Char Conversion under Suspension Fired Conditions in O₂/N₂ and O₂/CO₂ Atmospheres

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Abstract
The aim of this investigation has been to model char conversion under suspension fired conditions in O₂/N₂ and O₂/CO₂ using intrinsic kinetics found by burning Entrained Flow Reactor (EFR) chars in a ThermoGravimetric Analyzer (TGA). Experiments were carried out in an electrically heated EFR at temperatures and inlet O₂ concentrations between 1173 – 1673 K and 5 – 28 vol. %. In these experiments char was sampled at different residence times covering the onset of heterogeneous combustion to complete char burnout. The EFR-char was used to determine conversion profiles and in the TGA experiments. The TGA experiments were carried out at 5 vol. % O₂ in N₂ or CO₂ for char-O₂ kinetics and at 80 vol. % CO₂ in N₂ for char-CO₂ kinetics. The COal COmbustion MOdel (COCOMO) includes the morphologies cenospheres, network- and dense chars and it predicts EFR conversion profiles well using TGA kinetics. TGA experiments did not show a difference in char-O₂ reactivity between EFR-chars formed in N₂ and CO₂. The experimental EFR conversion profiles does not show an effect of CO₂-gasification but COCOMO suggests that it may play a role in O₂/CO₂ combustion at high reactor temperatures and low O₂ concentrations.

Keywords: Modelling, Oxy-fuel, combustion, kinetics, coal, char

1. Introduction
Global focus on anthropogenic CO₂ emission and its influence on the earth’s climate have initiated research into clean-coal-technologies all over the world as coal is projected to be a necessary feedstock in energy production for decades to come [1]. A promising technology to mitigate the CO₂ emission from power plants is Oxy-Fuel Combustion (OFC). In OFC a near pure O₂ stream is mixed with Recycled Flue Gas (RFG) at the entrance to the boiler thereby creating a plant exit stream of almost pure CO₂. This CO₂ can subsequently be sequestered in suitable geological formations such as saline aquifers and depleted oil- and gas fields [2,3].

As OFC is an emerging technology with current pilot plants in scales up to 30 MWe technical several aspects still remains to be clarified before industrialization. One important aspect is the nature of fuel conversion in an O₂/CO₂ environment as this will
affect the heat transfer profile in the boiler, its size and burnout efficiency. Predictive modelling tools, validated for O₂/CO₂ combustion, are also needed in the design process. There are at present a number of studies on fuel conversion in O₂/N₂ and O₂/CO₂ available in the literature from both TGA and Wire Mesh Reactors (WMR) [4-9] and different types of Flow Reactors (FR) [10-20]. These studies have developed an understanding of coal pyrolysis and combustion in O₂/CO₂ environments and accentuated areas where more research is needed.

The role of CO₂-gasification is still disputed and published experiments are not immediately comparable as they have been conducted under different conditions and with different coals. Pyrolysis experiments in CO₂ using TGA’s [4,5], WMR’s [9] and FR’s [10-13] have been carried out with low to medium rank coals and char conversion in O₂/CO₂ has been investigated using TGA’s [6-8,11,12] and FR’s [10,11,13-16,19,20] also with low to medium rank chars. The effect of CO₂-gasification in pyrolysis is difficult to evaluate from TGA experiments as the low heating rates and hence high residence times favours CO₂-gasification compared to the conditions in a boiler. The WMR and FR pyrolysis studies report additional weight losses in CO₂ compared to N₂ of up to 25 wt. % depending on coal and operating conditions. From TGA combustion of low to medium rank chars no differences in reactivity between O₂/N₂ and O₂/CO₂ have been found [6-8,11]. FR studies on char combustion often report overall burnout [11,14-16,19,20] but actual char conversion profiles, suitable for model validation, obtained at industrially relevant conditions are rare [10,13]. When comparing char burnouts and conversion profiles in O₂/N₂ and O₂/CO₂ the literature is unambiguous. With respect to intrinsic kinetics, applicable to modelling, there are no studies that report parameters obtained from char that have undergone treatment similar to that experienced in industrial boilers in O₂/N₂ and O₂/CO₂ environments.

In order to contribute to the understanding of fuel conversion in OFC environments this study presents char conversion profiles obtained under suspension fired conditions in an isothermal electrically heated EFR in O₂/N₂ and O₂/CO₂ atmospheres under a broad range of industrially relevant O₂ concentrations and reactor temperatures. Char sampled during these experiments have been combusted in a non-isothermal TGA. From the TGA experiments intrinsic kinetic expressions have been found for the char-O₂ and char-CO₂ reactions. The intrinsic kinetic expressions have been implemented in a detailed char combustion model and compared with char conversion profiles in the EFR.

2. Experimental
2.1 EFR Experiments
The EFR experiments are previously described in the literature [21]. All data presented in this text are taken directly from this reference. The reactor is cylindrical and measures 2 meters in length, 0.08 m in diameter and is shown schematically in figure 1 along with its utilities. The reaction zone is heated by 7 electrical heating elements and is capable of reaching temperatures up to 1773 K. On top of the reactor a 0.8 m long gas preheater, consisting of two heating elements, preheats the secondary gas stream to a prescribed temperature. Coal is fed to the reactor at a constant rate of 50 g hr⁻¹ using an air tight dosing system consisting of a silo and a screw feeder connected to a vibration transporter. Coal injection into the top of the reaction zone is done through a water cooled probe going through the center of the gas preheater.
During experiments char has been sampled at different reactor positions using a water cooled sampling probe with an outer radius of 0.017 m. The sampling end of this probe is shaped as a funnel. Sampling has been done iso-kinetically with an average gas velocity of 1.81 m s\(^{-1}\) in all the experiments. Through the probe, gas sampling for analysis for CO, CO\(_2\) and O\(_2\) has also been done at each sampling point. Except when experiments were carried out in air all gaseous environments used in the experiments were created by mixing bottled gases. Experiments were carried out in the temperature interval 1173 K – 1673 K with increments of 100 K.

Inlet O\(_2\) concentrations were in the range 5 – 28 vol. %, corresponding to stoichiometric ratios between 2 and 15, with either N\(_2\) or CO\(_2\) as carrier gas. O\(_2\) concentrations given in this paper are however lower, as these are measured after complete devolatilization and are the concentrations experienced by the burning char particles. During experiments the aim has been to obtain char conversion profiles at near constant O\(_2\) concentrations, in order to use them for model validation. The only consideration towards stoichiometry has therefore been to ensure sufficient amounts of O\(_2\).

![Experimental setup used in the EFR experiments. Solid lines are tubes and dashed lines are wiring in the data logging system. All streams leaving the equipment are sent to a central ventilation system.](image)

Table 1: Proximate and ultimate analysis of the coal used for experiments. In the column “Corrected” the original data has been corrected for the ash content of the particle size fraction 90 – 106 \(\mu\)m.

<table>
<thead>
<tr>
<th>Proximate Analysis</th>
<th>Original</th>
<th>Corrected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper heating value</td>
<td>MJ/kg ar</td>
<td>28.19</td>
</tr>
<tr>
<td>Effective heating value</td>
<td>MJ/kg ar</td>
<td>27.09</td>
</tr>
<tr>
<td>Moisture</td>
<td>Wt. % ar</td>
<td>5.0</td>
</tr>
<tr>
<td>Ash</td>
<td>Wt. % ar</td>
<td>9.6</td>
</tr>
<tr>
<td>Volatiles</td>
<td>Wt. % ar</td>
<td>34.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultimate Analysis</th>
<th>Original</th>
<th>Corrected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>Wt. % ar</td>
<td>68.9</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Wt. % ar</td>
<td>4.61</td>
</tr>
<tr>
<td>Oxygen (diff.)</td>
<td>Wt. % ar</td>
<td>9.82</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Wt. % ar</td>
<td>1.44</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Wt. % ar</td>
<td>0.62</td>
</tr>
</tbody>
</table>

At each of the experimental temperatures a devolatilization experiment was also carried out in order to correct char conversion for volatile weight loss. Due to problems with tar...
clogging the probe the devolatilization experiments were carried out at approximately 5 vol. % O$_2$ corresponding to a stoichiometric ratio of approximately 3. This did however not affect coal mass losses at the low residence times used for sampling and the presence of O$_2$ during devolatilization was not found to affect char reactivity.

El Cerrejón coal sieved to the size range 90 – 106 $\mu$m has been used in all the experiments. Ash tracing on the sieved coal fraction revealed an ash content of 5.9 wt. %, which is lower than that of proximate analysis on the unsieved coal. The proximate and ultimate analysis of the coal in table 1 is therefore shown both as received from the lab and corrected for ash content using the same fractional correction factor for all coal constituents.

2.2 TGA Experiments

All experiments presented here have been carried out in a TGA of the type Netzsch STA 449 F1 where gaseous atmospheres have been created by mixing bottled gases. Samples were placed in alumina crucibles and positioned automatically on a highly sensitive balance located in a chamber that was purged with 20 ml min$^{-1}$ of N$_2$. This N$_2$ made up 20 vol. % of the total flow in all experiments. The weight of the sample and the crucible temperature were recorded continuously as reaction progressed. Temperature programs dictating heating rates and maximum temperatures were specified for the Netzsch STA 449 F1 and for each program a calibration curve was made to ensure that possible fluctuations caused by the TGA did not influence the experimental measurements. By repetition of experiments the deviation in weight losses was found to be less than 1 %.

Three different types of experiments have been carried out. The first type of experiments, with particles of El Cerrejón coal sieved into the size ranges 63 – 90, 90 – 106 and 150 - 180 $\mu$m, were done to establish experimental conditions where mass transfer limitations did not influence the combustion rate and to investigate at what temperature CO$_2$ gasification could be expected to influence the sample consumption rate. The ultimate and proximate analysis of the unsieved coal is shown in table 1. The coal particles in all of these experiments were pyrolized in situ using N$_2$ and heating rates between 5 and 20 K min$^{-1}$ to a maximum temperature of 1273 K. After pyrolysis the samples were allowed to cool to a temperature of 473 K at what point a heating rate of 5 or 10 K min$^{-1}$ were used for non-isothermal char combustion at 5 vol. % O$_2$ in N$_2$ or CO$_2$. The maximum temperature of char combustion was 1373 K in all experiments and to evaluate the influence of sample mass on combustion regime samples of 2, 5 and 10 mg were used.

The second type of experiments was conducted using chars obtained from devolatilization and combustion in the EFR. Based on experience from the first type of TGA experiments a heating rate of 5 K min$^{-1}$ were used to reach a maximum temperature of 1123 K and sample masses between 1.2 and 1.5 mg were combusted in 5 vol. % O$_2$ in either N$_2$ or CO$_2$ to ensure that the process took place in zone I.

The third type of experiment was carried out using the same char as in the second type of experiments, the same heating rate and the same sample masses. However the gas atmosphere consisted of 80 vol. % CO$_2$ and 20 vol. % N$_2$ and the peak temperature was 1473 K.

In the following, the reactivity, listed in the figures as $d(X) dt^{-1}$, is defined by equation (1) where $m_0$ is the initial mass of char (dry and ash-free) and $m$ is the mass of char at time $t$ (dry and ash-free).
\[
\frac{d (X)}{dt} = - \frac{1}{m_0} \frac{d (m)}{dt}
\]  

(1)

3. Results and Discussion

3.1 TGA Results

From the first type of TGA experiments it was found that CO₂-gasification did not affect char consumption rate in the temperature window used for combustion. This was the case both for in situ pyrolyzed char and char sampled in the EFR. Similar conclusions have been published by Li et al. [4], Várhegyi et al. [6] and Rathnam et al. [11] and the remaining TGA combustion experiments in this text have therefore been carried out in O₂/N₂.

The effect of gaseous atmosphere in the EFR on resulting intrinsic char kinetics is shown in figure 2 where TGA reactivity profiles of chars obtained by devolatilization at 1573 K and 1673 K in N₂ and CO₂ are compared. It is seen from the figure that the switch of carrier gas from N₂ to CO₂ at the high temperatures in the EFR where the chars were formed does not cause a significant change in combustion reactivity. The same conclusion can be drawn from reactivity profiles of chars devolatilized at lower temperatures and from reactivity profiles of samples partly converted in the EFR. The small differences in combustion reactivity between N₂ and CO₂ chars observed in figure 2 is within the experimental repeatability of the EFR as discussed in [21] and particle to particle variations in the small sample masses used in the TGA.

Figure 2: Combustion reactivity of EFR char obtained from devolatilization at 1573 K and 1673 K in N₂ and CO₂. A TGA heating rate of 5 K min⁻¹ has been used to reach a maximum temperature of 1123 K in 5 vol. % O₂ and 95 vol. % N₂. Sample masses were within 1.2 – 1.5 mg.

The effect of gaseous atmosphere in the EFR on resulting intrinsic char kinetics is shown in figure 2 where TGA reactivity profiles of chars obtained by devolatilization at 1573 K and 1673 K in N₂ or CO₂ are compared. It is seen from the figure that the switch of carrier gas from N₂ to CO₂ at the high temperatures in the EFR where the chars were formed does not cause a significant change in combustion reactivity. The same conclusion can be drawn from reactivity profiles of chars devolatilized at lower temperatures and from reactivity profiles of samples partly converted in the EFR. The small differences in combustion reactivity between N₂ and CO₂ chars observed in figure 2 is within the experimental repeatability of the EFR as discussed in [21] and particle to particle variations in the small sample masses used in the TGA.

Figure 3 and figure 4 show Arrhenius plots for combustion and gasification of EFR chars obtained by devolatilization in CO₂. Due to a limited amount of char only three Arrhenius plots are shown in figure 4 for gasification by CO₂. Reaction rates covering char consumption between 10 % and 90 % conversion in the TGA are represented in both figures. The rate constants have been found from equation (2) with a specific char surface area, \( S_0 \), of 240 m² g⁻¹ found from BET measurements [21].

\[
k = \frac{d (X)}{dt} \cdot (1 - X)^{-1} \cdot S_0^{-1} \cdot (C^n)^{-1}
\]  

(2)

The concentrations of O₂ or CO₂, \( C \), are found using the temperature measurements at each data point. The kinetic parameters found from the TGA data will be used in
modelling work at the conditions in the EFR and a decision must therefore be made when determining the reaction orders $n$ as these are known to vary between temperatures. For combustion intrinsic reaction orders between $0.5 - 1$ have been reported for the temperature interval used in the TGA [22] while intrinsic reaction orders between $0 - 1$, though with the majority being 0, have been reported at the temperature interval used in the EFR [23]. To make the kinetic parameters as consistent as possible when they are found at low temperatures but used at high temperatures a reaction order of 0.5 has been chosen for use in equation (2). For gasification, intrinsic reaction orders found in the literature varies around 0.5 [24,25] and this value of reaction order has therefore been chosen for use in equation (2).

Linear regression on the data in figure 3 and figure 4 yields average activation energies, $E_{A,\text{Avg}}$, of 137.5 +/- 7.4 kJ mol$^{-1}$ for combustion and 230.8 +/- 8.6 kJ mol$^{-1}$ for gasification, both of which are nearly constant across the interval of devolatilization temperatures. The pre-exponential factors, $A_0$, are however varying. As char consumption between $X = 0.1 - 0.9$ is taking place in a narrow temperature window of $110 - 130$ K an average combustion temperature, $T_{\text{Avg}}$, is found for the individual chars.

Using equation (3) a new pre-exponential factor, $A_0'$, is then defined for each char using the average activation energy of all chars and the average combustion temperature of the individual char.

$$A_0' = A_0 \cdot \exp \left( \frac{1}{R \cdot T_{\text{Avg}}} \left( E_{A,\text{Avg}} - E_A \right) \right)$$ (3)

When equation (3) is used for the gasification data in figure 4 and average pre-exponential factor of 7.3282 +/- 0.24 kg m$^{-2}$ s$^{-1}$ (mol m$^{-3}$)$^{-0.5}$ is found. The pre-exponential factors, $A_0'$, of the combustion data in figure 3 show however a clear trend ($R^2 = 0.79$) of deactivation, as the devolatilization temperature increases, with a deactivation energy, $E_D$, of 20.5 kJ mol$^{-1}$ and a pre-exponential factor, $A_0''$, of 1.4359 kg m$^{-2}$ s$^{-1}$ (mol m$^{-3}$)$^{-0.5}$.

![Figure 3: Arrhenius plots of combustion rate constants for char obtained by devolatilization in the EFR in CO$_2$.](image)

![Figure 4: Arrhenius plots of gasification rate constants for char obtained by devolatilization in the EFR in CO$_2$.](image)
The resulting kinetic expressions for combustion and gasification can be seen in equations (4) and (5), respectively.

\[ k_{O_2} = 1.4359 \cdot \exp \left( \frac{20500}{R \cdot T^*} \right) \cdot \exp \left( \frac{-137500}{R \cdot T} \right) \left[ \text{kg m}^{-2} \text{s}^{-1} (\text{mol m}^{-3})^{0.5} \right] \]  
\[ k_{CO} = 7.3282 \cdot \exp \left( \frac{-230800}{R \cdot T} \right) \left[ \text{kg m}^{-2} \text{s}^{-1} (\text{mol m}^{-3})^{0.5} \right] \]  

When equation (4) is used, \( T^* \) is the highest temperature a particle has reached at any degree of conversion, which assumes a rapid deactivation to a pseudo steady value at any given \( T^* \).

### 3.2 EFR Results

The kinetic expressions in equations (4) and (5) have been implemented into a COal COmbustion MOdel (COCOMO). The model describes the char as being composed of the three morphologies; cenospheres, network- and dense chars, shown schematically in figure 5.

The morphologies in figure 5 are distributed between six fixed particle sizes determined by laser diffraction [21]. The distribution of char between particle sizes is temperature dependent in order to account for swelling and is determined from Particle Size Distributions (PSD) for devolatilized char. Reaction is assumed to take place on both interior and exterior particle surface though consumption takes place by radial shrinkage. Internal mass transfer limitations of reactants are accounted for multiplying an effectiveness factor to the internal reaction rates. This entails a shrinking spherical particle of constant density and eases calculations considerably. Energy balances are also solved for each type of particle. In figure 6 – 11 simulations of COCOMO are compared to experimental conversion profiles obtained in the EFR. In figure 9, the contribution from each morphological group to the overall char conversion profile can also be seen. In all the simulations shown in figures 6 – 11 CO\(_2\)-gasification is active in the calculations though it does not influence the behaviour of the conversion profiles except for figures 10 and 11. In these figures simulated O\(_2\)/CO\(_2\) profiles are shown with and without CO\(_2\)-gasification.
Figure 6: COCOMO profiles and experimental profiles obtained at 1173 K in N₂ and CO₂. The O₂ concentrations are the averages of the local concentrations at each sampling position. λ ~ 2.7 – 15.2.

Figure 7: COCOMO profiles and experimental profiles obtained at 1273 K in N₂ and CO₂. The O₂ concentrations are the averages of the local concentrations at each sampling position. λ ~ 2.5 – 10.5.

Figure 8: COCOMO profiles and experimental profiles obtained at 1373 K in N₂ and CO₂. The O₂ concentrations are the averages of the local concentrations at each sampling position. λ ~ 2.3 – 9.8.

Figure 9: COCOMO profile and experimental profile obtained at 1473 K in N₂. The O₂ concentration is the average of the local concentrations at each sampling position. λ ~ 3.7. Also shown are COCOMO conversion profiles of each of the three morphologies.

Figure 10: COCOMO profiles and experimental profiles obtained at 1573 K in N₂ and CO₂. The thin dashed line is the simulation in O₂/N₂ and the thin unbroken line is the simulation in O₂/CO₂ with gasification included. The O₂ concentrations are the averages of the local concentrations at each sampling position. λ ~ 2.

Figure 11: COCOMO profiles and experimental profiles obtained at 1673 K in N₂ and CO₂. The thin dashed line is the simulation in O₂/CO₂ with gasification included and the thin unbroken line is the simulation in O₂/N₂. The O₂ concentrations are the averages of the local concentrations at each sampling position. λ ~ 1.9.
Figures 6 - 11 show in general reasonable agreement between simulations and experiments. In figure 6 it can be seen that COCOMO over predicts the conversion at high and low O2 concentrations and it over predicts the conversion in figure 7 at low O2 concentrations. In both figures it can be seen that there exists a delay in the onset of char conversion for low O2 concentrations in the EFR, possible caused by problems with heterogeneous ignition at the low temperatures and O2 concentrations. Though this is not captured by COCOMO the model predicts conversion rates fairly accurate. At the high O2 concentrations in figure 6 it can be seen that the char deactivates rapidly in the EFR at a reactor position of approximately 0.5 m. COCOMO also captures this abrupt deactivation though it predicts it to occur at a reactor position of approximately 0.2 – 0.4 m. The reason for this inconsistency is likely found in the nature of the deactivation. COCOMO predicts a homogenous deactivation of each particle size and morphology according to equation (4), depending on particle peak temperature, though this is not likely to be the case at the high O2 concentrations. Simulations and TGA reactivity profiles have suggested that two distinctively different phases in the char is formed at these conditions due to the high over temperatures and heating rates some particle sizes and morphologies experiences upon ignition. One of these phases is reactive and is converted at a normal combustion rate whereas the other phase is highly inactive and remains in the char. As the inhomogeneous nature of the char is not accounted for in COCOMO the char deactivates homogeneously and prematurely in the simulations.

In figure 9 it can be seen that the transient behaviour of the conversion profile is highly sensitive to the abundance of char morphologies. The general abundance of morphologies in COCOMO is taken from Cloke et al. [26] and is assumed constant across the devolatilization temperatures. Judging from the fit of the simulations to the experimental profiles this approach is sufficiently accurate.

The influence of CO2 gasification on char conversion in figures 6 – 9 is not significant. COCOMO finds no differences and from the experimental profiles in the figures there are no trends that could suggest an influence from CO2 gasification on conversion rate. In figures 10 and 11 the experimental profiles show a lower conversion rate in O2/CO2 than in O2/N2 (most clearly seen in figure 11). This behaviour witness of an effect from external mass transfer limitations where the lower diffusion coefficient of O2 in CO2 (~22 %) lowers the char conversion rate compared to combustion in N2. The COCOMO profiles in the two figures do however suggest a positive contribution from CO2 gasification on char conversion. This could be due to an over prediction of the gasification rate in equation (5).

4. Conclusion
A combustion model encompassing dense, network and cenospheric char each distributed between six discrete particle sizes have been compared to experimental char conversion profiles obtained in O2/CO2 and O2/N2 mixtures under suspension fired conditions. In the temperature interval 1173 K – 1673 K reasonable consistency was found between experiments and simulations at inlet O2 concentrations between 5 and 28 vol. %. The model applies kinetic parameters for char oxidation and CO2 gasification obtained from TGA experiments with char formed at the experimental temperatures under suspension fired conditions. The expressions for the rate constants include the effect of thermal char deactivation only on the reaction with O2, since no deactivation was observed for CO2
gasification. The kinetic expression for O₂ combustion has proven to work satisfactorily under a wide range of suspension fired conditions while that for CO₂ gasification show slight over prediction at high temperatures.

From experimental EFR profiles obtained in a range of operating conditions, covering zone I - III, no evidence suggesting a positive effect of CO₂-gasification on char conversion has been found. In fact the only indication of an effect of CO₂ on char conversion rate is seen in zone III where the lower diffusion coefficient of O₂ in CO₂ appears to slow down the reaction rate compared to O₂/N₂.

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6. REFERENCES


