[Review Paper]

Recent Progress on Microwave Processing of Biomass for Bioenergy Production

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Recent studies on microwave processing of biomass for bioenergy production are reviewed. Statistical review of published research papers related to microwave and biomass was used to classify microwave processing used in bioenergy production. Microwaves have potential for use in various processing methods such as pretreatment, gasification, pyrolysis, transesterification, extraction, liquefaction and drying, to achieve low energy consumption, rapid reaction time, and high production yield. Microwave-assisted processing technologies for the second generation biomass (lignocellulosic biomass) and third generation biomass (algae and seaweeds) are described, as first generation biomass (food crops such as sugar canes, corns and grains) is often discussed as a “fuel versus food” issue. Scale-up strategies and discussions on energy consumption, cost, and efficiency of the microwave processing are also described with reference to specific examples of microwave reactors. Understanding of dielectric properties of biomass mixture is crucially important for designing an efficient and robust microwave reactor. Microwave processing is a future promising technology for renewable energy production, although its industrialization is still unfulfilled.

Keywords
Biomass, Bioenergy, Microwave, Scale-up, Dielectric property

1. Introduction

Renewable energy resources have great potential as alternatives to fossil fuels for transportation and electricity generation. The International Energy Agency (IEA) reported that worldwide renewable electricity generation will exceed 7000 TWh by 2020\(^1\), so that over 26% of all electricity generation in the world will be provided by renewables.

Bioenergy, a type of the renewable energy obtained from biomass or renewable biological materials, is expected to reduce atmospheric levels of greenhouse gases because plants can absorb CO\(_2\) in the photosynthetic process. The IEA reported that world biofuel production will slowly grow to 144.4 billion L in 2020\(^1\). Currently, the United States and Brazil are the two major countries involved in biofuel production derived from corn and sugar cane. In contrast, OECD Asia-Oceania countries including Japan produce less than 1% of the total world production of biofuels\(^1\).

Bioenergy is categorized into three generations based on the feedstock: the first generation of bioenergy depended on sugars, starch, seeds and edible oils derived from food crops such as sugar canes, corns and grains; the second generation of bioenergy was produced from lignocellulosic biomass and non-edible oils derived from non-food crops, wood and agricultural residues; and the third generation uses algae and seaweeds. First generation bioenergy is already utilized as biofuels in various countries; but often raises “fuel versus food” issues. In addition, biodiesel from first generation bioenergy is not a cost-effective source to reduce greenhouse gas emission\(^2\). Therefore, second and third generation bioenergy is extensively studied to reduce injudicious food crop consumption as well as control greenhouse gas emissions. The United States aims to produce 36 billion gallons of bioenergy, of which 21 billion will be obtained from cellulosic biomass, by 2022\(^3\).

The key problems of second and third generation bioenergy are the financial and environmental balances between energy production and consumption in the biofuel production process. In first generation bioenergy, sugars or starch are directly obtained from food crops, then biofuels are produced through saccharification (starch to sugar) and fermentation (sugar to alcohol) processes. Moreover, crop wastes such as sugar cane bagasse or corn stover can be effectively utilized as energy resources for electricity generation, which is directly consumed in the biofuel production process. In contrast, further processes are required to convert biomass into biofuels before the saccharification/fermentation processes in the second and third generation.
bioenergy. These extra energy and cost requirements require development of efficient processes to commercialize bioenergy production from the lignocellulosic materials and algae.

Microwave irradiation is expected to feature in energy and cost-saving processes for second and third generation bioenergy production based on the characteristics of rapid, internal and selective heating. The number of studies on microwave irradiation in bioenergy production has drastically increased. The present paper reviews recent progress on the use of microwaves in the processing of biomass.

2. Statistical Review of Published Research Papers Related to Microwave and Biomass

Recent trends in research on microwave processing for bioenergy production were identified through Google Scholar with search terms “microwave” and “biomass.” Figure 1 shows the number of searched annual published research papers. Note that only papers related to bioenergy production were counted and other papers (for example, microwave-band radar for investigating biomass distribution) were ignored. Around 100 papers were published every year from 2012 to 2015, since then the number has more than doubled since 2016. Figure 2 shows the percentage of the searched papers by country. China, Malaysia, the United States, India and the United Kingdom are the top five countries; whereas published papers from Japan accounted for less than 2% of the total. The journals Bioresource Technology, Journal of Analytical and Applied Pyrolysis, Green Chemistry, Fuel, Energy & Fuels, and Energy Conversion and Management were mainly searched. Various types of biomass feedstock were used over all the generations. Types of produced bioenergy were wide-ranging; biofuels including bioethanol and biodiesel, biogas (syngas), biochar, bio-oil, activated carbons and other organic compounds or value-added chemicals including reducing sugars and lipids.

3. Classification of Microwave Processing Used in Bioenergy Production

Microwave processing technologies, especially for second and third generation biomass, were classified. Figure 3 shows a rough schematic of the bioenergy process from biomass, summarized with the references2). 4). 5). The outline shows that utilization of microwaves has been studied. Various types of microwave processing have been studied to develop rapid, effective, efficient and inexpensive bioenergy production, except saccharification and fermentation. Microwave technology apparently did not contribute to first generation biomass, but many studies on microwave processing of sugarcane bagasse were reported on the processes of pretreatment6. 14), pyrolysis15. 17), hydrolysis18), activation19) and wet torrefaction20).
3.1. Pretreatment

Pretreatment is an essential process for converting lignocellulosic biomass into biofuels or value-added chemicals, because of the complex structure of lignocellulosic biomass, which consists of cellulose, hemicellulose and lignin. Efficient production of biofuels requires enhanced effectiveness of cellulosic and hemicellulosic enzymes in the subsequent saccharification process.

The pretreatment process is also important from the economical viewpoints, because this is an additional process to obtain biofuels compared with first generation biomass, as described in Sec. 1. Energy and cost saving methods are essential to establish viable bioenergy production from second generation biomass. Pretreatment processes based on steam explosion, ammonia fiber/freeze explosion, ammonia recycle percolation, hydrothermolysis, milling, microwave irradiation, electron beam irradiation, and pretreatments with alkalis, acids, supercritical carbon dioxide, lime, white rot fungi, peroxide and organic solvents (organo-solvolysis) have been extensively investigated.

Microwave irradiation or heating is expected to provide an alternative and reliable option to conventional pretreatment systems based on the use of different chemistry due to the internal heating, and rapid heating rates up to the target temperature. Numerous studies on pretreatment of various raw materials have been reported.

3.2. Gasification

Gasification is a thermochemical conversion process to obtain biogas (syngas), which can be used as the raw materials of hydrocarbon biofuels. Noncatalytic gasification requires an extremely high temperature of 1300 °C; whereas catalytic gasification can be achieved at substantially lower temperatures.

A microwave-assisted catalytic gasification system was developed for syngas production and tar removal from corn stover. In this system, SiC particles were used as the microwave absorbent bed, to reach a temperature of 900 °C. More syngas of H2 and CO could be produced with Ni/Al2O3 catalyst compared to without catalyst. Microwave-driven plasma gasification for biomass waste was also reported.

3.3. Pyrolysis

Pyrolysis is a thermal degradation method in the absence of oxygen. In the pyrolysis process, biomass is converted to biochar, bio-oil, biogas, and activated carbon depending on the biomass feedstock characteristics and pyrolysis conditions. Pyrolysis is categorized into three types: slow, fast and flash pyrolysis processes, according to the reaction rate, residence time, and heating rate. The heating rate and reaction temperature of the slow, fast and flash pyrolysis processes are 0.1-1 °C/s and 280-680 °C, 10-200 °C/s and 580-980 °C, and more than 1000 °C/s and 780-1030 °C, respectively.

Microwave-assisted pyrolysis, which is one of the most discussed microwave processes, is expected to achieve fast and high yielding chemical reactions. Several review papers have described microwave-assisted pyrolysis. Microwave-assisted pyrolysis generally depends on a microwave absorber such as carbonaceous, inorganic, and metal oxide materials. Microwave-assisted pyrolysis without the absorber is possible, but requires high microwave power of 1000-2000 W.

3.4. Transesterification

Transesterification is a reaction of fats with alcohol to obtain esters and glycerol. Basic transesterification is a reversible stepwise reaction in which triglycerides and methanol are converted to methyl esters and glycerol. Methyl esters are well known as biodiesel, and glycerol is a high value alcohol widely used for medical and food applications. The transesterification reaction is generally catalyzed by a liquid base or a liquid acid. Recently, many microwave-assisted transesterification studies of algae and microalgae, third generation biomass, have been reported as well as palm oils, nuts, seeds, and used vegetable oils.

Microwave irradiation are very advantageous for transesterification, because triglycerides and alcohols, especially methanol, are susceptible to 2.45 GHz microwaves, which are used for microwave ovens all over the world. Microwave heating provides partial high temperature spots called “hot spots” in the mixture. Consequently, the local reaction temperature under microwave-assisted transesterification would be much higher than for conventional heating transesterification. This unique advantage contributes to the reduction of reaction time and energy consumption.

3.5. Extraction

Extraction is a process in which desired substances are selectively removed from raw materials. The extraction process is mainly classified into chemical extraction and physical extraction. The chemical extraction process usually utilizes a solvent, in which the desired materials are dissolved and subsequently separated. The physical process includes several methods such as mechanical pressure, microwave-assisted extraction, ultrasound assisted extraction, negative pressure cavitation, and supercritical fluid extraction.

Microwave-assisted extraction is expected to afford much shorter reaction time, higher extraction yield, and much less solvent consumption, compared with conventional extraction methods. In addition, microwave-assisted extraction has the unique possibility to carry out integrated extraction of multiple products from a single matrix. Integration of microwave-assisted extractions with other physical extraction technologies as well as enzyme-assisted extraction and hydro-
diffusion has been investigated for food components\(^4\)). Microwave-assisted extraction of lipid from third generation biomass has also considerable potential\(^2\)). For example, microwave-assisted hydrothermal extraction of sulfated polysaccharides from green algae has been studied in Japan\(^3\)).

3. 6. Liquefaction

Liquefaction is a process to convert biomass mainly to liquid products. The presence of water in the biomass sometimes has a negative effect on pyrolysis\(^4\)). Drying, as described in the next subsection, is an option to solve the moisture problem, but liquefaction is a powerful technique to liquefy biomass with any level of water content. In the liquefaction process, macromolecules of the feedstocks are decomposed into fragments of light molecules by dehydration, dehydrogenation, deoxygenation and decarboxylation\(^5\)). The fragments are converted to oily compounds through condensation, cyclization and polymerization. Liquefaction can be classified into high-temperature and high-pressure liquefaction, direct catalytic or non-catalyst liquefaction, hydrothermal liquefaction, and supercritical liquefaction.

Microwave-assisted liquefaction has the advantages of reduction of energy consumption and reaction time. For examples, microwave-assisted direct liquefaction of algae was studied for bio-oil production\(^6\)). Under microwave power of 600 W for 30 min at 180 °C, the maximum liquefaction yield was 84.81 %. Microwave-assisted hydrothermal liquefaction of lignin was also reported for the preparation of phenolic formaldehyde adhesive\(^7\)). The maximum liquefaction yield was 78.69 % after 30 min at 200 °C.

3. 7. Drying

Drying, which is not shown in Fig. 3, is also an important required preprocessing step to improve the net energy balance of bioenergy production. Reduction of water content from raw materials both reduces weight directly, and critically affects the energy efficiency of subsequent biomass processing, quality of products, and longevity of the product shelf life\(^8\)). Microwave drying is also an effective energy-saving method. Drying rate and water removal from feedstocks was faster using microwave heating (6 min at 600 W) than the conventional oven (40 min at 105 °C)\(^9\)). Moreover, the yields of bio-oil and char increased and the gas yield decreased in the subsequent pyrolysis process after microwave drying.

4. Scale-up Strategies for Microwave Processing

Future industrialization of microwave processing depends completely on the development of methods to scale up the process. The penetration depth \(d\) of microwaves into materials, as expressed in Eq. (1), limits the reactor size in any process,

\[
d = \frac{\lambda}{4\pi} \sqrt{\frac{2}{\varepsilon_r' \left(\sqrt{1 + \tan^2 \delta} - 1\right)}}
\]

where \(\lambda\) is the wavelength, \(\varepsilon_r'\) is the relative permittivity of the material, and \(\tan \delta\) is the dielectric loss tangent of the material, respectively\(^8\)). Unplanned enlargement of the reactor size will fail to propagate microwaves into the center of the target material, resulting in inhomogeneity of reaction temperature, decline in production yield, and deterioration in quality.

In this section, scale-up strategies for microwave processing, mainly our microwave pretreatment process, are introduced. As described above, simple scale-up of the reactor size would be less than successful for microwave processing unlike the conventional heating methods. Therefore, the continuous flow-type reactor would be more suitable for industrialization of microwave processing than the batch-type.

4. 1. Continuous Flow-type Microwave Reactors for Pretreatment of Wood Biomass

As examples of scaled-up microwave systems, three continuous flow-type reactors with total microwave power of 3.6, 12 and 15 kW were developed for the pretreatment process of wood biomass\(^9,10\)).

Figures 4 and 5 show photographs of the 3.6 kW and 15 kW microwave pretreatment reactors, respectively\(^9\)). These reactors have quite similar structures. Raw materials (slurry consisting of wood biomass, water,
solvents and catalysis) are passed through a metal pipe with agitation pumps, and irradiated with 2.45 GHz microwaves at the T-junction metal pipe sections. Three 1.2 kW microwave generators are connected to the three T-junction metal pipes in Fig. 4. Similarly, three 5 kW microwave generators are connected to the three T-junction metal pipes in Fig. 5. Considering the microwave generator and T-junction metal pipe as a microwave unit, the number of units can be changed depending on the amount of slurry, reaction time and temperature. The diameters of the reactors (metal pipes) are 75 mm and 80 mm for the 3.6 kW and 15 kW reactors, respectively.

Figure 6 shows a photograph of the tower-type 12 kW microwave pretreatment reactor. Unlike the previous two reactors, the slurry is poured from the top of the reactor and the products exit from the bottom. This reactor consists of 8 microwave generators, with frequency and power of 2.45 GHz and 1.2 kW, respectively. The 8 microwave generators are positioned in two tiers of four units aligned at 90° in the same plane. The diameter of the reactor is 254.2 mm, more than tripled compared to the other two reactors. The reactor volume reaches around 50 L.

Using the tower-type microwave reactor, pretreatment of Eucalyptus globulus wood chips was conducted for bioethanol production. Liquefaction was followed by simultaneous saccharification and co-fermentation (L+SSCF). From 150 g (dry weight) of the Eucalyptus globulus woodchips, the final ethanol density of 64 g/L was achieved at the production rate of 1 g/L per hour and recovery ratio of 90%.

4.2 Scalable Processing Concepts of Microwave-assisted Pyrolysis

Various scale-up studies of microwave-assisted pyrolysis for bio-oil production have been reported. Five different concepts were introduced: gravity transport with rotary kiln, conveyor transport with conveyor belt, conveyor transport with rotating ceramic-based disc, pneumatic transport with microwave fluidized bed, and extrusion transport with auger reactor. Although some concepts were only designed in electromagnetic simulators and not yet constructed, these concepts show great potential for assisting the needs of the industrial bioenergy community.

4.3 Dielectric Properties of Biomass Mixtures

Understanding of the dielectric properties of biomass mixture is crucially important for designing an efficient microwave reactor, because the permittivity of the mixture affects not only the penetration depth as expressed in Eq. (1), but is also sensitive to the reflection coefficient between the microwave generator and reactor. In addition, the permittivity is dependent on the microwave frequency and temperature. Without knowing the dielectric properties, the microwave reactor design would be much less efficient, and will not reach the desired temperature due to the high reflected power at the boundary of the microwave generator and reactor.

Thorough measurements of dielectric properties at various frequencies and temperatures will directly contribute to development of an efficient and robust microwave reactor via computer-aided design. In the continuous flow-type microwave reactors as described in Sec. 4.1, the dielectric properties were carefully measured before design of the reactors via electromagnetic simulators. Various studies on dielectric properties of biomass mixture have shown that the relative permittivity depends extensively on moisture content. Permittivity determination sensors for biomass and microwave moisture sensors for flowing biomass pellets have also been reported for monitoring and measurement of biomass mixtures.

5. Discussions of Energy Consumption, Cost and Efficiency of Microwave Processing

Energy consumption, cost and efficiency of microwave processing are all crucial aspects for replacement of the conventional process in industries.

The energy requirement of 1 g essential oil from rosemary is reported as 0.25 kWh for microwave-assisted extraction and 4.5 kWh for the conventional hydrodistillation. Moreover, microwave-assisted extraction was completed in 30 min; whereas the conventional process took 2 h. However, degradation of the compounds in the essential oil was observed if the extraction time was shortened by excessive microwave power.

Cost assessments of microwave processing were reported by Chinese and Italian groups. In the Chinese case, a moving bed microwave-assisted pyrolysis auger reactor of 1 t/day feed rate based on sawdust costs 700,000 CNY (1 CNY = ~17 JPY);
whereas the same pyrolyzer using electric heaters costs 500,000 CNY. Despite the higher cost, this study insisted that microwave-assisted pyrolysis was profitable. Assuming 50 wt% of biochar production by microwave-assisted pyrolysis, the income from the biochar was estimated at 2000 CNY/day, which exceeded the costs of raw materials, operation and maintenance: 1200 CNY/day. In the Italian case\(^6\), pectine and limonene productions were assessed by microwave-assisted extraction from waste orange peel. The income of these products was 19,100 EUR/day; whereas the daily operational cost of electricity was 168 EUR. The latter case suggests that production of value-added chemicals by microwave processing is extremely attractive.

Microwave processing and conventional pre-treatments of Japanese cedar wood chips\(^6\) and ground beach wood\(^9\) were compared by a Japanese group. Although wood biomass is one of the most difficult lignocellulosic biomasses for pretreatment, the maximum sugar yields in these pretreatments were 53.55 % at 180 °C for 6 min and 59.5 % at 140 °C for 30 min, respectively. In the latter case, pretreatment by conventional heating in an autoclave provided a sugar yield of 41.8 %. Therefore, microwave-assisted pretreatment can provide great potential for an effective bioenergy production system compared with conventional processing. Another case study compared microwave-assisted pyrolysis and conventional electric heating pyrolysis of waste oil\(^3\). Microwave-assisted pyrolysis yielded bio-oils and reduced chars better than the conventional pyrolysis. In addition, the carbon components in the produced bio-oil were mainly C5-C18 hydrocarbons in the microwave-assisted pyrolysis; whereas heavier C19-C35 hydrocarbons were obtained in the conventional pyrolysis. This finding indicates that microwave-assisted pyrolysis can enhance cracking reactions.

An interesting evaluation of microwave processing efficiency compared continuous microwaves and pulsed microwaves at the same energy consumption\(^7\). Esterification conversion of free fatty acid with a heterogeneous catalyst was improved from 39.9 to 66.1 % by using square-pulsed microwaves at 400 Hz repetition rate and 10-20 % duty cycle, compared to continuous microwaves under the same reaction condition.

### 6. Conclusion

Microwaves have great potential in the processing of biomass for bioenergy production, especially from the viewpoints of low energy consumption, rapid reaction time, and high production yield. Nevertheless, industrialization of microwave-assisted processing is still unfilled due to the difficulty of scale-up. In the future, "speed-up" as well as "scale-up" of the microwave processing will be the keys for successful industrialization.

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### Nomenclatures

| Symbol | Description                                      | Unit |
|--------|--------------------------------------------------|------|
| \(d\) | penetration depth                                 | m    |
| \(\lambda\) | wavelength of microwaves                          | m    |
| \(\varepsilon_r\) | relative permittivity of material                 |      |
| \(\tan \delta\) | dielectric loss tangent of material               |      |

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要 旨
バイオエネルギー生産を目指したバイオマスマイクロ波処理の最近の進展

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バイオエネルギー生産を目指したバイオマスマイクロ波処理の最近の動向について解説する。最近の新著論文の統計的解析に続いて、バイオマスマイクロ波処理手法の分類を説明する。マイクロ波は、前処理、ガス化、熱分解、エステル交換、抽出、液化、乾燥などの様々な処理で重要な役割を果たしており、処理エネルギーの低減、反応時間の高速化、生産量の改善の観点でマイクロ波は大いに期待されている。本論文では第2世代バイオマス（リグノセルロース系バイオマス）および第3世代バイオマス（藻類、海藻）のマイクロ波処理を中心に取り上げる。また、マイクロ波処理の大型化の問題や、マイクロ波処理のエネルギー消費、コスト、およ且の効率の議論についても、具体的な開発事例を挙げて説明する。バイオマス混合物の誘電特性を知ることは、効果的なマイクロ波処理容器を設計する上で極めて重要である。マイクロ波処理の工業化は未だ道半ばであるが、再生可能エネルギー生産に対する将来の処理方法としてマイクロ波は今後も期待される手法であろう。