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Biodiesel Synthesis Via Transesterification Reaction Using Chemically-Based Heterogenous Catalysts Under Microwave Irradiation

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ABSTRACT

This review paper has reviewed, albeit not thoroughly, biodiesel synthesis via transesterification reaction of non- edible and waste oils using chemically- based heterogenous catalysts induced by microwave irradiation. Synthesis of biodiesel from such feedstock oils can help boost biodiesel commercialization since it is an economical alternative to fresh edible oils in order to reduce the cost of raw materials. Another cost cut- off might arise from the use of heterogenous catalysts with microwave heating which consumes less energy and requires a shorter transesterification reaction time with a better reaction kinetics without compromising the overall biodiesel yield, in comparison to conventional heating. Results of the reviewed work have indicated that microwave heating could outperform conventional heating in all aspects considered, although reaction conditions are moderated in the former mode of heating. Also, it has been observed that acceleration of a transesterification reaction by microwave heating cannot be compared to that under conventional heating under; otherwise, identical reaction conditions. In addition, microwave- assisted heterogeneously- catalyzed transesterification reactions are featured with the generation of hot- spot zones, superheating and selective species heating. Out of these phenomena, the efficiency of heating process is increased; thus, rate of transesterification reaction is accordingly increased while production of by- products is decreased. The performance of heterogenous catalysts in catalyzing transesterification reactions, with their high reactivity, stability and selectivity under the influence of microwaves, has been superb.

Keywords: transesterification, free fatty acid, microwaves, heterogenous, impregnation.

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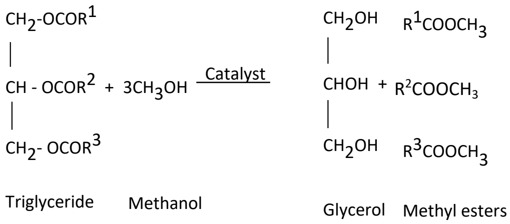
1. INTRODUCTION

Due to its environmental benefits including biodegradability and nontoxicity, biodiesel, as an alternative to classical fossil fuels, has become a more attractive fuel. Due to some challenges, commercialization of biodiesel synthesis through catalytic transesterification reaction has not been significantly effective; however. Of these challenges are: high operating cost, low production efficiency due to kinetic limitations, high energy consumption, long time and complication of product-catalyst separation and high cost as well as lack of sustainability of raw material(s), fresh edible oils, used as a feedstock for biodiesel synthesis. Such oils include but not limited to oils of: barley, canola, coconut, copra, corn, cotton seeds, ground nut, oat, palm, rape seed, rice, safflower, soybean and wheat. To slightly overcome such challenges, biodiesel has been synthesized based on the use of waste cooking oils which are of no value and can environmentally be a burden if; otherwise, disposed off. Also, another alternative has been the use of non- edible oils such as oils of: almond, babassu, jatropha curcas, palm, rice bran, sesame, salmon and tobacco seeds, etc.

Transesterification (alcoholysis) is a reversible modification reaction out of which glycerol is removed from the triglycerides of the starting feedstock oil/fat in the presence of a catalyst to produce the corresponding fatty acid alkyl esters (biodiesel) with respect to the alcohol used [1-5]. A typical transesterification reaction in which methanol (methanolysis) is employed as an alcohol is depicted in Fig. (1).



$$\begin{array}{l} CH_2\text{-}OCOR^1 \\ | \\ CH\text{ - }OCOR^2 \\ | \\ CH_2\text{- }OCOR^3 \end{array} + 3CH_3OH \xrightarrow{\text{Catalyst}} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} R^1COOCH_3 \\ \\ R^2COOCH_3 \\ \\ R^3COOCH_3 \end{array}$$

Fig. (1): Transesterification Reaction, redrawn from Ejikeme, et al. [5].

In order for a catalytic transesterification reaction to progress: 1- a catalyst of a certain characteristics must be used unless the route followed is the supercritical heating mode which is non- catalytic and 2- a certain temperature has to be maintained depending on the feedstock oil/fat as well catalyst used. Catalysts in use for transesterification reactions for biodiesel synthesis have included: enzymes [6], homogenous [7] and heterogenous [8-9]. In general, heterogenous catalysts for biodiesel synthesis require drastic reaction conditions: reaction temperatures reach up to 476 °C, catalyst amount up to 10 wt.% and alcohol to oil molar ratio between 10:1 and 25:1 or even higher. These harsh costly conditions are required in order to make- up low mass transfer rates due to small surface area of such catalysts by which a low contact with the reactants is caused. Thus, to achieve a certain biodiesel yield, reaction duration has to be prolonged. Other issues that may arise due to using heterogenous catalysts to catalyze a transesterification reaction include: poisoning, sintering, coking and leaching by which deterioration of the catalytic reactivity of the catalyst is inevitable. High cost and difficulty of removal of small catalyst particles via filtration from the produced biodiesel are also hurdles that might limit use of heterogenous catalysts in this application. Nevertheless, heterogenous catalysts; in general, are tolerant to oils with high levels of free fatty acids and water, as the case with waste feedstock oils, when used for biodiesel synthesis, resulting in no formation of undesirable soap. Also, use of such heterogenous catalysts in biodiesel synthesis could ensure no corrosion effects on equipment used. Heterogenous catalysts are also featured with high reactivity, stability, selectivity as well as long lifetime; in particular, if a solid material support is integrated in their design such as alumina or silica, etc. Another good feature of such catalysts is their regeneration for subsequent use(s) exhibiting no or trivial catalytic deterioration. Besides, product (biodiesel) purification, which is costly and complicated, can; to a large extent, be eliminated if heterogenous catalysts are employed [9].

Equally crucial is maintaining the be-spoke temperature throughout the transesterification reaction to ensure the progress of the reaction. Nature of the feedstock oil/fat as well as catalyst used, *do* play a role in deciding the transesterification reaction's temperature. In order to attain the required temperature, some sort of heat must be supplied to the transesterification reaction mixture. Heating can be via conventional, supercritical or non- conventional modes. Among non- conventional modes are: ultrasonic, plasma and microwaves (dielectric). Of these modes, microwaves are further examined in this review. Whilst applying the conventional heating (wall heating), in which, as previously mentioned, a certain catalyst of a certain type must be used, which usually requires a separation procedure unless being heterogenous, transesterification reaction temperature is between 60 and 476 °C with atmospheric pressure being sufficient. In terms of heat loss, it is evident since heat is lost to the environment via conduction and convection while transferring heat through reactor's wall and reactants; respectively [10-11]. One additional problem of conventional heating is that it creates a non- uniform temperature distribution through the heated medium. Also, properties of the heated medium, e.g., density, heat capacity and thermal conductivity play a major role in the efficiency of heating. However, in supercritical heating mode, there is no need to use a catalyst; thus, there is no procedure required for catalyst removal. Absence of the catalyst(s) is; however, supplemented by the employment of severe reaction conditions of too high pressure and temperature, up to 60 MPa and 400 °C; respectively. This can be a safety concern and requires a high capital cost. The need to use a catalyst, at certain reaction conditions of pressure and temperature as the case with conventional heating, is again what features microwave heating. However, heat loss is minimal since heating the reactor's wall is not involved and that molecules of the entire liquid within the heated medium are subjected to microwaves which constitute electric and magnetic fields each of which interact differently with molecules to be heated [11]. This is governed by ionic conduction and one kind of dipolar polarization whether displacement, orientation or interfacial polarization. In microwave heating, almost 65% of electrical energy can be converted into heat via a microwave equipment [12]. In addition, microwave heating is advantageous over conventional and supercritical heating modes in terms of short reaction time [13], higher process efficiency and cleaner products [11,14-18]. To this end, use of microwaves as a heating means has seen versatile applications including: biodiesel synthesis, methane conversion, coal and biomass conversion, desulfurization and carbon dioxide separation, materials synthesis, etc. [12]. The aim of this paper is to review the research published on biodiesel synthesis from different non- edible and waste oils via transesterification reaction using different chemically-based heterogenous catalysts under microwave irradiation. For comparison purposes, use of conventional heating in this regard is touched upon.

2. Biodiesel Synthesis Via Chemically-Based Heterogenous Catalysts Under Microwave Irradiation

Basic and Acidic heterogenous catalysts have been synthesized based on chemical material(s) and recently based on the use of waste materials. Use of acidic chemically- based heterogenous catalysts in the synthesis of biodiesel has been reviewed elsewhere [9]. Investigations reported in this review were all, opposing to this current review, relying on conventional heating methods to facilitate the desired transesterification reaction's temperature [9]. This paper; however, focuses on the employment of such heterogenous catalysts for the purpose of transesterification of different non- edible and waste oils under microwave heating. Microwaves are electromagnetic waves that form when electric and magnetic fields are coupled perpendicularly to each other. Among the electromagnetic spectrum, microwaves sit at the middle between radio waves and infrared waves. The wavelengths of microwaves range from 0.01 to 1 m. Frequencies of microwaves are broad and extend thousand times from 0.300 to 300 GHz, although most common frequencies applied industrially are between 0.915 and 2.450 GHz. Thus, a successful chosen heterogenous catalyst should be capable to absorb microwaves with such frequencies beyond its skin depth. In terms of frequency, wavelength and energy content, microwaves with higher frequencies possess shorter wavelengths while a higher energy content. Also, the response of materials exposed to microwaves varies from a material to another according to their polarity, viscosity, density, temperature, concentration and molecular wight [12]. To avoid digression, further details on principles, theory and mechanism of microwave heating, the requirement(s) of equipment used with microwave heating and microwaves- assisted organic reactions are left to the reader and can be found elsewhere [19-20].

In order to enhance the synthesis process of biodiesel, Kord and his coworkers have investigated the transesterification reaction of castor oil under microwave irradiation while using methanol as an alcohol and KOH as a heterogenous catalyst. The alcohol used and the ingredients of the catalyst used are all with high dielectric properties which are of great contribution towards absorption of microwaves. Only two minutes were required to obtain a biodiesel yield of 92.15% [21]. In another work, Yuan and co- workers have investigated the synthesis of biodiesel from castor oil under microwave irradiation. In this work, the performance of two acid homogenous catalysts and a heterogenous base catalyst, in catalyzing the transesterification reaction of castor oil with methanol, was evaluated. Acid homogenous catalysts used included $NaHSO_4.H_2O$ and $AlCl_3$ while the heterogenous base catalyst was Na_2CO_3. The required temperature for the transesterification reaction was secured by conventional heating and microwave heating. Among heating modes and catalyst used, microwave heating when used with Na_2CO_3 catalyst, biodiesel yield was the highest at 90%. In terms of energy consumption, microwave heating consumed less energy than conventional heating in all experiments carried out [22].

In another study performed by Zhang and co-workers, higher than 96% of biodiesel yield was obtained in 10 min via a microwave-aided transesterification of yellow horn oil using 1 wt.% of heteropolyacid as a catalyst and methanol as an alcohol [23]. Using the same alcohol, in 2011, Hsiao et al. and Patil et al. have investigated the transesterification of soybean oil and camelina sativa oil using a powder of CaO and BaO, CaO, MgO and SrO, respectively. In both works, experiments were performed under conventional heating and microwave heating. Under microwave heating, biodiesel yield was 95% and 94% out of the first and second work, respectively [24-25]. Among the catalysts used in the second work, BaO and SrO were better than CaO and MgO in terms of the obtained yield. Also, the transesterification reaction rate while performing the experiments under microwave heating was two orders of magnitude higher than that obtained in conventional heating [25]. In the same year, work on microwave- assisted transesterification of *pongamia pinnata* seeds oil was also carried out for the production of biodiesel. Methanol and two alkali heterogenous catalysts; namely, NaOH and KOH were used as an alcohol and catalysts for the transesterification reaction, respectively. A biodiesel yield of 96% via both catalysts was obtained after 5 min as the reaction started [26]. In addition, Kamath, H. V. and Saidutta, R. M. B., have synthesized biodiesel from karanja oil using methanol as an alcohol and KOH as a catalyst for the transesterification reaction under the influence of microwave heating for 150 sec. However, this was not possible unless a pretreatment procedure, via an esterification reaction for 190 sec in order to reduce the content of free fatty acids of the oil to 1.04-1.18%, was followed. Satisfactory biodiesel yield was obtained out of this work, 90% [27].

Based on ceiba pentandra oil, Silitonga, et al., have synthesized biodiesel via a microwave- assisted transesterification reaction using methanol and KOH as an alcohol and a catalyst; respectively, with agitating the reactants continuously, in order to speed- up the reaction rate and shorten the reaction time. They have obtained biodiesel in a short time with an average yield of 95.42% in an energy-efficient fashion, keeping the production at a minimum [28]. Also, Lin, J. J. and Chen, W. C., have used this alcohol and catalyst with agitation again for the transesterification of jatropha seeds oil while applying conventional and microwave heatings employing mild conditions. Transesterification reaction rate obtained via microwave heating was much faster than that when a conventional heating reactor was used [29]. Pongamia pinnata oil, which is widely available in India, has been subjected to conventional and microwave heatings in an effort to synthesizing biodiesel using the same alcohol and catalyst used in the work just reported. Due to the high content of free fatty acids of the used oil, a pretreatment procedure was necessary in order to produce biodiesel with a low acid value. Compared to conventional heating, with microwave heating, significant improvements in the yield, reaction time and processing time of the produced biodiesel were reported [30]. Also, a yield of biodiesel of 99.40% was obtained in an investigation by Choedkiatsakul and others in 1.75 min as a reaction time of transesterification of palm oil under microwave conditions using methanol and only 1 wt. % of NaOH as a heterogenous catalyst [31].

Again, using methanol, biodiesel was also synthesized from a waste cooking oil in the presence of microwave irradiation and calcium diglyceride as a catalyst. The highest biodiesel yield reported is 94.86% obtained in 15 min [32]. In order to improve biodiesel yield based on use of a waste cooking oil, Chen and others have separately used CH_3NaO and NaOH as catalysts and methanol as an alcohol coupled with a microwave heating system. In this work, it was found that biodiesel yield increases as reaction power was increased up to 750 W. Higher reaction power(s); however, were found to be with a problematic effect on reactants molecules. Compared to NaOH, CH_3NaO was associated with higher biodiesel yield when both catalysts used at 0.75 wt.%. Reaction duration was as little as 3 min [33]. In another study, Hsiao and co- workers have compared the performance of a traditional water- heating path system and that of a microwave heating system in heating the transesterification reaction of a waste cooking oil. Methanol was used as an alcohol and a novel alkaline solid surface-modified CaO as a reaction catalyst. It was reported that, the modified CaO is characterized with a high thermal stability. Compared to the traditional water- heating bath system, with microwave heating system reaction time was significantly reduced. Also, biodiesel conversion was 98.20% while using microwave irradiation as a heating media compared to 53.66% when heating was through a traditional water- bath system, despite nearly doubling the reaction time from 75 to 140 min. In both arrangements, reaction temperature was 65 °C, methanol- to- oil molar ratio was 8:1 and concentration of CaO was 4 wt.% [34]. In another work, Hsiao and co-workers have performed a similar work using a low-quality oil with a high acid value, 4.84 mg KOH/g, in order to synthesize biodiesel via microwave heating but using NaOH as a catalyst instead of CaO. Reported conversion to biodiesel was up to 98.20% [35]. In Table (1), details of most of these above cited investigations in addition to other investigations on microwave- assisted transesterification of different non- edible and waste feedstocks employing different chemically- based heterogenous catalysts, are summarized; while, for comparison purposes, Table (2) summarizes details of some investigations previously reviewed elsewhere on transesterification of different feedstocks under conventional heating [9].

3. Performance of Chemically- Based Heterogenous Catalysts and Microwave Irradiation in Transesterification Reactions for Biodiesel Synthesis

Although satisfactory biodiesel yields have been obtained while using various efficient chemically- based heterogenous catalysts under conventional heating as reported in Table (2), conditions of transesterification reaction; however, had to be intensified in all works cited. Reaction temperature is elevated up to 476 °C, catalyst amount used is high, 10 wt.% as well as a high methanol to oil molar ratios, i.e., consumption of high amounts of methanol, up to 24:1, are used. Besides, duration of transesterification reaction ranged from two to eighteen hours. This, unfortunately, renders transesterification reaction via different chemically- based heterogeneous catalysts aided by conventional heating an energy intensive costly process.

However, based on investigations cited above, refer to Table (1), it can be observed that microwave heating is advantageous over conventional heating in terms of higher biodiesel yield and shorter time required for a transesterification reaction, with other reaction conditions are moderated. Required reaction temperature, catalyst amount and methanol to oil molar ratio are much lower than that exercised in transesterification reactions under conventional heating. In fact, as stated earlier, heterogenous catalysts are featured with high reactivity, stability and selectivity. These features could be further boosted by microwaves for the benefit of increased reaction rate, longer catalyst lifespan and increased production selectivity, respectively. The catalytic reactivity of a heterogenous catalyst is a measure of the extent of chemical bonds between its surface and reactants involved in the reaction. It depends on the structure and composition of sites on the surface of the catalyst. Microwaves with the aid of polarity of reactants molecules contribute to faster rates of rotation of these molecules leading to increased reaction rates. Furthermore; perhaps, one reason that all investigations under scrutiny have used methanol as an alcohol for transesterification reactions is its high polarity as well as its higher dielectric constant than other alcohols, that render it the fastest alcohol to heat up promoting its capability to absorb microwaves [60]. This can help improve the transesterification reaction under microwave irradiation, which as mentioned above, is governed by ionic conduction and dipolar polarization [11]. Moreover, it has been proposed that via microwave heating, inevitable catalyst deactivation, by poisoning, sintering, coking and leaching, could be retarded, i.e., a longer catalyst lifetime. The influence of microwave heating on the selectivity of a heterogenous catalyst can be understood through rapid heating rates and high temperatures that localize on certain sites on the surface of the catalyst, by which a non- uniform distribution of electromagnetic field develops, due to the presence of some metals when impregnated on the surface

Table 1 A summary of some investigations on microwave-assisted transesterification of different non-edible and waste feedstocks

Feedstock Oil	Catalyst	Transesterification Reaction Parameters				Biodiesel Yield/ Conversion, %	Reference
		Reaction Temperature, °C	Maximum Reaction Time, min	Maximum Catalyst Concentration	Methanol to Oil Molar Ratio		
Yellow horn oil	Heteropolyacid catalyst	-	10	1 wt.%	12:1	Y= 96.22	23
Palm oil	NaOH	70	1.75	1 wt.%	12:1	Y= 99.40	31
Pongamia pinnata seeds oil	NaOH	60	5	0.5 wt.%	1:6	Y= 96	26
Pongamia pinnata seeds oil	KOH	60	5	1 wt.%	1:6	Y= 96	26
Jatropha oil	Potassium fluoride modified hydrotalcite		30	10 wt.%	2:10	Y= 97	36
Jatropha curcas oil	20% KOH impregnation on CaO		68	3.17 wt.%	8.42:1	Y= 97.1	37
Soybean oil	Alumina/silica loaded with potassium sodium tartrate	65	45	8 wt.%	13:1	Y= 96.5	38
Soybean oil	Potassium hydroxide (KOH) impregnated alumina (KOH/ɣ- Al_2O_3)	65	35	3 wt.%	12:1	Y= 97.30	39
Wet microalgal biomass	Ionic liquid	-	25	-	4:1	Y= 42.22	40
Camelina sativa oil	BaO	-	4	1.5 wt.%	9:1	Y= 94	25
Soybean oil	Amorphous SiO2 loaded with 10 wt.% of sulfonic groups	-	-	1 wt.%	1:10	-	41
Waste cooking oil	Heterogeneous base catalyst- calcium diglyceroxide	62	15	1.03 wt.%	7.46:1	Y= 94.86	32
Jatropha oil	KF-Modified Natural Halloysite	-	30	Catalyst/oil:1/30	8:1	Y= 83.77	42
Waste cotton seed and cooking oil	CaO	-	9.7	1.33 wt.%	9.6:1	Y= 89.94	43
Soybean oil	Nano powder calcium oxide	60	60	3 wt.%	7:1	Y= 96.60	24
Corn oil	Diphenylammonium salt	150	20	20 mol. %	5:2, g/g	Y= 100	44
Castor oil	55% H_2SO_4/C	58	2	1.44 wt. %	7.12:1	Y= 92.15	21
Castor oil	H_2SO_4 immobilised in SiO2	60	30	10 wt. %	6:1	C= 95	45
Rapeseed oil	KSF montmorillonite	170	60	10 wt. %	9:1	Y= 51	46
Free fatty acid stearic acid	Macroporous styrene chelate resin, with -NHCH2PO3H2 functional groups	80	420	9 wt. %	11:1	C= 90	47
Waste lard fat	35% CaO/zeolite	-	1.25	8 w/v	30:1	90.89	48
Chlorella vulgaris lipid	SiC-NaOH/GO	85	5	4 wt. %	48:1	Y= 81	49
Canola oil	ZnO/La2O2CO3	85	5	1 wt. %	12:1	Y>95	50

Table 2 A summary of some investigations on transesterification of different feedstocks under conventional heating

Catalyst	Transesterification Reaction Parameters				Biodiesel Yield/ Conversion, %	Reference
	Reaction Temperature, °C	Maximum Reaction Time, min	Maximum Catalyst Concentration	Methanol to Oil Molar Ratio		
Sulfated zirconia	150	240	7.61 wt.%	9.88:1	Y= 90	51
KOH	65	120	1 wt. %	9:1	Y= 95	52
Sulfated zirconia and KOH	63.50	-	1.439 wt. %	7.472:1	Y= 84.51	53
Sulfonated poly (vinyl alcohol), SPVA, and zirconium sulfate ($Zr(SO_4)_2$),	65	120	4 wt. %	12:1	Y= 95.1	54
Tungstophosphoric acid (TPA), impregnated on four different supports such as hydrous zirconia, silica, alumina and activated carbon	200	-	3 wt. %	9:1	Y= 90	55
$AlCl_3$	100	1080	5 wt. %	24:1	C= 98	56
Zeolite	65	-	10 wt.%	16:1	Y= 84	57
Ion exchanger using natural zeolite	60	120	100 g KOH/100 ml	-	Y= 95.24	58

Table 3 Comparison Between Conventional and Microwave- Assisted Transesterification Reactions of Some Non-Edible and Waste Feedstock Oils

Feedstock Oil	Conventional Heating						Microwave Heating					
	Catalyst	Catalyst Concentration, wt. %	Molar Ratio	Reaction Temperature, C	Reaction Time, Min	Yield/Conversion, %	Catalyst	Catalyst Concentration, wt. %	Molar Ratio	Reaction Temperature, C	Reaction Time, Min	Yield/ Conversion, %
Canola Oil	$AlCl_3$	5	24:1	100	1080	C= 98	$ZnO/La_2O_2CO_3$	1	12:1	85	5	Y >95
Jatropha Curcas Oil	Sulfated Zirconia	7.61	9.88:1	150	240	Y= 90	KOH	3.17	8.42:1	-	68	Y= 97.1
Waste Oil	Zeolite	10	16:1	65	-	Y= 84	Calcium Diglyceroxide	1.03	7.46:1	62	15	Y= 94.86

of that catalyst; for instance. This has the outcome of increasing product selectivity through rapid activation of reactants [12] while reducing the production of by-product(s), i.e., a simpler and shorter time of downstream separation [61-62].

Also, in contrast to conventional heating, phenomena like generation of hot- spots, superheating and selective species heating *do* accompany microwave heating which positively influence heating process efficiency and accordingly transesterification reaction rate by which a higher biodiesel yield can be obtained in a shorter reaction time. Due to non- uniform distribution of electromagnetic field on the surface of the heterogenous catalyst, hot- spot zones generate aligning on the catalyst's surface, creating a temperature gradient between 15- 200 °C. Intensity of the formed temperature gradient largely depends on the thermal conductivity of the catalyst used. This leads to a localization of high temperatures in that region which promotes product (biodiesel) formation as a result of increased reaction rate. Also, due to the temperature gradient, product formed on the surface of the heterogenous catalyst in its active sites will have to migrate back to the bulk where the temperature is ubiquitously lower. In another study, it was found that the intensity of electric field is utmost at the point of contact between two adjacent catalyst particles [63]. Formation of hot- spot zones is further promoted if the heterogenous catalyst used in transesterification reaction consists of metal(s) impregnated on its surface. Furthermore, due to the contact of microwaves with metal(s) involved, local micro-plasmas and electrical arc at metal sites are formed which positively affect the reaction through forming another temperature gradient within the catalyst, i.e., between the body of the catalyst and metal sites [64]. In addition, heterogenous catalyst particle geometry, morphology and content of electrically conductive particles within its matrix, all play a role in enhancing the formation of hot- spot zones. It was found that, a spiked heterogenous catalyst exhibited better dielectric properties than that of a cubed one. Understandably, conductive particles when added to the matrix of a heterogenous catalyst were found to support the formation of hot-spot zones [65]. In addition to this, minimal heat loss renders microwave heating a superb heating means. Finally, selective species heating via microwaves can be explained through different responses of metals loaded to the surface of the heterogenous catalyst to microwave irradiation. Depending on these different responses, certain part of the heterogenous catalyst (selective species) will be heated the most leading to increased reaction rate [12**].**

4. Comparison Between Conventional and Microwave- Assisted Transesterification Reactions of Some Feedstock Oils

Although yields/conversions obtained out of all microwave-assisted transesterification reactions are always higher than that obtained out of transesterification reactions of the same feedstock oils in which conventional heating is used while using different catalysts, a proximity of the values of these yields/conversions obtained can be noticed. However, this proximity is not available when comparing catalyst concentrations, methanol to oil molar ratios, reaction temperatures and times applied in both transesterification reactions. In transesterification reactions heated- up conventionally, these parameters are evidently higher by several orders of magnitude when compared to those applied in microwave- assisted transesterification. Numerical values that support this argument are displayed in Table (3).

4. CONCLUSION

High energy consumption and; thus, high operating cost, that have been among the challenges that hinder commercialization of biodiesel synthesis through catalytic transesterification by means of heterogenous catalysts, may be diminished if transesterification reaction is assisted by microwaves. This is also applicable to the time required for product- catalyst separation owing to the good features of heterogenous catalysts mentioned above. Furthermore, cost of raw materials used for biodiesel synthesis can also be reduced if waste or non- edible oils are used instead of fresh edible oils. According to results reported in works under scrutiny in this paper, yield of biodiesel based on waste and non- edible oils has not been compromised and is comparable to that obtained from fresh edible oils. Heterogeneously- catalyzed transesterification reactions heated- up by conventional heating suffer from the need of high temperatures, heat loss and non- uniform temperature distribution. In heterogeneously- catalyzed transesterification reactions supplemented by microwaves; however, reaction conditions are moderated, heat loss and reaction time are little while process efficiency is high. Shortened transesterification reaction time and high process efficiency might be attributed to the improved reaction kinetics while heating via microwaves in comparison to conventional heating. This improvement is due to the productive integration between microwaves and the high reactivity, stability and selectivity of the heterogenous catalyst used, through faster movement of reacted molecules, low catalyst deactivation and rapid heating rates and high temperatures that localize on certain sites on the surface of the catalyst, respectively. Furthermore, polarity and high dielectric constant of the used alcohol for transesterification reaction could contribute towards better reaction kinetics. Perhaps, this is the reason why all investigations under scrutiny have used methanol as an alcohol for their transesterification reactions. In addition, microwave- assisted heterogeneously- catalyzed transesterification reactions are featured with the generation of hot- spot zones, superheating and selective species heating. Out of these phenomena, the efficiency of heating process is increased; thus, rate of transesterification reaction is accordingly increased while production of by- products is decreased.

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