



# A review of catalytic microwave pyrolysis of lignocellulosic biomass for value-added fuel and chemicals



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## HIGHLIGHTS

- Review of catalytic upgrading of microwave-assisted pyrolysis (MAP) of biomass to desired products.
- Review of catalytic MAP of biomass for phenol rich and hydrocarbon rich bio-oil.
- Review of MAP and its increased efficiency in thermo-chemical conversion of biomass.
- Kinetics study and prospects for MAP of biomass are discussed.

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## ABSTRACT

Lignocellulosic biomass is an abundant renewable resource and can be efficiently converted into bio-energy by a bio-refinery. From the various techniques available for biomass thermo-chemical conversion; microwave assisted pyrolysis (MAP) seems to be the very promising. The principles of microwave technology were reviewed and the parameters for the efficient production of bio-oil using microwave technology were summarized. Microwave technology by itself cannot efficiently produce high quality bio-oil products, catalysts are used to improve the reaction conditions and selectivity for valued products during MAP. The catalysts used to optimize MAP are revised in the development of this article. The origins for bio-oils that are phenol rich or hydrocarbon rich are reviewed and their experimental results were summarized. The kinetics of MAP is discussed briefly in the development of the article. Future prospects and scientific development of MAP are also considered in the development of this article.

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## 1. Introduction

The diminishing supply of petroleum fuels and the negative effects that their continuous use has had on our environment has prompted many new investigations that are aimed to discover new sources of energy. Although there have been advances in renewable sources of energy such as solar, geothermal, and hydro-electric, these still does not come close to solving the global energy crisis because of the form in which it is obtained (Bridgwater and Peacocke, 2000; Guéhenneux et al., 2005). The new alternative source of energy has to be in liquid form for it to be a suitable replacement for petroleum based fuels. This new

energy source is believed to be bio-based fuel and products which are derived from lignocellulosic biomass. Lignocellulosic biomass is predominantly obtained from plant sources and is composed of three major components; cellulose, hemicelluloses and lignin. The structural characteristics of these components determine that they are recalcitrant during the transformation of biomass (Mohan et al., 2006). Raw bio-oil is obtained from pyrolysis of organic material at 350 °C to 600 °C in the absence of oxygen (Bridgwater and Peacocke, 2000; Marcilla et al., 2013). In recent studies scientists have come to understand that this product is not readily available for consumption, there are many issues that negatively affect the ability for raw bio-oil to be used as a source of fuel or for value added chemical. Its complex chemical composition is one of the main reasons it cannot be utilized directly in combustion systems. Bio-oil has a low heating value of 16–18 MJ/kg because of a 15–30 wt% of water and 35–50 wt% of oxygen; it's high acidity of pH

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2–3 also contribute to its undesirable qualities (Duan and Savage, 2011; Mohan et al., 2006; Peterson et al., 2008). Upgrading is used to improve the chemical and physical properties of the raw bio-oil/pyrolysis oil (Gunawan et al., 2013; Zhang et al., 2016). The production process of bio-oil has limitations, so in recent years scientists have been trying to understand its complexity. One of the main difficulties that occur during biomass pyrolysis is the selectivity of the desired compounds in the bio-oil. Different feedstock sources leads to different ratios in the chemical composition of the bio-oil/pyrolysis-oil (Umeki et al., 2016), this has spawned a never ending variety of possibilities when it comes to the production of the raw product. With this problem at hand the objective of this review was to analyze investigations that are geared towards improving the bio-oil yield during the pyrolysis process as well as improving the selectivity of the desired compounds in the pyrolysis oil. Catalytic microwave assisted pyrolysis has been at the center of many recent investigations whose aim is to improve selectivity and yield of bio-oil. The use of catalysts are being investigated that targets desired compounds in the bio-oil produced. Traditionally Zeolite catalyst have been employed in the oil industry for its refinement (Wang et al., 2012). With the improvement of technology scientists find themselves employing the same zeolite catalysts in the production process. Recently Zeolite structure and chemical composition have been modified to improve its performance (Zhang et al., 2015a). Apart from zeolite catalysts, metal oxides have also been the subject of recent MAP experiments. The use of metal oxides as catalysts have proven to be just as good as the traditional zeolite catalyst and can be produced at a much cheaper price (Kuan et al., 2013). Of the *in situ* and *ex situ* use of catalysts; majority of the experiments conducted using metal oxides have employed its *in situ* use (Huang et al., 2013b; Wan et al., 2009). At the moment in science there seems to be two desired types of bio-oil, those that have a high hydrocarbon content and those that have a high phenol content (Jeong et al., 2016; Norouzi et al., 2016; Wang et al., 2016b). The two types of oil give rise to the different properties in each of their upgraded versions. The functionality of microwave technology on the production process of these types of oil is discussed in the development of this article. This recent technology has attracted a lot of attention recently because of the efficiency at which the overall process is capable of producing bio-oil. In the development of the article the kinetics of the pyrolysis process in relation to bio-mass feedstock is briefly discussed. The future prospects for the continuation of this type of research and the benefits that it will have on the environment as well as the economic possibilities are also discussed in the development of this article.

## 2. Biomass resources

### 2.1. Composition of plant biomass sources

Biomass is all organic matter that exists here on earth; it fulfils one of the criteria of life. It is also one of the most abundant sources of energy available to mankind (Wang et al., 2016c); biomass has been used as a source of fuel since the dawn of civilization when man discovered fire. The burning of wood has proven to be instrumental in the foundation of our civilization and here in the 21st century the burning of wood seems to be just as fascinating as the day it was discovered. This source of energy can potentially make the use of fossil fuel a thing of the past. The most abundant source of biomass comes from plants, there are three components that are most abundant within the plants' structure, cellulose, lignin and hemicellulose (Mohan et al., 2006). Cellulose and hemicellulose are both polysaccharides. Cellulose is a linear polysaccharide of  $\beta$ -D-glucopyranose units (Jenkins et al., 1998). Hemicellulose is

a mixture of various polymerized five- and six-carbon monosaccharides such as glucose, mannose, galactose, xylose, arabinose, methylglucuronic acid, and galacturonic acid (Jenkins et al., 1998; Mohan et al., 2006). Lignin is an amorphous polymer with no exact structure and consists of an irregular array of variously bonded phenylpropane units (Mohan et al., 2006). Cellulose is generally the largest fraction, representing approximately 40–50 wt% of the biomass, Lignin is the second largest fraction that is approximately 16–33 wt% depending on the feedstock source and the Hemicellulose portion occupy majority of the remaining mass. Some other compounds present include organic extractives and inorganic compounds (McKendry, 2002).

### 2.2. Variation in plant source and resulting bio-oil

Each plant species differ from one another genetically, this genetic variation allows the chemical compositions of the plants to vary so the percentages of cellulose, lignin and hemicellulose are not necessarily constant. Plants are generally classified into groups such as softwood, hard wood and grasses. While both groups will contain the same materials, the quantities may vary, typically softwood would contain 42% cellulose, 19% hemicellulose (C6-sugars), 7% hemicellulose (C5-sugars), 27% lignin, with 2% extractives and only 3% of other components. On the other hand hardwood would normally contain 42% cellulose, 4% hemicellulose (C6-sugars), 26% hemicellulose (C5-sugars), 23% lignin with 3% extractives and only 2% of other components. Grasses typically contain 38% cellulose, 1% hemicellulose (C6-sugars), 24% hemicellulose (C5-sugars), 24% lignin with 3% extractives and about 10% of other components (Mohan et al., 2006). These small differences in the composition of hardwood, softwood and grasses have effects on the properties of their derived bio-oil; bio-oils that are rich with hydrocarbons or bio-oils that are rich with phenols. Some of the major organic compounds found in bio-oil after biomass pyrolysis are acids, alcohol, ether, ketone, aldehyde, phenol, ester, sugar, furan and nitrogen compounds (Bridgwater and Peacocke, 2000). The phenolics compositions (phenol, guaiacol and other substituted phenol compositions) are formed by the decomposition of lignin. While other components such as alcohols, acids, ketones, sugars, esters and others are formed from the decomposition of cellulose and hemicellulose (Huber et al., 2006). Investigations has proven that multi step upgrading to the raw bio-oil is necessary and will have positive and profitable results.

### 2.3. Availability of biomass resources

In the pyrolysis process for the production of bio-oil, biomass can be obtained from a variety of sources. The variety of sources of biomass is necessary for maintenance of the system at industrial scales. Motasemi and Afzal (2013) explained that the biomass needed to maintain a functioning system can be obtained from three distinct sources. The three groups that they divided it into were virgin resources, residues and municipal solid waste. Table 1 shows the variation of composition fractions for different biomass sources. Virgin resources were further subdivided into forest resources and oil crops. Motasemi explained that forest resources would be any type of wood like pine beetle wood, or new types of woody and forest biomass such as willow, hybrid poplar, balsam poplar or aspen including others. They also explained that oil crops are crops that are actually grown for oil or food; these may include wheat barley, tame hay, corn, canola, palm oil, soybean, flax, oat, straw, pasture grasses and others. Residues, however was subdivided into three sources, wood residues, agricultural residues and wastes, and livestock residues. Residues is the waste material from other production processes, wood residues may include bark, branches, leftover treetop, and leaves from harvest and thinning

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