Coal depolymerization using permanganate under optimal conditions

Chunjie Xia¹, Tomasz Wiltowski^{2,3}, Satya Harpalani⁴, Yanna Liang^{1,5}

¹. Department of Civil and Environmental Engineering, Southern Illinois University Carbondale,
1230 Lincoln Dr. Carbondale, IL 62901, USA

². Department of Mechanical Engineering and Energy Processes, 1230 Lincoln Drive, Southern
Illinois University Carbondale, Carbondale, IL 62901, USA

³. Advanced Coal and Energy Research Center, 405 West Grand Ave., Southern Illinois
University Carbondale, Carbondale, IL 62901, USA

⁴. Department of Mining and Mineral Resources Engineering, 1230 Lincoln Drive, Southern
Illinois University, Carbondale, IL 62901, USA.

⁵. Materials Technology Center, 1230 Lincoln Drive, Southern Illinois University, Carbondale,
IL 62901, USA.

* Corresponding author phone: 618-453-7808; fax: 618-453-3044

E-mail: liangy@siu.edu

Abstract:

For the purpose of solubilizing coal for liberating valuable chemicals, permanganate was used as an oxidant. To obtain the highest yield of soluble compounds from coal, permanganate was studied at different concentrations and different temperatures with different loading of bituminous coal from the Illinois basin. The optimal condition for dissolving 60% of the bituminous coal was: KMnO_4 at 0.45 mol/L; temperature at 25 °C; coal loading at 50 g/L in a

tumbler set at 45 rpm for 21 days. A mathematical equation was developed for predicting yield of soluble compounds from coal based on experimental data. Upon verifying the results predicted by the model, coal treatment also included samples from the San Juan basin and the Powder River Basin. After treatment, the residual coal was characterized in terms of elemental composition. The aqueous phase was subjected to analysis of total organic carbon (TOC), volatile compounds by HPLC and dichloromethane solubles by GC-MS. Considering the high TOC content demonstrated from this study, this work provided a cost-effective way for obtaining value-added chemicals from coal at different locations.

Key words: Coal, KMnO_4 , Value-added chemicals, TOC, GC-MS, Optimization

1. Introduction

Coal played a critical role as a primary source of organic chemicals throughout the world until the 1950s and has also maintained its role as a primary energy source in the 20th century (Schobert and Song, 2002). In the past decades, coal has increased its share of the global energy mix from 23% in 2000 to 29% in 2015 although the momentum behind coal's surge is starting to ebb (International Energy Agency, 2015). It is recognized that the total world proved reserves of coal in the end of 2014 were 891 billion tons, which are sufficient to sustain 110 years of global consumption, by far the largest reserves-to-consumption ratio for any fossil fuel (BP, 2015). Therefore, coal could still be an abundant and important resource in the next century.

Coal's use as a "non- fuel" has also been explored over the years, due in part to its low cost. Biological, thermochemical, and chemical processes have been considered for the

conversion of coal to valuable chemicals. The aerobic biological conversion of coal using pure strains of bacteria and fungi, as well as the extracellular enzymes produced from these microorganisms was extensively studied in the 1980s and 1990s. (Fakoussa and Hofrichter, 1999; Hofrichter et al., 1997a, b; Willmann and Fakoussa, 1997; Wilson et al., 1987). As a result, pure bacterial and fungal strains have been isolated from different environments and well characterized (Fakoussa and Hofrichter, 1999; Huang et al., 2013a). In recent years, anaerobic conversion or biogasification of coal has been on the rise. This approach focuses on producing methane from coal (Park and Liang, 2016; Zhang et al., 2016a; Zhang et al., 2015a; Zhang et al., 2015b; Zhang et al., 2016b). Although various microbes do have the potential and capability to convert coal to methane under mild conditions, this direction does have the drawbacks of being relatively slow (days vs. minutes in chemical reactions) and sometimes inefficient and thus requires more efforts to make it cost-effective at large scales.

Thermochemical coal conversion is featured by using high temperatures. Along this line, many attempts have been made to increase the yields of tar and aromatic compounds, such as benzene, toluene and xylene (BTX) through controlling either the primary reactions or the secondary gas phase reactions (Miura, 2000). Even though different forms of pyrolysis at different temperatures have been performed and the yield of total volatiles and BTX are improved, thermochemical conversion needs to overcome the expensive energy cost in addition to other challenges (Siefert et al., 2012; Steynberg and Nel, 2004).

In terms of severity of reaction conditions, chemical conversion of coal is in between biological and thermochemical. Throughout the years, different chemicals, such as strong acids, strong bases and oxidants have been investigated regarding their effects on solubilizing coal (Alvarez et al., 2003; Hayatsu et al., 1981; Huang et al., 2013b). For subbituminous coal sampled

from the Powder River Basin (PRB), nitric acid at 3.33 mol/L was found to depolymerize the coal the best compared to sodium hydroxide, hydrogen peroxide and permanganate (Huang et al., 2013b). However, the compounds in the water soluble phases derived from nitric acid and sodium hydroxide treatments were shown to be relatively recalcitrant. Of the chemicals evaluated, the treatment using permanganate at 0.1 mol/L was shown to be the most bioavailable, even though only 5.4% of the total coal carbon was dissolved into the aqueous phase. When used at a higher concentration of 0.25 mol/L at 80 °C, permanganate liberated around 25% of the coal carbon from lignite to organic acids and 15.9% to humic acids (Hayatsu et al., 1981). In addition to these studies, permanganate as an oxidant has been successfully used to remediate groundwater and soil at contaminated hazardous waste sites (Ighere et al., 2015; Urynowicz, 2008) and also for coal structure studies (Bone et al., 1930; Burke et al., 1990; Forsey et al., 2010; Haenel, 1992; Moore and Swanson, 1993; Novikova et al., 2010; Zhang, 2016). However, although permanganate is a promising oxidant in dissolving chemicals from coal, use of this chemical for producing value-added products from coal has not been investigated in detail. Thus, the objectives of this study aimed to: (1) identify and verify optimal conditions for solubilizing bituminous coal from the Illinois basin in the USA through use of permanganate as an oxidant; (2) characterize the residual coal together with those derived from another two coal basins in the USA; and (3) characterize the soluble compounds generated from three kinds of coals in terms of total organic carbon (TOC) and chemical compositions through gas chromatography-mass spectrometry (GC-MS) and high performance liquid chromatography (HPLC).

2. Materials and methods

2.1. Coal

Three coal samples were investigated in this study. One was from #6 (Herrin seam) of the

Illinois basin, and the details of geographical location was previously reported by Zhang et al (Zhang et al., 2015a). The other two samples were collected from southwest of the San Juan basin and west central Wyoming in the Powder River Basin, respectively. These coal samples were referred to as IL coal, SJ coal and PRB coal in the following. For all three coal samples, blocks of freshly cut coal were picked from the working face of underground operations. They were brought to the surface where they were sealed in boxes and kept immersed under water to prevent dehydration and exposure to sunlight. The boxes were then transported to laboratories at Southern Illinois University Carbondale and kept at room temperature. It needs to be noted that the operations practiced continuous mining. No drilling or injection of chemicals was involved. Thus, the coals were not contaminated and were in their native states. Prior to testing, the outer layers of the coal blocks were peeled and only the inner portion of the coal was ground. Those passed through a 40 mesh (< 0.42 mm) screen were stored in re-sealable ziploc bags and maintained in a humidity chamber at room temperature to avoid water loss (Zhang et al., 2015a; Zhang et al., 2016b). Elemental analyses of the coal samples were conducted using a Fisher Thermo Scientific Flash 2000 Organic Elemental Analyzer (Thermo Fisher Scientific, Waltham, MA, USA). Proximate analyses were performed by Standard Laboratories, Inc. (Freeburg, IL, USA). Results of these analyses were presented in Table 1.

2.2. Coal pretreatment by KMnO_4 : identifying optimal values for each of three parameters

Four parameters were evaluated as part of the KMnO_4 pretreatment study: concentration, temperature, coal loading, and treatment duration. The IL coal was used to evaluate the optimal value for the first three parameters using a Box-Behnken factorial design. The experiments were performed with initial KMnO_4 concentrations of 0.1, 0.28 and 0.45 M, temperatures of 25, 33 and 40 °C, and coal loadings of 50, 125 and 200 g coal per liter solution. (Table 2). For coal

loading of 50, 125 and 200 g coal per liter solution, 2, 4.5 and 8 g coal were added to 40 ml of KMnO_4 solution, respectively. A total of 17 reactors were established using 120-mL serum bottles containing 40 mL of KMnO_4 solution at desired concentration and coal at designated loading and maintained at set temperatures in shakers at 120 rpm. After 21 days, the content of each reactor was centrifuged at $4,000 \times g$ for 20 min to separate the liquid and residual coal. The liquid fraction was then filtered through a $0.45 \mu\text{m}$ cellulose filter. Three aliquots of each filtrate were dried in the fume hood by air and weighed to determine the dry weight of the soluble compounds which was the response. Additionally, after aliquots of filtrate were used for gravimetric analysis for obtaining yield of soluble compounds, the remaining filtrate was adjusted to a neutral pH with 6 M HCl, filtered again to remove any precipitates, and stored at 4°C for further analysis. The solid fraction was washed with deionized and distilled water (DDW) 3-5 times to remove any soluble compounds associated with coal. The washed coal was kept at 4°C for later use.

The experimental results were analyzed using the Design-Expert (Stat-Ease, Inc., Minneapolis, Minnesota, USA). Once the optimal value for each parameter was calculated by the software, a verification experiment was performed to confirm the predicted response in terms of the concentration the yield of soluble compounds. In addition, the mixing approach of shaking was compared to tumbling in a tumbler set at 45 rpm. Other treatment durations, including 5, 7, 12, 21, 25, and 30 days were also investigated. Once the optimal condition was finalized for the IL coal, the SJ and PRB coals were treated under the same conditions and analyzed in a similar fashion as the IL coal.

2.3. Analysis

Total organic carbon (TOC) in each filtrate sample was analyzed with a TOC analyzer (TOC-5000A, Shimadzu Corporation, Kyoto, Japan). TOC was determined by performing separate total carbon (TC) and total inorganic carbon (TIC) analyses and subtracting the results. The samples were diluted by DDW with different dilution factors in order to fit the calibration range.

The residual coal solids that was washed as detailed above was homogenized and dried in an oven at 105 °C until the solid weight was constant. Analysis of carbon, hydrogen, nitrogen, sulfur and oxygen was conducted by using Thermo Flash 2000 Elemental Analyzer (Hudson, New Hampshire, USA) according to manufacturer recommended procedures.

To understand the composition of the filtrate, nonadecanoic acid (C19:0) (98%, Acros organics, New Jersey, USA) was used as an internal standard and added to each 5 mL sample. After the pH was adjusted to 2.0 using 12 M HCl, 5 mL dichloromethane (DCM) (99.9%, Fisher Chemical, Pittsburgh, Pennsylvania, USA) was added. The glass tube was then vortexed vigorously for 10 min. When phase separation was complete, the DCM layer was withdrawn from the bottom of the tube. The remaining aqueous phase was extracted by DCM twice. All DCM fractions were pooled together, passed through dried sodium sulfate powder and evaporated to dryness under a gentle stream of nitrogen. Methanol (1.0 mL) was then added to dissolve the dried powder followed by transferring to a GC vial where 0.1 mL tetramethylammonium hydroxide (TMAH) stock solution (20 g/L) was added for derivatization.

GC-MS analysis (Agilent 7890A/5975C) was performed using helium (1 mL/min) as the carrier gas and a capillary column, HP-5MS (30 m 5% phenyl methyl siloxane × 0.25 mm i.d.;

0.25 μm film thickness, Agilent). The GC oven was heated to 50 $^{\circ}\text{C}$ for 1 min then to 300 $^{\circ}\text{C}$ at a rate of 4 $^{\circ}\text{C}/\text{min}$ with an isothermal period of 5 min. Spectra were recorded in the EI mode (electron energy = 70 eV), with a scan range from 33 to 650 m/z in 0.42 s/scan. The injection volume was 1 μL . The identification of each compound was achieved by matching each peak's mass spectrum with that in the spectral library (NIST 11 database).

Concentrations of volatile products (formic acid and acetic acid) in filtrates were analyzed using a HPLC (Shimadzu Scientific Instrument, Inc. Columbia, MD, USA) through establishing an external calibration curve for each target compound. This HPLC had a refractive index detector and used an Aminex HPX-87 column (5 μm , 30 $\text{cm} \times 4.6$ mm, Bio-Rad, CA, USA). This column was installed in an oven set at 40 $^{\circ}\text{C}$. Sulfuric acid at 0.005 M was used as the mobile phase with a flow rate of 0.6 mL/min . The injection volume was 20 μL .

3 Results and Discussions

3.1. Coal composition

As shown in Table 1, the IL coal contained carbon, nitrogen, hydrogen, sulfur and oxygen at the following percentages; $70.07 \pm 0.36\%$, $1.39 \pm 0.01\%$, $5.21 \pm 0.03\%$, $0.63 \pm 0.03\%$ and $15.41 \pm 0.20\%$, respectively. The SJ coal samples had similar content of carbon, nitrogen, hydrogen, and sulfur as those of the IL coal, but a higher concentration of oxygen. The PRB coal had even a higher oxygen content of $26.56 \pm 0.59\%$, which was significantly higher than those of IL and SJ coals. In addition, the carbon, nitrogen, hydrogen and sulfur contents of the PRB coal were all lower than those the other two coal samples studied.

The proximate analysis demonstrated that the IL coal was indeed high volatile bituminous B. Compared to the IL coal, the SJ coal had lower content of ash and volatile matter, but higher content of fixed carbon. However, the heating value of $12,410.65 \pm 80.36$ BTU/lb put it into the

same category as the IL coal. Compared with the IL coal, the PRB coal had higher content of ash and fixed carbon, but lower content of volatile matter. The heating value of $10,786.25 \pm 29.80$ BTU/lb indicated that it was close to high volatile bituminous C. Even though the IL and SJ coal had similar heating values, they had different colors. The former appeared to be black while the latter looked brownish. The PRB coal was even more brown than the SJ coal and looked like a typical brown coal.

Generally, the IL, SJ and PRB basins are recognized as rich deposits of bituminous, subbituminous and lignite coal, respectively. However, the coal from the sampling locations in the SJ and PRB basins did not belong exactly to subbituminous and lignite. Similar observations were reported by Green et al. (Green et al., 2008) who reported that subbituminous B Wyodak coal from the PRB basin had a content of 69.74% of carbon, 0.94% of nitrogen, 5.55% of hydrogen, 0.35% of sulfur, 14.83% of oxygen and 8.59% of ash. The calculated heating value of 12,652.3 BTU/lb would categorize it as high volatile bituminous B. Therefore, even though different basins have signature characteristics, ranking of coals varies with different locations and the coal investigated in this study represented those locations identified above.

3.2. Identifying optimal parameters for maximum yield of soluble compounds

Analysis of soluble compounds yield (g/g coal) (Table 2) under different conditions revealed that coal loading and KMnO_4 concentration, each had a p value less than 0.0001, had statistically significant effects on coal depolymerization. Effect from temperature was not significant. In addition, interactions between AB, AC, BC and A^2 and C^2 were significant, too (Table 3). As indicated by Fig. 1, decrease of coal loading and increase of KMnO_4 concentration resulted in higher yield of soluble compounds than those with high coal loading and low concentration of KMnO_4 . All experimental results can be fitted by a reduced quadratic model. This model had a R^2 of 0.9999, adjusted R^2 of 0.9997, predicted R^2 of 0.9988 and adequacy precision of 313.892.

If parameters in the units in Table 2 were used, yield of soluble compounds in natural log could be expressed as:

$$\begin{aligned} \text{Ln (Soluble components yield)} = & - 2.25093 - 0.021827 \times \text{Coal loading} + 0.01301 \times \\ & \text{Temperature} + 10.57827 \times \text{KMnO}_4 \text{ Concentration} - 4.68\text{E-}05 \times \text{Coal loading} \times \text{Temperature} + \\ & 2.48\text{E-}03 \times \text{Coal loading} \times \text{KMnO}_4 \text{ Concentration} - 0.030472 \times \text{Temperature} \times \text{KMnO}_4 \\ & \text{Concentration} + 4.46\text{E-}05 \text{ Coal loading}^2 - 10.00733 \times \text{KMnO}_4 \text{ Concentration}^2 \end{aligned}$$

According to this model, the optimal condition for achieving the highest yield of soluble compounds of 0.596 g/g coal was: solid loading, 50 g/L; temperature, 25.104 °C; and KMnO₄, 0.45 mol/L. To confirm the predicted results, experiments were conducted by adopting the optimal value for each parameter. At the end of 21 days, yield of soluble compounds was 0.580 ± 0.01 g/g coal, which matched the predicted results well. In addition, the yield obtained through using a tumbling mixer was 0.684 g/g coal with the same temperature, coal loading and permanganate concentration (Fig. 2). Thus, the method for mixing did play an important role on reaction rate as it impacted the contact between coal and the liquid reactants. In terms of treatment duration, from day 5 to day 21, the yield of soluble compounds increased with increasing of time. After day 21, however, the yield basically leveled off. Thus, it could be concluded that at day 21, the reaction of coal and KMnO₄ was complete due to the exhaustion of the permanganate. Under the optimal conditions attained for the IL coal, the yield of soluble compounds was 0.901 ± 0.006 g/g SJ coal and 0.953 ± 0.033 g/g PRB coal. Therefore, the best condition for solubilizing the IL coal can also be applied to the SJ and PRB coals evaluated in this study.

3.3. Characterization of the residual coal solids

As a result of the pretreatment by KMnO_4 , the residual coal samples all contained less carbon, nitrogen, hydrogen, and sulfur (Fig. 3). In particular, the decrease of carbon content, 87.2% for the PRB coal, 89.8% for the SJ coal and 84.5% for the IL coal, was dramatic, which demonstrated that using KMnO_4 at 0.45 mol/L was effective in removing carbon from coal. It needs to be noted that the lost carbon has two forms: dissolved in the aqueous phase and as CO_2 in the gas phase. The oxygen content, however, varied depending on specific coal samples. Regarding the PRB coal, the oxygen content became $27.007 \pm 0.464\%$ from $26.561 \pm 0.590\%$. For the SJ basin coal, the oxygen content increased from $17.967 \pm 0.057\%$ to $27.838 \pm 0.679\%$. The same trend was observed for the IL coal. The oxygen percentage increased from $15.408 \pm 0.197\%$ before treatment to $24.925 \pm 1.569\%$ after treatment. As a consequence of treatment, the residual coal had much lower heating values. Based on the elemental analysis, all three kinds of residual coals comprised approximately 62% of other elements rather than carbon, hydrogen, nitrogen, sulfur and oxygen. Considering the reaction between coal and KMnO_4 , the uncharacterized elements should be mainly those from the reagent used, such as K and Mn. As the former might reside in the aqueous phase, Mn was supposedly staying with coal as MnO_2 . However, this assumption needs to be further confirmed.

3.3. Characterization of the soluble compounds

Analysis of TOC in the aqueous phase samples disclosed similar concentrations of inorganic carbon and organic carbon for the IL and SJ coal (Table 4). The inorganic carbon, such as bicarbonate and carbonate might be from dissolution of CO_2 resulted from coal oxidation by the added permanganate. With regard to the PRB coal, the TOC content of 0.120 g/g coal carbon was higher than the inorganic carbon of 0.096 g/g coal carbon. The TOC concentration increased from 2,732.333 mg/L for the IL coal to 3,073.800 mg/L for the SJ coal and to 3,364.333 mg/L

for the PRB coal. Similarly, the TOC in g/g coal carbon increased in the same order. These TOC contents were significantly higher than 1,200 mg/L and 0.054 g/g coal carbon reported for PRB subbituminous coal (Huang et al., 2013c). The reported TOC results were obtained at a solid loading of 33.3 g/L and KMnO_4 at 0.1 mol/L for 21 days at room temperature and a tumbling speed that was not specified. In addition, the contents of TOC in samples derived from the SJ and PRB coals were higher than 3,038 mg/L, the highest value obtained from treating different PRB coal samples with nitric acid, sodium hydroxide, permanganate and hydrogen peroxide. This TOC content was from pretreatment that was conducted with nitric acid at 3.33 mol/L for 4 months (Huang et al., 2013b). Although results obtained from different studies may not be comparable owing to different mechanisms, the optimal value determined in this study for the critical parameters did lead to more efficient coal depolymerization and dissolution compared with those reported so far.

Analysis of the DCM soluble samples by GC-MS identified a total of 37, 30 and 34 compounds derived from the IL, SJ and PRB coal, respectively (Fig. 4, Supplemental Fig. 1 and Fig. 2). All of these compounds (Table 5, Supplemental Table 1 and Table 2) matched those in the MS library at over 90% of confidence. These compounds were grouped into seven different categories (Table 6). For the DCM solubles derived from the SJ and PRB coals, fatty acids and their derivatives comprising 55.4% and 72.9% of the total were the dominant group. For those derived from the IL coal, this group was 26.4% out of the total, which was less than dicarboxylic acids, 28.7% of the total. For these two groups, the carbon length varied between C_5 and C_{26} . Besides aliphatic acids, benzene-related compounds including benzoic acid and benzene derivatives were abundant in the DCM solubles from the three kinds of coals. These results were in agreement with those reported. For example, when lignite was exposed to 0.25 mol/L KMnO_4

at 80 °C, the oxidation products included unbranched aliphatic dicarboxylic acids ranging from C₄–C₁₈, branched dicarboxylic acids (C₅–C₁₀), tricarboxylic acids (C₆–C₈), and aromatic acids (Hayatsu et al., 1981). Specific to the IL coal, alcohol and hydrocarbons were identified although the contents were rather low.

For each kind of coal sample, the quantity of all of these identified by GC-MS was 762.70 ± 81.48; 840.14 ± 138.00; and 942.80 ± 257.32 µg/g coal daf for the IL, SJ and PRB coal, respectively (Table 7). Besides GC-MS, HPLC was also used to detect those that were volatile and missed by the GC. Formic acid and acetic acid were detected by HPLC with concentrations higher than the sum of those identified by GC-MS. Adding all together, the identified compounds were 22.9 mg/g IL coal, 21.1 mg/g SJ coal and 25.5 mg/g PRB coal. Compared to the total dry weight of chemicals in the aqueous phase samples, the majority of chemicals were not identified by both GC-MS and HPLC. It needs to be noted that only DCM solubles were subjected to analysis in this study. As reported by Liu et. al. (Liu et al., 2003), large fractions of compounds may not be organic solvent soluble, but stay in the solvent insoluble and water soluble phase. Thus, further investigation of those water soluble compounds needs to be carried out.

In summary, through using KMnO₄ under mild conditions, coal can be depolymerized and converted to water soluble compounds. Among those water solubles that could dissolve in DCM, a broad variety of compounds that are of high values were identified in addition to formic acid and acetic acid. However, further work is urgently needed to identify all possible chemicals and develop ways to utilize those derived from coal.

Conclusion

The optimal condition for depolymerizing bituminous coal from the IL basin through use of permanganate was identified. To obtain the highest yield of soluble compounds from the IL coal, permanganate needed to be used at 0.45 mol/L at a coal loading of 50 g/L and at room temperature with tumbling at 45 rpm for 21 days. Under this same condition, more TOC was detected in aqueous phase samples derived from the PRB and SJ basin than those from the IL basin. Although this study revealed the highest TOC content compared with reported results, the quantity of total identifiable compounds in the aqueous phase samples was between 2.1 and 2.6 % of coal (daf). This was mainly due to limitations posed by the GC-MS analysis. Nevertheless, this study demonstrated a cost-effective way for dissolving coal from three basins. The high yield of soluble compounds from the studied coals warrants further investigation with regard to chemical characterization and downstream separation for obtaining pure compounds for industrial uses.

Acknowledgement

We gratefully acknowledge support from the Department of Energy of the United States under Award Number DE-FE0024126.

Tables:

Table 1: Composition of coal samples studied in this work.

Table 2. The Box–Behnken design of the variables with yield of soluble compounds as the response.

Table 3. Analysis of variance (ANOVA).

Table 4. Results of TOC in different aqueous phase samples after treatment.

321 Table 5. Compound profile of the DCM solubles derived from treating the IL coal with KMnO_4 .

322 Table 6. Groups of compounds identified in DCM solubles by GC-MS.

323 Table 7. Yields of identified compounds in the aqueous phase samples derived from coal
324 treatment.

325 Supplemental Table 1. Compound profile of the DCM solubles derived from treating the SJ coal
326 with KMnO_4 .

327 Supplemental Table 2. Compound profile of the DCM solubles derived from treating the PRB
328 coal with KMnO_4 .

329

330 **Figure Caption**

331 Fig. 1: The effect of solid loading and KMnO_4 concentration on the yield of soluble compounds
332 from the IL coal.

333 Fig. 2: (a) The effect of mixing method on the yield of soluble compounds

334 (b) Yield of soluble compounds changing with reaction time.

335 Fig. 3: The comparison of elemental content and heating value before and after treatment. (A) IL
336 coal; (B) SJ coal; (C) PRB coal; (D) heating value.

337 Fig. 4: The GC chromatogram of the DCM solubles derived from treating the IL coal with
338 KMnO_4 .

339 Supplemental Fig. 1: The GC chromatogram of the DCM solubles derived from treating the SJ
340 coal with KMnO_4 .

341 Supplemental Fig. 2: The GC chromatogram of the DCM solubles derived from treating the PRB
342 coal with KMnO_4 .

343

344

References

- Alvarez, R., Clemente, C., Gómez-Limón, D., 2003. The influence of nitric acid oxidation of low rank coal and its impact on coal structure. *Fuel* 82, 2007-2015.
- Bone, W.A., Horton, L., Ward, S.G., 1930. Researches on the chemistry of coal. Part VI. Its Benzenoid Constitution as Shown by Its Oxidation with Alkaline Permanganate. *Proceedings of the Royal Society of London* 127, 480-510.
- BP, 2015. BP statistical review of world energy. <http://www.bp.com/content/dam/bp/pdf/Energy-economics/statistical-review-2015/bp-statistical-review-of-world-energy-2015-full-report.pdf>.
- Burke, S., Jarvie, A.W.P., Gaines, A.F., 1990. Phase transfer catalysed permanganate oxidation of three British bituminous coals. *Fuel* 69, 1370-1376.
- Fakoussa, R., Hofrichter, M., 1999. Biotechnology and microbiology of coal degradation. *Applied Microbiology and Biotechnology* 52, 25-40.
- Forsey, S.P., Thomson, N.R., Barker, J.F., 2010. Oxidation kinetics of polycyclic aromatic hydrocarbons by permanganate. *Chemosphere* 79, 628-636.
- Green, M.S., Flanagan, K.C., Gilcrease, P.C., 2008. Characterization of a methanogenic consortium enriched from a coalbed methane well in the Powder River Basin, USA. *International Journal of Coal Geology* 76, 34-45.

370 Haenel, M.W., 1992. Recent progress in coal structure research. Fuel 71, 1211-1223.
 371 Hayatsu, R., Winans, R.E., Scott, R.G., McBeth, R.L., 1981. Is kerogen-like material present in
 372 coal? 1. Buffer-controlled permanganate oxidation of coal. Fuel 60, 158-161.
 373 Hofrichter, M., Bublit, F., Fritsche, W., 1997a. Fungal attack on coal I. Modification of hard
 374 coal by fungi. Fuel Processing Technology 52, 43-53.
 375 Hofrichter, M., Bublit, F., Fritsche, W., 1997b. Fungal attack on coal II. Solubilization of low-
 376 rank coal by filamentous fungi. Fuel Processing Technology 52, 55-64.
 377 Huang, Z., Liers, C., Ullrich, R., Hofrichter, M., Urynowicz, M.A., 2013a. Depolymerization and
 378 solubilization of chemically pretreated powder river basin subbituminous coal by manganese
 379 peroxidase (MnP) from *Bjerkandera adusta*. Fuel 112, 295-301.
 380 Huang, Z., Urynowicz, M.A., Colberg, P.J., 2013b. Bioassay of chemically treated
 381 subbituminous coal derivatives using *Pseudomonas putida* F1. International Journal of Coal
 382 Geology 115, 97-105.
 383 Huang, Z., Urynowicz, M.A., Colberg, P.J.S., 2013c. Stimulation of biogenic methane
 384 generation in coal samples following chemical treatment with potassium permanganate. Fuel
 385 111, 813-819.
 386 Ighere, J.O., Honjaya, K., Chawla, R.C., 2015. Applications of potassium permanganate in the
 387 oxidative degradation of trichloroethylene. Journal of Materials Science and Chemical
 388 Engineering 03, 16-27.
 389 International Energy Agency, 2015. World Energy Outlook 2015 Executive Summary.
 390 [http://www.iea.org/publications/freepublications/publication/world-energy-outlook-2015---](http://www.iea.org/publications/freepublications/publication/world-energy-outlook-2015---executive-summary---english.html)
 391 [executive-summary---english.html](http://www.iea.org/publications/freepublications/publication/world-energy-outlook-2015---executive-summary---english.html).

392 Liu, Z.-X., Liu, Z.-C., Zong, Z.-M., Wei, X.-Y., Wang, J., Lee, C.W., 2003. GC-MS analysis of
 393 water-soluble products from the mild oxidation of Longkou brown Ccal with H₂O₂. *Energy &*
 394 *Fuels* 17, 424-426.

395 Miura, K., 2000. Mild conversion of coal for producing valuable chemicals. *Fuel Processing*
 396 *Technology* 62, 119-135.

397 Moore, T.A., Swanson, K.M., 1993. Application of etching and SEM in the identification of
 398 fossil plant tissues in coal. *Organic Geochemistry* 20, 769-777.

399 Novikova, L.N., Erdenechimeg, R., Purevsuren, B., Vakul'skaya, T.I., Kushnarev, D.F., Rokhin,
 400 A.V., 2010. Composition of humic substances in oxidized brown coal from Mongolia. *Solid Fuel*
 401 *Chemistry* 44, 78-88.

402 Park, S.Y., Liang, Y., 2016. Biogenic methane production from coal: A review on recent
 403 research and development on microbially enhanced coalbed methane (MECBM). *Fuel* 166, 258-
 404 267.

405 Schobert, H.H., Song, C., 2002. Chemicals and materials from coal in the 21st century. *Fuel* 81,
 406 15-32.

407 Siefert, N., Shekhawat, D., Litster, S., Berry, D., 2012. Molten catalytic coal gasification with in
 408 situ carbon and sulphur capture. *Energy & Environmental Science* 5, 8660-8672.

409 Steynberg, A.P., Nel, H.G., 2004. Clean coal conversion options using Fischer–Tropsch
 410 technology. *Fuel* 83, 765-770.

411 Urynowicz, M.A., 2008. In situ chemical oxidation with permanganate: assessing the
 412 competitive interactions between target and nontarget compounds. *Soil and Sediment*
 413 *Contamination* 17, 53-62.

414 Willmann, G., Fakoussa, R.M., 1997. Extracellular oxidative enzymes of coal-attacking fungi.
 415 Fuel Processing Technology 52, 27-41.

416 Wilson, B.W., Bean, R.M., Franz, J.A., Thomas, B.L., Cohen, M.S., Aronson, H., Gray Jr, E.T.,
 417 1987. Microbial conversion of low-rank coal: characterization of biodegraded product. Energy &
 418 fuels 1, 80-84.

419 Zhang, H.-X., 2016. Determination of aromatic structures of bituminous coal using sequential
 420 oxidation. Industrial & Engineering Chemistry Research 55, 2798-2805.

421 Zhang, J., Liang, Y., Harpalani, S., 2016a. Optimization of methane production from bituminous
 422 coal through biogasification. Applied Energy 183, 31-42.

423 Zhang, J., Liang, Y., Pandey, R., Harpalani, S., 2015a. Characterizing microbial communities
 424 dedicated for conversion of coal to methane in situ and ex situ. International Journal of Coal
 425 Geology 146, 145-154.

426 Zhang, J., Liang, Y., Yau, P.M., Pandey, R., Harpalani, S., 2015b. A metaproteomic approach
 427 for identifying proteins in anaerobic bioreactors converting coal to methane. International
 428 Journal of Coal Geology 146, 91-103.

429 Zhang, J., Park, S.Y., Liang, Y., Harpalani, S., 2016b. Finding cost-effective nutrient solutions
 430 and evaluating environmental conditions for biogasifying bituminous coal to methane ex situ.
 431 Applied Energy 165, 559-568.

432

433

Table 1: Composition of coal samples studied in this work

Parameter	Source of Coal		
	Illinois Basin #6	San Juan Basin	Powder River Basin
Ultimate analysis (dry basis)			
Carbon	70.07 ± 0.36	70.29 ± 0.38	64.19 ± 0.23
Nitrogen	1.39 ± 0.01	1.36 ± 0.01	1.09 ± 0.04
Hydrogen	5.21 ± 0.03	5.12 ± 0.05	4.59 ± 0.07
Sulfur	0.63 ± 0.03	0.83 ± 0.03	0.56 ± 0.01
Oxygen	15.41 ± 0.20	17.97 ± 0.06	26.56 ± 0.59
Proximate analysis (dry basis)			
Ash	7.50 ± 0.05	5.09 ± 0.00	8.08 ± 0.03
Volatile matter	49.93 ± 0.18	44.15 ± 0.09	44.23 ± 0.01
Fixed carbon	42.58 ± 0.17	50.76 ± 0.10	47.69 ± 0.01
Heating value (BTU/lb)	12547.50 ± 36.06	12410.65 ± 80.6	10786.25 ± 29.80

Table 2. The Box–Behnken design of the variables with yield of soluble compounds as the response.

Run	Solid loading (g/L)	Temperature (°C)	KMnO ₄ Concentration (M)	Soluble compounds yield (g/g coal)
1	50	25	0.28	0.378
2	200	25	0.28	0.071
3	50	40	0.28	0.382
4	200	40	0.28	0.064
5	50	33	0.10	0.134
6	200	33	0.10	0.022
7	50	33	0.45	0.580
8	200	33	0.45	0.110
9	125	25	0.10	0.041
10	125	40	0.10	0.044
11	125	25	0.45	0.206
12	125	40	0.45	0.191
13	125	33	0.28	0.123
14	125	33	0.28	0.126
15	125	33	0.28	0.125
16	125	33	0.28	0.124
17	125	33	0.28	0.125

Fig. 1: The effect of solid loading and KMnO_4 concentration on the yield of soluble compounds from the IL coal.

Table 3. Analysis of variance (ANOVA)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	11.34	8	1.42	6935.03	< 0.0001
A-Coal loading	5.96	1	5.96	29187.4	< 0.0001
B-Temperature	6.68E-04	1	6.68E-04	3.27	0.1082
C-KMnO4 Concentration	4.73	1	4.73	23149.2	< 0.0001
AB	2.77E-03	1	2.77E-03	13.56	0.0062
AC	4.24E-03	1	4.24E-03	20.76	0.0019
BC	6.40E-03	1	6.40E-03	31.31	0.0005
A^2	0.27	1	0.27	1301.07	< 0.0001
C^2	0.4	1	0.4	1940.77	< 0.0001
Residual	1.64E-03	8	2.04E-04		
Lack of Fit	1.26E-03	4	3.14E-04	3.3	0.1369
Pure Error	3.80E-04	4	9.50E-05		
Cor Total	11.34	16

Fig. 2: (a) The effect of mixing method on the yield of soluble compounds
(b) Yield of soluble compounds changing with reaction time.

Fig. 3: The comparison of elemental content and heating value before and after treatment (A) IL coal; (B) SJ coal; (C) PRB coal; (D) heating value.

Table 4. Results of TOC in different aqueous phase samples after treatment.

Parameter	IL coal	SJ coal	PRB coal
Total Carbon (g/g coal carbon)	0.147 ± 0.007	0.179 ± 0.002	0.215 ± 0.008
Inorganic Carbon (g/g coal carbon)	0.075 ± 0.003	0.087 ± 0.012	0.096 ± 0.005
TOC (mg/L)	2732.333± 171.523	3073.800± 326.255	3364.333± 270.806
TOC (g/g coal carbon)	0.072 ± 0.005	0.093 ± 0.011	0.120 ± 0.009

Fig. 4: GC chromatogram of the DCM solubles derived from treating the IL coal with KMnO_4

Table 5. Compound profile of the DCM solubles derived from treating the IL coal with KMnO₄

Group	Number*	RT (min)	Compound name	µg/g daf
<i>Fatty acid and derivatives</i>				
	7	23.31	Methyl 8-methyl-nonanoate	0.349
	12	26.354	Dodecanoic acid	1.322
	19	31.999	Methyl tetradecanoate	4.525
	23	34.615	Pentadecanoic acid	2.387
	25	37.136	Hexadecanoic acid	76.205
	28	39.534	Hexadecanoic acid, 14-methyl	2.083
	8	23.394	Dimethyl phthalate	0.731
	32	41.075	9,12-Octadecadienoic acid (Z,Z)-	1.079
	33	41.218	11-Octadecenoic acid	19.047
	34	41.382	9-Octadecenoic acid	12.380
	35	41.827	Methyl stearate	87.036
<i>Bezene related, oxygen containing</i>				
	2	12.317	Benzoic acid	27.744
	5	20.604	Benzoic acid, 2-methoxy	1.730
	6	21.732	Benzoic acid, 4-methoxy	0.612
	24	36.135	Benzene, 2-methyl-1,4-bis(1-methylethyl)-	3.334
	15	28.483	Benzothiazole, 2-(methylthio)-	16.570
	9	24.279	Dimethyl phthalate	90.450
	10	24.633	2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	1.246
	11	25.608	1,4-Benzenedicarboxylic acid	0.503
	17	29.955	Benzene, 1,1'-(1,3-propanediyl)bis-	1.340
	18	31.809	Methyl propyl phthalate	27.619
	20	33.069	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	2.217
	26	38.015	Dibutyl phthalate	5.552
	30	40.488	Benzene, 1,1'-(1-methylethylidene)bis[4-methoxy-	1.764
	37	46.424	Methyl dehydroabietate	20.428

Table 5. Compound profile of the DCM solubles derived from treating the IL coal with KMnO₄ -cont.

Alcohol

3	14.038	1,6-Hexanediol	87.380
---	--------	----------------	--------

Compounds containing hetero atoms

1	10.987	Tricyclo[3.3.3.0(1,5)]undec-6-ene-2,3,6-tricarbonitrile	1.051
16	29.717	Benzenesulfonamide, N,N,4-trimethyl-	21.609
14	27.917	3-Methyl-3H-benzothiazol-2-one	7.087

Hydrocarbon

21	33.773	1-Nonadecene	0.464
22	33.948	Octadecane	3.292
27	38.883	Heptadecane	2.123
29	39.905	10,18-Bisnorabieta-8,11,13-triene	10.811
31	40.811	1-Docosene	0.910

Dicarboxylic acid

4	17.495	Hexanedioic acid	221.572
8	24.04	Octanedioic acid	0.696
13	27.064	Nonanedioic acid	2.614

Aromatic compound

38	48.266	Pregna-5,17(20)-dien-3-ol, (3.β.,17E)-	15.312
----	--------	--	--------

*: Peak #36 was the internal standard added for quantification.

Table 6. Groups of compounds identified in DCM solubles by GC-MS.

Group	$\mu\text{g/g coal daf}$		
	IL coal	SJ coal	PRB coal
Fatty acid and derivatives	207.15	499.92	655.00
Bezene related, oxygen containing	201.11	288.66	193.30
Alcohol	87.38	NA	NA
Compounds containing hetero atoms	29.75	NA	3.26
Hydrocarbon	17.60	NA	NA
Aromatic compound	15.31	25.74	6.41
Dicarboxylic acid	224.88	88.88	40.89

Table 7. Yield of identified compounds in the aqueous phase samples derived from coal treatment

Yield (µg/g coal daf*)	IL coal	SJ coal	PRB coal
All soluble compounds identified by GC/MS	762.70 ± 81.48	840.14 ± 138.00	942.80 ± 257.32
Formic acid detected by HPLC	9404.25 ± 287.75	5647.94 ± 37.10	8863.01 ± 1542.81
Acetic acid detected by HPLC	12753.41 ± 110.03	14590.16 ± 358.74	15737.97 ± 2989.47
All soluble compounds detected	22920.36 ± 310.02	21078.23 ± 372.87	25543.78 ± 4738.13

* daf: dry and ash free