



# 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.  $\gamma$ - $\text{Al}_2\text{O}_3$  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  $\gamma$ - $\text{Al}_2\text{O}_3$  was shown to have excellent de-oxygenation activity [11].

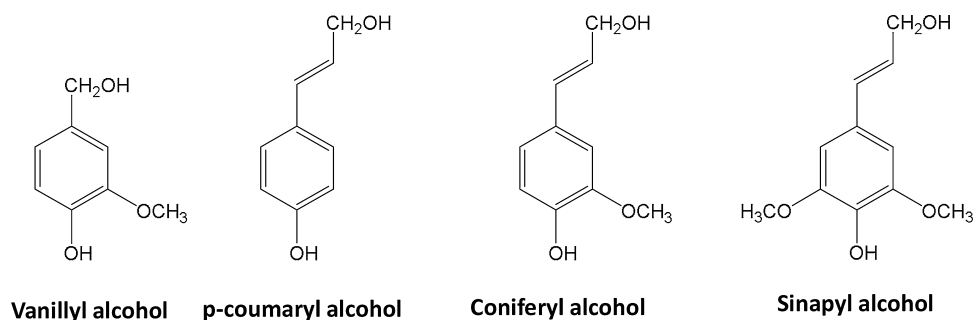
Lignocellulosic biomass is mainly composed of cellulose, hemicellulose, and lignin. Cellulose (a crystalline polymer of glucose) and hemicellulose (an amorphous polymer, whose major component is a xylose monomer unit) make up 60–90 wt% of terrestrial biomass [1]. Lignin, a large polyaromatic matrix made 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.%  $\text{Na}_2\text{CO}_3/\gamma$ - $\text{Al}_2\text{O}_3$  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  $\text{CO}_2$ , 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

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**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  $\beta$ -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 <sup>a</sup>
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

<sup>a</sup> 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 lignocellulosic biomass, i.e. lignin in the presence of cellulose and hemicellulose, over those catalysts.

## 2. Material and methods

### 2.1. Materials

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> (catalyst support) was obtained from Akzo Nobel, Na<sub>2</sub>CO<sub>3</sub> (reagent grade >99.5%) and quartz reference material from Sigma–Aldrich. 20 wt.% Na<sub>2</sub>CO<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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<sup>-1</sup>) under air flow (200 mL min<sup>-1</sup>). 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<sup>-1</sup>. 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 consecutive 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

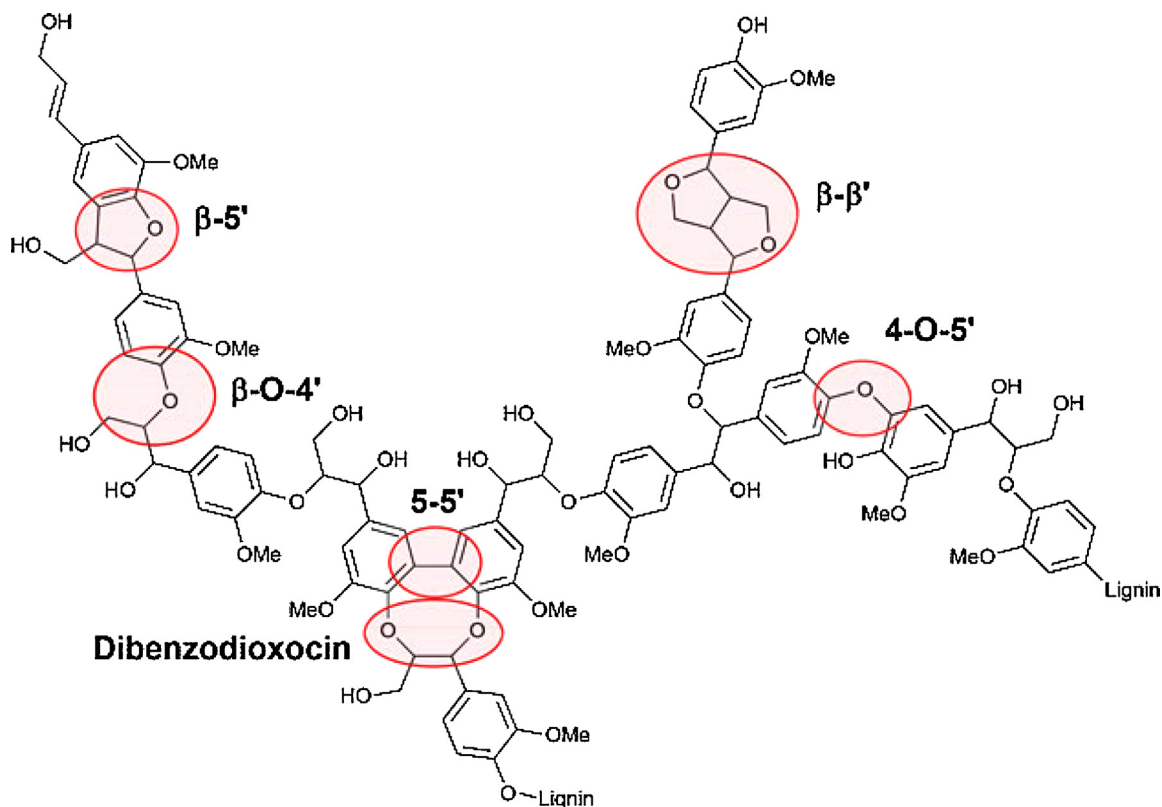


Fig. 2. Representative structure of lignin with some highlighted common linkages.

were identified comparing their mass spectra with the NIST mass spectral data library NIST08. Information about the database can be found in the NIST website [24]. In order to determine the distribution of these components, a semi-quantitative study was made by means of the percentage area of the total ion chromatogram (TIC) peaks. Detected components in the condensable phase were classified into five main groups based on their functionalities, namely: aromatic hydrocarbons, methoxy aromatic hydrocarbons, phenols, methoxy phenols, and cyclic pentenones. TIC area % of these groups were used to compare the differences in composition of the condensable fraction and calculated by summing up the area % of all corresponding members in those groups. The yield of the condensable phase is determined by the change in weight of the condensers before and after experiment. The yield of coke formed on catalysts was determined by carrying out TGA experiment of the catalyst-coke mixture in air. The gas yield was calculated by difference, assuming that the yields of the condensable phase, coke and gas make up to 100% of the original mass of VA.

### 3. Results and discussion

#### 3.1. Reference experiment

In the reference experiment, 1 g of an inert material, *i.e.* quartz, was used. The detected components in the condensable (liquid) phase are shown in Table S.1 along with their structures, group, and TIC area %. As can be seen, most of the starting material vanillyl alcohol was not converted during the reference experiment, shown by the highest area % of this component (*ca.* 85%). The two components with the second and third highest area % were vanillin and 2-methoxy-4-methylphenol (8.4% and 4.8%, respectively). They are likely the products from the self-oxidation of VA. There are other products presenting in small area %, resulted from the thermal decomposition of VA over quartz (Table S.1).

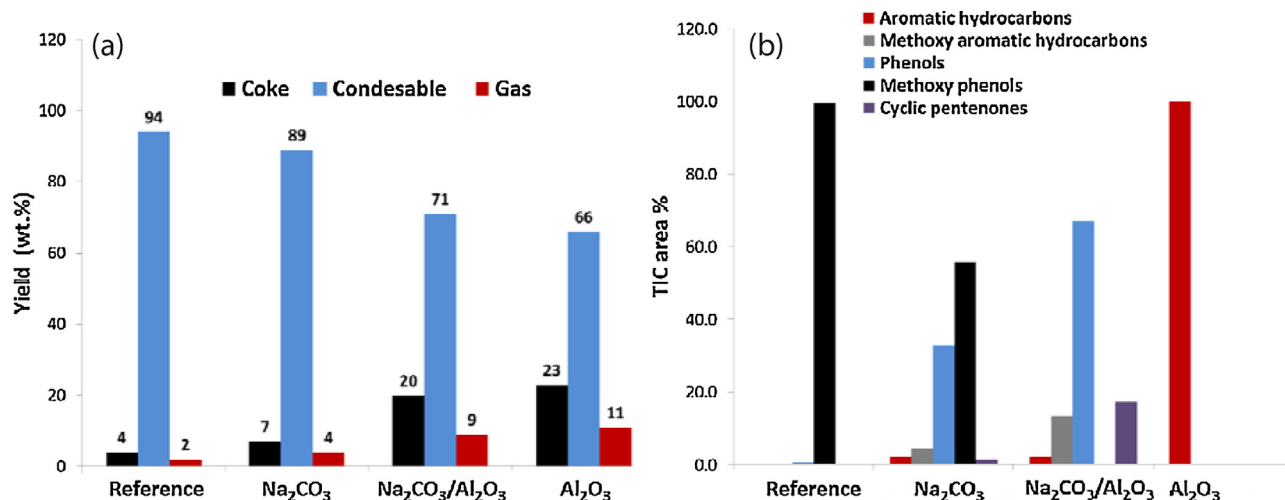
The yields of the three products, *i.e.* condensable, coke and gas, from the thermal and catalytic conversion of vanillyl alcohol are summarised in Fig. 3a. It can be seen that only minor amount of coke (4 wt.%) and gas (2 wt.%) were formed in the reference experiment, which correlates to the low conversion of this model component as mentioned previously.

Previous studies on non-catalytic, thermal pyrolysis of monomeric model components of lignin showed them to occur *via* a free radical mechanism [22,23]. The mechanism of vanillin pyrolysis was studied by Shin *et al.* using mass spectrometer and multivariate analysis at the pyrolysis temperatures of 500, 650 and 800 °C [25]. It was shown by Shin that at 500 °C vanillin was hardly converted, which agrees well with our result of the reference experiment. The low conversion of vanillyl alcohol observed in the non-catalytic experiment can be explained by the fact that the formation of free radicals requires the homolytic cleavage of chemical bonds; and at 500 °C there is not enough thermal energy for the necessary for the necessary bond scission to occur.

Fig. 3b illustrates the change in TIC area % of different groups of components in the condensable phase under the influence of different catalytic materials. It can be seen that there is hardly any de-oxygenation occurring on the quartz material and almost all products obtained in the reference experiment are methoxy phenols. This is expected because of the inertness of quartz material and de-oxygenation requires the presence of an acid catalyst. Typically thermal pyrolysis of lignocellulosic biomass results in a bio-oil which has similar oxygen content (~42 wt%) as that in the starting material [2].

#### 3.2. Catalytic experiments

In catalytic experiments, quartz material was replaced with different catalysts. All reaction conditions were the same as those in the reference experiment. Compositions of the condensable



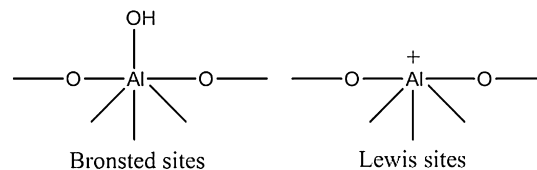
**Fig. 3.** The effect of different catalysts to: (a) yields of coke, condensable, gas products, wt.% and (b) TIC area % of different groups in the condensable fraction. Reaction conditions: 500 °C, 2 s, 1 g of VA and 1 g of catalyst.

fractions obtained with Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and γ-Al<sub>2</sub>O<sub>3</sub> catalysts are shown in Table S.2, S.3 and S.4, respectively. TIC area % of the five groups of components are compared in Fig. 3b and the mass balances shown in Fig. 3a. It was shown that in an inert atmosphere Na<sub>2</sub>CO<sub>3</sub> was stable up to 850 °C whereas Na<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> decomposed readily into Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> starting from 135 °C [11]. This suggests that during the model compound experiment with Na<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, which was carried out at 500 °C, the actual catalyst is Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>. Compared to Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>O is more basic and this might lead to completely different catalytic effects.

It can be seen in Tables S2–S4 that vanillyl alcohol was not detected in any of the catalytic experiments, which suggests that it was fully converted in presence of the catalysts. Similar to the reference experiment, methoxy phenols are the most abundant in the condensable fraction obtained with Na<sub>2</sub>CO<sub>3</sub> catalyst, as can be seen in Fig. 3b. However, the amount of phenols has increased significantly, along with the formation of other groups of components, for e.g. cyclic pentenones, aromatic hydrocarbons, etc. which were not present in the reference experiment. This trend continues with Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst, with which methoxy phenols were not detected in the condensable phase and instead phenols became the dominant group in terms of TIC area (67%). Moreover, compared to Na<sub>2</sub>CO<sub>3</sub> catalyst, the area % of aromatic hydrocarbons in presence of Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> is similar but those of methoxy aromatic hydrocarbons and cyclic pentenones have increased as shown in Fig. 3b. Finally, there is a tremendous change in the composition of the condensable phase obtained with γ-Al<sub>2</sub>O<sub>3</sub>, which separates this catalyst from the rest of the materials used in this study (Table S.4 and Fig. 3b). As can be seen, oxygenates are no longer detected in the condensable phase in presence of γ-Al<sub>2</sub>O<sub>3</sub>. Detected components all fall into the aromatic hydrocarbons category. It can be seen in Fig. 3a that compared to the reference case, there is more coke and gas and less condensable products obtained in all of the catalytic experiments; and the coke and gas yield was maximised on γ-Al<sub>2</sub>O<sub>3</sub> catalyst.

### 3.3. Proposed pathways for the conversion of vanillyl alcohol

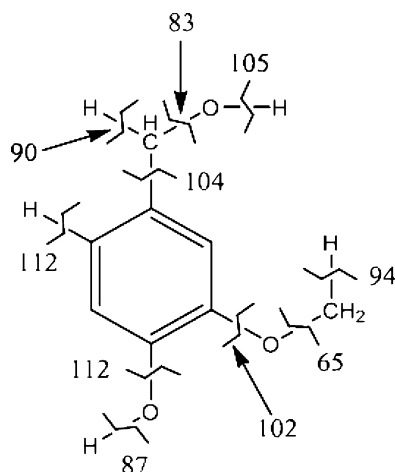
Earlier studies in which γ-Al<sub>2</sub>O<sub>3</sub> was placed in contact with a series of indicator dyes of varying basicity suggest that the surface has modest acidity [26]. <sup>13</sup>C NMR studies of n-butylamine adsorbed on γ-Al<sub>2</sub>O<sub>3</sub> demonstrate that both Lewis and Bronsted acid sites co-exist on the surface [27]. These two types of acid sites are illustrated in Fig. 4.



**Fig. 4.** Illustration of Bronsted and Lewis acid sites in γ-Al<sub>2</sub>O<sub>3</sub> [30].

A trend that can be easily seen in Fig. 3b that the more acidic the catalyst is, the more deoxygenated products were obtained. As discussed previously, with the non-acidic quartz and Na<sub>2</sub>CO<sub>3</sub>, methoxy phenols were the dominant products. The lack of acid function in the two materials prevented the catalytic conversion into phenols and aromatic hydrocarbons. On the catalysts with acid sites, such as Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and γ-Al<sub>2</sub>O<sub>3</sub>, VA was deoxygenated into phenols and aromatic hydrocarbons, thus decreasing the yield of the condensable phase and increasing the yield of the coke and gas, as can be seen in Fig. 3a. It was shown in our previous study [11] that there is an interaction between Na<sub>2</sub>CO<sub>3</sub> and the acid sites on the surface of alumina, thus the number of acid sites in Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> is expected to be less than that in γ-Al<sub>2</sub>O<sub>3</sub>. This explains the higher aromatic hydrocarbon and coke yields in the presence of pure alumina. It was proposed by Ma et al., that acid sites in zeolites cause dehydration, decarboxylation, dealkylation, cracking, isomerisation, oligomerisation, etc. of lignin into aromatic hydrocarbons [28]. Mullen and Boateng also proposed two pathways to explain the formation of aromatic hydrocarbons in the catalytic pyrolysis of lignin over H-ZSM5 catalyst [29]. Both pathways begin with the de-polymerisation of lignin over HZSM-5 to form: (i) small olefins from the aliphatic linkers of the lignin matrix and (ii) alkoxy phenolic monomers. In the first pathway, aromatic hydrocarbons were formed via the aromatisation of the olefins over HZSM-5. The second pathway involves the direct de-oxygenation of the alkoxy phenols over the zeolite into the corresponding aromatic hydrocarbons. However, we never detected significant amounts of olefins in our experiments, which suggests that either: (i) the catalytic conversion of VA occurred via the second pathway or (ii) the olefins were rapidly converted into aromatics.

As mentioned previously the pyrolysis of vanillyl alcohol likely occurs via a free radical mechanism, initialised by the homolytic cleavage of C–C and C–O bonds in this molecule. Thus an important consideration to have is the corresponding bond disassociation energies. Although these bond disassociation energies have not

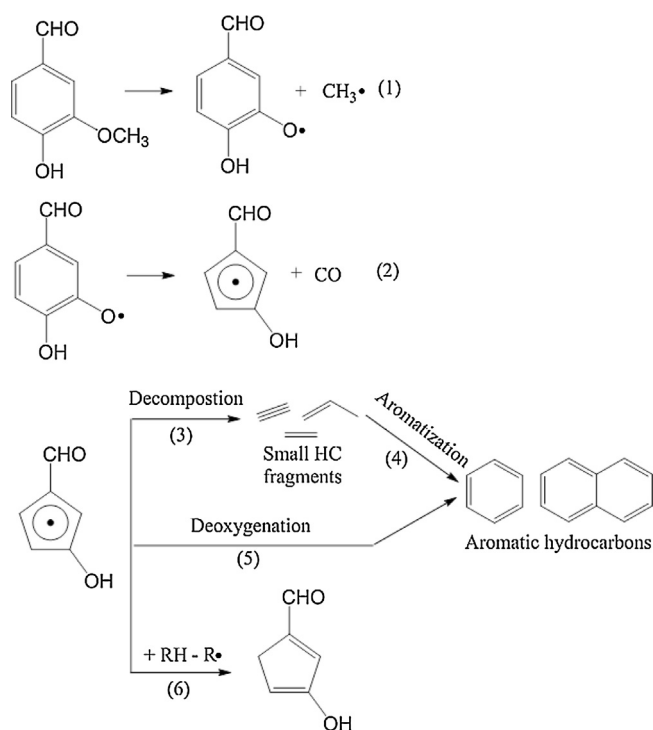


**Fig. 5.** Estimated bond dissociation energies in vanillyl alcohol molecule by Shin [25] and Blanksby et al. [31], shown in  $\text{kCal mol}^{-1}$ .

been measured directly, one can approximate their values as being close to anisole ( $\text{C}_6\text{H}_5\text{CH}_3$ ), phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) and benzyl alcohol ( $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ ) and are summarised in Fig. 5.

As can be seen, the disassociation energy of the C–O bond between a C atom of the aromatic ring and an O atom of the hydroxyl group is the highest ( $112 \text{ kCal mol}^{-1}$ ). It thus requires a large amount of thermal energy or a proper catalyst to facilitate the scission of this bond. For this reason most of the catalysts except for  $\gamma\text{-Al}_2\text{O}_3$  resulted in a condensable phase which is rich in phenol derivatives (methoxy phenols and phenols).

Shin et al. has carried out a study on the mechanism of vanillin pyrolysis using mass spectrometry and multivariate analysis [25]. He showed that the weakest bond in vanillin is the C–O bond on the methoxy group and suggested that the unimolecular decomposition of vanillin would be dominated by the scission of this bond, forming a substituted phenoxy radical (Fig. 6, step



**Fig. 6.** Multiple steps in the unimolecular decomposition of vanillin, proposed by Shin et al. [25].

1). Further unimolecular rupture could result in an expulsion of CO (de-carbonylation) to form a cyclopenta-di-enyl radical (step 2). The cyclopenta-di-enyl radical formed in step 2 can undergo different pathways to form aromatic hydrocarbon and cyclopenta-di-en products (step 3–6). Step 3 involves the decomposition of cyclopenta-di-enyl radical into small hydrocarbon fragments and molecules, *i.e.*  $\text{C}_3\text{H}_3$ ,  $\text{C}_2\text{H}_2$ , *etc.*, followed by aromatisation of these fragments into aromatic hydrocarbons (step 4). The cyclopenta-di-enyl can also be deoxygenated directly to form the corresponding aromatic hydrocarbons (step 5). Despite working with different feedstocks, *i.e.*, lignin or a monomeric model component of lignin (vanillin), both Mullen [29] (shown previously) and Shin [25] et al. arrived at a very similar conclusion regarding the pathways to aromatic hydrocarbons: either *via* the aromatisation of small unsaturated fragments or the direct de-oxygenation of monomeric species. Finally, the cyclopenta-di-enyl radical formed in step 2 can also abstract a H atom from other hydrocarbons to form a cyclopenta-di-ene (step 6). All the pathways described above can also be correlated to our study because of the similarities in: (i) the acidic nature of the catalysts, *i.e.*  $\gamma\text{-Al}_2\text{O}_3$  and HZSM-5 even though they possess different strengths, and (ii) the starting material, *i.e.* vanillyl alcohol, lignin, vanillin possess similar structures. The formation of the above-mentioned cyclopenta-di-enyl radical is likely the foundation for the generation of the cyclic pentenones detected in our study (Tables S2 and S3).

### 3.4. Correlation with the catalytic pyrolysis of biomass

So far in this study we have discussed the conversion of vanillyl alcohol as a model component of lignin-derived components over  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ , and  $\gamma\text{-Al}_2\text{O}_3$  catalysts. The same catalysts have also been employed in the upgrading of biomass pyrolysis vapour into bio-oil, of which the results were discussed thoroughly in our previous work [11]. Thus it is useful to establish if a correlation between the chemical profiles of the main products in biomass conversion, *i.e.* bio-oil, and that in model component conversion, *i.e.* the condensable phase, exists. The three chemical groups which were detected in both the bio-oil and the condensable phase are cyclic pentenones, phenol derivatives and aromatic hydrocarbons. The abundance of these 3 groups in bio-oil and condensable phase in presence of different catalysts, represented by the corresponding TIC area %, are illustrated in Fig. 7.

Various cyclic pentenones have been detected in both bio-oil and the condensable fraction from VA pyrolysis. The cyclic pentenones found in bio-oil can be the decomposition products of both the carbohydrate fraction (cellulose, hemicellulose) and the lignin fraction of biomass. On the other hand, the possible pathway leading to the formation of cyclic pentenones from VA has been discussed previously. One interesting trend observed in Fig. 7 is that the change in TIC area % of cyclic pentenones in both bio-oil and condensable phase are similar. The area % begins with an average value for  $\text{Na}_2\text{CO}_3$ , maximised with  $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalyst and becoming minimal with  $\text{Al}_2\text{O}_3$ . The only difference is, in bio-oil, the gap between the area % of cyclic pentenones obtained with  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalysts is small while that in the condensable phase obtained from the conversion of VA is much bigger. This suggests that  $\text{Na}_2\text{CO}_3$  might be more efficient in converting the carbohydrate part of biomass into cyclic pentenones compared to the lignin part.

The change in area % of phenol derivatives and aromatic hydrocarbons in bio-oil and condensable phase also have similar trend. However, the rates of change in the two cases are different. The rate of change of both phenol derivatives and aromatic hydrocarbons with the condensable phase is always faster, especially when  $\gamma\text{-Al}_2\text{O}_3$  is applied. Again, this can be attributed to the difference in

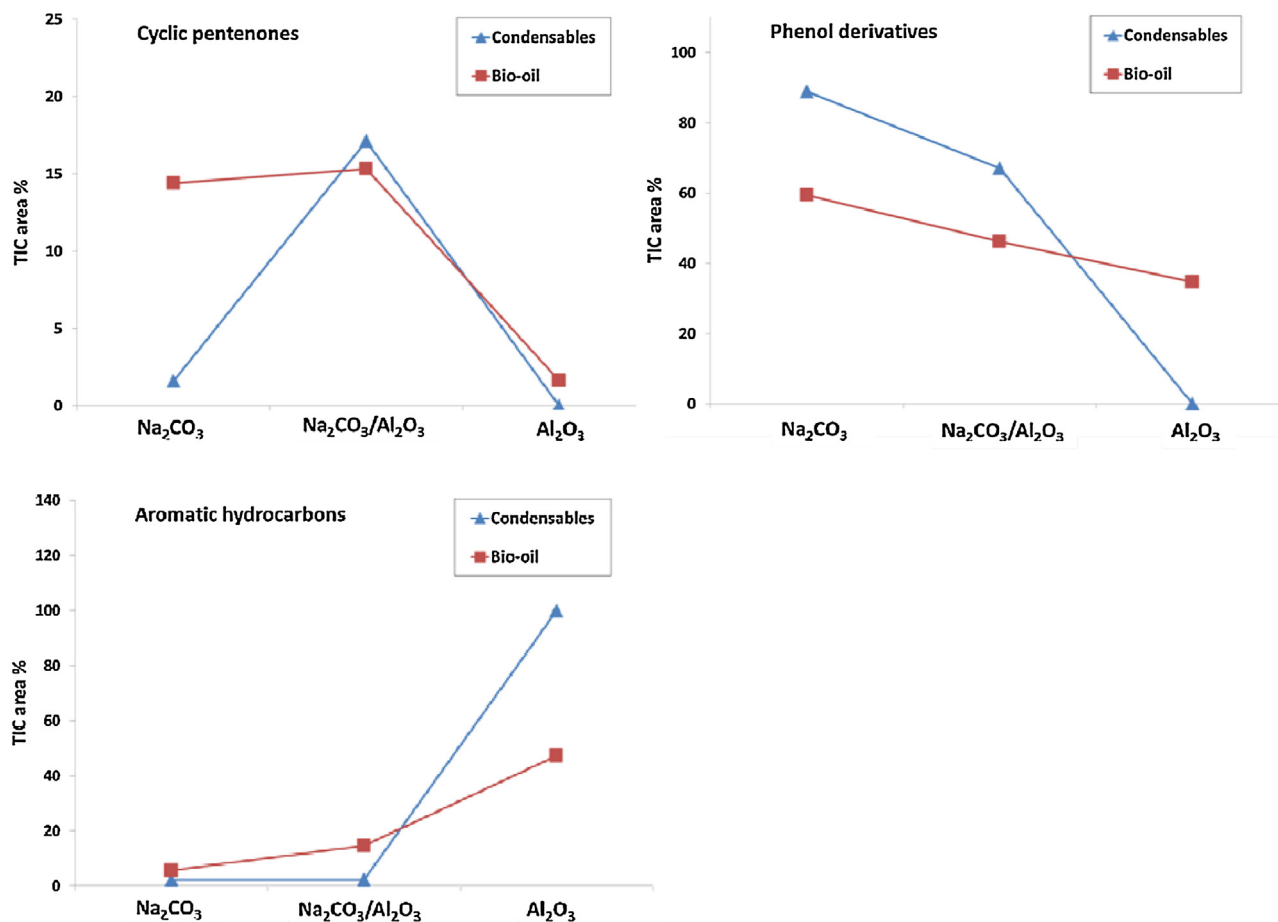


Fig. 7. The change in composition of bio-oil from biomass pyrolysis and condensable (liquid) phase from VA conversion over different catalytic materials.

catalytic efficiency of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> towards the conversion of carbohydrate and lignin fractions of biomass.

There are two conclusions that can be drawn based on the above discussion, which are: (i) lignin plays an important role in the chemistry of biomass pyrolysis and thus in determining the chemical profile and properties of the obtained bio-oil and (ii) vanillyl alcohol is a promising model component to study the behaviour of lignin in catalytic pyrolysis. However, more study should be carried out to gain deeper insight into this field, for e.g. comparison of lignin and vanillin alcohol pyrolysis over the catalysts.

#### 4. Conclusions

Extent of de-oxygenation of vanillyl alcohol increased with the increase in number of acid sites in the catalyst. Consequently,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the most acidic among the catalysts studied, was an efficient de-oxygenation catalyst, resulting in mostly aromatic hydrocarbon products. Two pathways have been shown leading to the formation of aromatic hydrocarbons from vanillyl alcohol, which are: (i) the decomposition of vanillyl alcohol into small olefinic hydrocarbon fragments and the subsequent aromatisation into final products and (ii) the direct de-oxygenation of vanillyl alcohol over the catalysts. Comparison of the chemical profiles between biomass and vanillyl alcohol pyrolysis has shown similarities between the two cases in terms of the trend of change. However, there are differences in the rate of change which can be attributed to difference in the catalytic efficiency towards different components of biomass (cellulose, hemicellulose, lignin).

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cattod.2015.04.043>

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