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Identification of Molecular Composition of Nascent Tar from Rapid Coal Pyrolysis

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Abstract

Understanding of mechanism/kinetics of tar conversion is a key factor to develop low temperature gasification for integrated coal gasification combined cycle (IGCC) since the tar may survive at temperature below 1000°C and cause problems at downstream processes. Though detailed chemical kinetic models (DCKMs) can predict the kinetics of vapor-phase reaction of various hydrocarbons, tar as oligomers is inapplicable due to difficulties in identification of the chemical composition. Thermal cracking of tar is a way to represent the composition. It decomposes oligomers into monomers that are acceptable to the DCKMs. Rapid pyrolysis, which is an initial step of gasification, of low rank coals was performed in this study. The composition of tar was expressed as a mixture of known compounds though total yield after pyrolysis was insufficient to describe the complete tar composition.

1. Introduction

Tar, a complex mixture that consists mainly of condensable aromatic compounds, is problematic in coal gasification when integrated into a gas/steam turbines combined cycle for power generation. The tar may survive in lower temperature gasification due to incomplete conversion of coal resulted from decreasing O_2 consumption that theoretically improves chemical energy of resultant gas by the gasification. The integrated gasification combined cycle is therefore operated at temperature well above 1000°C to avoid problems at downstream processes such as gas cleaning and combustion.

The tar is a major compound that composes volatile matters produced by pyrolysis as an initial conversion step of gasification. Coal primarily undergoes intra-particle pyrolysis that produces the volatile matters consisting of inorganic gases and light hydrocarbons as well as the tar and carbon-enriched solid termed char. Then, the volatile matters and char secondarily undergo exothermic oxidation with O_2 and endothermic oxidation with CO_2 or H_2O in parallel. During the conversion, it is believed that the tar vapor undergoes further aromatization (removal of aliphatic and oxygen containing substituents) and growth in ring size leading to formation of soot. Understanding of the mechanism/kinetics of the tar conversion is therefore essential for developing low temperature gasification.

Recent development of detailed chemical kinetic models (DCKMs) enables prediction of kinetics of vapor-phase reactions of hydrocarbons. However, tar is inapplicable directly to the DCKMs due to its complex chemical composition containing abundant oligomers of which complete identification is impossible even by modern analyses. Monomers, mono- and polyaromatic hydrocarbons, can be identified and are alternatively accepted by DCKMs.

This on-going study aims at development of an analytical pyrolysis to identify and quantify aromatic compounds in the tar from rapid coal pyrolysis as much as possible, and then simulate the vapor-phase reactions by a type of DCKM. This abstract reports results of the development of the analytical pyrolysis.

2. Experimental

2.1. Pyrolysis in Curie-point pyrolyzer

Two low rank coals, Loy Yang (LY) and Mulia (MU), were used for identification of composition. The coal samples wrapped by a ferromagnetic foil, of which Curie-point temperature is 920°C, were pyrolyzed in Curie-point pyrolyzer (CPP) under He atmosphere. The foil was inductively heated up to the designed temperature in a few seconds with heating rate of 1000°C s^{-1}, resulting in minimal secondary pyrolysis of volatile matters. The volatile matters were analyzed by gas chromatograph (GC) applying thermal conductivity detector (TCD) with a packed column and GC combined with mass spectrometer (GC-MS) with a capillary column.

2.2. Pyrolysis in two stage tubular reactor

Two-stage tubular reactor (TSTR) was employed for sequential occurrence of primary and secondary pyrolysis in divided two zones[1]. The coal samples wrapped by wire mesh were dropped into the primary pyrolysis zone separated by quartz wool, which was heated up to 920°C under He atmosphere.

Table 1. Molecular composition of product gas from primary pyrolysis in CPP at 920°C

Coal	LY [wt%]	MU [wt%]
Char	43.6	44.0
H_2	0.91	1.05
CO	10.5	11.1
CO_2	10.5	8.92
H_2O	14.0	12.9
CH_4	1.63	1.43
C_2-C_4 gases	0.80	1.32
Tar *(by difference)*	18.1	19.3

Then, nascent tar in volatile matters underwent secondary pyrolysis in the next zone and was analyzed by GCs applying TCD with a packed column and flame ionization detector (FID) with both a packed and capillary column. Residence time of the volatile matters in the secondary pyrolysis zone was around 3.5s.

3. Results and discussion
3.1. Primary pyrolysis

Table 1 presents the chemical composition of inorganic and light hydrocarbon gases. More than half mass of the coal sample was converted into volatiles by the pyrolysis, leaving around 44 wt% of char. The total yield of inorganic gases was 34-36 wt%, and the yield of the detectable light hydrocarbons (C_1-C_4) was less than 3 wt%. The GC left undetectable compounds with total yield of 18-19 wt%. It was believed that the unidentified fraction consisted of monomers (mono- and polyaromatic compounds) and oligomers. GC-MS detected some mono-aromatic compounds. Benzene was the most abundant aromatic compound among those detected, but its yield was as small as 0.1 wt%. Di-aromatics and greater aromatics were also detected, but the yields were all trace. It was clear that the total yield of the detected and identified was insufficient to represent the chemical composition of the nascent tar. It was thus concluded that the identification of the volatiles from the primary pyrolysis was far away from completeness. Performing the secondary pyrolysis of the nascent tar to an appropriate extent was therefore essential for representing the entire portion or at least a major one of the volatiles by identifiable compounds.

3.2. Sequential secondary pyrolysis

The coal pyrolysis in TSTR was conducted to examine the chemical composition of the volatiles by the secondary pyrolysis to a limited degree. Benzene was quantified by both columns, and the greater aromatics detected by the capillary column were quantified based on the ratio of benzene at the packed and capillary columns. Both LY and MU

Table 2. Molecular composition of product gas from sequential pyrolysis in TSTR at 920°C

Coal	LY [wt%]	MU [wt%]
Char	44.0	47.4
H_2	n.d.	n.d.
CO	5.91	5.63
CO_2	10.5	8.90
H_2O	8.47	7.69
CH_4	2.87	2.96
C_2-C_4 gases	2.03	2.43
Benzene	1.25	1.34
Mono-aromatics (except benzene)	0.34	0.32
Di-aromatics	0.81	0.87
Tri- or more aromatics	0.44	0.37
Sum of aromatics	2.84	2.90

coals showed similar molecular composition, resulting from the similar elemental composition[2]. Secondary pyrolysis showed lower yields of CO and H_2O, similar yields of char and CO_2, and higher yields of light hydrocarbons compared to that from primary pyrolysis. It is likely due to water-gas shift reaction and tar reforming by steam and CO_2[3]. Further, yields of the aromatic hydrocarbons increased significantly, considering that the benzene yield was 0.1 wt% from primary pyrolysis. The benzene yield after secondary pyrolysis was around 1.3 wt%, and the total yield of aromatic hydrocarbons was around 2.9 wt% that is still insufficient for complete molecular composition. Nonetheless, it is worth that the unknown nascent tar is expressed as a mixture of known compounds.

4. Conclusion

Rapid pyrolysis of low rank coals was performed to identify molecular composition of nascent tar. Identification of the tar was impossible by primary pyrolysis due to its presence as a form of oligomers. Sequential secondary pyrolysis decomposed the oligomers into monomers, resulting in significant increase of the yields of aromatic hydrocarbons. Though total yield of aromatics was insufficient for the complete identification of the composition, tar was expressed as a mixture of known compounds.

References
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