EFFECT OF OXYGEN COMPOUNDS ADDITION ON THE HYDROCRACKING OF ALKYLPHENOLS

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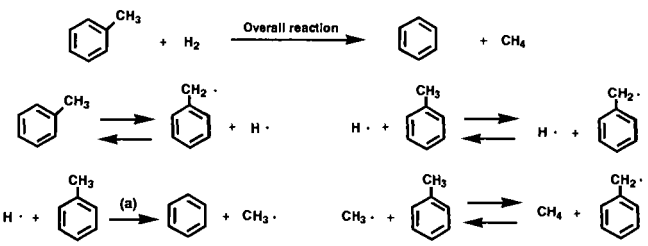
ABSTRACT

To produce and purify useful compounds in tar from coking and from low temperature pyrolysis of coal, hydrocracking of alkylphenol mixture is very important reaction. In this study, the effect of oxygen compounds such as dimethylcarbonate(DMC) addition on the hydrocracking of alkylphenols was investigated to decrease hydrogen loss by the production of water. Hydrocracking of three dimethylphenols(DMP) was carried out using atmospheric flow apparatus with quarts reactor at 700°C, residence time of 3-10 sec and hydrogen to reactant mole ratio of about 10. From the hydrocracking of 3,5-DMP without DMC, m-xylene and m-cresol were produced with the production ratio of 1:1.8. However the dehydroxylation to produce m-xylene was decreased by the addition of 10% DMC with the production ratio of 1:2.7. Similar reaction behavior was observed in the hydrocracking of 2,5-DMP. These are considered due to the strong interaction between DMC and hydroxyl group. Relationship between reaction behavior and molecular structure would be also discussed.

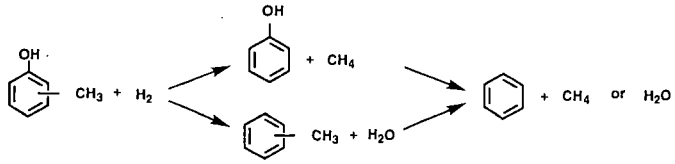
INTRODUCTION

Mild gasification and low temperature pyrolysis are considered to be the most promising process for high-moisture, subbituminous and lignite coal to produce upgraded solid fuel with high heating value and low sulfur, and to produce a useful liquid fuel. However these liquid products contain considerable amounts of oxygen, and are rich in alkylphenols with alkylbenzenes and alkylnaphthalenes.[1] Gas phase thermal demethylation of a series of methyl substituted benzenes under a excess hydrogen stream has been a subject of many investigators. Reaction behavior, including kinetics, and product distribution for toluene and methylbenzenes can be accounted for by the following free radical mechanism. [2]



In the above chain scheme, the propagation rate is effectively controlled by reaction (a). This reaction can be pictured as a perpendicular approach to hydrogen atom to phenyl carbon atom, to which methyl group is attached. We have found the same mechanism can be applied for the demethylation of methylnaphthalenes, and the relative reactivities of both methylbenzenes and methylnaphthalenes have been correlated with the reactivity indices, theoretically calculated by molecular orbital method. [3,4] According to the results for methyl substituted aromatic compounds and the reaction behavior for the other alkyl aromatic compounds, demethylation rates for methylnapthalenes are generally higher than that for methylbenzenes, and the removal of higher alkylgroup takes place competitively with demethylation. In this reaction, aromatic structure does not cracked, and simple aromatic compounds, without having alkyl substituents, are produced with high selectively in the presence of excess hydrogen.

On the other hand, kinetic studies of the thermal hydrocracking of cresols, and 2,4,6-trimethylphenol have been discussed in terms of the reaction mechanism by Davies et al [5], Kawase et al [6], and Moghul et al [7]. The same type of kinetic equation with dimethylation, and the following concurrent reaction scheme have been proposed to account for the experimental measurement of the reaction rate, and the product distribution.



However the relationship between molecular structure and kinetic observations has not yet been explained satisfactory. In this reaction, hydrogen was consumed to produce water by dehydroxylation.

In this study, the effect of oxygen compounds addition on the hydrocracking of alkylphenols was investigated to decrease hydrogen consumption due to the production of water.

EXPERIMENTAL

Commercial reagent grade dimethylphenols(DMP), dimethylcarbonate(DMC) and diethylcarbonate(DEC) were used as received. Thermal hydrocracking of DMP was carried out using a small atmospheric flow apparatus at temperatures of 700°C with residence times of 3-10 sec, and hydrogen-to-reactant molar ratio of more than 10. The reactor was made of a quartz tubing, 21.5 mm in inside diameter and 120 mm in length, and was equipped with a thermo-sheath placed along its central axis. Annular space of the vessel was filled with 10-20 mesh quartz tips, resulting in a free volume of about 18.3 ml. DMP were introduced into the reactor quantitatively by using a small liquid feeding pump, and hydrogen stream was supplied by using a mass flow controller. DMP was mixed with an adequate amount of toluene as a standard reference and 10% DMC or DEC in some of the experimental runs. Gaseous and liquid products were subjected to a conventional gas chromatographic analysis.

RESULTS AND DISCUSSIONS

Reaction behavior of DMP

From the hydrocracking of 3.5-DMP mixed with toluene, benzene from toluene, m-xylene and m-cresol with trace of phenol from DMP were mainly produced with methane. The conversion of toluene and 3,5-DMP with and without DMC were illustrated in Fig.1. These show good fittings of first-order kinetic equation with respect to both toluene and 3,5-DMP. Similar reaction behavior was also observed for 2,5- and 2,6-DMP, however, the conversion ratio of DMP to toluene calculated by first-order rate low was same in all three cases with and without DMC. Products distribution at 700°C from 3,5-DMP are shown in Fig.2 and Table 1. 63.5 mol % m-cresol and 34.5 mol % m-xylene were produced with production ratio of 1.8 from the hydrocracking of 3,5-DMP at 700°C with residence time of 5sec without DMC. This result indicates the rate of demethylation is faster than that of dehydroxylation. From the overall relative first-order cracking rate and the product distribution, the rate per one equivalent methyl and hydroxyl groups for three DMP's were calculated as shown in Fig. 3. The specific rates of demethylation and dehydroxylation are affected by both number and position of substituents of the reactant molecule. Removal of the substituent at ortho position of DMP is quite definitely easier than that of toluene.

Effect of DMC addition on the hydrocracking of DMP

From the hydrocracking of 3,5- DMP mixed with toluene and DMC, observed conversion for both toluene and 3,5-DMP with 10% DMC was higher than that without DMC as shown in Fig.1. The production of m-cresol increased and that of m-xylene decreased by the addition of 10% DMC as shown in Fig.2 and Table 1. The production ratio of m-cresol to m-xylene changed drastically from 1.8 to 2.7 by the addition of DMC. This indicates the dehydroxylation, caused by the attacking hydrogen atom to the phenyl carbon adjacent to hydroxyl group, was prevented by the strong interaction between DMC and

hydroxyl group in 3,5-DMP. Similar effect was observed by the addition of DEC. Contrary to these, demethylation was accelerated probably by the indirect electronic effect of DMC. However, in the case of 2,5-DMP, the effect of DMC addition on the products distribution was not strong, and the production ratio of cresols to p-xylene changed only from 3.0 to 3.6, as shown in Table 1. The decrease of p-xylene and the increase of cresols in the products distribution was less than 12 mol%. It was thought that the interaction between DMC and hydroxyl group in 2,5-DMP was slightly hindered by the neighboring methyl group at ortho position. Therefore the effect of DMC on the dehydroxylation was weakened by the steric hindrance.

On the other hand, there were no differences in the product distribution and the conversion from the hydrocracking of 2,6-DMP, as shown in Table 1. It was very clear that the interaction between DMC and hydroxyl group was almost completely disappeared by the neighboring two methyl groups at ortho position.

CONCLUSION

The strong effect of DMC addition on the products distribution was observed from the hydrocracking of 3,5-DMP at 700°C. The production ratio of m-cresol to m-xylene changed drastically from 1.8 to 2.7 by the addition of DMC. These are considered due to the strong interaction between DMC and hydroxyl group in 3,5-DMP. Similar reaction behavior was observed for the case of 2,5-DMP, however, the production ratio of cresols to p-xylene increased only 20% from 3.0 to 3.6. Moreover, there were no differences in the products distribution and the conversion for the case of 2,6-DMP. These indicate that the interaction between DMC and hydroxyl group in 2,5- and 2,6-DMP is slightly and strongly hindered by the neighboring methyl group in the molecule. These findings suggest that the addition of DMC can decrease hydrogen consumption on the hydrocracking of alkylphenols. These are also very valid to concentrate and purify phenol and cresols economically by the hydrocracking of coal derived tar.

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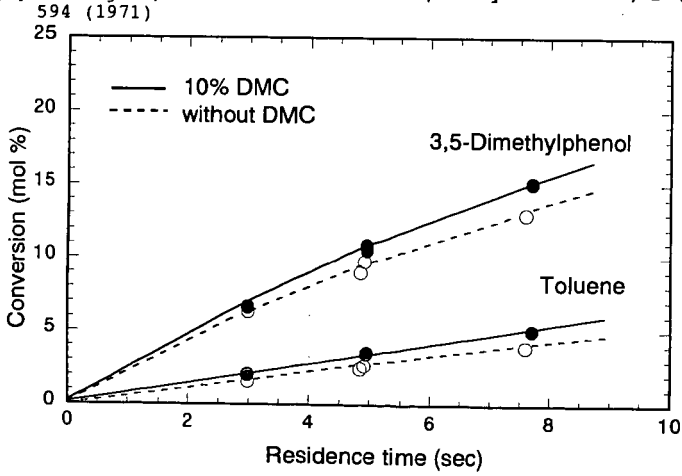

Fig. 1 Hydrocracking of 3,5-Dimethylphenol at 700°C

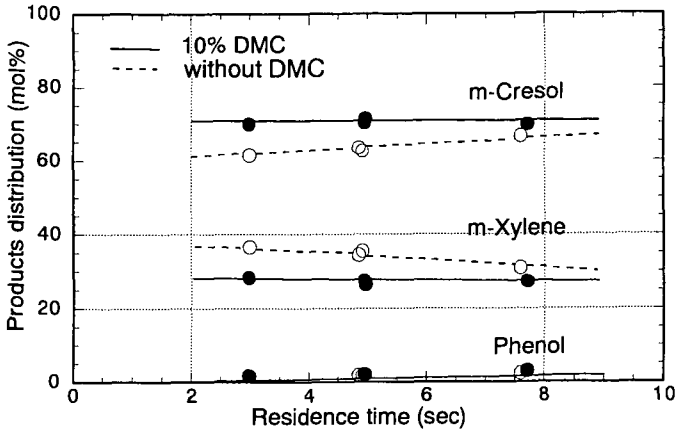

Fig. 2 Products Distribution from the Hydrocracking of 3,5-Dimethylphenol at 700°C

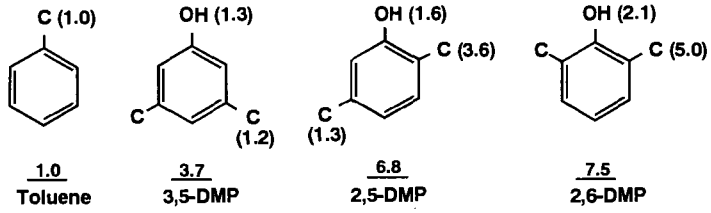

Fig. 3 Relative Rates of Demethylation and Dehydroxylation at 700°C

Table 1 Products Dstribution at 700℃, 5sec.

	3,5-DMP			2,5-DMP		2,6-DMP	
Additive	non	DMC	DEC	non	DMC	non	DMC
Conversion (mol%)							
DMP	9.0	10.5	8.8	20.3	20.9	23.3	23.9
Toluene	2.5	3.5	2.9	3.3	4.0	3.5	3.9
Product distribution (mol%)							
m-Xylene	34.5	26.5	26.4			28.0	28.0
p-Xylene				24.2	21.2		
Phenol	2.0	2.1	1.6	2.7	3.0	4.7	4.9
o-Cresol				19.7	20.8	67.3	67.1
m-Cresol	63.5	71.4	72.0	53.4	55.0		
Cresols/Xylene	1.8	2.7	2.7	3.0	3.6	2.4	2.4