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Research article

High-quality oil and gas from pyrolysis of Powder River Basin coal catalyzed by an environmentally-friendly, inexpensive composite iron-sodium catalysts

Bang Xu [a], Wenyang Lu [a], Zhao Sun [a], Ting He [b], Alexander Goroncy [c], Yulong Zhang [d], Maohong Fan [a,e,f,*]

[a] Department of Chemical Engineering, University of Wyoming, Laramie, WY 82071, USA
[b] Idaho National Laboratory, Idaho Falls, ID 83415, USA
[c] Department of Chemistry, University of Wyoming, Laramie, WY 82071, USA
[d] National Institute of Clean and Low Carbon Energy, Beijing 102211, China
[e] School of Energy Resources, University of Wyoming, Laramie, WY 82071, USA
[f] Department of Petroleum Engineering, University of Wyoming, Laramie, WY 82071, USA

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ABSTRACT

The objective of this research is to develop a cost-effective catalytic pyrolysis process for producing high-quality oil and gas from coal with low CO_2 emission. Catalytic pyrolysis of the Powder River Basin coal using composite Na_2CO_3-$FeCO_3$ catalysts has been investigated in a fixed bed reactor between 500 and 800 °C under atmospheric pressure to evaluate effects of catalyst on quantity and quality of the resulting oils and gases. The results indicate that high-quality oil and gas can be obtained with use of 4% Na_2CO_3 and 3% Na_2CO_3–1% $FeCO_3$ catalyst. Use of 3% Na_2CO_3–1% $FeCO_3$ catalyst can improve coal conversion by ~4.5% and 5% for Na_2CO_3 catalyst. The H/C ratio of the oil products obtained with catalysts are higher, while their O and S concentrations are reduced by as much as 36.1% and 50.6% for 4% Na_2CO_3 and 23.27% and 50.6% for 3% Na_2CO_3–1% $FeCO_3$ catalyst, respectively. The respective heating values of oil obtained with the 4% Na_2CO_3 and 3% Na_2CO_3–1% $FeCO_3$ catalysts increase by 833.3 kJ/kg and 541.7 kJ/kg. Moreover, these catalysts can reduce CH_4 and increase H_2 and CO concentrations of the produced gases at 700 °C, while 3% Na_2CO_3–1% $FeCO_3$ obtain better quality syngas (H_2/CO) at higher temperature. At 700 °C,4% Na_2CO_3 can reduce CH_4 concentration in the gas by 23.11% and increase H_2 and CO by 70.22% and 6.54%, respectively, 3% Na_2CO_3–1% $FeCO_3$ can reduce CH_4 concentration by 20.80% and increase H_2 and CO by 58.90% and 2.18%. All these results demonstrate that 4% Na_2CO_3 and 3% Na_2CO_3–1% $FeCO_3$ are both promising coal pyrolysis catalysts. The composite catalyst can not only synergize the advantages, but also overcome the challenges of pure iron or pure sodium based catalytic coal pyrolysis processes. In addition, GCMS test results show that Na_2CO_3 can change the reaction pathway way of pyrolysis, resulting in a decrease in the generation of furan and esters and increases in the productions of phenols, ketones, straight-chain olefins, and alicyclic hydrocarbons. The associated catalytic mechanism with addition of Na_2CO_3 is proposed.

1. Introduction

The atmospheric CO_2 is rising at an unprecedented rate and will continue to increase due to the world's ever increasing demand for energy and consequent consumption of fossil fuels such as coal, oil and natural gas [1,2,3]. If current trends continue, the world could soon see major disruptions to both natural ecosystems and human civilization, including sea level increases that could swamp many of the world's coastal cities. The control of CO_2 is a major challenge for the future use of fossil fuel, especially coal. The CO_2 emissions of coal-based power plants account for ~30% of total CO_2 emissions in the U.S [4]. Thus, there is an increasing interest in developing non-combustion based coal utilization and energy production technologies.

Pyrolysis is considered one of the promising method for low carbon-footprint coal utilzation. It is an efficent way for separating coal into three products: oil or tar, gas and solid. The oil or tar can be refined into liquid fuels. The gas can be used for producing liquids and chemicals such as diesel. The solid carbon/char has various applications including environmental protections.

However, there are several shortcomings with the conventional coal pyrolysis. First of all, its kinetics is slow. Coal pyrolysis occurs at relatively low temperatures [5,6]. Slow kinetics leads to high energy consumption. Also, the concentrations of undesired elements including O and S are high in pyrolysis-derived oils, which

* Corresponding author at: Department of Chemical Engineering, University of Wyoming, Laramie, WY 82071, USA.
E-mail address: mfan@uwyo.edu (M. Fan).

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Table 1
Proximate and ultimate analyses of coal.

Proximate analysis (wt%)			Ultimate analysis (wt%, daf)				
M_{ad}	A_d	V_{daf}	C	H	N	S	O[a]
10.27	8.72	48.73	78.87	3.72	1.01	0.47	15.93

[a] By difference.

considerably affect their applications as fuels. For example, the concentration of O in the coal tar produced by Fang et al. [7] through pyrolysis is up to 65%. It is well known that O in oil negatively affects the life span of engines [8] and increases the harmful NO_x emissions [9]. Moreover, the gases derived with the conventional pyrolysis process contain high concentrations of CH_4 and CO_2 and low H_2: CO ratio, which are undesired when the gases are used for synthesizing liquid fuels [10,11].

Therefore, the above-mentioned shortcomings need to be simultaneously overcome from the perspectives of economy, energy utilization efficiency, and environmental protection. As reported by Jin et al. [12], activated carbon catalysts exhibited better upgrading performances in a fixed-bed reactor over char. The upgrading performance of various metal-loaded HZSM-5 were examined by Liu et al. [13] and Ni-loaded presented the best performance for production of high quality tars with highest aromatics contents of 94.2% (area%). Xiao-Bo et al. [14] reported that organic oxygen species were applied to investigate the effects of pyrolysis temperature and gas resident time. Moreover, some results indicate that the additive of Na_2CO_3 can improve the quality of oil produces by oil sludge and biomass. The oxygen concentration of the bio-oil from biomass pyrolysis decrease from 47.5 wt% to 16.4 wt% [15,16]. In addition, transition metals are also effective catalysts for coal pyrolysis reaction. They can improve hydrogenation reaction [17,18]. Fe_2O_3 is also a promising catalyst because of its abundance, low cost and environmentally friendly for coal pyrolysis. In addition, Results obtained in our previous research, showing that the composite Na_2CO_3-$FeCO_3$ catalysts are efficient for PRB coal gasification, which not only can reduce the activation energy obviously, but also improve the generation of desired products H_2 and CO, compared to pure sodium and iron catalysts, respectively [5,19–21].

This research aims to address these issues. The effect of Na_2CO_3-$FeCO_3$ composite catalysts on coal pyrolysis was studied. Specifically, inexpensive $FeCO_3$ and Na_2CO_3 based catalysts and the corresponding composite catalysts have been explored to improve the qualities of coal-pyrolysis-derived oil and gases.

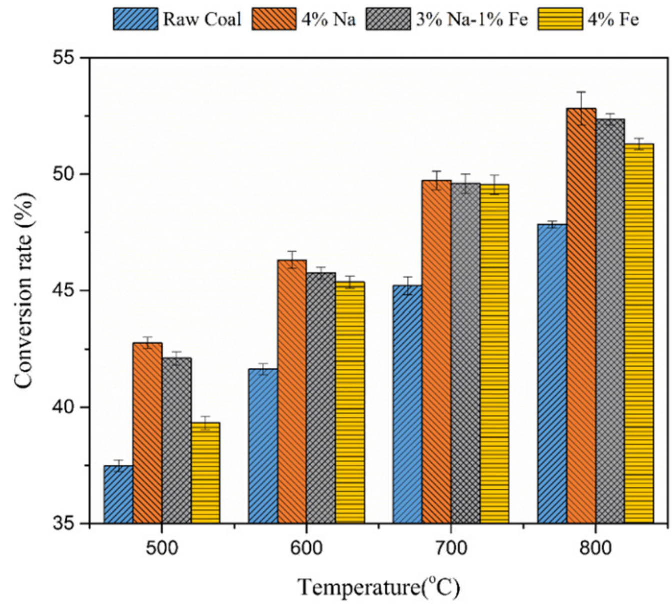

Fig. 2. Coal conversion rate from coal pyrolysis with and without use of catalysts at different temperatures.

2. Materials and methods

2.1. Materials

Raw coal used in this work was from the Wyoming Powder River Basin, provided by Wyodak Resources Development Corp. The proximate analyses were performed according to ASTM D5142 and D5016. The ultimate analyses were performed on PRB chars obtained by ASTM D5373, D5016, and D4239 methods. The results of proximate and ultimate analyses of the coal are shown in Table 1. Meanwhile the ash analysis of raw coal is shown in Table S1.

The incipient wetness impregnation (IWI) method was used to mix $FeCO_3$ and Na_2CO_3 with coal particles [22]. The specific preparation of the $FeCO_3$ catalyst has been described in detail elsewhere [21]. The catalyst and coal mixtures were prepared by adding the appropriate amounts of $FeCO_3$, Na_2CO_3 or $FeCO_3$-Na_2CO_3 to pulverized PRB coal to

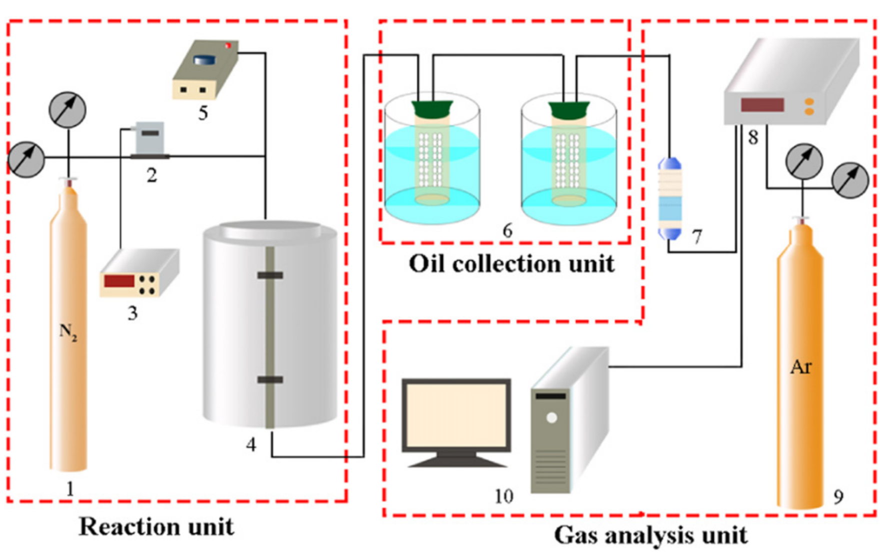

Fig. 1. Schematic diagram of catalytic PRB coal pyrolysis in a fixed-bed reactor. (1) N_2, (2) mass flow, (3) mass flow controller, (4) high-temperature furnace, (5) temperature controller, (6) collection unit, (7) dryer, (8) online GC, (9) Ar, (10) data acquisition unit.