



Reaction of volatiles – A crucial step in pyrolysis of coals



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HIGHLIGHTS

- Volatiles formed in coal pyrolysis experience temperature increase in all reactors.
- Volatiles' temperature increases in coking, fluidized-bed and rotary kiln are large.
- Volatiles' temperature increases in fixed-bed and moving-bed reactors are small.
- A large volatiles' temperature increase leads to a low particulate-free tar yield.
- Volatiles' temperature increase promotes cracking of volatiles and coke formation.

ARTICLE INFO

Article history:

Received 1 September 2014

Received in revised form 1 April 2015

Accepted 3 April 2015

Available online 11 April 2015

Keywords:

Coal pyrolysis

Volatiles reaction

Tar

Radical reaction

ABSTRACT

Coal pyrolysis is regarded by many as a simple method to produce liquid fuels and chemicals and has been studied extensively in the past. However, fast coal pyrolysis technologies intended for higher tar yields and higher productivities, in comparison to the successful slow pyrolysis technologies, had common problems such as poor tar quality and plugging of the volatile products lines. The failing of many technical efforts in solving these problems calls for more fundamental studies, especially on the reaction of volatiles in major pyrolysis reactors. This is because that thermal cleavage of covalent bonds in coal that generates volatiles is a single step and depends mainly on the temperature of the coal, while the reactions of the volatiles involve multiple steps and depend on many factors especially the gas phase temperature that is generally higher than that of the coal due to the large temperature gradient in fast pyrolysis reactors. This article analyzes temperature increases in volatiles' upon their generation from coal in various pyrolysis reactors and correlates the temperature increases with tar yield and composition. Experimental results on reaction of volatiles are also presented to enlighten the importance of the volatiles' reactions.

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1. Introduction

Pyrolysis of coal has been studied extensively in the past for production of coke, tar and fuel gas. Many processes were developed including fixed-bed, moving bed, fluidized-bed and rotary kiln technologies. These technologies are often categorized into two groups, slow pyrolysis with heating rates usually less than 1 K/s and fast pyrolysis with heating rates as high as 10^4 K/s [1].

The main slow pyrolysis technologies include those employing fixed-bed or moving bed reactors, such as coking for metallurgical coke or Lurgi retort and Lurgi gasifiers, which have been practiced

successfully for more than a century. Since the tar yields of the coking technology are low, about 3–5 wt%, and the productivity of the moving bed technologies is low due to long residence time of coal, in hours, fast pyrolysis technologies were studied and developed, because it was reported by many that tar yield increases with an increase in heating rate [2].

The fast pyrolysis technologies usually include fluidized-bed, rotary kiln and those heating coal with solid heat carriers. It is unfortunate however that none of these technologies has been commercialized up to date. The common problems are poor tar quality due to high solid and pitch contents as well as frequent plugging of the volatile product lines [3]. Extensive technical efforts have been made in the past to solve these problems, including further increases in heating rate of coal and in cooling rate of volatiles, application of multiple high temperature dust removal devices, pretreatment of coals and introduction of catalysts [4–6].

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These technical efforts, however, did not yield sufficient improvement in solving the problems. It seems to suggest that it is important to study the fundamental reactions involved in pyrolysis of coals in these reactors.

It is well accepted that pyrolysis of coals follows a two-step radicals mechanism: generation of volatile radical fragments and reactions of the volatile radical fragments to form volatile products (tar and gas) and nonvolatile products (char) [7,8]. It is noted that the generation of the volatile radical fragments results from thermal cleavage (or cracking) of covalent bonds in coals, which in principle is a single step governed mainly by the bond energy and temperature of the coal because catalytic activity of minerals in coal is usually low at temperatures lower than 600 °C [9]. The reactions of the volatile radical fragments involve multiple reactions and depend on many factors, such as concentration of the volatile fragments, catalytic effects of coke/coal and minerals in the coal, and the gas phase temperature. The effect of the gas phase temperature is worth to address because the temperature difference between the coal and the surrounding gas phase is large in fast pyrolysis due to the large temperature gradient in the reactors. The high gas phase temperature promotes cracking, coupling and condensation of the volatile radical fragments in the gas phase as well as on the coal/char surface, which alter the tar yield and composition [10,11]. For example, some of the tar-fraction radical fragments and/or pitch-fraction radical fragments may be converted into coke, light tars and gas. Furthermore, the volatile products formed may crack further to initiate more cycles of “bonds cleavage and reaction of radical fragments” in the gas phase.

The above discussion suggests that the reactions of volatile fragments, including radicals or non-radicals, occur at temperatures higher than that for the bonds cleavage in coal, especially in fast pyrolysis. This implies that the difference in temperature gradient in various pyrolysis reactors plays an important role in determination of pyrolysis products, especially the yield and composition of tars. This information, however, has not been reported in detail in the literature.

This article studies temperatures of coal and volatiles (the gas phase) in various pyrolysis reactors and discusses behavior of the volatile reactions caused by the temperature gradient in the reactors. The reactors analyzed include not only those used in fast pyrolysis technologies but also those used in slow pyrolysis technologies.

2. Temperature profiles of volatiles and coal in large pyrolysis reactors

2.1. Fixed-bed reactor

The fixed-bed pyrolysis reactor discussed here is an externally or indirectly heated coke oven, which pyrolyzes the largest amount of coal currently in the world. Fig. 1(a) is a cross-sectional sketch of a coke oven during operation. Modern coke ovens consist of a series of batteries, each having a height of 6–8 m and a width of 0.4–0.6 m, and a length of 17–19 m. Coal is charged in the ovens batchwise and a coking cycle is usually about 20 h. Since the heat is from the wall (the far left in Fig. 1(a)), the coal close to the wall pyrolyzes first while the coal at the center of coal bed in width (the far right in Fig. 1(a)) pyrolyzes last. The shrinkage of coke and cracks formed in coke form passages of the lowest pressure drop for volatiles to escape as indicated by the arrow.

Fig. 1(b) shows temperature profiles of volatiles and coal (not in scale) corresponding to Fig. 1(a). At any location in the oven, temperature of the coal increases with time (the dash line, not in scale) and the volatiles responsible for tar formation generate in a temperature range of 300–600 °C. The volatiles then flow to the zone

of lower pressure and higher temperature. The temperature of oven wall varies usually from an initial value of about 800 °C to higher than 1100 °C over time [12], and the volatiles' average temperature is about 950 °C and average residence time is about 11.6 s as estimated in Appendix A. This large temperature increase and long residence time of the volatiles cause them to crack significantly, resulting in a low tar yield, about 3.0–4.5%, and a high gas (rich in H₂ and CH₄) yield, about 15–19% [13]. The tars usually contain about 50–60 wt% pitch and less than 10 wt% particulates [14].

2.2. Moving-bed reactor

The moving-bed reactor discussed here is a vertical three stages Lurgi retort, known as Lurgi–Spuelgas (L–S), shown in Fig. 2(a) [15]. The coal enters the retort on the top and is dried at about 150 °C directly by the hot gas generated from the upper burner. Then the dried coal enters the second stage and is heated gradually to a final temperature, about 500–850 °C [12], directly by the hot gas generated from the lower burner. The volatiles generated are immediately in contact with the upcoming hot gas and are carried out by the gas to the low temperature zone and leave the reactor at a temperature of about 240 °C [16]. The char formed in the second stage moves down to the third stage where it is cooled by recycled low temperature pyrolysis gas and then discharged from the bottom of retort.

Fig. 2(b) shows the temperature profiles of volatiles and coal (not in scale) in the second stage of L–S retort where the final temperature of char is 720 °C. It can be seen that when volatiles generate from coal in the temperature range of 300–600 °C, responsible for tar formation, they are heated by the raising hot gas quickly to a temperature about 40 °C higher, which is estimated based on an energy balance shown in Appendix B. The residence time of volatiles vary in a range of 3–9 s depending upon the location of their generation, shown also in Appendix B. The residence time of volatiles generated at a lower temperature is shorter while that of volatiles generated at a higher temperature is longer. It is important to note that after the initial temperature increases the volatiles' temperature decreases while they move upwards and reach the exit temperature of 240 °C. This indicates that the volatiles undergo very limited cracking in comparison to that in a coke oven and some of the heavy fractions of volatiles, such as pitch, may condense on the coal surface of lower temperatures. This agrees with the fact that the L–S retorts usually yield more tars, with less heavy fractions and less gas in comparison with coking. For example, in some cases the tar yields are about 8 wt%, wherein the pitch contents are about 21–30 wt%, and the gas yields are about 12 wt% [12,15,17].

2.3. Pyrolysis using solid heat carriers

There are a number of fast pyrolysis technologies that employs high temperature solids as heat carriers, such as Lurgi–Ruhrgas (L–R) process [16,18], DG process [12,15,19] and some kiln processes [20,21]. The reactor discussed here is the L–R process which is a suitable example for understanding other processes. Fig. 3(a) is a schematic diagram of the major part of an L–R reactor, the screw feeder or mixer [18]. The hot solid heat carrier, coke of 800–850 °C in many cases, blends with coal in the screw feeder usually at a heat carrier to coal mass ratio of 5–8. The coal is thus heated up quickly to generate volatiles.

Fig. 3(b) shows temperature profiles of the heat carrier (not in scale) and the coal (not in scale) in the screw feeder. Since the temperature of heat carrier is always higher than that of coal at any location of the screw feeder, the volatiles generated from the coal in the temperature range of 300–600 °C, responsible for tar formation, are immediately heated by the heat carrier to its temperature

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