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Aromatic Production from Fast Pyrolysis and In Situ Reforming of Lignin

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Abstract

Fast pyrolysis and in situ reforming is such a simple and promising thermochemical conversion process to convert biomass into variety of high valuable products. Pyrolysis and catalytic process were carried out in separate zone, however it occurs simultaneously within a short time. Such process was performed to produce aromatics from lignin at 550°C in two-stage tubular reactor and atmospheric pressure under helium and hydrogen gas. A reactive carrier gas may affect either primary or secondary pyrolysis that involves vapor-vapor-solid interaction. The aim of helium carrier gas use is to compare product distribution of lignin pyrolysis at inert atmosphere. It is observed that hydrogen even at nearly atmospheric pressure still has an effect to enhance deoxygenation, aromatics production and limit the coke formation. Hydrogen as an active gas is also being combined with the feature of some catalysts that may selectively drive the reaction to form aromatics.

1. Introduction

A growing interest in biomass research still becomes an attractive topic to develop. The current biomass research is directed to observe its main substituent separately. Lignin is the lowest biomass substituent among cellulose and hemicellulose that took account for 10-25wt% [1]. Unlike cellulose and hemicellulose which can be easily degraded chemically or biochemically, lignin is recalcitrant to the degradation. It is characterized by highly cross-linked and branched of three-dimensional aromatic structure. Its utilization is simply limited to the use as burning fuel, contained very low energy density. An attempt to increase its economic value has to be developed using an effective and efficient conversion method.

In this study, fast pyrolysis and in situ reforming were chosen as the way to degrade lignin. Feedstock and catalyst were placed separately in the different zone. During fast pyrolysis, biomass will undergo devolatilization releasing vapor-phase compound and remaining solid unconverted char. While at reforming stage, all the vapors simultaneously pass through catalyst bed undergo a complex chemical reaction to produce the desirable product.

This study investigated experimentally in situ catalytic reforming of volatiles derived from lignin involving gas-solid and vapor-vapor interaction between char-vapor, vapor-vapor and catalyst-vapor. Various type of catalyst performance was examined in order to find the optimum yield of aromatics. Beside helium, hydrogen is also being used as carrier gas to investigate the effect of non-inert gas during fast pyrolysis and reforming.

2. Materials and Methods

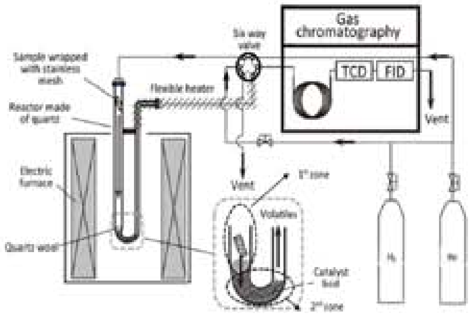

Figure 1. Experimental setup.

Enzymatic hydrolysis lignin with the size of 75-150 µm was used as a feedstock. Approximately 1.0 mg of sample wrapped using wire mesh SUS316 and stored overnight in a desiccator to remove the moisture. In order to reach very inert condition, small quartz tube is also used to put in the sample. Elemental analysis of enzymatic hydrolysis is given as follows (wt%): C=63.3; H=5.9; O=28.9; N=1.9.

Figure 1 shows a schematic diagram of experimental setup for fast pyrolysis and in situ reforming of lignin as used by Uemura et al [2]. It is composed of an electric furnace, microtubular reactor, GC TCD/FID (Shimadzu GC 2014 and GC 2010), and gas supply. All the experiments were carried out at 550°C within less than 1 s of residence time in quartz TS-TR (two stage tubular reactor) connected online with GC. Hydrogen and helium were used as a carrier gas of GC and play a role to sweep the volatiles passing through catalyst bed.

3. Result and Discussion

In this study, around 56 compounds were sucessfully detected and classified into some groups, inorganic gas (CO, CO_2, H_2O), C_1-C_5 hydrocarbon, oxygenated compound, mono-aromatics, tricyclic aromatics and char. The char was calculated by the difference of solid lignin before and after pyrolysis. The rest of the number was unidentified compounds could be lighter or heavier compound than that detected, denoted as unknown.

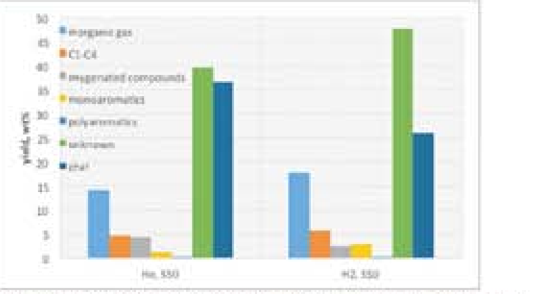

Figure 2. Product Distribution under Helium and Hydrogen Carrier Gas.

From Figure 2, it can be observed that after thermally proceeds, solid lignin remaining approximately 10% lower solid char under hydrogen compared to helium as the carrier gas. The lower char indicates higher conversion of lignin to volatiles. The low char in hydrogen case was accompanied by the increase of inorganic gas, light hydrocarbon, aromatics and also unknown. The increase of inorganic gas and light hydrocarbon is probably due to the contribution of effective deoxygenation. Oxygenated compound seemed to be split into light hydrocarbon by releasing inorganic gas.

In this experiment, the mass of char defined as unconverted lignin including coke. Therefore the decrease in char yield under hydrogen could be caused by the reduction of coke formation instead of char itself. This explanation is supported by the black surface that covers the outer surface of wire mesh when using helium. Seemingly, under hydrogen the precursor of coke did not undergo excessive reaction to form condensable complex molecular compound, which is known as coke. It is responsible also for the high yield of unknown that mainly composed of heavy molecular compound. Metal content in the wire mesh also may has an ability to catalyzed the reaction or inhibit coke removal [3]. An inert quartz tube accordingly employed to load the lignin. The result showed that char yield loaded on quartz tube is 8 wt% higher than that of wire mesh. This fact indicates that hydrogen in the presence of metal tends to make hydrogen dissociated. Thereby, it actively reacts and terminates the radical avoiding the further repolymerization.

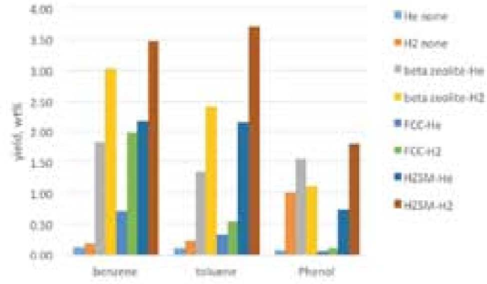

Figure 3. Product Distribution over 3 different catalysts.

Figure 3 present aromatic production over 3 different catalysts, β-zeolite, FCC (Fluid Catalytic Cracking) and H-ZSM-5 via catalytic reforming of lignin volatiles. As we can see, the effect of catalyst presence overall can effectively and selectively boosted the yield of aromatics regardless the type of carrier gas we used. The aromatics yield become much larger when the experiment was carried out under hydrogen. It denotes the combination of hydrogen effect as a reactive gas and the catalytic effect of zeolite resulting in higher degree of aromatization. Selectivity of above catalyst to aromatics follow this order: HZSM-5 > β-zeolite > FCC.

4. Conclusion

HZSM-5 can convert the primary volatiles into mono -aromatics such as benzene, toluene and phenol most effectively. Nearly atmospheric hydrogen is still effective to reduce char and coke formation, enhancing the formation of aromatics with the yield of 13wt% at 550°C.

5. References

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