

Effects of catalyst acidity on upgrading of biomass pyrolysis vapors

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Introduction

The conversion of biomass into liquid transportation fuels has gained attention because of concerns about the sustainability of petroleum-derived fuels. Pyrolysis is a process capable of converting biomass to a liquid bio-oil with a 75wt% yield.¹ This bio-oil has the potential to be further upgraded and blended to create a finished fuel product. However, raw pyrolysis oil has undesirable properties of high acidity, high oxygen content, instability, and immiscibility with hydrocarbons.¹ In order to improve the quality of this bio-oil, however, it can either be hydrotreated after it has condensed or upgraded *in-situ* while it is still in the vapor phase. The upgrading of pyrolysis vapors has been achieved using acidic zeolites, as they have been shown to produce aromatic hydrocarbons and could be condensed to form oils with low oxygen content, but at low yields.^{2,3} Both the pore structure and acid properties of the zeolites are thought to play a role in the deoxygenation chemistry and resulting slate of reaction products. In this study, a series of catalysts with varying pore structures, acid strengths, and acid site density were explored to generalize the effects of acid strength and nature on catalysis of biomass pyrolysis vapors.

Materials and Methods

Materials used in this study consisted of commercially obtained BEA and ZSM-5 zeolites (Alfa Aesar) with various Si/Al ratios (BEA SAR = 25, 36, and 80; ZSM-5 SAR = 23, 30, 50, 80, and 280) as well as sulfated and tungstated ZrO₂ (Alfa Aesar). The sulfated and tungstated ZrO₂ and Al₂O₃ supports were prepared using incipient-wetness impregnation with aqueous solutions prepared with ammonia sulfate or ammonia metatungstate, respectively, as the precursors. Samples were then calcined in air at 500°C. The result catalysts nominally consisted of [0.1%, 1.0%, and 5.0wt% S] and [0.57%, 1%, and 5.7wt% W] on ZrO₂ and Al₂O₃ supports.

A micropyrolyzed coupled with a GC/MS was used to carry out reaction experiments. In this experiment, pine samples were loaded in the bottom of a stainless steel cup, covered with a quartz filter, covered with catalyst, which was covered with another filter. The catalyst-to-biomass ratio was 20:1. These catalyst + pine cups were then dropped into a pyrolysis reactor at 500°C and the He carrier gas took the vapors to a liquid N₂-cooled trap prior to injection into the GC/MS.

Results and Discussion

The primary pine pyrolysis vapors consist of a mixture of oxygenated hydrocarbons such as CO₂, carboxylic acids, phenolic compounds, and aldehydes. Additionally, guaiacol derivatives appear as a result of lignin break-down. **Figure 1** shows the GC chromatograms of pine pyrolysis vapors at 500°C, and also chromatogram after passing over ZSM-5 catalysts of varying Si/Al ratio. When the ZSM-5 catalysts were introduced, many of the pine primary vapors were eliminated, and the increase in catalyst acidity led to a more complete removal of the pine primary vapors. This is evident by the decreased intensity

of the peaks associated with uncatalyzed pine pyrolysis vapors as the ZSM-5 Si/Al ratio decreases. The acidic zeolites were also active for producing deoxygenated, aromatic compounds such as benzene, toluene, naphthalene, and their methylated derivatives. The increasingly acidic ZSM-5 catalysts (lower Si/Al) had a tendency towards smaller aromatics (e.g., benzene, toluene) whereas the less acidic zeolites tended towards heavier deoxygenated aromatics (e.g., naphthalene, methyl-naphthalenes, di- and tri-methyl benzene). In addition to zeolites of varying acidity, other acid-doped metal oxide catalyst supports (ZrO₂ and Al₂O₃) were evaluated and the interplay between acid strength and reaction product distribution was investigated.

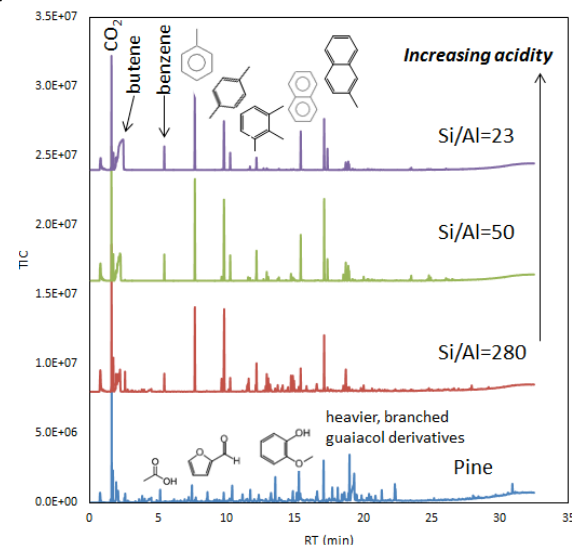


Figure 1. GC chromatograms for pine pyrolysis vapor and after they have passed over ZSM-5 zeolites of varying Si/Al ratio.

Significance

Acid catalyzed reactions on biomass pyrolysis vapors are dependent on the acid type, strength, and physical structures of the catalyst. This information can be used to determine a trade-off between bio-oil yield and composition during catalytic pyrolysis.

References

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