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Ex situ thermo-catalytic upgrading of biomass pyrolysis vapors using a traveling wave microwave reactor

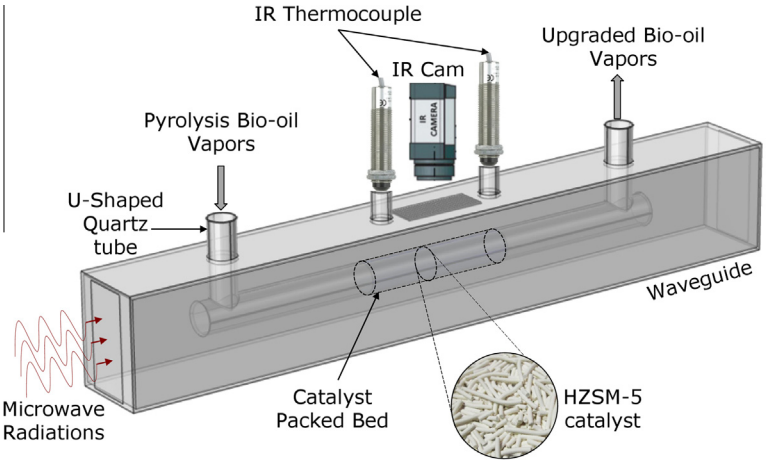
P.D. Muley [a], C.E. Henkel [b], G. Aguilar [b], K.T. Klasson [c], D. Boldor [b,*]

[a] Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803, United States
[b] Department of Biological and Agricultural Engineering, Louisiana State University Agricultural Center, Baton Rouge, LA 70803, United States
[c] United States Department of Agriculture, Agricultural Research Service, New Orleans, LA 70214, United States

HIGHLIGHTS

- *Ex-situ* microwave reactor was used to heat catalyst bed for pyrolysis upgrading.
- Results were compared with conventional catalytic reactor.
- Microwave heating yielded higher aromatic compounds.
- Catalyst deactivation due to coking was lower in microwave reactor.
- 30% decrease in energy input for microwave reactor.

GRAPHICAL ABSTRACT



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ABSTRACT

Microwave heating offers a number of advantages over conventional heating methods, such as, rapid and volumetric heating, precise temperature control, energy efficiency and lower temperature gradient. In this article we demonstrate the use of 2450 MHz microwave traveling wave reactor to heat the catalyst bed for thermo-catalytic upgrading of pyrolysis vapors. HZSM-5 catalyst was tested at three different temperatures (290°, 330° and 370 °C) at a catalyst to biomass ratio of 2. Results were compared with conventional heating and induction heating method of catalyst bed. The yields of aromatic compounds and coke deposition were dependent on temperature and method of heating. Microwave heating yielded higher aromatic compounds and lower coke deposition. Microwave heating was also energy efficient compared to conventional reactors. The rate of catalyst deterioration was lower for catalyst heated in microwave system.

1. Introduction

Pyrolytic bio-oil is a complex mixture of different sized organic molecules such as phenols, furans, levoglucosan, and other compounds, [1,2] formed as a result of the depolymerization and

* Corresponding author at: 149 EB Doran Building, Department of Biological and Agricultural Engineering, LSU AgCenter, Baton Rouge, LA 70803, United States.
E-mail address: DBoldor@agcenter.lsu.edu (D. Boldor).

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fragmentation of the biomass feedstock components (cellulose, hemicellulose, and lignin) during pyrolysis. Although bio-oil produced from fast pyrolysis of biomass has a potential to be directly used as a liquid fuel, this fuel has certain limitations such as high viscosity, acidity, low heating value, high ash content, etc. [3]. Pyrolytic bio-oil also has high oxygen content of about 40% which marks a major difference between pyrolysis fuel and hydrocarbon fuel (oxygen content < 1%) [3]. High oxygen content leads to a decrease in energy density [1] and catalytic deoxygenation of bio-oil is the most effective way to reduce oxygen content [4,5]. In this process, pyrolysis vapors are upgraded with the catalyst; where deoxygenation and cracking reactions takes place, and oxygen is released in the form of water, CO_2, and CO.

Numerous studies have been performed over the years to study the effect of various catalysts on pyrolysis vapor upgrading, with most of them using the 300° to 500 °C as the operating temperature range [1,6–11]. Zeolites such as HZSM-5 have proved to be one of the most effective catalyst for deoxygenation of bio-oil when operating in the temperature range of 250–400 °C [7]. The major disadvantages of catalytic upgrading of pyrolysis bio-oil are heat loss by heat transfer medium such as sand, non-uniform heating of catalyst in externally heated reactors and the issues associated with the deactivation of catalytic sites via either coke deposition or poisoning [1,12]. In spite of smart heat transfer designs, conventional heating technologies lack a rationally designed method for efficient and optimum use of imparted energy to achieve a desired temperature distribution.

Use of electromagnetic energy in the microwave region (300–6000 MHz) is an effective heating mechanism as microwaves impart energy directly to the material and eliminates the need of a heat transfer medium [13]. These qualities of microwave heating make it an efficient heating method, with a conversion efficiency of electrical energy to heat of 80–85% [14]. Apart from increased heating efficiency, microwave heating of catalyst may improve catalyst performance compared to conventional heating, mainly due to an increase in rate of reaction as described by Arrhenius equation [15]

$$K = Ae^{\frac{-Ea}{RT}} \quad (1)$$

where K – Rate constant, Ea – Activation energy (J mol^{-1}), R – Gas constant (J K^{-1} mol^{-1}), T – Temperature (K), A – pre-exponential factor.

The frequency factor A represents molecular mobility and depends on the frequency of vibration of reacting molecules at the reaction interface which is directly affected by the microwave irradiation. An increase in frequency factor indicates increased rate of collision, thus, increases the rate of reaction [15]. Moreover, microwave heating of catalyst is known to reduce coke deposition on the surface due to self-gasification of coke peculiar to microwave reactions only [16]. Microwave irradiated coke tend to desorb from the surface of the catalyst, and microwave heating is also an effective means of desorption of polar molecules [17]. These advantages of microwave technology make it a viable option for catalyst heating.

Microwave heating has been previously studied for pyrolysis of biomass as well as catalytic upgrading [18–20]. However, all the studies reported were *in situ* catalytic upgrading. *In-situ* catalytic upgrading puts limitations on the pyrolysis temperature as most catalysts are efficient at 200–500 °C [7], while pyrolysis is most efficient above 500 °C for maximum liquid yields. Moreover, *ex situ* catalytic upgrading has shown to increase both yield and deoxygenation rate compared to *in situ* upgrading [21,22]. The objective of this study was to develop an *ex-situ* microwave-assisted catalytic upgrading process for pyrolysis vapors that will help promote the understanding of fundamental catalytic requirements for deoxygenation of pyrolysis vapors and the role of microwaves in catalyst activity and heating efficiency.

Pyrolysis of biomass was performed in an induction heater and the exiting bio-oil vapors were passed over a hot catalyst bed heated using a traveling wave microwave reactor. The performance of the microwave process was compared to conventionally and inductively heated catalyst bed processes in terms of yield and quality of the produced bio-oil, as well as with respect to catalyst performance. The conversion of biomass using the proposed method can lead to significant improvements in energy production from renewable resources in terms of increased energy efficiency and biofuel quality, as well as toward developing sustainable energy systems.

2. Materials and methods

2.1. Material

Pine sawdust was obtained from scrap wood at Biological and Agricultural Engineering wood shop at the Louisiana State University Agricultural Center. The sawdust was finely ground and its moisture content was measured. Nitrogen gas cylinder was supplied by Air Liquide (Houston, TX, USA). The HZSM-5 catalyst was supplied by Sigma Aldrich (St. Louis, MO, USA). The biomass pyrolysis reactor was a 5 kW RDO induction heater operating at a frequency range of 35–100 kHz (RDO Induction LLC, Washington, NJ). The reaction tube was a 310-stainless steel tri-clamp tube, 419 mm in length with an inner diameter of 34.4 mm. Reaction tube temperature was controlled using a calibrated Omega IR2C series infrared feedback controller (Omega, Stamford, CT) and an IR sensor to monitor the temperature.

For upgrading reaction, the catalyst was heated by three different methods;

1. Conventional heating using a 13 mm × 1220 mm high temperature heavy insulated heating tape with 313 W output operating at 120 V (Briskheat Corporation, Columbus OH, USA) surrounding the reaction tube. The temperature was measured using a K type thermocouple and controlled using a bench top temperature controller from Briskheat Corporation (Columbus, OH).
2. Induction heating using a 5 kW RDO induction heater operating at frequency range of 135–400 kHz (RDO Induction LLC, Washington, NJ) to heat the catalyst bed. The reaction tube temperature was controlled using a calibrated Raytek MI3 series infrared remote temperature sensor (Raytek Corporation 1999–2014) that was coupled with a PID controller (Red Lion P-1641100, Red Lion Controls Inc. York, PA, USA). For both conventional and induction heating methods, the reaction tube was a 310-stainless steel tri-clamp tube, which was 270 mm length with inner diameter of 25.4 mm [23].
3. Microwave heating using a 1.2 kW, 2450 MHz microwave system. A 2450 MHz microwave traveling wave applicator was modified to accommodate the catalytic bed. The reaction tube was fabricated from quartz with 28.0 mm inner diameter and 472.7 mm in length. The tube was designed to meet the microwave waveguide safety requirement, where a hole in the waveguide is less than 1/3 of the wavelength. The length of the tube was selected such that two IR pyro sensors measured the catalyst temperature at two different points and a thermal camera measured the temperature of the catalyst through a metallic mesh region of the waveguide.

In addition to the microwave safety criteria described above, the dimensions and configuration of the tube were selected considering the ease of loading and unloading of the catalyst and cleaning the tube. Catalyst bed temperature was controlled by using a PID