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Upgrading of lignin-derived bio-oil in non-catalytic plasma reactor: Effects of operating parameters on 4-methylanisole conversion

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ABSTRACT

This article investigated an atmospheric pressure dielectric barrier discharge (DBD) plasma reactor to explore the effects of carrier gas type, applied voltage and pulse repetition frequency on upgrading of 4-methylanisole as a lignin-derived bio-oil. A series of experiments were designed to realize the effects of argon (Ar) and hydrogen (H_2) on upgrading. The results showed that argon yields higher conversion of 4-methylanisole compared to hydrogen, and both voltage and frequency had positive effects on the conversion of 4-methylanisole. Increasing voltage and frequency led to an increase in the number of active species and subsequently, the number of effective collisions as a result 4-methylanisole conversion and discharge power (DP). In the experiments with applied voltage of 9 kV, frequency of 20 kHz and existence of Ar as carrier gas, the conversion reached to 29.80% at the DP of 77 W. The most abundant products were 4-methyphenol and 2,4-dimethylphenol, which were formed from transalkylation and hydrogenolysis reactions. It was found that the increase in the applied voltage, frequency and Ar percentage of carrier gas (as adjustable parameters), has the same effects on product distribution; since their variation resulted in the same changes in core plasma parameters such as electron energy, temperature and density.

1. Introduction

Nowadays, changes in human life style, technological and economical advances, increase in the population and thereby higher use of transportation vehicles have resulted in the growth rate of the total energy consumption (Taghvaei et al., 2015; Mortensen et al., 2011). Moreover, the feedstock for production of energy is provided from fossil fuels, where their consumption has led to problems such as CO_2 emission and global warming. Besides, the fossil fuel resources are limited (Dehkordi and Ghasemi, 2012). These issues altogether manifest the significance of using alternative sources of energy. In this regard, biomass, as a renewable source of energy, has attracted the attention of many researchers due to its potential of being converted to fuel. Although there are some complexities affiliated with biomass conversion, several advantages such as sustainable source of organic carbon (Hakim et al., 2013) and the ability to provide energy in liquid, gas and solid

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phases (Pham et al., 2013), have convinced industries to use biomass as the feed source for bio-fuels production (Jacobson et al., 2013).

Generally, biomass refers to the agricultural wastes, forest wastes, wood, byproducts of biological materials, organic sector of sewages and sludge. Through the photosynthesis process, biomass converts CO_2 and solar energy to chemical energy in the form of carbohydrates (Kumar et al., 2009).

Two general methods that have been investigated for conversion of the biomass are biochemical and thermochemical conversions. Thermochemical conversion is performed through gasification, (fast/slow) pyrolysis, liquefaction and hydrogenation. These processes could convert biomass to oils, fuel gases and charcoals (Chaiwong et al., 2013). Fast pyrolysis, which operates under the temperature range of 400 °C to 800 °C (Gorling et al., 2013), and has a relatively short vapor residence time (about 2 s) and high heating rate (near 104 °C/s) (Nguyen et al., 2013), converts biomass to high oxygen content compounds called bio-oil. After analysis, it has been proved that the bio-oil from fast pyrolysis contains anisole, 4-methyl anisole, cresol, guaiacol and lignin-derived phenolic compounds (Popov et al., 2013; Paenpong et al., 2013; Taghvaei et al., 2014a,b).

Bio-oils obtained from pyrolysis have higher energy densities than the original biomasses. The reported energy density for bio-oils and the original biomasses are 19 kJ/kg and 15 kJ/kg, respectively (Nguyen et al., 2013). Bio-oils produced from the conversion processes can be used as fuel or chemical feedstock, however, some problems should be eliminated (Wang et al., 2013).

Bio-oils obtained from fast pyrolysis process have high oxygen content (about 30–40 wt%), which leads to some undesirable properties such as low heating value (Leng et al., 2013), significant thermal instability and low volatility (Maggi and Delmon, 1994), high corrosiveness and immiscibility with gasoline and diesel fuels (Nimmanwudipong et al., 2011). Besides, such bio-oils have high water content (about 20 wt%) (Gunawan et al., 2013), high viscosity (Sharma and Bakhshi, 1993), high acidity (pH about 2.5) (Bridgwater, 2012), high solid content (Gutierrez et al., 2009), and high polymerization potential, which causes large molecules (Dang et al., 2013).

Due to the aforementioned issues, these types of bio-oils cannot be used as common fuels directly. They could be utilized only as heavy fuel oil (Sharma and Bakhshi, 1991; Wei-cheng et al., 2013). Therefore, the bio-oils must be upgraded to be used as common fuels. The products obtained from upgrading of bio-oils are very similar to hydrocarbon oils. Hydrodeoxygenation (HDO) and zeolite cracking are two conventional upgrading methods (Bridgwater et al., 1999). Hydrodeoxygenation usually occurs at high pressures (near 20 MPa) and medium temperatures (about 400 °C). From economical point of view, hydrodeoxygenation is not an economical method due to the high consumption of hydrogen and high pressure (Mechold et al., 2004; Diebold and Czernik, 1997). Zeolite cracking upgrading occurs at atmospheric pressure and high temperature (300–600 °C) in gas or liquid phase. In contrast to HDO process, this method has an advantage of no H_2 requirement. However, the high degree of coke formation leads to the fast deactivation of catalyst within seconds (Nguyen et al., 2013; Nimmanwudipong et al., 2012; Park et al., 2006).

Given the problems mentioned for common upgrading methods, researchers have tried to find better catalysts and alternatives that do not involve catalysis. In the last few years, research has been done on the use of non-catalytic plasma reactor for bio-oils upgrading (Taghvaei et al., 2014a,b).

In chemical sciences, plasma is defined as a partially ionized gas, which includes ions, atoms, metastable and free radicals that creates a quasi-neutral media (Jahanmiri et al., 2012; Taghvaei et al., 2012).

Plasma-processing systems are traditionally divided into two major categories: thermal and non-thermal ones. In thermal plasmas, the number of collisions between electrons and heavy particles increases due to high pressure. As a result, electrons and gas molecules reach thermal equilibrium and therefore, the gas bulk temperature attains to 2000 K (Tao et al., 2010; Khani et al., 2011, 2014).

In non-thermal plasma, the electrical energy goes into the production of energetic electrons rather than into gas heating, which is due to its low pressure. Therefore, the electrons temperature can reach up to 10^4–10^5 K, while the gas remains at room temperature (Hooshmand et al., 2013).

Among the NTP types, dielectric barrier discharge (DBD), corona discharge and spark discharge can be noted (Nozaki and Okazaki, 2013), where DBD is more efficient for plasma essence due to its simple design and operation (Rahimpour et al., 2013a,b), ability to work at atmospheric pressure and high efficiency in generation of radicals in gas phase (Xia et al., 2008).

In our previous works, the non-catalytic upgrading of anisole was carried out in a DBD plasma reactor. The plasma technology was responsible for the progress of upgrading of anisole at room temperature. Moreover, deactivation of the catalysts was eliminated by the plasma (Rahimpour et al., 2013a,b).

In this study, the effects of the carrier gas type, applied voltage and frequency were investigated on upgrading of 4-methylanisole in an atmospheric pressure dielectric barrier discharge (DBD) plasma reactor. A self-made DBD plasma reactor was used for the intended purpose. Argon, hydrogen and their combinations were used as the carrier gas.

2. Experimental

2.1. *Experimental equipment*

A schematic diagram of the plasma reactor used to investigate upgrading of 4-methylanisole is shown in Fig. 1.

The plasma reactor was made of quartz glass with an overall length of 65 cm. This relatively high length is because the reactor requires a relatively long-term use of internal electrons to reduce energy loss of the sharp electrode. Inner and outer diameters of the reactor were 10 and 13 mm, respectively. This thickness (about 1.5 mm) plays the role of dielectric insulation. An inner electrode with a length of 45 cm and diameter of 2.68 mm was placed in the middle section of the reactor. The electrode was made of stainless steel and centered within the reactor using two plexiglass pieces that were neutral with respect to reactions.

The inner electrode was connected to a high voltage source and was able to produce voltages up to 10 kV with fall and rise times less than 80 ns, pulse width of less than 50 ns and frequency range between 1 and 20 kHz by given voltage of 220 V and frequency of 50 Hz as input. The applied voltage and current were respectively measured by Tektronix P601A high voltage probe and Pearson 150, 2A/V current probe.

The outer electrode, which was made of brass and determined the range of discharge zone, was rolled on the outer wall