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Energy Procedia 105 (2017) 642 – 647

Energy Procedia

The 8th International Conference on Applied Energy – ICAE2016

Gasification of high heating-rate biomass-derived chars at elevated temperatures

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Abstract

In this study, gasification behavior of high heating-rate chars were investigated using an entrained flow reactor with an optical particle-sizing pyrometer. Two biomass chars produced from forest residue and torrefied forest residue as well as one coal char produced from low sulfur Black Thunder subbituminous coal have been gasified at temperature over 1700 K. Both the char surface temperatures and surrounding gas temperatures were precisely measured. Despite large discrepancies in constituents, the two biomass chars showed rather similar surface temperatures at the tested conditions. However, a slight lower surface temperature was obtained by the coal char gasification. A comprehensive model was also applied to aid understanding of the conversion process of char gasification. One set of intrinsic kinetic parameters for both the heterogonous water-gas reaction and the Boudouard reaction were found to effectively capture the experimental data at the two investigated conditions.

Peer-review under responsibility of the scientific committee of the 8th International Conference on Applied Energy.

Keywords: Char; Biomass; Gasification; Surface temperature; Torrefaction; Kinetics

1. Introduction

Biomass is one of the most attractive alternative carbon sources because of its renewability and availability. It is particularly interesting to convert biomass into syngas that contains mainly hydrogen and carbon monoxide. The biomass-derived syngas has a big potential to produce liquid transportation fuels and important industrial intermediates such as lower olefins [1]. However, because of the inherent fuel properties of biomass, certain pretreatments are often required for an efficient conversion process, such as

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Peer-review under responsibility of the scientific committee of the 8th International Conference on Applied Energy.
doi:10.1016/j.egypro.2017.03.369

torrefaction. Compared to raw biomass, torrefied biomass has better grindability, higher energy density, and significantly improved hydrophobic behavior. Gasification of biomass is a complex process in particular the rate-limiting step of char conversion. Increased efforts have been given to investigate the behavior of high heating rate char conversion at high temperature conditions that are relevant to industrial reactors [2–6]. However, time-resolved char temperature profiles are rarely reported at such conditions, especially for chars produced from biomass and torrefied biomass. The temperature history of the char particle is a direct reflection of the char conversion process. In addition, an accurate profile of the char temperature is very valuable for validating numerical models.

In the current work, an entrained flow reactor with an optical particle-sizing pyrometer was used to investigate gasification of high heating-rate chars produced from biomass and torrefied biomass. High precision surface temperatures of chars were obtained. Moreover, a sophisticated char conversion model was applied to examine kinetic parameters of the heterogonous water-gas reaction and the Boudouard reaction. One char produced from a low sulfur coal was also studied for comparison reason.

2. Experimental methods

The biomass investigated is a type of forest residue consisting of tops and branches of trees. The corresponding torrefied biomass was produced in a torrefaction reactor consisting of four electrically heated screw conveyors [7]. In the torrefaction process, the biomass were preheated at 498 K for 5 min and then torrefied at 548 K for 30 min. The coal examined in this study is for comparisons a low sulfur subbituminous coal from the Powder River Basin coal region named Black Thunder. The biomass char (BC), torrefied biomass char (TBC), and coal char (CC) were produced in an electrically heated drop tube reactor (DTR) located at the Combustion Research Facility of Sandia National Laboratories [8]. The wall temperatures of both the reactive section and the preheater section were 1200 °C. A bulk gas stream of 182 slpm (liters per minute at 0 °C and 1 atm) of preheated N_2 was introduced into the reactor to generate the desired pyrolysis atmosphere. It is worth noticing that the coal char was produced at slightly different atmosphere, which is a mixture of a stream of 180 slpm of N_2 and a stream of 5.5 slpm of O_2. The details of the char production have been presented elsewhere [8,9]. To aid data acquisition, both the biomass chars were sieved to 71-90 μm, and the coal char was sieved to 75-90 μm. Proximate and ultimate analyses of the feedstocks and chars have been summarized in Table 1. Due to the low char yields of biomass and torrefied biomass, proximate analysis of the corresponding chars were not performed.

Table 1. Proximate and ultimate analysis

	Biomass	Torrefied biomass	Coal	Biomass char	Torrefied biomass char	Coal char
Proximate analysis (wt. %, as received)						
moisture	6.3	4.2	9.3			3.7
ash	2.2	2.7	4.8			9.5
volatile	70.0	61.6	42.3			12.1
fixed carbon	21.5	31.5	43.6			74.1
Ultimate analysis (wt. %, dry ash free)						
C	52.1	59.5	69.0	69.8	78.1	89.6
H	6.1	5.6	5.0	2.7	2.2	0.8
O (by diff.)	41.3	34.3	25.4	27.0	19.0	1.3
N	0.5	0.6	1.0	0.5	0.7	8.0
S	<0.02	<0.02	0.5	<0.02	<0.02	0.4

The gasification of chars were examined using Sandia's optical entrained flow reactor, described in more detail in a previous work [10]. As shown in Fig. 1, the combustion-driven reactor features a diffusion-flamelet-based Hencken burner, which provides a high-temperature gas flow at ambient pressure (1 atm). The char reactor consists of a 46 cm tall, 5 cm×5 cm quartz chimney that prevents cold surrounding air from disturbing the post-combustion gas flow. The pulverized char particles were carried by a small flow of N_2 or CO_2 and injected at the furnace centerline through a 0.75 mm stateless-steel tube. The temperature along with velocity and diameter of individual burning char particles were measured using a particle-sizing pyrometer. Two gas atmospheres were achieved by burning mixtures of hydrogen and ethylene and diluting with N_2 (case 1) or CO_2 (case 2). The compositions of the post-combustion gas are 13.9 vol-% H_2O, 6.4 vol-% CO_2 and 79.7 vol-% N_2, and 13.9 vol-% H_2O and 86.1 vol-% CO_2, respectively, whereas, the total product flow rate was 60.0 and 57.2 slpm.

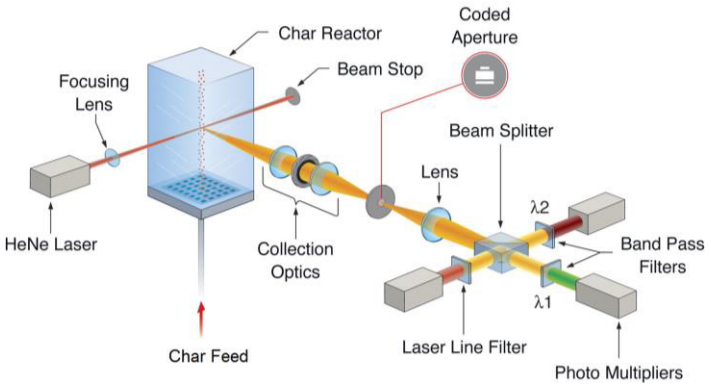

Fig. 1. Schematic of Sandia's optical entrained flow reactor [10]

3. Numerical analysis

As a support and extension of the experiments, a comprehensive char conversion model using intrinsic kinetics was applied to investigate the tested char gasification process. The model considers the carbon gasification by both H_2O and CO_2. Furthermore, the model allocates the ash liberated at the particle surface to a) form an ash film, b) diffuse back into the particle and participate as a dilution effect, or c) act as an arbitrary combination of the two effects in tandem, which as employed here. The integration of ash film and ash dilution is essential for simulating biomass char. The inherent highly porous nature of biomass char improves ash penetration rather than forming an ash film completely. The initial char particle is divided into several equally spaced concentric shells. The particle is idealized as consisting of an external ash film and an internal char core where ash and carbon are distributed uniformly. Some ash components liberated during the conversion of each burned shell is used to thicken the ash film, whereas, the rest is assumed to penetrate and be uniformly distributed in the char core. When the outmost shell of the char core is burned out, the adjacent internal shell develops a new 'outmost' shell. More details regarding the char conversion model can be found in previous work [11].

4. Results and discussion

Fig. 3 shows the gas temperatures along the central line of the reactor at the two tested conditions. The temperatures were measured by a 25-μm, type-R fine-wire thermocouple, and were corrected for the

radiative losses. Due to the injection of the cold solid feeding gas (around 0.03 slpm) in the middle of the reactor, the gas temperatures below the height around 25 mm were relative low. The gas temperatures peaked around 1930 K with N_2 diluent and 1880 K with CO_2 diluent at the height between 50 to 70 mm. Because of the heat losses via the quartz windows, the gas temperatures decreased with increasing height at both conditions. However, the measurement data for char particles were mainly collected between 25 and 300 mm above the burner, where the gas temperatures were relatively high.

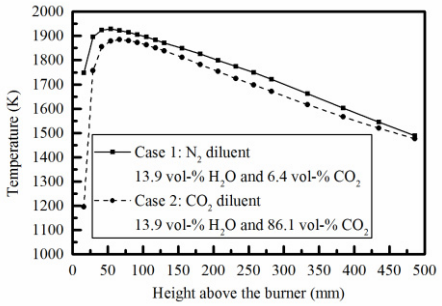

Fig. 3. Measured gas temperatures along the central line of the reactor at N_2 diluent and CO_2 diluent conditions

Fig. 4 shows the comparisons between measured char temperatures and simulation results as function of residence time. The char surface temperatures were collected at various heights above the burner. Additionally, the residence times of char particles were calculated based on the particle velocities, which were measured using the particle-sizing pyrometer. The velocity differences between different types of char particles were very small. Therefore, only one series of representative residence time was given in Fig. 4 in each condition. Every temperature measurement point shown in Fig. 4 was made of roughly 100 char particles. There was very little spread in the temperatures for each type of char respectively. The deviation constantly lay within the error of the temperature measurement (estimated at ±20 K).

All the investigated chars showed similar temperature profiles. Temperatures firstly increased when chars were injected into the reactor, and then slowly decreased. It is worth noticing that the char surface temperature was always lower than the temperature of the surrounding gas at the particle location. This implies the decline of surface temperature is caused primarily by the endothermic heterogonous water-gas reaction and Boudouard reaction. Therefore, the surface temperature can be viewed as an indication of char reactivity. In general, lower temperature correlates with higher gasification reactivity.

It can be seen from Fig. 4 that there were no notable differences regarding surface temperatures between the two biomass chars, thus, suggesting a similar reactivity. It is interesting to note that the TBC showed lower CO_2 reactivity than the BC in the previous study [8]. One major difference between the two studies is the size of the char particle. In this study, chars were sieved into a narrow size fraction (71-90 μm), whereas, in the previous study, chars were in their original form with a wide distributions. Several potential explanations had been raised in the previous study to explain the effects of torrefaction on char reactivity. Based on the current study, the effect of char size may seem to contribute most to the observed effect. Compared to the biomass chars, the surface temperature of coal char was found to be relatively low in both conditions. This is somewhat counterintuitive since generally biomass char has higher reactivity than coal char. However, different from the biomass chars, the coal char were produced with additional oxygen. Although only around one vol-% oxygen was added when the char was produced, it might effectively prevent recondensation of tar on the char surface. Therefore, a more porous structure might be developed for the coal. The conversion of char is most likely controlled by both chemical kinetics and pore diffusion (zone II) in the current study, particularly, at the higher temperature Case 1. The more porous coal char led to a faster conversion than the biomass chars due to the higher diffusion rate of the gaseous reactants.

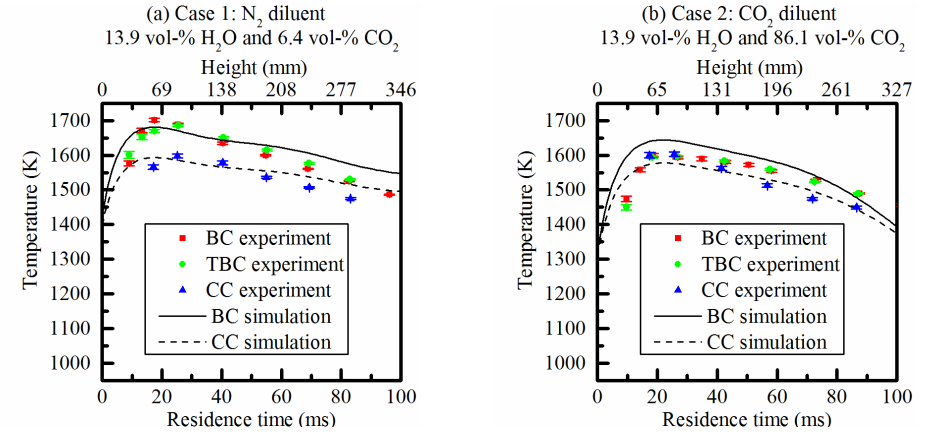

Fig. 4. Comparison between measured char surface temperatures and simulated char surface temperatures

A preliminary analysis of intrinsic kinetic parameters of gasification reactions was thereafter carried out using the char conversion model. Due to the similarities between the BC and the TBC, only one biomass char, the BC char, was investigated in this study. The intrinsic reaction orders of both the heterogeneous water-gas reaction and the Boudouard reaction were set to be 0.5 in the model, based on the previous study, which was performed in similar conditions [11]. Furthermore, according to the suggestions given by Hecht et al. [12,13], the activation energies were limited to 190-270 kJ/mol for the heterogeneous water-gas reaction (E_{H2O}) and 230-251 kJ/mol for the Boudouard reaction (E_{CO2}). Since the pre-exponential factor is highly depended on the fuel type and charring condition, the pre-exponential factors of the heterogeneous water-gas reaction (A_{H2O}) and the Boudouard reaction (A_{CO2}) were solely determined by the experiments. The intrinsic kinetic parameters were found for both the biomass char (A_{H2O}=20000 g/s/cm^2/atm$^{0.5}$, E_{H2O}=190 KJ/mol, A_{CO2}=20000 g/s/cm^2/atm$^{0.5}$, and E_{CO2}=220 KJ/mol) and the coal char (A_{H2O}=70000 g/s/cm^2/atm$^{0.5}$, E_{H2O}=190 KJ/mol, A_{CO2}=100000 g/s/cm^2/atm$^{0.5}$, and E_{CO2}=251 KJ/mol) by comparing to the measured char surface temperatures. As shown in Fig. 4, with the fitted intrinsic kinetic parameters, the simulated char temperatures were very close to the experimental data in both conditions, especially the case 1 with low CO_2 concentration. To understand the discrepancies between the measured data and the predicted results, a more detailed study on the kinetic parameters are being conducted, in which a more rigorous global fitting scheme will be used. In addition, an in-depth analysis of the char gasification process using the conversion model will be given in future work.

5. Conclusion

The gasification behaviour of two biomass-derived chars and one subbituminous coal char produced at high heating-rate were investigated at high temperatures using Sandia's optical entrained flow reactor. Moreover, the gas temperatures along the central line of the reactor were well characterized. As an indication of the char reactivities, the surface temperatures of chars were accurately recorded at various heights above the burner surface. The two biomass chars were found to convert in a very similar way, regardless of the environments. In conjunction with the previous studies, the most predominant effects of torrefaction on reactivity of biomass char might come from the differences of char size. The measured temperature data was also interpreted with the comprehensive char conversion model using intrinsic kinetics. The kinetic parameters of the heterogeneous water-gas reaction and water-gas reaction Boudouard reaction were preliminary determined with the apparent reaction order of 0.5, which well predicted experimental results.

6. Copyright

Acknowledgements

This publication has been funded by CenBio–Norwegian Bioenergy Innovation Centre. CenBio is co-funded by the Research Council of Norway (193817/E20) under the FME scheme and the research and industry partners. Special thanks to Christopher Shaddix and Manfred Geier for their assistance with the experiments at Sandia.

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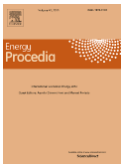

Biography

The corresponding author of this paper Dr. Tian Li is now working as a Postdoc researcher in the Department of Energy and Process Engineering at Norwegian University of Science and Technology. Main research interests of Dr. Tian Li are thermochemical conversion of biomass and numerical modelling of multiphase reacting flow.