Study on the catalytic conversion of lignin-derived components in pyrolysis vapour using model component

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ABSTRACT

Vanillyl alcohol was chosen as a model component for lignin-derived components in bio-oil. The catalytic conversion of vanillyl alcohol over different catalysts was studied and it has been shown that this model component has undergone consecutive reactions to form methoxy phenols, phenols, and eventually hydrocarbons with increasing degree of de-oxygenation. The degree of de-oxygenation of vanillyl alcohol was shown to increase with the increase in number of acid sites in catalysts. γ-Al_2O_3 material with the highest number of acid sites has resulted in the highest yield of aromatic hydrocarbons, accompanied by the highest yields of coke and gas compared to other materials used in this study. Two pathways have been shown leading to the formation of hydrocarbons from vanillyl alcohol, which are: (i) decomposition of vanillyl alcohol into small olefinic hydrocarbon fragments and the subsequent aromatisation into final products and (ii) direct de-oxygenation of this model component over catalysts.

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1. Introduction

The pyrolysis of biomass is receiving tremendous interest as a potential method for converting solid biomass into liquid transportation fuels [1–7]. Lignocellulosic biomass is one of the most promising renewable resources because it is cheap and abundant [8–10]. Our previous works aimed to develop an efficient catalyst for the pyrolytic conversion of lignocellulosic biomass, via de-polymerisation and simultaneous de-oxygenation, into a high quality fuel/fuel precursor [2,11]. Different catalysts have been tested and a catalytic system of sodium carbonate supported on γ-Al_2O_3 was shown to have excellent de-oxygenation activity [11].

Lignocellulosic biomass is mainly composed of cellulose, hemicellulose, and lignin. Cellulose (a crystalline polymer of glucose) and hemicellulose (an amorphous polymer, whose major component is a xylose monomer unit) make up 60–90 wt% of terrestrial biomass [1]. Lignin, a large polyaromatic matrix made up of alkoxy substituted phenyl propyl units, is the other major component of biomass and occupies about 15–30% by dry weight [12].

During pyrolysis, decomposition of cellulose and hemicellulose results in a variety of components such as (substituted) furans, carboxylic acids, aldehydes, ketones. Catalytic pyrolysis of cellulose and hemicellulose carried out in the presence of the 20 wt.% Na_2CO_3/γ-Al_2O_3 catalyst resulted in the formation of mainly aliphatic hydrocarbons, furans and carbonyls. The results of such experiments carried out by us are summarised in Table 1. Among those products, aliphatic hydrocarbons and furans are desirable as fuel precursors because of their high energy content, very low oxygen content and neutrality in acid/base scale. It can be seen in Table 1 that there is hardly any carboxylic acid present in the product formed in the catalytic pyrolysis of cellulose, hemicellulose or lignin. This acid removal function of the sodium-based catalyst is already discussed in our previous study [11]. Carboxylic acids are either decomposed to CO_2, which occurs to a large extent, or to form carbonyls via condensation, acetone from acetic acid is one such example. Our most recent work has shown that that carbonyls can be reduced significantly combining catalytic de-oxygenation and hydrogenation over a dual-bed catalyst system. In short, among the 5 groups of components shown in Table 1 two are desirable (aliphatic hydrocarbons, furans) and two are undesired but can be catalytically treated (carboxylic acids, carbonyls) to desirable components.

The sharp increase in aromatic products in the case of lignin pyrolysis (Table 1) reflects the structure of this component, which is a three dimensional amorphous polymer containing
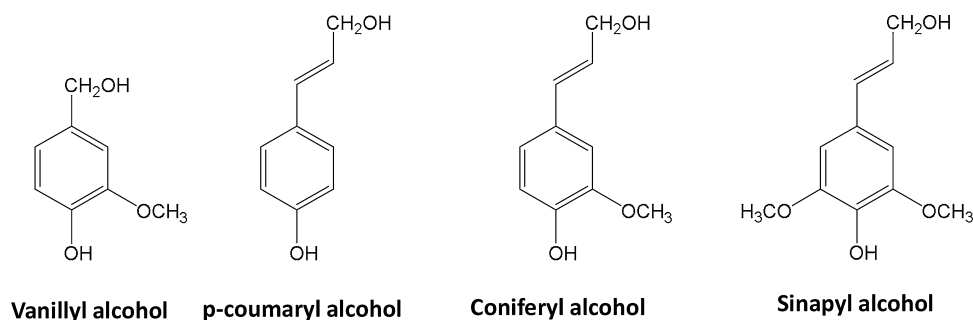
Fig. 1. Structures of the model compound vanillyl alcohol and the three building blocks of lignin, namely p-coumaryl, coniferyl and sinapyl alcohols.

methoxylated phenyl propyl matrix made up of p-coumaryl, coniferyl and sinapyl alcohols (Fig. 1) [13]. Aromatics, possess high energy content and they are often allowed in limited concentration in fuels to increase their octane number. However, they are also known to be carcinogenic and can be corrosive (for e.g. phenols). Moreover, biomass pyrolysis oil contains up to 30 wt.% of lignin-derived aromatic components, mainly in phenolic form [14,15]. Formation of various phenols during catalytic pyrolysis and their further conversion is thus of great interest while considering the need to form fuel compatible components.

Over eight types of linkages have been identified in lignin structure [16]. Some of the common linkages in the structure of lignin are shown in Fig. 2. The β-O-4 bond is the major type of linkage which occupies 46–60% of the total linkages depending on the type of wood [17].

Pyrolysis of lignin has been studied by a few of people over the decades. In 1970s, Iatridis et al. pyrolysed lignin in a "captive sample" reactor at temperature of 400–700 °C and only identified a limited number of components by gas chromatography which included hydrocarbons, methanol, acetone, phenol and guaiacol due to the limitation in analytical technology [18]. Recently, Guozhan Jiang et al. identified ~50 components from lignin pyrolysis at a temperature range of 400–800 °C [19]. The phenolic components yield was 16.2 wt.% for Alcell lignin and individual yield of most of the components were less than 1 wt.%. The thermal decomposition and weight loss of various lignin sources were studied by D. J. Nowakowski [19]. He found out that the major decomposition of lignin occurred at a temperature range of 350–450 °C and that the heating rate affected the amount of volatile products.

Several so called "lignin model components" have also been studied to avoid complexity. These lignin model components have simple structures and product distributions compared to real lignin. Guaiacol is the simplest monomeric model component and its pyrolysis behaviour was studied by Bredenberg in 1987 [20]. Catechol and phenol were shown to be the dominant products at 400 °C. A free radical reaction combined with a concerted reaction mechanism were suggested to explain guaiacol pyrolysis. Other substituted monomeric phenolic components such as syringol, isoeugenol, vanillin, anisole and dimethoxy-phenols were tested by Klein in 1981 [21]. It was concluded that the principal reactions of those compounds during pyrolysis are de-methylation, isomerisation and de-methoxylation. A free radical mechanism has been proposed by Schlosberg [22] and Masuku [23] to explain the pyrolysis of monomeric lignin components.

In this study, the pyrolysis conversion of vanillyl alcohol (VA) as a model component is studied. The structure of vanillyl alcohol is compared to those of the three building blocks of lignin and illustrated in Fig. 1.

The catalysts applied in this chapter are the same materials which were used in the catalytic upgrading of lignocellulose (pine

Table 1
Selectivities based on TIC area % of main groups of products formed in the catalytic pyrolysis of cellulose, hemicellulose and lignin.

Component of biomass	Aliphatic HCs	Furans	Carbonyls	Acids	Aromatics[a]
Cellulose	20.2	33.3	36.9	1.9	1.6
Hemicellulose	25.9	63.6	6.6	0.0	3.9
Lignin	11.8	52.4	1.3	0.0	32.3

[a] Consists of substituted phenols and aromatic hydrocarbons.

wood) in our previous study [11]. Vanillyl alcohol was selected since it contains all three types of functional groups attached to the aromatic ring as in lignin derivatives, namely: (i) alkyl group, via C–C bonds (ii) alkoxy group, C–O bonds and (iii) hydroxyl group, C–O bonds. The object of such a model component study is to (i) investigate the chemistry of the catalytic upgrading of lignin-derived components, (ii) comparing the effectiveness of different catalytic materials to cleave different bonds and (iii) determine the possible correlations between the conversion of lignin model component, vanillyl alcohol, and the conversion the lignocelluosic biomass, i.e. lignin in the presence of cellulose and hemicellulose, over those catalysts.

2. Material and methods

2.1. Materials

γ-Al$_2$O$_3$ (catalyst support) was obtained from Akzo Nobel, Na$_2$CO$_3$ (reagent grade >99.5%) and quartz reference material from Sigma–Aldrich. 20 wt.% Na$_2$CO$_3$/γ-Al$_2$O$_3$ catalyst was prepared applying wet impregnation. The catalyst were dried over night at 110 °C to remove all excess water and finally calcined at 550 °C for 12 h (10 °C min^{-1}) under air flow (200 mL min^{-1}). Vanillyl alcohol (>98%), cellulose (microcrystalline, colloidal, >90%), hemicellulose (as xylan from beechwood, >90%), lignin (organosolv, >90%) were purchased from Sigma Aldrich.

2.2. Catalytic testing

The experimental set-up and applied definitions are described in detail in an earlier publication [2]. In each experiment, 1 g of vanillyl alcohol and 1 g of catalyst were loaded into the pyrolysis and catalyst chambers, respectively. Temperature of the catalyst bed was maintained at 500 °C for all experiments. The flow of Ar carrier gas was 70 mL min^{-1}. At the beginning of each experiment, vanillyl alcohol was quickly brought to its boiling point (ca. 293 °C) in less than 5 sec. The formed vapour was then pushed by the Ar flow into the catalyst bed. The condensable products were collected in two consecutives condensers kept at −40 °C. The condensable products were dissolved in acetone with the mass ratio of acetone: products of 95:5 and was subjected to GC-MS analyses. Components