

Kinetic Studies of Catalytic Upgradation of Biomass Model Compounds Using Analytical Py-GC/MS

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Global energy demand and depletion of fossil-derived fuels have posed an alarming need for alternate fuels. Lignocellulosic biomass is one of the most promising sustainable carbon-rich feedstocks that can be directly converted to biofuels via fast pyrolysis technique. It involves thermochemical decomposition at very high heating rate ($\sim 10^4$ °C s⁻¹), moderate temperatures (400-600 °C) and short residence time (1-5 s) in inert ambience to yield bio-oil. However, significant presence of oxygen-containing chemicals in bio-oil is the root cause of various unenviable properties. The prime objective is to minimize the substantial amount of oxygen content in bio-oil by selectively altering the organic oxygenates into hydrocarbons through deoxygenation pathways. Accordingly, catalytic upgrading of pyrolysis vapours in hydrogen ambience is a promising strategy to tailor the chemical composition of bio-oil to a greater extent via hydrodeoxygenation (HDO). However, it is mandatory to understand the ex-situ upgradation kinetics of organic vapours on the catalyst surface. To this end, mechanistic insight into deoxygenation of catalytically upgraded representative biomass pyrolysates such as guaiacol and furfural over protonated Zeolite Y catalysts of different Si/Al ratios were investigated in this study. Analytical pyroprobe connected with Gas Chromatograph/Mass Spectrometer (Py-GC/MS) served in testing the HDO activity of catalysts. The use of catalysts significantly led to better HDO producing remarkable aromatic hydrocarbons in the condensed phase. Protonated Zeolite Y (Si/Al ratio: 5.1:1 and 30:1) catalysts converted guaiacol into valuable chemicals, viz. benzene, toluene, and xylene (BTX) in major quantities. Notably, 100% conversion of guaiacol and furfural were achieved with Zeolite Y (5.1:1).

1. Introduction

The most promising alternative to petroleum based fuels and chemicals could be biomass, the key source of renewable carbon. Importantly, the fuels and chemicals derived from biomass not only caters to the energy demand but also stands out in terms of less greenhouse gas emission, waste resource recovery, production of green chemicals, near carbon neutrality in the environment. Hence, lignocellulosic biomass consisting of three major parts: cellulose, hemicellulose and lignin can be utilized for the production of fine chemicals and refinery ready fuel blendstocks. However, there are several technological and economical setbacks in bringing this technology into existence. Fast pyrolysis is a potential technique for the effective utilization of lignocellulosic biomass, in which the feedstock is thermally degraded at a very high heating rate ($\sim 10^4$ °C s⁻¹), short residence time (1-5 s), and moderate temperatures (400-600 °C) to produce $\sim 75\%$ of liquid product called "bio-oil" (Xiu et al., 2012). The characteristics of the biomass have a strong correlation with the pyrolysis behavior (Braz et al., 2014) and product composition (Huber et al., 2006). Bio-oil is a complex mixture of several organic compounds. Nevertheless, the existence of high amount of oxygen content in bio-oil due the structural backbone of biomass, leads to various practical issues such as polymerization during storage, immiscibility with existing fuels, low heating value, and high moisture content (Czernik et al., 2004). Hence, catalytic upgrading of pyrolysis vapours could help greatly in altering the chemical composition of bio-oil into gasoline range aromatic hydrocarbons via deoxygenation routes. Deoxygenation of the organic compounds is plausible through dehydration (-H₂O), decarbonylation (-CO), and decarboxylation (-CO₂) routes. However,

dehydration is more favorable than the other two routes mainly because of the carbon loss in the latter. In catalytic fast pyrolysis (CFP), the pyrolysis vapours from degraded biomass are upgraded on the surface and in the pores of the catalyst, resulting in the production of permanent gases (CO, CO₂, H₂O, CH₄), linear and cyclic oxygenates, and hydrocarbons. Deoxygenation is an acid catalyzed reaction and especially Zeolite, known for their acid sites, can be well utilized for this purpose (Adjaye et al., 1994). Understanding the deoxygenation chemistry of pyrolysis vapours from biomass is highly complicated due to the complex mixture of various organic compounds. Hence, studies on representative compounds from thermal pyrolysis could play an important role in understanding the reaction mechanism and consequently, aid in the development of suitable deoxygenation catalysts. In this study, two model compounds, viz. guaiacol and furfural representing lignin and sugar fraction of biomass, respectively are selected for understanding their conversion mechanisms over protonated Zeolite Y catalysts of different Si/Al ratios.

Guaiacol, a monomer of lignin, is considered to be a plausible prototypical compound as it consist of both hydroxyl and methoxy functional groups, representing a large number of substituted guaiacol and phenolic groups in bio-oil. Moreover, the existence of guaiacol and substituted phenols with high selectivity leads to the formation of heavy hydrocarbons during storage and cause stability issues. There are several works reported in literatures on guaiacol conversion over various catalysts. In one of the works, zirconia supported noble metal catalysts (Rh, Pd, Pt) exhibited high hydrogenation and hydrodeoxygenation activity on guaiacol at 100 °C and 300 °C, respectively (Gutierrez et al., 2009). Whereas, platinum metal supported on H-MFI Zeolite exhibited 100% conversion and > 90% selectivity to cyclohexane (Hellinger et al., 2015). The mechanism clearly stated hydrogenation to be the first step, and acid catalyzed dehydration along with hydrogenation to be the second step. Studies on hydrodeoxygenation of guaiacol over carbon nanofibre supported W₂C and Mo₂C catalysts executed at 55 bar hydrogen pressure yielded more of phenolics at 300-375 °C (Jongerius et al., 2013). The key finding of this work reported reaction temperature and time to play a crucial role in the formation of fully hydrodeoxygenated products like benzene and toluene. The metal and metal deposited acidic matrices are responsible for aromatic ring hydrogenation and hydrodeoxygenation of oxygenates, respectively (Lee et al., 2012). This was elucidated using guaiacol as the model compound using various combinations of noble metals (Pt, Rh, Pd, Ru) and acid matrices (Al₂O₃, SiO₂-Al₂O₃). Furfural is a heterocyclic compound consisting of a furan, with a hydrogen atom at position 2 substituted by a formyl group. It is one of the key intermediates in the production of valuable chemicals (Gallezot, 2012). Adsorption and reaction of furfural on the surface of the catalyst plays an important role in determining the end product (Shi et al., 2015). On a Pt (111), furfural was found to bond using the aromatic ring, whereas on a Zn-modified Pt (111), it adsorbs via aldehyde carbonyl. Hence, desired end product can be produced by designing the suitable catalysts. Hydrodeoxygenation of furfural and guaiacol were carried out in an analytical pyrolyzer as a function of Zeolite Y catalyst acidity at atmospheric pressure.

2. Experimental section

2.1 Materials

In this study, guaiacol and furfural (99% purity, purchased from Alfa Aesar) were used as representatives of biomass pyrolysates. These compounds were used as received. Protonated Zeolite Y (ZY) catalysts of different Si/Al mole ratios (5.1, 30, 60, and 80) purchased from Alfa Aesar were used for evaluating the deoxygenation activity. The catalysts were calcined at 700 °C for 7 hours prior to use. The characteristic properties of the catalysts were determined as mentioned below in Table 1.

Table 1: Properties of catalysts

Catalysts	Si/Al (mole ratio)	Total Acidity (mmol g ⁻¹)	T _{max} of h peak (°C)	Micropore area (m ² g ⁻¹)	External surface area (m ² g ⁻¹)	BET surface area (m ² g ⁻¹)	Average pore diameter (Å)	Micropore volume (cm ³ g ⁻¹)
Zeolite Y	5.1:1	1.3614	245	594	53	647	55.7	0.29
Zeolite Y	30:1	0.5553	354.6	555	193	748	129.9	0.27
Zeolite Y	60:1	0.3332	353.5	548	226	775	63.9	0.26
Zeolite Y	80:1	nd	nd	454	264	718	56.1	0.22

nd- not determined

2.2 Catalytic conversion experiments

The CDS Pyroprobe[®] 5200 analytical pyrolyzer was used for testing the deoxygenation activity along with gas chromatograph (GC) and mass spectrometer (MS) (Agilent 7890, 5975). Typically, 0.3 ± 0.005 mg of pure model compound i.e. guaiacol/furfural was weighed accurately using a Sartorius CUBIC series microbalance. The weighed sample was placed in the middle of a 2 mm i.d. and 20 mm length quartz tube. Quartz wool packed on either side of the quartz tube aided in preventing the spillage of the sample. Subsequently, the quartz tube was inserted horizontally into the platinum coil and resistively heated. Guaiacol/furfural was programmed to vaporize at 200 °C with a ramp rate of 10 °C ms⁻¹ for 60 s. Vapours of model compound were carried by hydrogen gas to the catalyst upgradation zone maintained at 500 °C. Ex-situ conversion of model compounds occurs over the ZY catalyst of different Si/Al mole ratios (5.1, 30, 60, 80) with a catalyst to compound weight proportion of 10:1. The upgraded vapours were carried to GC injector maintained at 300 °C with a split ratio of 83.333:1. Agilent HP-5ms column (30 m length × 250 μm diameter × 0.25 μm thickness) with a flow rate of 1.2 mL min⁻¹ enabled the separation of various organics employing the following program: 40 °C for 5 min, ramped at 5 °C min⁻¹ to 280 °C and held for 10 min. The vapours were scanned with MS ionization voltage of 70 eV and mass-to-charge range of 10-300 Da. MS ion source and quadrupole were set at 250 °C and 150 °C, respectively. Mass spectra of various peaks (with high match factor, >85%) in the total ion chromatogram (TIC) were compared with the NIST library to perform the product identification. The identified compounds with higher relative peak area% were calibrated in GC using standard pure samples through manual injection method. This was plausible using known concentrations of the samples prepared using dichloromethane (DCM) as the solvent. Henceforth, the HDO products obtained from the experiments are depicted in terms of yield (wt. %) and carbon yield (wt. %). The carbon yield (wt. %) depicts the closure of carbon balance and it is very important because analysis of permanent gases was not possible in this work. All the experiments were repeated twice and the data reported is an average with 4-8% error.

3. Results and discussions

3.1 Catalytic Conversion of Guaiacol

The conversion of guaiacol was carried out over various ZY catalysts of different Si/Al ratios (5.1, 30, 60 and 80) with catalyst bed maintained at 500 °C. The TIC obtained from non-catalytic and catalytic experiments are depicted in Figure 1. Non-catalytic vaporization of guaiacol showed a clear single peak of guaiacol in MS, whereas catalytic conversion resulted in the formation of benzene, toluene, and phenol with high absolute area. Absolute areas of major compound peaks obtained from TIC plots were converted into yield (wt. %) using the calibration values.

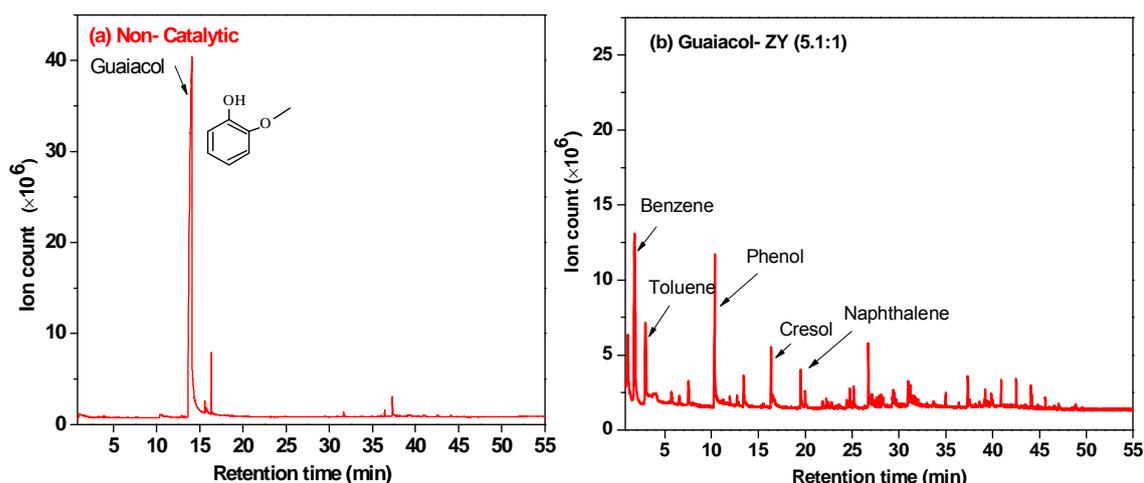


Figure 1: GC/MS TIC of guaiacol conversion. (a) Non-catalytic, (b) using ZY (5.1:1) catalyst.

From Figure 2a, it is observed that in the non-catalytic vapourization of guaiacol, it is possible to achieve a mass closure of ~94%. On the other hand, catalytic conversion over Zeolites resulted in the overall average yield (wt. %) range of 40-50%. The overall yield of products using ZY 5.1, 30, 60 and 80 are 40.1%, 48.9%, 35.4% and 36%, respectively. Higher yield with ZY (30) correlates with the high pore volume and average pore diameter, preventing the occurrence of pore blockage during evolution of volatiles from the pores of the catalyst. The blockage of pores due to volatiles could be accounted to the coke formation on the catalyst. There is almost complete conversion of guaiacol using highly acidic ZY catalysts of low Si/Al ratio. The notable HDO products with ZY (5.1 and 30) were phenol, benzene, toluene and naphthalene derivatives. However, the yield of partially deoxygenated product i.e. phenol is very low. In addition to the above products, traces of xylene and other phenols derivatives were also seen. Notably, the presence of naphthalene derivatives in the product stream with ZY (5.1 and 30) could be attributed to the higher pore volume. Higher pore volume would allow access to the bigger aromatic moieties. Although ZY (5.1) is highly acidic compared ZY (30), high BET surface area and pore diameter of ZY (30) promoted high deoxygenation activity than ZY (5.1). As the Si/Al ratios increase, which is an indication of lowering acidity, conversion of phenols and its derivatives to aromatic hydrocarbons were lower over less acidic ZY (60 and 80) catalysts. This is evident from the presence of guaiacol, phenol, and other phenols derivatives in significant quantities as depicted in Figure 2a. Traces of toluene are also observed. Unlike ZY (5.1 and 30), there was no formation of naphthalene derivatives and xylene. On comparison of the evolved products, it could be observed that the complete deoxygenated products i.e. aromatic hydrocarbons were produced over ZY catalysts of low Si/Al ratio. Whereas, partially deoxygenated products were produced using ZY of high Si/Al ratio. This strongly emphasizes the influence of acidity on deoxygenation chemistry.

Figure 2b depicts the overall carbon yield of various products evolved from guaiacol. The carbon yield obtained using ZY 5.1, 30, 60 and 80 were 52.8%, 63.7%, 41.1% and 44%, respectively. Remaining yield of carbon could be attributed to the formation of coke on catalysts and gases (CO, CO₂). Conversion of guaiacol to phenol occurred through a direct demethoxylation pathway in hydrogen ambience. Consequently, phenol underwent dehydration step in the presence of hydrogen to benzene. Dehydration mechanism was facilitated by the acidic sites in the ZY catalysts.

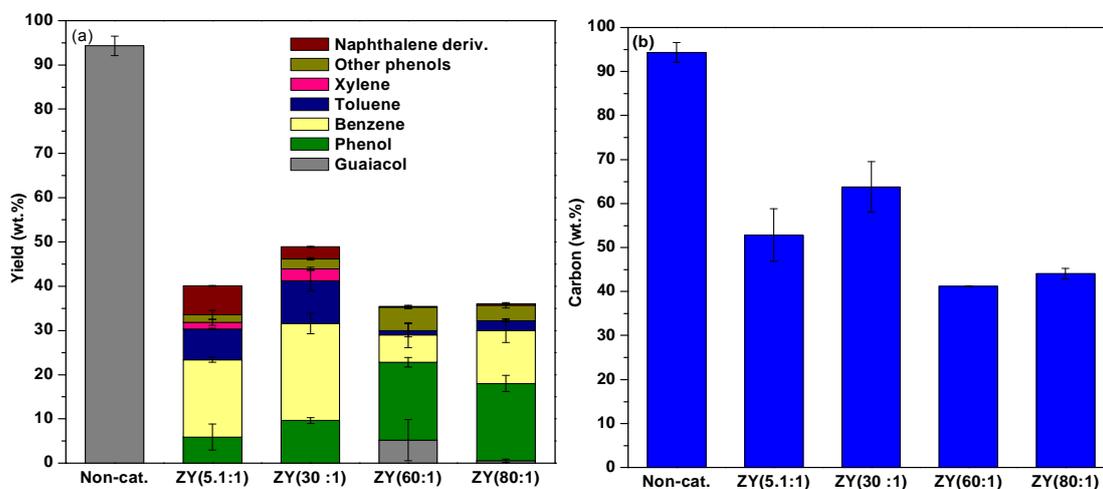


Figure 2: Comparison of product distribution from non-catalytic and catalytic conversion of guaiacol represented in terms of (a) yield (wt. %), (b) carbon yield (wt.%)

3.2 Catalytic Conversion of Furfural

Catalytic conversion of furfural over ZY catalysts will be discussed in this section. Figure 3 depicts the TIC plots of non-catalytic and catalytic conversion of furfural. In general, furfural was converted to furan and 2-methyl furan over ZY catalysts as depicted in Figure 4a. Furfural was not observed to appear in the product stream indicating its complete conversion, irrespective of the Si/Al ratio. There is no significant difference in the yield of pyrolysates with increase in Si/Al ratios. Also, the yield of furan and 2-methyl furan were independent of catalyst acidity. With non-catalytic experiments, the yield of furfural was ~80%. In catalytic experiments, on an average the yield of partially deoxygenated products was 35±5%. On the basis of carbon balance as shown in Figure 4b, the overall yields were non-catalytic (82.4%), ZY-5.1(43.8%), ZY-30 (47.6%),

ZY-60 (45.1%), ZY-80 (43.1%). Furan is produced by decarbonylation of the furfural. There are two routes for the production of 2-methyl furan. One could be by initial hydrogenation of furfural to furfuryl alcohol and a second stage hydrogenation of furfuryl alcohol to produce 2-methyl furan. Whereas, the second route is as follows: furfural selectively adsorbs onto the catalyst site via aldehyde group and cleavage of C-O bond occurs. Later, the $(C_4H_3O)-CH=$ intermediate would then be hydrogenated to produce 2-methyl furan. These are the possible mechanisms for the formation of furan and 2-methyl furan.

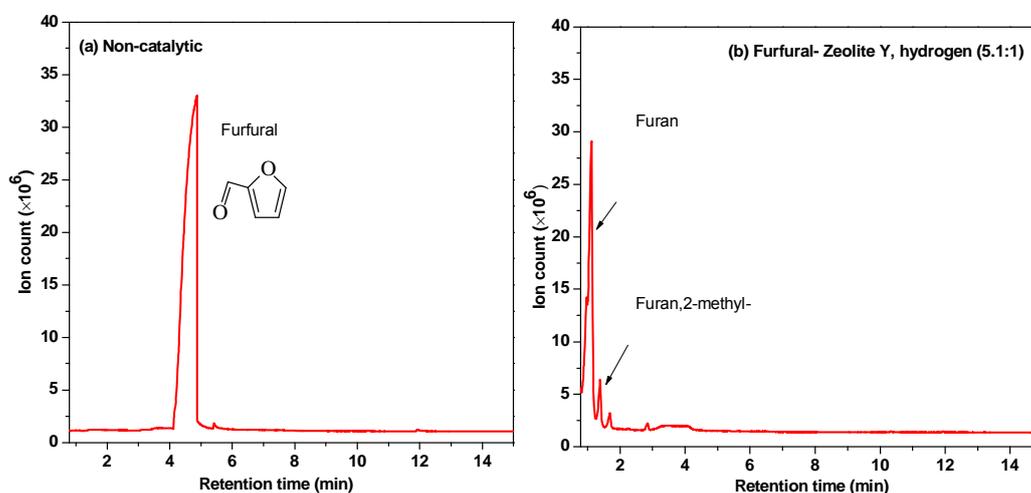


Figure 3: GC/MS TIC of furfural conversion. (a) Non-catalytic, (b) using ZY (5.1:1) catalyst.

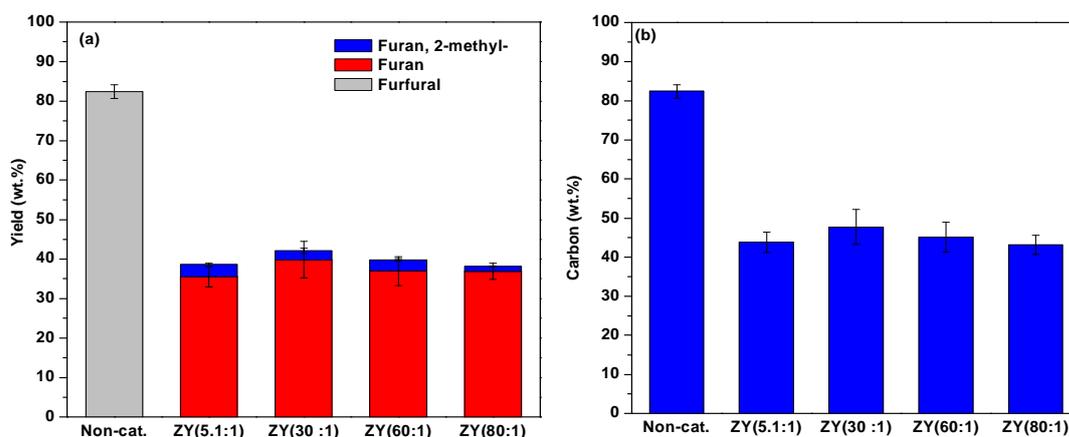


Figure 4: Comparison of product distribution from non-catalytic and catalytic conversion of furfural represented in terms of (a) yield (wt.%), (b) carbon yield (wt.%)

4. Conclusions

The product composition from catalytic conversion of guaiacol and furfural over ZY catalysts of different Si/Al ratios was investigated. Conversion of guaiacol over ZY catalysts of low Si/Al ratios, viz. 5.1 and 30, resulted in the production of aromatic hydrocarbons. The main hydrodeoxygenation products were benzene, toluene, xylene, and phenol. The yield of benzene was highest with ~19.5 wt. % over ZY (30:1). The yield of BTX in guaiacol conversion followed the trend: ZY-30 (30.5%) > ZY-5.1 (28.1%) > ZY-80 (12.0%) > ZY-60 (6.4%). This is possibly due to the interplay between pore diameter, BET surface area and total acidity of the catalysts. Importantly, the acidity of the catalyst played an important role in deoxygenation of the methoxy and hydroxyl groups of guaiacol. However, there was no significant effect of catalyst acidity on deoxygenation of furfural. Understanding the reaction chemistry can give us an insight to design more effective zeolite catalysts and reactors for efficient utilization of biomass resource. This study would be especially important in probing an economically and technically viable process for the conversion of biomass to fuels and thus transform transportation sector which is currently dependant on fossil fuels

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