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Steam gasification of a refuse derived char: Reactivity and kinetics

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ABSTRACT

A char was obtained from a commercial pilot-scale gasifier, which had been operating with a refuse derived fuel (RDF). Using this char, steam gasification experiments were then performed in a 15.6 mm i.d. packed bed tubular reactor. The effect of reaction temperature was studied (800 °C to 900 °C), and also the partial pressure of steam were in the range 33.3 kPa to 66.7 kPa. With the aid of the Shrinking-Core and the Uniform-Reaction models, kinetic parameters were estimated (apparent activation energy varied from 96 kJ mol^{-1} to 162 kJ mol^{-1}). It was also found that at lower carbon conversions (e.g. 10% to 60%) the RDF-derived char appeared to be more reactive than other bio-chars reported in the literature. However, at higher conversions (>60%), its apparent reactivity decreased with carbon conversion, thereby behaving in a similar manner to chars derived from coal.

1. Introduction

There is much interest in the development of processes in which biomass (e.g. wood) and refuse derived fuels (RDFs) may be converted into a gaseous stream, which could then be used as a fuel to produce energy, or act as a chemical intermediate. Based on information in the literature, it is well recognized that when biomass is gasified in the presence of air, then a gas mixture of CO, H_2, CO_2, N_2 and H_2O is produced, and a char stream is also produced as a by-product (Wu et al., 2009; Knoef, 2005; Chaudhari et al., 2003; Kolaczkowski et al., 2011). In such processes, the char arises from the nature of the gasification process, where some of the carbon in the feedstock remains, combined with the residual ash, which needs to be removed from the process. As such biomass gasification processes are being developed, there has been great interest in the conversion of the residual carbon in the char into a gaseous fuel, and such a process could be developed using steam to gasify the char.

1.1. Motivation for the gasification of RDF derived char

In their discussions with a number of different companies that were developing such biomass to energy processes, the authors of this paper were made aware of the importance that such companies placed on the need to find economically viable ways of converting the carbon in the char into a useful form of gaseous fuel. Otherwise, the char produced had to be disposed of off-site, which created a disposal cost and a loss in revenue from the potential of converting the carbon in the char into gaseous fuel. These considerations led to the work described in this study. In such processes, there is thermal energy available, which could be used to produce steam on-site. So using steam in such a process makes sense.

Although there have been many kinetic studies performed on the steam gasification of char (Paviet et al., 2008; Ahmed and Gupta, 2010; Wu et al., 2006), these in general have been performed on char from wood, food waste, and coal. There is relatively little data on the gasification of char produced from

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Nomenclature

A	pre-exponential factor ($bar^{-n}\,s^{-1}$)
d_q	diameter of char particle (μm)
$\bar{d}_q$	mean char particle diameter (μm)
$(\Delta d_q)_i$	char particle size interval i (μm)
E	activation energy ($kJ\,mol^{-1}$)
F_i	molar flow rate of species i ($mol\,min^{-1}$)
k	specific (or apparent) reaction rate coefficient ($bar^{-n}\,s^{-1}$)
m_i	mass fraction of char particle in size interval i
n	reaction order
P_{H_2O}	partial pressure of steam bar(a)
q	differential frequency mass (or fixed carbon content) distribution of char particle size (μm^{-1})
q_i	differential frequency mass (or fixed carbon content) fraction of size interval i (μm^{-1})
Q	cumulative frequency mass (or fixed carbon content) distribution of char particle size
Q_i	cumulative frequency mass fraction of particles smaller than size $(d_q)_i$
r	specific (or apparent) reactivity of char in gasification (s^{-1})
R_g	universal gas constant 8.314 $J\,mol\,K^{-1}$
t	time (s)
Δt	time interval (s)
T	temperature (°C)
w	char sample weight at any reaction time t (g)
w_0	initial char sample weight (g)
w_{ash}	ash content measured after gasification reaction of char (g)
X	carbon conversion at any reaction time t (%)

a process using a refuse derived fuel (RDF). However, it is well recognized that char reactivity depends not only on operating parameters (e.g. temperature, pressure, steam ratio), but also on the source of the char and how it was produced. For example, wood char reactivity is reported to increase with carbon conversion (Mermoud et al., 2006a), whereas that of coal char decreases with carbon conversion (Liu et al., 2006). The presence of inorganic elements in the char may also have a favourable catalytic effect, e.g. (Wu et al., 2009)

1.2. *Effect of temperature*

Many of the studies in the literature on the steam gasification kinetics of chars are performed at temperatures in the region of 700 °C to 1000 °C, reflecting the temperature range inside the reaction zone of a gasifier (fluidized/fixed bed), for example, in:

Paviet et al. (2007)—char gasification experiments are performed with steam at 850 °C, 900 °C, 950 °C and 1000 °C.

Khor et al. (2006)—charcoal gasification experiments are performed with steam and air at 800 °C to 950 °C in the bed.

Chaudhari et al. (2003)—steam gasification of chars at 700 °C, 750 °C, and 800 °C.

According to Blasi (2009), at such high temperatures (<1000 °C), the rate of diffusion through the pores of reacting chars plays no role in determining the overall rate of reaction, so measurements at such high temperatures are considered to be in the kinetically controlled regime. In some of the studies reported in the literature, by making comparisons between the time-scales of the different phenomena involved, a simplified approach to kinetic analysis has been adopted. Such a technique is described in Dupont et al. (2007), who applied it to a study on the gasification of biomass with steam.

Particle size will also have an effect, and this is discussed in Section 1.4.

1.3. *Effect of gas velocity*

The effect of gas velocity was also considered in some studies. For example, Paviet et al. (2008) reported that gas velocity had influence on the external mass transfer resistance, and at high gas velocity (from 10 $cm\,s^{-1}$ to 20 $cm\,s^{-1}$) this influence could be considered to be negligible. Mermoud et al. (2006a) also suggested that gas velocity had a gentle influence on gasification.

1.4. *Effect of particle size*

Char particle size was reported to have no effect by some authors (e.g. Paviet et al., 2008), while others (e.g. Mermoud et al., 2006a; Mani et al., 2011) have reported that as the particle size is increased, then this has a retarding effect on the rate.

Paviet et al. (2008), in an investigation of the effects of diffusional resistance on wood char gasification in a tubular kiln reactor, reported no significant influence on wood char gasification for mean char particle sizes of 0.1 mm and 0.47 mm. They suggested that internal mass transfer effects at these conditions could be considered to be negligible (experiments at T = 900 °C to 1000 °C, and steam partial pressure from 10.1 kPa to 70.9 kPa).

Mani et al. (Dupont et al., 2007), in an investigation of reaction kinetics and mass transfer of wheat straw char with CO_2 using a thermo gravimetric apparatus (TGA), found that particle size (from less than 60 μm to 925 μm) had much influence on the char gasification reaction, and reactivity decreased as the particle size increased (experiments performed at T = 750 °C to 900 °C, with CO_2 partial pressure of 101 kPa).

Mermoud et al. (2006a) formed similar conclusions as Mani et al. (2011). However, they investigated the steam gasification of single wood charcoal particles (10 mm to 30 mm in size) at different temperatures (830 °C to 1030 °C), and at different steam partial pressures (10.1 kPa to 40.5 kPa). They concluded that internal mass transfer was influencing the reaction under these operating conditions—although this is not surprising as the charcoal particles were relatively large.

1.5. *Effect of alkali and alkaline metallic (AAEM) species*

It is well-known that AAEM species can act as good catalysts for the combustion and gasification of solid carbonaceous fuels such as biomass or biochar (Wu et al., 2009; Yip et al., 2010). As reported in Yip et al. (2010), during char gasification, the reactivity of the raw biochars generally increased, while that of all acid-treated biochars (for removal of AAEM species) remained relatively unchanged with conversion. The results indicate that Na, K, and Ca retained in the biochars were the key catalytic species, with the catalytic effect appearing to be in the order K > Na > Ca during the steam gasification of the biochar.