



# Controlling the selectivity to chemicals from lignin via catalytic fast pyrolysis

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## ARTICLE INFO

### Article history:

Received 3 November 2011

Received in revised form 16 February 2012

Accepted 17 February 2012

Available online 24 February 2012

### Keywords:

Aromatic hydrocarbons

Biomass

Fast pyrolysis

Lignin

Zeolites

## ABSTRACT

The catalytic fast pyrolysis of alkaline lignin to useful chemicals was investigated using zeolite catalysts with different acidity and pore size. The catalyst played dual roles in this process. In its acid form, it catalytically converted the depolymerized intermediates into desirable and more stable products. This and their surface prevented repolymerization and coke formation. The yield of liquid and the selectivity to desired products can be controlled by tuning of the acidity and pore size of the catalyst. Using no catalyst yielded 40 wt.% of liquid, which mainly consisted of 6 wt.% (carbon yield) of phenols and 19 wt.% (carbon yield) of phenol alkoxy species. The highest yield of phenol alkoxy species was obtained over H-ZSM5 of extremely low number of acid sites; liquid yield of 51 wt.% and carbon yield of 24 wt.%. The highest yield of liquid (75 wt.%) was obtained over H-USY, which had the largest pore size and lowest Si/Al ratio, thus the largest number of acid sites among all the catalyst tested; the carbon yield of aromatic hydrocarbons was around 40 wt.% at 650 °C. Depolymerized lignin products undergo consecutive reaction to form phenol alkoxy, phenols, and eventually aromatic hydrocarbons.

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## 1. Introduction

Lignocellulosic biomass is the most abundant and inexpensive sustainable source of carbon, and consists of three main components: lignin, cellulose and hemicellulose [1]. Concerns over energy shortage and CO<sub>2</sub> emission make lignocellulosic biomass attractive as feedstock for the production of renewable fuels and commodity chemical feedstock [2–4]. Fast pyrolysis of lignocellulosic biomass produces an inexpensive and renewable liquid, also called bio-oil. Such process is cheaper than conversion based on other technologies, such as gasification, liquefaction, and fermentation [5]. The product of fast pyrolysis, bio-oil, cannot be directly used as a replacement of gasoline and diesel fuels because of the high oxygen content, which makes its upgrading essential. Catalytic pyrolysis aims at producing a better quality product [6,7].

Considerable work has been done regarding biomass catalytic fast pyrolysis, especially on cellulose and hemicellulose [8–14]. For reviews on the production of transportation fuels from biomass via catalytic routes, the reader is referred to the reviews of Huber et al. [6] and Chheda et al. [15]. Zeolites are effective catalysts to remove oxygen and produce desired products from biomass, resulting in

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increased C/O ratio. Also significant progress has been made in the catalytic upgrading of bio-oil into fuels and chemicals [16,17]. These studies showed that upgrading of bio-oil is possible. However, the yield of these upgrading products is limited by the efficiency of bio-oil formation itself. Because under typical pyrolysis conditions, significant amounts of gas and coke/char (generally up to 40 wt.%) are formed, there is significant potential for improvement. Lignin conversion has received relatively little attention compared to cellulose with regards to its utility, because lignin is known as difficult to be converted, which would produce more residual than cellulose and hemicellulose [18–20]. Amen-Chen et al. published a review on the production of monomeric phenols obtained by the thermochemical conversion of biomass, mainly focusing on non-catalytic conversion of lignin [21]. Some reports focused on lignin catalytic fast pyrolysis [20,22–28]. Thring et al. reported the production of gasoline-range hydrocarbons from Acell lignin using H-ZSM5 as a catalyst in a fixed bed reactor, and the highest yield of liquid (43 wt.% of lignin) was obtained at 550 °C [24]. Zhao et al. reported that the selectivity to aromatic hydrocarbons was more than 87% during high temperature pyrolysis of isolated lignin after low temperature pyrolysis over a ZSM5 catalyst [27]. Mullen and Boateng pyrolyzed four different lignin sources over H-ZSM5 and CoO/MoO<sub>3</sub> catalysts, and found that the H-ZSM5 catalyst was the most effective for the conversion of lignin into aromatic hydrocarbons [20]. Recently, the same group studied the effect of the framework and acidity of the catalysts on producing aromatic hydrocarbons from eight types of lignocellulosic biomass and its components [28]. H-ZSM5 was the most effective catalyst, which produced aromatic