Gasification Kinetics of Waste Tire Char and Sewage Sludge Char with Steam in a Thermobalance Reactor

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Abstract: The effects that the gasification temperature (550 ~ 850°C) and partial pressure of H₂O (25 ~ 101.3 kPa) have on the steam gasification rates of tire-char and sludge-char have been determined in a thermobalance reactor. The gasification rates followed the order: tire > coal > sludge. Among the tested gas-solid reaction models, the modified volumetric reaction model was most appropriate to predict our conversion data and, thus, the kinetic parameters were determined on the basis of a modified volumetric reaction model. From the Arrhenius plot (κ vs. 1/T), the activation energy and the pre-exponential factor were 39.1 kJ/mol and 0.2669 s⁻¹, respectively, for tire-char and 156.5 kJ/mol and 5.8611 × 10⁶ s⁻¹, respectively, for sludge-char. The reaction orders were 0.87 for tire-char and 0.96 for sludge-char, with respect to H₂O partial pressures of 0.25 ~ 101.3 kPa. The gasification reaction rate can be expressed as dX/dt=(0.2699)exp(-39090/RT)(P_{H₂O})^{0.87}(1-X) for tire-char and dX/dt=(58611)exp(-156510/RT)(P_{H₂O})^{0.96}(1-X) for sludge-char.

Keywords: waste tire scrap, sewage sludge, gasification, thermobalance

Introduction

Large numbers of sewage sludge and used tires are produced in Korea. The number of waste tires generated has now reached 20 million per year. Their recycle ratio remains below 50% and the majority of them are dumped in landfill sites. Because they are normally not mixed with other types of waste, they are very good resources for energy recovery. Numerous studies [1-3] have been carried out in efforts to recover energy and chemical feedstocks from waste tires through direct incineration, pyrolysis, and gasification. The gasification of waste is a very attractive means of recovering energy without further processing [4]. Furthermore, the gasification greatly reduces gaseous pollutant and the gas produced can be used as a fuel for power plants, fuel cells, or hydrogen production. The gasification of carbonaceous waste proceeds in two steps: devolatilization and pyrolysed char gasification [5]. Because the gasification rate is much slower than the devolatilization rate, the volume of the gasifier depends on the gasification rate of the pyrolysed char [6]. Knowing the kinetics of waste-char gasification is important in understanding the reaction mechanism and in designing and optimizing the gasification processes. The main gasification reaction with steam is

\[ C + H₂O = CO + H₂ \quad \Delta H = 118.9 \text{ kJ/mol} \quad (1) \]

This endothermic reaction is favored by elevated temperature and pressure and, in the absence of a catalyst, occurs slowly at temperatures below 930°C. The objective of this study was to determine the effects that the gasification temperature and partial pressure of water have on the gasification rate of tire-char and sludge-char and to evaluate suitable kinetic equations to determine the gasification rates.

Kinetics of Steam Gasification

The carbon conversion during steam gasification of a carbonaceous solid is defined as

\[ X = \frac{W_e - W}{W_i - W_{ash}} \quad (2) \]

where \( W_i \) is the initial mass of the char, \( W_{ash} \) the mass of ash
Table 1. Analyses of Tires, Sewage Sludge, and Coal (As Received)

<table>
<thead>
<tr>
<th></th>
<th>Waste tire</th>
<th>Bituminous coal</th>
<th>Sewage sludge</th>
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<tr>
<td>Ultimate analysis, wt%</td>
<td></td>
<td></td>
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<tr>
<td>Carbon</td>
<td>84.65</td>
<td>72.30</td>
<td>34.26</td>
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<tr>
<td>Hydrogen</td>
<td>7.38</td>
<td>4.30</td>
<td>1.00</td>
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<tr>
<td>Nitrogen</td>
<td>0.39</td>
<td>0.36</td>
<td>5.24</td>
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<tr>
<td>Sulfur</td>
<td>2.11</td>
<td>0.21</td>
<td>0</td>
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<tr>
<td>Oxygen*</td>
<td>5.47</td>
<td>11.70</td>
<td>0</td>
</tr>
<tr>
<td>Proximate analysis, wt%</td>
<td></td>
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<tr>
<td>Volatile</td>
<td>61.72</td>
<td>27.38</td>
<td>6.39</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>33.05</td>
<td>57.19</td>
<td>2.29</td>
</tr>
<tr>
<td>Moisture</td>
<td>0.70</td>
<td>7.05</td>
<td>84.50</td>
</tr>
<tr>
<td>Ash</td>
<td>4.53</td>
<td>8.38</td>
<td>6.82</td>
</tr>
<tr>
<td>HHV, kcal/kg</td>
<td>7057</td>
<td>6087</td>
<td>-</td>
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<tr>
<td>HHV**</td>
<td>9200</td>
<td>6829</td>
<td>3115</td>
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Ash component, wt%  

<p>| | | | |</p>
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<tr>
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<tr>
<td>SiO₂</td>
<td>13.40</td>
<td>65.5</td>
<td>11.62</td>
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<tr>
<td>Fe₂O₃</td>
<td>2.00</td>
<td>2.24</td>
<td>1.95</td>
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<td>CaO</td>
<td>9.98</td>
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<td>0.76</td>
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<td>MgO</td>
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<td>TiO₂</td>
<td>2.92</td>
<td>1.50</td>
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<td>3.90</td>
<td>27.94</td>
<td>7.89</td>
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<tr>
<td>Na₂O</td>
<td>11.13</td>
<td>0.43</td>
<td>0.32</td>
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<tr>
<td>K₂O</td>
<td>1.10</td>
<td>1.40</td>
<td>0.71</td>
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<tr>
<td>MnO</td>
<td>0.01</td>
<td>0.02</td>
<td>0.06</td>
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<tr>
<td>Cr₂O₃</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

HHV: higher heating value; *: by difference; **: calculated using Dulong's formula.

Table 2. Kinetic Parameters from the Gas-solid Reaction Models for the Steam Gasification of Sewage Sludge

<table>
<thead>
<tr>
<th>Model</th>
<th>k (h⁻¹)</th>
<th>E (kJ/mol)</th>
<th>k₀ (sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (℃)</td>
<td>650 700 750 800 850 (kJ/mol) (sec⁻¹)</td>
<td></td>
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<tr>
<td>Modified</td>
<td>0.33</td>
<td>1.4 2.09</td>
<td>5.6 14.47</td>
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<tr>
<td>Volumetric</td>
<td>0.42</td>
<td>0.78 2.06</td>
<td>5.51 13.48</td>
</tr>
<tr>
<td>Shrinking core</td>
<td>0.16</td>
<td>0.43 1.61</td>
<td>6.69 12.23</td>
</tr>
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</table>

in the char, W is the final mass of the char. To analyze the gasification rate of char and to evaluate its reactivity, three gas-solid reaction models for the heterogeneous reaction have been used. The unreacted shrinking core model in the chemical reaction control regime [7] gives the time-conversion behavior as Equation (3), whereas the volumetric reaction model [8] gives Equation (4). The modified volumetric reaction model suggested by Kasaoaka and coworkers [9] has two constants in their conversion equation, Equation (5).

Ψt = 1 - (1 - X)²/³ (3)

\[ r_t = - \ln(1 - X) \] (4)

\[ k = \sum_{0}^{1} k_{a}(X) dX \] (9)

\[ k_{a}(X) = \frac{1}{1 - X} \frac{dX}{dt} = \frac{3\psi}{[1 - X]^{1/5}} \] (6)

\[ k_{a}(x) = \frac{1}{1 - X} \frac{dX}{dt} = \Omega \] (7)

\[ k_{a}(x) = \frac{1}{1 - X} \frac{dX}{dt} = \alpha^{1/\beta} \ln(1 - X)^{(\beta - 1)/\beta} \] (8)

As a measure of char reactivity, the average reaction rate is defined as

\[ k(t) = \frac{-1}{t} \ln(1 - X) \] (5)

\[ \alpha t = - \ln(1 - X) \] (4)

\[ \beta = - \ln(1 - X) \] (5)

where \( \psi \) and \( \Omega \) are constants [1/sec] and the constants \( \alpha \) and \( \beta \) are determined from conversion vs. time data through least-square fitting. When \( \beta = 1 \), Eq. (5) is the same as the volumetric reaction model. For \( \beta < 1 \), the maximum reaction rate occurs at \( t = 0 \) and after that the rate decreases. For \( \beta > 1 \), a sigmoid shape appears in the rate vs. time curve. The specific reaction rate (reactivity), the rate per unit mass of residual fixed carbon, varies with the carbon conversion and can be easily derived as Equations (6), (7), and (8) from Equations (3), (4), and (5), respectively.

Experimental

The waste tire scraps were obtained from a tire shredding plant (Korea Resources Recovery & Reutilization Co.). The tire granules were free of steel cords, but they contained steel materials below 0.1%, and measured approximately 0.6–1.2 mm in size. The wet sludge from Ilbons waste water treatment plant has a moisture content of 85%. The wet sludge was dried in an oven for 48 h and the dried particles were sieved to an average diameter of 0.5 mm. Analyses of the waste tire scraps and the sewage sludge are shown in Table 1. The corresponding values of an Austrian bituminous coal are shown together as a reference. The heating value of sludge is very low, but that of tire scraps (ca. 7000 kcal/kg) is higher than that of coal. Therefore, waste tires can be a good supplementary fuel for the gasification process. A separate charring step was not adopted; the solid waste was placed directly into the sample basket and devolatilization and gasification of the waste were carried out consecutively in the thermobalance reactor at atmospheric pressure.

The schematic diagram of the thermobalance reactor is
shown in Figure 1. The main part of the thermobalance is a 0.055-m i.d. × 1.0-m-high stainless-steel tube equipped with a 3 kW external electrical heater. The reactant steam was generated from an electric steam generator that is a 1/8” copper tube of 1.0 m length on which a flexible electrical heating wire was coiled. The flow rate of steam was controlled by a micro-pump. The temperature of the thermobalance was controlled using a K-type thermocouple located 5 mm below the sample basket. The sample basket, made of stainless-steel mesh, was suspended from an electronic balance (Mettler Toledo) and the mass signal at the balance was transferred to a personal computer (the change of mass is indicated as a dotted curve on the monitor).

When the reactor was heated to the desired reaction temperature under a nitrogen flow, the waste sample (0.7 ~ 1.0 g) was placed in the sample basket through the hatch and the sample basket was moved down to the center of the reactor using a motor-driven winch. There was an initial mass loss due to the evolution of moisture and volatile matter from the waste sample. Volatile matter (over 60 wt%) evolved rapidly within two min for the 0.6 ~ 1.2-mm-size tire granules. After 15 min, the sample mass became constant and then a mixture of steam and N₂ was admitted to the reactor for gasification of the residual carbon in the char sample. During gasification, the variation of the sample mass was recorded continually every 6 sec. When the sample mass became nearly constant again, the gaseous reactant was switched to air to burn the final residual carbon out. The content of ash then could be determined.

Results and Discussion

Rate Controlling Step

When gaseous diffusion is fast through a particle and the exterior of a particle, the overall reaction rate will be controlled by the chemical reaction between carbon and water. The dominant control step can be easily determined by applying the shrinking core model in the chemical reaction control regime to the time-conversion data. When the conversion data of log[1-(1-X)^(3/2)] is plotted with respect to log t, according to Equation (3), the slope of the plot determines the control step: a slope of 1 means chemical control, whereas a slope of 2 implies diffusion control. The conversion data of several
runs from the gasification of tire-char and from that of sewage sludge-char are plotted in Figure 2; most of the data lie in a linear mode. This result indicates that the steam gasification of tire-char and the gasification of sludge-char are chemically controlled.

Comparison with the Models

The three gas-solid reaction models were tested to predict gasification behavior of the tire and sludge chars. The time-conversion equations from the unreacted shrinking core model, volumetric reaction model, and modified volumetric reaction models are given as Equations (3), (4), and (5), respectively. Because these equations can be expressed in linear form, the linearity of the data indicates their degree of fitness to the experimental values. It should be noted that the line from Equation (5) does not cross the origin. The time-conversion data of the tire-char are plotted in Figure 3 according to the three gas-solid reaction models. The modified volumetric model shows good linearity of data at most temperatures, but the other two models show deviations of data from linearity at low temperatures. This situation may arise because the modified volumetric model has two constants in the equation, whereas the others have only one constant. Lee and Kim [10] reported that the modified reaction model was good at expressing the conversion behavior during their gasification of shredded tires.

The conversion data of the sludge-char are given in Figure 4. It is strange that it is very difficult to notice differences in the goodness of fit of the models. All three models provide the experimental data with good linearity. Dried sludge particles (ca. 1 g) were used for the thermobalance experiment. After devolatilization, the remaining char and fixed carbon for the gasification reaction can be calculated from proximate analysis data. The char of the sludge was 59% of the sample (ca. 0.6 g
Gasification Kinetics of Waste Tire Char and Sewage Sludge Char with Steam in a Thermobalance Reactor

The gasification rate is very sensitive to temperature because the reaction is endothermic. The initial rates were relatively high and after that the gasification rates decreased. At high temperatures (over 800°C) all the models predict the data very well, whereas at the lower temperatures only the modified reaction model gives reasonable predictions. The modified volumetric model is the best at describing the conversion behaviors not only for gasification of tire-char but also for the gasification of sludge-char. Because the physical structure of the dried sludge particle should be very different to that of a tire granule, a further study of the particle structure will be helpful to examine gas-solid reaction models for sludge particles.

The changes of the specific gasification rate with respect to carbon conversion for the gasification of sludge-char at various temperatures are shown in Figure 6 together with the model predictions. The specific rate increases with respect to conversion at high temperature, but decreases at low temperature. The gasification rate is usually limited by gaseous diffusion resistances when the rate is high. However, the diffusion resistance can be reduced at high temperature because of the enlargement of the pores; thus, the apparent reaction rate can increase upon increasing the carbon conversion, as shown in this plot. The shrinking core model suggests that the specific rate increases somewhat as the conversion approaches unity, but the prediction deviates significantly at higher temperatures (750 and 800°C). The specific rate from the volumetric model always remains constant, as is clear in Equation (4). In contrast, the modified volumetric model describes the experimental specific rate relatively well.

From the Arrhenius-type plot (k vs. 1/T) for the steam gasification of sludge-char at a steam partial pressure of 50 kPa, the activation energy from the average reaction rates determined by the modified volumetric model was found to be 156.51 kJ/mol, the activation energy determined by the volumetric reaction model was 152.59 kJ/mol, and the activation energy determined by the shrinking core model was 197.74 kJ/mol. The differences in these activation energies from the three models are not too large. Various kinetic parameters, such as the average reaction rates, the activation energy, and pre-exponential factor, from the three models are summarized in Table 2. Because the modified volumetric reaction model predicts the conversion behavior most accurately, the average reaction rate from the modified volumetric reaction model is used in the remainder of this paper.

**Activation Energy**

Arrhenius plots for the steam gasification of tires, coal, and sludge at a steam partial pressure of 50 kPa are presented in Figure 7. The activation energy can be determined from the slope of the line from linear regression of the average reaction rates. The activation energy for
the steam gasification of waste tire-char was found to be 39.1 kJ/mol and the pre-exponential factor was 0.2669 s⁻¹. Lee [11] reported an activation energy of 51.1 kJ/mol from the gasification of waste tire at 750～900°C and a steam pressure of 25～61 kPa. Park and coworkers [12] carried out non-isothermal pyrolysis of waste tires and reported an activation energy of 60～113.2 kJ/mol. Lee and Kim [10] presented a value of 238.7 kJ/mol for the CO₂ gasification of waste tires. On the other hand, the activation energy for the coal-char was determined to be 99.3 kJ/mol in a previous study [13] and that for sludge-char was found to be 156.5 kJ/mol. Kayembe and Pulsifer [14] reported an activation energy of 60～310 kJ/mol for the steam gasification of coal. The activation energy for the steam gasification of tire-char seems to be small when compared to the corresponding values for coal.

The reactivities of tire-char, coal-char, and sludge-char that are shown in Figure 7 were calculated based on the modified volumetric model and Equation (9). The reactivity of tire-char is higher than that of bituminous coal. This rank is the same as the rank of their higher heating value in Table 1. Such a high reactivity of tire-char may be explained by the ash components of the tire. The tire is relatively rich, when compared to coal or sludge, in ash components, such as CaO, TiO₂, and Na₂O, which can have catalytic effects on the gasification reaction [14]. This phenomenon also explains the low activation energy of the tire-char in this study. On the other hand, the higher reactivity of bituminous coals (than that of tires) was reported in the gasification with CO₂ [10]. It should be checked here whether the sample mass had an effect on the gasification rate, because the initial sample mass of tire-char used was different to the mass of coal-char. The tire-char had a mass of ca. 0.3 g after the volatile was removed from the tire granule of mass 0.7 g in the sample basket, whereas an already-prepared coal-char of 0.7 g mass was placed in the sample basket in the study of Jang [13]. However, these differences in the char samples do not affect the char reactivity according to studies on the effect that the sample mass has on the rate of gasification in thermobalance reactors [10,15,17]. These reports suggest that the char reactivity is relatively independent of sample mass in the range 0.3～0.7 g, but decreases with a further increase in sample mass because of increased resistance to diffusion of the reactant gas through the char.

**Reaction Order**

The effect of the steam pressure on the average reaction rate is shown in Figure 8. The average reaction rates are proportional to the steam partial pressure for both the coal and tire gasifications. From the slope of the log-log plot of k vs. H₂O partial pressure, the reaction order for the gas reactant was 0.87 for a steam partial pressure of 25～101.3 kPa at 800°C in the gasification of waste tire and 0.96 for a steam partial pressure of 25～101.3 kPa at 850°C in the gasification of sewage sludge-char. The order of 0.96 was reported from the gasification of Australian sub-bituminous coal-char at 850°C [18] and an order of 0.87 from coal gasification at 1000°C [19]. The gasification of waste tire scraps presented an order of 0.78 [11], and the CO₂ gasification of tires gave an order of 0.68 [10]. Therefore, the reaction order determined in this experiment seems to be reasonable. It was reported for coal-char that the gasification rate increased...
linearly with respect to steam pressures up to 101.3 kPa, with the rate approaching a constant value at higher steam pressures [19]. The reaction rates for the steam gasification of waste tire char and sewage sludge char, respectively can be expressed by the following kinetic equations:

\[
\frac{dX}{dt} = (0.2388) \exp\left( \frac{-29000}{RT} \right) (P_{H_2}O)^{0.587} (1 - X) \tag{9}
\]

\[
\frac{dX}{dt} = (5.8611 \times 10^4) \exp\left( -\frac{156510}{RT} \right) (P_{H_2}O)^{0.95} (1 - X) \tag{10}
\]

**Conclusions**

The gas-solid reaction models indicate that the steam gasification of waste tire char and that of sewage sludge char are mainly controlled by chemical reactions. The modified volumetric reaction model is the best at predicting the gasification conversion. The gasification reaction rates follow the order: waste tire > bituminous coal > sewage sludge. The activation energy was 39.1 kJ/mol and the pre-exponential factor was 0.2669 s\(^{-1}\) for the waste tire char over the temperature range 550 \text{–} 800°C at a steam partial pressure of 50 kPa. An activation energy of 156.5 kJ/mol and a pre-exponential factor of 5.8611 \times 10^4 s\(^{-1}\) were found for the sewage sludge-char over the temperature range 650 \text{–} 850°C at a steam pressure of 50 kPa. The reaction order was 0.87 for tire-char and 0.96 for sludge-char. The gasification rates observed in the present study are represented by two proposed kinetic equations [Equations (9) and (10)].

**Acknowledgment**

This work was supported by the Korea Energy Management Co. for the Ministry of Commerce, Industry and Energy, Korea, and the Kunsan Automotive Technology Innovation Center. The author greatly appreciates the contribution of Mr. Yongwon Jang who conducted a part of the experimental work.

**Nomenclature**

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<th>Symbol</th>
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<th>Unit(s)</th>
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<td>E</td>
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<td>(k_0)</td>
<td>Pre-exponential factor</td>
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<td>Specific reaction rate based on the remaining carbon in the solid</td>
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<tr>
<td>(k)</td>
<td>Average reaction rate defined by Equation (9)</td>
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<td>(P_{H_2}O)</td>
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<td>R</td>
<td>Gas constant</td>
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<td>T</td>
<td>Reaction temperature</td>
<td>[K]</td>
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<tr>
<td>t</td>
<td>Reaction time</td>
<td>[sec]</td>
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<tr>
<td>W</td>
<td>Sample mass at certain time</td>
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<tr>
<td>(W_{ash})</td>
<td>Mass of ash</td>
<td>[kg]</td>
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<tr>
<td>(W_0)</td>
<td>Initial mass of char on dry base</td>
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<tr>
<td>X</td>
<td>Carbon conversion</td>
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**Greek Letters**

<table>
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<tr>
<td>(\Omega)</td>
<td>Constant in volumetric reaction model in Equation (4)</td>
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**References**