



In situ catalytic pyrolysis of lignocellulose using alkali-modified amorphous silica alumina

M. Zabeti^a, T.S. Nguyen^a, L. Lefferts^a, H.J. Heeres^b, K. Seshan^{a,*}

^a Catalytic Processes and Materials, Faculty of Science and Technology, MESA+, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

^b Chemical Technology, Institute for Technology, Engineering and Management, Faculty of Mathematics and Natural Sciences, Nijenborgh 4, 9747 AG Groningen, The Netherlands

HIGHLIGHTS

- ▶ Alkali-modified amorphous silical alumina (ASA) catalysts are effective for bio-oil upgrading.
- ▶ Among the alkalis tested, Cs/ASA catalyst is promising for: Cracking of lignin fraction of biomass.
- ▶ Deoxygenating of substituted phenols.
- ▶ Producing hydrocarbons.

ARTICLE INFO

Article history:

Received 15 March 2012

Received in revised form 5 May 2012

Accepted 9 May 2012

Available online 17 May 2012

Keywords:

Alkali
Bio-oil
Cesium
Pyrolysis
Renewable

ABSTRACT

Canadian pinewood was pyrolyzed at 450 °C in an Infrared oven and the pyrolysis vapors were converted by passing through a catalyst bed at 450 °C. The catalysts studied were amorphous silica alumina (ASA) containing alkali metal or alkaline earth metal species including Na, K, Cs, Mg and Ca. The catalysts effectiveness to reduce the bio-oil oxygen content, to enhance the bio-oil energy density and to change the liquid and gas product distribution were evaluated using different techniques including gravimetric analysis, elemental analysis, Karl–Fischer titration, GC/MS and micro-GC analysis. According to the results K/ASA found to be the most effective catalysts for conversion of hollocellulose (hemicellulose and cellulose)-derived vapors of pinewood while Cs/ASA catalyst was the most effective catalyst for conversion of lignin-derived vapors and production of hydrocarbons.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Depletion of fossil resources, increasing demand for petroleum fuels and concerns over global warming have created interest in renewable feedstock's. Biomass is a renewable source of energy, consists mainly of carbon, hydrogen and oxygen and has a nominal composition of C₈H₄O₆. It also contains certain amounts of alkali and alkali earth metals, depending on the biomass source (Fassinou et al., 2011). Compared to fossil fuel resources biomass has lower H/C ratio and higher O/C ratio and as a consequence the energy density is lower than crude oil (16 vs. 44 MJ kg⁻¹ for crude oil) (Mortensen et al., 2011). Liquefaction of solid biomass is proposed to be advantageous for reasons of logistics, transport and processing

issues. The product of liquefaction is an intermediate energy carrier and can be used as “bio-crude oil” for refineries (Kersten et al., 2007). The most used liquefaction process is fast pyrolysis, a process in which biomass is liquefied by rapid heating to temperatures around 450–550 °C in the absence of oxygen. The liquid product is a complex mixture of organic components and water and is named “bio-liquid”, “bio-oil” or “pyrolysis oil”. It cannot be directly used as a transportation fuel because it (i) is very viscous due to the presence of large molecules (up to 1500 D), (ii) corrosive due to the presence of organic acids, (iii) thermally unstable owing to a large content of reactive components and (iv) has a very low heating value (19 MJ kg⁻¹) due to its low hydrogen and high oxygen content.

Accordingly, the development of technologies to reduce the product acidity and to increase stability and energy content of bio-oil is essential. One of the options to achieve this is by reducing the oxygen content of bio-oil. Oxygen removal can be achieved by (i) hydro-deoxygenation (HDO) using (standard) hydrotreating catalysts around 300–500 °C and high hydrogen pressures (Ardiyanti

* Corresponding author. Tel./fax: +31 53 4893254/4683.

E-mail addresses: m.zabeti@utwente.nl (M. Zabeti), T.S.Nguyen@utwente.nl (T.S. Nguyen), l.lefferts@utwente.nl (L. Lefferts), h.j.heeres@rug.nl (H.J. Heeres), k.seshan@utwente.nl (K. Seshan).