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Chemical structure and reactivity alterations of brown coals during thermal treatment with aromatic solvents

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ABSTRACT

Thermal treatments of two brown coals (Chinese and Australian brown coals) -slurries with four different aromatic solvents (hydrogen donor and non-donor, polar and non-polar solvents) were conducted with bench-scale apparatus, and the treated samples (TSs) were separated and characterized in detail to investigate the structural alterations of the coals, as well as the interactions between the solvents and the coals. It is observed that the thermal treatments in aromatic solvents are effective in upgrading the brown coals, but the reactivity of brown coals towards pyrolysis is reduced due to the extraction of small molecules and the enhancement of cross-linking reactions. The solvents are tightly combined with the brown coals owning to the formation of new chemical forces (such as hydrogen bonds or π–π conjugations) as well as the physical disruptions such as the collapse of pores during slurry-heating. Different solvents behave variously with their unique properties, especially tetrahydroquinoline (THQ), which is more tightly combined with the brown coals than the other solvents, including tetralin (THN), 1-methylnaphthalene (1-MN), recycle solvent (RS) due to the electron-affluent nitrogen atom on its aromatic ring. Hydrogen-donor solvent is superior to non-donor solvent for thermal treatment of brown coals.

1. Introduction

Direct coal liquefaction (DCL) technology is widely recognized as an important utilization for brown coals and a potential method to alleviate the petroleum shortage for countries with huge petroleum consumption but limited crude oil reserves, such as China [1]. The main objective of DCL is to crack the macromolecular structure of coal into radical fragments, and then capping or hydrogenating the radical fragments into liquid products. However, liquid fuels produced from DCL are not economically competitive with those from crude oil refineries at the existing technical conditions.

Based on the extensive studies and industrial demonstrations of DCL process [2–6], the key factor that influences the yield of target product (oil) during DCL is how to balance or match the generation rate of radicals (or reactive fragments) and that of the hydrogenation. It is generally agreed that few radicals are generated at low temperatures thus resulting in low yield of oil. With the temperature rises more radicals are generated, which potentially enhances the oil yield if radicals are adequately stabilized and hydrogenated. On the other hand, the rate of radical generation is possibly faster than the rate of hydrogenation at high temperatures, leading to the condensation of a great amount of radicals into solid coke, a group of products chemically more stable than coal, thus lowering the yield of oil according to previous literatures [5,7,8].

Therefore, numerous studies have been conducted through the years to increase the rate of hydrogenation and/or provide sufficient hydrogen to free radicals at liquefaction temperatures. Previous literatures show that the hydrogen used for capping radicals are mostly derived from solvents, and the contribution of H_2 is less than 10 wt % although the partial pressure of H_2 is usually high (≥ 14 MPa) under liquefaction conditions [7,9–11]. Thus, the research and development of effective solvents for DCL have always been an interest for researchers. For instance, Sangon et al. [12] conducted liquefaction of lignite and bituminous coal in supercritical toluene–tetralin mixture with a semi-continuous reactor. They observed that supercritical toluene could extract the coals effectively and the addition of tetralin could stabilize the radicals thus inhibiting their recombination, which was conductive to improve the yield of oil (45 wt %, daf) at 490 °C. Ding et al. [13] developed two-stage co-processing of coal with plastic and found that waste plastic-derived liquids could be utilized as solvent for thermal and catalytic coal liquefaction. Further, they carried out thermal and catalytic liquefaction experiments of DECS-6 coal using plastic-derived liquids as solvent and investigated the kinetics of the reactions. They believed that the hydrogen-rich fragments of plastic-derived oil could

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react with coal and yield liquid products of higher quality than those obtained from coal alone [14]. Orr et al. [15] performed liquefaction of a high-volatile bituminous coal using oil derived from vacuum pyrolysis of waste rubber tires with the presence of molybdenum catalyst. They reported that the vacuum-pyrolyzed tire oil contained various polyaromatic molecules which were beneficial to coal liquefaction, and over 90 wt % (daf) of coal was converted into gas, oil and asphaltenes at 430 °C under 6.9 MPa (initial pressure) of hydrogen.

At present, most commercial DCL processes generally consist of four steps: coal-slurry preparation, liquefaction, distillation of products and hydrogenation of solvents. Among the four steps, comparatively, less attention is paid to the step of coal-slurry preparation. The coal-slurry preparation includes slurry-making and slurry-heating in practice. Specifically, the crashed coals are firstly mixed with the DCL solvents to make coal-oil slurry, which is then pumped to a pre-heater, where it is gradually heated to a relatively high temperature (such as 400 °C) before being sent to the liquefaction reactors [16]. In most circumstances, commercial DCL plants take brown coals as the feedstock due to their low prices and high reactivity towards liquefaction [17]. Brown coals are generally considered as low rank coals owning to the low coalification and large amounts of functionalities such as hydroxyl, phenolic, and carboxyl groups. Thus, it is not difficult to envision that brown coals will undergo significant structural alterations during the slurry-heating treatment. However, most of the studies reported on the roles of solvents are related to the liquefaction at high temperatures, and less attention is focused on the interactions between brown coals and the solvents before the start of liquefaction reactions. The solvents used in DCL are mostly hydrogenated aromatics with 2–4 rings, paraffins and small amount of aromatics with heteroatoms (N, S, etc.). It is well accepted that DCL solvents could donate/shuttle hydrogen to coal fragments, dissolve coal particles and disperse catalysts during liquefaction [18,19]. In addition, during slurry-heating, solvents are also likely to interact with brown coals due to the high content of labile functionalities such as carboxyl and hydroxyl groups of brown coals [20]. Swelling and extraction also occurred when coals were heated in solvents [18], and cross-linking of brown coals occurred at 200–400 °C as well [21]. All the above interactions would inevitably lead to the alterations of chemical structure and reactivity of brown coals toward liquefaction.

It is widely recognized that reactivity of the feed coal significantly influences the efficiency and economy of DCL plants, thus it is necessary to investigate the structural and reactivity alterations of brown coals during slurry-heating and to explore the interactions between the solvents and the coals at this stage. Therefore, in this work, we simulated the coal-slurry preparation process with laboratory-scale apparatus and separated the coal samples after the heating treatment. The resultant samples were then characterized with FTIR, ^{13}C NMR, TG-MS and swelling experiments to analyze the changes of chemical structures and reactivity. The solvents employed were tetralin (THN, $C_{10}H_{12}$), 1-methylnaphthalene (1-MN, $C_{11}H_{10}$), tetrahydroquinoline (THQ, $C_9H_{11}N$) and a recycle solvent (RS) from a PSU liquefaction apparatus, which can be classified as hydrogen donor and non-donor, polar and non-polar aromatic and hydrogenated aromatics. This work would deepen our understanding of interactions between brown coals and the DCL solvents during slurry-heating process, as well as enrich the knowledge of coal chemistry about the liquefaction of brown coals, which are contributable to improve the economy and efficiency of the existing DCL technology.

2. Materials and methods

2.1. Materials

Two brown coals from China (Yunnan province) and Australia (Victoria) were used and denoted as YN and AU, respectively. The samples were crushed, ground to less than 154 μm and sealed in a plastic bag filled with N_2 and stored in a desiccator for analysis. The properties of the samples are listed in Table 1.

The solvents employed were three chemical reagents including THN, 1-MN, THQ, and RS provided by the Synfuels China Inc. THN was purchased from Sinopharm Chemical Reagent Co. Ltd. with purity higher than 99.0%. (1-MN) was purchased from Shanxi Tianyu Coal Chemical Co., Ltd. and the purity is above 96.0% (with 2–3% methylbenzothiophene and 1–2% 2-methylnaphthalene and biphenyl). THQ was purchased from TCI Shanghai Development Co., Ltd., and the purity is above 95.0% (the major impurity is quinolone, C_9H_7NO). RS mainly consists of hydrogenated aromatics, condensed aromatics with 2–4 rings, paraffins and small amount of pyrene, thiophene, etc. The detailed compositions of RS are shown in Table 2. All the chemical reagents were used without further purification.

2.2. Thermal treatments of coal-slurries

Thermal treatments of the brown coals with the solvents were carried out with a 100 mL micro-autoclave (Parr 4598, USA). In each run, 10.0 g of raw coal and 20.0 g of solvent were charged into the reactor. After airproofing, the reactor was flushed with N_2 (purity $\geq$ 99.5%) five times and then pressurized with N_2 to 2.0 MPa at room temperature. Afterwards, the reactor was gradually heated to 300 °C at 5 °C/min with stirring at 500 rpm. After soaking for 120 min at 300 °C, the oven/heater was taken off and the autoclave was cooled down to room temperature by air. The gaseous products were collected and analyzed with a gas chromatography (GC, Haixin Co Ltd, GC-950, China). An Al_2O_3 column was used with FID detector to analyze C_1–C_4 hydrocarbons and a carbon sieve column with TCD detector was employed for H_2, CH_4, CO, and CO_2 analyses. The solid–liquid mixtures in the reactor were separated by filtration under reduced pressure. The filter cakes were then ultrasonicated three times with benzene (10 min each time) to remove the solvents and filtered again. The solid products were then dried under vacuum at 80 °C overnight and stored in the desiccator for further analysis. The treated samples (TSs) were denoted with the abbreviation of solvents combined with the raw coals, such as THN-YN, THN-AU, (1-MN)-YN, and (1-MN)-AU. The mass of the TSs on daf basis was defined as m,and the mass of raw coal on daf basis was defined as M, thus the solid yield was calculated as: Yield (solid) $= \frac{m}{M}$. The error of the yield of solid in repeated runs is within $\pm$1.00%. Distributions of products after the treatment are shown in Table 3. The yield of liquid (small molecules extracted) was obtained by the difference between 1 and the sum of the yield for gaseous and solid products.

2.3. Infra-red spectra characterization

FTIR spectra of the raw coals and TSs were obtained on an IR spectrometer (VERTEX 70, Bruker, Germany) at room temperature. All samples were fully grounded to guarantee high homogeneity prior to tests. The samples were uniformly mixed with dried KBr powder at the mass ratio of 1:300 and the mixture was then finely milled and pressed into a pallet under 12 MPa for 2 min. The spectra were recorded at the wavenumber ranges from 400 to 4000 cm^{-1} and the baselines of the spectra were corrected.

2.4. ^{13}C NMR spectra characterization

Molecular structures of the samples were also investigated with solid-state ^{13}C CP/MAS NMR spectroscopy. The experiments were performed on a 600 MHz NMR spectrometer (Avance III, Bruker, Germany) at a carbon frequency of 151.0 MHz. Coal samples were finely milled to less the 74 μm and packed into a 4 mm zirconia rotor with a Kel-F cap. The spectra were recorded at a spinning speed of 9 kHz using a Bruker MAS double resonance probe. Measurement conditions were as follows:The contact time was 2 ms, with a recycle delay of 5 s