

## Hydrodeoxygenation of Woody Tar and Model Compounds

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### Introduction

Due to the increase in the crude oil prices and environmental problems, it is desired to use transportation fuels produced from renewable sources. In addition, foods such as corn and vegetable oils soar in price on account of growing demand of biofuels. From these backgrounds, transportation fuels produced from non-edible biomass have lately attracted considerable attention. Among non-edible biomass, pyrolysis oil derived from woody biomass is a promising resource [1, 2]. Because pyrolysis oil contains various oxygenated compounds, the deoxygenation is required to produce fuel. In the study, hydrodeoxygenation of woody tar derived from charcoal manufacture and its model oxygenated compounds were examined.

### Materials and Methods

Guaiacol, phenol, anisole, 2,3-dihydrobenzofuran (2,3-DBF), 3-phenyl-1-propanol (3-P-1-P) and propiophenone (PP) were selected as the model compounds. A woody tar was obtained from Nara Tanka Kogyo Co. Ltd. (Japan). Hydrodeoxygenation was carried out in a batch reactor with commercial CoMo and NiMo sulfided catalysts. The catalysts were sulfided in 5%H<sub>2</sub>S/H<sub>2</sub> stream before reaction. The compositions of feedstock and product oil were analyzed using GC and GC-MS.

### Results and Discussion

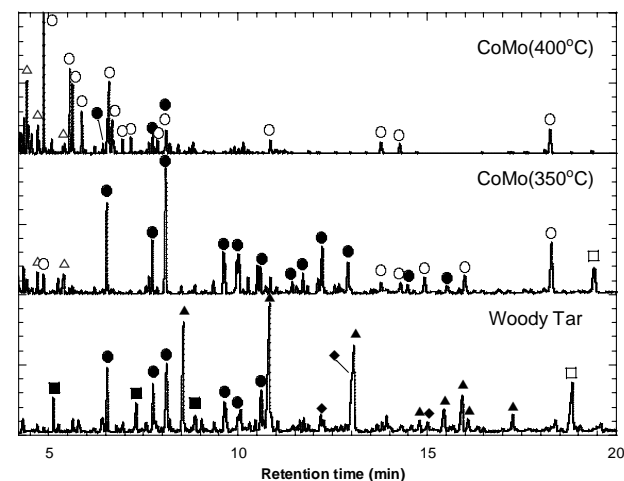
The results of hydrodeoxygenation of 5wt%various model compounds/tetradecane mixture over CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst are shown in Table 1. The reaction was carried out at 300°C for 1 h under 5MPa hydrogen pressure. 3-phenyl-1-propanol and propiophenone were easily deoxygenated and gave propylbenzene. The reactivity of phenol was low and main products are naphthenes and aromatic hydrocarbons. Conversions of guaiacol, anisole and 2,3-dihydrobenzofuran were high. However, those compounds gave phenols as intermediate

**Table 1. Hydrodeoxygenation of model compounds**

Compound	Conversion(%)	Aromatics	Product composition (%)		
			Naphthenes	Phenols	Other oxygenate
Guaiacol	100	11.3	39.8	47.4	1.5
Phenol	72.3	23.2	44.2	32.6	0
Anisole	94.5	21.1	35.2	38.2	5.5
2,3-DBF	97.7	8.6	6.4	82.6	2.4
3-P-1-P	100	98.8	1.2	0	0
PP	100	99.0	1.0	0	0
Benzene	3.1	96.9	3.1	-	-

products and the selectivity of hydrocarbon formation was low. These results indicate that the key reaction of pyrolysis oil upgrading is hydrodeoxygenation of phenols. Under this reaction condition, hydrogenation of benzene slightly occurred and 3.1% of cyclohexane was formed. This result indicates that naphthenes seem to be formed not from aromatic hydrocarbon, but from phenols via cyclohexanols. Phenols were completely deoxygenated at 350°C for 3 h under 5MPa hydrogen pressure.

The hydrodeoxygenation of woody tar was carried out at 350°C or 400°C for 5 h under 5MPa hydrogen pressure over CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. The reactivity of woody tar was much lower than those of model compounds. The gas chromatograms of feedstock and product oils are shown in Figure 1. At 350 °C, alkyl phenols could not be deoxygenated and still remained. However, they could be converted to hydrocarbons by hydrodeoxygenation at 400°C. The catalytic activity depended on metal and support species.



**Figure 1.** Gas chromatograms of woody tar and its hydrodeoxygenated products ▲ alkylguaiacol, ● alkylphenol, ◆ alkylcatechol, ■ other oxygenated compounds, ○ aromatic hydrocarbon, △ naphthene, □ terpene

### Significance

This work can contribute to the production of transportation fuel from woody biomass.

### References

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