



## Original Research Paper

## Biodiesel production from high FFA feedstocks with a novel chemical multifunctional process intensifier

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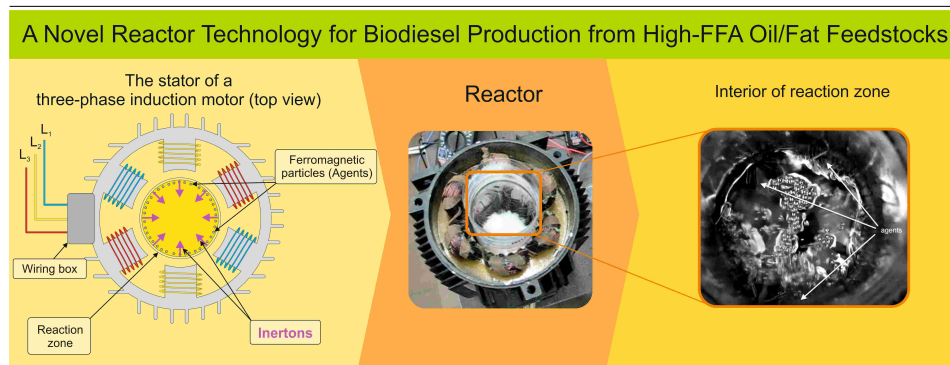
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### HIGHLIGHTS

- A novel chemical multifunctional process intensifier is described.
- Both alkali transesterification and acid esterification reactions are examined.
- Biodiesel production from high FFA oil/fat feedstock is addressed.
- Complete conversion of oils/fats to biodiesel is achieved at very short reaction times and at ambient temperature.
- Using this technology, feedstocks with FFA contents of up to ~9% could be efficiently converted by alkali catalyzed transesterification.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Biodiesel production is generally accomplished by the transesterification of vegetable oils and animal fats with a short chain alcohol (mostly methanol) in the presence of an alkali catalyst (mostly potassium or sodium hydroxide) in continuous stirred tank reactors. This chemical reaction requires heating at around 60°C and usually takes about 60 to 120 min. When using oil/fat feedstocks containing high free fatty acids (FFA) contents, acid esterification is often required to prevent the saponification of fatty acids with the base catalyst in the subsequent transesterification. These impose high energy and time requirements. In the present study, we introduce a novel chemical multifunctional process intensifier involving a reaction zone with magnetostrictive cylindrical particles (agents) subjected to an oscillating electromagnetic field for efficient biodiesel production from high FFA content feedstocks. The results obtained revealed that the esterification and transesterification reactions could be substantially intensified under the action of an oscillating electromagnetic field that forces magnetostrictive agents to rapidly vibrate and intensify the mixing of the reagents. Complete conversion of oils was observed at an extremely short reaction time (30–180 s) and at the ambient temperature. Using the investigated technology, oil/fat mixtures with higher initial FFA contents, i.e., ~9%, could be used in alkali catalyzed transesterification processes compared with conventional reactors (capable of handling FFA contents of ~2.5%).

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## 1. Introduction

Production of renewable fuels and biodiesel in particular has increased during the last years due to the need for alternative and cleaner sources of energy. There are various processes for biodiesel production including homogeneous alkali (base) catalyzed transesterification (Ma and Hanna, 1999; Jeong et al., 2004), homogenous acid catalyzed transesterification (Fukuda et al., 2001), heterogeneous base or acid catalyzed transesterification (Furuta et al., 2006), enzyme catalyzed transesterification (Nelson et al., 1996; Shimada et al., 1999), supercritical alcohol transesterification (Vyas et al., 2010), etc. Microwaves and ultrasound have also been demonstrated to intensify the transesterification process (Ji et al., 2006; Gole and Gogate, 2012a, 2012b, and 2013; Maddikeri et al., 2012; Subbedar et al., 2015; Joshi et al., 2018). Other approaches for the intensification of transesterification reaction include cavitation (Mohod et al., 2017) and high-speed homogenizers (Joshi et al., 2017). Tabatabaei et al. (2019) reviewed conventional and advanced biodiesel production technologies with an in-depth state-of-the-art focus made on transesterification reactors, including tubular/plug-flow, rotating, simultaneous reaction-separation, cavitation, and microwave reactors, with 18 reactor types in total.

The transesterification of oils is a reaction where alcohol (usually methanol) reacts with triglycerides contained in the oil feedstock in the presence of a catalyst (usually alkali) producing fatty acid esters and glycerin. The reaction is carried out in three consecutive steps, leading to the breakdown of each mole of triglycerides into three moles of esters and one mole of glycerin (Noureddini and Zhu, 1997). Transesterification is mainly affected by molar ratio of oil or fat to alcohol, catalyst, reaction time, temperature, free fatty acids (FFA) content, and water content of the feedstock (Freedman et al., 1984; Ma and Hanna, 1999). Oils and fats should ideally be free from water and FFA in order to achieve better conversion rates, however, this is not possible in practice. Various studies demonstrated that water content should be less than 0.06% and FFA less than 0.5% in order to get a desirable conversion (Bradshaw and Meuly, 1944; Freedman et al., 1984; Ma et al., 1998).

Stoichiometrically three moles of methanol are required for each mole of oil or fat. However, in order to promote the reaction, higher molar ratios are used. Bradshaw and Meuly (1944) suggested that favorable molar ratios should be between 3.3–5.25:1 depending on the quality of oils and also on the process (reaction steps). In general, higher molar ratios result in shorter conversion times. A commonly reported molar ratio for promising conversion results is 6:1 (Feuge and Gros, 1949; Freedman et al., 1984 and 1986).

The basic catalyst used is typically sodium hydroxide (NaOH) or potassium hydroxide (KOH). Typical amounts of catalyst are 1% w/w for the transesterification of raw vegetable oils (Freedman et al., 1984). In reactors, the hydroxide reacts with methanol to produce an alkoxide which will be the catalyzing force of the reaction (Ma and Hanna, 1999). Water is also produced in the reaction resulting the production of alkoxide, which leads to the saponification of the oils/fats. The direct use of an alkoxy, either sodium or potassium methoxide, is recommended for that reason. Over the last few decades, different studies have attempted to compare the performance of various alkaline catalysts. For instance, Freedman et al. (1984) found that at 6:1 methanol to oil molar ratio and 1 h reaction time, ester conversion was the same when using 0.5% NaOCH<sub>3</sub> and 1% NaOH. Singh et al. (2006) compared the efficiency of four different alkali catalysts: NaOH, KOH, sodium methoxide (NaOCH<sub>3</sub>), and potassium methoxide (KOCH<sub>3</sub>). They reported that the most efficient catalyst was KOCH<sub>3</sub> (1.59% w/w) at 50°C and at methanol to oil molar ratio 4.5:1.

The reaction temperatures for transesterification may vary from 20°C to 60°C. Higher temperatures result in higher conversion rates (Singh et al., 2006). It is common in the industry to perform transesterification at 60°C due to the limitations of the low boiling point (65°C) imposed by methanol (Gerpen, 2007). The conversion of oils increases with time, as expected. Freedman et al. (1984) transesterified various types of vegetable oils at 60°C, methanol to oil molar ratio of 6:1 and 0.5% NaOCH<sub>3</sub> and found that after 1 min the yield was approximately 80% while after 1 h it reached 93–98%.

Industrially, biodiesel is mainly produced in continuous processes using alkaline catalysts, as described above. Continuous stirred tank reactors (CSTR) are used at 55–60°C for that reason. Typically, a two-step reaction process is used, where two CSTRs are placed in series having a reaction time of 1 h at each reactor. The yield after the first reactor generally reaches 75–90% (Gerpen, 2007).

When oils or fats with high FFA contents are used, acid esterification is often used to overcome the saponification problem of the fatty acids with the alkalis used (Encinar et al., 2011). Strong acid catalysts, such as sulfuric acid and hydrochloric acid, are used in this case (Freedman et al., 1984; Di Serio et al., 2005), since their activity is not affected by the presence of FFA and they can catalyze the esterification of FFA and triglycerides to methyl esters. One major drawback of acid-catalyzed transesterification is the reaction rate, which is quite low. Freedman et al. (1986) investigated the transesterification of soybean oil with methanol using 1 wt% concentrated sulfuric acid (based on oil mass). It took 69 h to obtain more than 90% oil conversion to methyl esters at 60°C and at a methanol to oil molar ratio of 30:1, far longer than 2–8 h generally taken by using base catalysts. Canacki and Gerpen (2001) studied the effects of alcohol to oil molar ratio, reaction temperature, catalyst loading, and reaction time on ester conversion by acid-catalyzed transesterification. They found that the increased conversion rates of esters could be obtained at increased alcohol to oil molar ratios, increased reaction temperatures, increased concentration of sulfuric acid, and longer reaction times.

The acid-catalyzed process is especially advantageous in the pre-transesterification of waste cooking oils, where the FFA content is usually greater than 2% (Watanabe et al., 2001; Zhang et al., 2003). This is a common practice in the biodiesel industry. Dias et al. (2009) studied the acid pre-transesterification of acid waste lard and reported the optimal conditions to be 65°C, 2% H<sub>2</sub>SO<sub>4</sub>, and 5 h reaction time, with catalyst concentration and temperature being the most important conditions. Lin et al. (2009) investigated a two-step acid esterification of the crude rice bran oil (acidity of 40 mg KOH/g; 20% FFA) with 1% H<sub>2</sub>SO<sub>4</sub> and methanol to oil molar ratios of 6:1 and 7:1 for 60 and 30 min reaction times, respectively, to obtain a final product with an acidity of less than 1 mg KOH/g. In a different study, some strong organic acid catalysts (loading of 0.5 wt%) were used in a mixture of soybean and lard oil at 60°C, methanol to oil molar ratio of 6:1, and a reaction time of 4 h. The acidity was reduced from the initial value of 7.2 mg KOH/g to 0.6 mg KOH/g (Canoira et al., 2008). Diarylammonium was also used as a catalyst in the acid esterification of greases where the FFA content of 12–40% was successfully esterified to produce a product with FFA < 1% (Lin et al., 2009). Issariyakul et al. (2007) reported a successful acid esterification of waste fryer grease with 5–6% FFA at 2 wt% H<sub>2</sub>SO<sub>4</sub> and a reaction time of 5 h. They deduced that successful acid esterification of high FFA feedstocks required a temperature higher than 50°C, a catalyst amount between 0.5–3 wt% (preferably sulfuric acid), methanol more than 5:1 mol/mol (18 g/100 g oil), and a reaction time between 90 min and 5 h.

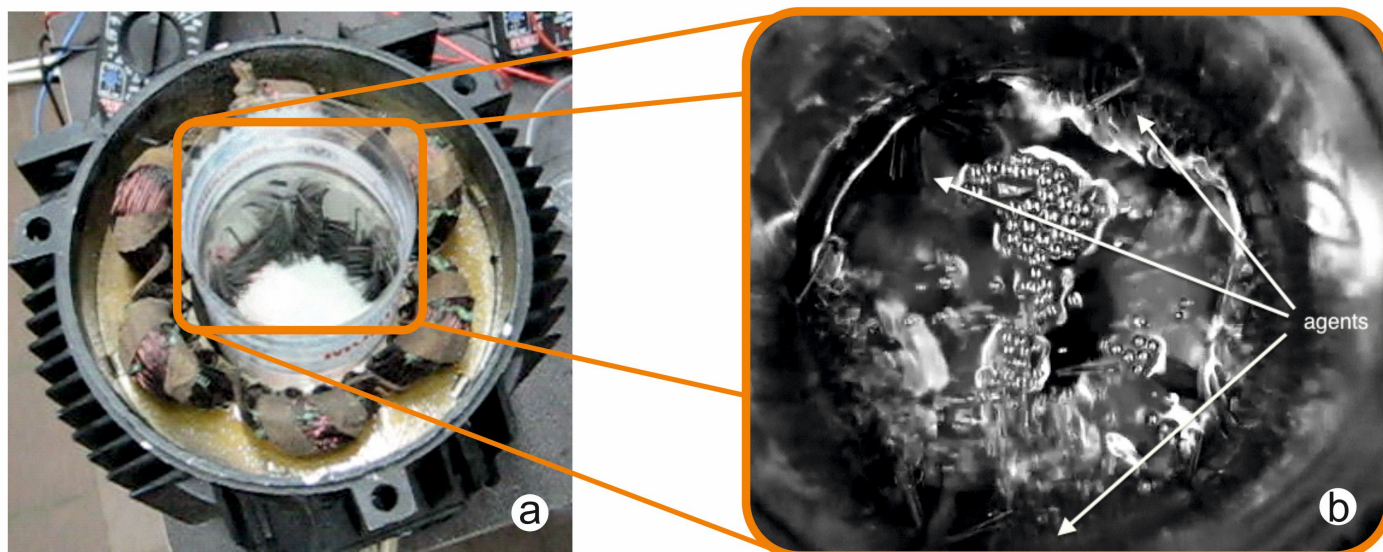
The esterification reaction can also be intensified by using enhanced reactor technologies (Mohod et al., 2017). For instance, Aghbashlo et al. (2018) developed a low power high frequency ultrasonic reactor and claimed more promising exergoeconomic and exergoenvironmental performance of the investigated reactor for biodiesel synthesis from waste cooking oil.

The aim of the present work is to investigate the effect of a novel chemical process intensifier involving a reaction zone with magnetostrictive cylindrical particles subjected to an oscillating electromagnetic field on the reaction time and biodiesel yield, specifically in the case of high-FFA feedstock.

## 2. Experimental

### 2.1. Physical principles

We used an experimental chemical process intensifier involving a reaction zone with ferromagnetic iron (or nickel) particles (agents) subjected to an oscillating electromagnetic field, generated in the working zone of the reactor (Krasnolovets, 2017). The ferromagnetic iron particles, which are set in vibration by the electromagnetic field (Fig. 1a), can give rise to various physical phenomena like ultrasound and cavitation in a fluid placed inside of the reactor (Logvinenko and Sheliakov, 1976). These processes intensify the mixing of the reagents. Furthermore, since iron is a magnetostrictive material, the oscillations of the magnetic field lead to a periodic instant contraction of small iron rod cylinders introduced in the reaction zone, followed by the restoration of their size. The magnetostrictive contraction and expansion of the iron particles inside the



**Fig. 1.** (a) Configuration of the electromagnetic field and ferromagnetic agents (iron particles) in the reactor zone: the agents are fastened to the walls by the electromagnetic field and oscillate near their equilibrium positions. (b) Interior of the reaction zone. The vegetable oil is intensively mixed with methanol by the vibrating ferromagnetic agents.

reactor lead to the periodic release of the so-called inertons (quasi-particles) of the matter waves, i.e., the carriers of the quantum mechanical interaction (Krasnoholovets, 2017). In the moments of contraction, inertons are released from the iron agents into the mixture of the oil and methanol. They are absorbed by these fluids and affect the strength of the chemical bonds between different atoms and molecules contributing to the breakage of some bonds and the formation of others. Such processes can facilitate and intensify chemical reactions like transesterification.

## 2.2. Materials

All the materials used in this study were supplied by the Elin Biofuels' biodiesel plant (Magnisia, Greece). The following oils/fats were used: refined sunflower oil (SUN), used cooking oil (UCO), animal fat (AF). The reagents used during the biodiesel synthesis were methanol (99.5%), potassium methoxide solution (32% w/w in methanol) as alkali catalyst, and sulphuric acid ( $H_2SO_4$ , 96%) as acid catalyst.

## 2.3. Experimental procedure

A laboratory scale Biaktor Lx 1002 reactor (Indra Scientific SA, Brussels, Belgium) was used for the chemical process intensification. The description of the reactor can be found in Krasnoholovets (2017). This technology can be used as a replacement for typical continuous stirred tank reactors (CSTR) frequently used for biodiesel production. The apparatus can operate at various combinations of raw materials, catalysts, and operation modes, i.e., low-frequency (LF) and high-frequency (HF). In the LF mode, the vibration frequency is fixed at 50 Hz while in the HF mode, the low-frequency vibrations are superimposed with a short-wave envelope where the vibration frequency can vary from 0 to 413 Hz. The LF mode is much similar to the approach used by Logvinenko and Sheliakov (1976), but in the Logvinenko's technology, the field configuration inside the reactor is different (the ferromagnetic agents revolve in circular orbits inside the reactor instead of vibrating as in the present case).

The operation of the reactor loaded with typical oil blends (combination of raw vegetable oils and used cooking oils), alcohol, and catalyst was evaluated. Moreover, the oils that are not suitable for the commercial alkali process (high FFA and water contents) were also used in the process. In addition, the homogenous acid catalyst (sulphuric acid,  $H_2SO_4$ ) was also used in the reactor for the acid pre-treatment of high FFA oils in order to evaluate the efficiency of the technology for the acid esterification reaction.

Batches of 250–400 g were prepared and each was introduced into the reactor for 30–120 s. The operational procedure is described below:

- Initially, the oils were mixed in the reactor vessel (one section plastic bottle) with methanol and catalyst;
- the ferromagnetic agents were added into the vessel (approximately 75 g); then, the vessel was shaken in order to obtain a homogenized reaction mixture and was placed in the reaction chamber (Fig. 1b);
- the operation mode (LF or HF) and reaction time (0–60 s) were set and the reactor was launched.

All the batches leaving the reactor were further processed in order to obtain the final biodiesel product prior to product characterization, following the same procedure taking place in commercial biodiesel plants upon the completion of the reaction. The steps following the reaction were gravitational separation, washing (3 rounds), drying, and filtering.

The experimental treatments investigated were as follows:

- I. preliminary tests;
- II. high FFA oil feedstock, alkali catalyzed / LF mode;
- III. high FFA oil feedstock, acid catalyzed / LF mode;
- IV. high FFA oil feedstock, alkali catalyzed / LF mode vs. HF mode.

Preliminary tests were performed using the reactor in order to assess its operation and to define the protocols required for biodiesel production. A full report of all these tests and results are not presented here. In the second treatment, a high FFA oil feedstock was used in an alkali catalyzed process using the reactor's LF mode in order to assess the capability of the reactor to transesterify oils that cannot be processed in the typical commercial alkali process. In the third treatment, high FFA oil feedstocks were used again but this time with a homogeneous acid catalyst ( $H_2SO_4$ ) in order to determine the reactor's operability as an esterification pre-treatment process intensifier. Finally, in the last series of experiments, the modes of operation of the reactor were evaluated using the same feedstocks and catalyst. The modes tested were the LF mode, HF mode at 50 Hz, HF mode at 200 Hz, and HF mode at 400 Hz.

## 2.4. Analytical procedures

The final products were evaluated according to the European Quality Standard for biodiesel EN 14214:2003. Biodiesel characterization was conducted by Elin Biofuels' chemical laboratory (Magnisia, Greece). The

parameters used to estimate the rate of oil conversion to biodiesel were concentrations of glycerides (mono-, di-, tri-) and the ester content. It should be noted that ester content is generally indicative of the oil conversion rate, but not in cases where cooking oils or animal fats are used, due to the presence of polymerized triglycerides resulting in the production of polymerized esters, which are not taken into account in the ester content calculation. This means that it is possible for the ester content of biodiesel to be out of the EN 14214 specifications, i.e., < 96.5%, in spite of the completion of the reaction. In order to overcome this problem, the glycerides levels can be used as an indicator of the amount of oil which was not converted into biodiesel. Mono-, di-, and triglycerides were analyzed using a Shimadzu GC 2010 gas chromatograph with a capillary column MEGA-5 HT (12 m × 0.20 mm × 0.10 μm film thickness). The glyceride levels were quantified using the gas chromatograph method EN 14105:2003. The calibration curve for the above method was set between 0–0.4 wt% for diglycerides and triglycerides and between 0–0.9 wt% for monoglycerides. The ester content was determined by using a Shimadzu gas chromatograph (GC) with a fused silica capillary column SP-2330 from Supelco (30 m × 0.25 mm × 0.2 μm film thickness).

### 3. Results and Discussion

#### 3.1. Preliminary test runs

A series of preliminary tests were performed with various oil types and conditions. The objective of these tests was to assess the degree of transesterification of oil (triglycerides) to biodiesel (fatty acid methyl esters, FAMES). Only three tests (out of multiple test runs conducted) are presented herein **Table 1**. The oil mixtures used in the three experiments represent typical raw materials used for biodiesel production. “Oil 1” is a SUN with a very low FFA content of 0.1 wt%, “Oil 2” is a mixture of UCO with SUN with an FFA content of 1.51 wt%, and while a 100% UCO with a high FFA content 4.2 wt% was also used, designated as “UCO1”. According to the literature, the recommended FFA content of oils used in the transesterification process is 1 wt% (Bradshaw and Meuly, 1944; Feuge and Gros, 1949; Ma et al., 1998), however, industrial experiences indicate that oils/fats of up to 2.5 wt% FFA content can still be used in the transesterification process. Higher FFA contents lead to extended soap formation that emulsifies the reaction mixture making the biodiesel/glycerine phase separation impossible.

Thus, “Oil 1” and “Oil 2” are the oils that can be processed in the typical alkali transesterification process. The investigated laboratory reactor was capable of transesterifying these oils within very short reaction times (30–180 s) as compared to the conventional processes performed by CSTRs (1.5–2 h) (Freedman et al., 1984; Ma and Hanna, 1999; Gerpen, 2007). Moreover, the transesterification was conducted at low temperatures (2 to 40°C) which are substantially lower than the values practiced in the conventional processes, i.e., 55–60°C (Freedman et al., 1984; Gerpen, 2007). The ester content of the final biodiesel product was within the EN 14214 limits (i.e., > 96.5 wt%) only for “Oil 1”, while the diglyceride and triglyceride contents were out of the EN 14214 specifications (i.e., 0.2 wt% for di and tri-glycerides) for both tests

**Table 1.**

Process and biodiesel parameters in the preliminary tests.

Process parameters	Oil 1	Oil 2	UCO1
Composition	100% SUN	64% SUN + 36% UCO	100% UCO
FFA (wt%)	0.10	1.51	4.20
Methanol/Oil (w/w)	0.14	0.14	0.16
CH <sub>3</sub> OK (wt% in oil)	1.5	1.5	1.5
Operation mode (-)	LF	LF	HF
Reaction time (s)	30	180	60
Reaction temperature (°C)	25	25	25
<b>Biodiesel parameters</b>			
Ester content (wt%)	97.1	94.5	80.3
Monoglycerides (wt%)	0.45	0.48	0.65
Diglycerides (wt%)	0.49	0.50	1.61
Triglycerides (wt%)	0.76	1.85	5.22

involving “Oil 1” and “Oil 2”. Although the “UCO1” oil had a rather high FFA content, presumably making its treatment with the typical alkali process impossible, there was a possibility to process it by using the investigated reactor. This would be considered a promising result as the introduced technology could allow the base catalyzed transesterification of oils and fats with higher FFA contents (> 2.5%).

The reaction times of the preliminary test runs varied from 30 to 180 s (**Table 1**). According to the results obtained, the reaction time for the subsequent test runs was fixed at 60 s.

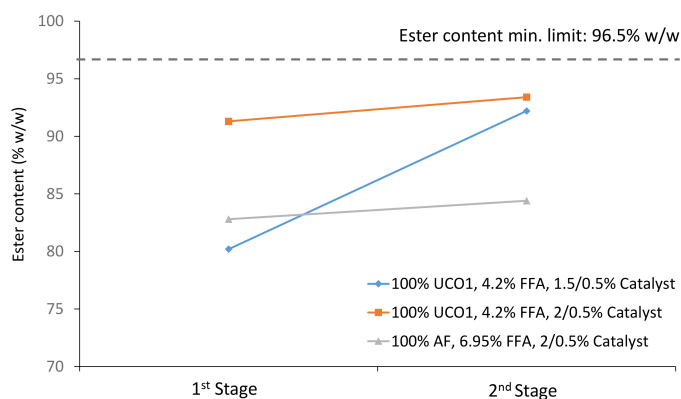
#### 3.2. High FFA feedstock, alkali catalyzed / LF mode

UCO1 and AF were transesterified by the alkali catalyst using the LF mode. The process parameters and the results are tabulated in **Table 2**. The ester contents of different experiments after two stages of reaction are shown in **Figure 2**. UCO1 was initially transesterified at a catalyst concentration of 1.5 wt% and a methanol to oil mass ratio of 0.16 for 60 s. The oil could be transesterified even at such a short reaction time and at the ambient temperature, although the FFA content was almost twice the accepted value for the transesterification reaction. Then, to further boost the ester content, the 2<sup>nd</sup> stage was performed with a methanol to oil weight ratio of 0.03 and catalyst loading of 0.5 wt%, while the other reactor parameters were the same as the 1<sup>st</sup> stage. Similar experiments were conducted using UCO1 and AF with an initial catalyst loading of 2 wt%.

**Table 2.**

Process and biodiesel parameters for the two-staged alkali catalyzed transesterification of high FFA oil/fat feedstocks.

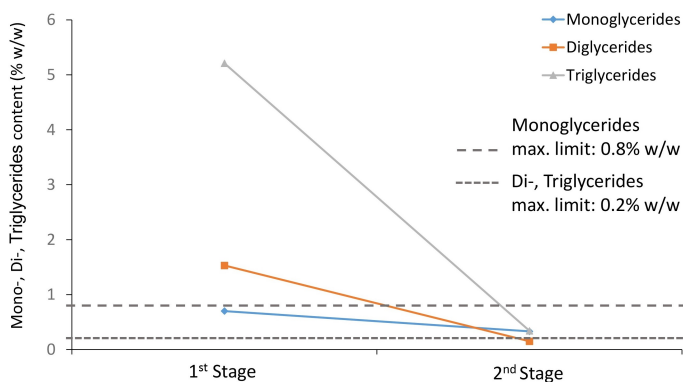
Process parameters	UCO1		UCO1		AF	
	100% Used cooking oil		100% Used cooking oil		100% Animal fat	
	1 <sup>st</sup> Stage	2 <sup>nd</sup> Stage	1 <sup>st</sup> Stage	2 <sup>nd</sup> Stage	1 <sup>st</sup> Stage	2 <sup>nd</sup> Stage
FFA (wt%)	4.20	4.20	4.20	4.20	6.95	6.95
H <sub>2</sub> O (wt%)	0.20	0.20	0.20	0.20	0.06	0.06
Methanol/Oil (w/w)	0.16	0.03	0.16	0.03	0.16	0.03
Catalyst (wt% in oil)	1.5	0.5	2	0.5	2	0.5
Operation mode (-)	LF	LF	LF	LF	LF	LF
Reaction time (s)	60	60	60	60	60	60
<b>Biodiesel parameters</b>						
Ester content (wt%)	80.2	92.2	91.3	93.4	82.8	84.4
Monoglycerides (wt%)	0.70	0.33	0.49	0.24	0.50	0.50
Diglycerides (wt%)	1.53	0.15	0.52	0.05	1.57	1.25
Triglycerides (wt%)	5.21	0.34	1.00	0.09	4.74	1.33



**Fig. 2.** Ester contents for the 1<sup>st</sup> and 2<sup>nd</sup> reaction stages using UCO1 (catalyst loadings of 1.5 wt% and 2 wt% at the 1<sup>st</sup> stage and 2 wt% at the 2<sup>nd</sup> stage) and AF (catalyst loading of 2 wt% at the 1<sup>st</sup> stage). The catalyst loading at the 2<sup>nd</sup> stage for all the experiments was 0.5 wt%

However, after two rounds of reactions, none of the product met the standard requirement for ester content (i.e., > 96.5 wt%).

As for the glyceride contents, after the first reaction stage using UCO1 as feedstock and with the catalyst loading of 1.5 wt%, the triglyceride and diglyceride levels were still higher than the 0.2 wt% limit set forth by the EN 14214, namely, 5.21 wt% and 1.53 wt%, respectively. These results indicated that the reactions did not complete during the 1<sup>st</sup> stage, with the remaining oil compounds detected in high concentrations in biodiesel. Therefore, to complete the process, the 2<sup>nd</sup> stage was performed using a less quantity of the same catalyst and methanol, 0.5% and 3 wt%, respectively, resulting in improved conversion rates (Fig. 3). It should be noted that the implementation of a second reaction stage is common in the industry in order to achieve higher conversion rates. The biodiesel produced after the second reaction stage had considerably better characteristics, but the triglyceride level was still above the limit (0.34 wt% triglycerides). This could be attributed to the consumption of catalyst by the high amount of FFA and water present in the reaction mixture.

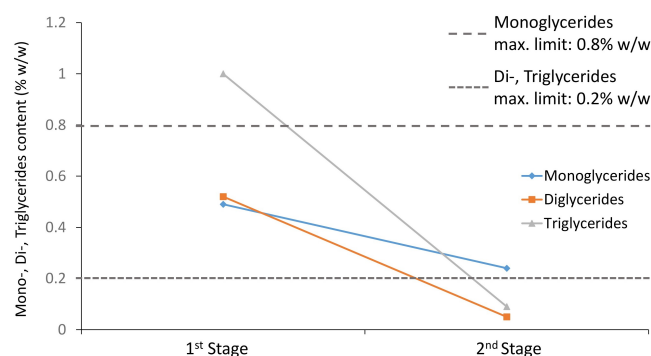


**Fig. 3.** Glycerides contents after the 1<sup>st</sup> and 2<sup>nd</sup> reaction stages using UCO1 as feedstock (catalyst loadings of 1.5 wt% at the 1<sup>st</sup> stage and 0.5 wt% at the 2<sup>nd</sup> stage).

With potassium methoxide used as catalyst and oleic acid considered as the main FFA compound, 0.25 g of catalyst would be consumed by each g of FFA present in the sample. This means that at the catalyst loading of 1.5 wt%, the catalyst available for transesterification would be approximately 0.5 wt%. The catalyst could also be depleted because of the water content in the oil/fat reaction mixture. In better words, triglycerides could be hydrolyzed in the presence of water producing additional FFAs, rendering more catalyst unavailable (available catalyst < 0.5 wt%). Nevertheless, it is not possible to predict the accurate amount of catalyst consumed since the hydrolysis reaction

never comes to completion and thus, not all the water available reacts with the oil/fat. Assuming that all the water be consumed in the hydrolysis of the oil/fat, then the consumption of catalyst would be 12.16 g catalyst/g H<sub>2</sub>O. In spite of that, industrial experiences prove that the real consumption of catalyst is substantially less than the above-mentioned amount, and it can even be ignored if the water content is lower than 0.05%. According to the published literature, a water content of less than 0.06% would be required to achieve the most favorable conversion rates (Ma et al., 1998; Ma and Hanna, 1999). UCO1 had a water content of 0.20%, which was high but still within the acceptable limits for the transesterification reaction (oils/fats of up to 0.3% are used in the industry without posing any problems to the conversion rates of triglycerides). In spite of that and as mentioned earlier, the available catalyst would be less than 0.5 wt%. This value would not be sufficient to effectively drive the transesterification reaction. It has been well documented that the amount of catalysts required for efficient transesterification of oils and fats range from 0.5 to 1.59 wt% (Bradshaw and Meuly, 1944; Canoira et al., 2008; Lin et al., 2009).

Thus, in order to overcome the problem of catalyst consumption, catalyst loading of 2 wt% was used at the first reaction stage following the catalyst loading of 0.5 wt% at the second stage. The results obtained showed that the final product was within the EN 14214 specifications with regard to the glyceride contents, confirming the complete conversion of the oil feedstock (Fig. 4).



**Fig. 4.** Glycerides contents after the 1<sup>st</sup> and 2<sup>nd</sup> reaction stages using UCO1 as feedstock (catalyst loadings of 2 wt% at the 1<sup>st</sup> stage and 0.5 wt% at the 2<sup>nd</sup> stage)

In spite of the favorable glyceride contents, however, the ester content obtained was 93.4% which was out of the specifications (Fig. 2). This can be attributed to the origin of the oil; used oils are generally subjected to high temperatures during their use, long storage time in imperfect conditions, and they are also in contact with water contained in food debris. All these factors can lead to the polymerization of glycerides, which in turn results in the presence of polymerized triglycerides and esters in the biodiesel. Those compounds are dissolved in biodiesel and a distillation step would be required to remove them.

Conversion of AF was performed using the catalyst loadings of 2 wt% and 0.5 wt% at the first and second stages, respectively. It was observed that upon the completion of the reaction, the main products streams (i.e., methyl esters phase/glycerol phase) were separated by gravity in spite of the high FFA content of the feedstock. This is generally not feasible in conventional stirred tank reactors because of the formation of emulsions at high concentrations of soaps. AF had a very low water content (0.06%), indicating that the consumption of catalyst because of water was negligible. However, the high FFA content might have resulted in a theoretical catalyst consumption of 5.4 wt%, which was more than twice the added catalyst. Therefore, theoretically, all the catalyst must have been consumed leading to formation of soaps. Nevertheless, given the results obtained, this was not the case in practice given the ester content recorded (Table 2 and Fig. 2). This finding could be explained by the excellent mixing provided in the reactor allowing more efficient catalysis while minimizing the consumption catalyst and soap formation. In spite of that, the data presented in Figure 5

reveal that the conversion was not complete, given the fact that the diglyceride and triglyceride levels measured after the second reaction stage were higher than the specified limits (i.e., 1.25% and 1.33%, respectively).

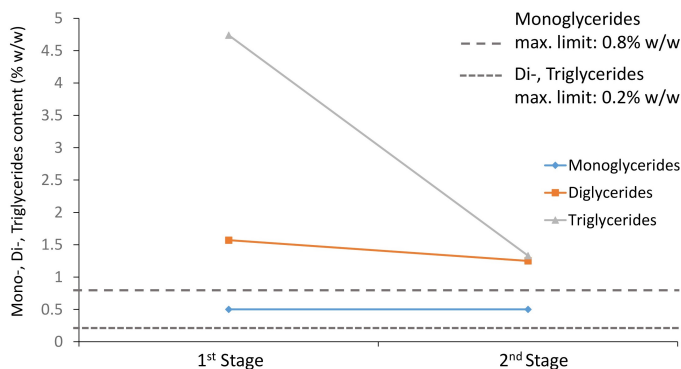


Fig. 5. Glycerides contents after the 1<sup>st</sup> and 2<sup>nd</sup> reaction stages using AF as feedstock (catalyst loadings of 2 wt% at the 1<sup>st</sup> stage and 0.5 wt% at the 2<sup>nd</sup> stage).

Higher amounts of catalyst are not recommended because of high production costs and the possibility of oil saponification. Moreover, the FFA present in the high-FFA feedstock would be lost, even if the transesterification reaction could be completed without the occurrence of the emulsification problem. Therefore, in order to efficiently such oil feedstocks for biodiesel production, an acid esterification step is recommended prior to transesterification, where the FFAs are converted to their respective FAMES.

### 3.3. High FFA feedstock, acid catalyzed / LF mode

Two feedstocks, i.e., UCO2 (FFA content of 8.4 wt%) and UCO3 (FFA content of 13 wt%) were pretreated with sulfuric acid (3 g H<sub>2</sub>SO<sub>4</sub>/g oil) and methanol (30 g methanol/100 g oil or methanol/oil mole ratio of 8.3:1) using the reactor's LF mode at the ambient temperature and a reaction time of 60 s, as in the previous tests. The results are shown in Figure 6.

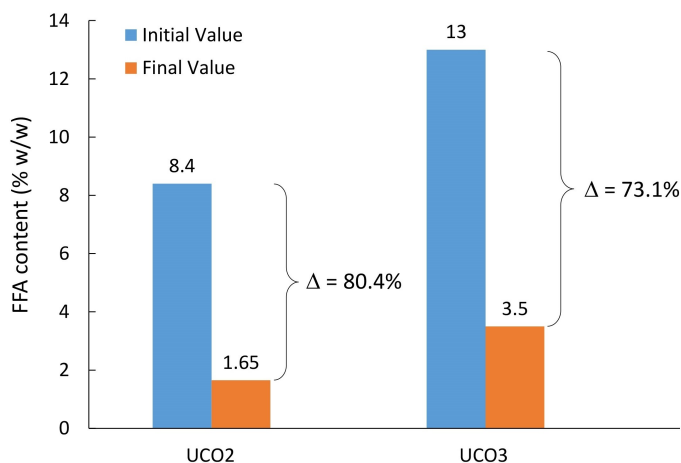


Fig. 6. Acid esterification of the high FFA feedstocks using the LF mode of the reactor.

The objective of acid esterification as a pretreatment step prior to the alkali transesterification is to reduce the FFA levels to acceptable levels (i.e. < 2%). The pretreatment of UCO2 resulted in an FFA content of 1.65 wt% while the pretreatment of UCO3 resulted in an FFA content of 3.5 wt%. The former value is acceptable for the alkali transesterification while the latter is still rather high.

Both feedstocks seemed to be equally affected by the acid pretreatment, since the conversion of FFA was in the same order, 80.4% for UCO2 and 73.1% for UCO3. Thus, it can be concluded that the maximum FFA content that can be treated under the same conditions using the developed technology would be close to 9 wt%.

The most noticeable finding is that the esterification of FFAs was promoted to acceptable levels even at the ambient temperature and within a very short reaction time (60 s), while temperatures of 50–90°C and reaction times of 2–5 h are generally employed for this reaction (Issariyakul et al., 2007; Canoira et al., 2008; Ngo et al., 2008; Dias et al., 2009; Lin et al., 2009). So, to the best of our knowledge, this is the first report on accomplishing the esterification reaction within such a short reaction time and at the ambient temperature.

### 3.4. High FFA feedstock, alkali catalyzed: effect of operation mode (LF vs. HF)

In this set of experiments, the reactor's HF mode was tested and compared with the LF mode. Three frequencies were selected for testing the HF mode of operation: 50 Hz, 200 Hz, and 400 Hz. In all the experiments, the reaction was performed in two stages, as in the previous tests. The amount of catalyst and methanol (based on oil) were 2 wt% and 16 wt% at the 1<sup>st</sup> stage and 0.5 wt% and 3 wt% at the 2<sup>nd</sup> stage, respectively. The results obtained are shown in Figure 7.

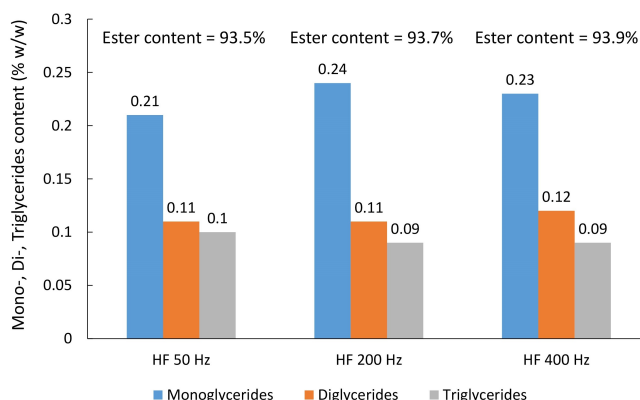


Fig. 7. Ester contents and glyceride levels through alkali catalyzed transesterification of UCO1 at varying frequencies in the HF mode of the reactor.

From the data presented in Figure 7, it can be concluded that the frequencies investigated did not result in significant differences in terms of the ester and glyceride contents. Considering the results obtained for the same feedstock (UCO1) under the same conditions using the LF mode (ester content: 93.4 wt%, monoglycerides: 0.24 wt%, diglycerides: 0.05 wt%, and triglycerides 0.09 wt%), it can be deduced that there was no significant difference between the operation modes (LF vs. HF) nor between different frequencies from the viewpoint of conversion rates.

## 4. Conclusions and future prospects

A novel chemical process intensifier involving a reaction zone with magnetostrictive particles subjected to an oscillating electromagnetic field was employed for the esterification and transesterification of oils and fats into biodiesel. The investigated technology efficiently converted high-FFA content UCO into FAMES (total potassium methylate catalyst consumption of 2.5 wt% and total methanol to oil mass ratio of 0.19; through a two-stage process at the total reaction time of 120 s). Moreover, high FFA-content AF was also converted into biodiesel under similar conditions; however, the conversion was incomplete, which can be attributed to the catalyst depletion due to its reaction with FFAs.

The esterification of UCO as a pretreatment step prior to transesterification was also carried out. Based on the results obtained, the

investigated technology could efficiently reduce high FFA levels of up to approx. 9% to less than 2 wt% (suitable for alkali catalyzed transesterification) in 60 s using 3 wt% H<sub>2</sub>SO<sub>4</sub> catalyst and methanol to oil mass ratio of 0.3. It should be highlighted that the process intensifier was operated at ambient temperature; a feature of significant importance from the energy and environmental conservation perspectives. Moreover, given the short reaction times achieved, it could be deduced that the intensification of chemical physical processes indeed took place in the experimental reactor used in the present study. **Table 3** compares some other reactor types described by Tabatabaei et al. (2019) with the reactor technology investigated in the present study. Further research works may include further investigation of the developed technology by using other feedstocks and catalysts as well as using ethanol instead of methanol. Moreover, scrutinizing the sustainability aspects of the technology using advanced sustainability assessment tools such as life cycle assessment (LCA), exergy, etc. (Rosen, 2018) could be the subject of future investigations. It should be noted that the technology described herein could also be used for the intensification of various chemical reactions that usually require special conditions and long reaction times.

**Table 3.**

Comparison of a number of reactor types in terms of the process intensification mechanisms involved during their operation with the reactor technology investigated in the present study.

Reactor type	Process intensification				
	Intensive Mixing	Ultrasonic	Microwave	Cavitation	Striction/Inertons
This study (Multifunctional process intensifier)	✓	✓	-	✓	✓
Sonochemical	-	✓	-	-	-
Microwave	-	-	✓	-	-
Hydrodynamic	✓	-	-	-	-
Cavitation	✓	-	-	✓	-
CSTR*	-	-	-	-	-

\* CSTR: continuous stirred tank reactor

## References

- [1] Aghbashlo, M., Tabatabaei, M., Hosseinpour, S., 2018. On the exergoeconomic and exergoenvironmental evaluation and optimization of biodiesel synthesis from waste cooking oil (WCO) using a low power, high frequency ultrasonic reactor. *Energy Convers. Manage.* 164, 385-398.
- [2] Bradshaw, G.B., Meuly, W.C., 1944. Preparation of detergents. US Patent, 2, pp. 360-844.
- [3] Canakci, M., Gerpen, J.V., 2001. Biodiesel production from oils and fats with high free fatty acids. *Trans. ASAE.* 44(6), 1429-1436.
- [4] Canoira, L., Rodríguez-Gamero, M., Querol, E., Alcántara, R., Lapuerta, M., Oliva, F., 2008. Biodiesel from low-grade animal fat: production process assessment and biodiesel properties characterization. *Ind. Eng. Chem. Res.* 47(21), 7997-8004.
- [5] Dias, J.M., Alvim-Ferraz, M.C., Almeida, M.F., 2009. Production of biodiesel from acid waste lard. *Bioresour. Technol.* 100(24), 6355-6361.
- [6] Di Serio, M., Tesser, R., Dimiccoli, M., Cammarota, F., Nastasi, M., Santacesaria, E., 2005. Synthesis of biodiesel via homogeneous Lewis acid catalyst. *J. Mol. Catal. A: Chem.* 239(1-2), 111-115.
- [7] Encinar, J.M., Sánchez, N., Martínez, G. and García, L., 2011. Study of biodiesel production from animal fats with high free fatty acid content. *Bioresour. Technol.* 102(23), 10907-10914.
- [8] Feuge, R.O., Gros, A.T., 1949. Modification of vegetable oils. VII. Alkali catalyzed interesterification of peanut oil with ethanol. *J. Am. Oil Chem. Soc.* 26(3), 97-102.
- [9] Freedman, B., Butterfield, R.O., Pryde, E.H., 1986. Transesterification kinetics of soybean oil. *J. Am. Oil Chem. Soc.* 63(10), 1375-1380.
- [10] Freedman, B.E.H.P., Pryde, E.H., Mounts, T.L., 1984. Variables affecting the yields of fatty esters from transesterified vegetable oils. *J. Am. Oil Chem. Sci.* 61(10), 1638-1643.
- [11] Fukuda, H., Kondo, A., Noda, H., 2001. Biodiesel fuel production by transesterification of oils. *J. Biosci. Bioeng.* 92(5), 405-416.
- [12] Furuta, S., Matsushashi, H., Arata, K., 2006. Biodiesel fuel production with solid amorphous-Zirconia catalysis in fixed bed reactor. *Biomass Bioenergy.* 30(10), 870-873.
- [13] Gerpen, J.V., 2007. Biodiesel Production, in: *Improvement of crop plants for industrial end uses*, Ranalli, P. (Ed.), Springer. 281-289.
- [14] Gole, V.L., Gogate, P.R., 2012a. A review on intensification of synthesis of biodiesel from sustainable feed stock using sonochemical reactors. *Chem. Eng. Process. Process Intensif.* 53, 1-9.
- [15] Gole, V.L., Gogate, P.R., 2012b. Intensification of synthesis of biodiesel from nonedible oils using sonochemical reactors. *Ind. Eng. Chem. Res.* 51(37), 11866-11874.
- [16] Gole, V.L., Gogate, P.R., 2013. Intensification of synthesis of biodiesel from non-edible oil using sequential combination of microwave and ultrasound. *Fuel Process. Technol.* 106, 62-69.
- [17] Issariyakul, T., Kulkarni, M.G., Dalai, A.K., Bakhshi, N.N., 2007. Production of biodiesel from waste fryer grease using mixed methanol/ethanol system. *Fuel Process. Technol.* 88(5), 429-436.
- [18] Jeong, G.T., Park, D.H., Kang, C.H., Lee, W.T., Sunwoo, C.S., Yoon, C.H., Choi, B.C., Kim, H.S., Kim, S.W., Lee, U.T., 2004. Production of biodiesel fuel by transesterification of rapeseed oil. *App. Biochem. Biotechnol.* 113-116 (1-3), 747-758.
- [19] Ji, J., Wang, J., Li, Y., Yu, Y., Xu, Z., 2006. Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation. *Ultrasonics.* 44, e411-e414.
- [20] Joshi, S., Gogate, P.R., Moreira Jr, P.F., Giudici, R., 2017. Intensification of biodiesel production from soybean oil and waste cooking oil in the presence of heterogeneous catalyst using high speed homogenizer. *Ultrason. Sonochem.* 39, 645-653.
- [21] Joshi, S.M., Gogate, P.R., Kumar, S.S., 2018. Intensification of esterification of karanja oil for production of biodiesel using ultrasound assisted approach with optimization using response surface methodology. *Chem. Eng. Process. Process Intensif.* 124, 186-198.
- [22] Krasnoholovets, V., 2017. *Structure of space and the submicroscopic deterministic concept of physics.* Apple Academic Press, Oakville, Canada; Waretown, USA.
- [23] Lin, L., Ying, D., Chaitep, S., Vittayapadung, S., 2009. Biodiesel production from crude rice bran oil and properties as fuel. *Appl. Energy.* 86(5), 681-688.
- [24] Logvinenko, D.D., Sheliakov, O.P., 1976. Intensification of technological processes in apparatuses with vortex layer. *Izdatel'stvo Tekhnika, Kyiv.*
- [25] Maddikeri, G.L., Pandit, A.B., Gogate, P.R., 2012. Intensification approaches for biodiesel synthesis from waste cooking oil: a review. *Ind. Eng. Chem. Res.* 51(45), 14610-14628.
- [26] Ma, F., Clements, L.D., Hanna, M.A., 1998. The effects of catalyst, free fatty acids and water on transesterification of beef tallow. *Trans. ASAE.* 41(5), 1261-1264.
- [27] Ma, F., Hanna, M.A., 1999. Biodiesel production: a review. *Bioresour. Technol.* 70(1), 1-15.
- [28] Mohod, A.V., Subudhi, A.S., Gogate, P.R., 2017. Intensification of esterification of nonedible oil as sustainable feedstock using cavitation reactors. *Ultrason. Sonochem.* 36, 309-318.
- [29] Nelson, L.A., Foglia, T.A., Marmor, W.N., 1996. Lipase-catalyzed production of biodiesel. *J. Am. Oil Chem. Soc.* 73(9), 1191-1195.
- [30] Ngo, H.L., Zafiroopoulos, N.A., Foglia, T.A., Samulski, E.T., Lin, W., 2008. Efficient two-step synthesis of biodiesel from greases. *Energy Fuel.* 22(1), 626-634.
- [31] Noureddini, H., Zhu, D., 1997. Kinetics of transesterification of soybean oil. *J. Am. Oil Chem. Sci.* 74(11), 1457-1463.
- [32] Rosen, M.A., 2018. Environmental sustainability tools in the biofuel industry. *Biofuel Res. J.* 5(1), 751-752.

- [33] Shimada, Y., Watanabe, Y., Samukawa, T., Sugihara, A., Noda, H., Fukuda, H., Tominaga, Y., 1999. Conversion of vegetable oil to biodiesel using immobilized *Candida antarctica* lipase. *J. Am. Oil Chem. Soc.* 76 (7), 789-793.
- [34] Singh, A., He, B., Thompson, J., Gerpen, J.V., 2006. Process optimization of biodiesel production using alkaline catalysts. *Appl. Eng. Agric.* 22(4), 597-600.
- [35] Subhedar, P.B., Botelho, C., Ribeiro, A., Castro, R., Pereira, M.A., Gogate, P.R., Cavaco-Paulo, A., 2015. Ultrasound intensification suppresses the need of methanol excess during the biodiesel production with Lipozyme TL-IM. *Ultrason. Sonochem.* 27, 530-535.
- [36] Tabatabaei, M., Aghbashlo, M., Dehghani, M., Panahi, H.K.S., Mollahosseini, A., Hosseini, M., Soufiyan, M.M., 2019. Reactor technologies for biodiesel production and processing: a review. *Progress Energy Combust. Sci.* 74, 239-303.
- [37] Vyas, A.P., Verma, J.L., Subrahmanyam, N., 2010. A review on FAME production processes. *Fuel.* 89(1), 1-9.
- [38] Watanabe, Y., Shimada, Y., Sugihara, A., Tominaga, Y., 2001. Enzymatic conversion of waste edible oil to biodiesel fuel in a fixed bed bioreactor. *J. Am. Oil Chem. Soc.* 78(7), 703-707.
- [39] Zhang, Y., Dube, M.A., McLean, D.D.L., Kates, M., 2003. Biodiesel production from waste cooking oil: I. process design and technological assessment. *Bioresour. Technol.* 89(1), 1-16.