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Biofuel production from catalytic microwave pyrolysis of Douglas fir pellets over ferrum-modified activated carbon catalyst

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ABSTRACT

The presented study aims to improve the quality of bio-oils by catalytic upgrading of bio-oil from microwave pyrolysis of Douglas fir pellet using transition metal modified activated carbon (AC) catalyst. A central composite experimental design (CCD) was used to optimize the reaction conditions for high quality bio-oil production. The effects of reaction temperature and reaction time on product yields were investigated. GC/MS analysis indicated that the main chemical compounds (including furans, phenols, guaiacols, and ketones/ethers) of bio-oils were in the range of 80–87% of bio-oils for most of the samples. The ketones/ethers were mainly composed of 2-cyclopen-1-one; straight chain ethers were increased up to about 38% of bio-oil; and the phenols increased from 2.5% to about 10% of the bio-oils after upgrading accompanying with the decrease of guaiacols in comparison with raw biomass pyrolysis. The reaction mechanism of this process was analyzed.

1. Introduction

The global energy crisis and non-negligible effects of burning fossil fuels on the environment is becoming a global challenge that facilitates governments and scientists to seek and develop renewable and environmental friendly alternatives of fossil fuels. As one of the most significant renewable resources on earth and currently, the only renewable resource that can be directly converted to liquid fuels, biomass has received considerable attention in the search for alternative fossil fuels [1,2]. The major components of biomass are cellulose, hemicellulose and lignin. Cellulose and hemicellulose consist of complex polysaccharides [3], while lignin is highly substituted and mononuclear phenolic amorphous polymers consisting of phenylpropane units [4,5]. In general, there are two major methods for biomass conversion to chemicals and fuels: biochemical conversion through enzymatic hydrolysis in mild conditions and thermochemical conversion performed under high temperature or high pressure. Three major pathways in thermochemical conversion can be used to convert cellulosic biomass: syngas production by gasification, bio–oils production by pyrolysis or liquefaction, and aqueous sugar by hydrolysis [6–8].

Pyrolysis of biomass is a thermal decomposition process in which organic compounds in the absence of oxygen are decomposed into bio-oil, syngas, and biochar. It has been widely used for production of renewable fuels and chemicals [7–10]. Microwave pyrolysis of biomass is a process in which heat is generated within the biomass through its interaction with high intensity microwave field. Comparing with conventional pyrolysis, the most significant advantages of microwave pyrolysis include energy efficiency since no size reduction or drying of feedstock is required. Microwave pyrolysis of biomass can be very rapid due to selective heating [11,12]. Microwave pyrolysis using different feedstocks, such as wood, sewage slude, and microalgae, has been reported recently [12–14]. Douglas fir is a soft wood which belongs to the coniferous family. It is an important commercial wood and one of the abundant species in Northwestern American. Wood pellets provide a renewable energy source for power generation and residential heating due to easier handling for transportation, storage, and biomass conversion. It was estimated that there were 800,000 wood pellet stoves in use with a total of about 1500,000 tons of annual pellet consumption in North American in 2008 [15]. Although pyrolysis of Douglas fir pellets has been previously reported [9,16], research on the catalytic pyrolysis of Douglas fir pellets for biofuels production is quite insufficient.

Pyrolysis bio-oils are complex mixtures of more than 300 compounds derived from the flash depolymerization and fragmentation

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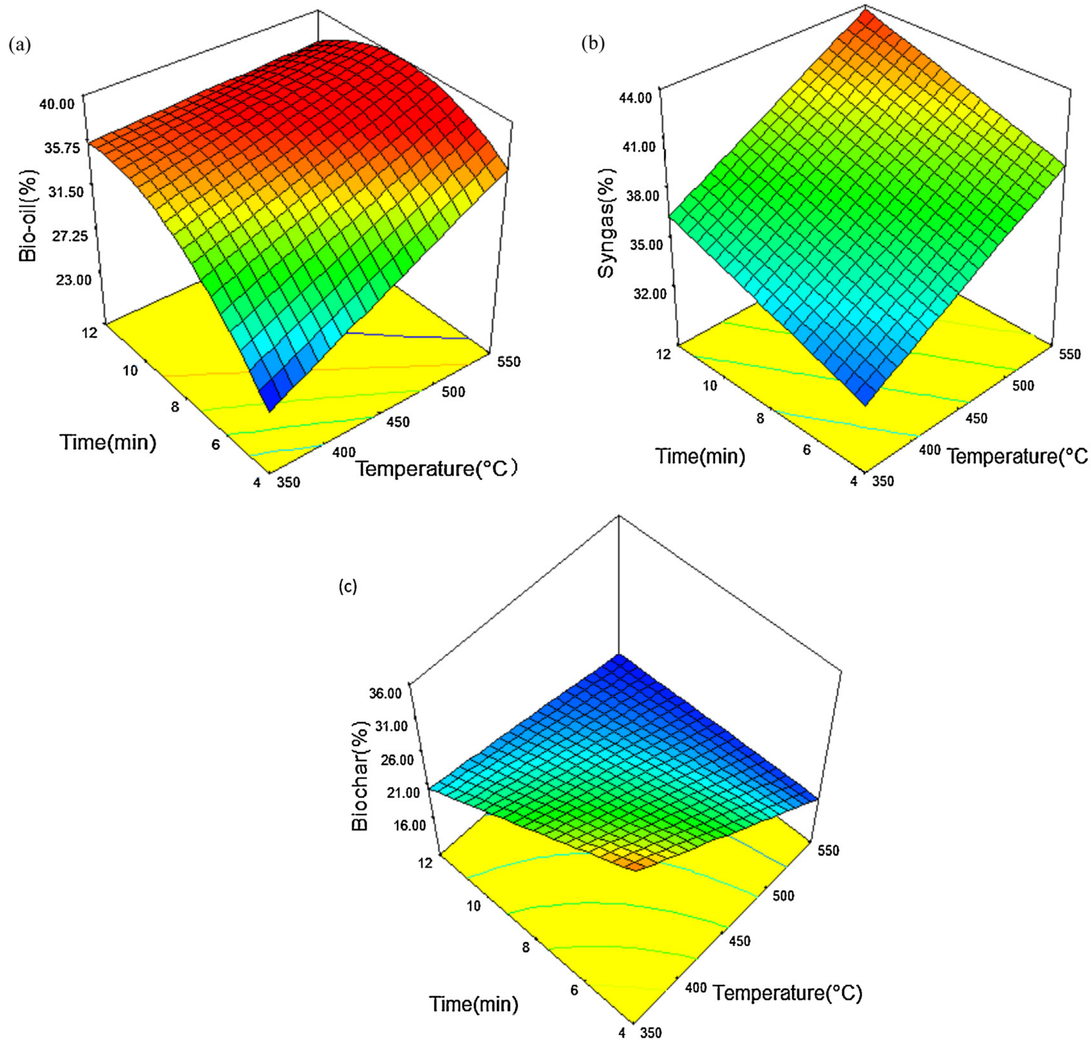

Fig. 1. The response surface and contour line of product yields as a function of reaction temperature and time: (a) bio-oil, (b) syngas, and (c) biochar.

reactions of cellulose, hemicellulose, and lignin. The major organic compounds are acids, alcohols, ethers, ketones, aldehydes, phenols, esters, sugars, furans, and nitrogen compounds. The physical properties of bio-oils, such as low pH, high oxygen content and low viscosity due to complex mixtures of reactive chemical compounds, cause bio-oils to be unstable intermediates [17]. Therefore, these unfavorable characteristics of bio-oils make their direct utilization challenging. Upgrading is necessary before bio-oils can be used as competitive substitutes of petroleum fuels and as chemical feedstocks in the chemical industry. Due to the low reactivity of some compounds such as phenols, considerable attention has been directed to catalytic upgrading of bio-oils using phenols as model compound which becomes one of the key reactions in pyrolysis oil upgrading [18].

Recently, some transition metal based catalysts including noble metals such as Pt, Pd and Ru on varied supports including Al_2O_3 and carbon were used for catalytic upgrading of bio-oils [19–23]. However, Al_2O_3 was shown to be an unsuitable support because the water formed in HDO and the oxygen containing compounds may convert it to boehmite (AlO(OH)) [20,24,25]. Observations showed that an indication of high affinity for carbon formation existed on the alumina support because of the relatively high acidity of Al_2O_3 [26]. As a result, carbon has been found to be a promising alternative to Al_2O_3 due to its neutral nature and high surface area [19,24]. Whether the activation of the oxy-compound is achieved through the metal sites or at the metal support interface is still unclear, though it is generally accepted that the metals contain the hydrogenation active sites [18].

Previous research [9,27] found that phenolic rich bio-oils were obtained during microwave pyrolysis of Douglas fir pellets. Therefore, the present study aims to improve bio-oil quality for biofuel production by catalytic microwave pyrolysis of Douglas fir using transition metal modified AC catalyst. The effects of reaction temperature and reaction time on product yield were investigated and models to predict the products yields were obtained. The chemical compositions of the resulting bio-oils were characterized by GC/MS analysis. The reaction mechanism of catalytic Douglas fir pyrolysis was analyzed.

2. Materials and methods

2.1. Materials

Douglas fir sawdust pellet (7 mm in diameter and 14 mm in length, ~8% moisture content) was used as biomass feedstock as received (Bear Mountain Forest Products Inc., USA). Acid-washed granular activated carbon, GAC 830 PLUS, with high purity produced by steam activation of selected grades of coal was purchased from Norit Americas Inc., (Marshall, TX). Iron powder was purchased from Sigma–Aldrich Corporation (St. Louis, MO, USA).