Full Length Article

Production of light aromatic hydrocarbons by catalytic cracking of coal pyrolysis vapors over natural iron ores

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A B S T R A C T

Four iron ores including limonite, siderite, hematite and magnetite are examined for their catalytic effects on coal pyrolytic products. Experiments were conducted at a pyrolyzer combined with gas chromatography/mass spectrometry (Py-GC/MS). The results show that limonite has the highest catalytic activity for light aromatic formation as a result of the conversion of aliphatic hydrocarbons and oxygenates. The total peak area of light aromatics such as benzene, toluene, ethylbenzene, xylene, and naphthalene (BTEXN) has increased by 52% after the catalysis of limonite. The good performance of limonite can be attributed to its large surface area. Multi-cycle tests were conducted over limonite to get the knowledge of its stability. The effect of valence state of iron is discussed by making comparison of the performances between the limonite and the reduced limonite. It is found that the reduced limonite has a more reactive catalytic activity for light aromatics production. Coal effect is also studied.

1. Introduction

Low rank coals such as lignite and sub-bituminous coal generally have high oxygen and moisture contents as well as low heating values. The characteristics significantly limit their utilizations in consideration of the low thermal efficiency for direct combustion, high cost in transportation and the tendency of spontaneous combustion in storage despite their vast reserves [1]. These problems could be avoided or greatly improved by application of pyrolysis as the first step.

Pyrolysis can simultaneously produce char, tar and incondensable gases. The char is subsequently combusted or gasified. The tar can further be processed into liquid fuels and valuable chemicals, which strongly enhances the entire process economics [2]. This is especially true in China since there is a lack of petroleum and gas reserves. Accordingly, various pyrolysis technologies have been developed for utilization of low rank coals [3–6]. However, the tar from coal pyrolysis usually contains high molecular weight compounds, which can be as high as 50% [7]. The presence of heavy compounds significantly increases the difficulty in further processing the tar. Moreover, these high molecular weight compounds readily condense in the downstream of equipment of the pyrolysis process, leading to abnormal operation due to pipe blocking. Thus, how to minimize the production of heavy components in tar during coal pyrolysis and increase the selectivity to light liquids becomes a concerned issue for the pyrolysis process

industrialization.

An integrated coal pyrolysis process with iron ore reduction has been put forward recently by the Institute of Process Engineering of Chinese Academy of Sciences [8]. In the proposed scheme, the coal pyrolytic vapors from the pyrolyzer directly pass through a secondary reactor, where natural iron ore is placed to decompose/reform heavy components in tar into light species. Simultaneously, the iron ore is reduced under the reduction atmosphere and recycled as the feedstock of iron- and steel-making industry.

Iron is very active in the catalytic chemistry [9]. Iron can largely facilitate bonds breaking such as C—C and C—O [10,11]. Research has indicated that iron ore can promote the production of light aromatics at the expense of oxygenated compounds and aliphatics [12]. Light aromatics such as benzene, toluene, ethylbenzene, xylene and naphthalene (BTEXN) are important raw materials in chemical industries. There are various natural iron ores such as limonite, siderite, hematite and magnetite. The differences in textural properties and structures, valence state of iron and its content as well as its existing forms among these natural ores may result in quite different performance in tar cracking. In this work, various iron ores including limonite, hematite, siderite and magnetite are studied with regard to their in-situ tar cracking/reforming performances by using a pyrolyzer combined with gas chromatography/mass spectrometry (Py–GC/MS), aiming at obtaining a general knowledge of the tar cracking performances of these iron ores

Table 1
Ultimate and proximate analyses of the coal sample.

Coal sample	Proximate analysis (wt%, dry)			Ultimate analysis (wt%, dry)				
	V	A	FC	C	H	N	S	O[a]
BR	44.0	12.0	44.0	62.6	4.3	0.8	0.3	20.1
SM	33.8	7.7	58.5	73.8	4.9	1.2	0.3	12.2
XL	31.8	26.4	41.8	55.0	3.9	0.8	1.0	13.0
TS	23.6	30.4	46.0	57.8	3.2	0.9	0.9	6.8

[a] Oxygen by difference.

and screening out an effective natural iron ore with high selectivity to the light aromatics. Surface areas of the natural ores are accounted for their performance. Multi-cycle tests are performed for investigation of the stability of iron ore performance. Effects of the valence state of iron are also discussed since the valence state of iron could be changed during the in-situ tar cracking reactions. The performance of limonite with different coals is examined.

2. Experimental

2.1. Coal and iron ores

A lignite from Baori, Inner Mongolia (BR), was used for the pyrolysis test throughout this study. Three coals from Xilinguole, Inner Mongolia (XL), Shenmu, Shaanxi (SM) and Tangshan, Hebei (TS) were also tested to investigate the effect of coal on the catalysis of iron ores. They were ground and sieved to particle sizes of below 75 μm and dried in a forced air convection drying oven at 105 °C for 4 h prior to experimentation. The proximate and ultimate analyses performed according to GB/T 212-2008 (for moisture, ash and volatile) and GB/T 31,391-2015 (for C, H, N, S) are shown in Table 1.

Four iron ores including limonite, hematite, siderite and magnetite purchased from the Research Academy of Shandong Metallurgy are employed as catalysts. Chemical analyses of the as-received ore samples are presented in Table 2. Iron in the limonite takes the form of Fe(OOH) while siderite is a mineral mainly composed of iron carbonate ($FeCO_3$). Prior to experimentations, limonite was calcined at 450 °C for 1 h in a muffle furnace to remove combined water. Siderite was calcined at 600 °C for 1 h for de-carbonation. After the pretreatment, the iron in both limonite and siderite is in the form of Fe_2O_3. The limonite and siderite mentioned hereafter indicate the ones after the calcination.

2.2. Catalyst characterization

The chemical phase of these iron ores was analyzed by X-ray diffraction method (XRD, Rigaku Smartlab, Japan) with D/teX-Ultra detector and CuK$_\alpha$ radiation (45 kV, 200 mA). The scanning range was 2θ = 5–90° with a step size of 15°/min. The specific surface area was measured by nitrogen adsorption-desorption isotherms at −196 °C on Tristar 3020II,Micromeritics, USA. The coke deposition on iron ores were analyzed using Elemental analyzer (Vario Macro Cube, Elementar, Germany). Thermogravimetric analyses were done on STA 449C (NETZSCH, Germany) like this: the sample (5 mg) was placed on the

sample plate, and then it would be heated to 900 °C at heating rate of 10 °C/min. The flow rate of air is 50 ml-NTP/min.

2.3. Experimental set-up

The pyrolysis tests were conducted at a platinum filament pyrolyzer (CDS 5200, CDS Analytical, Oxford, PA). The pyrolyzer can be operated in two modes: Py mode and trap mode. A detailed description of the operation modes can be found in the literature [13]. The trap mode was employed throughout this study in order to detect the gas compositions. In the trap mode, the released volatiles first go to an adsorption trap, which is kept at 40 °C. Simultaneously the incondensable gases from coal pyrolysis was carried into the GC sample loop for measurement. Then the adsorbed volatiles by the trap are desorbed at an elevated temperature (300 °C) with helium as a purging gas, analyzed with a GC/MS analyzer (Trace GC, ISQ MS, Thermo Scientific Co.).

Specific information about the instruments (the GC and GC/MS) and the methods are introduced in the previous study [12]. The term of tar is defined as a mixture of condensable organic compounds. The peak area is used in this work to indicate the variation of tar yield since the chromatographic peak area of a compound given by GC/MS is generally considered linear with its quantity [14]. Nearly exactly same amount of the coal sample is used for each test in this work. The gas yield is determined by GC via an external standard method.

For each run, a coal sample of 1.0 ± 0.03 mg and a catalyst of 1.0 ± 0.03 mg separately loaded in a small quartz tube (2.5 mm in outside diameter × 25 mm in length). Quartz wool is placed in between and at both ends of the samples to prevent the particles from moving by a purging gas. The samples are then heating to 700 °C at a rate of 20,000 °C/s under an argon atmosphere and holding for 25 s. All of the experiments were conducted 3 times. The relative errors are less than ± 5%, indicating good repeatability.

3. Results and discussion

3.1. Comparison of pyrolytic products over iron ores

Fig. 1 presents the total peak areas of tar obtained over different iron ores as well as the gas yields. It is seen that the tar yield is significantly reduced in the presence of both limonite and siderite. In comparison, hematite and magnetite have relatively weak effects. As expected, the gas yield appears a corresponding variation as a result of tar cracking as shown in Fig. 1. The gas yield significantly increases after the catalysis of limonite and siderite while there is a slight increase with hematite and magnetite.

Both limonite and siderite exhibit strong de-oxygenation capability as shown in Fig. 2. The oxygenated compounds such as phenols, aliphatic oxygenates and aromatic oxygenates in tar are dramatically
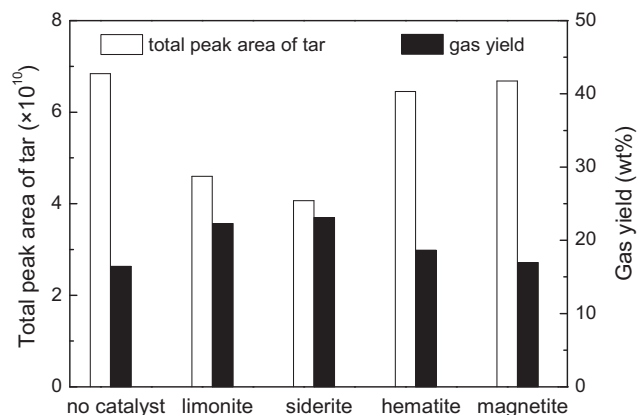
Table 2
Composition of iron ores.

Type	Composition (wt%)						
	TFe	SiO$_2$	Al$_2$O$_3$	CaO	MgO	P	S
Limonite	40.24	8.4	0.65	11.95	1.17	0.041	0.087
Hematite	64.66	4.34	1.8	0.011	0.082	0.02	0.0091
Siderite	43.66	3.99	0.6	3.38	3.84	0.034	1.46
Magnetite	62.65	4.2	0.39	0.71	4.73	0.011	0.114

Fig. 1. Total chromatographic peak areas of the tar and gas yields.