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# **Sustainable biofuel and bioenergy production from biomass waste residues using microwave-assisted heating: A comprehensive review**

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## **Abstract**

With drastic fossil fuel depletion and environmental deterioration concerns, a move towards a more sustainable bioenergy-based economy is essential. The application of microwave (MW) irradiation for waste processing has been attracting interest globally lately. MW-assisted heating possesses several advantages such as the provision of high microwave energy into dielectric materials with deeper penetration for internal heat generation, showing beneficial features in improving the heating rate and reducing the reaction time. Consequently, the most recent literature regarding the applications of MW-assisted heating for biomass pretreatment as well as biofuel and bioenergy production was reviewed and consolidated in this study. An impressive increase in the product yield and improvement of the product properties are reported, with the use of MW-assisted heating in several conversion routes to produce biofuels. Despite being a promising technology for biofuel production, some major fundamental data of MW-assisted heating have not been comprehensively identified. Therefore, the feasibility of this technology for large-scale implementation is still subpar. Understanding the interaction between the feedstock and the

microwave electromagnetic field, and the optimization of several operational and mechanical parameters are the two main keystones that would propel the industrialization of MW heating in the near future. This provides key insights leading to increased feasibility and more advanced application of MW heating.

**Keywords:** Microwave-assisted heating; biofuel and bioenergy; waste to energy processing; torrefaction and pyrolysis; hydrothermal carbonization and liquefaction; gasification.

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## 1. Introduction

Interconnected with the rapid growth of the global population and modernization of people's way of life, peaking global energy demand is observed since the start of the 21st century and is expected to rise through 2040 [1]. As a result, conventional resources, namely, coal, oil, and natural gas, where most nations are currently heavily relied on, deplete rapidly. This rapid exhaustion of fossil fuels contributes to greater environmental degradation including air pollution, ozone layer depletion, and continuous increase in the global temperature [2]. The renewable energy (RE) sector has paved its way to the limelight not only because of the crucial challenges aforementioned but also due to the initiative of the United Nation member to implement the Sustainable Development Goals (SDGs) wherein affordable and clean energy resources is one of the priorities [3]. Positive results are observed which REs now account for about a quarter (~25%) of the power output and 45% of the electricity output globally [4], and are expected to grow significantly to around 80% by 2100 [5].

The viability of replacing fossil fuels with biomass is high for several reasons: biomass is readily available, abundant in nature, and most of all, renewable. Biomass resources can be considered as organic matters coming from four major categories (generations). First-generation biomass feedstocks are crops that are purposively grown for energy generation. However, the issue with competition for food security arose and gave way to the utilization of second-generation feedstocks which are coming from lignocellulosic materials such as forest residues and organic fractions from agricultural, industrial, and domestic wastes. Third- and fourth-generation feedstocks are from microalgae, though the only difference is that the latter is genetically modified to increase its productivity [6, 7].

With the ability to sequester carbon throughout the life cycle, biomass-driven products are labeled as carbon-neutral and gained much attention around the world. Since various fuels such

as bioethanol, biohydrogen, and biodiesel can be derived from biomass, it holds the greatest potential to compete and even replace conventional fossil fuels in the international market [8]. However, the extent by which we can realize the impact of biomass with CO<sub>2</sub> reduction and economic growth will heavily rely on the amount and degree of its utilization to substantially replace the conventional sources [9]. On top of that, biomass still has limitations that greatly affect its energy conversion efficiencies such as elevated moisture content, hydrophilic nature, and poor calorific value [10, 11].

To counteract these disadvantages, biomass conversion processes will play a vital role in biofuel production. Bioenergy products, or biofuels, are evaluated according to its suitability for specific energy applications which are deeply impacted by how the feedstock's characteristics concur with its conversion process. Physical, biochemical, and thermochemical processes are the major conversion technology pathways applied to biomass to counteract the limitations. Physical conversion processes mainly involve precleaning and size reduction of biomass. [12-14] Microwave-assisted pretreatment of the biomass wastes are done before they undergo subsequent biochemical processes such as anaerobic digestion and bioethanol production. Additionally, microwave-assisted heating has also been widely used for several thermochemical routes which include pretreatment methods, such as drying, torrefaction, and hydrothermal carbonization, and subsequent intensive routes, such as pyrolysis, gasification, liquefaction, and transesterification. **Figure 1** describes the schematic of biomass conversion routes that utilize microwave-assisted heating.

The application of microwave (MW) irradiation for residual waste processing has been attracting interest globally in recent years. MW-assisted heating involves direct delivery of energy to the material via molecular interaction with electromagnetic waves ranged between 300 MHz and 300 GHz of frequency and wavelength ranging from 1 mm to 1 m. In contrast, conventional heating transfers energy mainly via conduction, convection, and/or radiation from

the surfaces of the material [15-17].

In comparison to conventional heating, MW-assisted heating poses several advantages such as the provision of high microwave energy into dielectric materials with deeper penetration for internal heat generation, showing beneficial features in improving the heating rate and reducing the reaction time. It is relatively easy to operate and control parameters such as irradiation time and power level [18, 19]. Coupled with these advantages, new technical issues arose as well with the introduction of a new heating mechanism [17]. The inherent nature of standing wave patterns of microwaves inside the microwave cavity could cause the non-uniform distribution of heat within the biomass. Physical and structural transformations during waste conversion may cause the dielectric properties of these biomass waste residues to be altered, which results in varying heat generation. In line with this varying heat generation within the microwave cavity, this may bring some difficulties concerning process modeling and control. Therefore, understanding the microwave heating mechanisms and their interaction with various feedstock is critical [18, 20].

The literature survey suggests that several review papers have been published regarding microwave-assisted heating for bioenergy. However, to the best of our knowledge, a comprehensive review of the applications of microwave-assisted heating for biomass pretreatment as well as biofuel and bioenergy production is still absent. For this reason, this review paper aims to provide a range of application of MW-assisted heating to biomass waste residue conversion into bioenergy products. This study also discusses the latest advancements in the applications of microwave-assisted heating to biofuel production to fill the gap between the recently developed technologies and other reviews. The focus of this review is structured in three main parts. The first part introduces the principle of microwave heating, including its operating parameters and conditions. The second part reviews and discusses the most recent developments and novel pathways of applying microwave heating in several conversion routes

within the sustainable energy spectrum. The last part discusses several perspectives of the MW system such as challenges, benefits, and areas for improvements of the technology for it to be applied in an industrial setting. This review will provide beneficial insights and findings on the application of MW technology in sustainable biofuel and bioenergy production.

## **2. Statistical review of microwave applications in bioenergy and biofuel production**

The current trends in research regarding the application of microwave heating for bioenergy production were distinguished with the program, VOSViewer and search terms “microwave”, “waste”, “biomass” and “biofuel” in Web of Science. **Figure 2** summarizes the major keywords associated with the search terms. Recently, microwave heating was found to be applied mostly as a pretreatment to biochemical processing. In particular, the thermochemical processing of microalgae is also one of the focuses of microwave applications. From the past 10 years, the number of papers concerning microwave application to bioenergy production has exponentially grown from 83 in 2009 to 669 in 2019 (Web of Science), as shown in **Figure 3**. This depicts that the interest in microwave-assisted heating as an alternative heating route for biofuel production has steadily increased.

## **3. Fundamentals of microwave-assisted heating**

Microwaves (MWs) are electromagnetic waves within 300 MHz to 300 GHz of frequencies with 0.001 to 1 m of wavelength [21-25]. MWs used for domestic purposes are strictly assigned to be in the 2.45 GHz frequency to not interfere with other purposes such as satellite communication, cellular connections, or other industrial purposes [23]. Three major mechanisms are involved in MW-assisted heating, namely, dipolar reorientation, ionic conduction, and interfacial polarization [21, 22]. Moisture or water, in general, are dipolar and tries to realign its polarization with the electrical field which rapidly alternates at higher frequencies. This change in direction produces friction, resulting in the internal heating of the



medium. In the second mechanism, ions within the feedstock migrate under the influence of constantly changing the electrical field. However, the movement of the ions cannot keep up with the frequency the electrical field oscillates, causing collisions and then heat generation [21, 22]. Interfacial polarization, also known as the Maxwell-Wagner-Sillars effect, is viewed as the combination of dipolar reorientation and ionic conduction. The movement of charged particles forms positive and negative space charges at the interfaces between different materials which, in turn, modifies the field distribution. It is considered as an important mechanism for heating with heterogeneous dielectric properties. [24, 25]

Materials react differently to MWs and can be categorically classified as insulative, reflective, and dielectric materials. **Figure 4** shows the nature of MW irradiation for each category. MWs penetrate the insulative materials without any loss from it (**Figure 4.a**). In contrast, MWs bounce off with reflective materials (**Figure 4.b**). Lastly, dielectric materials absorb MW irradiation (**Figure 4.c**) [26].

Metals are usually excellent reflectors of microwaves wherein no heating is produced. On the other hand, other materials absorbing microwaves depend on their properties like composition and structure. In constructing the primary components of a microwave unit, metals are usually used while accessories inside are made of transparent materials. Quartz is usually used as a reactor during microwave heating since it is transparent to microwaves while water is used as a microwave absorber for faster heating.

Since MWs are electromagnetic waves, their heating mechanism greatly depends on its capacity to convert electromagnetic energy into thermal energy. This property is known as the dissipation factor or dielectric loss tangent ( $\tan \delta$ ), and is given by the ratio of the dielectric loss factor ( $\epsilon''$ ) to the dielectric constant ( $\epsilon'$ ), as shown in the following equation [21, 27]:

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (1)$$

The dielectric loss factor expresses the material's conversion efficiency of electromagnetic energy to thermal energy, while the dielectric constant defines the molecule's ability to be polarized by an electric field [28]. Generally, MW absorbers with higher microwave absorbance are observed to have higher  $\tan \delta$  values.

The absorption of MW irradiation varies greatly with several factors such as temperature as well as microwave density and frequency. Microwave power controls the processing temperature, and an increase in microwave power results in an elevated temperature. It also increases the microwave density and specific energy input (SEI) in the cavity, thereby increasing the microwave absorption of biomass, which, in turn, intensifies the interaction between the microwave field and the biomass waste. Power density and specific energy input (SEI) are closely alike since the density measures the amount of microwave power supplied in a unit mass of biomass while SEI measures the amount of energy provided in a unit mass of biomass as well. A higher microwave power level leads to a higher heating rate, resulting from the enhancement of the absorptive properties of the biomass waste. The reaction time is also an important parameter in microwave-assisted heating. If the duration is not long enough, the process would not be completed or may not even occur at all [29]). On top of that, biomass' heterogeneous physical and chemical properties such as moisture, fixed carbon, volatile matter, and ash contents of a substrate, and lignocellulosic structure also affect the propagation of MWs. Biomass waste residues are typically dielectric since they are predominantly composed of hemicelluloses and cellulose. These two fiber components contain aliphatic C-C bonds, C-H bonds, C-O-C bonds, C-O-H bonds, and a small amount of carboxylic groups which contributes to the polarizability of biomass [30]. The aforementioned dielectric properties ( $\tan \delta$ ,  $\epsilon''$ , and  $\epsilon'$ ) will be important indicators whether particular biomass will be suitable for MW heating. **Table 1** shows the summary of microwave absorbing performance of some biomass materials

[27]. It includes a wide range of biomass, including agricultural residues such as rice husk, corn stover, sugarcane residues, and even municipal solid wastes (MSW), and the majority were found out to absorb microwaves poorly. In response, the addition of carbon-based and water-based absorbers as MW absorbers is essential for increased absorbance efficiency [27, 31].

#### **4. Microwave applications in bioenergy and biofuel production**

Mostly, microwave-assisted heating has been applied for second-generation (biomass waste residues) and third-generation (microalgae) feedstock to produce biofuels.

##### *4.1. Pretreatment for biochemical processes*

Physicochemical processing, often used in pretreatment, is commonly performed to initially deconstruct the cell wall's complex structure and internal lignocellulosic bonds within the biomass, thus providing a feedstock that is easier to break down for further biochemical processing such as fermentation and anaerobic digestion [32].

MW-based pretreatment for bioethanol production has been performed commonly with water [33], organosolvs [34], alkalis [35-37], and dilute-acid based solutions [38-41], as shown in **Figure 5**. Alkali pretreatment with sodium hydroxide (NaOH) results in lignin removal from oil palm empty fruit bunch (EFB) and cotton stalks by breaking the ester linkages between lignin and xylan [42, 43]. An increase in the sugar yield was also observed when NaOH-MW pretreatment was employed before the enzymatic hydrolysis of switchgrass. A similar sugar yield was achieved with NaOH pretreated cassava pulp under MW-assisted heating and it was achieved at a much shorter duration compared to that achieved by conventional heating [44]. Organic solvents were also coupled with MW-assisted heating as pretreatment and revealed that the breakdown of sugarcane bagasse during hydrolysis was improved [45]. Recently a NaOH-glycerol co-solvent mix was coupled with MW-assisted heating as a pretreatment approach, and this resulted in improved enzymatic hydrolysis yield and significantly induced surface

disruptions to the biomass [46]. **Table 2** summarizes the different residual wastes, the operating parameters, and important findings regarding the MW-assisted pretreatment for bioethanol production.

Pretreatment in the process of anaerobic digestion (AD) can aid in the breakdown of polymers into smaller molecules resulting in hydrolysis [47]. Theoretically, pretreatments shall disintegrate the bacterial cell wall and help to transfer extracellular polymeric substances (EPS) into the digestate, resulting in better-digesting capability [48] and reducing the retention time of the slurry mixture inside the digester [49, 50]. Same with bioethanol production, MW-assisted heating can also be incorporated with acids [51], alkalis [52-54], and  $H_2O_2$  [55, 56] as a pretreatment, as shown in **Figure 5**. MW-assisted heating applied as a pretreatment to AD could elevate biogas production, reduce the resulting sludge viscosity, and increase the soluble chemical oxygen demand to total chemical oxygen demand ratio (SCOD/TCOD) from 2 to 22% [57]. **Table 3** shows recent findings when MW-assisted pretreatment was utilized for anaerobic digestion. Combining MW-assisted heating with NaOH for pretreatment of waste activated sludge (WAS) was reported to significantly enhance chemical oxygen demand (COD) solubilization by 46%, as compared to MW-assisted heating and alkali pretreatment alone with only 8.5 and 18 %, respectively [58]. Enhancement in COD solubilization was also observed when  $H_2O_2$  was coupled with MW-assisted heating as a pretreatment route for anaerobic digestion of sludge [55]. However, it has been found that large fractions of  $H_2O_2$  remained in the AD system after pretreatment, inhibiting the hydrolysis-acidification and methanogenesis of municipal solid waste (MSW) sludge [51], thus, it was resolved by optimizing the amount of  $H_2O_2$  used and by understanding its catalytic mechanism.

#### 4.2. Pretreatment for thermochemical processes

The most promising methods of biomass waste pretreatment are drying, torrefaction, and

hydrothermal treatment because these are the only thermochemical processes with proven commercial and environmental feasibility and are still operated to this day. Therefore, these three processes are discussed in this section.

#### 4.2.1. *Drying*

The primary objective of drying is to reduce or remove moisture from the biomass waste residues without causing adverse effects on its physicochemical properties [59]. This results in enhancing energy yield and calorific value, as shown in **Figure 6** [60]. Additionally, pre-drying is required to avoid phase separation of the remaining moisture from the bio-oil after processing [61]. Basically, conventional oven drying and microwave-assisted drying are the two most utilized methods of drying [62].

MW-assisted drying is widely utilized because of its energy efficiency and better heating rate than conventional oven drying and is commonly applied to treat various raw foods (i.e., fruits, vegetables, and meat) [22, 63, 64]. MW-assisted drying improves the pore structure of biomass by reducing the moisture content, and eventually reduces the crystallinity of the cellulose within the biomass. The pore enlargement due to the liberation of moisture increases the effective surface area within biomass fibers and enhances the reactivity of the waste residues for further conversion processes [65, 66]. Drying in the context of pretreatment for thermochemical processes is a relatively new area of research, and limited resources can be found in the literature. **Table 4** shows a summary of the recent findings of microwave-assisted drying.

MW-assisted drying as a pretreatment for biomass waste torrefaction was done with rice straw, sugarcane bagasse, rice husk, and cotton stalk at two different temperature levels (250 and 300 °C) with 30 min residence time. Drying time was achieved 60% faster with the use of microwave compared to oven drying. More volatiles were released, the surface was more ruptured and crystallinity was also found to be lower which resulted in lower heating value,

energy yield, and elemental carbon content for all biomass wastes aside from the cotton stalk due to its woody nature that reduced devolatilization [67]. MW-assisted drying was also investigated as a pretreatment for pyrolysis using three different feedstocks, including corn stover, peanut shells, and pinewood sawdust at different power levels (200-800 W). Comparing to conventional oven drying at 105 °C for 40 min, a more rapid moisture reduction was observed with MW-assisted drying under 600 W for only 6 min [62]. The moisture reduction enhanced the porosity of waste vegetable leaves after undergoing MW-assisted drying at 1500 W, consequently, the combustion characteristic index was increased by 35%. The combustion kinetics of the food wastes was accelerated by reducing its activation energy at low temperatures while increasing its activation energy at elevated temperatures [68]. A higher comprehensive pyrolysis characteristic index (S) of *C. vulgaris* was also observed after microwave drying as opposed to conventional drying. Additionally, energy consumption and activation energy (E) after microwave drying were lower [69].

A drying efficiency of 76% was obtained when MW-assisted drying under 600 W was utilized to produce bio-oil from microalgae [70]. It has been reported that 20 W g<sup>-1</sup> of the microalgae *Chlorella vulgaris* was a viable power intensity for biofuel production, retaining a high lipid content for a lower specific energy requirement [71].

Although MW energy consumption was found to be higher than conventional oven drying, the significant reduction of processing time and upgrade in the product's quality will be a great offset to the aforementioned issue [47]. This proves that MW-assisted drying as a pretreatment for thermochemical conversion processes to produce biofuels is a promising technique.

#### 4.2.2. Torrefaction

Torrefaction is a mild thermal pretreatment of biomass waste residues with temperature ranging from 200 to 300 °C in an oxygen-free environment [72, 73]. Biochar is the main solid product of torrefaction with combustible properties nearly comparable to those of coal [74]. As

waste residue's hemicelluloses are thermally degraded, while cellulose and lignin are partially decomposed during torrefaction, the energy density, carbon content, and calorific value of the waste residues are greatly improved, as shown in **Figure 7** [75]. Conventionally, most researches have performed torrefaction either using a tube reactor or fixed bed reactor [76-78]. However, considering the potential of microwave-assisted heating for torrefaction, the research interest has grown utilizing different residual wastes from agricultural residues [79-84] to the organic fractions of sewage sludge [85-88], municipal solid wastes [89], and even co-torrefaction of waste oil fractions and other feedstock [90]. **Table 5** summarizes different biomass materials utilized as feedstocks, the parameters observed, and important findings in the context of MW-assisted torrefaction (MAT). Co-torrefaction of two residual wastes has been the recent trend either with two different agricultural residues or mixing it with sewage sludge to further enhance the solid yield and energy yield of the resulting biochar [87, 88]. Torrefaction as a pretreatment for more thermally intense processes such as pyrolysis and gasification provides a significant difference in the product outcome. For example, a better furfural production was observed when microwave-assisted catalytic torrefaction (MACT) was employed as a pretreatment for pyrolysis of Douglas fir sawdust pellets [91].

Some process variables significantly affect the yield and product properties of torrefaction. MW power level is found to be the most influencing factor in the quality of torrefied products [91-93] wherein the reaction time, heating rate, and maximum temperature are dependent. Recommended MW power levels are between 150 – 300 W since higher MW power levels lead to the secondary cracking of biomass (onslaught of pyrolysis) due to the elevated temperature levels and impact the quality of biochar negatively [87, 88, 94].

Particle size negatively affects the higher heating value of rice husk and sugarcane bagasse due to the larger surface area and concentration of MW energy in one spot [83]. The addition of microwave absorbents/ catalysts such as carbonaceous and water-based absorbers in the

context of MW-assisted torrefaction will be essential to provide higher heating rates and reduce the reaction times. Optimization of parameters is a must since an excessive amount of MW absorbers might cause the occurrence of selective heating (hotspots) wherein if the proper amounts are used, the desired temperature can be achieved at a shorter duration (20 min), thus lessening the energy consumption [89-91, 95, 96]. Overall, MW torrefaction can achieve comparable energy yields (70-90%) to conventional heating methods but with greater MW power levels are required at significantly shorter durations [79, 81, 97, 98].

#### 4.2.3. Hydrothermal carbonization

Hydrothermal carbonization (HTC), sometimes also termed as wet torrefaction, refers to the heating of biomass waste residues suspended in subcritical water or acid solution [99] with reaction time (30 min to several hours) and temperature range (200-300 °C) comparable to dry torrefaction [100-102]. The main solid product is referred to as hydrochar [103, 104] and accounts for nearly 88% to 90% of the mass and energy from raw biomass [105]. A schematic overview of the microwave-assisted hydrothermal carbonization is shown in **Figure 8**. Compared to dry torrefaction which involves decarboxylation, dehydration, demethoxylation, decarbonization, intermolecular rearrangement, condensation, and aromatization chemical reactions, hydrothermal carbonization is significantly different due to the presence of the submerging fluid [106]. The degradation of hemicelluloses is significantly increased with the lowered activation energies required for depolymerization as a result of ester and ether bond splitting from hydrolysis [107]. It has been reported to be more efficient and environment-friendly than dry torrefaction since water, inert gas, and raw biomass are the only inputs. Additionally, the higher heating value (HHV) and energy density of the derived hydrochar are exceptionally higher than biochar obtained from dry torrefaction. Besides, no pre-drying of feedstocks is required. Since microwave-assisted hydrothermal carbonization (MAHTC) can produce hydrochar with excellent fuel properties, improved grindability, and pelletability



without the prerequisite of drying, it is one of the best options to sustainably process biomass into biofuels [100, 108].

Limited studies can be found about the application of MAHTC for biofuel production. However, some researchers have started evaluating the viability of this process. Some of the most recent studies are summarized in **Table 6**. Chen et al. [109] found that sugarcane bagasse torrefied under HTC with the use of microwave-assisted heating improved its energy density by as much as 20.3% when compared to dry torrefaction. Elaigwu and Greenway's study [110] on MAHTC of rapeseed husks in deionized water at 150-200 °C at different reaction times revealed that higher reaction time and longer reaction duration favored greater energy yield of hydrochar garnering an increase of 32% at 200 °C and 25% for 30 min. When bamboo was subjected to MW-HTC in dilute hydrochloric acid, results revealed that the higher heating value of the hydrochar produced from MW-HTC was comparable to coals that were already commercially available [103].

Nizzamudin et al. [111] revealed that at a lower temperature (220 °C), shorter reaction time (5 min), lower biomass-to-water ratio (1:10), and higher particle size (3 mm), MAHTC produced more hydrochar (62.8% ) from rice husk, while higher heating value (HHV) was improved significantly from 6.80 MJ/kg of rice husk to 16.10 MJ/kg of hydrochar. Bach et al. [112] used microalgae (*Chlorella vulgaris* ESP-31) as the feedstock for MW-HTC and showed a 21% increase in the calorific value while retaining 61.5% of the energy originally in the raw microalgae. A more notable finding from this study was the significant reduction of ash content in the resulting hydrochar.

This elevated the potential to further explore the viability of using microalgae and macroalgae as feedstocks for MAHTC [99, 113]. The utilization of *Ascophyllum nosodum*, a brown seaweed, in the context of MAHTC with an additional acid catalyst not only resulted in energy yield of more than 50% but also produced an aqueous product rich in sugar [114]. A

greater and more critical exploration of the microwave hydrothermal carbonization process will provide a better vision for technological advancements to further improve product yield and quality, especially for the feedstocks such as seaweed and other biomass with high moisture and ash content [115, 116]. The feasibility of catalysis and operation in vacuum conditions are some of the innovations that can be ventured with MW-assisted hydrothermal carbonization. And to further enhance MAHTC's overall efficiency, proper handling and treatment with the aqueous by-product from hydrolysis is also a great path to explore.

#### 4.3. Pyrolysis

Pyrolysis refers to the thermal degradation of feedstock in the absence of oxygen, which produces three different products: the solid coal-like residue (biochar), the condensable heavy molecular weight compounds (bio-oil), and the non-condensable light molecular weight gaseous product containing syngas [117, 118]. Among all the thermochemical processes employed with MW-assisted heating, pyrolysis is the most researched path to turn biomass feedstocks into value-added products. [119, 120]. New pathways and findings with MW-assisted pyrolysis (MAP) are given in **Table 7**. MW pyrolysis can be subdivided, depending on its working temperature, heating rate, and residence time (see **Table 8**) [119].

Comparing to conventional pyrolysis, MW-assisted pyrolysis product yields and properties reported more drastic changes. More product vapors are released by the devolatilization that occurred during MW-assisted pyrolysis, hence more hydrocarbons in the vapors are converted into permanent gases. The product distributions of microwave and conventional pyrolysis are shown in **Figure 9** [121].

MW-assisted pyrolysis produces relatively clean and uniform biochar with higher surface area and better pore volume compared to the biochar produced from conventional pyrolysis [117, 122]. Thus, MAP can provide a new technique for making more porous biochar, which

can be used in sorption applications or as a precursor for producing activated carbon. Moreover, the produced biochar can be inserted in the microwave reactor as an MW absorber and increase the heating rate [122]. MAP of cylindrical wood blocks produced char with a larger specific surface area of  $450 \text{ m}^2 \text{ g}^{-1}$ . A few pyrolysis carbon-particles were found in the micropores in the SEM analysis [123]. Char formation plays an integral part in MW-assisted heating. Quicker char formation enhances the absorption of MW energy which, in turn, enhances the heating rate, thus elevating the reaction temperature more rapidly. It was observed that when oil palm fiber and oil palm shell undergone MAP, since oil palm fiber was less dense and smaller in size, char formed faster than the oil palm shell and reached the required pyrolysis temperature faster [124]. The char yield pine sawdust with the MAP, however, was observed to be relatively lower compared to conventional pyrolysis, mainly because of the higher internal heating rate and the event of self-gasification between the char and  $\text{CO}_2$ . Moreover, at elevated temperatures of MAP, char became less reactive due to char meltdown, pore shrinkage, and decrease in pore specific surface area which were observed from other literature [82].

The bio-oil shows greater carbon content and higher calorific value with a significant reduction in oxygen content [125-127]. The bio-oil yield generally increased with increasing reaction duration; however, an opposite trend was observed when sage wastes were pyrolyzed in a microwave reactor. The bio-oil yield decreased from 16.51 wt% to 3.92 wt% when the reaction time increased from 3 to 4 min, respectively [62]. Regardless of the biomass waste residue used, the composition of the bio-oil is predominantly composed of oxygenated compounds, carboxylic acids, phenols, etc. [62, 128, 129]. The distribution, on the other hand, is highly dependent on the reaction temperature. Increasing the temperature leads to a decrease in carboxylic acids and sterols due to the splitting of larger compounds into smaller compounds, predominantly alkanes, nitrogenous, and aromatic compounds [129].

The gaseous product which dominantly consists of  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{CO}_2$ , can be burned

and used for hydrogen production [130, 131]. MAP was also found to produce comparable non-condensable gas yield efficiently at lower temperatures (120-180 °C) compared to conventional pyrolysis (250-400 °C). When corn stalk bale was pyrolyzed using MW-assisted heating, more valuable products were obtained due to the rapid and uniform heating. The content of H<sub>2</sub> reached a maximum value of 35 vol% while the syngas (H<sub>2</sub> and CO) was above 50 vol%. A schematic overview of the microwave-assisted pyrolysis is shown in **Figure 10**.

The effects of feedstock type, particle size, operating temperature, residence time, and power level are the most studied parameters [121, 132-136]. The reaction temperature is regarded to be the one with the greatest influence. Generally, with increasing temperature, a significant increase in gas yield is observed with an opposite trend for the bio-oil yield, while biochar changes insignificantly [121]. Prolonged exposure of the pyrolysis vapors to irradiation enhances the thermal cracking which results in reducing bio-oil yield but an increase in the biochar yield [133]. The MW power level is also found to affect the product yields and property. As the heating rate increases with increasing MW power, more oxygen in the form of heavy molecular weight volatile compounds are liberated from the thermal decomposition of hemicelluloses, cellulose, lignin, proteins, and water, thus enhancing the bio-oil yield. The calorific value and yield of the biochar are also improved with increasing power levels [125].

Co-pyrolysis of biomass waste residues with polymers [137-139] or other wastes [140] has been regarded as an ideal process for liquid fuel production since it improves bio-oil yield and its quality. Another emerging technique is the use of additives or catalysts which enhances the desired product yield and selectivity [141, 142]. Catalyst introduction can be done *in situ* or *ex situ* wherein with *in situ* catalytic MW pyrolysis, biomass and catalyst samples are premixed in the quartz reactor before the experiment [143] while with *ex situ*, biomass and catalysts are within the microwave cavity but in separate reactors [144, 145]. Among the widely used catalysts, zeolite-based catalysts are highly regarded due to its excellent performance in

enhancing selectivity and product yields [146-149]. MW-assisted pyrolysis in vacuum condition has also proved its efficacy in improving the yield and quality of bio-oil [139, 150] and was even heightened when it was coupled with *ex-situ* catalysis with activated carbon [151]. A novel pathway of microwave steam activation via pyrolysis was recently introduced to convert waste palm shells into highly microporous activated carbon [152, 153]. Even though MW-assisted pyrolysis is thought to be widely studied already, there are still innovative pathways that can be walked upon to achieve better product yields without compromising sustainability and adaptable to be commercialized. Aside from piling studies regarding MW-assisted catalytic pyrolysis for enhanced product selectivity, coupling catalysis with pyrolysis in a vacuum environment has been extensively studied lately.

#### 4.4. Hydrothermal liquefaction

Hydrothermal liquefaction (HTL), also known as direct liquefaction, refers to the fragmentation of larger molecules into smaller ones which then recombine to produce bio-oil product (biocrude) in the absence of oxygen with temperatures ranging from 250 to 375 °C and pressure between 4 to 22 MPa [154-158]. The conversion takes place with hot compressed water acting as a reactant, solvent, and catalyst. Alternatively, methanol and ethanol are now also investigated as alternatives to water [154, 155, 159]. A schematic overview of the MW-assisted HTL is shown in **Figure 11**.

Microwave-assisted hydrothermal liquefaction (MA-HTL) has recently emerged as a sustainable alternative to the conventional HTL due to the wide range of advantages it offers. Mostly, MA-HTL is compared with the conventional HTL but not in the context of biofuel production [160-165]. Only a few studies are available and below are some of the highlights of MA-HTL in the context of biofuel production particularly biocrude (see **Table 9**). Zhuang et al. [158] investigated the effects of MW power, time, and temperatures on the HTL of *Ulva*

*prolifera*, and revealed that an increase in the three parameters resulted in increasing biocrude yield. However, at a certain MW power level, the yield started to decline and a maximum biocrude yield was registered at 84.81% and the greatest calorific value was 15.05 MJ/kg. The same feedstock was used by Liu et al. [166] to perform MA-HTL, reporting that a greater performance was observed with a maximum yield of 93.17% and a calorific value of 17.36 MJ/kg when optimum conditions were employed. Guo et al. [157] reported an 87.7% maximum biocrude yield when *Sargassum polycystum* C. Agardh underwent MA-HTL. From these results, it can be inferred that the maximum yields under varied conditions were obtained at 165 to 180 °C, significantly lower than that Elliot et al. [156] reported (38-64 MJ/kg). Thus, the results from Guo et al. [157] confirm that MA-HTL was more efficient than the conventional liquefaction. The addition of catalysts to feedstocks to enhance the selectivity of compounds in the biocrude produced has been the latest advancement in MA-HTL. Remon et al. [167] revealed that transforming 27% of the original biomass into a phenol-rich (47%) bio-oil with a relatively high HHV (20 MJ kg<sup>-1</sup>) is feasible by using optimized conditions such as temperature as low as 250 °C, the pressure at 80 bar, and employing 0.25 g catalyst/g biomass for 1.9 h. The properties of the bio-oil suggest that it is not only a suitable source of bioenergy but also a sustainable source of aromatics and phenolic-rich antioxidant additive.

#### 4.5. Gasification

Gasification is the process by which carbonaceous materials such as biomass and wastes are converted into combustible gas, termed as synthesis gas. Gasification can be categorized as direct or indirect gasification, depending upon the presence or use of an oxidant (air, O<sub>2</sub>, or steam) with the former using a limited amount and the latter using no oxidant at all [168-170]. Although synthesis gas (syngas) is its major product, it also produces a small amount of liquid fraction such as oil and tar, and a solid fraction (biochar) [168-171]. A schematic overview of microwave gasification is shown in **Figure 12**. The exothermic oxidation reactions during direct

gasification suffice the heat required to sustain the whole process. On the other hand, indirect gasification requires an external source of energy such as heat transfer or electrical means [168-172].

The advantages offered by microwave heating over the aforementioned conventional heating routes have led to several studies to utilize the microwave heating mechanism for gasification, as summarized in **Table 10**. Ismail and Ani [173] reported an optimal CO<sub>2</sub> flowrate for empty fruit bunch biochar and oil palm shell biochar at 3 L min<sup>-1</sup> and 2 L min<sup>-1</sup>, respectively, for the maximum biochar conversion into syngas of 75.07 % and 66.83 %. In another study, Ismail et al. [174] analyzed the impact of adding activated carbon (10%) and reported an enhanced gasification efficiency of 69.09 % from 66.83 % for oil palm shells, while an increase in the specific gas yield of 1.55 m<sup>3</sup> kg<sup>-1</sup> from 1.22 m<sup>3</sup> kg<sup>-1</sup> was reported for empty fruit bunches. Xie et al. [175] investigated the effect of different metal oxides in the context of MW-assisted gasification (MAG) and found out that Ni/Al<sub>2</sub>O<sub>3</sub> with the optimal ratios of catalyst-to-biomass of 1:3-1:5 were the best catalyst for maximum gas yield (80 %) and HHV (15.1 MJ/kg) of syngas. Due to the better heating mechanism of MAG, higher conversion efficiency and better fuel properties could be achieved at shorter reaction durations (13.7 times faster than conventional thermal driven reaction) [176-178]. An outstanding 49% biochar conversion efficiency was observed with MAG as compared to the conventional gasification [178].

The integration of plasma into the gasification system to enrich temperature and energy density in gasification has been gaining interest recently. Microwave plasma gasification systems are gaining attention because of its longer durability, smaller size, and flexibility, and it doesn't require an electrode compared to direct current (DC) and radio frequency (RF) gasification systems [179, 180]. Sturm et al. [179] presented a short gasification experiment with cellulose as the model biomass compound in air plasma. The energy efficiency of 1.84 was observed, that is, the chemical energy present in the resulting fuel gas was higher by as much

as 84% than the energy supplied into the microwave reactor over a range of operating conditions. Their results gave confidence that their concept could eventually be developed into a small-scale decentralized gasification technology. Zhang et al. [180] developed a pilot plasma gasification melting (PGM) reactor as a new waste disposal technology for municipal solid wastes. The overall gas yield increased significantly with high-temperature steam gasification compared to air gasification, which was attributed to the steam reforming in the steam gasification. The maximum energy efficiency reached 58% while the main energy loss was associated to the formation of tar. Sanlisoy et al. [181] reported a syngas production rate between 2.31 and 2.57 g s<sup>-1</sup>. The process energy efficiency and system energy efficiency were in the ranges of 36-86% and 27-61%, respectively. The hot gas energy efficiency was between 34 and 68%. A significant increase in syngas temperature was observed with increasing plasma power, mainly because of the increasing energy density within the plasma region.

Although there are several studies on MAG, it is still quite scanty compared to MW-assisted pyrolysis and this represents a huge avenue for further research.

#### 4.6. Transesterification

Biodiesel refers to fatty acid methyl esters (FAME) that are commonly produced with extracted oils and fats from biomass and other waste residues with alcohol [21, 182]. The process, which is popularly known as transesterification, can be done without a catalyst or employed with an acid [183-186], alkali [187-189], enzyme [190, 191], or metal oxides [192] as a catalyst. A schematic overview of the microwave-assisted transesterification (MATr) is shown in **Figure 13**. The parameters being investigated include MW power, time, agitation speed, and ratios between alcohol and oil or catalyst used with respect to the biodiesel yield. Among all these, MW power and reaction time are reported to have more significant effects on the yield than the other parameters [183, 184, 187, 188, 193, 194]. MATr has been widely used



in recent years because of its notable benefits over conventional heating such as faster chemical reaction rates, reduced reaction time, and thus lower energy consumption [195-197].

A summary of recent advancements with biodiesel production with microwave-assisted heating is provided in **Table 11**. Since microwaves have already been used for oil extraction prior to the use of MATr, a single combinatory process of extraction and transesterification using microwaves have been reported [195]. The majority of the papers published with MATr reported a direct relationship with the increase of FAME yields and the increase of parameters such as microwave power level, reaction time, and temperature. However, other papers reported that the increase with FAME yields was only up to a certain level and the yield eventually decreases with a continuous increase of the parameters. Ani and Elhameed [198] reported that this phenomenon may be associated with the promotion of saponification instead of biodiesel production at more elevated temperatures. Similarly, Azcan and Yilmaz [199], Cancela et al. [200], Choedkiatsakul et al. [201], and Martinez-Guerra and Gude [202] conferred that this sudden shift is a product of the reverse reaction of the feedstock over elevated temperatures. MW-assisted catalytic transesterification (MACTr) has been the recent trend with biodiesel production researches, where higher FAME yields have been obtained with faster reaction time and lower microwave power. However, the downstream processing to purify/ separate the catalyst from the biodiesel and reuse it has been a negating factor. Therefore, several new pathways could still be pursued to identify which treatment has the greatest techno-economic potential for future large-scale industrialization.

## **5. Advantages, challenges and other perspectives on MW-assisted heating**

### *5.1. Advantages of MW-assisted heating over conventional heating*

The various advantages of microwave heating over its conventional counterpart have been mentioned in the different applications for biofuel production reviewed in the sections above.

The majority gave credits to the improved energy efficiency by the use of microwave heating [203, 204]. The greater electric energy requirement of microwave to produce higher yields and better fuel properties was offset by the shorter duration times required to process biomass [22, 47, 63, 64, 79, 81, 97, 98, 111, 125, 156, 176, 178]. Due to the unique heating mechanism of microwaves, several other advantages are reported and summarized in **Table 12**. Aside from improved energy efficiency, the heating mechanism of MW-assisted heating is also an advantage as it illustrates the ability of MW to deliver the energy directly to biomass residue, unlike the contact heating where superficial heating occurs in the surface that results in heat and energy loss. Improved yields and product properties are also achieved at shorter durations as a result of the better heating rate in microwaves.

### 5.2. *Challenges with MW-assisted heating*

Although microwave heating offers a wide range of advantages, still, some aspects of this technology must be thoroughly investigated to further increase its efficiency and obtain better product yield and properties. A triple bottom approach is utilized to assess the challenges that need to be addressed to create a more sustainable microwave technology appropriate for biofuel production. This includes the discussion of challenges not only in the technical aspect but also in the environmental and economic aspects [205].

MW heating is highly dependent on the dielectric properties of biomass [206]. It has been mentioned from the fundamentals section that biomass is a poor absorber of microwaves, but a few publications report the dielectric properties of some biomass materials [47]. As an integral part of MW heating, this property needs to be fully understood to fully harness the advantages of microwave heating behavior. As dielectric properties determine the permittivity of microwave penetration, it is of great emphasis when designing a relatively more efficient microwave reactor. Permittivity is dependent on microwave frequency and temperature,

therefore, without the knowledge with dielectric properties of the feedstock, the reactor design would fail to reach the desired temperature due to the high reflected power in the boundary of the microwave generator and reactor [207]. Additionally, the use of MW absorbers will be of great necessity due to biomass' low dielectric properties in general [122, 125].

The formation of local heating or “hotspots” due to the heterogenous electrical field in the MW cavity is also a challenge. Unfortunately, the distribution of the electromagnetic field concerning power or frequency within the MW cavity is scarcely investigated [121]. The majority of the published researches utilized modified domestic microwave oven operating at 2.45 GHz, however industrial microwave heating equipment operates at 896 to 922 MHz. The effect of the operative microwave frequency might affect the products differently [208]. Proper modeling and simulation tools for the design of the equipment makes it possible to produce very accurate models, however, the lack of knowledge with the microwave and materials interaction has been a primary hindrance for scaling up. The need to explore new reactor concepts that ensures controllability and monitoring arises. Understanding with the variables such as electric field intensity, power dissipation rate, frequency, and temperature are needed to be harnessed.

When MW-assisted heating is used in pretreatment for biochemical processes such as fermentation and anaerobic digestion, toxic compounds may be generated that inhibit microbial activities and, in turn, decrease bioethanol and biomethane production. Furan derivatives and weak acids are formed during the decomposition of waste's carbohydrates, while the decomposition of lignin produces phenolic compounds [44-46, 51, 55, 58]. It is a must that the effects of the inhibitors are managed without causing drastic effects on carbon production. Some strategies suggested include the acclimatization of microorganisms to inhibitors before the production of biofuels or by using larger substrates to prevent inhibitor formation [209].

### 5.3. *Techno-economic analysis of MW-assisted processes*

There is only limited information available that accounts for the energy efficiency and energy consumption of MW-assisted heating in different biofuel conversion techniques. Likewise, cohesive evidence on energy balance, economics, and efficiency with MW-assisted processes was provided by a few studies to some of the different routes that utilize MW-heating. Performing a techno-economic analysis (TEA) determines the viability of a technology to sustainably produce biofuel and bioenergy products. The inputs for the model include investment and financial assumptions, processing capacity, biomass feedstock options, product options, operation costs, land costs, and revenues [210]. **Table 13** summarizes some of the techno-economic analysis performed to some MW-assisted processes.

The energy generation efficiency of microwaves from electrical energy is in the range of 50-65%. This means 35-50% of electrical energy is not converted into microwave energy. Again, in chemical reactions, it is an assumption that all of the microwave energy has been absorbed by the materials participating in the reaction. Having said that MW-assisted heating is more energy-efficient than conventional heating, some reports had questioned the actual energy savings when using microwave heating in some processes, and had highlighted the need to optimize each particular process and to carry out a thorough assessment of energy usage [211].

Technically, MW-assisted heating has been successfully applied to several biomass conversion processes for enhanced biofuel and bioenergy production. However, energy efficiencies were mostly negative which suggested that the improved product yield was not enough to compensate with the energy input from microwave systems.[209] For example, lower energy efficiency has been reported in the case of microwave pyrolysis [212]. It should be noted though that this efficiency depends on the suitability of microwave oven design for the process requirements, which may not be optimum when considering lab-scale rigs [210]. On the other

hand, biodiesel production was the sole MW-assisted process that actually is more energy-efficient than the conventional process. Yari et al. [213] have shown that microwave irradiation was a fast and energy-saving method compared to the conventional transesterification method for biodiesel production. However, innovative ways such as microwave vacuum pyrolysis [151] and microwave disintegration with the aid of zeolites [214], biosurfactants [215], ultrasonication [216], induction with  $H_2O_2$ -acidic pH [217], induction with disperser [218] and deflocculation [219] have proven that innovations with the current processing routes could alleviate the economic viability and energy balance in addition to the technical enhancement they have already provided. With microwave pretreatment alone, the net profits were negative and became positive when coupled with the supplementary pretreatments mentioned above.

Results from sensitivity analyses determine the relation strength of the output to the potential sources of uncertainty in the input. Since some cost variables are assumed from base scenarios, the impact of varying these variables are highly significant to be cited to assess the economic feasibility of the MW technology applied.

#### *5.4. Opportunities for enhancements and scalability of MW heating for industrial applications*

To fully utilize the potential of MW-assisted heating in biofuel production, the challenges aforementioned are required to be addressed. The scalability of MW-assisted heating as applied to large-scale industrial implementation in the future will require process modeling of the different conversion routes. This will require more parametric and kinetics researches, especially with MW-assisted conversion processes where available literature is scarce. Since only a few studies reported the dielectric properties of biomass [47, 206], the researches with more varied feedstocks will be beneficial to providing data for modeling purposes. The optimization of several parameters such as MW power, reaction duration, temperature, pressure, and catalyst loading ratio will also help to further improve the MW heating efficiency and

reduce the energy input required [121, 125]. Understanding the dielectric properties of the biomass feedstock and optimizing the parameters will ensure that the MW-assisted heating conversion will be performed in a more sustainable way where the release of undesirable substances will be reduced, and inputs such as raw materials and energy will be maximized without sacrificing the system's overall efficiency.

The MW cavity design is also an essential factor that can boost the efficiency of MW-assisted heating. Researches that focus on the cavity design and electromagnetic field correlation can also be pursued. Variations in cavity size and geometry, operating frequency, and provision of agitation are some of the strategies that can be employed and thoroughly studied. Beneroso et al. [220] for example, introduced potential scalable concepts of microwave-assisted pyrolysis for biofuel production. Five different concepts were introduced, including the rotary kiln, the conveyor belt, the rotating ceramic-based disc, the microwave fluidized bed, and lastly the auger reactor. Although most of these concepts were only modeled from electromagnetic simulators, the potential they possess would be great to enhance the industrial bioenergy sector in the near future.

MW penetration is inversely proportionate to MW frequency where higher MW frequencies result in lower penetration depth. The idea of using magnetrons with lower MW power is one of the scale-up ideas that arise. Basically, the most economic solution is to employ systems with multiple low-powered magnetrons since they are relatively cheaper.

Research regarding MW-assisted catalytic conversion processes is relatively a new path. The mechanism behind catalysis must be carefully identified so that the suitability of using MW absorbers (catalysts) for different conversion routes may be studied on a larger scale. Feasibility studies on MW-assisted catalytic conversion of waste residues will help in understanding the behavior of microwaves as applied to larger volumetric heating. The selectivity of product

properties can also be significantly improved with the introduction of catalysts. These opportunities, if pursued, may lead to positive large-scale implementation of MW heating for biofuel production and may even be commercialized to fully replace the conventional route of processing biomass to achieve a more sustainable future.

## 6. Conclusions

A review of the most recent publications regarding MW heating has uncovered how flexible the technology can be applied in biofuel production. An impressive increase with the product yield and improvement in the product properties are reported with the use of MW heating in several conversion routes to produce biofuels. The sustainability and advantage of MW heating are rooted in its higher energy efficiency compared to the conventional heating method. Descriptive researches on the effect of several parameters are already established, however, as a novel technology for biofuel production, some major fundamental data of the system have not been fully accounted for, thus, the feasibility of this technology for large-scale implementation is still subpar. Understanding the interaction between the feedstock and electromagnetic field, and the optimization of several operational and mechanical parameters are the two main keystones that would propel the industrialization of MW heating in the near future.

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Table 1. Summary of microwave absorbing performance of some biomass.

Poor absorber	Good absorber
Rice husk	Sewage sludge
Sugarcane residues	Pennisetum
Wood biomass	Oils
Rice straw	Carbon-based materials
Empty fruit bunch (EFB) of palm	Leucaena
Oil palm shell	Coconut activated carbon (AC)
Mesocarp fiber	Coal
Aspen bark	
Douglas fir	
Cornstalk	
Wheat straw	
Corn stover	
Rapeseed husk	
Municipal solid wastes (MSW)	



Table 2. Summary of MW-assisted pretreatment for bioethanol production

Feedstock	Reaction Conditions	Findings	References
Rice Straw	680 W, 24 min	Maximum enzymatic saccharification efficiencies were observed at 30.6% and 43.3% for cellulose and hemicellulose respectively and overall efficiency of 30.3%. It is thus concluded that MW pretreatment of straw could break down its lignocellulosic complex and partially remove silicon and lignin.	[33]
Rice Straw Sugarcane Bagasse	240 W, 10 min	Sugar production has increased more than twice when enzymatic saccharification was carried out under MW-assisted heating compared with the conventional one.	[34]
Rice Straw	700 W, 30 min	Microwave heating coupled with alkali pretreatment of rice straw produced more ethanol with lower enzyme loading and shorter duration time than the conventional method.	[35]
Wheat Bran Rice hulls	450 W, 3 min	Pretreatment time and MW power level have no significant effect in cellulase production even though the highest yield was obtained at 450 W and 3 min.	[36]
Rice Straw Rice Hull	200 – 800 W, 10 - 30 min	Rice straw and hulls' saccharification was mainly affected by alkali concentration, heating duration, and substrate concentration.	[37]
Rape Straw	900 W, 1 min	An outstanding 92.9% energy savings in producing 1 g of ethanol was observed higher in this study compared to previous ethanol production studies.	[38]
Oil Palm Empty Fruit Bunch Fiber	180 W, 12 min	Under 3% (w/v) NaOH loading, optimal loss in lignin and holocellulose were reported to be at 74% and 24.5% respectively and reduced 411 mg of sugar per gram EFB with a cellulose enzyme loading of 20 FPU.	[42]
Cassava Pulp	90 °C, 30 min	MW-alkali pretreatment gained a maximum yield of reducing sugar of 723 mg/g pulp with 1.5 % NaOH during the enzymatic saccharification with 400 IU amylase dosage.	[44]
Corn Straw and Rice Husk	1300 W, 2 min	The novel combination of MW-assisted heating and alkali glycerol pretreatment reported a drastic improvement in enzymatic hydrolysis of corn straw and rice husk	[46]

Table 3. Summary of MW-assisted pretreatment for anaerobic digestion

Feedstock	Reaction Conditions	Findings	References
Sewage Sludge	600 W	A 13.34 % increase in the total methane production was observed with MW-H <sub>2</sub> O <sub>2</sub> -OH as compared to the control. Capillary suction time was only at 9.85 sec thus proving that MW-H enhances sludge dewaterability.	[51]
Sewage Sludge	170 °C, 1 min	Combined MW-heating and alkali pretreatment (0.05 g NaOH/g sewage sludge) is a great method to biologically degrade thickened waste activated sludge particularly in a full-scale, thermophilic digestion digesters	[52]
Sewage Sludge	1000 W, 10 min	MW-NaOH pretreatment of sludge revealed 18 times better solubilization degree as compared to raw sludge. The best properties of pretreated sludge were achieved with a lower hydraulic retention time of 5 days (shorter than the raw sludge).	[53]
Sewage Sludge	600 W, 16 min	Soluble COD to total COD (SCOD/TCOD ratio of waste activated sludge increases as pH of the alkali pretreatment also increases. Deteriorated dewaterability was also improved when MW-assisted heating was combined with alkali pretreatment.	[54]
Sewage Sludge	600 W	Optimizing the H <sub>2</sub> O <sub>2</sub> : mixed liquor suspended solids (MLSS), H <sub>2</sub> O <sub>2</sub> dosage was reduced by 80% and the utilization rate was increased up to 3.87 times. The comparable release rate of SCOD was observed with optimized (0.2) and unoptimized (0.5) H <sub>2</sub> O <sub>2</sub> dosage.	[55]
Sewage Sludge	10 °C/min	MW-S <sub>2</sub> O <sub>2</sub> was found out to be a more promising pretreatment than MW-H <sub>2</sub> O <sub>2</sub> for sludge treatment at a lower oxidation dosage and temperature	[56]
Sewage Sludge	600 W, 2 min	MW-assisted alkali pretreatment achieved 46% solubilization of COD, even larger than the additive solubilization of MW-assisted heating and alkali pretreatment performed separately 8.5 + 18% = 26.5%).	[58]



Table 4. Summary of MW-assisted drying as applied to biofuel production

Feedstock	Reaction Conditions	Findings	References
Fruit Peels	900 W, 8.5 min	MW-assisted drying of fruit peels such as orange, mango, and passion fruit obtained a higher heating value (HHV) of 16,25kJ/g, 19,62kJ/g, 16,35kJ/g respectively. The energy consumed during the MW-assisted drying process was 85% lower than conventional drying.	[60]
Pinewood sawdust, peanut shell, and maize stalk	600 W, 6 min	Yields of solid char were increased however the content of the organic compound decreased. The same behavior with the bio-oil yield was observed together with its increased HHV and viscosity due to the lower moisture content. The gas yield on the other hand although higher CO <sub>2</sub> concentration was observed.	[63]
Kitchen waste	1500 W	The effect of MW-assisted drying was more evident to the vegetable leaves rather than cooked rice garnering an increase of about 34.47% in its combustion characteristic index compared to 8.12% in cooked rice.	[68]
Microalgae ( <i>Nannochloropsis sp.</i> )	630 W	A drying efficiency of as high as 76% was recorded when 130 g of microalgae was utilized per batch under a microwave power level of 630 W.	[70]
Microalgae ( <i>Chlorella vulgaris</i> )	20W g <sup>-1</sup>	A drying rate of 20 W g <sup>-1</sup> was recommended to obtain a good quality of the remaining lipid in the dried microalgae at a lower specific energy requirement.	[71]

Table 5. Summary of MW-assisted torrefaction

Feedstock	Reaction Conditions	Findings	References
Wheat Straw and Aspen wood	20 °C/min	Hydrophilic extractable chemicals were formed during the MW-assisted torrefaction for wheat straw and aspen wood and reported to be most significant in the temperature range of 250-280 °C.	[79]
<i>Prosopis juliflora</i>	250 °C	MW-assisted torrefaction of <i>Prosopis juliflora</i> revealed that not only hemicellulose is being degraded significantly but lignin as well. Results were from a detailed compositional analysis of its bio-oil.	[80]
Palm Kernel Shell	450 W, 8 min	Characteristics of Palm kernel shells such as oxygen content, carbon content and O/C ratio, were improved while increasing MW power level and reaction duration. Carbon content and higher heating value comparable to untreated MB coal was also obtained.	[81]
Leucaena	250 W, 30 min	With a fuel ratio (3.7) greater than those of bituminous coal ( $\leq 3$ ), and a maximum energy return on investment (ROI) of 34 when 200 g of leucaena is utilized, it can be used to replace or co-fire with coal in the industry.	[82]
Rice husk and Sugarcane residues	250 - 300 W	With increasing water content, maximum temperature and mass reduction ratio also increased and with the optimized reaction duration, the calorific value of rice husk and sugarcane bagasse can increase by as much as 26% and 57% respectively.	[83]
Rice straw and pennisetum	150 W, 10 min	A mass yield and energy yield for torrefied biomass of 70% and 80% was obtained at 150 W power level and 10 minutes reaction duration. Additionally, the remaining percentages are from the byproducts (bio-oil and gas) which can also be used as an additional source of heat and electricity.	[84]
Sewage Sludge	200 W	200 W was reported to be the optimum power level for MW-assisted torrefaction of sewage sludge to maximize bioenergy production since HHV of sewage sludge decreases as power level increases. The energy ROI including the by-product recovery is 16.4, which means that the process is feasible for bioenergy production,	[85]

Sewage sludge and Leucaena wood	250 W	The biochar produced from MW-assisted torrefaction of Leucaena and sewage sludge contains higher carbon content and was observed to adsorb CO <sub>2</sub> better than the raw counterparts. Optimization of the amount of Leucaena in the mixture leads to greater adsorptive properties of the biochar.	[86]
Sewage sludge and Leucaena wood	400 W	Both properties of biochar produced are significantly improved such as reduction of volatile matters and higher HHV and fuel ratio. However, the performance of the MW-assisted torrefaction of Leucaena was better than sewage sludge.	[87]
Sewage sludge and rice straw	200 - 300 W	The synergistic effect of adding rice straw with sewage sludge during MW-assisted torrefaction improved the system's performance wherein higher maximum temperature and improved HHV are observed.	[88]
Municipal Solid Waste	650 W	Highest HHV, improved energy yield and reasonable volatile matter are observed when biochar from sugarcane bagasse was added to the MW-assisted torrefaction of municipal solid waste at 650 W.	[89]
Oil palm waste and waste oil	250-300 °C, 5 - 8 min	MW-assisted co-torrefaction of oil palm empty fruit bunch and used engine oil reported a 100% energy yield with 85% mass yield at 250 °C, while the highest HHV (28 MJ/kg) was observed at 300 °C.	[90]
Douglas fir sawdust pellets	600 W, 6 min	The HHV of 20.90–25.07 MJ/kg of torrefied biomass shows a roughly 6%–31% increase from the raw biomass. Energy yield was at 67.03%–90.06% which means that most energy was stored with the torrefied biochar.	[92]
Douglas fir sawdust pellets	250 °C, 10 min	Increasing time, temperature and catalyst loading negatively impacted the yield of torrefied biochar while an opposite trend was observed with the bio-oil yield.	[91]
Corn stover	275 °C, 30 min	MW-assisted torrefaction as a thermal pretreatment indicates an improvement in the quality of pyrolytic oil such as increased content of hydrocarbons and phenols.	[93]
Oil Palm Empty Fruit Bunch	385 W	MW-assisted torrefaction of an empty fruit bunch increased the fixed carbon content in the biomass thus, increasing its HHV (22.4MJ/kg) while decreasing the amount of VM. Moisture was also reduced therefore improving its grindability.	[94]

Table 6. Summary of MW-assisted hydrothermal carbonization

Feedstock	Reaction Conditions	Findings	References
Microalgae ( <i>Chlorella vulgaris</i> )	160 °C, 10 mins	The enhancement in the HHV and energy yield was 40 and 45% respectively. The use of phosphoric acid (0.1 M) produced the highest ash content for ESP-31 and FSP-E with 1.61% and 11.60% respectively.	[99]
Bamboo	180 °C, 30 mins	As the torrefaction index was increased (3.27 to 3.89), a slight decrease was reported with the solid yield while hemicellulose content went down from 31.78% to 25.71%.	[103]
Phoenix tree leaves	220 °C, 60 mins	A direct relation was observed with the reaction severity and HHV of the hydrochar while the opposite was observed with its mass yield. The highest energy retention was observed at pH=7 with an increment of 2.7% higher than the raw feedstock.	[104]
Sugarcane bagasse	180 °C, 30 mins	A calorific value change of up to 20.3% via dry torrefaction can be achieved with hydrothermal carbonization at a temperature of 100 °C lower than dry torrefaction.	[109]
Rapeseed husk	150 – 200 °C, 5 – 30 mins	As reaction temperature and residence time were increased, mass yield decreased thus, improved the energy properties of the torrefied hydrochars.	[110]
Rice husk	220 °C, 5 mins	Lower temperature, lower residence time, lower feedstock to water ratio, and higher particle size favors the production of hydrochar. The HHV significantly improved from 6.80 to 16.10 MJ/kg.	[111]
Microalgae ( <i>Chlorella vulgaris</i> )	170 °C, 30 mins 180 °C, 10 mins	Results from MW-assisted HTC of microalgae improved the energy properties such as increased HHV (21%), hydrochar energy yield (61.5%), and hydrophobicity with reduced ash content.	[112]
Cellulose	250 °C, 90 mins	The improved fuel properties of hydrochar from MW-assisted HTC can be obtained with 5 to 10 times faster reaction time than conventional HTC.	[115]
Corn Stalk	182 °C, 40 mins	At optimum conditions (3.8 g/ 50 mL H <sub>2</sub> O), the highest energy yield is observed to be 80.55%, and with (2 g/ 50 mL H <sub>2</sub> O), the highest HHV was obtained to be at 22.82 MJ/kg.	[116]

Table 7. Summary of MW-assisted pyrolysis

Feedstock		Reaction Conditions	Findings	References
Waste paper	office	1200 W	The organic bio-oil yield was observed to be at 19% while the aqueous phase is at 23%. As applied for Al plates after 8 hours of curing at 160 °C, approximately 2300 N maximum tensile strength can be achieved.	[126]
Coffee hulls		130 – 420 W, 5 min	More gas and less oil were produced when coffee hulls were MW-assisted pyrolyzed and, notably, more H <sub>2</sub> and syngas (40 and 72 vol.%, respectively) were produced in this system rather than the conventional ones (30 and 53 vol.%, respectively).	[130]
Rice straw		300 W	As high as 50.67% H <sub>2</sub> comprises the gas product of the MW-assisted pyrolysis of rice straw which may be accounted due to the hotspot in the microwave cavity.	[131]
Sewage sludge		1000 °C, 20 min	Up to 94% vol syngas was produced with MW-assisted pyrolysis compared to conventional pyrolysis. Concentration CO <sub>2</sub> and CH <sub>4</sub> were at 50% and 70% respectively, lower than conventional pyrolysis.	[132]
Glycerol		800 °C	MW-assisted catalytic pyrolysis of glycerol with carbonaceous catalysts produced higher syngas content (81% vol) and increased selectivity of gas product towards hydrogen even at low temperatures comparing with conventional pyrolysis	
Waste polyolefins and waste cooking oil		800 W, 20 min	MW-assisted pyrolysis was observed to be more energy-saving due to shorter reaction time and lower power consumption. The process is also considered more sustainable because of lower nitrogen content and the absence of sulfur.	[139]
Used frying oil and plastic waste		500 °C, 10 min	MW-assisted co-pyrolysis of used frying oil and plastic waste generated 81% wt bio-oil yield and 18% wt gas with the provision of faster heating rate (50 °C min <sup>-1</sup> ) at a lower reaction time of 25 min.	[140]
Corn Stover		750 W	From the studied SiO <sub>2</sub> deposition range, the coke yield continually increased while the yield of water and gas reached a peak then decreased however, oil fraction behaved inversely.	[142]

Bamboo	30 °C/min, 20 min	The resulting carbon fiber reported low moisture content, inorganic elements, and ash. Fixed carbon was also reported to be high at 80% wt. and the carbon element at 87%.	[143]
Corn Stover	750 W, 45 min	Maximum bio-oil yield and best quality were considered to occur at the optimum temperature of 500 °C.	[145]
Corn Stover and Scum	500 °C	The effect of catalyst mixture (1:4 CaO to HZSM-5 ratio) in the MW-assisted co-pyrolysis of corn stover and scum at 550 °C reported the highest yield of bio-oil and aromatics more than half compared with using HZSM-5 alone.	[146]
Jatropha	65 °C, 90 min	MW-assisted catalytic pyrolysis of Jatropha with NaNH <sub>2</sub> (1% wt) obtained a 96.2% bio-oil yield. With a total energy consumption that is 10 times lower than the conventional.	[147]
Douglas fir	700 W, 12 min	Phenols (38.9%) and phenolics (66.9%) are the main constituents of the bio-oil produced and was related to the decomposition of lignin. However, when Zn powder was introduced as a catalyst, esters (42.2%) were observed to be of the highest concentration.	[148]
Douglas fir sawdust pellets	480 °C, 10 min	MW-assisted catalytic pyrolysis of Douglas fir pellets at 550 °C under 0.25 catalyst to biomass ratio reported the maximum carbon content of desired aromatics at 24.76%	[149]
Palm kernel shell	700 W, 25 min	Activated carbon from MW-assisted vacuum pyrolysis of biochar derived from kernel shells of oil palm demonstrated high adsorption capacity for metal atoms.	[150]
Waste plastic and used cooking oil	581 °C, 20 min	MW-assisted catalytic vacuum pyrolysis with activated carbon shows excellent potential for bioenergy production after producing 84% wt bio-oil with HHV of 9 MJ/kg and contains light hydrocarbons.	[151]
Waste palm shell	500 °C, 15 min	A gram of activated carbon from steam activation under microwave-assisted heating at 550 °C and 10 min can remove up to 38.5 methylene blue.	[152]
Waste palm shell	700 °C, 10 min	A conversion rate of 45% wt of microporous activated biochar (MAB) was observed after the provision of a high heating rate of 70 °C min <sup>-1</sup> as compared to the 12-17% of the conventional method.	[153]

Table 8. Classifications of Pyrolysis

	Temperature (K)	Heating Rate (K s <sup>-1</sup> )	Residence Time (s)
<b>Slow</b>	550 - 950	0.1 – 1	450 – 550
<b>Fast</b>	850 -1250	10 – 200	0.5 – 10
<b>Flash</b>	1050 – 1300	> 1000	< 0.5

Table 9. Summary of MW-assisted hydrothermal liquefaction

Feedstock	Reaction Conditions	Findings	References
<i>Sargassum polycystum</i> C.Agardh	170 °C, 30 min	A maximum liquefaction yield of 87.70% was achieved under optimum conditions including ethylene glycol (EG) to feedstock ratio of 18.5:1 (w/w), H <sub>2</sub> SO <sub>4</sub> loading of 9.6% (w/w%) and microwave power level of 400 W.	[157]
<i>Ulva prolifera</i>	180 °C, 30 min	With power level set to 600 W, solvent to feedstock ratio of 16:1 and H <sub>2</sub> SO <sub>4</sub> loading of 6%, MW-assisted HTL of <i>U. prolifera</i> achieved a maximum yield of 84.81%.	[158]
Wood meal	150 °C, 7 min	MW-assisted catalytic liquefaction of wood with H <sub>2</sub> SO <sub>4</sub> reduced the wood residue content to zero in just 5 minutes wherein the resulting liquefied wood polyols are deemed suitable for the preparation of PU foams.	[160]
Corn stover	160 °C, 5 - 30 min	The hydroxyl and carbonyl group contents of liquefied products via MW-assisted heating and conventional heating are found out to be significantly different according to the FTIR analysis.	[161]
Sweetgum sawdust	150 °C	The bonded phenols' chemical components and substitution patterns were found out to be similar to MW-assisted heating and conventional heating. Additionally, hemicellulose was the most susceptible to liquefaction while crystalline cellulose was the most recalcitrant.	[162]
Poplar sawdust	500 W, 2 min 300 W, 5 min	The synergistic effect of glycol in the liquefaction efficiency is more evident with the use of simple glycols like ethylene glycol and propylene glycol than higher analogues.	[163]
Wheat straw alkali lignin	300 W, 10-60 min	Optimize temperature and reaction time to avoid recondensation of degraded lignin fragments to obtain high yield monophenolic compounds.	[165]
<i>Ulva prolifera</i>	165 °C, 30 min	MW-assisted HTL of <i>U. prolifera</i> achieved a maximum yield of 93.17% with power level set to 600 W, solvent to feedstock ratio of 18.87:1 and H <sub>2</sub> SO <sub>4</sub> loading of 4.93%.	[166]
Pine and spruce	250 °C, 114 min	Optimized parameters such as the temperature at 250 °C, pressure of 80 bar, catalyst loading of 0.25 g/ g of biomass for 1.9 hrs yields phenol-rich bio-oil with high HHV.	[167]



Table 10. Summary of MW-assisted gasification

Feedstock	Reaction Conditions	Findings	References
Oil Palm Biochar	800 W, 5 min	Carbon conversion efficiency was observed to be at 75.07% and 66.83 % while a higher heating value of 12.84 and 13.03 MJ/kg for empty fruit bunches (3 lpm) and oil palm shells (2 lpm) respectively.	[174]
Oil Palm Biochar	800 W, 5 min	Best gasification efficiency was recorded at 72.34% and 69.09% for empty fruit bunches (with 10% AC and 12% unreacted carbon) and oil palm shell (with 12% AC and 18% unreacted carbon) respectively.	[173]
Corn stover	750 W	MW-assisted catalytic gasification with Ni/Al <sub>2</sub> O <sub>3</sub> (1:3 - 1:5 catalyst loading) was observed to favor syngas production and tar removal at the same time garnering a gas yield of greater than 80%.	[175]
Oil Palm Shell and Empty Fruit Bunch	900 °C, 60 min	The synergistic effect was highly evident with the CO <sub>2</sub> conversion of MW-assisted catalytic gasification (93%) which almost doubled as compared to the conventional thermal gasification of OPS biochar (58%) at the same condition.	[176]
Oil Palm Shell char	750 °C, 60 min	The very much lower activation energy was reported with MW-assisted catalytic gasification with iron-catalyzed char (36 KJ/mol) more than twice the non-catalytic MW-assisted gasification (74.2 KJ/mol) and almost 6 times lower than the conventional thermal gasification (247.2 KJ/mol). 99% CO <sub>2</sub> conversion can be maintained in this system for at least 60 minutes.	[177]
Rice straw	550 °C, 60 min	MW-assisted catalytic gasification with K <sub>2</sub> CO <sub>3</sub> (5%) and KOH (5%) increased the carbon conversion efficiency although the CO <sub>2</sub> content also increased. Syngas and H <sub>2</sub> yields were reported at 90% and 60% vol respectively. Ca(OH) <sub>2</sub> was regarded as an excellent catalyst as well for MW-assisted gasification and CO <sub>2</sub> absorption.	[178]

Table 11. Summary of MW-assisted transesterification.

Feedstock	Reaction Conditions	Findings	References
Microalgal lipid ( <i>Scenedesmus obliquus</i> )	1000 W, 10 min	MW-assisted catalytic transesterification of microalgal lipid with chromium-aluminum's efficiency is comparable to sulfuric acid (homogenous catalyst). FAME conversion of 98.28 was achieved when methanol to oil molar ratio was optimized at 20:1, and the catalyst amount of 15%.	[183]
Jatropha oil	65 °C, 60 min	MW-assisted catalytic transesterification of jatropha oil's performance was proven to be even better than with sulfuric acid. FFA conversion reached 99.13% with optimized parameters such as methanol/oil molar ratio of 12:1, catalyst loading of 7.5 wt%, and rotational speed of 350 rpm.	[184]
Waste cooking oil	140 °C, 15 min	With the optimum temperature and reaction time, FAME yields reached 90% and were associated with the increased SO <sub>3</sub> H groups in the biochar surface.	[185]
Palm oil	120 W, 8 h	MW-assisted transesterification can reduce reaction time and save up energy up to 44% more compared to the conventional method while reaching an outstanding 98.93% biodiesel yield.	[186]
Jatropha oil	65 °C	Even with milder reactions as compared to conventional transesterification, an oil conversion of 90% was achieved after 10 seconds due to the provision of a better heating rate from MW-assisted heating.	[187]
Waste cooking oil	325 W, 3.30 min	A power level of 325 W, the reaction time of 200 seconds, the temperature of 70 °C, and catalyst loading of 1 g/g oil the highest bio-oil yield of 97% was achieved with MW-assisted catalytic transesterification of waste cooking oil.	[188]
Papaya oil	700 W, 3.30 min	Methanol to oil ratio and temperature were the two parameters that have significantly affected the MW-assisted torrefaction of papaya oil.	[189]
Waste cooking oil	44.2 °C, 24 hrs	MW-assisted catalytic transesterification of WCO with lipase (0.782 g) can reduce the cost of the conventional transesterification with maximum FAME yield of 86%.	[190]

Waste cooking oil	70 W, 4 hrs	Optimized parameters such as enzyme loading, reactant ratio, temperature, water content and addition of surfactants intensified the conversion from 83% to 94%.	[191]
Jatropha-Castor oil	65 °C, 35 min	MW-assisted catalytic transesterification of mixed Jatropha and Castor oil with Ca and Fe (7:1 Ca: Fe ratio) optimized the yield of methyl esters by 95% under a methanol/oil ratio of 12:1. The catalyst was also found to be stable, reusable and easily recyclable.	[192]
Olive oil	500 W, 9 min	MW-assisted transesterification effectively increased the methyl ester yields while reducing reaction time and ultimately the energy consumption of the system. The increase in methyl ester yield is associated with the observed parameters such as the amount of catalyst, reaction time, methanol to oil molar ratio, and power level.	[193]
Animal Waste Fats	70 W, 60-120 hrs	MW-assisted catalytic transesterification of animal waste fats with sulfuric acid (2.0 wt/wt%) under optimum conditions, achieved a 93% FFA conversion which indicates that this process is a faster route to produce high FFA reduction for AWF.	[195]
Waste cooking oil	62 °C, 15 min	With optimal methanol (MeOH) to WCO molar ratio of 7.46:1, MW-assisted catalytic transesterification of WCO with catalyst loading (1.03 w/wt of feedstock) achieved a maximum biodiesel yield of 94.86%, which is twice as much as the conventional method can produce (42.59%).	[196]
Soybean oil	50 °C, 30 min	The optimized reaction conditions of FAME production using MW-assisted heating include methanol to oil ratio of 15:1 and 12 % wt. catalyst loading. Similar yields from fresh and reused catalysts were observed thus proving the reusability of the catalyst.	[197]
Soybean oil and waste cooking oil	300-500 W, 2-4 min	Highest biodiesel conversion rates of 97% and 93% were obtained from soybean oil and WCO respectively at an MW power level of 300 W (soybean oil, 2-3 min) up to 500 W (WCO, 4 min).	[221]
Canola oil	270 W, 30 min	Optimal conditions for the MW-assisted reaction of Canola oil with nanocomposite (4 % wt.) achieved a conversion rate of 98.8% under 15:1 MeOH: oil ratio.	[222]

Table 12. Advantages of MW-assisted Heating Over Conventional Heating

	Conventional Heating	Microwave Heating	Remarks
Mode of Heating	Contact Heating	Non-contact Heating	Microwaves penetrate the wall of the container and the biomass residue directly as opposed to conventional heating which involves conduction and convection which results in heat and energy loss
	Superficial	Volumetric	Volumetric heating ensures uniform heat distribution in the material, unlike superficial heating which occurs at the surface.
Energy Consumption	High	Low	As mentioned earlier, the higher power requirement was offset by the shorter reaction duration due to improved heating rate
Reaction Duration	Long	Short	Comparable yield and properties are observed as the heat transfer efficiency of microwaves are better
Ease of operation	Lower level of control	Higher level of control	MW warming can be promptly turned on and off. With new controls, microwave power and duration can be pre-determined dependent on its mass or volume.
Product	Lower product yield and fuel properties	Improved product yield and fuel properties	Results from the majority of the literature reported the improvement due to the more efficient heating rates at shorter durations

Table 13. Techno-economic analysis of some MW-assisted bioenergy and biofuel production processes

Feedstock	Process	Result of Analysis			References
		Technical	Economic	Energy	
Waste activated sludge	Pretreatment for Liquefaction	The result of the MW disintegration shows that the solids reduction and lysis rate of Ze-MWL sample with the optimum (0.04 g/g SS) dosage of zeolite was 33.1% and 42.8% comparatively more than MWL (21% and 26.8%) sample alone.	Comparing the net profit among two samples (MWL and ZeMW), the net gain of about (27 and 26 V/Ton of SS) was achieved. However, a higher net profit was achieved for Ze-MWL samples. Therefore it was concluded that Ze-MWL can be scalable at larger extent.	The net energy for both the samples (MWL and Ze-MW) was estimated to be 101.8 kWh and 254.5 kWh. While comparing the input energy of both MWL and Ze-MWL samples, MWL samples demand nearly double the energy to achieve the same 30% SCOD lysis rate	[214]
Waste activated sludge	Pretreatment for Liquefaction	The biosurfactant rhamnolipid under alkali conditions enhances the liquefaction at alkali pH of 10 with maximal liquefaction of 55% compared to RMD and MD with 45.7 and 33.7% respectively.	A net yield of (0.39 USD/ton) was achieved via the novel ARMD technique indicating its suitability at large scale execution when compared to RMD and MD only having net costs of −31.34 and −84.23 USD /ton net cost, respectively.	ARMD implies input energy of - 282.27 kWh proving the study's scalability.	[215]
Waste activated sludge	Pretreatment for Anaerobic Digestion	A higher suspended solids (SS) reduction and biomass lysis efficiency of about 22.5% and 33.2% was achieved through UMWD	A better net gain of 2.67 USD/Ton and nearly 50% of net energy savings were achieved for UMWD. On the other hand, an amount	MWD process demands a microwave energy input of −362.7 kWh to achieve 20% biomass lysis. However, UMWD demands only an MW energy	[216]

		when compared to MWD only (15% and 20.9%)	of –37.04 USD/Ton was spent towards MWD.	input of –189.1 kWh to achieve a similar extent of biomass lysis	
Waste activated sludge	Pretreatment for Anaerobic Digestion	Higher liquefaction of about 46.6% was achieved in HAMW-D when compared to that of MW-D (30%). It subsequently improved the methane yield of about 250 mL/g VS in HAMW-D, which was 9.6% higher than MW-D.	The addition of chemical cost did not cause any major impede to HAMW-D process as the net profit was (49 €/Ton of sludge) found to be comparatively higher than MW-D (10.2 €/Ton of sludge).	On evaluating the results of MW-D and HAMW-D samples, HAMW-D demands considerably lesser energy (68.8 kWh) to obtain 30% liquefaction when compared to MW-D process (482 kWh).	[217]
Waste activated sludge	Pretreatment for Anaerobic Digestion	The solids reduction and solubilization of floc disrupted (disperser induced microwave pretreated) sludge was found to be 17.33% and 22% relatively greater than that achieved in microwave pretreated (9.3% and 16%) sludge alone.	A positive net profit of about (104.8 USD) and a negative net profit of about -15.9 USD was achieved for disperser induced microwave pretreated and microwave pretreated alone sample.	The total energy consumed for both the samples (microwave pretreated and disperser induced microwave pretreated) to attain 20% solubilization was calculated to be 675.5 kW h and 480 kW h, respectively.	[218]
Waste activated sludge	Pretreatment for Anaerobic Digestion	Chemical oxygen demand (COD) solubilization of 31% and suspended solids (SS) reduction of 37% were achieved from the deflocculation of sludge, much higher than the 21% and 22% of flocculated sludge respectively.	A positive net profit of about 215 €/Ton of sludge was achieved with deflocculation and was also attractive compared to a flocculated sample with - 268.2 €/Ton of sludge.	The Deflocculated sample has a net (output–input) energy profit of 1915 kW h/tonne TS.	[219]

Sewage Sludge	Pretreatment for Anaerobic Digestion	In terms of the methane yield, the digestion's efficiency was observed to increase. The release of extracellular polymeric substances (EPS) and volatile fatty acids (VFAs) was also significantly improved due to the breakage of the sludge structure.	The cost of the Sulfur Citrate (SC) dosage is counterbalanced by the decrease in sludge disposal costs. For both treatments (MW20, MW40), there is no positive net gain at this point. Therefore, they are not attractive from an economic point of view.	The MW pretreatments demands a lot more energy than the extra methane produced can provide: MW20 demands the 5-fold in energy, MW40 requires almost 10 times as much energy. The large gain in methane yield did not compensate for the energy used to produce them, thus, a negative energy balance.	[211]
Douglas fir pellets	Pyrolysis	-	The assessment showed profitability for microwave-assisted ex-situ catalytic pyrolysis. The total capital investment was mainly from equipment costs, while the feedstock and chemical costs contributed significantly to the total annual production cost.	-	[210]
Hybrid Poplar	Pyrolysis	-	The design without heat integration turned out to be the most economically unfavorable since the contribution of coproduct credits was minimal. The liquid fuel yield in this study is lower compared to	Energy balance analysis indicated that in all 4 scenarios, the production process is completely self-sustainable. Additionally, significant energy savings can be achieved using heat integration. For instance,	[212]



			other literature. Yet, the benefit of co-production makes the overall production cost still cost-competitive.	energy consumption was cut off by 70% after heat integration.	
Waste plastic and used cooking oil	Pyrolysis	The combined use of microwave vacuum pyrolysis and activated carbon reaction bed produced up to 84 wt% yield of liquid oil, containing light hydrocarbons and higher heating value (49 MJ/kg) than diesel and gasoline, hence showing promise for application as fuel. The use of activated carbon reaction beds showed beneficial effects by averting the formation of oxygenated by-products.	The production cost of liquid oil for the scaled-up MVP system was estimated to be about USD 0.25/L, more than half the price of diesel fuel in Malaysia (USD 0.523/L, based on diesel price in August 2019). In comparison to biodiesel, the production cost of liquid oil is significantly lower than biodiesel (USD 0.53–2.04/L)	The lower energy consumption suggests that MVP could be an energetically viable means to co-process waste (WP, UCO) for waste reduction and energy recovery. The shorter pyrolysis time also led to a low electric consumption (0.38 kWh), indicating the lower energy consumption and potentially higher energy efficiency by this pyrolysis approach.	[151]
Waste fish oil	Transesterification	-	Economic efficiency was also achieved at 1.6637 kg.\$-1. In other words, in this work, the price of produced biodiesel per gasoline gallon equivalents (GGEs) will be 3.72 USD.	The total amount of input and output energy in this reaction was 48.839 and 50.866 MJ/L respectively. Specific energy consumption of 0.0167 kg/MJ and an energy ratio of 1.041 were also observed.	[213]

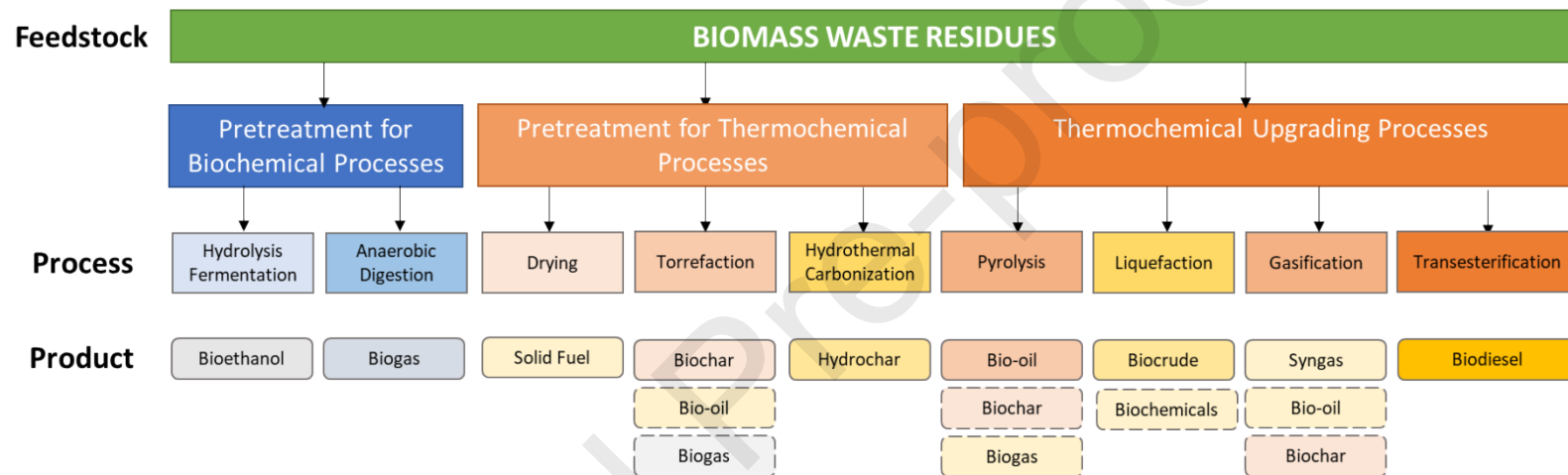


Figure 1. Biomass conversion routes for biofuel production with microwave applications.

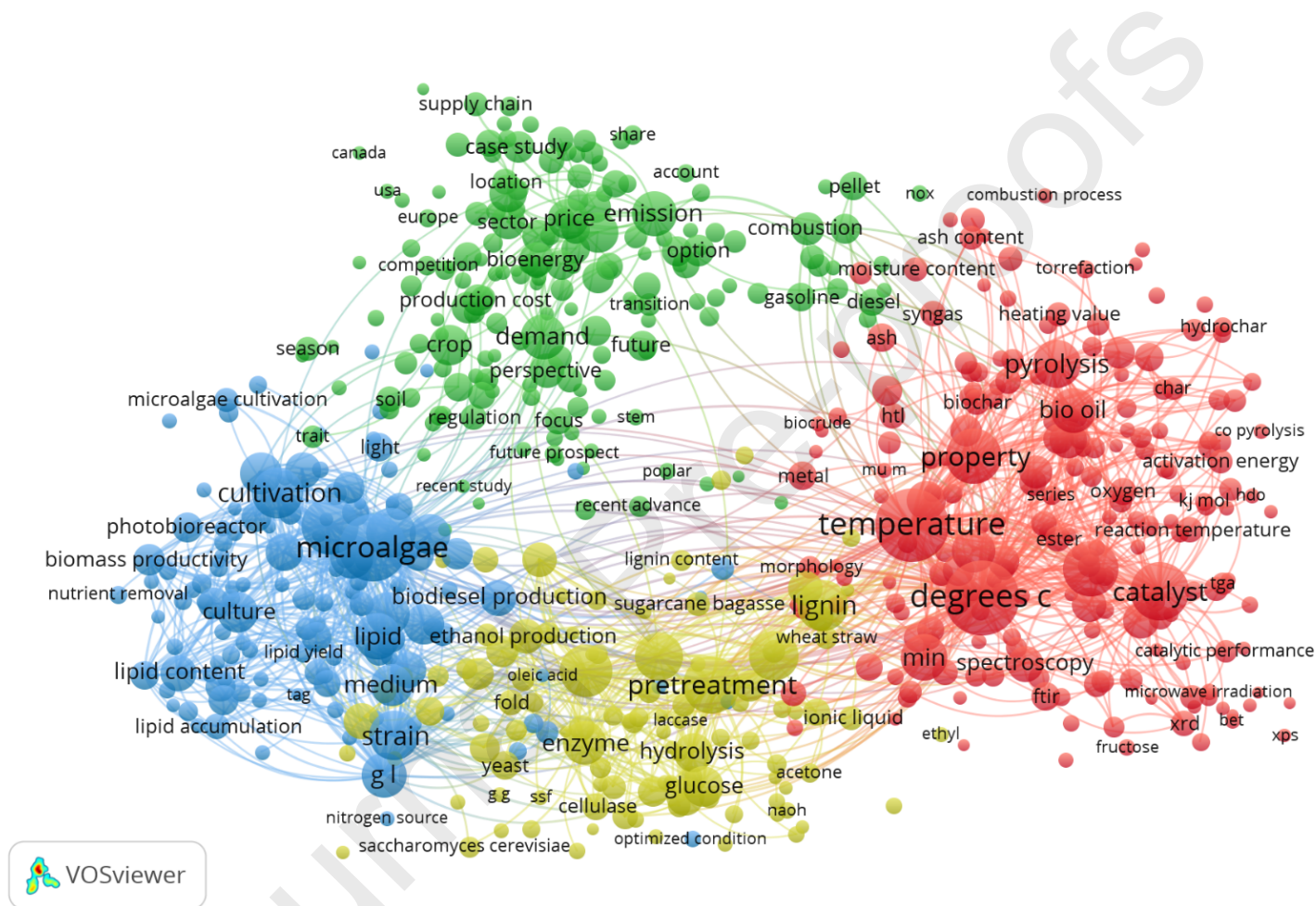


Figure 2. Network visualization of terms associated with microwave-assisted biofuel production from biomass waste residues

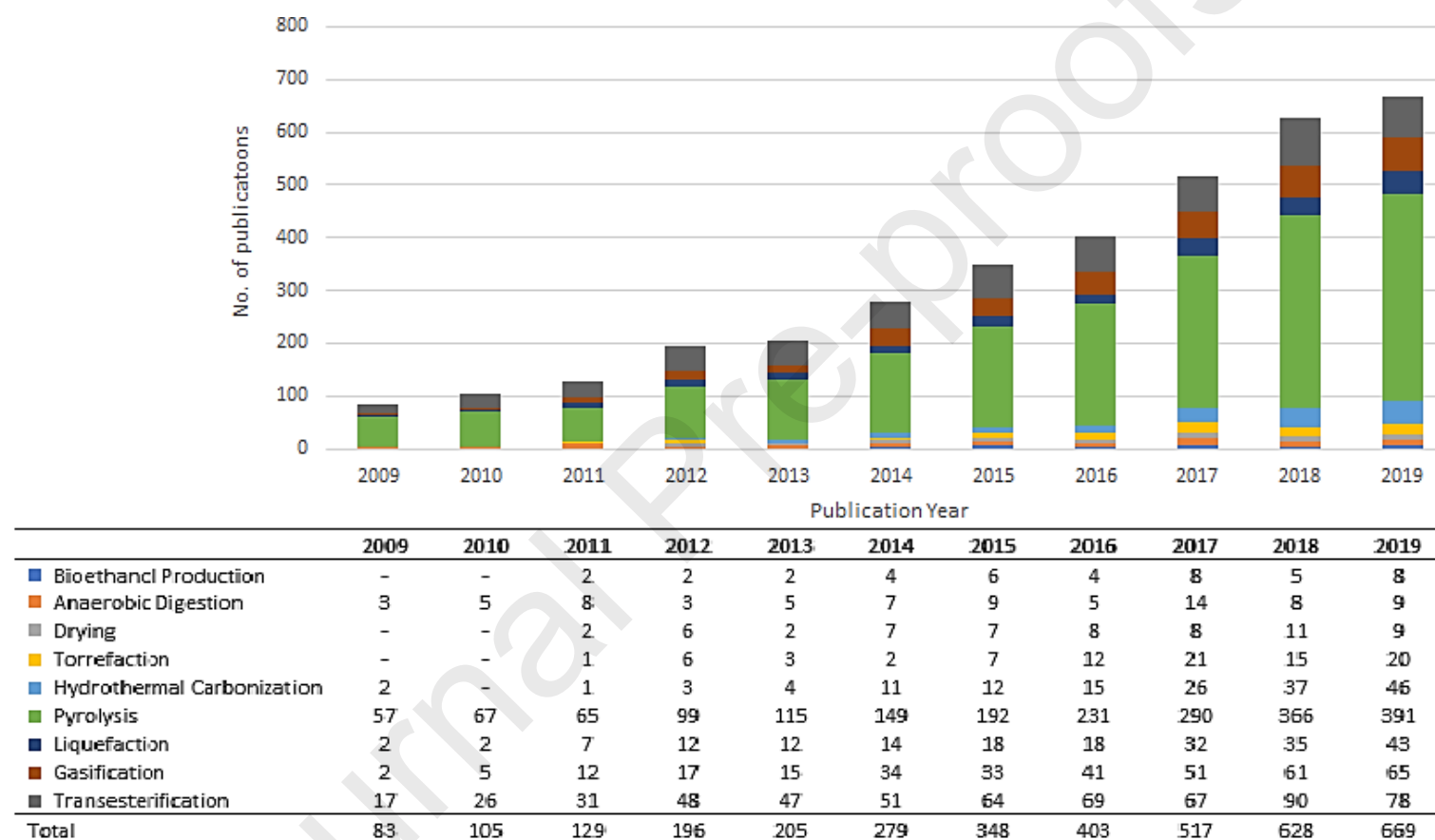


Figure 3. Total publications related to microwave-assisted processing of biomass wastes into biofuel and bioenergy (2009-2019).

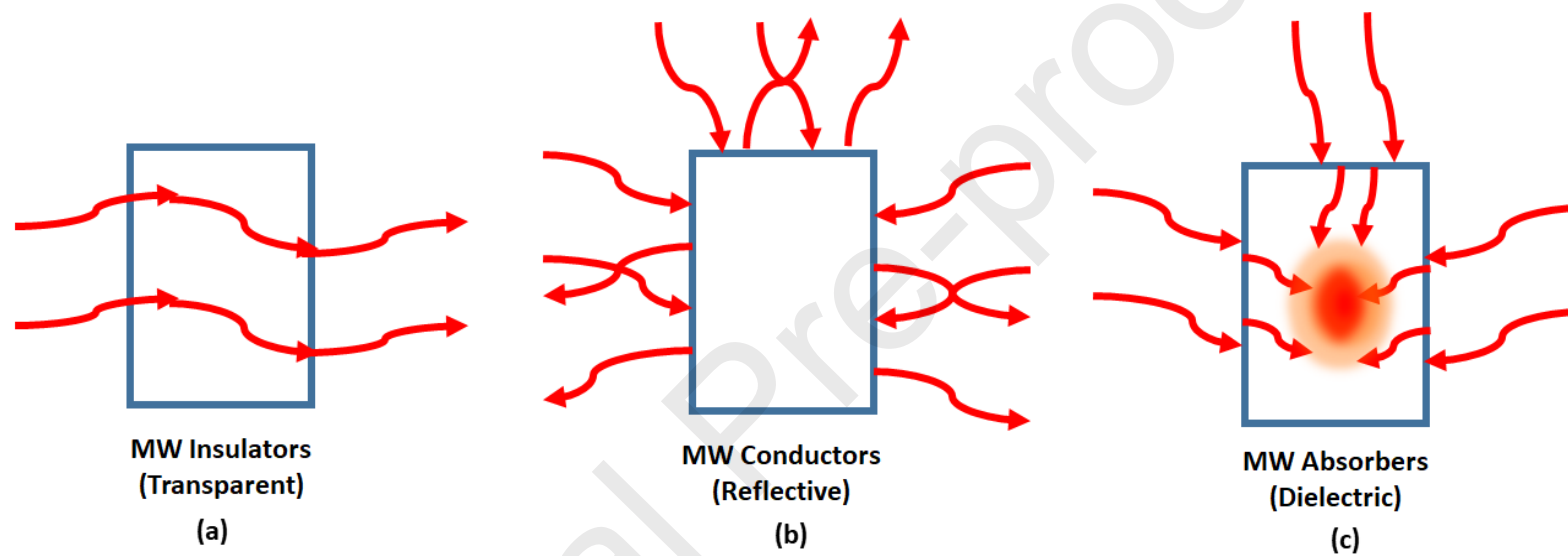


Figure 4. The reaction of different materials to microwave irradiation

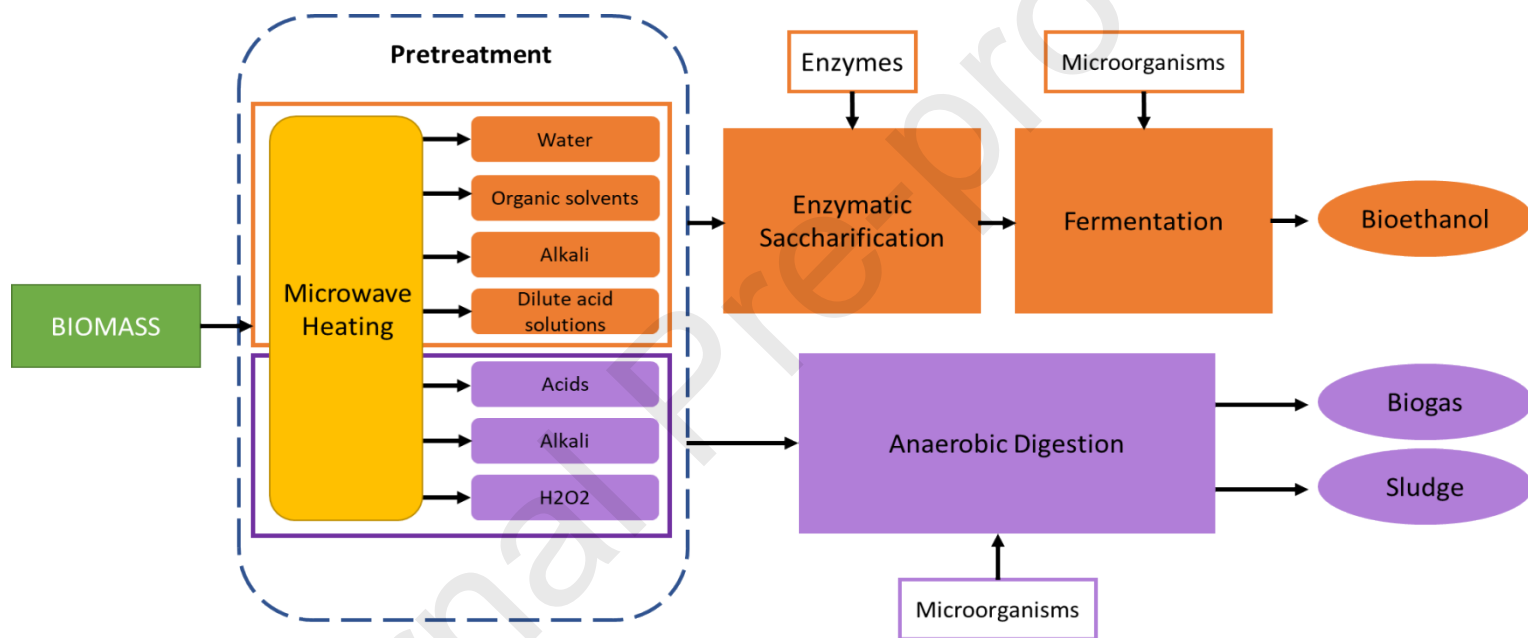


Figure 5. Schematic diagram of MW-assisted pretreatment as applied to biochemical conversion routes

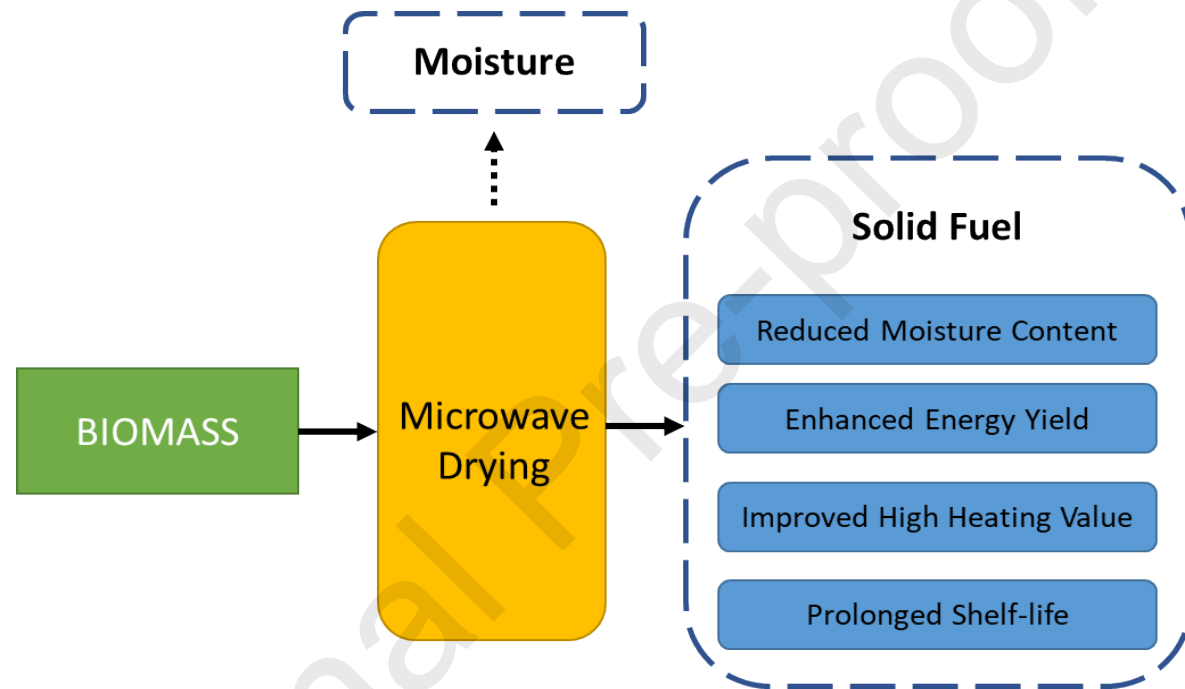


Figure 6. Schematic diagram of MW-assisted drying



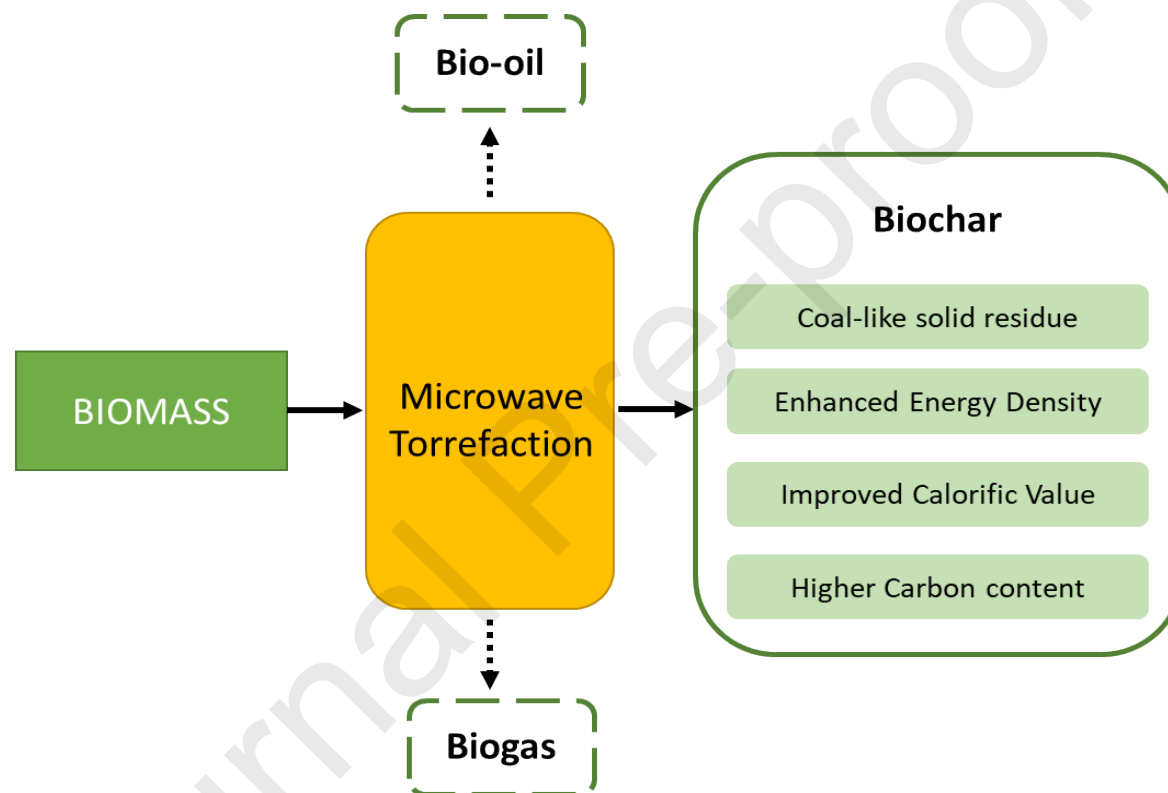


Figure 7. Schematic diagram of MW-assisted torrefaction

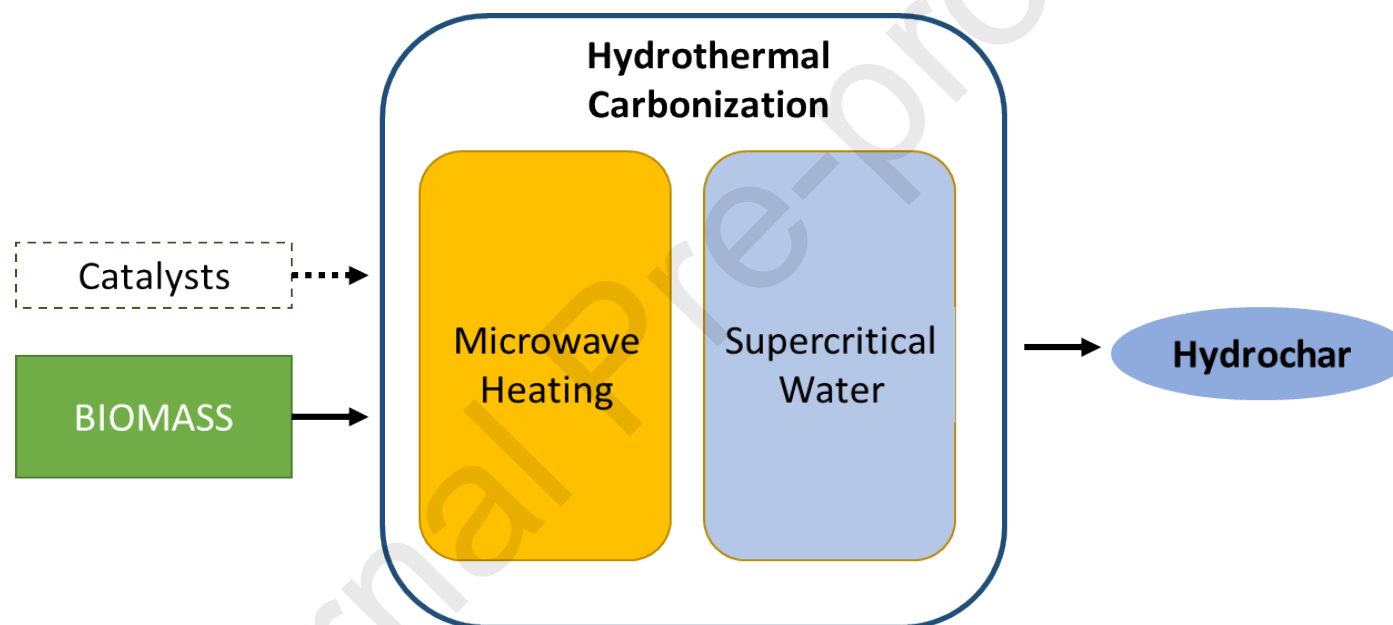


Figure 8. Schematic diagram of MW-assisted hydrothermal carbonization

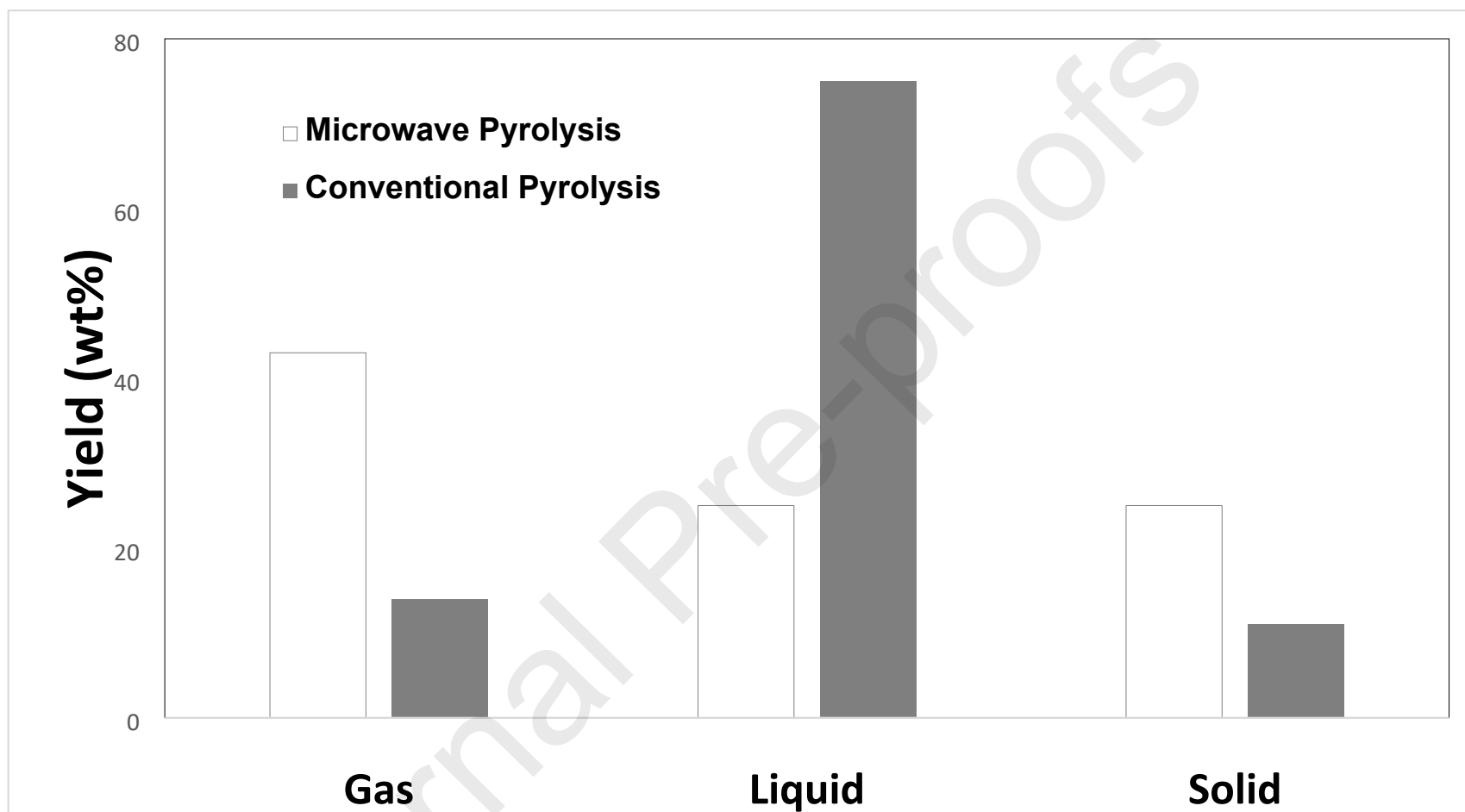


Figure 9. Product distributions of microwave and conventional pyrolysis

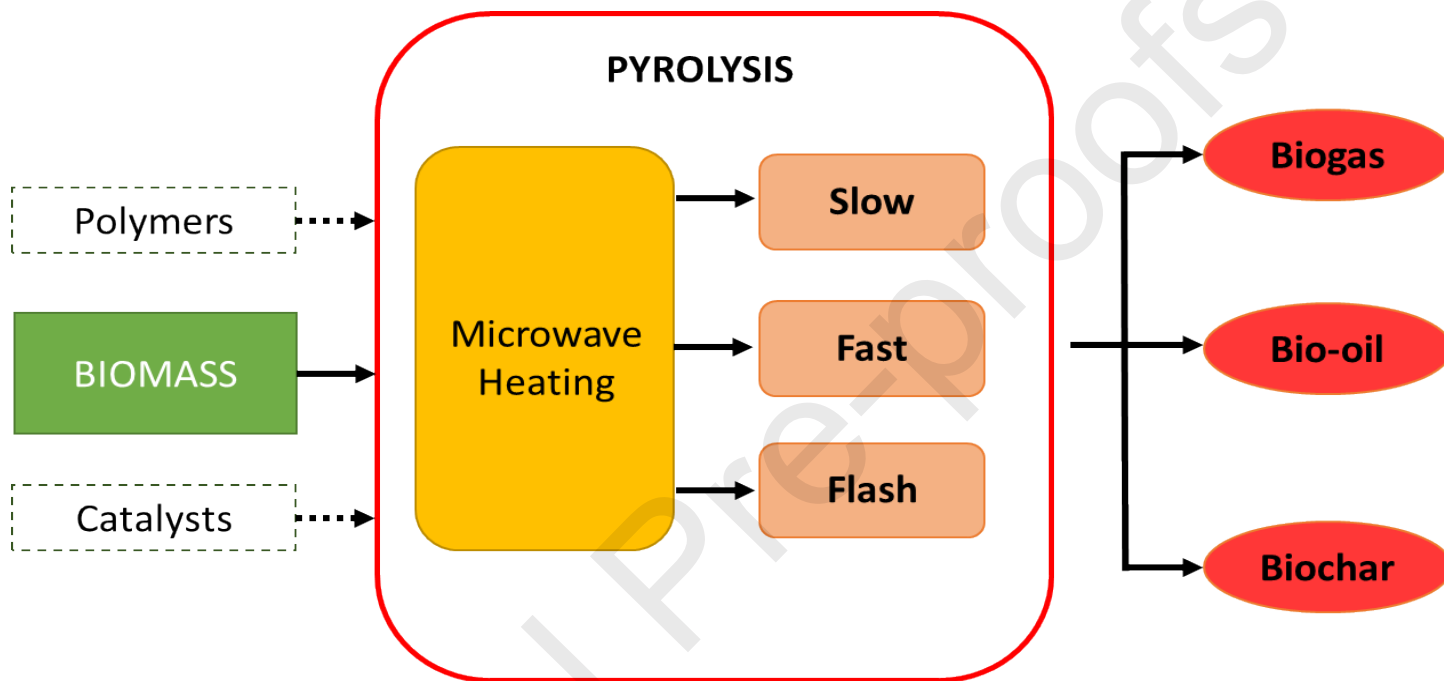


Figure 10. Schematic diagram of MW-assisted pyrolysis

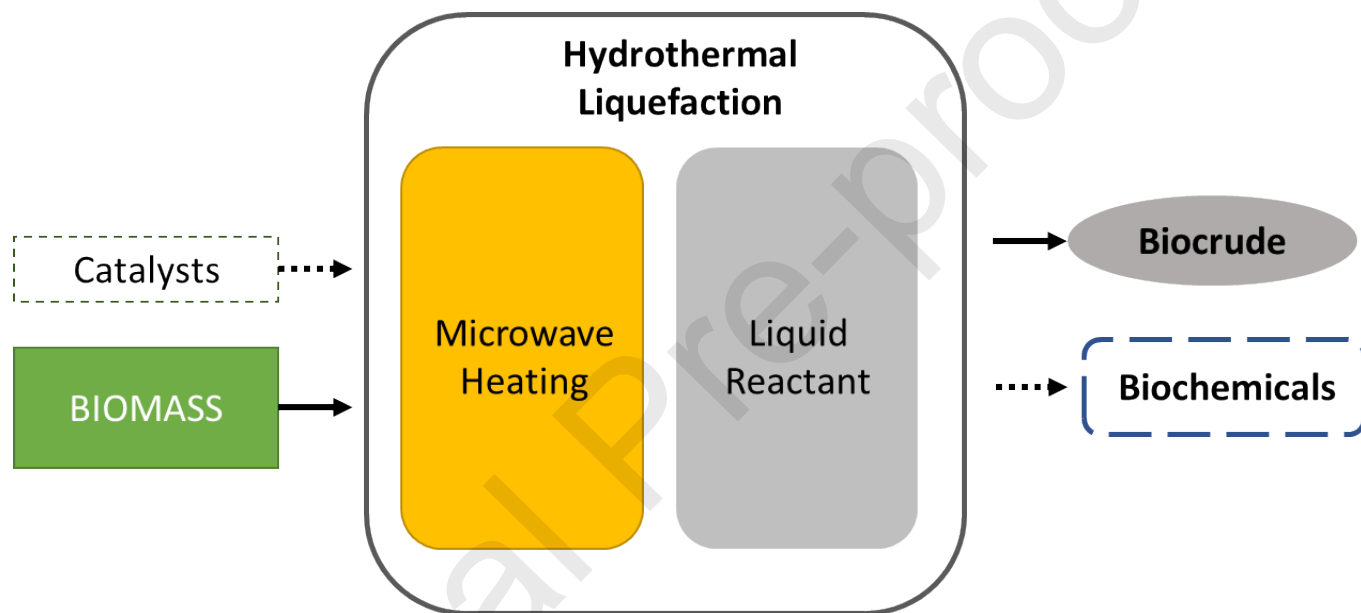


Figure 11. Schematic diagram of MW-assisted hydrothermal liquefaction

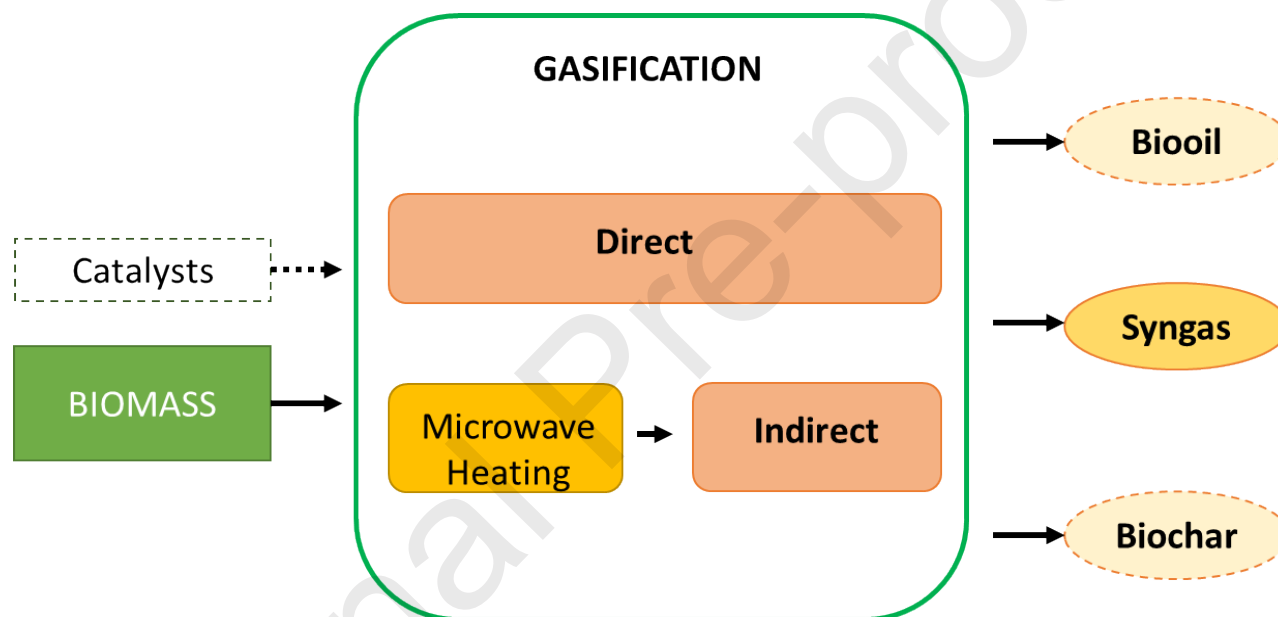


Figure 12. Schematic diagram of MW-assisted gasification

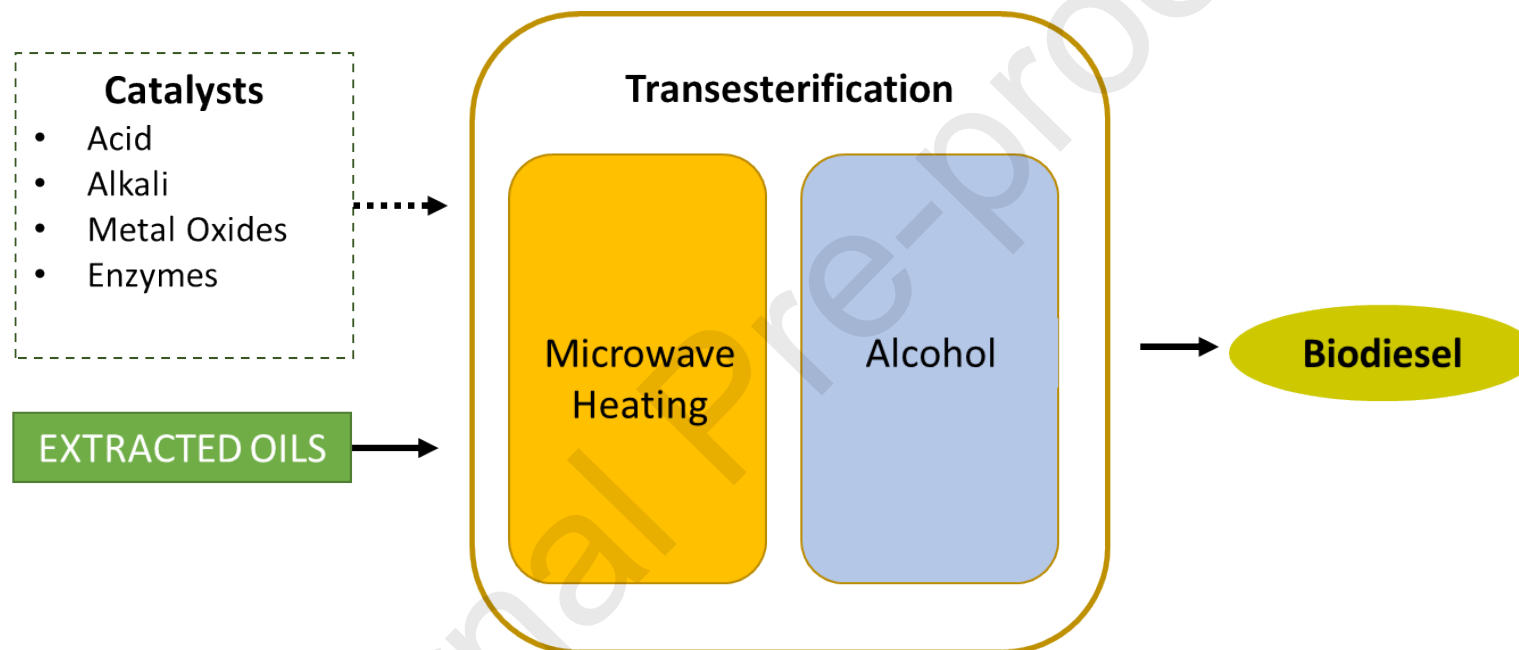
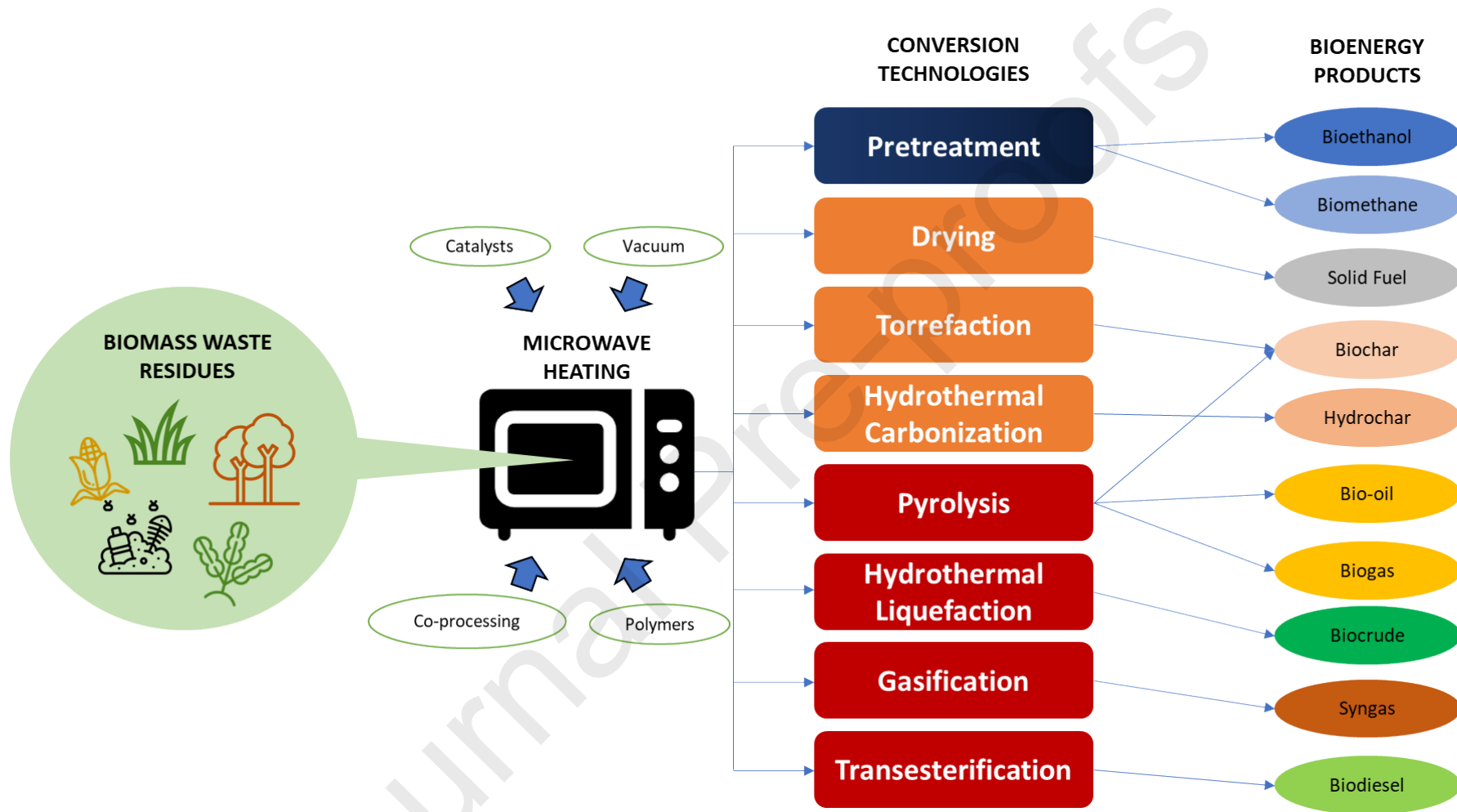


Figure 13. Schematic diagram of MW-assisted transesterification.



## **Graphical Abstract**



## Highlights

1. Eight conversion routes for waste residues using microwave-assisted heating are reviewed.
2. Microwaves' high energy use was offset by shorter duration and better product quality.
3. MW-assisted pyrolysis is the most studied route while other routes are still undermined.
4. Catalysis and co-processing of two wastes are the recent trends with several routes.
5. MW-assisted pyrolysis in a vacuum environment is some of the most recent advancements.