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Coal depolymerization using permanganate under optimal conditions

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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.

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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 studies in the 1980s and 1990s. (Fakoussa and Hofrichter, 1999; Hofrichter et al., 1997a, 1997b; 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).

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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. (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

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)	12,547.50 ± 36.06	12,410.65 ± 80.6	10,786.25 ± 29.80

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 KMnO4 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 × *g* for 20 min to separate the liquid and residual coal. The liquid fraction was then filtered through a 0.45 μm 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

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

Run	Solid loading (g/L)	Temperature (oC)	KMnO4 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