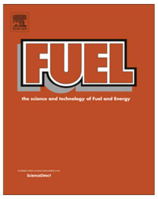
Fuel 143 (2015) 476–483

Contents lists available at ScienceDirect

Fuel

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



Gasification of pyrolysis chars from sewage sludge

Lech Nowicki, Maciej Markowski *

Lodz University of Technology, Faculty of Process and Environmental Engineering, Wolczanska 213, 90-924 Lodz, Poland

HIGHLIGHTS

- TG–MS study of the gasification of sewage sludge chars was performed.
- Three reaction rate models for gas–solid reaction with CO_2 and H_2O were identified.
- The original quasi-quantitative analysis of TG–MS data was proposed.

ARTICLE INFO

Article history:
Received 5 June 2013
Received in revised form 16 October 2014
Accepted 21 October 2014
Available online 6 November 2014

Keywords:
Steam reforming
Gasification
Sewage sludge char
Kinetic modelling

ABSTRACT

Gasification of char derived from sewage sludge was studied by using the TG–MS system. Experiments were carried out at different temperatures and steam concentrations. The temperatures of 700–900 °C were necessary to complete the conversion in reasonable time. Three reaction rate models for gas–solid reaction were applied to describe the effect of char conversion on the reaction rate. In comparison to the shrinking core model for reaction-controlled regime and random pore distribution models, simple pseudo-homogeneous first-order kinetics was found to be the best for predicting the rate of char steam gasification. Kinetic parameters estimated from the experimental data are in accordance with the literature for lignocellulosic char gasification and are the first ones published for sewage sludge char gasification.

1. Introduction

Sewage sludge, the inevitable by-product of wastewater treatment, can be considered a valuable raw material for energy generation. Carbon-containing sewage sludge can be used to obtain heat or electricity from direct combustion or co-combustion with coal [1]. However, as a rather low energy–density fuel, it could be convenient to convert it into a synthesis gas (mixture of CO and H_2) by means of gasification [2]. The production of gaseous fuels from wastes such as sewage sludge seems to be a very appealing idea because the use of such materials to produce clean energy could significantly contribute to sustainable development.

Gasification consists of two main chemical steps: pyrolysis and conversion of a solid devolatilization product—char composed of carbon and ash. Pyrolysis is a relatively fast thermal decomposition of organic matter in solid fuel, whereas char gasification is a slow gas–solid heterogeneous reaction [3]. Thus, the kinetics of char gasification is crucial for the design and development purposes [3]. Therefore, knowledge of the reaction kinetics of char gasification is essential for proper design and operation of the gasification reactor [3].

The reaction of char with the gasification reagent occurs at higher temperatures when most thermal decomposition processes are finished. The type of the gasification agent used has a major impact on the composition of the resulting gas product. Gasification is usually carried out with oxygen and steam or the mixtures thereof. The gasification process is very often performed with steam because the product of steam gasification of chars, which is rich in hydrogen, can be considered not only a fuel but also a useful raw material for chemical industries, not to mention its use as clean fuel [4]. Recently, we have witnessed a growing interest in the so-called dry gasification by means of CO_2 [5,6]. The presence of CO_2 can improve char conversion and decrease the volume of gasification residue [7].

The rate of gasification is affected by char reactivity, type and concentration of the gasifying agent used and the operating conditions, such as pressure and temperature [8,9]. On the other hand, the reactivity of the char depends on the raw material, from which the char was produced, as well as on pyrolysis conditions [8,10].

Most publications available in the literature on the gasification of sewage sludge relate to the process in which dewatered and dried sewage sludge is used as a starting material [9,11–19].

---

* Corresponding author.
E-mail addresses: nowicki@wipos.p.lodz.pl (L. Nowicki), markowski.m.p@gmail.com (M. Markowski).

http://dx.doi.org/10.1016/j.fuel.2014.10.056
0016-2361/© 2014 Elsevier Ltd. All rights reserved.

Nomenclature

α	conversion (–)	n	number of moles (mol)
C_t	concentration of active size (mol g^{-1})	R	universal gas constant (kJ mol^{-1} K^{-1})
E	activation energy (kJ mol^{-1})	t	time (s)
k	reaction rate constant (s^{-1})	T	temperature (K)
m	reaction order in respect to H_2O partial pressure (–)	y_g	concentration of oxidizing agent (mole frac.)

Studies on the steam or carbon dioxide gasification of chars from sewage sludge are fairly limited. The influence of different pyrolysis conditions (temperature and heating rate) on the reactivity of sewage sludge char in air and CO_2 gasification was studied by Inguanzo et al. [20]. Scott et al. [10] measured the rate of CO_2 gasification of three chars, including one derived from sewage sludge. They found that the sewage sludge char was the most reactive; as a result, the char contained large amounts of inorganic material, components of which catalyse the reaction of carbon with CO_2. The effect of inorganic constituents of waste biomass chars (from municipal solid wastes, sewage sludge and waste paper) on CO_2 gasification was studied by Vamvuka et al. [21]. Based on thermogravimetric measurements, they found that sewage sludge char was the most reactive due to alkaline and alkaline earth carbonates and sulphates contained in the ash. The CO_2 and steam gasification kinetics of char from dried sewage sludge was measured in a laboratory-scale fluidized bed by Nillson et al. [22]. It was found that the rate of both reactions depends on temperature, partial pressure of gas reactant and degree of conversion. For the whole range of conversion, the char reactivity in steam/N_2 was roughly three times higher than that in a mixture with the corresponding partial pressure of CO_2. In tests with steam at 900 °C, reactivity was influenced only by particle size greater than 1.2 mm.

In our previous study [23], we analysed gasification of char that originated from anaerobic sewage sludge produced in urban waste water treatment plants using thermogravimetric analysis to obtain rate equations and kinetic parameters for different oxidizing agents (O_2, H_2O, CO_2). The purpose of this work is to study the CO_2 and steam gasification of pyrolysis char derived from two sewage sludge samples of different origin and composition in order to compare gas product yields, product composition and carbon conversion kinetics.

2. Material and methods

A thermobalance, Netzsch STA 409 PG, coupled with a mass spectrometer, Balzers ThermoStar QMS 200, were was used for measurements. The thermobalance was equipped with a water vapour furnace, enabling measurements in the atmosphere containing a controlled amount of steam. The mass spectrometer was connected with the thermobalance by means of a heated quartz capillary with an internal diameter of 0.2 mm maintained at 200 °C. The intensity of selected ions was measured at different times, together with sample temperature and mass. Gasification tests were performed in an alumina crucible with a diameter of 5 mm and height of 3 mm.

Two types of sewage sludge were used in this study to obtain the pyrolysis char: stabilized sewage sludge from an urban wastewater treatment plant (WWTP) in a big city (designated as SS1) and row sludge from a small WWTP in rural area (designated as SS2). Both types of sludge differ mainly with ash (mineral fraction) content, which was about 41 and 27.9 wt.%, respectively (Table 1).

Proximate analysis of moisture, volatiles (including fixed carbon) and ash was performed in preliminary experiments in which the samples were heated to 1000 °C in inert gas (argon) and then kept at this temperature in air atmosphere to burn out the char formed during the pyrolysis. The contents of C, H, N and S elements were determined by an elemental analyser (CE Instruments NA 2500).

The char was obtained by devolatilization of sewage sludge or of an oil cake in a horizontal quartz fixed-bed reactor (with a 20 mm internal diameter) heated by an electric furnace. The sample of dried and ground material was heated under the stream of argon at a constant heating rate of 100 °C/h, held in the final conditions (1000 °C) for about 60 min and then cooled to room temperature. The fraction of the char particles with a diameter of 70–125 μm was used for gasification tests. Characteristics of the pyrolysis char are given in Table 2.

2.1. Evaluation of TG/MS data

Each chemical compound present in the gas phase can be represented by characteristic ions (charged molecules and molecule fragments) formed from its ionization and fragmentation process occurring during the mass spectrometric analysis. Individual ions are indicated by their mass-to-charge (m/z) ratio. Table 3 shows normalized (the largest peak corresponding to 1) intensities of the peaks on mass spectrum for the ions that can be formed from selected chemical species important for this study. These values are assumed according to the Spectra library supplied with QUADSTAR 422 apparatus. As can be seen from the table, some ions can be formed from the fragmentation of different molecules, which makes mass spectrometry data analysis difficult. However, only a limited number of main species evolved during the char gasification can be chosen to make further analysis possible.

To obtain an approximate composition of gas from MS measurements, the following procedure was applied. Evolution profiles (ion current values for selected m/z ratios recorded during the whole analysis) were normalized to the intensity of the $m/z = 40$ signal corresponding to the carrier gas (argon) in order to minimize errors caused by the shift in the mass spectrometer sensitivity.

Normalized signals, $S_j(t)$, were integrated during the whole process to obtain an integrated evolution profile, Q'_j, for all considered $(m/z)_j$ ratios

$$Q'_j = \frac{1}{t_k}\int_0^{t_k} S_j(t)dt, \quad j = 1\ldots5, \tag{1}$$

where t_k is the duration of the process.

Generally, the signal measured for some $(m/z)_j$ ratios can involve the contributions arising from the fragmentation of different components. According to the data in Table 3, the problem concerns CO and CH_4. The values of integrated profiles for these two components were corrected using the following formulas:

$$Q_3 = Q'_3 - 0.11Q'_4 \tag{2}$$

$$Q_5 = Q'_5 - 0.08Q'_4 \tag{3}$$

For other components, Q_j equals Q'_j. Then, a molar fraction of each component evolved from the sample was calculated from

$$y_i = \frac{Q_i/RCF_i}{\sum_{k=1}^{N} Q_i/RCF_k}, \tag{4}$$