



Two-stage hydrogasification of different rank coals with a focus on relationships between yields of products and coal properties or structures



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HIGHLIGHTS

- Different rank coals were hydrogasified using a two-stage pressurized reactor.
- Yields of CO, CO₂, CH₄, C₂–C₃, water and light aromatics were determined.
- Coal structures were characterized by chemical titration, solid state ¹³C NMR and FTIR.
- The highest sums of CH₄ and C₂H₆ yields were obtained for two lignite coals.
- Relations between products and coal properties or structures were surveyed.

ARTICLE INFO

Article history:

Received 13 November 2015
Received in revised form 6 April 2016
Accepted 10 April 2016
Available online 19 April 2016

Keywords:

Different rank coals
FTIR
¹³C NMR
Hydrogasification
Hydrocracking

ABSTRACT

The pressurized hydrogasification of different rank coals was carried out using a laboratory two-stage reactor to investigate the influences of volatile matter hydrocracking on the formations of gaseous products (CO₂, CO, CH₄ and C₂–C₃) and liquid products (water and light aromatics). Experiments were conducted by way of comparison under the N₂ atmosphere. Fourier transform infrared spectroscopy (FTIR), solid state ¹³C nuclear magnetic resonance technique (¹³C NMR) and chemical titration analysis were used to semi-quantitatively or quantitatively determine the main functional groups in the coals. It was found that through the hydrocracking at 700 °C, the summed yields of CH₄ and C₂H₆ from two lignite coals reached as high as 21.2–22.9% (daf. coal), higher than those even from two subbituminous coals. This result was associated with the abundance of longer alkyl groups in two lignite coals. Two lignite coals were the most enriched with carboxyl groups, which was proved to be the principal precursor of CO₂. The hydrocracking at 700 °C allowed a distinct part of CO₂ to convert into CO by the reversal gas water shift reaction, while the changes in the yields of H₂O were indistinct. The hydrocracking at 700 °C was also favorable for the production of BTX (benzene, toluene and xylene) and naphthalene. The simple linear regression was used to assess the correlations of the yields of main gaseous products (CH₄, C₂H₆, CO₂ and CO) and liquid products (H₂O and BTX) obtained under varying conditions to some relevant coal properties such as volatile matter content and total oxygen content as well as to some structural parameters such as aliphatic ratio and carboxyl group content.

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1. Introduction

The development of efficient and clean technologies of coal utilization never ceases to attract researchers' attention worldwide [1–5]. Coal hydrogasification is one of coal gasification processes, which uses hydrogen as a gasifying agent. It has an advantage over

the steam/oxygen gasification of having a better harvest of hydrocarbon gasses and light aromatics. This technique had been vigorously developed in 1970 s and 80 s owing to the oil shortage crisis [6,7]. Only a few pilot and demonstration plants were constructed, but no hydrogasification processes were taken to commercial scale, in part due to the drop in oil/gas prices in the late 1980s and 1990s. Only one commercial scale coal-to-natural gas chemical plant was built in the U.S. This plant used a steam/oxygen gasification process followed by the catalytic methanation from syngas rather than a direct hydrogasification process [8,9]. In recent years, the

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world consumption of natural gas (NG) has risen rapidly, mainly due to the economic growth in developing countries.

China is short in NG reserve but has vast coal resources. On the other hand, many coal mines are located remotely away from the economically centralized districts, leading to a low efficiency of bulky coal transport. More importantly, a huge amount of coal is utilized less cleanly, bringing about the intractable problems of environmental pollution in China. It is imperative in every respect to develop new techniques for converting coal, especially low-rank and low-grade coals, into cleaner and pipeline-transportable synthetic natural gases (SNG) [10]. Coal hydrogasification, as a state-of-the-art technique, has thereby attracted a renewed research interest. A pilot-scale coal hydrogasification process has recently been developed in ENN Group Co. Ltd., China, with the handling capacity of 10 t/d coal.

The coal hydrogasification process can be broadly divided into a rapid coal hydrolysis and a slow char hydrogenation [6,11]. For the reactors with short residence time, such as entrained gas flow reactor and fluidized bed reactor, the coal hydrolysis is a dominant process determining the yields of gaseous and liquid products. Coal properties are an intrinsic factor for hydrolysis. Researchers have devoted to studying the relationships between the yields of gaseous and liquid products and the coal properties. Chen et al. investigated the hydrolysis of eight U.S. coals on a flash heating tube reactor with the heating time of 10 s and the residence time of 0.6 s [12]. They observed that overall, the yield of CH_4 obtained at a hydrogen pressure of 101.3 MPa and a temperature of 800 °C decreased appreciably with increasing the carbon content from 70% to 86% (dmmf.), whereas the yield of BTX exhibited a maximum at the mid-point of this range. Strugnell and Patrick employed a heat-grid apparatus to shed light on the rapid hydrolysis [13]. The total gas and liquid yields were found to be a function of the volatile matter contents. No significant correlations were established between the yields of any single gas of CH_4 , C_2H_6 , CO and CO_2 and the proximate and ultimate properties. From the rapid coal hydrolysis on a small entrained flow reactor at a hydrogen pressure of 4.0 MPa and a temperature of 750 °C, Tang et al. [14] observed that the yield of either C_2H_6 or $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ displayed a near linear increase with the H/C molar ratio increasing, but the yield of CH_4 was virtually unchanged from the H/C molar ratio of 0.6 to 1.1. Meanwhile, they reported that the yield of CO_2 was proportionate to the oxygen content from 3% to 20%, whereas the yield of CO varied exponentially with the oxygen content. Xu et al. performed the coal hydrolysis using a continuous free fall reactor [15]. Although the weight losses obtained at 800 °C and 7 MPa roughly had a direct proportion to the contents of volatile matter in coals, the yields of CH_4 showed no such a variation trend. From the above studies, we can cognize that the relations between the yields of products and the coal properties remain rather intriguing. Moreover, seldom literature refers to the relations to coal structures.

In a previous article, we reported the influences of post hydrocracking of volatile matter on the gas and liquid formations for a subbituminous coal using a two-stage reactor [16]. It was evident that the yield of either CH_4 or BTX was enhanced by raising hydrocracking temperature (500–750 °C) and hydrogen pressure (0.1–5.0 MPa). The yields of CO, CO_2 and H_2O were affected not only by the hydrocracking but also by the gas-phase reactions. The present work is undertaken to further investigate the hydrogasification behaviors of different rank coals using the same two-stage reactor. A focus is brought on the dependences of the yields of products obtained under varying conditions on coal properties and structures. For this purpose, chemical titration method, FTIR and solid state ^{13}C NMR have been used to quantitatively or semi-quantitatively determine the main functional groups in coal with the help of previous studies [17–19]. The study would be

valuable to deeply understand the behaviors of coal hydrogasification and to appropriately design a hydrogasification reactor and process.

2. Experimental

2.1. Coals samples

Five coals including two lignite coals (LC-1 and LC-2), two subbituminous coals (SBC-1 and SBC-2) and a bituminous coal (BC) were used in this study. The coal samples were ground and sieved to the particle size of less than 0.15 mm. The proximate and ultimate analyses of the coal samples are listed in Table 1.

2.2. Determination of total acidity and carboxyl groups

The total acidity (carboxyl plus phenolic hydroxyl groups) in coals were determined by a chemical titration method [17]. This method includes the following steps: (1) an excess amount of a $\text{Ba}(\text{OH})_2$ solution was mixed with coal at a boiling point under stirring to neutralize the acidic groups in coal; (2) a proper amount of a HCl solution was added to neutralize the remnant $\text{Ba}(\text{OH})_2$; (3) the overplus HCl amount was titrated with a NaOH solution. The carboxyl groups were determined by an ion-exchange and titration method via the following steps: (1) The coal sample was pretreated with a HCl solution to convert the carboxylate to the carboxylic acid; (2) calcium acetate was added to thoroughly exchange proton in the carboxyl groups at a boiling point; (3) the amount of released proton was titrated with a NaOH solution. The amount of phenolic hydroxyl groups in coal were calculated by the difference between the total acidity and the amount of carboxyl groups. The contents of total acidic groups, carboxyl groups and phenolic hydroxyl groups are shown in Table 1.

2.3. Spectral analyses

All coal samples were degassed and dewatered overnight at 60 °C in a vacuum oven prior to the use for FTIR and ^{13}C NMR analyses. For FTIR measurement, a 1 mg coal sample was uniformly mixed with 150 mg of potassium bromide in an agate mortar. The mixture was transferred into a glass bottle, and then was dried again at 60 °C in a vacuum oven for 12 h. A sample of the dried mixture was weighed and then molded into a tablet, and soon analyzed on a Nicolet 6700 analyzer. The spectra were recorded by co-addition of 32 scans in the range of wavenumbers 400–4000 cm^{-1} at a resolution of 4 cm^{-1} . Unfortunately, no measure was taken to avoid the contact of the sample with air during the sample molding and scanning. The spectra were fitted with the Gaussian functions coupled with Lorentz functions for the first and last peaks according to the literature [20–23]. Some modifications were made in our spectral deconvolution, and the detail will be described later. The fitting was implemented using an Originlab software until the square coefficients of correlation (R^2) of the fitted curve with the experimental spectrum reached 0.998 or better. The procedures of FTIR spectra curve fitting are described in the supplementary information (SI).

Solid state ^{13}C NMR coupled with cross polarization/magic angle spinning/total sideband suppression (CP/MAS/TOSS) techniques was conducted on a Bruker Avance II 500 NMR solid state spectrometer (11.7 T) equipped with a double resonance probe at the frequency of 125.77 MHz for carbon and 500.13 MHz for proton. The ^{13}C NMR spectra were recorded at a spinning speed of 5.65 kHz, a polarization contact time of 1 ms, a data acquisition time of 27 ms, a recycle delay time of 5 s, and a scan number larger than 2000. The ^{13}C chemical shifts were given relative to the

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