TG–GC–MS study of volatile products from Shengli lignite pyrolysis

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HIGHLIGHTS

- TG–GC–MS was used for the lignite pyrolysis analysis.
- DTG curve was fitting to 7 sub-curves to analyze the breakage of different bonds.
- Released gas at different temperatures was identified by GC–MS.
- Aliphatic and aromatic compounds were classified to understand the pyrolysis process.

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ABSTRACT

Thermal degradation of Shengli lignite was studied by thermogravimetry coupled with gas chromatography–mass spectrometry (TG–GC–MS) for a temperature range from room temperature to 1200 °C at a heating rate of 5 °C/min. The volatile products released from the lignite gradually with the programmed temperature. The main reaction of pyrolysis took place between 350 °C and 800 °C. Seven sub-curves were used to fit the DTG curve to analyze the breakage of different bonds. More than 100 different substances were identified at different temperatures from the GC–MS results. Alkanes and benzene series were the major constituents of the released volatile products along with alcohol, naphthalene, benzofuran, indane, indole, biphenyl, etc. Most of the aliphatic compounds were released around 430 °C with chain lengths up to C21, with the majority being between C1 and C5. Aromatic hydrocarbons were also released mostly at around 430 °C. The number of substituents in a single aromatic compound was found between 0 and 4. The length of the substituent was C1–C6 (sometimes heteroatom instead) and C1 accounted for the most. Generally, TG–GC–MS results presented the mass loss and released gas information with the programmed temperature to bring a better understanding of the structure of the lignite and the pyrolysis process.

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1. Introduction

The total global resources of lignite amount to 4345 billion ton [1,2], 21% of global total coal reserves. Lignite has a high water content and a low calorific value. It is difficult to transport and store, because of a tendency for spontaneous ignition tendency [3–5]. Despite being low rank coal, the outlook for lignite as a raw material for meeting the energy demand of the future is still quite important. Many countries have taken advantage of lignite: it supplies about 52% of Turkish primary energy and 50% of Greece's

energy need [6]. Lignite satisfies 91% of the state of Victoria, Australia's electricity generation [7–9]. There are more than 130 billion tons of lignite resources (approximately 13% of the total coal reserve) in China [10,11]. But currently predominantly anthracite coal satisfies China's energy demand, while the use of lignite possesses huge potential.

Many researchers have attempted to understand the coal pyrolysis process [12–17]. Most coal utilization processes (combustion [18–19], liquefaction and gasification [20]) is related to pyrolysis, in which valuable products include gaseous fuels, liquid tar or solid char [7–9]. Lignites with high volatile contents decompose at relatively low temperatures compared with other coals with low volatile products. Therefore research on pyrolysis of lignite is extremely important to understand gasification and combustion of these coals. During pyrolysis, the small molecules [21] in the

lignite vaporize first. Then some weak bridges break and release some liquid products such as tar until all the volatiles are exhausted. And at high temperature, only condensation of the carbon skeletons takes place [12,22,23]. Functional groups also decompose during the process [22]. Various techniques are used in coal pyrolysis research, and their advantages and disadvantages are briefly described by Jia et al. [24].

Thermogravimetric analysis (TGA) has been widely used to study the decomposition behavior at higher treatment temperatures (up to 1600 °C). The mass-loss (the yield of gas, tar and char) and the pyrolysis rate are obtained from the TG curve and the differential mass-loss (DTG), respectively. A gas analyzer connected with TG provides information of the volatiles evolved during the process and information on the pyrolysis behavior. Thermogravimetry coupled with mass spectrometry (TG/MS) and Thermogravimetry coupled with Fourier transform infrared spectroscopy (TG/FTIR) are the most popular methods. TG/MS [25–27] can detect small molecules H_2, CH_4, H_2O, CO, CO_2, and phenol, while TG/FTIR [27–32] is an effective method used in studying functional-group decomposition. For TG/MS and TG/FTIR systems, without separation of the released gas, it is difficult to identify the compounds due to overlapping of many signals when the thermal degradation of coal and other polymers produces a wide range of low-molecular weight compounds [25].

TG–GC–MS system is another powerful method for volatile gas analysis. Coal decomposes in a programmed-temperature process, and the released gas is transferred to GC. GC separates the complex products and then MS analyzes them. The TG–GC–MS system has been used in the research of sol–gel [33] and poly (propylene sebacate)/nano-composites [34]. TG–GC–MS shows the specific products at different temperatures with qualitative or semi-quantitative gas phase analysis and gives some knowledge of the reaction. Therefore gradual sample decomposition information can be collected. In some degree, TG–GC–MS is similar to Pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS), another advanced hybrid technique [26,35,36]. A sorbent tube is usually used for adsorbing the released gas during pyrolysis and desorbing after the pyrolysis process which is then subjected to GC/MS analysis. TG–GC–MS can analyze the products when they are released at a specific temperature without mixing gases released in the process, helping to understand the pyrolysis process better. The mass loss information of the sample and the released gas information can be obtained at the same time at a specific temperature. TG–GC–MS results can provide much information on coal structure and help to identify the reaction point of pyrolysis process. Different products could be analyzed with different reaction parameters, for example, the conversion process of coal to oil or gas can be optimized to specific products.

In this study, TG–GC–MS is used to identify thermal decomposition of Shengli lignite from room temperature to 1200 °C at a rate of 5 °C/min. TG, DTG curves combined with the GC/MS results are used to identify the pyrolysis process.

2. Experimental section

2.1. Coal sample used

Lignite from the Shengli (SL) coalfield mine in Inner Mongolia, in the northeast of China was used in experiments. The lignite, as received was ground to 200 mesh, dried using a vacuum oven at 105 °C for 4.5 h (no further mass change was detected). Ultimate and proximate analysis was carried out by using Vario MACRO cube from Elementar Co. Ltd. and 5E-MAG6700 from Changsha Kaiyuan Instrument Co. Ltd. respectively. Table 1 shows the ultimate [37] and proximate analyzes of the coal used for the experiment.

2.2. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the untreated and vacuum dried lignite samples were carried out using Nicolet 6700 (Thermo Fisher Scientific, USA) in the wave number range of 4000–500 cm^{-1} by using a KBr disc containing about 1% finely ground samples. Fig. 1a shows the FTIR spectra of the raw lignite and vacuum dried samples. The peaks were analyzed using the procedure as described by other researchers [23,25,27,38–40].

2.3. X-ray diffraction analysis

Mineral content of the raw coal was analyzed using X-ray diffraction with D8 Advance from the Bruker Company. The samples were scanned from 3° to 80° in 2θ range. The analysis (Fig. 1b) shows that most of the mineral content in the lignite was quartz (the peak Q), which is stable during pyrolysis and similar finding was reported by other researchers [41,42]. The second abundant mineral is kaolinite (the peak K), which may have a mass loss between 440 °C and 580 °C associated with the dehydroxylation process [43,44].

2.4. Experimental Setup

The overall TG–GC–MS experimental set-up is shown in Fig. 2.

The Thermogravimetric Analyzer (TGA) (SETARAM Labsys™ Evo instruments) was used to carry out pyrolysis experiments. In TGA, high purity helium (99.999%) at a flow rate of 50 ml min^{-1} was used to ensure an inert atmosphere and also as the carrier gas to remove the pyrolysis products. About 23 mg sample (<74 µm approximately 200 mesh) was pyrolysed in the TGA for a range of temperatures between 30 °C and 1200 °C at a heating rate of 5 °C min^{-1}. The evolved gas at a target temperature was sampled via an Automation Autoinjector™ system that is connected with the TGA system. The gas sample loop was 1 ml and the injection time was 10 s. The remainder of the gas is purged to the atmosphere. All transfer lines of the autoinjector are maintained at 280 °C to avoid any condensation of volatile gases whose boiling temperature is less than 280 °C.

Gas analysis was carried out with a Thermo Scientific ISQ™ single quadrupole GC–MS system. The GC instrument was equipped with TG-SQC GC Column (30 m length, 0.25 mm I.D. and 0.25 µm film). The oven temperature was held at 50 °C for 1 min, and then increased from 50 °C to 150 °C at a rate of 2 °C min^{-1}, 150 °C to 240 °C at a rate of 10 °C/min and 240 °C to 280 °C at a rate of 20 °C/min. A helium flow rate of 1 ml min^{-1} was used as the carrier gas for the column. The detector consists of a mass selective detector and electron impact mass spectra are acquired with 70 eV ionizing energy with a scanning range from 50 to 600 m/z (The m refers to the molecular or atomic mass number and z to the charge number of the ion) and with a scan rate of 5 scans s^{-1}. The MS transfer line and the ion source temperature was maintained at 280 °C. The system software is used to match each separated compound of mass spectrum with that in the spectral library (NIST 08 database) to identify the products and the accepted limit for the quality of recognition with the database was 600.

The whole analysis time depends on the GC separating time. The whole separation process of GC was approximately 62 min, and GC oven needed another 2–3 min to cool down to initial temperature of 50 °C. So the total lag time between sample injections of GC–MS system was about 65 min. The time between different injection temperatures in a single TG test was not long enough for the GC–MS analysis, so the injections were from the repeated TG tests. Blank GC–MS tests were run before every test to make sure that the GC column was purged clean after each injection.