Oxidation of Zhundong subbituminous coal in aqueous Fe2+/ glacial acetic acid solution with H2O2

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Research

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Abstract

The improvement of the reactivity of H$_2$O$_2$ and Zhundong subbituminous coal (ZS) was focused on in this work. The mild oxidation of ZS was carried out under different conditions. The liquid oxidation products were analyzed using gas chromatography /mass spectrometry (GC/MS). The results suggest that Fe$^{2+}$ and glacial acetic acid (GAA) have a synergistic effect on the H$_2$O$_2$ oxidation of ZS, which can significantly promote the conversion of ZS and the production of liquid products. In total, 40 compounds are identified, which could be categorized as 8 group components. Most of them are valued-added chemicals. Among the detected compounds, carboxylic acids (CAs) is the most abundant, accounting for 47.22% of all the group components in TRC. Moreover, according to the compounds detected by GC/MS, condensed aromatic rings are significantly abundant than aliphatic moieties in organic matter of ZS. -CH$_2$CH$_2$- are predominant bridged linkages connecting aromatic rings in ZS. The existing forms of organic nitrogen and sulfur species contain quinolins, pyrroles, pyrimidins, quinoxalines, enamides, oxazoles, isoquinolines, thiazols, sulfonamides in ZS.

1. Introduction

Low-rank coals (LRCs) are plentiful fossil resources, but they have low calorific value, high water content, high ash yield, poor thermal stability, and easy spontaneous combustion, which make LRCs difficult in the current industrial use, such as combustion, pyrolysis and gasification (Doskočil et al. 2014; Liu et al. 2019b; Liu et al. 2016; Liu et al. 2013a; Liu et al. 2013b; Liu et al. 2013c; Liu et al. 2018; Liu et al. 2015; Mae et al. 2001; Miura et al. 1996; Wang et al. 2013; Wang et al. 2012; Wang et al. 2014; Yu et al. 2014). Therefore, it is necessary to exploit a new conversion method for utilizing LRCs efficiently based on its structural characteristics (Liu et al. 2019b; Liu et al. 2018).

As is known to all, oxygen-containing functional groups, such as −OH, −COOH, −COOR, etc., are abundant in LRCs, which make LRCs have the potential to produce value-added oxygenated organic chemicals via the liquid oxidation (Doskočil et al. 2014; Liu et al. 2016; Mae et al. 2001; Miura et al. 1996). Hence, the oxidation of LRCs have attracted much attention from researchers. Classified by the kinds of oxidants, the method of oxidative depolymerization of LRCs includes RuCl$_3$-NaIO$_4$ oxidation (Huang et al. 2008; Liu et al. 2014; Lv et al. 2016; Murata et al. 2001; Stock and Wang 1986), O$_2$ oxidation (Wang et al. 2013; Wang et al. 2012), NaClO oxidation (Liu et al. 2013a; Lv et al. 2018; Wang et al. 2014; Yao et al. 2010) and H$_2$O$_2$ oxidation (Doskočil et al. 2014; Liu et al. 2019b; Liu et al. 2018; Liu et al. 2015; Mae et al. 2001; Miura et al. 1996; Tahmasebi et al. 2015; Wang et al. 2018). The high cost of RuCl$_3$-NaIO$_4$ makes it difficult for industrial applications. O$_2$ oxidation of LRCs needs high temperature, high pressure and strong acids or alkalis. NaClO oxidation of LRCs produces large amount of chloro-substituted species, leading to the difficulties in separating liquid oxidation products (Liu et al. 2015; Wang et al. 2015b). H$_2$O$_2$ oxidation of coal can be carried out at mild condition, and cannot be involved in other elements except H and O. Moreover, H$_2$O$_2$ is low price, easy availability, and eco-friendliness. Based on the above factors, H$_2$O$_2$ oxidation is a suitable way to utilize LRCs.
Miura et al. (Miura et al. 1996) found that the oxidation of LRCs using \( \text{H}_2\text{O}_2 \) under mild conditions could produce small molecule fatty acids in high yield and in high selectivity in 1996. After that, \( \text{H}_2\text{O}_2 \) oxidation of coal was used to produce carboxylic acids, including aliphatic carboxylic acids and benzenepolycarboxylic acids, and reveal molecular structure of coal (Doskočil et al. 2014; Liu et al. 2018; Liu et al. 2015; Wang et al. 2015b; Wang et al. 2018). However, to our knowledge, few reports were issued on improving the reactivity of \( \text{H}_2\text{O}_2 \) and coal.

Oxidation of coal with \( \text{H}_2\text{O}_2 \) was a free radical reaction, which hydroxyl radicals (\( \cdot \text{OH} \)), derived from the decomposition of \( \text{H}_2\text{O}_2 \), reacted with coal to achieve oxidative depolymerization of coal (Liu et al. 2018; Pan et al. 2013). \( \text{Fe}^{2+} \) is prone to catalyze \( \text{H}_2\text{O}_2 \) decomposition to form \( \cdot \text{OH} \), as shown in Eq. 1 (Jiang et al. 2013). Moreover, the yield of the liquid products abundant in value-added organic chemicals produced via oxidative depolymerization of coal with \( \text{H}_2\text{O}_2 \) is improved with the aid of glacial acetic acid (GAA) (Liu et al. 2015). In this paper, we extend the above ideas and propose to improve the yield of liquid products produced through \( \text{H}_2\text{O}_2 \) oxidation of coal by introducing \( \text{Fe}^{2+} \) and GAA. We investigated conversion of Zhundong subbituminous coal (ZS) at different reaction conditions and the liquid products were separated and analyzed with gas chromatography/mass spectroscopy (GC/MS). The result suggests that \( \text{Fe}^{2+} \) and GAA exists in a synergistic effect on the oxidation of ZS in aqueous \( \text{H}_2\text{O}_2 \) solution, which can significantly promote the conversion of ZS and the production of liquid products.

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^-
\]

(1)

2. Materials And Methods

2.1 Materials

ZS was collected from Zhundong Coal Mine in Xinjiang Province, China. It was pulverized to pass through a 200-mesh sieve (<74 μm) and then dried in a vacuum oven at 80 °C for 24 h before use. The proximate and ultimate analyses of the samples are listed in Table 1. \( \text{H}_2\text{O}_2 \) (30%), \( \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \), glacial acetic acid (GAA), butanone, anhydrous \( \text{MgSO}_4 \), \( \text{Na}_2\text{SO}_3 \), diethyl ether and diazomethane are analytical reagents. All the reagents were purchased from Aladdin. All the organic solvents were distilled before use.

| Table 1 | Proximate and ultimate analyses (wt%) of ZS |
### Proximate analysis

| Sample | Proximate analysis | Ultimate analyses (d) |
|--------|--------------------|-----------------------|
|        | $M_{ad}$ | $A_{ad}$ | $V_{ad}$ | $FC_{ad}$ | C | H | N | S | O$^a$ |
| ZS     | 15.87    | 3.71    | 27.36    | 53.06    | 72.50 | 3.56 | 0.69 | 0.49 | 22.76 |

$d$: dry base; $ad$: air dried base.

$^a$ By difference.

### 2.2 Experimental procedure

As displayed in Fig. 1, ZS (1 g), FeSO$_4$·7H$_2$O (0.06 g) and GAA (10 mL) were added to a 100 mL three-necked spherical flask under magnetic stirring. While stirring the mixture, 30% H$_2$O$_2$ (20 mL) was dropwise added into the mixture using a constant pressure drop funnel. The oxidation was performed in a water bath at 60 °C. After the reaction for 4 h, 2 g Na$_2$SO$_3$ was added into the reaction mixture to resolve excess H$_2$O$_2$, then the reaction mixture was separated by filtration to afford filter cake (FC) and filtrate (F). The FC was dried in a vacuum oven at 80 °C for 24 h. F was extracted five times with 100 mL butanone to attain extraction solution (ES). ES were dried with anhydrous MgSO$_4$ and filtrated to remove MgSO$_4$·nH$_2$O. Then the organic solvents in ES were removed by rotary evaporation to attain liquid products (E). Finally, E was methylated with diazomethane in diethyl ether to afford methyl esterified E (MEE) (Wang et al. 2015a).

The conversion of coal, and the yield and selectivity of E were calculated using the following Equations.

\[
\text{Conversion} = \frac{(m_0-m_1)}{m_0} \times 100\% \tag{2}
\]

\[
\text{Yield} = \frac{m_2}{m_0/(1-M_{ad}-A_{ad})} \times 100\% \tag{3}
\]

\[
\text{Selectivity} = \frac{\text{Yield}}{\text{Conversion}} \times 100\% \tag{4}
\]

where $m_0$, $m_1$ and $m_2$ are the weights of raw coal, FC and E, respectively.
2.3 Sample analyses

MEE was analyzed using an Agilent 7890/5977 GC/MS equipped with a DB-EUPAH capillary column and a quadrupole mass analyzer with a split flow rate of 10:1, a flow velocity of 1.0 mL/s, and operation under electron bombardment (70 eV) mode. The mass scanning range was from 30 to 500 amu. and the electron bombardment voltage is 70 eV. The capillary column was held at 45 °C for 3 min, and then heated at 10 °C min\(^{-1}\) from 45 to 310°C, and held at 310 °C for 20 min. Data were obtained and processed using GC/MS software, and the compounds were identified by comparing the mass spectra to the NIST05 spectral library data and referring to available references. The relative content (RC) of the compound was determined by normalization of the peak area, which was defined as the peak area of the compound divided by the sum of the peak areas of all identified compounds in the total ion chromatogram (Wang et al. 2015b). The total relative content (TRC) was acquired by the sum of the RC from a class of compounds.

3. Results And Discussion

3.1 Oxidation of Zhundong subbituminous coal

Conversion of ZS at different reaction conditions is shown in Table 2. When ZS is converted into liquid products abundant in value-added organic chemicals with H\(_2\)O\(_2\) as oxidant, conversion of ZS is dependent on the amount of the amount of hydroxyl radicals (·OH) derived from the decomposition of H\(_2\)O\(_2\). The more the amount of ·OH produced the decomposition of H\(_2\)O\(_2\), the higher the conversion of ZS. In the absence of FeSO\(_4\)·7H\(_2\)O and GAA (entry1, Table2), the conversion is 31.84% and the yield of liquid products is 15.06%, which could be related to the rate at which H\(_2\)O\(_2\) decomposes to ·OH is slow at current reaction conditions. ·OH can be rapidly generated from the decomposition of H\(_2\)O\(_2\) with the aid of Fe\(^{2+}\). Therefore, the addition to FeSO\(_4\)·7H\(_2\)O into the mixture of ZS and H\(_2\)O\(_2\) aqueous solution (entry2, Table2) increases the ZS conversion to 72.31%. Miura et al. (Miura et al. 1996) proposed that H\(_2\)O\(_2\) first broke weak -C-O- linkage to produce a large amount of water-soluble organic compounds and CO\(_2\), and a plurality of carboxylic groups are formed.
around the condensed aromatic rings of the compound. Then, the aromatics rings with the carboxylic groups gradually decomposed to produce small molecule fatty acids. At the same time, when the amount of \( \cdot \text{OH} \) produced from the decomposition of \( \text{H}_2\text{O}_2 \) is excessive, watersoluble organic compounds and small molecule fatty acids are further oxidized into CO\(_2\).

Under present experimental conditions, the excessive \( \text{H}_2\text{O}_2 \) is used, thus large amounts of \( \cdot \text{OH} \) are generated in the presence of \( \text{Fe}^{2+} \), which not only enhances the conversion of ZS, but also leads to the deep oxidation of liquid products. Therefore, though the conversion of ZS is very high, the yield and selectivity of liquid products is 9.74\% and 13.46\%, respectively (entry2, Table2). Interestingly, when adding \( \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \) and GAA into the mixture of ZS and \( \text{H}_2\text{O}_2 \) aqueous solution, the conversion of ZS is 75.18\%, and the yield and selectivity of liquid products is 59.49\% and 79.13\%, respectively (entry3, Table2). The result indicates that there is a synergistic effect of \( \text{Fe}^{2+} \) and GAA, which can significantly promote the conversion of ZS and the production of liquid products.

### Table 2 Conversion of ZS at different reaction conditions

| entry | 30\% \( \text{H}_2\text{O}_2 \) /mL | \( \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \) / g | GAA / mL | Conversion /\% | Yield /\% | Selectivity /\% |
|-------|-------------------------------|-------------------|---------|----------------|------------|----------------|
| 1     | 20                            | 0                 | 0       | 31.84          | 15.06      | 47.31          |
| 2     | 20                            | 0.06              | 0       | 72.31          | 9.74       | 13.46          |
| 3     | 20                            | 0.06              | 10      | 75.18          | 59.49      | 79.13          |

### 3.2 GC/MS analysis

As displayed in Fig. 2 and Table 3, 40 compounds are identified by GC/MS analysis in total. Their parent products can be classified into hydrocarbons (HCs), alkanoic acids or
alkenoic acids (AAs), alkanedioic acids or alkenedioic acids (ADAs), alkanetricarboxylic acids or alkenetricarboxylic acids (ATCAs), benzene carboxylic acids (BCAs), nitrogen containing species (NCSs), sulfur containing species (SCSs), and others species (OSs) (Liu et al. 2019a; Liu et al. 2013b; Liu et al. 2013c; Wang et al. 2014).

As shown in Table 3 and Fig. 3, 19 carboxylic acids (CAs) are detected by GC/MS analysis, including 2 AAs, 7 ADAs, 3 ATCAs and 7 BCAs. CAs is the most abundant, accounting for 47.22% of all the group components in TRC. Arylalkenes or arylalkanes, α,ω-diarylalkenes or α,ω-diarylalkanes and condensed aromatics are the precursors of AAs, ADAs and BCAs, respectively (Liu et al. 2013b). Pan et al. (Pan et al. 2013) proposed the mechanism of the H$_2$O$_2$ oxidation: First, ·OH are produced from the decomposition of H$_2$O$_2$. Then, ·OH reacts with the cluster ring, producing a large amount of water-soluble organic compounds. Meanwhile, Liu et al. (Liu et al. 2018) supposed that ·OH can break condensed aromatic rings in Xianfeng lignite-derived residue followed by rupturing the condensed aromatic rings to produce aromatic carboxylic acids. Among the detected CAs, BCAs are the most abundant in detected compounds, accounting for 34.89% of all group components in TRC, suggesting that that condensed aromatic rings are significantly abundant than aliphatic moieties in organic matter of ZS. Interestingly, benzene-1,2,3,4,5,6-hexacarboxylic acid, accounts for 25.03% of all the group components in TRC. The resulting benzene-1,2,3,4,5,6-hexacarboxylic acid could be derived from the oxidation of highly condensed aromatic rings (Scheme 1). Among the detected ADAs, succinic acid is predominate, accounting for 4.3% of all the group components in TRC, implying that $\text{-CH}_2\text{CH}_2\text{-}$ is dominant bridged linkages connecting aromatic rings in ZS. Moreover, most of the detected CAs are valued-added chemicals. For example, palmitic acid can be used as a precipitant, chemical reagent and waterproofing agent. Succinic acid can be used to produce surfactant, detergent additive and foaming agent. Benzene-1,2,3,4,5,6-hexacarboxylic acid is a useful polydentate ligand (Liu et al. 2018).

As shown in Table 3 and Fig. 3, 7 HCs, 8 NCSs and 6 SCSs were detected by GC/MS analysis, respectively. According to the detected NCSs and SCSs, we deduce that the existing forms of organic nitrogen and sulfur species in ZS contain quinolins, pyrroles, pyrimidins,
quinoxalines, enamides, oxazoles, isoquinolines, thiazols, sulfonamides. Moreover, some of them are useful chemicals. For example, (Z)-docos-13-enamide, which accounts for 10.21% of all the group components in TRC, can be used as an excellent lubricant for extruded films of polyvinyl chloride, polyethylene and polypropylene.

[Please see the supplementary files section to view Scheme 1.]

**Table 3** Compounds detected in the product from ZS oxidation with H$_2$O$_2$ in the presence of Fe$^{2+}$ and GAA. Reaction conditions: ZS, 1g; temperature, 60 °C; 30% H$_2$O$_2$, 20 mL; FeSO$_4$·7H$_2$O, 0.06g; oxidation time, 4 h; glacial acetic acid, 10 mL.
| Peak   | Parent compound                                      | Relative content/% |
|--------|------------------------------------------------------|--------------------|
| HC     | icosane                                              | 0.22               |
| 19     | henicosane                                           | 0.49               |
| 22     | docosane                                             | 0.87               |
| 27     | tricosane                                            | 1.08               |
| 31     | tetracosane                                          | 1.14               |
| 32     | pentacosane                                          | 0.84               |
| 33     | hexacosane                                           | 0.69               |
| AA     | 3-(2-hydroxyethoxy)-3-oxopropanoic acid              | 0.7                |
| 18     | palmitic acid                                        | 0.36               |
| ADA    | fumaric acid                                         | 0.38               |
| 1      | 2-hydroxysuccinic acid                               | 1.36               |
| 2&8&11 | 2,3-dihydroxysuccinic acid                           | 0.81               |
| 6      | maleic acid                                          | 0.29               |
| 7&21&26| succinic acid                                        | 4.3                |
| 10     | 4-oxoheptanedioic acid                               | 0.25               |
| 14&15  | 5-oxotetrahydrofuran-2,3-dicarboxylic acid           | 0.8                |
| ATCA   | 2-hydroxypropane-1,2,3-tricarboxylic acid            | 0.75               |
| 9&25   | 1-hydroxypropane-1,2,3-tricarboxylic acid            | 0.73               |
| 12&13  | propane-1,2,3-tricarboxylic acid                     | 1.6                |
| BCA    |                                                     |                    |
|   | Chemical Structure | Molecular Formula | Concentration |
|---|--------------------|-------------------|---------------|
| 5 | phthalic acid      |                  | 0.29          |
| 28&29 | benzene-1,2,4-tricarboxylic acid |                  | 3.55          |
| 30 | benzene-1,3,5-tricarboxylic acid |                  | 1.14          |
| 35&36 | benzene-1,2,3,5-tetracarboxylic acid |                  | 1.5           |
| 38 | benzene-1,2,3,4-tetracarboxylic acid |                  | 0.94          |
| 39 | 2,2'- (isophthaloylbis(oxy))diacetic acid |                  | 2.44          |
| 49&51&54&56 | benzene-1,2,3,4,5,6-hexacarboxylic acid |                  | 25.03         |
| NCSs |                      |                  |               |
| 16 | 2-methylquinolin-3-ol |                  | 0.43          |
| 17 | quinoline-2-carboxylic acid |                  | 0.29          |
| 40&42&43 | ethyl 9-methyl-1-phenyl-1,2,3,3a,9,9a-hexahydro-4H-pyrrolo[2,3-b]quinoxaline-4-carboxylate | 6.48 |
| 44 | 5-benzyl-4,6-diphenylpyrimidin-2(1H)-one |                  | 11.82         |
| 48 | 2,3,8,9-tetramethoxy-11,12-dihydrobenzo[c]phenanthridin-6(5H)-one |                  | 1.04          |
| 50 | (Z)-docos-13-enamide |                  | 10.21         |
| 52 | 7-(4,5-dimethoxy-2-methylnaphthalen-1-yl)-3- |                  | 0.82          |
methyl-1,2,3,4-
tetrahydroisoquinolin-8-ol

|    |                |       |
|----|----------------|-------|
| 53 | 7-methyl-6,7,7a,8-| 4.13  |
|    | tetrahydro[1,3]dioxolo[4,5-i] |       |
|    | [1,3]dioxolo[4',5':5,6]indeno |       |
|    | [2,1-c][2]benzazepine |       |

SCSs

|    |                  |       |
|----|------------------|-------|
| 23 | N,4-             | 5.41  |
|    | dimethylbenzenesulfonamide |       |
| 45 | (Z)-6,7-dimethyl-2-(3-| 2.08  |
|    | nitrobenzylidene)benzo[4,5]i|       |
|    | midazo[2,1-b]thiazol-3(2H)-|       |
|    | one              |       |
| 47 | 2,4-             | 0.8   |
|    | dimethylbenzo[4,5]imidazo[1|       |
|    | ,2-|               |       |
|    | c]pyrido[3',2':4,5]thieno[2,3-e]pyrimidine |       |
| 55 | N,4-dimethyl-N-   | 0.89  |
|    | tosylbenzenesulfonamide |       |

OSs

|    |                  |       |
|----|------------------|-------|
| 34 | dimesitylmethanone | 0.89  |
| 41&46 | bis(6-methylheptyl) | 2.16  |
|      | phthalate         |       |

4. Conclusion

Fe$^{2+}$ and GAA have a synergistic effect on the H$_2$O$_2$ oxidation of ZAS, which can significantly promote the conversion of ZS and the production of liquid products. More organic matter is converted into soluble species, including HCs, AAs, ADAs, ATCAs, BCAs, NCSs, SCSs and OSs)by oxidation of ZS with H$_2$O$_2$ in the
presence of Fe$^{2+}$ and GAA. In total, 19 carboxylic acids (CAs) are detected by GC/MS analysis, including 2 
AAs, 7 ADAs, 3 ATCAs and 7 BCAs. Among the detected compounds, CAs is the most abundant;
accounting for 47.22% of all the group components in TRC. Moreover, according to the compounds
detected by GC/MS, condensed aromatic rings are significantly abundant than aliphatic moieties in
organic matter of ZS. -CH$_2$CH$_2$- is predominant bridged linkages connecting aromatic rings in ZS. The
existing forms of organic nitrogen and sulfur species contain quinolins, pyrroles, pyrimidins, quinoxalines,
enamides, oxazoles, isoquinolines, thiazols, sulfonamides in ZS.

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**Figures**

**Figure 1**

Procedure for oxidation of ZS with H$_2$O$_2$ in the presence of Fe$^{2+}$ and GAA.
Figure 2

Total ion chromatograms of the methyl esterified products from ZS with H2O2 in the presence of Fe2+ and GAA. Reaction conditions: ZS, 1g; temperature, 60 °C; 30% H2O2, 20 mL; FeSO4·7H2O, 0.06g; oxidation time, 4 h; glacial acetic acid, 10 mL.

Figure 3

Distribution of group components in the MEE from oxidation of ZS with H2O2 in the presence of Fe2+ and GAA. Reaction conditions: ZS, 1g; temperature, 60 °C; 30% H2O2, 20 mL; FeSO4·7H2O, 0.06g; oxidation time, 4 h; glacial acetic acid, 10 mL.

Supplementary Files
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- Scheme1.PNG