Fuel 207 (2017) 244–252

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Free radical reaction mechanism on improving tar yield and quality derived from lignite after hydrothermal treatment

Peng Liu [a,b,*], Jiawei Le [a,1], Dexiang Zhang [a,*], Shengchun Wang [a,d], Tieying Pan [c]

[a] Key Laboratory of Coal Gasification and Energy Chemical Engineering of Ministry of Education, Department of Chemical Engineering for Energy Resources, East China University of Science & Technology, Shanghai 200237, China
[b] National Institute of Clean and Low-Carbon Energy, Beijing 102209, China
[c] Analysis and Research Center, East China University of Science & Technology, Shanghai 200237, China
[d] College of Chemical Engineering, North China University of Science and Technology, Tangshan 063009, China

HIGHLIGHTS

- Free radical properties of hydrothermal treatment is characterized.
- Correlated free radical with weight loss during lignite pyrolysis.
- Relation of free radical variation after hydrothermal treatment to coal tar yield is found.
- Described free radical mechanism on improving tar yield and quality after hydrothermal treatment.

ARTICLE INFO

Article history:
Received 13 February 2017
Received in revised form 24 April 2017
Accepted 20 June 2017

Keywords:
Free radical
Lignite pyrolysis
Tar
Hexane soluble
Hydrothermal treatment

ABSTRACT

Coal pyrolysis process is accompanied by free radical generation, stabilization and condensation. Free radical concentration plays a crucial role in pyrolysis product distribution. Hydrothermal treatment of lignites is used as a pretreatment method to regulate pyrolysis product distribution analyzed by free radical reaction mechanism. The free radical concentration in lignite and char was monitored by electron paramagnetic resonance (EPR). The results show that free radical concentration in lignite increases during hydrothermal treatment, Hydrolysis of oxygen functional group and dissociation of the small molecules in the lignite interlayer stacking structure generate free radicals with medium molecular weight during hydrothermal treatment. Meanwhile, the increase of hydrogen radical donated from water through the interaction of water and lignite is utilized to stabilization of free radical with medium molecular weight to hinder the second cleavage and cross-linking of free radical during pyrolysis. The increasing rate of free radical concentration decreases to a minimum at a turning point temperature. The turning point temperature of hydrothermal treatment of lignites is different because of the difference in their structure. The pyrolysis tar yield increases around 20% after hydrothermally treated at the turning point temperature. The light tar (hexane soluble in tar) yield from lignite pyrolysis increases also. According to analysis of free radical in char, it shows that the pyrolysis weight loss numerically correlated to variation of free radical concentration during pyrolysis after hydrothermal treatment. The results can provide the data for the application of hydrothermal treatment on regulating gas and liquid fuel quality from carbon-based material for energy supply and environment protection.

1. Introduction

Coal supplies primary energy for many countries, it also contributed to more amount of the associated environmental burden for nearly all impacts on human health and ecosystems[1–3]. Traditional coal combustion to power generation is leading to increment of particulate matter ($PM_{2.5}$) which threatens human health [4–5] and global-warming [3]. The clean and efficient coal technology should be introduced into modern coal conversion process.

* Corresponding authors at: Key Laboratory of Coal Gasification and Energy Chemical Engineering of Ministry of Education, Department of Chemical Engineering for Energy Resources, East China University of Science & Technology, Shanghai 200237, China (D. Zhang and P. Liu).
E-mail addresses: pengjuehui@126.com (P. Liu), zdx@ecust.edu.cn (D. Zhang).
[1] The author has the equal contributions to first author.

http://dx.doi.org/10.1016/j.fuel.2017.06.081
0016-2361/

Nomenclature

Symbols and definitions

A	the percentage of ash in coal, %
C	carbon
EPR	electron paramagnetic resonance
f_a^B	bridging ring junction aromatic carbon, %
f_a^{CC}	carboxyl, quinone and Carbonyl carbon, %
f_a^H	protonated aromatic carbon, %
f_{al}	aliphatic carbon contents, %
f_{al}^*	quaternary sp^3C, %
f_{al}^1	methyne, quaternary sp^3C, %
f_{al}^2	methylene, %
f_{al}^3	aliphatic methyl, %
f_{al}^a	aromatic methyl, %
f_{al}^O	oxygen aliphatic carbon, %
f_a^O	oxygen aromatic carbon, %
f_a^S	aliphatic substituted aromatic carbon, %
FC	Fixed carbon, %
H	hydrogen
IM	inner Mongolia lignite
M	moisture, %
m	mass, g
N	nitrogen
Ng_{char}	free radical concentration in char, g^{-1}
Ng_{coal}	free radical concentration in lignite, g^{-1}
ΔNg	the difference of free radical concentration between char and lignite, g^{-1}
NMR	nuclear magnetic resonance
O	oxygen
S	sulfur
XF	Xianfeng lignite
XLT	Xiaolongtan lignite
V	volatile matter,%
w_{HS}	the yield of Hexane soluble matter, %
w_{tar}	the yield of lignite tar

Many researchers explored numerous amounts of ways for clean coal conversion [6–11]. However, coal pyrolysis-based poly-generation, which is able to efficiently convert coal into tar while producing electricity [12], is an important strategy to deal with the serious issue of energy saving and greenhouse gas emission reduction. The overall efficiency of coal utilization in the system of pyrolysis-based poly-generation increases [13]. The emission of CO_2 and noxious gas from the system of pyrolysis-based poly-generation is easily controlled [14].

Low rank coal is about half of the world's coal deposits, which are relatively inexpensive, at just 20–30% of the price of high ranked coal. Low rank coals have not been utilized as much as high rank coal, because they have many drawbacks, such as high moisture, low energy density, and high spontaneous combustion tendency. In order to overcome these drawbacks and make low rank coals characteristics comparable with those of high rank coals. Low rank coals should be treated by upgrading process before use. The first step of the upgrading process is dewatering. Dewatering of coal by hydrothermal treatment [15–17] is an attractive technology which improves thermal efficiency. In the other hand, the water can participate in one or more roles with the existing of oxygen functional groups in lignite [18]: as a catalyst, reactant, and solvent in the aquathermolysis chemistry at the treatment temperature. Li [19] studied the behavior of free radicals in coal at temperatures up to 573 K in various organic solvents, indicated that the radical intensity increased slightly as temperature increased, however, the radical intensity in heat-treated coal in a hydrogen-donating solvent decreased sharply from 473 to 573 K due to the stabilization of radicals by hydrogen transferred from solvent. Miura [20–21] also proposed the mechanism of radical transfer during the flash pyrolysis of solvent-swollen coal. The degree of hydrogen transfer from the solvent to coal is controlled by the hydrogen donability of solvent and the hydrogen acceptability of coal. In one hand, the water can act as solvent to donate hydrogen to lignite during hydrothermal treatment. Chen [22–23] presents calculations from a single-particle model to illustrate the effects of thermo-physical properties and operating variables on the inversion point temperature; above this temperature, the vaporization rate in steam is greater than that in other atmospheric conditions. Pretreatment in aqueous and thermal system is efficiently for upgrading lignite to utilize. Hydrothermal treatment has an improvement in the slurry ability of coal [24–27] and can reduce the viscosity of the coal-water slurry. Moreover, hydrothermal treatment not only promotes the hydro-liquefaction activity in coal liquefaction [28] but also increases the coal concentration of coal-solvent slurry [29–30] because of the lower porosity for the treated coal. The treated lignite has a greater calorific value [31–32] compared with the raw lignite. Most important of all, the water from hydrothermal treatment can be utilized circularly in the system and hydrothermal treatment can reduce the emission of CO_2 during pyrolysis. The water can be utilized as catalysis, solvent and reactant during hydrothermal treatment to obtain near zero discharge during coal conservation. Also, the pyrolysis tar yield [33–34] increases 20% after hydrothermal treatment.

Free radicals are formed during the coalification and exist in the coal stably. The concentration of free radical increases with the change of external condition. Thermal conversion of coal is also well recognized as a series of free radical reactions [35–37]. Hydrothermal treatment and coal pyrolysis progress are both accompanied by free radical generation, stabilization and condensation. Seehra et al [38] indicated that the variation of free radical concentration was in three distinct stages during coal pyrolysis with temperature increasing. The free radical concentration increases observably after 700 K because of the covalent bonds begin to break in bituminous coal. Flower et al [39] showed the same phenomenon using a bituminous coal. Murakami [40] also indicated that the free radical concentration increases observably after 673 K. The coal tar was formed largely at 673–873 K. Coal structure with different coalification environment is various leading to the difference in free radical reaction and transfer during coal pyrolysis. Wu et al [41] studied the evolution of free radical concentration in coals during pyrolysis at different temperature. They found that the free radical concentration of lignite increases to a maximum at 823 K, lower than that of sub-bituminous coal (873 K). The free radical concentration in lignite increases to the maximum and then decreases as time goes on at 823 K. The radicals come through the formation and stabilization during pyrolysis obviously from the data. Zhang et al [42] reported co-pyrolysis of coal and tar distillation residue to generate more free radicals during pyrolysis. The tar yield and quality are regulated and controlled by the free radicals. The free radicals play a significant role in controlling pyrolysis product distribution. However, the properties of free radical in coals during hydrothermal treatment were ambiguously studied. The free radical reaction mechanism on increasing of tar yield should be researched further.