*Review*

# Microwave Assisted Biodiesel Production Using Heterogeneous Catalysts

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**Abstract:** As a promising renewable fuel, biodiesel has gained worldwide attention to replace fossil-derived mineral diesel due to the threats concerning the depletion of fossil reserves and ecological constraints. Biodiesel production via transesterification involves using homogeneous, heterogeneous and enzymatic catalysts to speed up the reaction. The usage of heterogeneous catalysts over homogeneous catalysts are considered more advantageous and cost-effective. Therefore, several heterogeneous catalysts have been developed from variable sources to make the overall production process economical. After achieving optimum performance of these catalysts and chemical processes, the research has been directed in other perspectives, such as the application of non-conventional methods such as microwave, ultrasonic, plasma heating etc, aiming to enhance the efficiency of the overall process. This mini review is targeted to focus on the research carried out up to this date on microwave-supported heterogeneously catalysed biodiesel production. It discusses the phenomenon of microwave heating, synthesis techniques for heterogeneous catalysts, microwave mediated transesterification reaction using solid catalysts, special thermal effects of microwaves and parametric optimisation under microwave heating. The review shows that using microwave technology on the heterogeneously catalysed transesterification process greatly decreases reaction times (5–60 min) while maintaining or improving catalytic activity (>90%) when compared to traditional heating.

**Keywords:** microwave-assisted transesterification; heterogeneous catalyst; biodiesel; reaction time; thermal effects

## 1. Introduction

In the twenty-first century, it has become a significant constraint for the scientific community to rigorously address the present energy issue while also taking into account ecological concerns about global climate change. The threat of diminishing fossil fuels and ongoing global warming challenges prompted scientists to search for sustainable and renewable energy resources to address the energy demands of the world's growing population. As a result, eco-friendly and renewable fuels are recommended to be sought after and investigated at this time. Biofuels such as biodiesel and bioethanol are proposed as renewable fuels obtained from renewable resources that may be used to replace fossil-derived diesel and gasoline fuels [1–4]. In addition to ensuring the availability of renewable

and sustainable fuels, their quick production techniques must be discovered to fulfil the demands of the rising population.

Transesterification is the most prominent method generally used for biodiesel generation [1,5]. It entails the deployment of homogeneous, heterogeneous or enzymatic catalysts to speed up the reaction [6,7]. Although homogeneous catalysts demonstrate good catalytic activity in transesterification, the difficulties associated with their removal from the mixture and additional washing stages implied extra operational expenses and hence made the overall process less cost-effective [8,9]. These issues can be effectively resolved by the application of heterogeneous catalysts [10,11]. A number of heterogeneous catalysts, either synthetic or derived from waste resources, have been developed to effectively transform oil sources into biodiesel [12–16]. After achieving the optimal performance of these catalysts, research has now shifted in other directions, such as applying non-conventional techniques such as plasma, ultrasonic, microwave-assisted methods for getting rapid conversions [11].

The electromagnetic rays with wavelengths of 0.01–1 m along with frequency varying from 0.3 to 300 GHz are called microwave irradiation. For instance, radar transmissions operate at wavelengths ranging from 0.01 to 0.25 m and telecommunications practice the spare portion of wavelengths. All household microwave ovens and reactors for chemical manufacturing function at a frequency of 2.45 GHz, holding a wavelength of 12.25 cm with attention to evade the interferences with mobile phone frequencies and telecommunications. The microwave region stays between infrared and radio waves [17]. The electromagnetic spectrum is seen in Figure 1. At the right, the tiny visible light range is expanded.
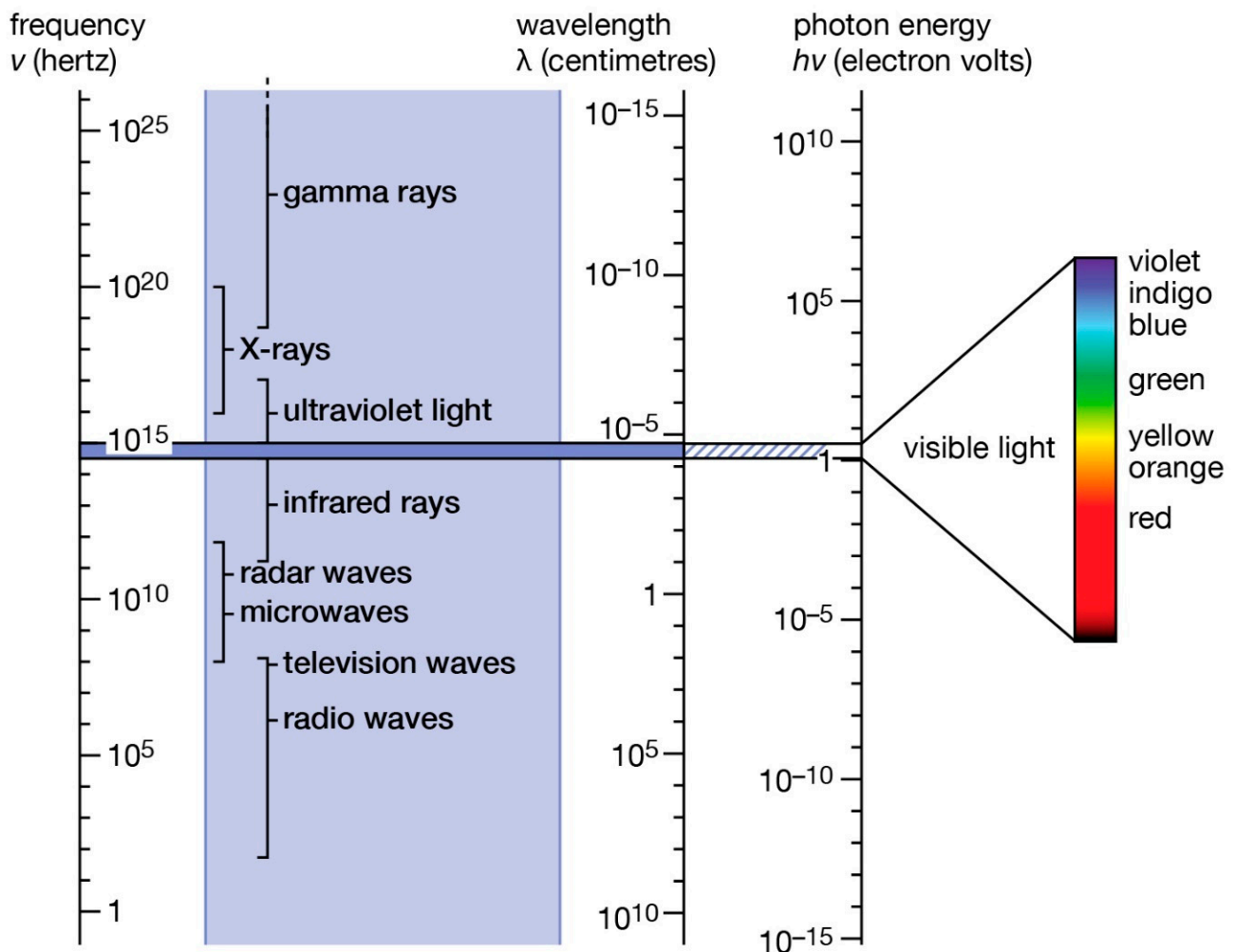


**Figure 1.** Electromagnetic spectrum and their corresponding wavelengths and frequencies.

Microwaves improve and accelerate chemical reactions because of the direct accessibility of energy to the reactants. In the case of microwaves, heat transfer is even more efficient than normal heating, therefore leading to short reaction times [18]. In the case of normal heating, an oil bath or furnace is employed, which initially heats the walls of the container by conduction or convection and later heat is transmitted to the centre of the sample. At the same time, microwaves heat the target compounds without heating oil bath or furnace, which conserves energy and time. It boosts the reaction speed and makes the separation mechanism simpler in comparison with normal heating. It has been stated that the reaction accelerates via thermal effect only, also called the kinetic effect, which is associated with instant temperature rise during the ionic conduction/dipolar polarisation under microwave heating [19,20]. It has also been concluded that microwave heating also significantly lessened the reaction time while keeping the kinetic mechanisms of the same reactions alike. The other advantages of microwave heating include selective heating, diffusional radiation, reduced adverse emissions, clean energy and reaction trend, molecular level heating, etc. [21]. In addition, along with the utilisation of efficient technologies, optimisation of reaction parameters is still necessary to get the highest yield of biodiesel. Nowadays, various researchers have also targeted the application of different techniques such as artificial neural network (ANN), adaptive neuro-fuzzy inference system (ANFIS) and response surface methodology (RSM) and hybrid approaches such as support vector machine-RSM (SVM-RSM) and extreme learning machine-RSM (ELM-RSM) to optimise reaction parameters to get the maximum yields of biodiesel [22,23].

This mini review has concentrated on reviewing the research carried out to date on microwave-assisted heterogeneously catalysed biodiesel generation. It incorporates the phenomenon of microwave heating, synthesis techniques for heterogeneous catalysts, microwave mediated transesterification reaction using solid catalysts, special thermal effects of microwaves and parametric optimisation under microwave heating. It suggests that the application of microwave technology on the heterogeneously catalysed transesterification process significantly reduces the reaction times with better catalytic activity compared to conventional heating.

## 2. Synthesis Techniques for Heterogeneous Catalysts

There are a variety of techniques that have been employed in the literature for the manufacturing of heterogeneous catalysts ranging from the direct use of material after grinding to the other modification techniques such as calcination, physical mixing, bifunctional modification, wet impregnation, co-precipitation, calcination-hydration-dehydration, and sol-gel method etc. [24]. Either heterogeneous catalysts can be produced synthetically from chemicals or can be derived from waste resources such as eggshells, waste bones and other agricultural waste. For instance, some of the heterogeneous catalysts based on metal and mixed metal oxides such as calcium oxide ($CaO$), strontium oxide ($SrO$), magnesium oxide ($MgO$), calcium-diglyceroxide, calcium methoxide, aluminium oxides-based catalysts and sulphated zirconia, etc., are commercially available and others such as $LiAlO_2$, $Li_4SiO_4$ etc., can be synthesised from variable sources by adopting suitable techniques for catalysts synthesis [25–29]. Moreover, nowadays, it has become decisive to carefully select sustainable and renewable sources from which heterogeneous catalysts should be prepared to avoid the ill effects on the environment. Therefore, research has been directed towards waste-based resources and environmentally friendly techniques for catalyst synthesis. The synthesis methods for heterogeneous catalysts, along with their brief description, are provided in Table 1.

**Table 1.** Categorisation of heterogeneous catalysts synthesis methods.

| Method | Description | Ref. |
|---|---|---|
| Impregnation method | A solution of precursor/active components is taken, and carrier is immersed in it. After a while, when equilibrium is achieved, the remaining liquid is withdrawn and the catalyst is acquired following the drying, calcination and activation | [30] |
| Precipitation | A precipitation agent is added in an aqueous solution of metallic salts to obtain the crystal of carbonates, hydrated oxides, or gels. | [31] |
| Precipitation-impregnation method | A method based on the combination of the impregnation and precipitation technique initially synthesised the precipitant matrix in the impregnation solution. Upon completion of impregnation, the precipitant is accumulated on the carrier's surface through heating. | [32] |
| Chemical deposition method | The films are produced on the substrate surface via chemical reactions using materials containing film components. | [33] |
| Sol-gel method | The butyl titanate and anhydrous ethanol are mixed slowly to another solution of demineralised water, anhydrous ethanol, nitric acid and suitable quantity of nitrate precursor at ambient temperature under strong mixing to perform hydrolysis | [34] |
| Physical mixing | The multiple materials in a ground form are well mixed or blended | [34] |
| Calcination | The substance is exposed to elevated temperature in a furnace | [34] |

## 3. Microwave Assisted Transesterification Using Heterogeneous Catalysts

The transesterification reaction involves oil, alcohol and catalyst, which are vigorously mixed under a specified temperature for the reaction to proceed. In the case of microwave aided biodiesel production, these three components are mixed and processed under microwave irradiation [35]. Upon completion of the reaction, biodiesel is separated and purified. Methanol is preferably used for microwave-assisted reactions because of its high polarity and capability to absorb microwaves. The transesterification procedure may be enhanced through ionic conduction and dipolar polarisation under microwave heating, which may have a higher reliance on the absorption ability and polarity of the reacting species [20]. Heterogeneously catalysed transesterification under microwave irradiation displayed short reaction times with better biodiesel yields as displayed in Table 2.

For instance, catalysts derived from waste eggshells provided more than 95% yield of biodiesel within 4 min under microwave mediated transesterification reaction [36]. In another study, corn cobs derived sulfonated activated carbon was utilised as a solid catalyst for microwave supported reaction process of soybean oil. The FAME yield of 88.7% was attained in 20 min with methanol/oil ratio of 6:1. It indicates the effectiveness of the heterogeneously catalysed transesterification reaction in the occurrence of microwaves [37]. Microwave supported transesterification of yellow horn oil utilising heteropolyacid catalyst depicted more than 96% yield of biodiesel in 10 min with catalyst amount of only 1 wt.% [38]. Similarly, in another investigation, Guinea fowl bone-based heterogeneous catalyst displayed 95.82% biodiesel yield within 20 min in the transesterification of oil (*Annona squamosa* L. seed) using microwaves [39]. In another place, natural hydroxyapatite synthesised from pork bone was applied as solid catalyst in microwave supported

transesterification of jatropha oil [40]. The greatest yield of 94% was achieved in 5 min using microwave power of 800 W (CH$_3$OH/oil: 18/1, catalyst weight: 4%). Additionally, the investigations mentioned above suggest a significant reduction in reaction times in the presence of microwaves while using heterogeneously catalysed systems for biodiesel generation.

Hsiao et al. [41] analysed the microwave mediated transesterification of soybean oil into methyl esters depicting above 95% yield of biodiesel while employing nano-powder CaO as a heterogeneous catalyst. As per their studies, microwave heating was appeared to be more proficient than a traditional bath for biodiesel generation. Patil et al. [42] studied the reaction kinetics of transesterification of oil (*Camelina sativa*) using metal oxides catalysts such as oxides of Barium, calcium, magnesium and strontium under the microwave and conventional heating conditions. The comparison between both heating methods indicated that the k values for the microwave-mediated process were of two orders of magnitude higher in comparison with the traditional heating scheme. It has been established that the heating technique displays a substantial effect in bettering the reaction kinetics.

In another study, Gupta and his coworkers [43] attempted to adjust the reaction parameters in the microwave mediated transesterification of WCO involved biodiesel generation using calcium diglyceride as a heterogeneous catalyst. As per their studies, under the optimised reaction variables such as methanol/oil 7.46:1, catalyst weightage of 1.03%, the temperature of 62 °C, the highest biodiesel yield of 94.86% was attained within 15 min using microwave heating whereas only 42.59% yield was achieved under the same reaction parameters using normal heating process.

The transesterification of palm oil employing hydrated heat-treated seashells as a heterogeneous catalyst has been examined for microwave heating and conventional heating conditions [44]. It was detected that yield of only 59.2% was achieved after 2 h in the conventional reactor at high temperature and pressure, whereas under microwave heating, the performance of the same catalyst enhanced, and a maximum yield of 96% was obtained after 10 min with a catalyst weight of only 0.5 g.

Therefore, it can be deduced from the studies that solid catalysts mediated reaction process occurring under microwaves displays short reaction times and better yields as compared to normal heating while using the same catalysts. Alongside, the microwave heating mechanism improves reaction kinetics by increasing rate constant values, which results in better conversions.

**Table 2.** Synopsis of recent works reported for microwave mediated biodiesel generation using various heterogeneous catalysts.

| Materials | Catalyst Preparation | Catalyst | Oil Used | Reaction Parameters | Yield | Ref. |
|---|---|---|---|---|---|---|
| Waste eggshells | Calcined at 800 °C for 4 h in air atmosphere (10 °C/min). | CaO | Palm olein oil | M/O: 18, catalyst: 15 wt.%, time: 4 min, temperature: -, mic. power: 900 W | Y = 96.7 | [36] |
| Corn cobs | First, activated carbon was obtained from corn cobs and then sulfonated by applying sulphonating agent. | Sulfonated activated carbon | Soybean oil | M/O: 6, catalyst: 20 wt.%, time: 20 min, temperature: -, mic. power: 0–600 W | Y = 88.7 | [37] |

**Table 2.** *Cont.*

| Materials | Catalyst Preparation | Catalyst | Oil Used | Reaction Parameters | Yield | Ref. |
|---|---|---|---|---|---|---|
| Waste shells of oyster and Pyramidella | Calcined at 900 °C for 2 h in air environment (10 °C/min) | CaO | Jatropha curcas oil | M/O: 15, catalyst: 4 wt.%, time: 5 min, temperature: -, mic. power: 800 W | Y = 93 | [45] |
| $ZrO_2$-supported bamboo leaf ash | First, addition of ZrOCl solution to isopropanol solvent and water while stirring to get the precursor $ZrO_2$ solution. Afterward, the mixing of the suspension of precursor solution and leaf ash accompanied by adding HCl and then refluxing for 4 h is needed to get $ZrO_2$/ash composite. The mixture was then dried and calcined. | Silica-based material with acid properties of $ZrO_2$ | Soybean oil | M/O: 15, catalyst:12 wt.%, time: 30 min, temperature: -, mic. assisted | Y > 90 | [46] |
| Cassava peel derived sulfonated acid catalyst | Initially, the biomass pyrolysis (slow) was carried out at 400 °C for 1 h. After that, the sulfonation for the catalyst functionalisation was executed by introducing $SO_3H$ groups into biochar to get biochar-based acid catalyst. The co-precipitation technique was applied for the synthesis of $Fe_3O_4$ magnetic nanoparticles. The nanomagnetic biocatalyst was synthesised by mixing magnetic nanoparticles and sulfonated biochar catalyst in demineralised $H_2O$ utilising an ultrasonicator at an ambient temperature for 8 h. Later, the nanomagnetic biocomposite was dried and stored in a desiccator. | weak hydroxyl and strong carboxylic and sulfonic acidic groups | Millettia pinnata seed oil | M/O: 11, catalyst: 3 wt.%, time: 45 min, temperature: -, mic. assisted | Y = 98.7 | [47] |
| Heteropolyacid catalyst | The catalyst was purchased as it is. | $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ | Yellow horn oil | M/O: 12, catalyst: 1 wt.%, time: 10 min, temperature: -, mic. power: 500 W | Y = 96.22 | [38] |
| Potassium fluoride (KF) modification of hydrotalcite (Sorbacite®) | The solid reaction technique was used for the catalyst production. The mixture of potassium fluoride and hydrotalcite was milled and heated at a specified temperature for 2 h. KF content was differed from 5–30 wt.% in range. | KF modified hydrotalcite | Jatropha oil | M/O: 2–10, catalyst: 3.33, 5, 10 wt.%, time: 2–30 min, temperature: -, mic. power: 0–900 W | Y = 97 | [48] |

**Table 2.** *Cont.*

| Materials | Catalyst Preparation | Catalyst | Oil Used | Reaction Parameters | Yield | Ref. |
|---|---|---|---|---|---|---|
| KOH impregnated CaO catalyst | KOH impregnated calcium oxide (CaO) catalysts were synthesised by wet impregnation method | 20% KOH impregnation on CaO | Jatropha curcas oil | M/O: 8.42, catalyst: 3.17 wt.%, time: 67.9 min, temperature: -, mic. assisted | Y = 97.1 | [49] |
| Guinea fowl bone | Calcined at 900 °C for 5 h | β-Ca$_3$(PO$_4$)$_2$ | *Annona squamosa* L. seed oil | M/O: 18, catalyst: 4 wt.%, time: 20 min, temperature: -, mic. power: 800 W | Y = 95.82 | [39] |
| Lignin based heterogeneous solid acid catalyst extracted from sugarcane bagasse | The alkaline pulping method was employed for lignin extraction from bagasse followed by the partial carbonisation in a furnace at 400 °C. Later, the product was mixed with conc. H$_2$SO$_4$ at a specified temperature for 2 h. | Sulfonic group, carboxyl group and hydroxyl group after effective chemical activation and sulfonation. | Waste cooking oil | M/O: 18, catalyst: 15 wt.%, time: 15 min, temperature: -, mic. assisted | Y = 89.19 | [50] |
| Alumina/silica loaded with potassium sodium tartrate | A one-step sol-gel method was employed for catalyst preparation. In the end, the catalyst was heat-treated at elevated temperature for 5 h. | Good dispersion of C$_4$H$_4$O$_6$KNa on the support | Soybean oil | M/O: 13, catalyst: 8 wt.%, time: 45 min, temperature: 65 °C, mic. assisted | Y = 96.5 | [51] |
| A sulfonated-glucose solid acid catalyst | The incomplete carbonisation of a specific quantity of D-glucose was carried out while heating at 400 °C for 12 h under N$_2$ gas. The product was ground and heated at 160 °C under inert atmosphere for 12 h in the presence of conc. H$_2$SO$_4$. Lastly, the suspension was further diluted with distilled water and the precipitate was acquired. | Glucose-SO$_3$H catalyst | Non-edible palm fatty acid distillate | M/O: 12, catalyst: 3 wt.%, time: 15 min, temperature: 75 °C, mic. assisted | Y = 96 | [52] |
| Potassium hydroxide (KOH) impregnated alumina catalysts | Wet impregnation method was employed for KOH/γ-Al$_2$O$_3$ catalysts preparation using the γ-Al$_2$O$_3$ support. The powdery material was heat-treated in a tube furnace under the air environment at the specified time and temperature. | K$_2$O | Soybean oil | M/O: 12, catalyst: 3 wt.%, time: 35 min, temperature: 65 °C, mic. assisted | Y > 95 | [53] |
| Ionic liquid (IL)-microwave heating | - | - | Wet *Nannochloropsis* sp. biomass | M/O: 4, catalyst: -, time: 14 min, temperature: -, mic. assisted, IL ratio maintained at 1:0.5 | Y = 42.22 | [54] |

**Table 2.** *Cont.*

| Materials | Catalyst Preparation | Catalyst | Oil Used | Reaction Parameters | Yield | Ref. |
|---|---|---|---|---|---|---|
| Strontium Oxide Agglomerates Depositing upon Titanium Plate | Strontium oxide powder deposited on a titanium plate picked as the support because of the possible formation of $SrTiO_3$ at their interface after heat treatment | $SrO/TiO_2\_P$ | Olive oil | M/O: 6, catalyst: 3 wt.%, time: 4 min, temperature: -, mic. assisted | C = 87.7 | [55] |
| Metal Oxide catalysts | Barium oxide | BaO | Camelina sativa oil | M/O: 9, catalyst: 1.5 wt.%, time: 4 min, temperature: -, mic. assisted | Y = 94 | [42] |
| The propyl-$SO_3H$ amorphous $SiO_2$ | The sol-gel technique was employed for the preparation of the propyl-$SO_3H$ (10 wt.%)/silica. The specified quantity of tetraethyl orthosilicate was added in ethanol and kept for stirring for 15 min at 45 °C. Next, a specific quantity of acetic acid aqueous solution (pH:5) was put on the mixture, followed by 3-mercaptopropyltrimethoxy silane and hydrogen peroxide. The solution was continuously mixed at 45 °C overnight under reflux followed by the increase in temperature up to 80 °C and remained same for 4 h. The gel was formed by heating up to 100 °C and finally dried. | Amorphous $SiO_2$ loaded with 10 wt.% of sulfonic groups | Soybean oil | Substrate/tert-butyl-methyl ether:1/10, catalyst: 1 wt.%, time: -, temperature: -, mic. power: 20 W | - | [56] |
| Heterogeneous base catalyst-calcium diglyceroxide | A specific quantity of calcined CaO was put into the glass reactor carrying methanol and glycerol. The resulting product was stirred at 60 °C for 3 h that lead to the formation of CaDG. | CaDG as a heterogeneous base catalyst | Waste cooking oil | M/O: 7.46, catalyst: 1.03 wt.%, time: 15 min, temperature: 62 °C, mic. assisted | Y = 94.86 | [43] |
| Pork bone derived natural hydroxyapatite | Calcination at 900 °C for 2 h | $\beta$-$Ca_3(PO_4)_2$ | Jatropha Curcas oil | M/O: 18, catalyst: 4 wt.%, time: 5 min, temperature: -, mic. power: 800 W | C = 94 | [40] |
| KF-Modified Natural Halloysite | The solid reaction method was applied for the catalyst synthesis. The mixture of potassium fluoride and halloysite was milled and heated at a specified temperature for 2 h. KF content was differed from 5–30 wt.% in range. | KF-Modified Natural Halloysite | Jatropha oil | M/O: 8, catalyst/oil: 1/30, time: 30 min, temperature: -, mic. assisted | Y = 83.77 | [57] |

**Table 2.** *Cont.*

| Materials | Catalyst Preparation | Catalyst | Oil Used | Reaction Parameters | Yield | Ref. |
|---|---|---|---|---|---|---|
| Waste eggshells | The crushed dried eggshells were heat-treated in a furnace at a temperature of 900 °C–950 °C for 4 h. | CaO | Lagenaria vulgaris seed oil | M/O: 40, catalyst: 5 wt.%, time: 40 min, temperature: 60 °C, mic. assisted | Y = 95.07 | [58] |
| Calcium oxide catalyst | $CaCO_3$ powder was calcined for 5 h at 900 °C. | CaO | Waste cotton-seed cooking oil | M/O: 9.6, catalyst: 1.33 wt.%, time: 9.7 min, temperature: -, mic. assisted | Y = 89.94 | [59] |
| Hydrated calcined Cyrtopleura costata seashells | Seashells were initially washed and dried accompanied by grinding and then calcined at 900 °C for 2 h, Hydration was attained by placing the heat-treated product into atmosphere for a week in a humidity-controlled room. | $Ca(OH)_2$ | Palm oil | M/O: 9, catalyst: 0.5 wt.%, time: 10 min, temperature: -, mic. assisted | Y = 96.7 | [44] |
| Nanopowder calcium oxide | Nano CaO (purity: 98%) were purchased and applied. | Nano-CaO | Soybean oil | M/O: 7, catalyst: 3 wt.%, time: 60 min, temperature: 60 °C, mic. assisted | Y = 96.6 | [41] |
| Diphenyla-mmonium salt catalysts | | Dipheny-lammonium salt | Corn oil | M/O: 5/2 (g/g), catalyst: 20 mol%, time: 20 min, temperature: 150 °C, mic. assisted | Y = 100 | [60] |
| Microwave Absorption Catalysts | $H_2SO_4/C$ catalyst was synthesised via impregnation method | $H_2SO_4/C$ catalyst | Castor oil | M/O: 12, catalyst: 5 wt.%, 55 wt% $H_2SO_4$ time: 60 min, temperature: 65 °C, mic. assisted | Y = 94 | [61] |
| Acidic silica gel as catalyst | A specified quantity of silica and sulphuric acid were mixed and agitated at ambient temperature for 30 min. The resulting solid was strained and finally dried and stored in a desiccator | $H_2SO_4$ immobilised in $SiO_2$ | Castor oil | M/O: 6, catalyst: 10 wt.%, time: 30 min, temperature: 60 °C, mic. assisted | C = 95% | [62] |
| Waste Cement Clinker Catalyst | Calcinated clinker is utilised to generate a limestone-based catalyst | CaO, Silica, Alumina, Iron oxide | Rubber seed oil | M/O: 5, catalyst: 6 wt.%, time: 60 min, temperature: 60 °C, mic. assisted | C = 96.8 | [63] |

**Table 2.** *Cont*.

| Materials | Catalyst Preparation | Catalyst | Oil Used | Reaction Parameters | Yield | Ref. |
|---|---|---|---|---|---|---|
| KSF montmoril-lonite | Catalysts have been purchased from Aldrich | | Rape oil | M/O: 9, catalyst: 10 wt.%, time: 60 min, temperature: 170 °C, mic. assisted | Y = 51 | [64] |
| Aminophosphonic acid resin D418 | Aminophosphonic acid resin D418 was purchased and used. | Macroporous styrene chelate resin, with -NHCH$_2$PO$_3$H$_2$ functional groups | Free fatty acid stearic acid | M/O: 11, catalyst: 9 wt.%, time: 7 h, temperature: 80 °C, mic. assisted | Y > 90 | [65] |
| Calcium oxide (CaO) loaded on zeolite | The manufacturing of an active solid catalyst via CaO loaded on high silica zeolite employing impregnation method | 35% CaO/zeolite | Waste lard fat | M/O: 30, catalyst: 8 $w/v$, time: 1.25 min, temperature: -, mic. power: 595 W | Y = 90.89 | [66] |
| K$_2$CO$_3$/Al$_2$O catalyst | The supported catalysts K$_2$CO$_3$/Al$_2$O$_3$, was attained via sedimentation subsequently, the calcination of the catalyst active mass. | 5% K$_2$CO$_3$/Al$_2$O | Sunflower oil | M/O: 16, catalyst: 2.5 wt.%, time: 30 min, temperature: 70 °C, mic. assisted | C > 60 | [67] |
| Graphene oxide-based catalyst | Graphene oxide was synthesised from graphite powders through modified Hummer's method. The SiC-NaOH/GO was synthesised by in-situ impregnation method. | SiC-NaOH/GO catalyst | Chlorella vulgaris lipid | M/O: 48, catalyst: 4 wt.%, time: 5 min, temperature: 85 °C, mic. assisted | Y = 81 | [68] |
| Elephant-ear tree pod husk | The dried pods were handpicked, and seeds were separated manually parting the sticky husk behind. One part of the husks was powdered, as the other portion was charred to ash in air. After that, part of the ash was exposed to calcination between 300 and 1100 °C for 4 h using a muffle furnace. | K, Mg, Ca and Fe | Esterified oil mix of neem and rubber seed oil | M/O: 11.44, catalyst: 2.96 wt.%, time: 5.88 min, temperature: -, mic. power: 150 W | Y = 98.77 | [69] |
| ZnO/La$_2$O$_2$CO$_3$ layered composite | The zinc–lanthanum-mixed oxide catalyst was synthesised through an in-situ precipitation technique and later calcined at 550 °C for 6 h | ZnO/La$_2$O$_2$CO$_3$ | Canola oil | M/O: 12, catalyst: <1 wt.%, time: 5 min, temperature: 85 °C, mic. assisted | Y > 95 | [70] |

## 4. Special Thermal Effects of Microwaves on Solid Catalysts

The dielectric materials captivate microwave energy and convert it into heat energy which is appeared as the total loss of microwave energy in materials. This phenomenon is called the thermal effect of the microwave. Figure 2 shows the special thermal effect, also called hot spot, uncovered by various investigators [71–73].
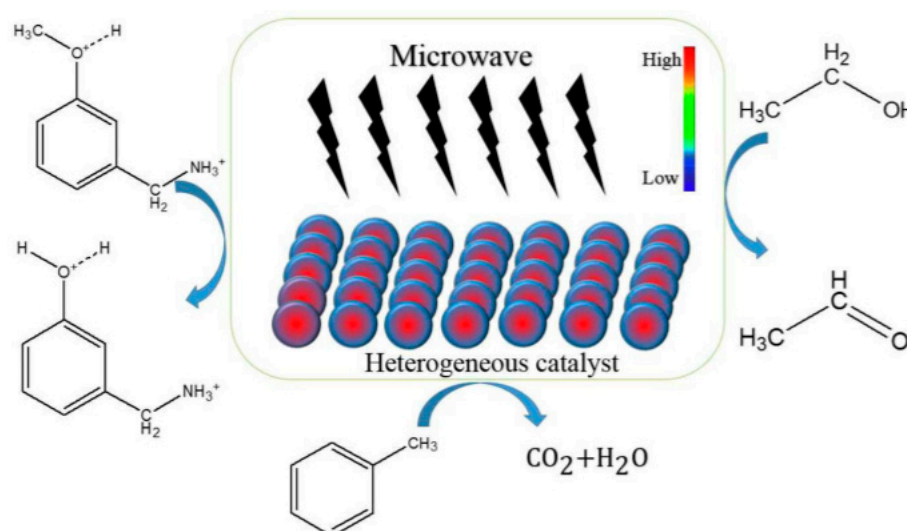


**Figure 2.** Thermal effect mechanism of microwave on heterogeneous catalysts.

Moreover, two mechanisms such as conduction in material and polarisation, are involved in dielectric heating. In conduction, variation in the electric field would oscillate the mobile charged particles or ions, which results in the electric current generation. Heat is generated owing to the internal resistance to this current provoked by the collision of molecules and charged particles. The conduction of charged ions moving randomly in the mixture may also lead to generating heat. If these ions are in a space circumscribed by other molecules and cannot freely couple with the varying electric field, the charge begins to accumulate, and the energy is dissipated as heat [11].

Whereas, in the case of polarisation, the displacement of charged particles from their equilibrium positions occurs within the dielectric material owing to the electric field, inducing dipoles. These dipoles begin to rotate with high frequency upon responding to the applied electric field may generate heat and friction. Polar materials have permanent dipoles that also result in polarisation [11].

Microwave-assisted biodiesel synthesis has been studied with various homogeneous and heterogeneous catalysts by Nayak and his coworkers [74]. The major benefit coupled with the usage of heterogeneous catalysts is their simple separation from the product and reclaim in comparison with homogeneous catalysts. There exists a number of acid or base heterogeneous catalysts synthesised for biodiesel generation. The multiple selectivities of solid catalysts permit the choice of the appropriate catalyst for the reaction [72]. For example, Yuan et al. [61] explored the use of $H_2SO_4/C$ solid acid catalyst for the transesterification reaction in microwave irradiation. Both sulfuric acid and activated carbon possess high dielectric properties and, therefore, absorb microwaves. Owing to this, microwave hotspots are generated on $H_2SO_4/C$ solid acid catalyst in the presence of microwaves which indicates that the temperature of the catalyst would be greater than that of liquid. The elevated temperature from microwave hotspots would offset the activity reduction owing to mass transfer resistance resulted in better catalytic activity. Moreover, in the case of solid catalysts, both internal and external surfaces are simultaneously available for reaction. The endothermal reaction favors high temperature as in the case of transesterification using $H_2SO_4/C$ solid acid catalyst for biodiesel generation, therefore, yield is improved under

microwave heating. In this case, a maximum yield of 94% was achieved under microwave heating compared with conventional heating.

Dipolar polarisation, interfacial polarisation and ionic conduction mechanisms are responsible for microwave energy transfer into microwave absorbing materials [75]. Another explanation stated by the researchers that methanol utilised in transesterification reaction holds a robust microwave absorption property, and hydroxyl groups connected with long-chain molecules act as if fastened to a stagnant raft, with the more localised rotations governing the microwave spectrum and ensuing a molecular level localised superheating, subsequently a substantial drop in activation energy that supports in accelerating the reaction [76,77]. Marwan et al. [44] described that the temperature attained at the catalyst surface could be much greater than the bulk temperature, which increased the biodiesel yield due to the localised superheating.

## 5. Optimisation of Reaction Parameters for Microwave Mediated Heterogeneously Catalysed Transesterification

The optimisation of reaction variables such as alcohol/oil ratio, catalyst weight percent, reaction time, temperature and microwave power etc., are still required for maximising the biodiesel yield under microwave irradiation, similar to the conventional heating scenario. It has been reported that for conventional heating, the optimised reaction parameters for four heterogeneous catalysts including BaO, SrO, CaO and MgO were found to be methanol/oil: 9:1, 12:1, 15:1 and 15:1 respectively, the reaction temperatures of 100, 60, 100, 80 °C, respectively and catalyst loading of 1%, 0.5%, 0.5% and 1% (wt), respectively [78]. On another side, the most favourable reaction conditions for microwave mediated reaction of C. sativa oil in the presence of BaO and SrO catalysts were observed to be methanol/oil: 9:1 and catalyst loading of 1.5% and 2%, respectively. While the reaction times have been significantly dropped for the case of microwave heating using the same catalysts as compared to the standard heating (Figure 3) [42]. However, it seems noteworthy that a higher catalyst amount is required for getting higher biodiesel yield in such a short reaction time. Nowadays, different optimisation techniques such as RSM, ANN, ANFIS, DoE, Taguchi method and some hybrid approaches such as SVM-RSM and ELM-RSM have also been employed for the optimisation of reaction parameters [22,23,79,80].
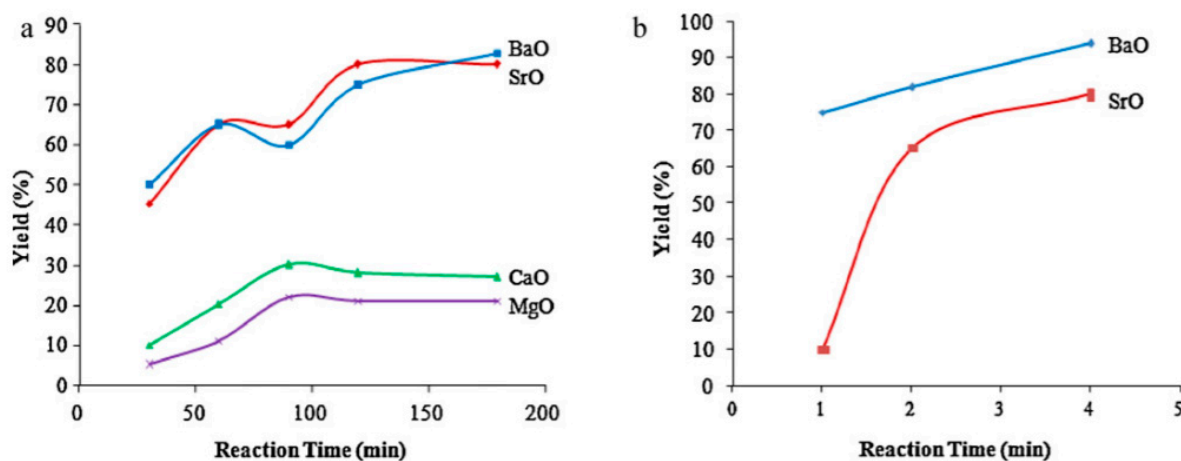


**Figure 3.** FAME yield vs. reaction time for same catalysts under (**a**) Normal heating, (**b**) microwave heating [42] (Licence number: 5196451338660).

## 6. Conclusions

With technological advancement, it has become necessary to adopt cutting-edge technologies to make the overall process more sustainable and time-efficient, particularly in renewable fuels production, such as biodiesel, which is required to avoid the threats of oil reserve depletion and resulting environmental damage. Many studies have been conducted

in recent years on biodiesel production from diverse feedstocks utilising heterogeneous catalysts and traditional heating techniques. Currently, research is being devoted to implementing microwave heating technology for biodiesel synthesis employing heterogeneous catalysts to improve the process's efficiency. This study focuses on the research done to date in microwave aided heterogeneously catalysed biodiesel generation. It examines the phenomena of microwave heating, synthesis strategies for heterogeneous catalysts, microwave mediated transesterification process employing solid catalysts, specific thermal effects of microwaves, and parametric optimisation under microwave heating. The application of microwave technology for biodiesel generation using heterogeneous catalysts has appeared to be quite efficient with respect to biodiesel yield, catalytic activity, reaction time and energy efficiency. It strongly suggests that the application of microwave technology on the heterogeneously catalysed transesterification process significantly reduces the reaction times with better catalytic activity compared to conventional heating. Although microwave mediated biodiesel production is considered fast and energy-efficient, but the major downside associated with it is its lower penetration depth that is a few centimetres. It displays the instant loss in microwave intensity, and this problem may amplify while scaling up the batch process. This issue is required to be rectified, or continuous mode can be adopted using film type reactor to overcome this problem. Moreover, there are other risks such as spark ignition, high-temperature zones at edges, microwave leakages etc., which must be tackled for large scale adoption of this technology. If the mentioned issues are properly managed, commercial adoption of microwave technology would be quite helpful in satisfying the rising demands of biofuels.

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