



Conversion of lignocellulosic biomass to green fuel oil over sodium based catalysts



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HIGHLIGHTS

- Biomass pyrolysis vapors was upgraded over Na₂CO₃/γ-Al₂O₃ catalyst.
- Catalytic bio-oil resembles fuel oil in its properties.
- The active specie is proposed to be Na⁺ ions hydrated by the OH groups of Al₂O₃.

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ABSTRACT

Upgrading of biomass pyrolysis vapors over 20 wt.% Na₂CO₃/γ-Al₂O₃ catalyst was studied in a lab-scale fix-bed reactor at 500 °C. Characterization of the catalyst using SEM and XRD has shown that sodium carbonate is well-dispersed on the support γ-Al₂O₃. TGA and ²³Na MAS NMR suggested the formation of new hydrated sodium phase, which is likely responsible for the high activity of the catalyst. Catalytic oil has much lower oxygen content (12.3 wt.%) compared to non-catalytic oil (42.1 wt.%). This comes together with a tremendous increase in the energy density (37 compared to 19 MJ kg⁻¹). Decarboxylation of carboxylic acids was favoured on the catalyst, resulting to an oil almost neutral (TAN = 3.8 mg KOH/g oil and pH = 6.5). However, the mentioned decarboxylation resulted in the formation of carbonyls, which correlates to low stability of the oil. Catalytic pyrolysis results in a bio-oil which resembles a fossil fuel oil in its properties.

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1. Introduction

Biofuels have gained considerable interest in recent years because of the high crude oil prices, energy security concerns and potential climate change consequences over the utilization of fossil fuel. The first generation of biofuels, *i.e.* bioethanol and biodiesel, are commercially available and have contributed significantly to the fuel supply in some countries, for *e.g.* Brazil. However, the production of these fuels requires the use of food crops, for *e.g.* sugar cane, corn, palm, *etc.* and there is a threshold above which they cannot be produced without threatening food supplies and biodiversity. Consequently more attention is focused on the production of liquid fuels from lignocellulosic biomass, which can be considered the second generation biofuels. The goal of second generation biofuels processes is to use sustainable lignocellulosic feed stocks including: (1) industrial waste such as woodchips, skins and pulp,

(2) the residual non-food parts of current crops such as stems, leaves, husks, *etc.*, and (3) other crops such as switch grass, *miscanthus*, *etc.*

One of the promising techniques to generate liquid fuels from lignocellulosic biomass is fast pyrolysis, in which the feedstock is heated rapidly ($\sim 10^4$ °C s⁻¹) in an inert atmosphere (1 bar, N₂) to a moderate temperature (400–550 °C) with short residence time (<2 s) and rapid quenching of the formed vapor. This process has drawn much interest because it produces high yields of a liquid product, named bio-oil, which can contain up to 70% of the energy of the biomass feed (Babich *et al.*, 2011; Bridgwater and Peacocke, 2000). However, certain detrimental properties of bio-oil such as its low energy content, acidity, instability, and incompatibility with standard petroleum fuels have significantly restricted its application (French and Czernik, 2010; Nguyen *et al.*, 2013). The undesirable acidic and unstable characteristics of bio-oil result from its high oxygen content due to the presence of oxygenates such as carboxylic acids, aldehydes/ketones, respectively. The removal of oxygen is thus necessary to convert bio-oil into a fuel which is universally accepted and economically attractive. Methods for rejecting oxygen from biomass mainly include catalytic

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de-oxygenation (Nguyen et al., 2013; Zabeti et al., 2012) and hydrogenation/hydrode-oxygenation (Busetto et al., 2011; Fernández et al., 2009; Fisk et al., 2009). De-oxygenation is a promising route (Czernik and Bridgwater, 2004; Huber et al., 2006b) since it does not require use of hydrogen, which is expensive and not widely available. To be efficient, de-oxygenation should attempt to remove harmful oxygenates such as carboxylic acids (to lower acidity), aldehydes/ketones which cause stability problems (Diebold, 2000; Oasmaa and Kuoppala, 2003) and retaining other oxygenates which have higher energy content. Catalyst design should attempt to optimize such selective de-oxygenation.

Recently, we showed that the presence of sodium ions in Faujasite matrix helped improve de-oxygenation of biomass pyrolysis vapors, reduced the amount of acids, aldehydes/ketones and enhanced the hydrocarbon content and thus the energy density of the oil (Nguyen et al., 2013). However, the de-oxygenation obtained with Na-FAU catalysts was still not optimal. Catalytic pyrolysis led to a bio-oil, with an oxygen content of 38 wt.% in comparison to non-catalytic case where it was 42 wt.%. However, we also showed that, with Na₂CO₃, extensive de-oxygenation could be achieved during the catalytic pyrolysis of *Chlorella Algae*, shown by the significant increase in the energy density of bio-oil from 21 MJ kg⁻¹ (non-catalytic) to 32 MJ kg⁻¹ (with Na₂CO₃) at 450 °C (Babich et al., 2011). It has been shown (O'Connor et al., 2012) that the incorporation of Na₂CO₃ to white pine during pyrolysis led to a catalytic bio-oil with a significant degree of de-oxygenation.

Sodium carbonate has low surface area and has a tendency to form clusters in presence of water, and is susceptible to attrition due to low mechanical strength. For a typical fluidised bed pyrolysis process, anchoring sodium carbonate on a mechanically strong support would be beneficial. It has been reported (Stefanidis et al., 2011) that in the presence of γ -Al₂O₃ oxygen content of bio-oil was 24 wt.% compared to that of 42 wt.% of non-catalytic oil, showing promise. γ -Al₂O₃ was also found to significantly increase the concentration of aliphatic and aromatic hydrocarbons in the bio-oil during the pyrolysis of *miscanthus* \times *giganteus* grass compared to non-catalytic tests (Yorgun and Şimşek, 2008). γ -Al₂O₃ is also mesoporous in nature, allow access to bulkier biomass oxygenates and the problem of coking/pore blockage may be less compared to microporous FAU zeolites.

Based on elemental composition, oxygen content of the bio-oil below 15 wt.% would be necessary to bring its heat content/energy density similar to that of fuel oil (Huber et al., 2006b). It is important to achieve such levels of oxygen content, via selective de-oxygenation/eliminating oxygenates that cause properties, as discussed above, that are detrimental for the use of bio-oil as a fuel. In this work the influence of Na₂CO₃/ γ -Al₂O₃ catalysts on the conversion of lignocellulosic biomass to various organic components is investigated with a view to establishing a catalytic pyrolysis process for a green refinery.

2. Methods

2.1. Materials

Wood chips of Canadian white pine (ThoroughBed, Long Beach Shavings, Co.) were used as the biomass feedstock in this study. Characteristics of the feedstock were described earlier (Nguyen et al., 2013). Prior to all experiments, the wood chips were ground by ball-milling and sieved to particle sizes of 0.3–0.6 mm.

2.2. Catalyst preparation

Extrudes of γ -Al₂O₃ (Akzo Nobel) were crushed and sieved to particle sizes of 0.3–0.6 mm. Na₂CO₃ (ACS reagent grade >99.5%)

was obtained from Sigma–Aldrich. The catalyst 20 wt.% Na₂CO₃/ γ -Al₂O₃ was prepared by wet impregnation. The catalysts 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).

2.3. Catalyst characterization

BET surface areas, and porosity of the catalysts were measured on an ASAP 2400 (Micromeritics). X-ray diffraction (XRD) patterns were collected over the range $2\theta = 20\text{--}90^\circ$ on a Bruker D2 Phaser XRD device using Cu K α 1 radiation source. The nature of the coke formed on the catalyst during upgrade of pyrolysis vapor is different from traditional hydrocarbon coke. This coke is high in oxygen content and proposed to be formed by the oligomerization of oxygenates presenting in pyrolysis vapor. For that reason, we would like to introduce the term heterogeneous char, instead of coke, for this type of material. This term will be used throughout the study. The traditional homogeneous char formed directly in biomass pyrolysis will be mentioned as char. Changes in mass of the catalysts due to changes in temperature was monitored by Thermogravimetric Analysis (TGA851e, Mettler Toledo) in 50 mL min⁻¹ Ar flow with temperature ramp of 10 °C min⁻¹. The amount of heterogeneous char in the spent catalyst were determined using the same set-up by heating the samples to 800 °C (10 °C min⁻¹ ramp, 50 mL min⁻¹ air flow). A Flash 2000 (Interscience) instrument was employed to analyze the elemental composition (C, H, and O mass fraction) of the heterogeneous char, char and bio-oil. The elemental composition of heterogeneous char will be calculated taken into account its known amount (obtained from TGA) in the spent catalyst. Additionally, Na₂CO₃ presenting in the catalyst can decompose to form Na₂O and CO₂. This will in turn influence the results from the above TGA and elemental analyses since:

- (1) In TGA analysis, the decomposition of Na₂CO₃ together with the burning of heterogeneous char both contribute to the decrease in weight of the spent catalyst.
- (2) In elemental analysis, the C content of a material is calculated based on the amount of CO₂ formed by the complete oxidation of that material. In the condition inside the C,H,O analyzer, both heterogeneous char and Na₂CO₃ are able to release CO₂.

In order to eliminate those interferences, all experiments were carried out two times in the same conditions, one using the actual sample (heterogeneous char + catalyst) and the other using a blank sample (catalyst only). The difference between the two results is thus the contribution of the heterogeneous char fraction. Scanning electron microscopy (SEM-Zeiss 1550) technique was used to study the morphology of the catalysts. The elemental distribution (mapping) on the surface of catalysts was done using Energy-dispersive X-ray spectroscopy (EDX) technique in the same device. ²³Na MAS NMR spectra was recorded using Bruker AV-750 spectrometer, equipped with 4 mm MAS probe using 13 kHz spinning frequency.

2.4. Catalytic testing

The experimental set-up used was described in detail in an earlier publication (Nguyen et al., 2013). Before each experiment, the whole system was purged with a 100 mL min⁻¹ flow of Ar for 60 min to guarantee an inert atmosphere during the pyrolysis. After this period the Ar flow was reduced to 70 mL min⁻¹ and kept constant during the experiments. The biomass was heated by an IR furnace to the pyrolysis temperature of 500 °C with a heating rate of 40 °C s⁻¹. The catalyst was packed in a separate bed

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