EKSAKTA
Journal of Sciences and Data Analysis

E-ISSN: 2720-9326
P-ISSN: 2716-0459
DOI: 10.20885/EKSAKTA.vol2.iss2.art6

Review Article

Microwave and Ultrasound Irradiations for the Intensification on Biodiesel Productions: A Mini Review

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Received: 22 September 2021; Accepted: 24 September 2021; Published: 24 September 2021

Abstract: This mini review discusses the roles of intensification process in biodiesel production. Due to the Twelve Principles of Green Chemistry as a foundation for sustainability, the shorter time and efficient energy consumption highlighted the use of microwave and ultrasound irradiation for increasing conversion of biodiesel. The principles and some examples for the process are exhibited. It can be summarized that the intensifications are important innovations, but some optimization and life cycle analysis are required in applicable scales.

Keywords: Biodiesel, Intensification, Microwave, Ultrasound.

Introduction

Renewable energy research is receiving increasing attention in the last decade. It is reported that the consumption of petroleum is 105 times faster than what nature can provide and until now the world's fossil fuel reserves will decrease until 2050 [1], [2]. Meanwhile, fuel consumption is expected to increase by 60% or more over the next 25 years. To reduce dependence on fossil fuels, many countries have committed to renewable energy production while anticipating an increase in greenhouse gas emissions at national and international levels [3], [4]. Biodiesel is one of the selected renewable energies which properly developed for Asian countries. The abundant potencies of plant oils are the main reason besides the easy and fast production of biodiesel [5], [6].

As many chemical processes, some technical factors an important in the productivity of biodiesel. Encouraged by this, in the last decade, the concept of green chemistry has become a central topic in the development of all aspects of chemistry, including synthetic organic chemistry [7]–[9] With 12 principles of green chemistry, the development of production technology that uses the mechanism of synthesis of organic compounds is directed towards environmentally friendly processes. Some of these aspects are the atomic economics of a reaction in which the principles of using as few chemicals as possible and preventing waste are adhered to[10]–[12]. By these principles, the use of low-cost catalysts is chosen. In this regard, catalysis using heterogeneous catalysts is the key to green conversion [12], [13]. In addition, by the concept of less energy such as the electrical energy needed to transfer kinetic energy in each molecule involved in the reaction and no less important is the reusability of components from a reaction mechanism. The developments cover the intensification of transesterification in biodiesel production. This mini review discusses the intensifications on biodiesel productions and the perspective for future developments. The review focused on the use of microwave and ultrasound methods for intensifications.

Intensification in Biodiesel Production

Intensification of the biodiesel production process is carried out by several factors in the principles of sustainability in chemical processes. Some intensification parameters include:

a. *E-factor:* the number (kg) of byproducts relative to the number (kg) of the main product
b. *Atom economy*: the ratio of the molecular weight of the main product relative to the reactant
c. Energy consumption is how much power is used in alternative processes compared to the power needed from conventional processes.
d. Renewable resources: This is related to the use of renewable materials in the production process[2], [14]–[18].

The use of microwave radiation, ultrasound, and supercritical conditions is widely used. Based on recent papers, microwave and ultrasound irradiation gave a shorter time in biodiesel production, which is closely related to the efficiency of the product[19]–[23]. Meanwhile, the supercritical to accelerate the kinetics and reaction mechanisms have also been developed. Not only for reactions but microwave radiation has also been introduced for various procedures such as digestion and extraction of materials/samples in analytical procedures[24].

For chemical reactions, microwaves are an alternative form of energy that significantly reduces reaction time. In the case of biodiesel production using microwave irradiation, studies put forward the energy conversion factor of a short reaction time, but the aspect of harmony with other aspects such as waste reduction and concise stages has not been widely studied. For example, in the conversion of biodiesel, NaOH catalysts are widely used in industry[25]–[29]. Its use in the system as a homogeneous catalyst makes it a consumable material because it cannot be reused. Substitution of NaOH catalyst with alkaline solids is more advantageous both in terms of minimizing material and reuse and easy separation[30]–[34].

The use of MW irradiation in biodiesel production processes is closely related to energy consumption whereby using MW the reaction can take place in a short time and is linear with the overall amount of energy needed in the process[35][36][10],[37],[38]. The publications related to the use of MW in biodiesel production increased from year to year as presented in Figure 1.

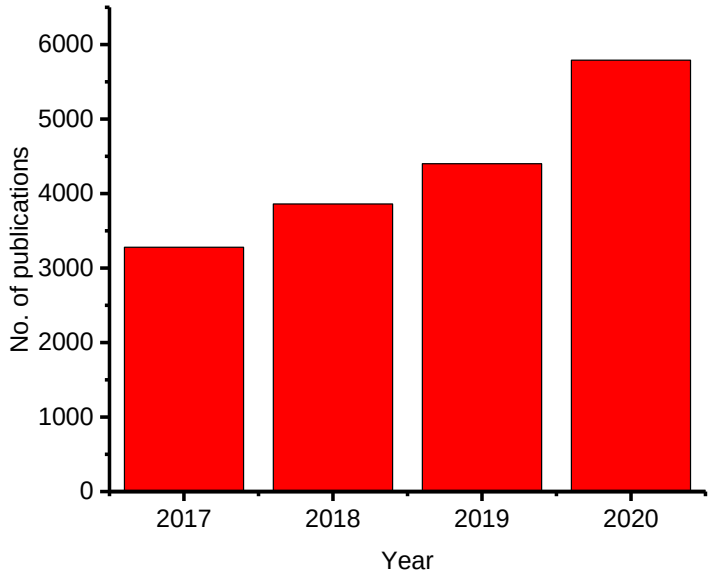


Figure 1. Number of publications on the use of MW in biodiesel production (Source: Scopus Database)

Microwaves (MW) are electromagnetic waves with frequencies between 0.3 GHz and 300 GHz and are forms of energy that are quite high in the electromagnetic spectrum. Because of its relatively short wavelength of MW radiation contributes great energy by the Max Planck equation (eq.1):

$$E = h\frac{c}{\lambda} \quad (1)$$

The MW spectrum is between infrared waves and radio waves between 0.01 and 1 m [39],[40]. In general, commercial MW ovens operate with a frequency of 2.45 GHz set to anticipate interference with telecommunication waves and cellular phone frequencies, while for industrial applications there are two frequencies namely 915 and 2450 MHz although the frequency of 2450 MHz (corresponding to the wavelength of 12.24 cm) is more widely used. In these waves, the absorption of microwaves by fluids is considered optimal.

When MW irradiation hits the material/reactant, there will be interactions between molecules including:

a. Dipoles interaction: The dipoles of the molecule will drain the electron charge as the oscillation field causes collisions between molecules and generates heat. The heat of each collision between these molecules is effectively used as energy in reactions.
b. Ionic conduction: Ionic conduction can occur if in the system there are free ions or ionic species. The electronic charge of the movement of the ions leads to more effective heating and interaction of the reaction process.

The schematic representation of the difference in conduction with regular heating and MW irradiation can be seen in Figure 2.

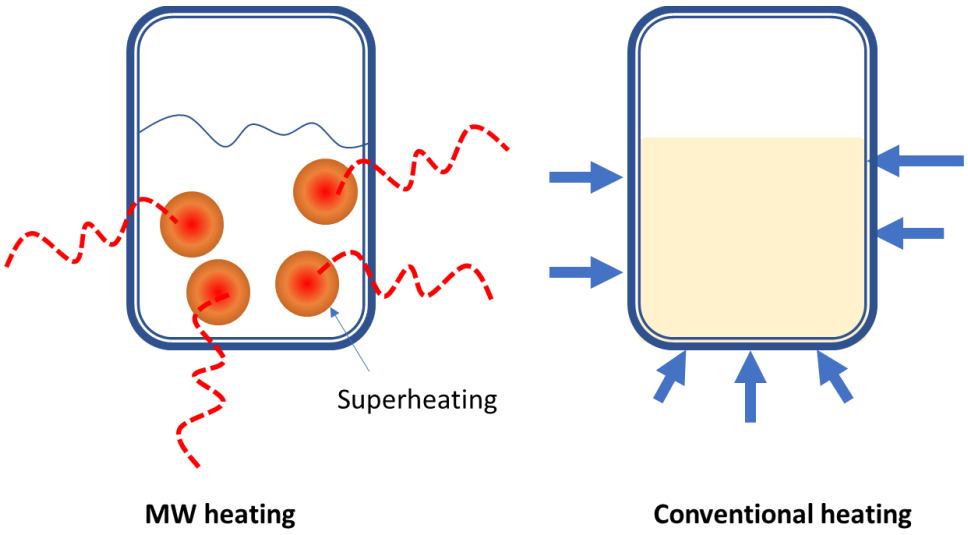


Figure 2. Differences in heat flow patterns in regular heating and MW

The MW irradiation is related to lower energy compared to the Brown's motion energy so it's not strong enough to break chemical bonds. The effect of MW irradiation on energy on chemical or biochemical reactions occurs both thermally and non-thermally. The frequency of microwaves (300 MHz - 300 GHz) corresponds to an energy of 1.24 × 10-6-1.24 × 10-3 eV, respectively. This energy is much lower than the ionization energy of biological compounds (13.6 eV), covalent bond energy such as OH- (5 eV), hydrogen bond (2 eV), van der Waals intermolecular interaction (lower than 2 eV), and even lower than the energy associated with Brown motion at 37 °C (2.7 10-3eV)[22],[41],[42]. Microwaves, as an energy source, generate heat by their interaction with matter at the molecular level without changing the molecular structure. Microwave heating offers several advantages over conventional heating such as heating without direct contact to reduce the risk of overheating on the surface of the material, energy transfer does not involve heat transfer or radiation penetrative, heating is fast.

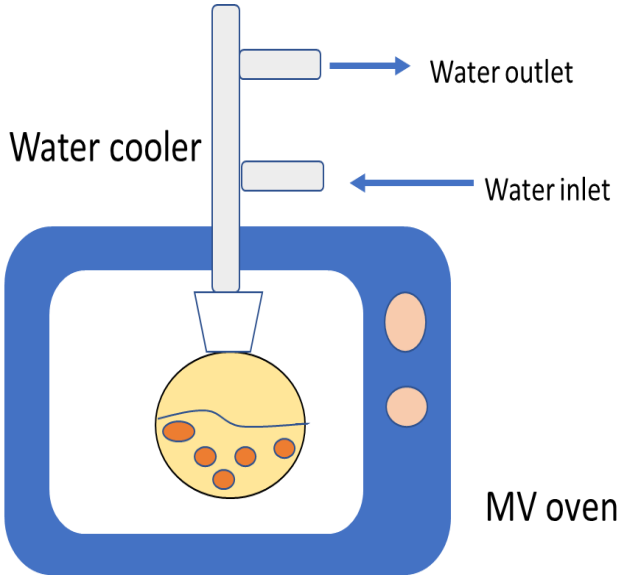
The use of MW energy in biodiesel production is carried out in two main objectives: oil extraction, and chemical transformation of oil into methyl ester through transesterification reactions.

a. Microwave-assisted oil extraction

In-plant seeds such as soybean seeds and corn kernels' energy sources are stored in the form of oil in the embryo. For example, most soybean seeds are made up of cotyledons, which are mainly composed of lipids, proteins, and carbohydrates (cell wall polysaccharides and sugars). Previous studies on the microchemical structure of soybean seeds have shown that lipids, carbohydrates, and proteins occur in the cotyledon unevenly but are in cluster form[35],[43],[44].

Lipids are biological tissues in parts of plants. Various interactions and forces between molecules such as van der Waals force, electrostatic force, hydrogen bonding, and covalent bonds exist between molecules so that sufficient energy is needed to separate oil/lipids from other materials or molecules[19],[23],[45]. For this purpose, several methods have long been developed including solvent extraction methods, Soxhlet extraction, super-critical extraction, ultrasonic wave assisted extraction

(US), physical pressure extraction, etc. Each extraction method provides advantages and disadvantages among others in the method of extraction socket required solvents in large quantities and required the re-separation of the oil with the solvent used. On the other hand, mechanical pressing methods are more suitable for seeds with high oil content (above 20%). For oilseed raw materials with a relatively low oil content (18-20%), solvent extraction is more suitable for use. In the extraction process, there will be contact between the oilseed and the solvent, so the solvent diffuses through the night, and the extraction occurs due to the breakdown of the hydrophobic and hydrophilic phases[46]–[48].



(b) Microwave Oven

Kinetic extraction can be explained through the Arrhenius equation. In general, solvent extraction occurs based on the principle of like dissolve like, namely compounds with the same hydrophobicity/equivalent will mix, and vice versa. The solubility of a compound or component is determined by Gibbs's free energy dissolution process and its value depends on the equilibrium between the two phases that insoluble refers to Eq.2:

$$\Delta G = RT ln\ K \qquad (2)$$

With ΔG is Gibb's energy (Joule), R is gas constant (Joule/K.mol), T is the temperature (K), and K is equilibrium constant. When more analytes (oils) are dissolved in the solvent phase, the equilibrium is greater, or Gibb's energy is getting negative which means the process is easier to take place. On the other hand, the function of Gibb's depends on changes in mixing enthalpy (ΔHmix) and changes in mixing entropy (ΔSmix). The more negative the change in mixing enthalpy and the more positive the change in mixing entropy the easier the extraction process is carried out[10][13],[49],[50].

The overall amount of energy that contributes relative to the intermolecular force that occurs between analyte molecules and solvents includes electrostatic force, London force, hydrogen bond, and hydrophobic bond. As a result, the development of a solvent-based extraction process should consist of a choice (mixture or co-solvent) of solvents that results in a series of chemical interactions between analytes and solvent molecules that are more beneficial than the chemical interaction between (i) the solvent with the solvent molecule itself (i.e., the associate force), and (ii) the analyte. with solvents[51]. This is the basis of the like-dissolve-like principle. The microwave-assisted microwave-assisted microwave extraction coefficient improvement process, called the Microwave Integrated Soxhlet (MIS) is tested for oil and fat extraction from different food matrices such as oleaginous seeds, meat, and bread products. The results showed that the MIS parameters did not affect the composition of the extract. For generalizations of studies with multiple food matrices, the results of MIS extraction obtained were then compared to conventional Soxhlet extraction in terms of coarse extract and fatty acid composition and showed that the oil was extracted with a quantitative and qualitative MIS like that obtained by conventional Soxhlet extraction. MIS lab station can be considered a new and common alternative to

E-ISSN: 2720-9326
P-ISSN: 2716-0459

lipid extraction using microwave energy. **Table 1** presents the use of MW on biodiesel conversion. The energy coordinate in the MW assisted process can be seen in Figure 3.

Table 1. Convert some oil with MW

Oil	Specific conditions	Reference
Used cooking oil	Transesterification using alcohol/oil ratio= 6:1 and KOH catalyst 1% in a very short period (1-3 minutes)	[30]
Used cooking oil	The use of MW and BaO and KOH catalysts provides effectiveness with energy consumption of less than 10% with the same result.	[52]
Corn oil	Biodiesel from corn oil transesterification using a methanol ratio of 10:1 oil and a 1.5% NaOH catalyst produces a methyl ester yield of more than 98% within 5 minutes.	[53]
Castor oil	The yield of methyl esters comparable to reflux/conventional methods is obtained in a shorter time (2 minutes). The reaction takes place with a KOH catalyst	[39]
Castor Oil	The maximum yield obtained 80.1% with methanol ratio: oil = 10:1 using KOH catalyst for 10 minutes of irradiation	[54]
Sunflower seed oil	Yield is achieved in a much shorter time compared to conventional conversions.	[55]

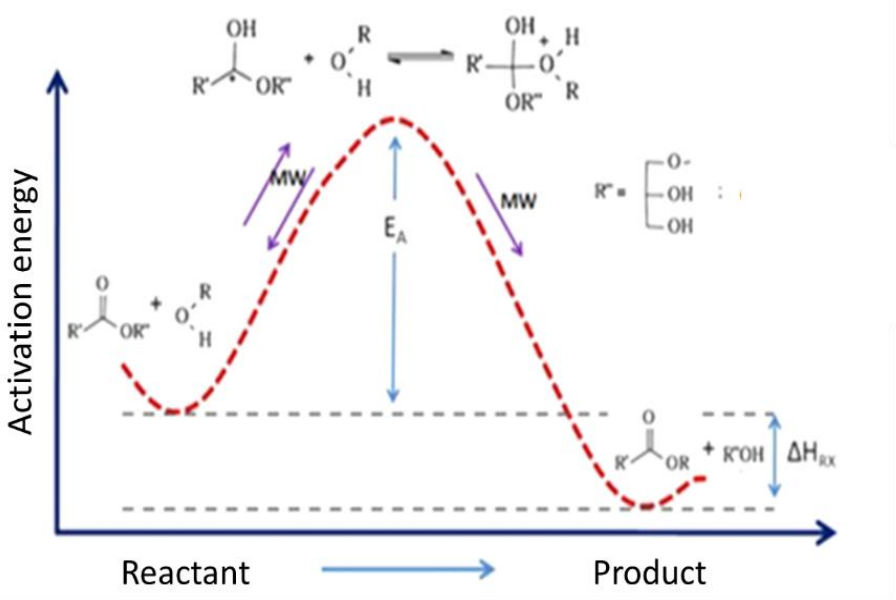


Figure 3 Catalysis scheme by MW

Table 1 Conversion of some oil with MW on various catalysts

Oil	Catalyst	Catalyst dose (% w)	Reactant	Ratio of oil: alcohol	Reaction conditions	Yield	Reference
Castor Oil	$NaHSO_4 \cdot H_2O$,	7.5	Methanol	1:8	120 min	74	[56]
	$AlCl_3$	1.5	Methanol	1:8	120 min	73	[56]
	Na_2CO_3	0.75	Methanol	1:8	120 min	90	[56]
Soybean oil	Nano-Fe_3O_4	2	Methanol	1:6	power of 560 W with a methanol-to-oil molar ratio of 6:1 using a 1.0% NaOH-methanol solution	93	[57]

Oil	Catalyst	Catalyst dose (% w)	Reactant	Ratio of oil: alcohol	Reaction conditions	Yield	Reference
Millettia pinnata seed oil	magnetic Fe_3O_4		Methanol	1:6		98.7	[58]
Waste cooking oil	CH_3ONa	0.75	Methanol	1:6	65 °C, 600 rpm, 3 min	97.9 (yield)	[46]
	NaOH					96.2 (yield)	
Soybean	$C_4H_6O_4KNa/ZrO_2$	10	Methanol	1:14	65 °C, 30 min, 1000 rpm	94.75 (yield)	[57]
Pongamia pinnata seed oil	KOH	1	Methanol	1:6	60 °C, 5 min	97 (yield)	[59]
	NaOH	0.5				96 (yield)	
FFA stearic acid	D418	9	Ethanol	1:11	80 °C, 7 h	>90 (conversion)	[60]
Waste cooking oil	CH_3ONa	1	Methanol	1:6	60 °C, 5 min	98.87 (conversion)	[47]
Palm oil	CaO derived from waste eggshells	15	Methanol	1:18	122 °C, 4 min	96.7 (yield)	[61]
Soybean	SrO	1.8	Methanol	1:6	60 °C, 40 s	97 (conversion)	[62]
	KOH	1				81 (conversion)	
	$Sr(OH)_2$	2.1				97 (conversion)	
Cooked oil	SrO	1.8			60 °C, 20 s	93.2 (conversion)	
						99.4 (conversion)	
Castor oil	SiO_2/50% H_2SO_4	10	Methanol	1:6	60 °C, 30 min	95 (conversion)	[48]
	Al_2O_3/50% KOH				60 °C, 5 min	95 (conversion)	
Karanja oil	H_2SO_4 (esterification)	3.73	Methanol	1:9.4	300 rpm, 190 s	87.5 (FFA reduction)	[41]
	KOH	1.33		1:9.3	300 rpm, 150 s	89.9 (yield)	
Ceiba pentandra	H_2SO_4 (esterification)	1.5	Methanol	1:6	500 rpm, 5 min, 60 °C	86.4 (FFA reduction)	[63]
	KOH	2.15		1:9.85	500 rpm, 3.29 min, 57.09 °C	89.9 (conversion)	
Soybean oil	KF-Halloysite	3	methanol	1:12	78 °C, 30 s	85	[64]
Vegetable oil	BaO	1	Methanol	1:6	67–78 °C, 30 s	97	[65]

In general, conversion using MW irradiation provides a shorter time, while the type of catalyst used will also affect the yield and characteristics of the product. **Figure 5** presents the magnitude of the methyl ester yield resulting from the conversion of sunflower seed oil into microwave irradiated biodiesel. The physical characteristics of the catalyst affect the conversion yield[66][19][41],[48],[62]. This is by the rule that in catalysis various factors determine the transport of reactants to the catalyst and the mechanism of surface reaction in the catalyst. The conversion rate of each component is different from each other, and this is reflected in the difference in the composition of the methyl ester produced. Differences in

energy consumption at varied catalysts (**Figure 4**) suggests that there are about 3-4 times higher energy consumed by the conventional method with respect to the MW assisted process.

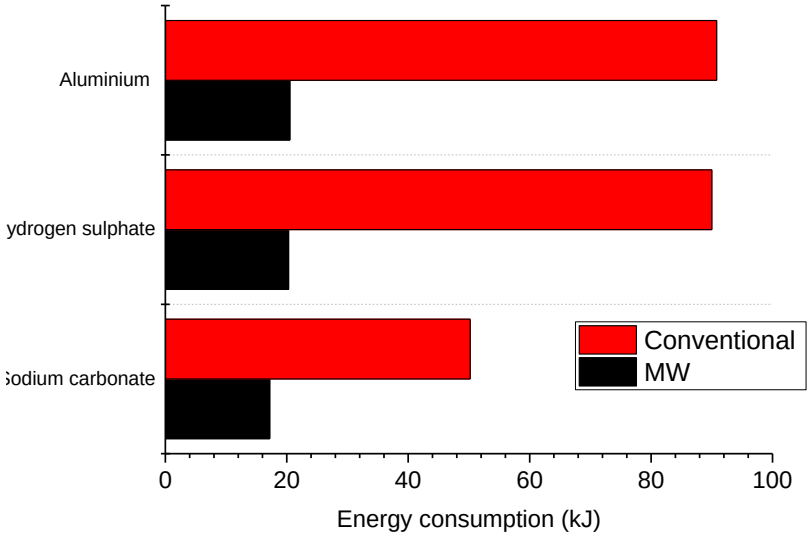


Figure 4. Consumed energy at varied catalyst and method

Besides the reduced energy, the catalyst also influences the conversion of biodiesel. Figure 5 depicts the effect of catalyst types on the methyl ester yield of sunflower seed oil.

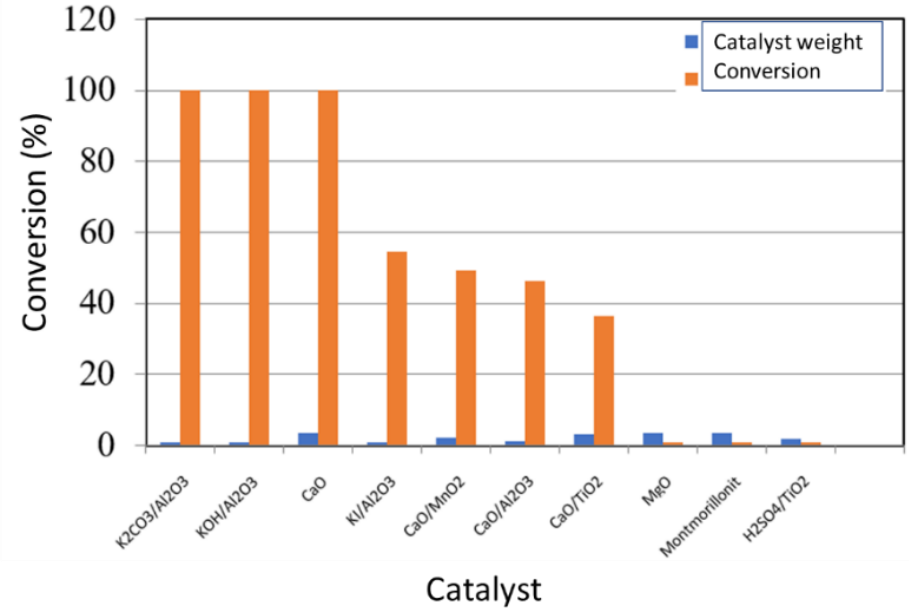


Figure 5. Effect of catalyst types on the methyl ester yield of sunflower seed oil (Reaction conditions of methanol: oil ratio = 16:1; Catalyst 10 wt.%; reaction time 2 hours, temperature 70 °C)

Intensification of the biodiesel production process using ultrasonic irradiation (US)

The ultrasound (US) is a voice with a tone over the human hearing. The use of U.S. reactions in some reactions is considered a 'green' technology because of its high efficiency, short time, and more economic efficiency in terms of its energy results and consumption. The frequency of the U.S. is classified into regions:

1. High-frequency and low-power (2-10 MHz) US, also called U.S. diagnostics, are used in medical imaging and chemical analysis.
2. U.S. low frequency and high power (20-100 kHz) ultrasound, used for cleaning and welding and also for sonochemistry[51],[67].

The interaction between U.S. and reactants in the sonochemistry system does not occur directly but through the phenomenon of cavitation: the formation, growth, and collapse of implosive cavities in a fluid that releases large amounts of energy at the location of a particular molecule. Cavitation can be classified into four types based on its formation: acoustic, hydrodynamic, optical, and particle. Of the four types, only acoustic and hydrodynamic cavitation can produce the intensity necessary to induce chemical or physical changes in a system. The US produces acoustic cavitation with very high spot temperatures (over 5000 K), high pressure (500 atm), and heating/cooling rates from solutions greater than 109 K/s. During acoustic cavitation, free radicals are formed by the dissociation of steam trapped in cavities; These radicals are used for the acceleration of chemical reactions at ambient temperatures that will not require more extreme conditions. Furthermore, the limited interaction is microcirculation (acoustic streaming) which can be utilized for increased mass transport. Some U.S. parameters, such as frequency, intensity, cycle, and length of irradiation, determine the potentially damaging effects on biological molecules. The molecular effects of the US are summarized and illustrated in **Figure 6**. There are some effects caused by the irradiation, consist of:

a. Thermal Physic:

Thermal: pyrolysis and combustion cover thermal effects do not pose a danger but depend on the absorbed energy and maximum temperature (I), partial or perfect lysis (II).
Non-thermal: cavitation (III), changes in enzyme stability (III), seller effect that can cause lysis (II), DNA damage (IV), and breaking of bonds in polymers (V).

b. Chemical Changes cover cavitation that produces radicals consists of the release of molecules such as nitric acid, H_2O_2 by formed radicals (VI), and decreased cell stability (VII).

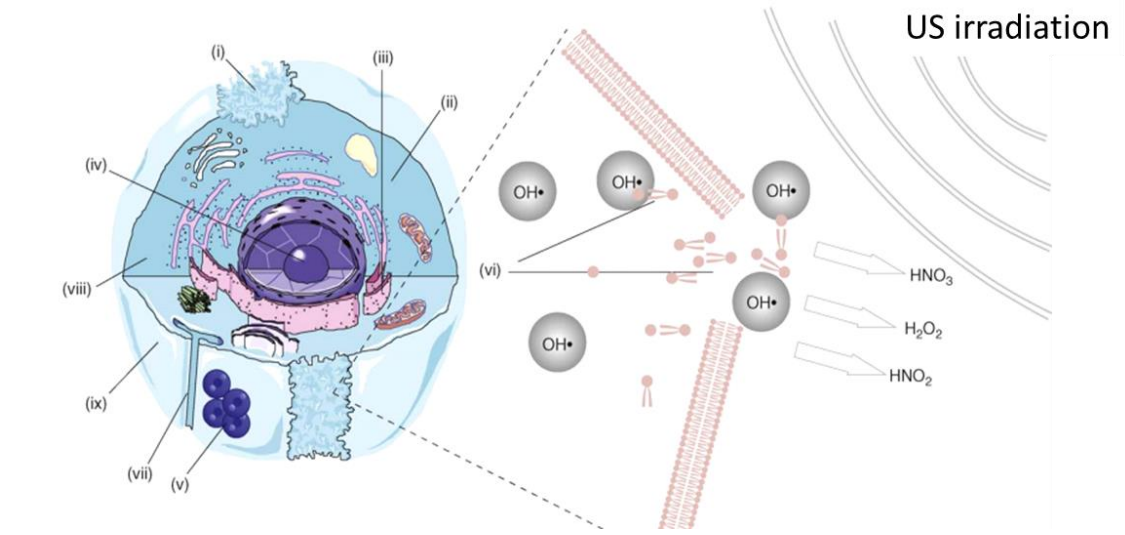


Figure 6. Molecular effects by US irradiation

US-assisted biodiesel processing enables continuous processing with conversion yields reaching more than 99%. Ultrasonic reactor reduces the processing time from conventional 1-4 hours of batch processing to less than 30 seconds. Furthermore, U.S. use reduces the separation time from 5 to 10 hours (using conventional agitation) to less than 60 minutes[68], [69]. The US. also helps to reduce the number of catalysts required by up to 50% as chemical activity increases in the presence of a cavity. Another benefit is the result of increased glycerin purity. U.S. biodiesel processing involves the following steps: vegetable or animal oil fats mixed with methanol (which makes methyl ester) or ethanol (for ethyl ester) and sodium or potassium methoxide or hydroxide mixture heated, e.g., temperatures between 45 and

65°C mixtures heated with moderate sonification for 5 to 15 seconds[68], [70]–[73]. Some US-assisted biodiesel conversions are listed in Table 3.

Table 2 Some biodiesel conversion research with the U.S.

Oil	Specific conditions	Reference
Waste cooking oil	US time between 30-90 minutes, NaOH catalyst 0.5 -1% b/b. methanol ratio: oil = 6:1, conversion value >60%.	[74]
Palm oil	US usage provides higher conversion results (>92.5%)	[68]
Waste cooking oil	A methanol ratio of 6:1 temperature of 30 °C and reaction time of 30 minutes with a catalyst of 0.75% KOH (wt/wt) resulting in >90% conversion	[70]
Soybean oil	Methanol ratio: 10.2:1 oil results in 100% conversion.	[71]
Oil (edible, soybean oil)	Methanol ratio: oil = 6:1 20 kHz, time 2-5 hours, resulting in conversion of 69,2%.	[73]
Nonedible oil: castor oil, Waste cooking oil	Ratio of methanol: oil = 6:1, alcohol variation (methanol, ethanol, propanol, butanol), homogeneous catalyst: NaOH and KOH (0.5-2.0 wt.%) or 30% CH_3ONa in methanol, us frequency 20-45 kHz or 581-611 kHz [157] Result: Best results of 98-99% obtained with a frequency of 28 kHz, higher frequency (40 kHz) gives a shorter time Longer alcohol provides lower conversion	[75]
Soybean oil	Intensification of U.S.-assisted semi-flow processes results in a 3-times conversion of the batch method. The reactor scheme presented in **Figure 96**	[72]

Conclusion and Future Perspective

Many literatures indicate considerable intensification procedures for biodiesel production. The use of MW and US for yield and effectiveness enhancements has been reported. However, due to many dependencies of biodiesel conversion to many other factors such as type of catalyst, reaction condition, and the sources, the optimization for each procedure for being applied on a larger scale is required. Moreover, study on the life cycle analysis for the applicable method is important.

References

[1] A. Demirbas, Progress and recent trends in biodiesel fuels, Energy Conversion and Management 50 (2009) 14–34.
[2] R. C. A. Lago, Castor and jatropha oils: Production strategies – A review, OCL - Ol. Corps Gras Lipides 16(4)(2009) 241–247.
[3] A. E. Atabani, A. S. Silitonga, I. A. Badruddin, T. M. I. Mahlia, H. H. Masjuki, and S. Mekhilef, A comprehensive review on biodiesel as an alternative energy resource and its characteristics, Renewable and Sustainable Energy Review 16(4)(2012) 2070–2093.
[4] S. K. Hoekman, A. Broch, C. Robbins, E. Ceniceros, and M. Natarajan, Review of biodiesel composition, properties, and specifications, Renewable and Sustainable Energy Review 16(1)(2012) 143–169.
[5] N. Ibrahim, S. K. Kamarudin, and L. J. Minggu, Biofuel from biomass via photo-electrochemical reactions: An overview, Journal of Power Sources 259(2014) 33–42.
[6] I. C. Emeji, A. S. A. Member, J. Kalala, and A. S. Abdulkareem, Optimization and Characterization of Biofuel from Waste Cooking Oil, in Proceedings of the World Congress on Engineering and Computer Science 2015 (2015) 2–5.
[7] J. H. Clark, Macquarrie, and T. Graedel, Green Chemistry and Sustainable Development, in Handbook Of Green Chemistry And Technology, Wiley publisher, 2007.
[8] R. L. Lankey and P. T. Anastas, Advancing Sustainability through Green Chemistry and Engineering, American Chemical Society, 2002.
[9] C. H. Zhou, An overview on strategies towards clay-based designer catalysts for green and sustainable catalysis, Applied Clay Science 53(2) (2011) 87–96.
[10] F. Jamil., Current scenario of catalysts for biodiesel production: A critical review, Review in Chemical Engineering 34(2) (2018) 267–297.

[11] S. Saka, Y. Isayama, Z. Ilham, and X. Jiayu, New process for catalyst-free biodiesel production using subcritical acetic acid and supercritical methanol, Fuel 89(7) (2010) 71442–1446.
[12] A. Yeboah, S. Ying, Y. Jiannong, L.Y. Xie, A.AMoaniamaa, A. Agyenim, B. Miao, C. Yin, Castor oil (Ricinus communis): a review on the chemical composition and physicochemical properties, Food and Science Technology 26(2020).
[13] A. Koh, Two-step biodiesel production using supercritical methanol and ethanol, 2011, [Online]. Available: http://ir.uiowa.edu/etd/1239/.
[14] K. Srinivasan, J. C. Manayil, and C. A. Antonyraj, Heterogeneous Catalysis for Perfumery Chemicals. Elsevier Inc., 2016.
[15] A. Tiwari, V. M. Rajesh, and S. Yadav, Biodiesel production in micro-reactors: A review, Energy for Sustainable Development 43(2018) 143–161.
[16] M. Emura and H. Matsuda, A green and sustainable approach: Celebrating the 30th anniversary of the asymmetric l-menthol process, Chemistry and Biodiversity 11(2014) 1688–1699.
[17] P. T. Anastas and M. M. Kirchhoff, Origins, current status, and future challenges of green chemistry, Account of Chemical Research 35(9) (2002) 686–694.
[18] S. S. Shams, L. S. Zhang, R. Hu, R. Zhang, and J. Zhu, Synthesis of graphene from biomass: A green chemistry approach, Material Letter 161(2015) 476–479.
[19] B. a. Roberts and C. R. Strauss, Toward rapid, 'green', predictable microwave-assisted synthesis, Account of Chemical Research 38(2005) 653–661.
[20] J. Jacob, Microwave Assisted Reactions in Organic Chemistry: A Review of Recent Advances, International Journal of Chemistry 4(2012) 29.
[21] H. Berthold, T. Schotten, and H. Hönig, Transfer hydrogenation in ionic liquids under microwave irradiation, Synthesis 11(2002) 1607–1610.
[22] I. Lavilla, V. Romero, I. Costas, and C. Bendicho, Greener derivatization in analytical chemistry, Trends in Analytical Chemistry 61(2014) 1–10.
[23] V. Gude, P. Patil, E. Martinez-Guerra, S. Deng, and N. Nirmalakhandan, Microwave energy potential for biodiesel production, Sustainable Chemical Process 1(2013) 1-5.
[24] C. H. Zhou, An overview on strategies towards clay-based designer catalysts for green and sustainable catalysis, Applied Clay Science 53(2011) 87–96.
[25] B. V. Badami, "Concept of green chemistry, Resonance 13(2008) 1041–1048.
[26] R. C. Fierascu, A. Ortan, S. M. Avramescu, and I. Fierascu, Phyto-Nanocatalysts: Green Synthesis, Characterization, and Applications, Molecules 24 (2019) 1–35, 2019.
[27] T. U. Eindhoven, Microwave heating in fine chemical applications : role of heterogeneity, Research Thesis, 2009.
[28] N. Remya and J. G. Lin, Current status of microwave application in wastewater treatment-A review, Chemical Engineering Journal 166(2010) 797–813.
[29] P. T. A. J. B. Zimmerman, The Twelve Principles of Green Engineering as a Foundation for Sustainability, Sustainability Science and Engineering 1(2006) 11-32.
[30] M. Zare, B. Ghobadian, and G. Fayyazi, Ebrahim., Najafi, Microwave-assisted Biodiesel Fuel Production from Waste Cooking Oil, International Journal of Agriculture and Crop Sciences (2013) 1314–1317.
[31] G. M. Hincapié, S. Valange, J. Barrault, J. A. Moreno, and D. P. López, Effect of microwave-assisted system on transesterification of castor oil with ethanol, Universitas Scientiarum 19(2014) 193–200.
[32] T. Lieu, S. Yusup, and M. Moniruzzaman, Kinetic study on microwave-assisted esterification of free fatty acids derived from Ceiba pentandra Seed Oil, Bioresource Technology 211(2016) 248–256.
[33] I. Fatimah, A. Taushiyah, F. B. Najah, and U. Azmi, ZrO2/bamboo leaves ash (BLA) Catalyst in Biodiesel Conversion of Rice Bran Oil, IOP Conference Series: Materials Science and Engineering 349(2018) 012027.
[34] J. Cheng, Y. Qiu, R. Huang, W. Yang, J. Zhou, and K. Cen, Biodiesel production from wet microalgae by using graphene oxide as solid acid catalyst, Bioresource Technology 221(2016) 344–349.
[35] N. A. Ibrahim and M. A. A. Zaini, Microwave-assisted solvent extraction of castor oil from castor seeds, Chinese Journal of Chemical Engineering 26(2018) 2516–2522.
[36] I. Fatimah, G. R. Aulia, W. Puspitasari, R. Nurillahi, L. Sopia, and R. Herianto, Microwave-synthesized hydroxyapatite from paddy field snail (Pila ampullacea) shell for adsorption of bichromate ion, Sustainable Environment Research 28(2018) 462–471.
[37] G. Nagendrappa, Organic synthesis using clay and clay-supported catalysts, Applied Clay Science 53(2011) 106–138.

[38] A. Buasri, T. Inkaew, and L. Kodephun, Natural Hydroxyapatite (NHAp) Derived from Pork Bone as a Renewable Catalyst for Biodiesel Production via Microwave Irradiation, Key Engineering Materials 659(2015) 216–220.
[39] S. A. El Sherbiny, A. A. Refaat, and S. T. El Sheltawy, Production of biodiesel using the microwave technique, Journal of Advanced Research 1(2010) 309–314.
[40] B. L. A. Prabhavathi Devi, M. S. L. Karuna, K. Narasimha Rao, P. S. Saiprasad, and R. B. N. Prasad, Microwave-Assisted Catalytic Transfer Hydrogenation of Safflower Oil, Journal of the American Oil Chemists' Society 80(2003) 1003–1005.
[41] H. Venkatesh Kamath, I. Regupathi, and M. B. Saidutta, Optimization of two step karanja biodiesel synthesis under microwave irradiation, Fuel Processing Technology 92(2011) 100–105.
[42] H. Mazaheri, H.. Ong, Z. Amini,H.H. Masjuki, M. Mofijur, C. H. Su, I.A. Badruddin T.M. Y. Khan, An overview of biodiesel production via calcium oxide based catalysts: Current state and perspective, Energies 14(2021). 1–23.
[43] S. Moradi, A. Fazlali, and H. Hamedi, Microwave-assisted hydro-distillation of essential oil from rosemary: Comparison with traditional distillation, *Avicenna J. Med. Biotechnol.*, 10(2018) 22–28.
[44] N. A. Ibrahim and M. A. A. Zaini, Solvent selection in microwave assisted extraction of castor oil, Chemical Engineering Transactions 56(2017) 865–870.
[45] A. T. Quitain, S. Katoh, and M. Goto, Microwave-Assisted Synthesis of Biofuels, 1999, 2006.
[46] K. S. Chen, Y. C. Lin, K. H. Hsu, and H. K. Wang, Improving biodiesel yields from waste cooking oil by using sodium methoxide and a microwave heating system, Energy 38(2020) 151–156.
[47] N. Azcan and O. Yilmaz, Microwave assisted transesterification of waste frying oil and concentrate methyl ester content of biodiesel by molecular distillation, Fuel 104(2012) 614–619.
[48] M. Salaheldeen, A. A. Mariod, M. K. Aroua, S. M. A. Rahman, M. E. M. Soudagar, and I. M. R. Fattah, Current State and Perspectives on Transesterification of Triglycerides for Biodiesel Production, Catalyst (2020) 1–37, 2021.
[49] C. H. Zhou, H. Zhao, D. S. Tong, L. M. Wu, and W. H. Yu, Recent advances in catalytic conversion of glycerol, Catalysis Reviews: Science and Engineering 55(2013) 369–453.
[50] P. Intarapong, S. Iangthanarat, and A. Luengnaruemitchai, Biodiesel Production from Palm Oil Using Potassium Hydroxide Loaded on ZrO 2 Catalyst in a Batch Reactor, Chiang Mai Journal of Science 41(2014) 2014.
[51] F. Chemat, N. Rombaut, A. G. Sicaire, A. Meullemiestre, A. S. Fabiano-Tixier, and M. Abert-Vian, Ultrasound assisted extraction of food and natural products. Mechanisms, techniques, combinations, protocols and applications. A review, Ultrasonic Sonochemistry 34(2016) 540–560.
[52] P. D. Patil, Biodiesel Production from Waste Cooking Oil Using Sulfuric Acid and Microwave Irradiation Processes, Journal of Environmental Protection 3(2012) 107–113.
[53] G. Ozturk, A. B. Kafadar, M. Z. Duz, A. Saydut, and C. Hamamci, Microwave assisted transesterification of maize (*Zea mays* L.) oil as a biodiesel fuel, Energy Exploration and Exploitation 28(2010) 47–58.
[54] G. M. Hincapié, S. Valange, J. Barrault, J. A. Moreno, and D. P. López, Effect of microwave-assisted system on transesterification of castor oil with ethanol, Universitas Scientiarum 19(2014) 193–200.
[55] E. L. Dall'Oglio, P. T. De Sousa, P. T. De Jesus Oliveira, L. G. De Vasconcelos, C. A. Parizotto, and C. A. Kuhnen, Use of heterogeneous catalysts in methylic biodiesel production induced by microwave irradiation, Química Nova 37(2014) 411–417.
[56] H. Yuan, B. Yang, H. Zhang, and X. Zhou, Synthesis of Biodiesel Using Castor Oil under Microwave Radiation, International Journal of Chemical Reactor Engineering 9(2012) 2562.
[57] C. H. Lin, Y. T. Chang, M. C. Lai, T. Y. Chiou, and C. Sen Liao, Continuous biodiesel production from waste soybean oil using a nano-fe3o4 microwave catalysis, Processes ((2012) 1–10.
[58] S. Chellappan, K. Aparna, C. Chingakham, V. Sajith, and V. Nair, Microwave assisted biodiesel production using a novel BrØnsted acid catalyst based on nanomagnetic biocomposite, Fuel 246(2019) 268–276.
[59] R. Kumar and A. K. Sethy, Microwave Assisted Energy Efficient Biodiesel Production from Crude Pongamia pinnata (L.) Oil Using Homogeneous Catalyst, Journal of Forest and Environmental Science 31(2015) 1–6.
[60] W. Liu, X. Liu, W. Chen, H. Chen, C. Liu, R. Qu, Q. Xu, Microwave assisted esterification of free fatty acid over a heterogeneous catalyst for biodiesel production, Energy Conversion and Management 76(2013) 1009–1014.
[61] P. Khemthong, C. Luadthong, W.Nualpaeng, P.Changsuwan, P.Tongprem, N.Viriya-empikul, K.Faungnawakij, Industrial eggshell wastes as the heterogeneous catalysts for microwave-assisted biodiesel production, Catalyst Today 190(2012) 112–116.

[62] M. Koberg, R. Abu-Much, and A. Gedanken, Optimization of bio-diesel production from soybean and wastes of cooked oil: Combining dielectric microwave irradiation and a SrO catalyst, Bioresource Technology 102(2010) 1073–1078.
[63] A. S. Silitonga, A.H.Shamsuddin, T.M.I.Mahlia, J. Milano, F.Kusumo, J. Siswantoro, S.Dharma, A.H.Sebayang, H.H.Masjuki, H. C. Ong, Biodiesel synthesis from Ceiba pentandra oil by microwave irradiation-assisted transesterification: ELM modeling and optimization, Renewable Energy 146(2020) 1278–1291.
[64] I. Fatimah and S. P. Yudha, KF-Modified Natural Halloysite as Green Catalyst in Microwave Assisted Biodiesel Conversion, Energy Procedia 105 (2017) 1796-1805.
[65] E. Martinez-Guerra and V. G. Gude, Transesterification of used vegetable oil catalyzed by barium oxide under simultaneous microwave and ultrasound irradiations, Energy Conversion and Management 88(2014) 633–640.
[66] S. Nomanbhay and M. Y. Ong, A Review of Microwave-Assisted Reactions for Biodiesel Production, Bioengineering 4(2017) 57-65.
[67] V. G. Gude, Synergism of microwaves and ultrasound for advanced biorefineries, Resource-Efficient Technologies 1(2015) 116–125.
[68] K. Somnuk, P. Smithmaitrie, and G. Prateepchaikul, Feasibility of Using Ultrasound-Assisted Biodiesel Production from Degummed-Deacidi fi ed Mixed Crude Palm Oil Using Small-Scale Circulation, 669(2012) 662–669.
[69] J. M. Encinar, A. Pardal, N. Sánchez, and S. Nogales, Biodiesel by transesterification of rapeseed oil using ultrasound: A kinetic study of base-catalysed reactions, Energies 11(2018) 11092229.
[70] O. Babajide, L. Petrik, B. Amigun, and F. Ameer, Low-cost feedstock conversion to biodiesel via ultrasound technology, Energies 3(2010) 1691–1703.
[71] F. F. P. Santos, S. Rodrigues, and F. A. N. Fernandes, Optimization of the production of biodiesel from soybean oil by ultrasound assisted methanolysis, Fuel Processing Technology 90(2009) 312–316.
[72] D. C. Boffito, S. Mansi, J.-M. Leveque, C. Pirola, C. L. Bianchi, and G. S. Patience, Ultrafast Biodiesel Production Using Ultrasound in Batch and Continuous Reactors, ACS Sustainable Chemistry and Engineering 1(2013) 1432–1439.
[73] J. Luo, Z. Fang, and R. L. Smith, Ultrasound-enhanced conversion of biomass to biofuels, Progress in Energy and Combustion Science 41(2015) 56–93.
[74] Á. Cancela, R. Maceiras, V. Alfonsín, and Á. Sanchez, Transesterification of waste frying oil under ultrasonic irradiation, European Journal of Sustainable Development 4(2015). 401–406.
[75] V.L. Gole and P.R. Gogate, Intensification of Synthesis of Biodiesel from Nonedible Oils Using Sonochemical Reactors, Industrial and Engineering Chemistry Research 11(51) (2012) 11866-11874.