiana and Saka 2001).

Several previous studies have proved that reaction temperature (Hanh *et al.* 2009, Colucci *et al.* 2005, Hanh *et al.* 2008, Koc 2009, Hsiao *et al.* 2010, Hsiao *et al.* 2011, Satyanarayana and Muraleadharan 2011) influence the transesterification significantly. Thus, this study focuses on the influence of power density, reaction temperature, the non-thermal effect of microwaves, and kinetics on transesterification.

## 2. Materials and methods

### 2.1 Materials

Sodium hydroxide (NaOH) (99% purity) and methanol (99.8% purity) were purchased from Shimakyu Co. Ltd. (Japan), and methyl laurate and acetic acid were purchased from Fluka Co. Ltd. (USA). Soybean oil was purchased from a local grocery store. The acid value (KOH mg/g) and saponification value (KOH mg/g) were determined using a standard titrimetric method (AOCS: American Oil Chemists' Society). The experimental results of acid value, saponification value, and molecular weight were 0.056, 194.985, and 863.314, respectively.

## 2.2 Experimental procedure

This process was carried out using a 6:1 methanol/oil molar ratio, 100 g of soybean oil, and 1 wt% (based on the weight of soybean oil) sodium hydroxide at various temperatures using microwave irradiation.

The water bath process experiment was carried out using a 6:1 methanol/oil molar ratio, 100g of soybean oil, and 1wt% (based on the weight of soybean oil) of sodium hydroxide at 65°C by mechanical stirring (350 rpm). All reactants were set to 30, 45, and 65°C preheating in the water bath before reaction, respectively, which kept the overall reaction temperature constant during microwave irradiation.

## 2.3 Equipment

Reactions were performed using a commercially available microwave apparatus (Milestone). The machine consists of a continuous microwave power delivery system with power output from 0 to 900 W. The microwave oven was modified by introducing a water condenser to conduct atmospheric pressure experiments (Fig. 1). The mixer shaft was equipped with a Teflon blade and the reactants were stirred at 350 rpm, which was sufficient to keep the system uniform in both temperature and suspension. Spherical glass reactors with volumes of 250 ml were loaded with the mixture and directly exposed to the microwave field. After the reaction, the mixture was allowed to settle and the FAME fraction that separated at the top was removed in a separating funnel. The methyl ester biodiesel phase was washed at least three times with acetate 30% and deionized water, and finally dried at  $378 \pm 3$  K in an oven (Cheng *et al.* 2006a, b).



Fig. 1 Modified microwave heating system used for transesterification reactions

### 2.4 Analytical methods

The samples were analyzed with a Perkin Elmer GC Clarus 600 equipped with a capillary column (SPBTM-WAX,  $30\text{ m} \times 0.75\text{ mm} \times 1.0\text{ }\mu\text{m}$ ) and a flame ionization detector (FID). Methyl laurate was added as an internal standard into the crude biodiesel. The sample was injected under the following conditions: the carrier gas was nitrogen, the injector temperature was  $280^\circ\text{C}$ , the split ratio was 1:20, and the temperature of the detector was  $300^\circ\text{C}$ . The oven temperature program was:  $210^\circ\text{C}$  for 4 min, increased to  $240^\circ\text{C}$  at a rate of  $4^\circ\text{C}/\text{min}$ , and held for 8 min (Wang *et al.* 2007).

### 3. Results and discussion

Fig. 2 shows the non-thermal effects of microwave irradiation on transesterification reactions evaluated at a constant reaction temperature ( $65^\circ\text{C}$ ) and power density ( $0.204\text{ Wg}^{-1}$ ). The biodiesel yield was 97.81% at 5 min with microwave irradiation. The biodiesel yield was only 27.77% at 5 min with mechanical stirring. Therefore, the non-thermal effects of microwave irradiation on transesterification reactions greatly increase the biodiesel yield.

Table 1 shows the non-thermal effects of microwave irradiation on transesterification reactions evaluated at a constant reaction temperature ( $65^\circ\text{C}$ ) and power density ( $0.204\text{ Wg}^{-1}$ ). Results show that microwave irradiation increased the reaction rates by 3.52 (at 5 min) to 7.06 (at 1 min) fold. The change in rate gradually decreased with reaction time. The non-thermal effects gradually decreased with increasing reaction time. This can be attributed to the microwave irradiation accelerating the methanol to achieve boiling point. Soybean oil has dielectric constants in a range of

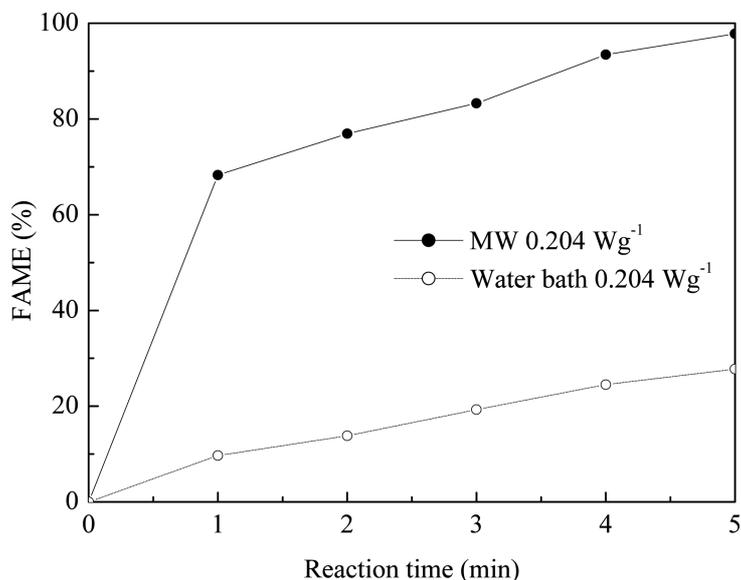


Fig. 2 Influence of microwave irradiation and water batch reaction time and mechanical stirring at 350 rpm on the yield of biodiesel production (experimental conditions: methanol/oil molar ratio of 6:1, NaOH 1 wt%, and temperature of  $65^\circ\text{C}$ )

Table 1 Non-thermal effect of microwave irradiation on transesterification

Reaction time (min)	Biodiesel yield (%)		Change in rate (MW/MS)
	MW	MS	
1	68.29	9.67	7.06
2	76.94	13.82	5.57
3	83.26	19.29	4.32
4	93.44	24.49	3.82
5	97.81	27.77	3.52

MW: Microwave

MS: Mechanical stirring

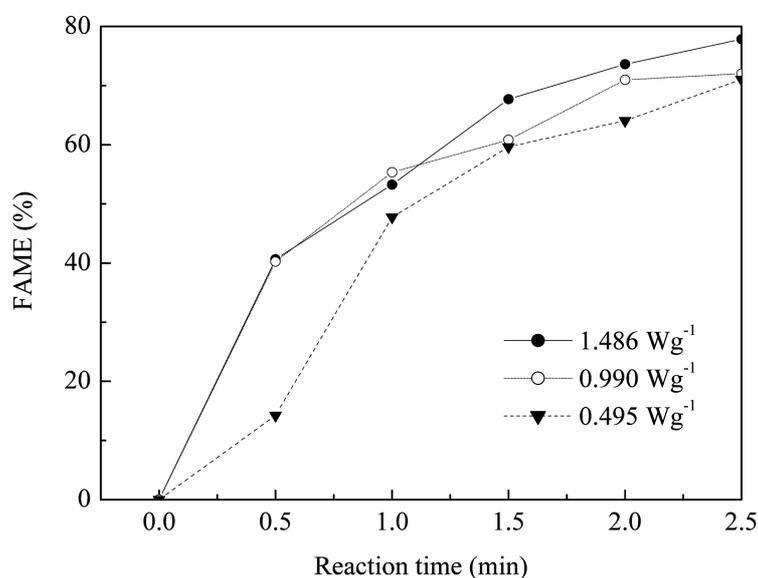


Fig. 3 Influence of microwave reaction time on the yield of biodiesel production (experimental conditions: methanol/oil molar ratio of 6:1, NaOH 1 wt%, and temperature of 30°C)

2 to 4. The dielectric constant of methanol is 33 (Carey and Hayzen 2001, Innawong *et al.* 2004, Navas *et al.* 2007). At the start of the reaction, the methanol absorbed a high level of microwave power. However, for the transesterification reaction after a few minutes at 65°C, the change in rate decreased due to dielectric loss caused by reduced methanol content.

The effects of power density, reaction time, and temperature of microwave irradiation on transesterification were investigated at 0.5-2.5 min. Figs. 3, 4, and 5 shows the influence of the reaction time on the yield of biodiesel production at 30-65°C. The biodiesel yield increased with increasing power density of microwave irradiation. This can be attributed to the power density inducing a mass transfer driving force, which increased the yield. It was observed that the yield was positively correlated with power density. In addition, the biodiesel yield increased with increasing reaction temperature at a given microwave power density. At a power density of 1.486 Wg<sup>-1</sup>, the FAME yield was 77.85% at 30°C (Fig. 3) and increased to 97.7% at 65°C (Fig. 5) for 2.5 min.

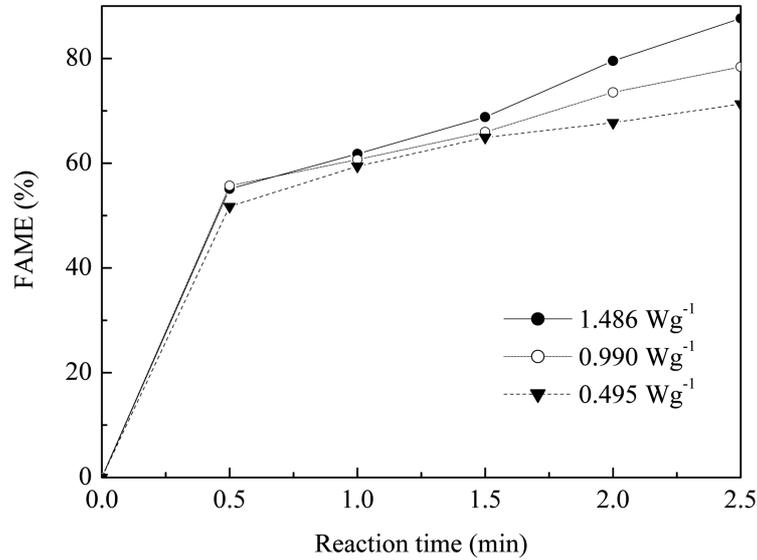


Fig. 4 Influence of microwave reaction time on the yield of biodiesel production (experimental conditions: methanol/oil molar ratio of 6:1, NaOH 1 wt%, and temperature of 45°C)

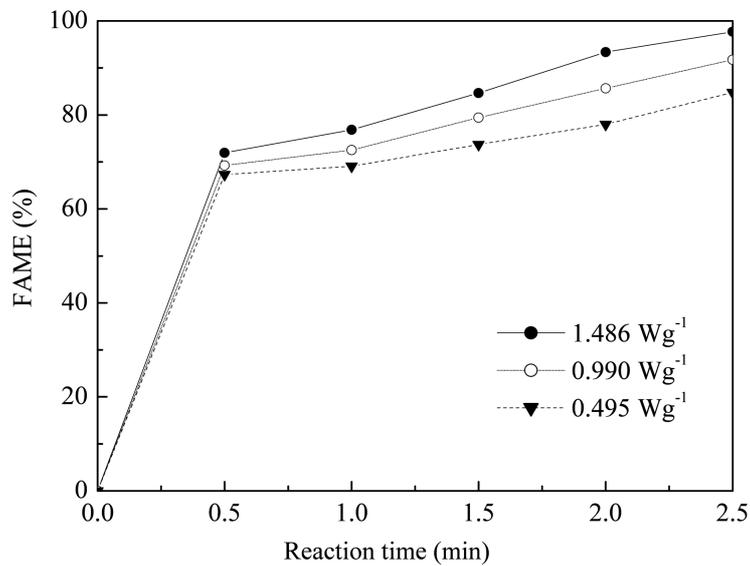


Fig. 5 Influence of microwave reaction time on the yield of biodiesel production (experimental conditions: methanol/oil molar ratio of 6:1, NaOH 1 wt%, and temperature of 65°C)

Therefore, the effect of reaction temperature on the FAME yield was greater than that of the power density. According to Carey and Hayzen (2001), as the temperature increases, the dielectric constant decreases as a result of the decreased polarizability of larger molecules.

According to Kusdiana and Saka (2001), the reaction proceeded as a first-order reaction as a

Table 2 Rate constant of transesterification reaction (experimental conditions: methanol/oil molar ratio of 6:1, catalysts 1 wt%, and reaction time of 2.5 min)

°C	$k$ (s <sup>-1</sup> )		
	Power density (Wg <sup>-1</sup> )		
	0.495	0.990	1.486
30	0.008	0.009	0.010
45	0.008	0.010	0.014
65	0.013	0.017	0.025

function of the concentration of triglycerides (TG) and reaction temperature. The rate constant of the reaction was determined based on the decreased amount of unmethyl-esterified [*uMEs*] compounds, which include triglycerides, diglycerides, monoglycerides, and unreacted free fatty acids.

$$\frac{-d[uMEs]}{dt} = k[uMEs] \quad (1)$$

Assuming that the initial concentration of *uMEs* = 100% and that it falls to *uMEs*, *t* at some reaction time *t*, the integration gives

$$\frac{\ln[uMEs, t] - [uMEs, 0]}{t} = k \quad (2)$$

A kinetic study of the transesterification of soybean oil was conducted under microwave irradiation at various temperatures, power densities, and reaction times.

Table 2 shows the rate constant of the transesterification reaction obtained from Figs. 3-5. The rate constant increased with increasing microwave power density and reaction temperature. The rate constant slightly increased from 0.008 to 0.010 s<sup>-1</sup> when the power density was increased from 0.495 Wg<sup>-1</sup> to 1.486 Wg<sup>-1</sup> at 30°C. The rate constant significantly increased from 0.008 to 0.013 s<sup>-1</sup> when the reaction temperature was increased from 30°C to 65°C. When the power density was increased from 0.495 Wg<sup>-1</sup> to 1.486 Wg<sup>-1</sup>, the rate constant greatly increased from 0.013 to 0.025 s<sup>-1</sup> at 65°C. Table 2 shows increase the reaction temperature with the increased rate constant by 1.5 times at power density 0.495 Wg<sup>-1</sup>. However, increase the reaction temperature with the increased rate constant approximately by 1.5-2.5 times at power density 0.990 Wg<sup>-1</sup> and 1.486 Wg<sup>-1</sup>, respectively. The rate constant significantly increased when the reaction temperature was at 65°C, due to the temperature change the phase equilibrium of the mixture and increase in the concentration of methanol in the vapor phase at 65°C (the methanol boiling point is 64.5°C) and increase the mixing rate in the liquid phase. Therefore, the rate constant increased with reaction temperature at a given power density.

#### 4. Conclusions

The non-thermal effect of microwaves and kinetics on transesterification was investigated. The biodiesel yield increased with increasing microwave power density. This can be attributed to the

microwave irradiation accelerating the methanol to achieve boiling point. The rate constant increased with increasing reaction temperature at a given power density. Therefore, the effect of reaction temperature on the rate constant is greater than that of the power density. Microwave irradiation was found increase the reaction rates by 3.52–7.06 fold. However, the non-thermal effects gradually decreased with increasing reaction time. This can be attributed to the lower reaction rate due to dielectric loss caused by reduced methanol content. The FAME yield was 97.7% at a power density of  $1.486 \text{ Wg}^{-1}$  for 2.5 min. Therefore, microwave irradiation has potential application in the biodiesel fuel industry.

## References

- Azcan, N. and Danisman, A. (2007), "Alkali catalyzed transesterification of cottonseed oil by microwave irradiation", *Fuel*, **86**(17-18), 2639-2644.
- Barnard, T.M., Leadbeater, N.E., Boucher, M.B., Stencel, L.M. and Wilhite, B.A. (2007), "Continuous-flow preparation of biodiesel using microwave heating", *Energ. Fuel*, **21**(3), 1777-1781.
- Bournay, L., Casanave, D., Delfort, B., Hillion, G. Chodorge, J.A. (2005), "New heterogeneous process for biodiesel production: A way to improve the quality and the value of the crude glycerin produced by biodiesel plants", *Catal. Today*, **106**(1-4), 190-192.
- Carey, A.A. and Hayzen, A.J (2001), *The Dielectric Constant and Oil Analysis*, Practicing Oil Analysis Magazine, September.
- Cheng, W.M., Raghavan, G.S.V., Ngadi, M. and Wang, N. (2006a) "Microwave power control strategies on the drying process I. Development and evaluation of new microwave drying system", *J. Food Eng.*, **76**(2), 188-194.
- Cheng, W.M., Raghavan, G.S.V., Ngadi, M. and Wang, N. (2006b), "Microwave power control strategies on the drying process II. Phase-controlled and cycle-controlled microwave/air drying", *J. Food Eng.*, **76**(2), 195-201.
- Colucci, J.A., Borrero, E.E. and Alape, F. (2005), "Biodiesel from an alkaline transesterification reaction of soybean oil using ultrasonic mixing", *J. Am. Oil Chem. Soc.*, **82**(7), 525-530.
- Diasakou, M., Louloudi, A. and Papayannakos, N. (1998), "Kinetics of the non-catalytic transesterification of soybean oil", *Fuel*, **77**(12), 1297-1302.
- Fan, L., Jin, R., Liu, Y., An, M. and Chen, S. (2011), "Enhanced extraction of patchouli alcohol from Pogostemon cablin by microwave radiation-accelerated ionic liquid pretreatment", *J. Chromatogr. B.*, **879**, 3653-3657.
- Ghadge, S.V. and Raheman, H. (2006), "Process optimization for biodiesel production from mahua (*Madhuca indica*) oil using response surface methodology", *Bioresour. Technol.*, **97**(3), 379-384.
- Hanh, H.D., Dong, N.T., Okitsu, K., Nishimura, R. and Maeda, Y. (2009), "Biodiesel production through transesterification of triolein with various alcohols in an ultrasonic field", *Renew. Energ.*, **34**(3), 766-768.
- Hanh, H.D., Dong, N.T., Starvarache, C., Okitsu, K., Maeda, Y., Nishimura, R. (2008), "Methanolysis of triolein by low frequency ultrasonic irradiation", *Energ. Conv. Manage.*, **49**(2), 276-280.
- Hernando, J., Leton, P., Matia, M.P., Novella, J.L. and Alvarez, B.J. (2007), "Biodiesel and FAME synthesis assisted by microwaves: Homogeneous batch and flow processes", *Fuel*, **86**(10-11), 1641-1644.
- Hsiao, M.C., Lin, C.C. and Chang, Y.H. (2011), "Microwave irradiation-assisted transesterification of soybean oil to biodiesel catalyzed by nanopowder calcium oxide", *Fuel*, **90**(5), 1963-1967.
- Hsiao, M.C., Lin, C.C., Chang, Y.H. and Chen, L.C. (2010), "Ultrasonic mixing and closed microwave irradiation-assisted transesterification of soybean oil", *Fuel*, **89**(12), 3618-3622.
- Innawong, B., Mallikarjunan, P., Irudayaraj, J. and Marcy, J.E. (2004), "The determination of frying oil quality using Fourier transform infrared attenuated total reflectance", *LWT-Food Sci. Technol.* **37**(1), 23-28.
- Koc, A.B. (2009), "Ultrasonic monitoring of glycerol settling during transesterification of soybean oil", *Bioresour. Technol.*, **100**(1), 19-24.
- Kusdiana, D. and Saka, S. (2001), "Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in

- supercritical methanol”, *Fuel*, **80**(5), 693-698.
- Leadbeater, N.E. and Stencel, L.M. (2006), “Fast, easy preparation of biodiesel using microwave heating”, *Energ. Fuels*, **20**(5), 2281-2283.
- Lopez, D.E., Goodwin, J.G. Jr., Bruce, D.A. and Lotero E. (2005), “Transesterification of triacetin with methanol on solid acid and base catalysts”, *Appl. Catal. A-Gen.*, **295**(2), 97-105.
- Navas, J.A., Tres, A., Bou, R., Codony, R. and Guardiola, F. (2007), “Optimization of analytical methods for the assessment of the quality of fats and oils used in continuous deep fat frying”, *Grasas Aceites*, **58**(2), 148-153.
- Roy, I. and Gupta, M.N. (2003), “Non-thermal effects of microwaves on protease-catalyzed esterification and transesterification”, *Tetrahedron*, **59**(29), 5431-5436.
- Satyanarayana, M. and Muraleedharan, C. (2011), “A comparative study of vegetable oil methyl esters (biodiesels)”, *Energy*, **36**(4), 2129-2137.
- Vicente, G., Martýnez, M. and Aracil, J. (2004), “Integrated biodiesel production: a comparison of different homogeneous catalysts systems”, *Bioresour. Technol.*, **92**(3), 297-305.
- Wang, P., Zhang, Q., Wang, Y., Wang, T., Li, X., Ding, L. and Jiang, G. (2010), “Evaluation of Soxhlet extraction, accelerated solvent extraction and microwave-assisted extraction for the determination of polychlorinated biphenyls and polybrominated diphenyl ethers in soil and fish samples”, *Anal. Chim. Acta.*, **663**(1), 43-48.
- Wang, Y., Ou, S., Liu, P., Xue, F. and Tang, S. (2006), “Comparison of two different processes to synthesize biodiesel by waste cooking oil”, *J. Mol. Catal. A-Chem.*, **252**(1-2), 107-112.
- Wang, Y., Ou, S., Liu, P. and Zhang, Z. (2007), “Preparation of biodiesel from waste cooking oil via two-step catalyzed process”, *Energ. Convers. Manage.*, **48**(1), 184-188.
- Zhang, Y., Dube, M.A., McLean, D.D. and Kates, M. (2003), “Biodiesel production from waste cooking oil: 1. Process design and technological assessment”, *Bioresour. Technol.*, **89**(1), 1-16.
- Zuo, Y., Zhang, K. and Lin, Y. (2007), “Microwave-accelerated derivatization for the simultaneous gas chromatographic-mass spectrometric analysis of natural and synthetic estrogenic steroids”, *J. Chromatogr. A.*, **1148**(2), 211-218.