



## Review of microwave-assisted lignin conversion for renewable fuels and chemicals



WANG Yunpu<sup>a,b</sup>, DAI Leilei<sup>a,b</sup>, FAN Liangliang<sup>a,b</sup>, SHAN Shaoqi<sup>a,b</sup>, LIU Yuhuan<sup>a,b,\*</sup>, RUAN Roger<sup>a,b,c,\*</sup>

<sup>a</sup> Nanchang University, Engineering Research Center for Biomass Conversion, Ministry of Education, Nanchang 330047, China, China

<sup>b</sup> Nanchang University, State Key Laboratory of Food Science and Technology, Nanchang 330047, China

<sup>c</sup> Center for Biorefining and Department of Bioproducts and Biosystems, Engineering University of Minnesota, 1390 Eckles Ave., St. Paul, MN 55108, USA

### ARTICLE INFO

#### Article history:

Received 2 November 2015

Received in revised form 14 March 2016

Accepted 17 March 2016

Available online 19 March 2016

#### Keywords:

Pyrolysis and solvolysis

Microwave

Lignin

Fuels

Chemicals

### ABSTRACT

Energy insecurity and resource shortage are driving societies to look for sustainable and renewable energy and resource supplies. Thus, converting biomass into useful energy and chemical products has attracted considerable attention in the past decades. As a carbon-rich renewable biomass source, lignin has been extensively studied as a raw material to produce bioenergy and value-added chemicals. Fuel gas and phenolic products can be obtained by converting lignin. This study strives to extensively review recent developments in the microwave-assisted pyrolysis and solvolysis of lignin. Lignin structural components and extraction techniques are described under different conditions. In addition, the fundamentals and advantages of microwave heating technology and the background of lignin pyrolysis and solvolysis are presented. The effectual parameters of the microwave-assisted pyrolysis and solvolysis of lignin and their advantages are also summarized. This review concludes that microwave-assisted technology is an effective method for significantly reducing reaction time and improving the yields and selectivity of target products. In the future, low-cost catalysts and microwave-assisted conversion units need to be developed to achieve large-scale production of renewable fuels and value-added chemicals from lignin.

© 2016 Elsevier B.V. All rights reserved.

### Contents

1. Introduction .....	105
2. Structure and extraction of lignin .....	105
2.1. Structure .....	105
2.2. Lignin extraction .....	105
3. Microwave heating technology .....	105
4. Microwave-assisted lignin conversion .....	107
4.1. Pyrolysis process of lignin .....	107
4.1.1. Conventional pyrolysis conditions .....	107
4.1.2. Conventional pyrolysis catalysts .....	107
4.1.3. Microwave-assisted pyrolysis technique .....	107
4.2. Solvolysis process of lignin .....	108
4.2.1. Conventional solvolysiscatalysts .....	108
4.2.2. Microwave-assisted solvolysis technique .....	109
5. Advantages of microwave-assisted lignin conversion technology .....	111
6. Conclusions .....	111
Acknowledgements .....	111
References .....	111

\* Corresponding authors.

E-mail addresses: [liuyuhuan@ncu.edu.cn](mailto:liuyuhuan@ncu.edu.cn) (L. Yuhuan), [ruanx001@umn.edu](mailto:ruanx001@umn.edu) (R. Roger).

## 1. Introduction

With the excessive use and depletion of fossil fuels as sources of fuels, chemicals, and energy, the production of such commodities from renewable biomass can be expected to increase in the near future. Therefore, researchers have conducted considerable studies on renewable, abundant, and clean alternatives to chemicals and fuels in recent years [1–3]. Given its abundance and affordability, lignocellulosic biomass that consists of cellulose, hemicellulose, and lignin has been extensively investigated and utilized to obtain fuels, such as bioethanol [4], biodiesel [5], hydrocarbon fuels [6], and chemicals [7,8]. Cellulose is a high molecular weight polymer that consists of linear  $\beta$ -1,4 glycosidic linked chains of D-glucose units [9], whereas hemicellulose is a heterogeneous polymer that comprises several different types of monosaccharides [10]. Lignin is one of the most abundant natural polymers (only second to cellulose), which constitutes 20%–30% of the weight of lignocellulosic biomass [11]. From the perspective of high energy content and polymer structure, lignin is considered a promising source of renewable fuels and chemicals. However, a majority of lignins have been burned as a source of heat and even discharged into rivers. Although lignin is mainly made up of three types of phenylpropane units, namely, guaiacyl alcohol, syringyl alcohol, and *p*-coumaryl alcohol, its 3D randomized net structure severely restricts its application in the production of valuable chemicals. In general, the conversion of lignin into fuels and chemicals relies on thermochemical and primary hydrolytic conversions to break down large polymers [12]. As a promising thermochemical conversion technology, pyrolysis can convert lignin into fuels and valuable chemicals in solid, liquid, and gas forms in the absence of oxygen, with or without a catalyst [7]. Lignin pyrolysis undergoes three consecutive stages, namely, the evaporation of water, the formation of primary volatiles, and the subsequent release of small-molecule gases [13]. Valuable pyrolysis products are volatiles such as phenols and gaseous products.

As an energy-efficient, fast, and environment-friendly heating source, microwave technology has been widely applied in lignin conversion, which considerably promotes the development of environmentally benign, innovative, and highly efficient lignin conversion processes [14–16]. Compared with conventional heating technology, microwave heating exhibits advantages in reaction control, energy efficiency, and high selectivity, which increase the application prospect of microwave-assisted lignin conversion. Researchers and scientists have mainly focused on microwave-assisted lignin conversion for fuel additives and high added-value chemicals. The complex and stable chemical bonds in lignin are difficult to cleavage; however, significant progresses have been achieved through microwave heating technology [17–19]. This study aims to present the advantages of applying microwave technology in lignin conversion. It reviews recent developments in microwave-assisted conversion of lignin for renewable fuels and chemicals using different types of catalyst.

## 2. Structure and extraction of lignin

### 2.1. Structure

Studies indicate that lignin is a natural phenolic random polymer with a 3D network structure; it is made up of three typical phenylpropane monomer units, namely, *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, through ether bond and C–C bond linkages (Fig. 1). The proportion of these linkages depends on the type of wood. In many cases, approximately two-third of the linkages in lignin are ether bonds, whereas the remaining linkages are C–C bonds. Since there are a number of phenylpropane

monomer units and the OH functional groups, lignin can be depolymerized into low molecular weight phenolic compounds, which can be converted into high value-added fine chemicals. The linkages between phenylpropane monomer units in the lignin structure mainly include ether bonds such as  $\beta$ -O-4,  $\alpha$ -O-4, and 4-O-5, as well as C–C bonds such as  $\beta$ -1,  $\beta$ -5, 5-5', and  $\beta$ - $\beta$ . Lignin has 48%–60%  $\beta$ -O-4 bonds and approximately 25% 5-5' linkages, which are the main bond types in lignin [20–22]. Therefore, the effective cleavage of  $\beta$ -O-4 bonds and 5-5' linkages is key to lignin decomposition. Promoting methoxy fracture with microwave pyrolysis may markedly reduce the activation energy of the depolymerization reaction.

The structure and functional groups of lignin have been characterized through a series of technologies, including chemical oxidation, thioacidolysis,  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy, thermogravimetric analysis, Fourier transform infrared spectroscopy (FTIR), and pyrolysis–gas chromatography (GC)–mass spectrometry (MS) [23,24]. Lignin composed of phenylpropane monomer units through different aryl ethers or other linkages. These irregular connection forms with different bond energy significantly affect the lignin depolymerization process. Theoretically, the required energy for cleaving ether bonds is significantly lower than that for cleaving C–C bonds.

### 2.2. Lignin extraction

Extracting lignin is an important first step in the biorefinery operations of the lignocellulosic biomass. However, the strong bonds between lignin molecule and cellulose and hemicellulose make separating lignin from the lignocellulose feedstock extremely difficult. Many researchers and scientists have conducted studies on high-quality and high-purity lignin extraction and have reported several effective extraction processes, including pH precipitation [26], precipitation with the  $\text{CO}_2$ - $\text{Alk}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  technique [27], and organic solvent extraction [28]. During these processes, undesirable changes in lignin structure may occur, which could severely affect and limit the economic value of lignin.

Wu et al. [29] reported a catalytic hydrothermal lignin extraction technology from cotton stalk using metal chlorides, including  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{ZnCl}_2$ , and  $\text{CrCl}_3$ , as catalysts. In this process, the acidity of the metal chloride catalysts helped cleaving of the  $\beta$ -O-4' linkages. In a subsequent study [30], these researchers also attempted to extract birch lignin using a microwave heating process in formic acid at 101 °C and characterized the extracted products through elemental analysis, FTIR, gel permeation chromatography (GPC),  $^1\text{H}$  NMR spectroscopy, and  $^{13}\text{C}$ - $^1\text{H}$  Heteronuclear Single Quantum Coherence. They concluded that microwave heating improved the lignin yield without dramatically changing the lignin structure, which was mainly guaiacyl–syringyl (GS)-type with  $\beta$ -O-4' ether bonds.

Lignin obtained from the pulping industry can be used as feedstock for added-value products production in a biorefinery. The pulping extraction process involves different conditions, including temperature, pressure, catalyst, pH, solvent, etc. These processing conditions significantly affect the structure of the lignin and the difficulty of the lignin depolymerization and the type of high added-value products that can be produced. Hence, optimal pretreatment and extraction conditions are important in the lignin biorefinery operation. A summary of different extraction techniques is provided in Table 1.

## 3. Microwave heating technology

In 1986, Gedye reported on the experimental results of esterification, hydrolysis, oxidation, and alkylation reactions under

Download English Version:

<https://daneshyari.com/en/article/7606577>

Download Persian Version:

<https://daneshyari.com/article/7606577>

[Daneshyari.com](https://daneshyari.com)