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Professor Stan Kolaczkowski  10 Dec 2015

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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 ºC to 900 ºC), 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 biochars 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.

Key words: Kinetic, steam gasification, RDF-derived char, biomass.

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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\textsubscript{2}, CO\textsubscript{2}, N\textsubscript{2} and H\textsubscript{2}O is produced, and a char stream is also produced as a by-product [1, 2, 3, 4]. 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

List of Abbreviations

<table>
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<tr>
<td>AAEM</td>
<td>Alkali and Alkaline Earth Metallic</td>
</tr>
<tr>
<td>QMS</td>
<td>Quadrupole Mass Spectrometer</td>
</tr>
<tr>
<td>RDF</td>
<td>Refuse Derived Fuel</td>
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<tr>
<td>TGA</td>
<td>Thermo Gravimetric Apparatus</td>
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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 [5, 6, 7], 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 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 [8], whereas that of coal char decreases with carbon conversion [9]. The presence of inorganic elements in the char may also have a favourable catalytic effect, e.g. [1].

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. [10] - char gasification experiments are performed with steam at 850 °C, 900 °C, 950 °C and 1000 °C.
Khor et al. [11] - charcoal gasification experiments are performed with steam and air at 800 °C to 950 °C in the bed.

Chaudhari et al. [3] - steam gasification of chars at 700 °C, 750 °C, and 800 °C.

According to Blasi [12], 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. [13], 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. [5] 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. [8] 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. [5]), while others (e.g. Mermoud et al. [8]; Mani et al. [14]) have reported that as the particle size is increased, then this has a retarding effect on the rate.

Paviet et al. [5], 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 $T = 900 \degree C$ to $1000 \degree C$, and steam partial pressure from $10.1 \text{kPa}$ to $70.9 \text{kPa}$).

Mani et al. [13], 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 $60 \mu m$ to $925 \mu m$) had much influence on the char gasification reaction, and reactivity decreased as the particle size increased (experiments performed at $T = 750 \degree C$ to $900 \degree C$, with CO$_2$ partial pressure of $101 \text{kPa}$).

Mermoud et al. [8] formed similar conclusions as Mani et al. [14]. However, they investigated the steam gasification of single wood charcoal particles (10 mm to 30 mm in size) at different temperatures ($830 \degree C$ to $1030 \degree C$), and at different steam partial pressures ($10.1 \text{kPa}$ to $40.5 \text{kPa}$). 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 [1, 15]. As reported in Yip et al. [15], 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.

A similar phenomenon of increased reactivity of biochar with conversion was also observed and reported by Wu et al. [1]. The catalytic effect of the inherent AAEM species seems in turn to depend on the carbon structure that probably affects the catalyst dispersion. It was emphasized that the surface area of biochar increased with conversion, suggesting the formation of new pores and/or opening of closed pores as a result of steam activation during gasification. Besides the effect of the carbon structure evolution, the inhibiting effect of some inorganic components such as Si and P was also discovered by Hugnon et al. [16], where K would tend to be encapsulated by P and Si with carbon conversion, and would then be unable to act as a catalyst.

Nevertheless, consideration of the effects of catalysts and evolution of carbon structure during gasification will not be considered in any detail in this paper; however, they will be used to explain the evolution of reactivity of RDF-derived char during the gasification process.

1.6. Decisions taken
Based on this review, it was decided that the influence of: char particle size, gas flow, char bed length, reaction temperature and steam partial pressure should all be explored. This would lead to the development of useful kinetic rate expressions, which in the future could be used to help estimate the residence time required in a reactor to achieve the desired conversion of carbon in the char. This work is clearly novel, as there is relatively little information in the literature on the gasification kinetics of RDF-derived char.

In developing the experimental technique, a number of important assumptions were made based on the following:

(a) In the literature, it has been suggested (e.g. Everson et al. [17] and Huang et al. [18]) that char-CO\textsubscript{2} and char-H\textsubscript{2}O reactions proceed on separate active sites at atmospheric pressure. Thus, in this present study, it was decided to study the steam (H\textsubscript{2}O) gasification of char as a set of experiments on their own.

(b) Although some authors (e.g. Everson et al. [17]; Huang et al. [18]) have presented evidence of the inhibition effects of CO in CO\textsubscript{2}-char reactions, and H\textsubscript{2} in steam-char reactions, in this study it is assumed that there are no inhibition effects.

(c) The partial pressure of the gasifying agent (H\textsubscript{2}O) is considered to remain unchanged along the reactor, even though it is inevitably consumed in reality. This assumption was also applied in other studies in the literature (e.g. Wu et al. [7]; Yip et al. [15]).

(d) Many of the kinetic experiments on char gasification have been performed using a TGA, and the carbon conversion was measured by the loss in the weight of the sample [8, 14, 17, 18, 19]. However, in this study, it was decided to perform
such experiments in a small packed-bed reactor, which is often used in heterogeneous catalytic experiments. A fast gas analysis method developed in [20] using a quadrupole mass spectrometer (QMS) was used to measure the product gas composition on-line, which was then used to calculate the rate of carbon conversion in the char.

2. Experimental Procedure

2.1. Experimental Apparatus

The experimental work was carried out using a packed-bed reactor (Figure 1), which operated at atmospheric pressure. The reactor consisted of a vertical stainless steel tube with an inner diameter of 15.6 mm, which was filled with RDF-derived char particles. The char bed depth could be varied from 1.6 mm to 23.7 mm. This tube was positioned inside an electrically heated furnace, and the temperature inside the char bed was measured using a thermocouple located at the top of the char bed. The char bed was supported by two quartz wool layers which retained the char and ash particles.

In experiments with steam, the water and nitrogen passed through a stainless steel tube put inside the furnace, which vaporized the water and preheated the gas. The nitrogen flow was adjusted with a rotameter, while that of the water was set using a metering pump.

The gas exiting from the top of the reactor flowed through a cooling coil, and condensate was trapped in two plastic vessels (connected in series). The gas then passed through a glass wool filter, and was finally discharged into the vent from the fume.
cupboard. A gas sample stream was passed to a quadrupole mass spectrometer (QMS) for on-line gas analysis.

**Figure 1 here**

### 2.2. RDF-derived Char Particle Size Distribution

Sieves were used to classify by size the RDF-derived char that had been obtained from the commercial pilot-scale gasifier. Information on the fixed carbon content in the different char size ranges will be also useful when designing a process.

The frequency mass fractions were calculated from:

\[ q_i = \frac{m}{\Delta d_q} \quad \text{or} \quad Q_i = \sum_{1}^{i} (q_i \Delta d_q) \]  

where: \( q_i \) is the differential frequency mass (or fixed carbon content) fraction of size interval \( i \), \( \mu m^{-1} \); \( Q_i \) is the cumulative frequency mass (or fixed carbon content) fraction of particles smaller than size \( (d_q)_i \); \( \Delta d_q \) is the size interval \( i \), \( \mu m \); and \( m_i \) is the mass fraction of char particle in size interval \( i \).

Then, the mean size of the RDF-derived char particles was estimated from:

\[ \bar{d}_q = \frac{1}{\sum_{a=1}^{a} \left( m_i / d_q \right)} = 305.52 \mu m \]  

The results of such a char particle distribution are presented, in Figure 2, from which it can be seen that particle size varied from 37.5 \( \mu m \) to 7,000 \( \mu m \). As the mean size of the RDF-derived char was 305 \( \mu m \), a sieve was used to obtain a char particle size range of 250 to 500 \( \mu m \) (representing mean particle size), and this size range was used for the experiments.
From the data on the fixed carbon content (Figure 2(c)), it is interesting to note that this changes slightly with particle size, and this is most probably related to the part of the process from which that carbon particle arose (e.g. carried in the gas stream and trapped in a cyclone, or retained in the char stream from the base of the gasifier).

The results of proximate analysis of the RDF-derived char are: moisture 4.59 wt.% wet basis; volatiles 10.71 wt.% dry basis; fixed carbon 34.18 wt.% dry basis; ash 55.10 wt.% dry basis. The proximate analysis of the RDF pellets was also performed, giving: moisture 7 wt.% wet basis; volatiles 43 wt.% dry basis; fixed carbon 31 wt.% dry basis; ash 26 wt.% dry basis.

From these measurements, it was decided to use char in the size range of 250 μm to 500 μm for the kinetic experiments.

### 2.3. Experimental Methodology

A bucket of RDF-derived char, obtained from an actual gasification pilot-plant that used RDF pellets as fuel, was supplied by Refgas Ltd, Sandycroft. This char was sealed and stored at room temperature, and used throughout this study to ensure the repeatability of the char resource.

Samples of char were first conditioned by heating for 3 hours in a flow of N₂ at 800 °C, and this removed any volatiles (checked with the QMS). Then N₂ was fed into the reactor (during the heating-up period) to achieve the desired operating temperature.
This was then followed by the addition of water which turned into steam, and the experiment was started. The system pressure was atmospheric (open end of reactor). After each run, air was passed through the reactor to burn out any residual carbon. Finally, the reactor was cooled, and the remaining ash was collected and weighed.

The rate of carbon conversion in the char can be inferred from the molar flow rate of CO and CO$_2$ from the reactor. This approach has been used in many studies [5, 6, 7, 9, 10], making use of the flow of an inert sweeping gas (e.g. N$_2$ or Argon) to perform such calculations. If the formation of CH$_4$ was significant then it would have to be included, but this was checked and found not to be the case in the experiments described.

The experimental conversion of carbon in the char, $X$, may be defined (e.g. in Paviet et al.[5]) as:

$$X = \frac{w_0 - w}{w_0 - w_{ash}}$$  \hspace{1cm} (3)

where: $w_0$ is the initial sample weight, $w$ is the sample weight at any time $t$ and $w_{ash}$ is the ash content measured after reaction.

The evolution of sample weight, $w(t)$, as a function of time is unknown, but it can be deduced from the gas composition. The experimental kinetic rate, at any time $t$, can thus be calculated (e.g. in Cozzani [19]) from:

$$\frac{dX}{dt} = \lim_{\Delta t \to 0} \left( \frac{X_{t_2} - X_{t_1}}{\Delta t} \right)$$ \hspace{1cm} (4a)

where: $X_{t_1}$ and $X_{t_2}$ are carbon conversion at time $t_1$ and $t_2$, respectively; and $\Delta t = t_2 - t_1 \approx 20$ s, which is the measurement step of the gas analysis method.

or (e.g. in Paviet et al. [5]) from:
\[
\frac{dX}{dt} = \frac{12(F_{CO} + F_{CO_2})}{w_0 - w_{ash}} \quad (4b)
\]

where: \(F_{CO}\) and \(F_{CO_2}\) are molar flow rates (mol/min) of CO and CO\(_2\), respectively, in the gas stream from the packed bed.

Both Equations (4a) and (4b) were tested, and they produced the same results. Equation (4b) was used in this work.

3. Results and Discussion

3.1. Experimental Results

To determine the operating conditions for the kinetic study the following set of preliminary experiments was performed:

3.1.1. Effect of char bed length

First of all, some preliminary experiments were performed with different char bed lengths (1.6 mm, 5.7 mm, 8.2 mm, 16.8 mm and 23.7 mm), corresponding to different initial mass quantities of char (0.1 g, 0.35 g, 0.5 g, 1.03 g and 1.45 g). The bulk density of the char is 500 kg/m\(^3\). Experiments were performed at: furnace temperature set at 900 °C; char particles from 250 μm to 500 μm; N\(_2\) flow set at 0.2 L min\(^{-1}\) (1 L = 1 dm\(^3\); 1 min = 60 s); H\(_2\)O flow set at 0.148 g min\(^{-1}\); and an calculated molar ratio of H\(_2\)O:N\(_2\) = 1:1.

It was observed that the performance of the reactor with bed lengths from 1.6 mm to 16.8 mm was very similar and about 70% of the carbon in the char was
consumed after eight minutes. This means that in such a sample the resistance to
external mass transfer is negligible.

For the planned kinetics study, it was decided to select a small initial bed length
to reduce any secondary reactions, and to minimize the change in the partial pressure of
steam along the char bed. However, if a bed length < 5.7 mm was used, then CO
concentration would be low, leading to measurement errors. Therefore, an initial char
bed length of 8.2 mm was selected for all subsequent experiments.

3.1.2. Effect of gas flow

Experiments were performed at different gas inlet flows (N₂ = 0.2 L min⁻¹, 0.4 L
min⁻¹, 0.6 L min⁻¹ and 0.7 L min⁻¹; H₂O = 0.148 g min⁻¹, 0.296 g min⁻¹, 0.444 g min⁻¹
and 0.518 g min⁻¹), which corresponded to different superficial velocities in the packed
bed (0.218 m s⁻¹, 0.437 m s⁻¹, 0.655 m s⁻¹ and 0.764 m s⁻¹). The experiments were done
at the following conditions: furnace temperature set at 900 °C; char bed length = 8.2
mm; char particles from 250 μm to 500 μm; calculated molar ratio of H₂O:N₂ = 1:1.

It was observed that at the high gas superficial velocities (0.437 m s⁻¹ to 0.764 m
s⁻¹), the gas velocity has little influence on char gasification, indicating that external
mass transfer resistance is low. In Paviet et al. [5], superficial gas velocities at 10 cm s⁻¹
to 20 cm s⁻¹ (0.1 m s⁻¹ to 0.2 m s⁻¹) had little influence on external mass transfer.

Although high gas velocities are preferred, this leads to higher errors in CO
measurements in the outlet gas stream; hence, a gas velocity of 0.218 m s⁻¹ was selected
for subsequent experiments.

3.1.3. Effect of char particle size
Experiments were performed with char particles that had the following size ranges: 180 μm to 250 μm; 250 μm to 500 μm; 1000 μm to 1180 μm; and 2000 μm to 4000 μm. The experiments were done at: furnace temperature set at 900 °C; char bed length = 8.2 mm; N₂ flow set at 0.2 L min⁻¹; H₂O flow set at 0.148 g min⁻¹; calculated molar ratio of H₂O:N₂ = 1:1.

The results obtained showed that the rate of carbon conversion increases slightly as the particle size was reduced. However, the increase was insignificant in the size range tested. Also, because the measured mean particle size of RDF-derived char was approximately 305 μm, particles in the range of 250 μm to 500 μm were chosen for the subsequent kinetic experiments.

3.1.4. Effect of Reaction Temperature

To explore the effect of reaction temperature, experiments were performed at: 800 °C, 850 °C and 900 °C. This set of experiments (at different reaction temperature) was repeated at various H₂O flows, while N₂ flow was kept constant at 0.2 L min⁻¹. This helps to determine kinetic parameters that will be described later. One example of the conditions in the reactor for one set of experiments was: N₂ flow rate = 0.2 L min⁻¹; char bed length = 8.2 mm; H₂O flow = 0.222 g min⁻¹; calculated molar ratio of H₂O:N₂ = 3:2, corresponding to steam partial pressure of 60 kPa.

As expected, reaction rates increased with temperature, see Figure 3.

Figure 3 here

3.1.5. Effect of Partial Pressure of Steam
As a reminder, for each reaction temperature (800 °C, 850 °C, or 900 °C), experiments were performed at different partial pressures of H₂O (33.3 kPa, 50 kPa, 60 kPa and 66.7 kPa), which corresponded to different H₂O flows (0.074 g min⁻¹, 0.148 g min⁻¹, 0.222 g min⁻¹ and 0.296 g min⁻¹), while N₂ flow was kept constant at 0.2 L min⁻¹. One example of the conditions in the reactor was: furnace temperature set = 850 °C; N₂ flow = 0.2 L min⁻¹; char bed length = 8.2 mm.

The results are presented in Figure 4, for experiments performed at 850 °C.

From these experiments, char reactivity increases with steam partial pressure.

3.2. Kinetic Analysis

There are several well established approaches which can be used to develop a model to describe reacting char. Because the ash content in the RDF-derived char is high, then according to Levenspiel [21] and Kunii and Levenspiel [22], then either the Uniform-Reaction Model or the Shrinking-Core Model for porous solids of unchanging size could be applied. In general, small particles follow the Uniform-Reaction Model, while large particles follow the Shrinking-Core Model - with ash diffusion controlling at high temperatures, but reaction controlling at low temperatures [22]. In this study, both of these models were considered.

3.2.1. Estimate of Kinetic Parameters for the Shrinking-Core Model
The theoretical development of this model is based on Levenspiel [21] and Kunni and Levenspiel [22]. In summary: for a Shrinking-Core model, the reaction front advances from the outer surface into the particle, leaving behind a layer of ash. Thus, at any time there exists an unreacted core of carbon which shrinks in size during the reaction. The driving force of the gasification is proportional to the available surface area, and char reactivity of a batch particle can be defined as:

\[
r = \frac{1}{(1 - X)^{2/3}} \frac{dX}{dt} = k \cdot P_{H_2O}^n
\]  

(5)

where: \( r = \frac{1}{(1 - X)^{2/3}} \frac{dX}{dt} \) is called specific (or apparent) reactivity of char in gasification reaction [15].

A similar equation to Equation (5) can also be seen in the literature (e.g. Liliedahl and Sjostrom [23]; Basu [24]).

For the steam gasification of char, an \( n \)-th-order reaction model is commonly used [6, 24]:

\[
r = k \cdot P_{H_2O}^n
\]  

(6)

where: \( P_{H_2O} \) is the partial pressure of steam, that is considered as the partial pressure of steam in the inlet gas stream.

From the experimental data of carbon conversion rate, the values of the rate constant \( k \), the reaction order \( n \), apparent activation energy \( E \) and pre-exponential factor \( A \) were calculated. Figure 5 shows an example of the plots to determine the values of \( k \) and \( n \) at 850 °C, and \( E \) and \( A \) at different degrees of conversion (\( X \)). These results are very encouraging as the data points are positioned close to the ‘best-fit’ straight lines. Values of \( k \) and \( n \), \( E \) and \( A \) are shown in Tables 1 and 2, respectively. From these, the
apparent activation energy varied from 96 to 106 kJ mol\(^{-1}\) across the 10 % to 70 % conversion range, and then it increased dramatically to 152 kJ mol\(^{-1}\) at 80 % carbon conversion.

Figure 5 here

Table 1 here

Table 2 here

Blasi [12] reviewed data on the steam gasification of a number of different biochars, and reported that \(E\) varied from 143 to 237 kJ mol\(^{-1}\) (with a large part of the values around 180 to 200 kJ mol\(^{-1}\)), depending on reaction conditions and biochar source. This indicates that the RDF-derived char used in this study may be very active.

From data in Table 2, the value of the pre-exponential factor increases slightly with conversion across the 10 % to 70 % range, but more rapidly after that. This change may be due to the evolution of the char structure with carbon conversion. Ahmed and Gupta [6] suggested that ash might have increased the adsorption rate of steam to the char surface, leading to an increase in the pre-exponential factor. However, (a) increased porosity, and (b) access to the ash (which may have catalytic and inhibiting properties), may also have a role to play [1, 7]. The effects of carbon structure on char reactivity are also discussed in Aarna and Suidberg [25], where they concluded that the micropores (< 2 nm) probably did not participate in the gasification reaction of chars, and that the surface developed by the macropores and the mesopores (2 nm < diameter < 50 nm) was a better indicator of the reactive surface, than the total pore surface area.

This conclusion is consistent with others (e.g. Paviet et al. [5]; Mermoud et al. [26])
In other studies on the steam gasification of biochars [1, 6, 8, 15, 27] pore surface area and reactivity of chars increased with conversion, while an opposite trend was observed for the steam gasification of coal chars [7, 23, 28].

It was decided, to examine the 70% to 80% carbon conversion region in more detail, and more data points were added. Figure 5(c) shows the Arrhenius plot for conversions from 71% to 80%. A ‘compensation effect’ is observed here, where there is a simultaneous increase in apparent activation energy and pre-exponential factor with conversion, see Table 2. This ‘compensation effect’ or ‘isokinetic effect’ has been observed and reported in the literature for char-gas reactions [6, 7], and explains the observed change that took place.

3.2.2. Estimate of kinetic parameters for the Uniform-Reaction Model

For the Uniform-Reaction Model, the driving force for the gasification is proportional to the mass of unreacted carbon in the particle, and char reactivity of a batch particle can be defined as:

\[ r = \frac{1}{1 - X} \frac{dX}{dt} = kP_{H_2O}^{n} \] (7)

A similar equation to Equation (7) can also be seen in the literature [22, 23, 24]. For this model, the values of the apparent activation energies (E) and pre-exponential factors (A) at different degrees of conversion (X) are calculated and presented in Table 3.

Table 3 here
It is interesting to note, that when comparing the values of the apparent activation energy \( (E) \) calculated in Table 3 (Uniform-Reaction Model), with the values in Table 2 (Shrinking-Core Model), then very similar results have been obtained. This means, that the two models would produce very similar results across the range of conditions tested. However, values of the pre-exponential factor \( (A) \) in the Uniform-Reaction Model are different from those in the Shrinking-Core Model. Mathematically, this comes from the fact that the pre-exponential factor in Shrinking-Core Model includes the factor that is a function of the density of carbon and diameter of the char particles, whereas that in the Uniform-Reaction Model does not (deduced from Kunii and Levenspiel [22]).

3.3. Comparison between RDF-derived char and wood charcoal

Finally, a few experiments were performed using a wood based charcoal, obtained from a small commercial gasification reactor that used wood chips as fuel. A bucket of this char, supplied by Refgas Ltd, Sandycroft, was sealed and stored at room temperature, and used throughout this study to ensure the repeatability of this char resource. Two different ranges of wood charcoal particles were used (250 \( \mu \text{m} \) to 500 \( \mu \text{m} \) and 2000 \( \mu \text{m} \) to 4000 \( \mu \text{m} \)) and tested. All of these experiments were performed at: furnace temperature set at 900 °C; char bed length = 8.2 mm; \( \text{N}_2 \) flow set at 0.2 L min\(^{-1}\); \( \text{H}_2\text{O} \) flow set at 0.148 g min\(^{-1}\); calculated molar ratio of \( \text{H}_2\text{O}:\text{N}_2 = 1:1 \).

The results are shown in Figure 6.

Figure 6 here
From these data, it is clear that at low carbon conversion (< 60 %), the RDF-derived char is much more reactive than wood charcoal. However, at higher carbon conversions the opposite is true.

In some studies [15, 28], the reactivity of gasification of char is presented as the specific (or apparent) reactivity, $r$. If the Shrinking-Core Model is selected, then

$$ r = \frac{1}{(1 - X)^{2/3}} \frac{dX}{dt} $$

Figure 6(c) shows the evolution of apparent reactivity of char with carbon conversion.

From Figure 6(c), above a carbon conversion of 60 %, the apparent RDF-derived char reactivity decreases sharply with carbon conversion. This behaviour of RDF-derived char is opposite to that of other biochars such as mallee-bimass-derived char [14] or food-waste-derived char [6]; however, it is similar to that of coal char (e.g. as presented in Wu et al. [7]; Liu et al. [9]; Liliedahl and Sjostrom [22]; Xu et al. [27]).

Mermoud et al. [8], in a study of steam gasification of single wood charcoal particles (with a diameter of 10 mm to 30 mm), observed that the reactivity of wood charcoal increased continuously with conversion due to a continuous increase in the surface area. However, Liu et al. [9] reported a decrease in coal char reactivity with conversion because of a decrease in the surface area.

The RDF-derived char contained 55 wt.% ash, which consisted of inorganic elements. It is well known that these elements can have a catalytic effect, which could be the main reason for the increase in reactivity at low carbon conversion (<60%). However, the presence of inorganic elements can also decrease the porosity to such an extent that the active surface area is also decreased [1, 6, 7, 12]. In addition, Hugnon et al. [16] noticed that during steam gasification of algal and lignocellulosic biomass, K
would tend to be encapsulated by P and Si with carbon conversion, and would then be unable to act as a catalyst. Therefore, from the results obtained in this paper, at higher (>60%) carbon conversion, a higher ash content is expected, which could result in an encapsulation of AAEM species, a decrease in porosity (and active surface area), and hence reactivity.

4. Conclusions

For the steam gasification of the RDF-derived char, the apparent activation energy $E$ varied from 96 kJ mol$^{-1}$ to 162 kJ mol$^{-1}$. The reactivity of the char (at carbon conversions from 10% to 60%) appears to be higher than other biochars reported in the literature. However, at high conversions (> 60%), the apparent reactivity of the RDF-derived char decreases with carbon conversion, behaving in a similar manner to coal structures.

Comparisons between the use of the Shrinking-Core Model and the Uniform-Reaction Model produced almost identical results.

Information has been presented in this paper, which provides data on the properties of an RDF-derived char and how it could be gasified in the presence of steam. This supports the viability of converting this type of char into a useful fuel gas, which would enhance the commercial viability of the overall ‘RDF to energy’ process. Such data on RDF-derived char are scarce in the literature, and this is probably the first detailed kinetic study of its type in which kinetic parameters for an RDF-derived char have been determined. These parameters could be used in modelling studies to explore
different design concepts (e.g. packed-bed, moving-bed, fluidized bed) for the ‘char-gasifier’, although they would of course then need to be tested in pilot-scale studies.

Acknowledgment

We are grateful for the support received from Refgas Ltd a company developing biomass to energy processes, and also for the support from the Vietnam Ministry of Education & Training, in the form of a research grant for C. D. Le.

Nomenclature

$A$ Pre-exponential factor \( \text{bar}^n \text{s}^{-1} \)

$d_q$ Diameter of char particle \( \mu \text{m} \)

$\bar{d}_q$ Mean char particle diameter \( \mu \text{m} \)

$(\Delta d_q)_i$ Char particle size interval $i$ \( \mu \text{m} \)

$E$ Activation energy \( \text{kJ mol}^{-1} \)

$F_i$ Molar flow rate of species $i$ \( \text{mol/min} \)

$k$ Specific (or apparent) reaction rate coefficient \( \text{bar}^n \text{s}^{-1} \)

$m_i$ Mass fraction of char particle in size interval $i$

$n$ Reaction order

$P_{H_2O}$ Partial pressure of steam \( \text{bar(a)} \)

$q$ Differential frequency mass (or fixed carbon content)

$q_i$ Differential frequency mass (or fixed carbon content) \( \mu \text{m}^{-1} \)
content) fraction of size interval $i$\(\mu{}m^{-1}\)

$Q$ 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 $s$

$\Delta t$ Time interval $s$

$T$ Temperature $^\circ{}C$

$w$ 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 $t$ $\%$

References


**Figure Captions**

**Figure 1.** Schematic of the kinetic study apparatus.

**Figure 2.** RDF-derived char particles: (a) differential frequency mass and fixed carbon content distributions, (b) cumulative frequency mass and fixed carbon content distributions, (c) fixed carbon content based on char particle size.

**Figure 3.** Influence of reaction temperature: (a) carbon conversion, (b) rate of carbon conversion.

**Figure 4.** Influence of steam partial pressure at 850 °C: (a) carbon conversion, (b) rate of carbon conversion.

**Figure 5.** Plots to estimate kinetic values: (a) Example of plot to determine the values of $k$ and $n$ at 850 °C (Shrinking-Core Model); (b) Arrhenius plot for conversions from 10 to 80 % (Shrinking-Core Model); (c) Arrhenius plot for conversions from 71 to 80 % (Shrinking-Core Model).

**Figure 6.** Comparisons between RDF-derived char and wood charcoal at 900 °C: (a) carbon conversion, (b) rate of carbon conversion, (c) apparent reactivity.
Figure 1
Figure 2
Figure 3
Figure 4

(a) Carbon conversion (%) vs. Time (min) at different pressures (0.333 bar(a), 0.5 bar(a), 0.6 bar(a), 0.667 bar(a)).

(b) dX/dt (s⁻¹) vs. Conversion (%) at different pressures (0.333 bar(a), 0.5 bar(a), 0.6 bar(a), 0.667 bar(a)).
Figure 5

(a) 

(b) 

(c)
Figure 6
Table 1. Values of $k$ and $n$ at various reaction temperatures (Shrinking-Core Model).

<table>
<thead>
<tr>
<th>Carbon conversion (%)</th>
<th>900 °C</th>
<th></th>
<th>850 °C</th>
<th></th>
<th>800 °C</th>
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<td>$n$</td>
<td>$k$</td>
<td>$n$</td>
<td>$k$</td>
<td>$n$</td>
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<td>0.889</td>
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<td>20</td>
<td>0.660</td>
<td>1.413</td>
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<td>0.261</td>
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<tr>
<td>30</td>
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<td>1.370</td>
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<td>1.429</td>
<td>0.239</td>
<td>1.179</td>
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<tr>
<td>40</td>
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<td>60</td>
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<tr>
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<td>0.252</td>
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<td>0.126</td>
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Table 2. Apparent activation energies and pre-exponential factors (Shrinking-Core Model).

<table>
<thead>
<tr>
<th>Carbon conversion (%)</th>
<th>Arrhenius equation</th>
<th>Apparent activation energy, $E$ (kJ mol$^{-1}$)</th>
<th>Pre-exponential factor, $A$ (bar$^{-n}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$y = 9.342 - 11620x$</td>
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<td>$1.14 \times 10^4$</td>
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</table>

Note: When the conversion was calculated, using the equations presented in this table, the match was within ± 5% of the experimental data obtained.
Table 3. Apparent activation energies and pre-exponential factors (Uniform-Reaction Model).

<table>
<thead>
<tr>
<th>Carbon conversion (%)</th>
<th>Arrhenius equation</th>
<th>Apparent activation energy, $E$ (kJ mol$^{-1}$)</th>
<th>Pre-exponential factor, $A$ (bar$^n$ s$^{-1}$)</th>
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<tr>
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<td>y=9.6351 – 11697x</td>
<td>97.2</td>
<td>1.53 x 10$^4$</td>
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<td>30</td>
<td>y= 9.684 – 11768x</td>
<td>97.8</td>
<td>1.61 x 10$^4$</td>
</tr>
<tr>
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<td>y=10.075 – 12182x</td>
<td>101</td>
<td>2.37 x 10$^4$</td>
</tr>
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<td>y=10.555 – 12598x</td>
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<td>3.84 x 10$^4$</td>
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<tr>
<td>60</td>
<td>y=10.725 – 12644x</td>
<td>105</td>
<td>4.55 x 10$^4$</td>
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<td>y=11.023 – 12941x</td>
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<td>7.54 x 10$^4$</td>
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<td>y=15.426 – 18220x</td>
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<td>50.1 x 10$^5$</td>
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Note: When the conversion was calculated, using the equations presented in this table, the match was within ± 5% of the experimental data obtained.