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Mild degradation of Powder River Basin sub-bituminous coal in environmentally benign supercritical CO_2-ethanol system to produce valuable high-yield liquid tar

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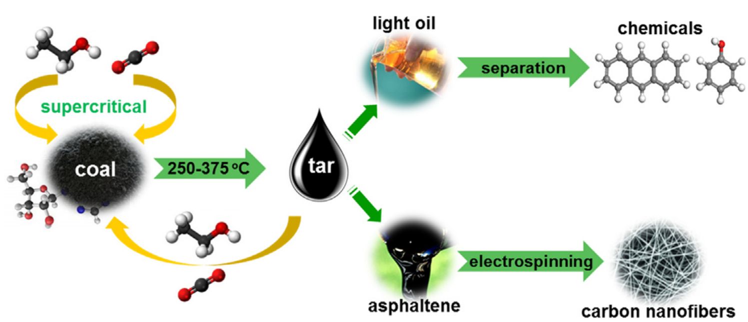
HIGHLIGHTS

- High yield liquid tar was produced from PRBSBC coal by degradation in $SCCO_2$-ethanol.
- The synergistic effect between ethanol and $SCCO_2$ can promote the liquid tar yield.
- Phenols and esters are the dominant small-molecular chemicals in the liquid tar.
- The liquid tar can be separated into light oil and asphaltene fractions by *n*-heptane.
- Asphaltene fraction has potential as the precursor to produce carbon nanofibers.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel and environmentally benign binary supercritical fluid system, comprised of supercritical CO_2 and ethanol ($SCCO_2$-ethanol), was employed to convert coal, a conventional energy resource, into high-value liquid tar which can be used as feedstock for the production of fuels/chemicals and carbon fibers. The $SCCO_2$-ethanol system shows good performance for producing valuable liquid tar in high yield from Powder River Basin sub-bituminous coal. The results show that the highest yield of liquid tar reaches up to approximate 38 wt% (38 g/100 g raw coal) at 350 °C, and that $SCCO_2$ can promote the liquid tar yield by 5.6 wt% compared to that using pure ethanol due to the synergistic effect between ethanol and $SCCO_2$. The liquid tars are better candidates as clean fuels than the raw coal or even bituminous coal due to their higher heating values and almost free from ash. The liquid tars from degradation in $SCCO_2$-ethanol (liquid $tar_{SCCO2\text{-}ethanol}$) and in ethanol without $SCCO_2$ (liquid $tar_{ethanol}$) at 350 °C were characterized with multiple analytical techniques. Fourier transform infrared analyses indicated that both liquid tars have similar distributions of functional groups. The proportion of volatile and small-molecular species in liquid $tar_{SCCO2\text{-}ethanol}$ is higher than liquid $tar_{ethanol}$ according to thermogravimetric analysis. Further, gas chromatograph/mass spectrometry analyses show that phenols and aliphatic esters are the dominant volatile compounds in both liquid tars. The ^1H and ^{13}C nuclear magnetic resonance analyses reveal that both liquid tars have low aromaticity and liquid $tar_{SCCO2\text{-}ethanol}$ contains more aromatic carbons than liquid $tar_{ethanol}$, especially highly condensed aromatic carbons. Methylene and aliphatic and aromatic CH_3 are

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the major aliphatic moieties in both liquid tars. The liquid tars can be separated into light oil and asphaltene fractions by extraction with *n*-heptane. In addition, the asphaltene fraction has potential to be used as the precursor for fabricating carbon nanofibers via electrospinning. Possible mechanisms for releasing volatile compounds and asphaltene from Powder River Basin sub-bituminous coal by $SCCO_2$-ethanol degradation were also discussed.

1. Introduction

With increasing environmental concerns alongside the rapid growth in clean fuels and chemicals demand, green chemistry has been the focus of both fundamental researches and industrial applications for more sustainable processes [1–3]. Most current chemical processes involving the use of chemicals have the potential for adverse environmental impacts. In coal utilization, direct combustion and conventional conversion processes (e.g., pyrolysis, gasification, and liquefaction) for generating energy and fuels/chemicals are not green or sustainable due to CO_2, NO_x and SO_x emissions, which constitute an unacceptable environmental pollution [4,5]. Therefore, it is desirable to develop environmentally benign, efficient, and value-added technologies of coal conversions to produce fuels/chemicals and carbon materials and reduce negative environmental impacts.

Coal has excellent advantages as feedstock for the production of value-added organic chemicals and advanced carbon materials because of its aromatic nature [5–7]. The major products from pyrolysis (or coking) and gasification processes are syngas and coke accompanied with low yield of liquid tar [8,9]. Further, processes converting coals to syngas then to fuels/chemicals have several disadvantages, including demanding strict operating conditions (> 800 °C), a lengthy production process, high production cost, high energy consumption, and significant pollution; as such, it is unsustainable for both economic and environmental considerations. Direct coal liquefaction is performed at relatively high temperature (ca. 450 °C) by using flammable and combustible H_2 and uses high boiling-point and toxic solvents such as tetralin and 9,10-dihydroanthracene [10]. Moreover, separation of the liquefaction products and the solvent recovery are time-consuming and complicated.

More eco-friendly and sustainable coal conversion processes that would employ mild reaction conditions and utilize CO_2 from other processes as a media or chemical precursor are highly desirable and attractive. In this regard, as a by-product from many processes, CO_2 is easily and abundantly available in high purity. Accordingly, focused research and development efforts should be made to realize environmentally benign processes and establish industrial applications for efficient coal utilization in the near future. Supercritical CO_2 ($SCCO_2$), with moderate critical pressure (73.8 bar) and temperature (31.1 °C), has received much attention as a green alternative solvent or reaction media for a wide range of applications due to its non-flammable, non-toxic, and easily available properties [1,11–13]. However, application of $SCCO_2$ as alternative solvent has been limited by its almost zero dipole and low solvation capacity for many targeted substances [14], including solid carbon resources like biomass, oil sand and coal. To overcome this limitation, $SCCO_2$ is usually used in combination with other fluids (i.e., co-solvents), especially polar solvents, to improve its performance.

The $SCCO_2$ combined with other fluids such as water, acetone, and/or ionic liquid has been used for producing aromatic chemicals (especially phenols) or reducing sugar from biomass and its derivatives [15–18]. In addition, $SCCO_2$ extraction technique has proved to be an effective pretreatment method for improving downstream processing of the biomass [19–21]. Rudyk et al. [22,23] investigated recovery of bitumen from oil sands by $SCCO_2$ extraction using water or alcohols as co-solvents and found that the yield of bitumen from oil sands can be enhanced by the co-solvents. The $SCCO_2$ was also used for extracting oil from oil shale with hexane or acetone as the co-solvent [24]. Some investigations have focused on drying coals using $SCCO_2$ [25–28]. To our knowledge, only one publication reported on $SCCO_2$ extraction of different coals with addition of *N*-methyl-2-pyrrolidone (NMP) [29]. Further, extraction yields of all the coals with different ranks are lower than 30 wt% and the recovery of NMP is difficult because of its high boiling-point. Low-carbon alcohols (e.g., methanol, ethanol, and isopropanol) with low-boiling point and low viscosity have been reported as solvents for thermal dissolution of coals under sub- or super-critical conditions [4,30,31]. To date, no reports have focused on the conversions of coals by using $SCCO_2$ in combination with low-carbon alcohols.

In the present study, an environmentally benign and low-toxicity $SCCO_2$-ethanol binary supercritical fluid is proposed for value-added utilization of a Wyoming sub-bituminous coal. Degradation of Powder River Basin sub-bituminous coal (PRBSBC) was carried out in $SCCO_2$-ethanol system under mild conditions (< 400 °C) for the production of valuable liquid tar which can be used as raw material for generating fuels/chemicals and carbon materials precursor. The possibility of forming an asphaltene fraction from the liquid tar as precursor for fabricating carbon nanofibers (CNFs) was also investigated.

2. Materials and methods

2.1. Materials

PRBSBC used in this study was from Wyodak coal mine in Powder River Basin, WY, provided by Black Hills Corporation. The coal sample was milled to pass through a 200 mesh sieve (with particle size < 75 μm). Proximate and ultimate analyses of raw PRBSBC are listed in Table 1. Anhydrous ethanol (99.9%, ACS) was purchased from Decon, Labs, Inc. Methanol (99.9%, ACS), isopropanol (99.9%, ACS), acetone (99.9%, ACS), toluene (99.9%, ACS), and *n*-hexane (99.9%, ACS), *n*-heptane (99.9%, ACS), and *N,N*-dimethylformamide (DMF, HPLC) were purchased from Fisher Scientific. Polyvinyl pyrrolidone (PVP, average M_w = 360, 000 Da) was purchased from Sigma-Aldrich. All the solvents were used without further purification. Liquid CO_2 (UHP, 99.999%) and N_2 (UHP, 99.999%) were supplied by United States Welding, Inc.

2.2. Degradation of PRBSBC in $SCCO_2$-ethanol to produce liquid tar

As shown in Fig. 1, the $SCCO_2$-ethanol degradation of PRBSBC was performed in a HPR-series high pressure chemical reactor (Supercritical Fluid Technologies, Inc., USA) with a 500 mL vessel. The reactor mainly consists of three units: liquid CO_2 cylinder, SFT 10 supercritical fluid pump, and integrated control box. Typically, 5 g of PRBSBC and 50 mL of ethanol were first loaded in the 500 mL vessel. The vessel was sealed

Table 1
Proximate and ultimate analyses (wt%) of PRBSBC.[a]

Proximate analysis			Ultimate analysis (daf)				$S_{t,d}$	H/C
M_{ad}	A_d	V_{daf}	C	H	N	O_{diff}		
16.00	8.18	48.73	78.87	3.72	1.01	15.93	0.47	0.5616

[a] Legend: daf, dry and ash-free basis; M_{ad}, moisture (air-dried basis); A_d, ash (dry basis, i.e., moisture-free basis); V_{daf}, volatile matter (dry and ash-free basis); O_{diff}, oxygen content, determined by difference; and $S_{t,d}$, total sulfur (dry basis).