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Research paper

Gasification characteristics of petcoke and coal blended petcoke using thermogravimetry and mass spectrometry analysis

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HIGHLIGHTS

- Pyrolysis and gasification characteristics of petcoke samples.
- Effect of petcoke particle size during steam gasification.
- Synergetic effects of coal blending with petcoke during gasification.
- Product gas compositions during gasification at different temperature ranges.
- Appropriate temperature range to gasification for different sized particles.

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ABSTRACT

The particle size effect of petcoke and blended samples of coal and petcoke with similar sizes were investigated during steam gasification. A simultaneous thermal analyzer and mass spectrometry was used to characterize the tested samples and the identification of the volatiles evolved during the heating up to 1150 °C under combustion cum gasification related conditions. The TG and DTA results are discussed for the investigations in steam gasification process. The effect of blending petcoke with coal was studied in order to determine the possible presence of synergetic phenomena. The TG-MS profile of the petcoke provides information on gasification performance on different particle size, reaction temperature and time. It gives the chemical changes of petcoke during gasification and gas evolution profiles. The size effects on temperature of petcoke and coal blended petcoke during gasification are discussed. It was found that temperature and particle size had the greatest influence on the gasification rate and final products. With the smaller sized particles, initial higher reaction stage is continued up to larger conversion level, whereas it is shifted to second stage of reaction for larger particles. The appropriate temperature range to the petcoke and blended petcoke gasification was evaluated for different particle sizes. A synergistic effect was ascertained during the gasification of coal and petcoke mixture in steam ambience.

1. Introduction

Petroleum coke (petcoke) is a viable economic and secure alternative fuel/feed stock for both power and hydrogen production due to the increasing demands of petroleum and the development of deep processing technology of crude oil. Particularly, CO_2 emission causes a significant climate change due to the repercussions of a wide variety of human activities. The gasification process has been developed to convert low grade coal and hydrocarbon into syngas [1], which is a mixture of hydrogen, carbon monoxide and along with a little content of methane which contribute as major intermediate raw material for further product syntheses. The produced syngas can be used in electricity generation (IGCC) and production of chemical feed stocks, hydrogen, etc., depending on the market demand. Energy systems based on the use of hydrogen are considered to offer great promise for the future. Some of the advantages of hydrogen energy include its low environmental impact and its attractive future application in fuel cell technology for producing electricity [2]. Nowadays, 98% of the hydrogen production comes from fossil fuels, mainly from natural gas reforming (approx. 50%) [3]. Gasification technology is a well-established method to produce syngas ($CO + H_2$), where

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hydrogen production can be increased by means of the water–gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$). With this technology, a highly concentrated stream of hydrogen can be generated, provided that CO_2 capture is also undertaken. Some studies have shown that electricity generation based on the combination of hydrogen fuel cells and CO_2 capture are less costly when compared to post combustion systems [4,5]. The energy producers are opted to buy and burn the cheapest fuel depending on the market opportunities for minimizing the operating cost to remain competitive and also to adhere with the environmental constraints. However, due to the uncertainty of natural gas supplies and the volatility of its price, in the medium term, the systems based on petcoke gasification may offer a better alternative. The use of petcoke in gasification technology has the advantage due to its versatility, and the variety of applications for the obtained product. As such, petcoke has been considered as an attractive feed stock for gasification. Main drawback of pure petcoke usage are higher SO_2 emissions and fireside fouling or corrosion problems as it contains considerable amounts of sulfur, vanadium and nickel. Moreover, it is difficult to ignite petcoke due to its low volatile matter content [6,7]. The internal structure (porosity, pore size, pore volume) and transport properties (diffusivity, tortuosity) of the carbon substrate also influence the mass transport limitations. The reactivity of petcoke is lower than that of coal, so that either a higher temperature or a larger residence time is required to achieve the same carbon conversion [8,9].

Several types of gasification technology available for carbonaceous feed stock gasification. In the fluidized bed gasification, the feed materials are in millimeter size range, and require more residence time to maximize the carbon conversion. The feed stock and gasification medium are in co-current flow in the entrained flow gasification system which is very well suited for petcoke gasification due to its operational conditions. Some commercial industries are already implemented the petcoke gasification in entrained flow reactors (EFG) [10–12]. Nagpal et al. [13] have simulated the petcoke gasification in slagging moving bed reactors to assess the effect of feed oxygen-to-coke and steam-to-coke ratios and feed coke rates on gasification performance for fixed particle size. They have reported that the particle sizes affect the reaction rate of the delayed petcoke only, but not the flexicoke samples. Malekshahian and Hill [14] have reported the intrinsic CO_2 gasification rates of petcoke at high pressures using thermogravimetry analysis and the kinetic parameters estimation. Sun et al. [15] have simulated the comprehensive three-dimensional numerical model for Shenfu bituminous coal and petroleum coke in the industrial Opposed Multiburner Entrained Flow gasifier in steam and CO_2 ambience. They have reported the catalytic effects on gasification due to the ash with minerals present in coal. Ren et al. [16] have estimated gasification reactivity of coal and petcoke in CO_2/steam at high temperatures using drop-in-fixed-bed reactor. They have reported that the overall gasification rate is limited by the surface chemical reaction, the rate of diffusion in the pores of char, and the rate of mass transfer to and from the exterior of the char particles. Another method to improve the low-volatile petcoke gasification feature is to co-gasify with other feed stocks such as a more reactive fuel with high volatile matter content lignite. The co-gasification of various hydrocarbon materials with coal might have some advantages, such as the reduction of the fossil fuel dependency and CO_2 emissions [17–19]. In order to use various hydrocarbons, such as lignite, petroleum coke, biomass, and so on, as the gasification feed stock, it is necessary to understand the gasification characteristics of each hydrocarbon material.

TGA (thermogravimetric analysis) coupled with MS (mass spectrometry) has been typically used for the study of the thermochemical conversion of different types of solid fuels, such as biomass, waste or coals [20–24]. However, most studies have been emphasized on pyrolysis and combustion processes. Comparatively, fewer gasification studies have been reported in literature, being most of them focused on the study of biomass and coal [25]. Trommer and Steinfeld [26] have modeled the combined pyrolysis and steam gasification kinetics of petroleum coke and also estimated the rate constants using thermogravimetry studies from 500 to 1520 K temperature range. Jayaraman and Gokalp [27] have investigated the size effects of high Indian coal and char particles using thermal characterization, gasification and kinetic analysis using the coupled thermogravimetric and mass spectrum analysis. Fermoso et al. [28] have investigated the effect of main operating variables (temperature, pressure, gasifying agent composition) on gas production and other process parameters during co-gasification of coal with biomass and petroleum coke. They have found that the temperature and oxygen concentration had the greatest influence on the final products and a synergistic effect was observed for blends of coal and petroleum coke. Hernandez et al. [29] have studied the synergy between biomass and coal-coke in the entrained flow, air-blown gasifier. They have concluded that the synergetic effects are caused by the content and composition of the blend ash catalytic effect of Ca and K which is coming from biomass ash, whereas Fe, Ni, and Zn contents from coal-coke ash. Goyal et al. [30] have modeled the co-gasification of coal and petcoke in a bubbling fluidized bed coal gasifier and reported that the increase in petcoke content significantly reduces the carbon conversion efficiency, whereas it increases the syngas production rate. Lee et al. [31] have examined the gasification characteristics of petcoke and mixture with coal in an entrained flow gasifier and found the synergetic effect in the mixtures with the particle sizes of around 75 μm. Gao et al. [32] have demonstrated that the reactivity of char obtained from biomass/coal with coke blends is lower at high temperatures from the thermogravimetric studies in CO_2 atmospheres, this effect being attributed to the particle agglomeration due to the melting of potassium silicates at high temperatures. Moreover, the nonlinear increase in the char reactivity when increasing the biomass content was justified by the interactions between the fuel components. The maximum methane conversion and steam decomposition rates were achieved in the co-gasification of petroleum coke and natural gas in a fixed bed gasifier, and also the H_2/CO ratio was higher than that of coal gasification [33].

On the other hand, some problems do still exist which is to be solved in gasification systems for petroleum coke and lignite mixtures due to the complex reactions involving based on chemical properties. Petcoke is different from coal chars, because of its different structure, pores, surface area and catalyst content. The test results of various sized petcoke and coal blended petcoke samples are necessary to develop the fuel flexible gasification systems. Therefore, the gasification properties of petcoke and mixture of petcoke and coal, including gasification temperature, syngas production rate and synergetic effects need to be assessed. This paper aims at a better understanding of the basic phenomena associated with thermogravimetric analysis of different sized petcoke and coal samples. The gases released during the gasification process were analyzed using online MS system. Moreover, synergetic effects of petcoke and coal blend haven't been documented so well under steam gasification, hence the need for the present research.

2. Experimental

2.1. Materials and thermogravimetry analysis

Petcoke samples were procured from Turkey. The size of the raw petcoke and high ash coal sample was in the range from few