Microwave-assisted biorefinery

Amr Sobhy* and Jamal Chaouki
Department of Chemical Engineering, Ecole Polytechnique de Montreal,
P.O. Box 6079, Station Centre-ville, Montreal, QC, Canada H3C 3A7
*Corresponding author Fax: ++1 514 340 4159 e-mail: sobhy.amr@gmail.com

Microwave heating has not received sufficient attention in the area of high-temperature biomass refining. This work summarizes the rationale behind investigating certain applications of microwave biorefining. The initial phase of this research will be carried out using a bench-scale microwave oven designed for processing under various conditions. The main objective of the initial phase of experiments is to determine the effect of microwave heating on pyrolysis of waste biomass and on tar cracking in biomass gasifiers. Proposed applications of microwave heating are expected to lead to biomass conversion with improved process control, lighter environmental impact, and higher efficiency than conventional heating processes.

1. Introduction

Biomass and domestic waste have been receiving attention as renewable sources of carbon. Substituting a fraction of global carbon dependence on fossil fuels with renewables could lead to significant reduction of carbon dioxide and green-house gas accumulation in the atmosphere. Sustainable clean technologies with high-quality products and light environmental footprints are now vital to the survival of human beings and their ecosystems. Biorefineries- biomass refineries- aim to extract energy (direct electricity generation in combined cycles), fuels (liquid bio-fuels), and chemicals (platform hydrocarbons extracted from biomass using an assortment of processing techniques) (Octave and Thomas 2009). These techniques range from high selectivity and low harshness (biological) to low selectivity and strong harshness (thermochemical) according to the characteristics of the material being processed. Members of our research group are experienced in high-temperature processing and up-scaling of chemical reactors (Fang et al. 2008; Mabrouk et al. 2005; Radmanesh et al. 2006; Sobhy et al. 2002; Sobhy et al. 2009; Sotudeh-Gharebaagh and Chaouki 2007). Biomass processing using microwave heating is one aspect of the multi-disciplinary high-temperature research undertaken in the group. Up-scaling microwave systems requires experience, intuition and trial-and-error (Thostenson and Chou 1999). Experience of the group members is vital for establishing microwave processing kinetics and up-scaling of microwave systems for full operation.

2. Heating and Microwaves

Beside moisture and trace minerals, biomass is mainly composed of hemicellulose, cellulose, and lignin. Lignin constitutes 25-30 wt-% of typical biomass. The high-molecular weight, three-dimensional branching structure of Lignin, which also interconnects with celluloses and hemicelluloses, is mostly composed of aromatic compounds. Lignin is the most complex and degradation-resistant component of biomass and constitutes the majority of biomass residues, such as agricultural, forestry, and municipal waste (Gani and Naruse 2007). Lignocellulosic composition and waste heterogeneity typically warrant the use of non-selective harsh conversion techniques based on high attrition and high temperatures. High-temperature processing is applied to simplify biomass hydrocarbons either into a complex pool of thousands organics in bio-oil (pyrolysis) or into syngas and permanent gases (gasification). Bio-oil and syngas are then further processed to extract or construct the desired fuels or chemicals.

The majority of high-temperature biorefining research and commercial attention is directed at conventional heating mechanisms where heat transfers to the target substance from an external source. Less-explored heating mechanisms induce heating within the core of the substance through a direct energy conversion. In that case, the substance becomes the heat source, thus altering reaction kinetics, and products.

In contrast with conventional heating mechanisms, where energy is first converted to heat then transferred along temperature gradients from the surface to the core of the material, microwaves induce heat at the molecular level by direct conversion of the electromagnetic field into heat. The electromagnetic field enters the solid and induces heating throughout the penetration depth through interaction with polarizable dipoles present in the target material. Two main factors affect the penetration depth and level of heating with microwaves: nature of the electromagnetic field (strength and frequency) and dielectric properties of the material being heated (polarizability of the dipoles and capacity for interacting with microwave energy) Microwave frequencies for heating are designated by the FCC (Federal Communications Commission) to prevent interference with aviation and telecommunication frequencies. Similar to home microwaves, our system also operates at 2.45 MHz. It follows that dipoles respond to phase changes in the electromagnetic field by re-aligning with the applied field 2.45 billion times per second. Bond resistance to this re-alignment causes the dipoles to lag behind the field. This resistance lag is accompanied by heat release (Thostenson and Chou 1999).

Advantages of microwave heating include: Strong selective heating of water content, selective heating of materials or phases according to dielectric properties, and avoiding heat loss in heating components and enclosures of the reaction chamber. Efficiency of conversion of electricity to microwaves could be as high 95% and the conversion of microwaves into heat within the material up to 85% (Thostenson and Chou 1999). Hence, there is potential for a more favorable product life-cycle where electricity is readily available and low in cost.

The *Engineer's handbook of Industrial Microwave Heating* states that the overall efficiency of a microwave heating system is 80-85% depending on the frequency in use. Microwave heating has some established applications in the areas of food processing and drying, chemical synthesis, and leaching. Surprisingly, full-scale microwave heating applications in bio-refining are virtually nonexistent. Literature on pyrolysisderived fuels/oil and carbon/char from processing using microwave heating has been growing over the past 5 years but remains rather limited (Domínguez et al. 2008; Huang et al. 2008; Wan et al. 2009).

The key obstacle to the effectiveness of microwave heating is sufficient microwave absorption by the material. In cases where microwave absorption is not effective in inducing sufficient heating, microwave-absorbing materials are added physically to the target material to incorporate polarizable dipoles. A common practice is to mix biomass with char. The C-C bonding in char absorbs microwaves and causes the char to heat. The heat is then transferred to the biomass material through conventional heat transfer. Heat transferred complements the microwave-induced heat within the biomass material to reach desired conversion temperatures.

This paper presents some basics of microwave heating and how it lays the foundation for the microwave-assisted biorefinery research being undertaken at Ecole Polytechnique at the moment. The work highlights two main areas of current research: microwave pyrolysis of Lignin and biomass to produce aromatics, bio-oil and bio-char, and microwave-assisted tar cracking for product gas cleaning in biomass gasification processes. Full experimental work has not yet commenced on the system. Results are expected in time for presentation at CISAP4 in March.

3. Experimental

The experimental assembly was based on an off-the-shelf microwave oven. The BP-211 (Microwave Research, Inc.) is a research-grade multi-mode microwave oven with power control features and mode stirrers to distribute the field and avoid localized hotspots. The microwaves are generated at a frequency of 2.45MHz and deliver maximum power of 3200W. The BP-211 was modified by cutting two opposing holes in the sidewalls of the microwave oven to allow for semi-batch and continuous processing investigations in the microwave. Glass and quartz components could be assembled and rearranged within the cavity and could be connected to gas inlets, pumps, feeders, condensers, cyclones. Different configurations shift operation between pyrolysis, gasification, combustion, batch, semi-batch, continuous, and fluidized bed modes. Temperature is measured using a 6-tip profile thermocouple probe inserted into the cavity through one of the holes in the walls. A microwave leakage meter is used on a regular basis to monitor radiation levels around the exits of the microwave. A GC-TCD will be connected for online analysis of non-condensable gases emitted by pyrolysis or gasification processes. A separate GC-FID will be used to analyze bio-oil.

4. Microwave pyrolysis of Lignin and biomass

Harshness of the biorefining technique depends on the target fraction of biomass composition. Finding an adequate harshness level for conversion of selected biomass could lead to important improvements in efficiency and product quality. Avoiding the unnecessary “over-processing” (pyrolysis and gasification) followed by re-construction cycle (distillation or Fischer-Tropsch). Microwave heating may facilitate reducing harshness while achieving high conversion by selectively targeting the resistant constituents to release the valuables intact. A possible application we are considering is microwave-assisted pyrolytic extraction of aromatics from Lignin.

More importantly, most biomass feedstocks contain considerable moisture levels. In conventional pyrolysis, as heat penetrates the particle, there is a simultaneous vaporization of moisture and devolatilization of aromatics within the pores of the biomass. This reaction proceeds from the surface of the particle to the moist, lower-temperature core. This mechanism favors reaction between water and organics and leads to partial oxidation and formation of permanent gases (CO, CO_2, H_2, CH_4).

Microwave-assisted biomass pyrolysis offers a different paradigm in particle heating where the electromagnetic field penetrates the solid and interacts directly with dipoles in the chemical structure. Due to the high affinity of water molecules to microwaves, moisture content within a given biomass particle is selectively targeted by incident microwaves. Microwaves vaporize moisture in the depth of the particle, prior to volatilizing organic content. This leads to tunneling and enhanced porosity. Once moisture is vaporized, the organic content remaining is volatilized by the incident microwaves. It would be expected that this would lead to lower permanent gas production and improved condensable pyrolytic organic gases with lower oxygen content and higher energy value.

Aromatic hydrocarbons are essential components in many chemicals and processes (Effendi et al. 2008). And in the case of synthesis of aromatics from biomass sources, the complexity and heterogeneity of biomass waste usually dictate the use of harsh processing to break the biomass down into much simpler components. These components are then reconstructed according to the target chemical. Both the breaking down and reconstruction processes consume energy. Under the framework of our microwave-assisted biorefineries project for converting biomass into value-added chemicals, we aim to cut this low-efficiency cycle by extracting the maximum possible yield of desirable aromatics from Lignin directly. Heat allows the aromatics to break free of the surrounding bonds while an oxygen-free extraction environment preserve of aromatic structures in the lignin. The key to this targeted pyrolytic extraction of aromatics from lignin would be optimization of the harshness of the thermochemical process applied.

Experimental work is currently being carried out on biomass pyrolysis in batch, semi-batch, and continuous regimes. Samples will be processed in quartz, glass, and Pyrex reactors inside the microwave cavity. Nitrogen gas will be used to purge oxygen from the reaction chamber continuously. Organic gas product will be condensed and dissolved outside the cavity to form pyrolysis oil. Non-condensable gases will be injected directly into a dedicated GC-TCD for online gas sampling. Solid char remaining after pyrolysis will also be analyzed for physical properties. Investigations for microwave-assisted extraction of aromatics from Lignin will be carried in reaction vessels similar to full pyrolysis. However, recuperation of the released aromatics will be based on dissolution/adsorption columns rather than condensation of organic fumes as is the case with pyrolysis oils.

5. Tar removal from biomass gasification

Technologies to process biomass feedstocks are based on petrochemical refinery processes and need to adapt to the new and variable nature of the materials being processed. Gasification is gaining wide attention as it allows hydrocarbons to retain a significant fraction of their energetic value to be eventually combusted cleanly and efficiently (compared to direct combustion). Gasification could be defined as conversion of solid hydrocarbons into combinations of CO_2 and H_2O for direct generation of electricity or CO and H_2 for combustion and chemical/biofuel synthesis. Gasification is carried out at high temperatures (700- 1400°C) under limited oxygen conditions (Yu et al. 2009). Due to the presence of moisture and oxygenated hydrocarbons in biomass, gasification suffers from formation of hazardous and undesirable tar. Tar is a complex mixture of condensed or polymerized oxygenated sticky hydrocarbons. Biomass gasification is hindered by excessive tar formation in gasification systems (Yu et al. 2009). We are investigating the feasibility and effect of microwaves being delivered locally to the zone of tar formation within the gasifier. Microwaves are generated by applying an orthogonal magnetic field to electrons accelerating along a large potential difference. The magnetic field causes the electrons to oscillate in a helix-shaped path. Resonant structures interact with the oscillating electrons and an electromagnetic field is generated at a specific frequency (usually 2.45GHz) according to the sizing of the structures. The most common and least expensive unit where microwaves are generated is called a magnetron (as used in home microwave ovens). Once the field is generated, the microwaves are relayed through a waveguide or transmission cables to the microwave cavity (Thostenson and Chou 1999). The proposed application would be a Magnetron-Cable Assembly (similar to a gun). It would be possible to deliver microwaves to a limited target volume/area by positioning the waveguide or transmission cable. A second approach involves tar capture and conversion in a stationary exhaust unit for targeting *only* the tar phase in gasification product with a microwave heating unit. In general, air and inorganic gases are not good absorbers of microwaves. On the other hand, organics and oxygenates, especially C-C and water bonds, are better absorbers of microwaves. The unit is expected to crack tar by preferentially heating the tar/emulsion/sticky phase rather than the whole gas matrix. Initial experimental work will establish tar cracking kinetics in microwave heating. Next, details of the required system components for targeting, capturing, and cracking tar will be developed with microwave experts here at Ecole Polytechnique.

6. Conclusion

Characteristics of microwave heating provide ample justification for microwave-assisted biomass processing research. We are currently conducting several experimental works involving microwave heating to cleanly and economically convert organic waste and biomass into higher quality value-added chemicals or liquid biofuels using an efficient and manageable microwave-assisted process. More specific targets include: (1) establishing a highly selective technology for extraction of valuables from biomass feedstocks, (2) higher quality yield of bio-oil and bio-char from pyrolysis of woody biomass, (3) improved yields and tar-free production of hydrogen and/or syngas (H_2 + CO) from biomass gasification, (4) improved favorability of product life-cycle analysis through energy and time savings, and (5) establishment of a novel clean and sustainable electrochemical biorefining technology for Quebec and Canada.

The microwave experimental system is in place and experiments are ongoing at the time of submitting this paper. Significant experimental results are expected in time for presentation and discussion at CISAP4