



## Study on pyrolysis characteristics of lignocellulosic biomass impregnated with ammonia source



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### HIGHLIGHTS

- Carbonyl compounds were converted into nitrogenous heterocyclic compounds (NHCs).
- The contents of NHCs and phenols in URL are very high.
- The quantity of compounds in SRL and PRL reduces remarkably.
- The reaction mechanism for the formation of NCHs was proposed.

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### ABSTRACT

The current study presents the pyrolysis characteristics of rice husk impregnated with different kinds of ammonia source (ammonium acetate, urea, ammonium sulfate and ammonium dihydrogen phosphate) in a fixed bed reactor. The introduction of ammonia source in pyrolysis process achieved the conversation from carbonyl compounds to nitrogenous heterocyclic compounds. The liquid product of urea-impregnated biomass has higher content of nitrogenous heterocyclic compounds (8.35%) and phenols (30.4%). For ammonium sulfate and ammonium dihydrogen phosphate-impregnated biomass, the quantity of compounds in liquid products reduces remarkably, and the gas products are rich in CO and H<sub>2</sub>. All the solid products of pyrolysis have great potential application in biochar-based fertilizer and activated carbon for their high N content.

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### 1. Introduction

Lignocellulosic biomass is the only renewable and clean energy resource existing as physical form. The development and utilization of lignocellulosic biomass draw increasing attention recently (Bilgili, 2012; Zhang et al., 2012). Biomass pyrolysis technology can be utilized with biomass to produce liquid, gas and solid products. The liquid product, also called bio-oil or pyrolysis oil, is universally regarded as a promising raw material for fuel and chemicals (Bridgwater, 2012; Mei et al., 2015). However, the poor physical and chemical instability of bio-oil resulting from high oxygen content, high water content, high viscosity, low pH and high-value chemicals content, hampered its wide application as raw material for chemical and fuel seriously. And there is a broad consensus that most of these undesirable characteristics are related to the presence of some oxygen containing reactive functional groups, especially carbonyl group. For example, a massive

amount of organic acids resulting in the strong corrosiveness of bio-oil (Aubin and Roy, 1990), and the chemical reactions of carbonyls with other organics in the bio-oil (including esterification, transesterification, homopolymerization, hydration, hemiacetal formation, acetalization, phenol/aldehyde reaction and resin, and so on), are conducive to the instability of bio-oil (Diebold, 2002; Chen et al., 2014).

Recently, many upgrading measures represented by catalytic pyrolysis (Zhang et al., 2009, 2013), catalytic cracking (Hew et al., 2010) and catalytic hydrogenation (Miskolczi et al., 2010) were taken to improve the quality and application value of bio-oil, and many positive results were also achieved, which has also been reviewed by Chen and Bridgwater comprehensively (Bridgwater, 2012; Chen et al., 2014). Nevertheless, the coking and deactivation of catalysts are still existing as obstacles having to face in the upgrading progress of bio-oil, resulting in the reduced efficiency and the increased cost of bio-oil catalytic transformation. Some recent researches demonstrated that the generation of coke is attributed to the existence of oxygenated organic compounds,

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especially the thermally unstable carbonyl compounds (Vispute et al., 2010; French and Czernik, 2010).

Therefore, finding a new way to reduce the yield of carbonyl compounds and convert them into more valuable chemicals has become one of the primary tasks during the biomass pyrolysis and bio-oil upgrading processes.

As an alternative to lignocellulosic biomass, algal biomass mainly consists of carbohydrates, lipids and proteins, which are different from the composition of lignocellulosic biomass with cellulose, hemicelluloses and lignin. Researchers have made comparative studies on the pyrolysis of algal biomass with lignocellulosic biomass, indicating that the bio-oil from the pyrolysis of algae feedstock has better stability compared to that from lignocellulosic biomass (Maddi et al., 2011; Campanella et al., 2012). Another noteworthy feature is that certain amount of nitrogenous heterocyclic compounds (NHCs) were generated in the bio-oil obtained from algal pyrolysis and the content of carbonyl compounds decreased, which is attributed to the Maillard reaction sequence combining carbonyl group and amino group (Campanella et al., 2012; Harman-Ware et al., 2013; Wang et al., 2013). Though the bio-oil obtained from algal pyrolysis has the recognized disadvantage of having high nitrogen content, the oil own better thermal stability since oil's NHCs are more stable than carbonyl compounds. Moreover, NHCs are the right raw material with high value-added for chemical industry.

According to the characteristic of lignocellulosic biomass with low N content, introducing exotic ammonia source in the pyrolysis process can induce Maillard reaction with carbonyl compounds. This is a promising new way to improve the quality of bio-oil from lignocellulosic biomass pyrolysis, which has been seldom reported in previous studies.

The biomass used in this study is rice husk, which is frequently used as typical representative of lignocellulosic biomass in pyrolysis process to study the pyrolysis characteristics of lignocellulosic biomass (Huang et al., 2012; Cai et al., 2013; Maddi et al., 2011). Rice husk, as the major agricultural residue in rice milling factory, is an abundant biomass resource with an annual production of more than 40 million tons in China (Zhang et al., 2015). It is usually considered as a potential source of renewable energy because of its low cost, easy availability and environmental sustainability. Ammonium acetate (AA), urea (UA), ammonium sulfate (SA) and ammonium dihydrogen phosphate (PA) are inexpensive, easily available and commonly used ammonia sources.

In this work, the rice husk impregnated with four kinds of ammonia source was prepared as samples for pyrolysis. And the pyrolysis experiments of those samples were carried out in a fixed-bed pyrolysis reactor at atmospheric pressure with pyrolysis temperature of 490 °C. Based on the analyses on yields and qualities of the pyrolysis products, the pyrolysis characteristics of rice husk impregnated with different ammonia sources were discussed and demonstrated, which can provide a reference basis for selecting right ammonium sources to improve the properties and application in chemical industry of pyrolysis products.

## 2. Methods

### 2.1. Materials preparation

The biomass used in this study was rice husk (RH) obtained from Anhui province in China. Prior to use, the biomass was milled and sieved to a particle size between 0.18 mm and 0.425 mm, and then dried at 50 °C. The elemental composition of rice husk was analyzed by an Elementary Vario EL-III cube analyzer. The contents of C, H, N, S and O are 41.75%, 5.74%, 0.63%, 0.20% and 33.63%. The moisture content in air-dried basis is 8.69%. The contents of ash,

volatile and fixed carbon in dry basis are 18.05%, 65.09% and 16.86%, respectively.

Ammonium acetate (AA), urea (UA), ammonium sulfate (SA), and ammonium dihydrogen phosphate (PA) (Analytical reagent, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. The corresponding impregnated samples were denoted as AR, UR, SR and PR, the corresponding products were ARX, URX, SRX and PRX, respectively (where X = L (liquid), G (gas) and S (solid)). While pyrolysis products of pure rice husk were named RHL, RHG and RHS, respectively. Prior to all experiments, 10 wt.% ammonia source aqueous solutions were prepared, and the impregnated samples were obtained by soaking 100 g of rice husk particles in 500 mL aqueous solutions with stirring by magnetic stirrer under 50 °C water bath for 4 h. Whereafter, the mixtures were filtered and dried at 50 °C in an air dry oven, and then stored in reagent bottles with screw cap for further use. The impregnation increments of four ammonia sources were determined by least square method based on the contents of carbon, hydrogen and nitrogen, and the results were 2.1 wt.%, 12.5 wt.%, 16.4 wt.% and 18.3 wt.%, respectively.

### 2.2. Pyrolysis process

The pyrolysis of sample was carried out in a laboratory scale fixed bed reactor under atmosphere pressure. As shown in Fig. 1, the reactor is made of a quartz tube reactor with dimension of 650 mm length and 60 mm inner diameter, a horizontal tubular resistance furnace with a digital temperature controller for heating, a two-stage condenser (liquid nitrogen and ice-water bath) used for collect liquid product, N<sub>2</sub> gas cylinder, acetic acid absorption bottle for the absorption of ammonia, gas drier and a gas bag for gas collection.

Before each pyrolysis run, about 20 g sample was kept in the quartz boat in the cooling zone of the reactor, and an inert gas (N<sub>2</sub>) flow of 100 ml/min was used to remove the air and maintain an inert atmosphere in the pyrolysis reactor during the whole run. When the temperature reached desired value (490 °C), the quartz boat containing sample was pushed to the flat-temperature zone of resistance furnace and lasted for 30 min. At the end of each run, the quartz boat was pulled out to the cooling zone again. Later, the solid, liquid and gas products were analyzed. The experiments were repeated at least three times for each sample.

The yields of liquid, solid and gas products were calculated by equation as following:

$$Y_i = m_i/m_f \times 100\%$$

In which, i = liquid, solid and gas, Y<sub>i</sub> is the yield, m<sub>i</sub> and m<sub>f</sub> stand for weight of the products and sample, respectively.

### 2.3. Product analysis

The liquid and solid products collected in each run were weighed. In order to collect all the liquid products including the partial attached to the wall of condenser and ensure good homogeneity, the liquid products were washed and diluted by equivalent weight anhydrous alcohol. The elementary compositions were also analyzed by the elemental analyzer mentioned above. The properties of diluted liquid product, such as water content and pH value, were measured by moisture analyzer and pH meter, respectively. The main components of the organic liquid products were further analyzed by GC/MS equipped with a capillary column coated with SE-30MS (50 m × 0.25 mm i.d. × 0.25 μm film thickness) and a quadrupole analyzer in electron impact mode at 70 eV. Helium with high purity of 99.999% was used as carrier gas. Before GC/MS analysis, the diluted liquid products were further diluted by anhydrous alcohol again and then dried by

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