Chemical routes to hydrocarbons from pyrolysis of lignocellulose using Cs promoted amorphous silica alumina catalyst

Masoud Zabeti [a], Jonas Baltrusaitis [b], K. Seshan [a],*

[a] Catalytic Processes and Materials group, Faculty of Science & Technology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands
[b] PhotoCatalytic Synthesis group, Faculty of Science & Technology, MESA+ Nanoinstitute, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

ABSTRACT

Lignocellulos biomass can be converted to bio-oil containing aliphatic hydrocarbons via catalytic pyrolysis at 500 °C in the presence of Cs modified amorphous silica alumina (Cs/ASA). The reaction routes for the formation of aliphatic hydrocarbons was studied using biomass constituent, *viz.* cellulose, hemicellulose, lignin, and single model components in a pyrolyzer system in conjunction with GC/MS. The pyrolysis behaviour of each biomass constituent was also studied using TGA. The results showed that in the presence of Cs/ASA catalyst aliphatic hydrocarbons can be formed from all the three constituents but mainly from lignin (35% of total peak area compared to 10% for cellulose) resulting in high quality bio-oil with 40 Mj kg^{-1} heating value. On the other hand, the pyrolysis of single model compounds did not result in the aliphatic hydrocarbons. However, pyrolysis of mixture of the model compounds yielded in aliphatic hydrocarbons indicating effect of intermolecular interactions such as hydrogen transfer over Cs^{+} ions.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Everyday life of people in modern societies is greatly depended on transportation which itself is depended mostly on liquid fuels. Liquid fuels have mainly been derived from fossil sources in the past decades since 19th century. However, depletion of fossil sources combined with increasing demand and emerging economies has driven societies towards use of alternative and sustainable sources for fuel production. With this context, lignocellulose biomass, which is mainly composed of holocellulose (cellulose and hemicellulose) and lignin, is the only current sustainable source of organic carbon for production of sustainable bio-fuels [1]. The major components of a fuel are hydrocarbons. Lignocellulose biomass can be converted to liquid containing hydrocarbons via catalytic cracking, *e.g.*, via pyrolysis reaction [2]. Acidic zeolites (H-FAU, H-MFI, H-MOR) [3–5], mesoporous silica alumina (SBA-5, MCM-41, MSU-S) [6,7], and alkali based catalysts (Na/Al$_2$O$_3$, Na/ASA, Na and K impregnated biomass) [8–10] were among the catalysts that have been studied for the catalytic pyrolysis of the lignocellulosic biomass. Triantafyllidis et al. [11]. investigated the effects of Al-MCM-41, MSU-S and H-BEA catalysts on the resulting bio-oil

product distribution obtained during *in situ* catalytic fast pyrolysis of lignocellulosic biomass at 500 °C. They found that all of the three catalysts led to the formation of aromatics including poly aromatic hydrocarbons (PAH), with MSU-S yielding the highest aromatic hydrocarbons. Mihalcik et al. [4]. investigated the role of zeolite catalysts including, H-BEA, H-FAU and H-MFI, on the bio-oil product distribution obtained from woody lignocellulose as well as its constituents, *i.e.*, cellulose, hemicellulose and lignin, and observed production of aromatic hydrocarbons in all the cases, as a result of deoxygenation. Aromatic hydrocarbons were also found to be formed *via* pyrolysis of alkali (*e.g.*, Na, K) impregnated woody biomass [12]. We reported earlier that supported sodium catalysts, Na/γ-Al$_2$O$_3$ [10], gave high yields of aromatic hydrocarbons (15.5% of total peak area) during pyrolysis of pinewood. More interestingly, we recently found out that Cs/ASA catalysts gave also aliphatic hydrocarbons in the product bio-oil from pinewood. One of the more common targets of catalytic biomass pyrolysis is to make the resulting bio-oil compatible with fossil fuels/feedstocks and hence formation of hydrocarbons is very appropriate. Understanding the reaction pathways for the production of the hydrocarbons from lignocellulosic biomass is a complicated task due to the structural complexity of the biomass. Hence, biomass constituents, as well as simple model compounds representing certain fragments of the lignocellulose structure have been used to postulate reaction pathways and mechanisms

[13–16]. Carlson et al [17]. used glucose as a model compound of cellulose and proposed that aromatic hydrocarbons can be formed from anhydrous sugars *via* simultaneous dehydration, decarbonylation and decarboxylation reactions during pyrolysis of cellulose on H-MFI catalyst at 500 °C. Yoshikawa et al. [18]. used dimeric components representing lignin, including di-phenylether and 2-benzyloxyphenol, to study chemical routes for the formation of aromatic hydrocarbons from lignin. They suggested that benzene and toluene can be formed by cleavage of C_{Ar}–C_{Al} (ß–1 and ß–5) and C_{Ar}–O–C_{Al} (ß–O–4 and α–O–4) bonds over $ZrO_2/Al_2O_3/FeO_x$ acidic catalysts.

Aliphatic hydrocarbons can be formed from pyrolysis of ligno-cellulose *via* catalytic hydrogenation reaction, but always requires a hydrogenation/hydrotreating step. Kunkes et al. [19]. claimed that they successfully produced gasoline and/or diesel range alkanes by catalytic conversion of biomass-derived monomer sugars *via* two step hydro-deoxygenation route involving (i) dehydration to make oxygenated heterocyclics, *e.g.* hydroxy methyl furfural (HMF) (ii) followed by its condensation/hydrogenation to C_4–C_{12} range hydrocarbons. Production of long chain aliphatic hydrocarbons (C_{10}–C_{18}) from hydrocracking of lignin at high hydrogen pressure (9.2 MPa) and in the presence of a hydrogenation catalyst (Ru modified SBA-15) was also reported [20]. Production of aliphatic hydrocarbons during the catalytic deoxygenation of lignocellulose without the use of an external hydrogen feed is interesting from the point of view of cost of hydrogen (2500 $/ton) and still remains a challenge.

We recently found out that the presence of Cs in amorphous silica alumina (ASA) led to the formation of considerable amount of hydrocarbons (22% of total peak area of total ion chromatogram in the GC/MS analysis of the bio-oil) during the catalytic pyrolysis of lignocellulos [21]. These hydrocarbons formed in the presence of Cs were mostly aliphatic including C_4 and C_5 alkanes/alkenes, C_6–C_9 chain and cyclic alkanes/alkenes and C_{10}–C_{16} linear alkenes. In the absence of Cs, only aromatic and poly aromatic hydrocarbons were formed. The production of aliphatic hydrocarbons was correlated to presence of Cs_2CO_3 in the vicinity of the Lewis acid sites on the ASA support.

In this article an effort is made to further investigate the routes to aliphatic hydrocarbon formation from lignocellulose using Cs/ASA catalyst. In an effort to minimise the complexity of the pyrolysis of woody biomass, the main constituents that make up lignocellulose, *i.e.* cellulose, hemicellulose and lignin, were selected and used for pyrolysis with the Cs/ASA catalyst. Further, three single model components to represent holocelluloses and lignin were also selected for pyrolysis experiments with Ca/ASA catalyst. An assessment of catalytic pyrolysis of the three constituents has been made to understand the potential of each constituent as feedstock for bio-fuel production.

2. Experimental

The biomass selected for this study was Canadian pinewood and its characteristics can be found elsewhere [22]. Wood constituents were commercially available as the followings: (i) Xylan (from beechwood, >90% xylose, Sigma–Aldrich, as representative of hemicellulose), (ii) lignin (Organosolv, Aldrich) and (iii) crystalline cellulose (microcrystaline colloidal, Sigma–Aldrich). Cyclopentanone (C_5H_8O, >99%, Sigma Aldrich), hydroxyacetone ($C_3H_6O_2$, >95%, Aldrich.) and vinyl-guaiacol ((2-methoxy-4-vinylphenol), $C_9H_{10}O_2$, >98%, Sigma–Aldrich) were selected as single model components for the cellulose, hemicellulose and lignin pyrolysis products, respectively, based on GC/MS analysis of the thermal pyrolysis of each biomass constituent.

2.1. Catalyst preparation

The amorphous silica alumina support (ASA) used in this study was provided by Sasol, Germany and had the following physical characteristics: BET surface area of 484 m^2 g^{-1}, SiO_2/Al_2O_3 ratio of 39.7/60.2; acidity was measured by NH_3-adsorption to be 0.90 μmol m^{-2} and the pore volume given by the supplier was 0.9 ml gr^{-1}. Cesium modified ASA catalyst (Cs/ASA) was prepared using a wet impregnation method. 1.46 g of $CsNO_3$ precursor was dissolved in 50 ml deionized water and then added to 9 gr of the ASA in an Erlen Meyer flask to give 10 wt.% of Cs. The reason to choose this concentration has been explained elsewhere [22]. The mixture was stirred for 180 min using a magnetic stirrer. After the reaction stopped, water was slowly removed at 80 °C at reduced pressure, using a rotary evaporator system. The catalyst was subsequently dried at 100 °C overnight. Finally, the catalyst was calcined at 600 °C for 300 min in air with 50 ml min^{-1} flow rate. The weight percentage of the alkali metal was measured using X-ray fluorescence (XRF) and was found to be 10% ± 0.5 wt.%.

2.2. Pyrolysis reactions

Pyrolysis reactions were performed in a Py-GC/MS system (CDS 2500HP), shown in Fig. 1.

The Pyrolyzer system is equipped with an (a) platinum coil-heated probe, (b) a stainless steel catalytic reactor and (c) a chemical adsorbent (CDS analytical, 60:80 mesh Tenax-TA trap). For each reaction, 0.5 mg of each sample was placed in a quartz tube (200 mm × 2 mm) and inserted into the probe. The tube was then rapidly heated (20 °C ms^{-1}) to 500 °C and the pyrolysis vapour were carried using a flow of He through the catalyst bed, which was placed downstream with the temperature maintained isothermally at 500 °C. After reacting with the catalyst, the vapour were carried through the adsorbent where condensable volatiles (C_3–C_{40}) were adsorbed and light (CH_4, C_2H_4 and C_2H_6) and permanent (H_2, CO, CO_2) gases, as well as water, passed through to the vent. After one minute, the desorption of the adsorbed gases was carried via rapid heating (40 °C s^{-1}) of the adsorbent to 300 °C and the resulting vapour was carried by a flow of He through a heated transfer line (300 °C) to the injector of the GC system.

Separation and identification of the vapour were done using an on-line GC/MS system. First, the components of the pyrolysis vapour entered to the split (100:1) injection port of GC at 280 °C and were subsequently separated through a GC (Agilent 6890 N) capillary column (Agilent VF–1701 ms, 60 m × 0.25 mm × 0.25 μm). The temperature of the column was initially kept at 40 °C for 5 min and was then elevated to 280 °C (3 °C min^{-1}), at which it was kept isothermally for 10 min. The separated components were analysed using MS (Agilent 5978) operating at Electron Impact (EI) mode. The mass spectra were obtained after ionization of the components at 70 eV and over a mass-to-charge ratio (m/z) of 33–550. Chromatographic peaks were identified according to the NIST (National Institute of Standards and Technology, The United States) mass spectra library.

Peak area percentage of total ion chromatogram (TIC) was employed to estimate the relative concentration of the GC/MS detected compounds. This method is acceptable for comparison purposes [23,24]. In this method, the area of each peak in TIC was calculated (using ChemStation software integrator) and then divided by the sum of total peaks areas. TIC peak area percentage of a certain component can be linearly correlated with the concentration of the corresponding component and since the initial weight of the feed was exactly the same for all the reactions, it can be used for the comparison of the components between the different chromatograms [25]. Conversion of each individual component was calculated by subtracting the TIC peak area percentage of the