HETEROGENEOUS KINETICS FROM CFD DIAGNOSTICS IN AN ENTRAINED FLOW REACTOR

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Abstract
A Computational Fluid Dynamics model of a pilot-scale entrained flow reactor is developed with the aim to shed light into the cloud of solid fuel particles. An iterative procedure is suggested to derive devolatilization kinetics: particle average residence times and heating rates are estimated from the numerical model, and a linear dependence of the particle temperature with residence time is assumed. In this manner the volatile release equation can be integrated analytically and subsequently kinetic parameters can be obtained from experimental conversion data. The procedure is shown for a Sebuku type coal in oxy-fuel conditions.

Introduction
The development of clean and efficient technologies for power generation from solid fuels such as biomass and coal, would benefit of detailed simulations tools as Computational Fluid Dynamics, able to handle a turbulent reactive multi-phase flow in a complex geometry without any need of scale-up procedures. Despite the huge increase in computational resources, still the large number of cells required for the spatial discretization of the burner/furnace, i.e. of the order of $10^6$ (but even more in Large Eddy Simulation), imposes a simplification of the physics. This means that global kinetic schemes should be adopted; however they are generally available only for conventional (air) combustion conditions.

Emissions of greenhouse gases from coal combustion can be drastically reduced through Carbon Capture and Sequestration (CCS) technologies. In oxy-fuel combustion, coal is burnt in a mixture of oxygen and recycled flue gas, obtaining a flue gas consisting of CO$_2$ and H$_2$O; flue gases are recycled to make up the volume of the missing N$_2$. Consequently, combustion occurs in a mixture of O$_2$ and CO$_2$ instead of O$_2$ and N$_2$; this affects gas properties (heat capacity, diffusivity and gas emissivity) and thus coal reactivity [1]. Hence new sub-models (devolatilization, char oxidation) able to describe coal combustion in a CO$_2$/O$_2$ atmosphere should be derived [3].

This requires the availability of experimental data, taken in conditions similar to those of industrial furnaces where the solid fuel is heated up quickly and loose volatiles in a very short time; indeed devolatilization is influenced by the heating
rate, so thermo-gravimetric analyses cannot be used to evaluate reliable kinetics. Conversely, entrained flow reactors (EFRs) are very interesting as they are able to provide heating rates and temperatures, typical of industrial combustion systems. EFRs are often used to estimate conversions in specific conditions and barely to derive kinetics, as in theory this would require the knowledge of the particle temperature [2]. Hence, the quick heating up of the particle is usually neglected, and particles are assumed to be at a temperature equal to the reactor one.

The present work is aimed at shedding light into some aspects that should be considered when estimating kinetics from EFRs and at suggesting a CFD-aided procedure for evaluating devolatilization kinetics from a pilot-scale EFR.

The entrained flow reactor
Experiments were performed in the Isothermal Plug Flow Reactor, which belongs to the International Flame Research Foundation and is shown in Figure 1. The reactor is cylindrical (diameter = 0.15 m, length = 4.5 m). At the walls electric resistances keep the temperature at a set point value. Several ports are available for injection or for the insertion of measuring instruments. Pulverized fuel particles are transported by a carrier gas and injected into a flue gas stream from a side through a radial probe bend at the edge to allow feeding in the axial direction. Flue gases come from a pre-heating combustion section that supplies gases of desired composition and temperature. In this manner solid fuel particles experience high temperatures (1000-1600 K) and heating rates ($10^4$-$10^5$ K/s).

![Figure 1. Scheme of the Isothermal Plug Flow Reactor.](image)
At the reactor bottom, flue gas and particles are quenched down to 500 K with N₂ and then treated in a separation and analysis system before being discharged. Particles exiting the EFR are sampled and analyzed through thermogravimetry in order to obtain the ash content, and thus to determine the conversion as:

$$X = \left( 1 - \frac{\text{ash}}{\text{ash}_{\text{max}}} \right)$$

The position of the sampling probe can be varied, allowing taking conversions with different residence times. Devolatilization runs were performed using three different nominal temperatures, i.e. $T_R = 1173, 1373$ and $1573$ K nearly in absence of oxygen (0 - 0.5%) and using CO₂ as carrier gas to emulate oxy-fuel conditions. The coal is a 65-90 µm Sebuku coal, whose analysis are reported in Table 1.

### Table 1. Sebuku coal proximate and ultimate analysis.

<table>
<thead>
<tr>
<th>Proximate Analysis [%dry]</th>
<th>Ultimate Analysis [%daf]</th>
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<tbody>
<tr>
<td>VM</td>
<td>FC</td>
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<tr>
<td>40.30</td>
<td>47.95</td>
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</table>

Numerical model

A two-way coupled Lagrangian tracking of the devolatilization tests was developed with ANSYS Fluent v. 15. Due to its symmetry, half IPFR was modeled. The domain corresponded to the run with the largest distance between the feeding and the sampling probe; then a post-processing Matlab® subroutine was used to vary virtually the position of the sampling probe in the reactor. A grid independency study leaded to a hybrid grid with 900k elements. Reynolds-averaged Navier-Stokes equations were solved using the standard k-ε turbulence model. About 1600 particle tracks were followed in the domain; gravity, drag and turbulent dispersion were applied to the particles. Devolatilization was described through a Single First Order Rate (SFOR), according to which the rate of devolatilization is first-order dependent on the amount of volatiles remaining in the particle.

$$\frac{d\text{VM}}{dt} = k_f(\text{VM}_{\text{m}} - \text{VM}) = \text{Ae}^{-\frac{E}{RT}}(\text{VM}_{\text{m}} - \text{VM})$$

where VM and VMₚ are the actual and maximum volatile matter content of the particle. The latter can be evaluated from the high temperature volatile yield; and VMₚ= 1, 1.2 and 1.38 were evaluated for $T_R = 1173, 1373$ and $1573$ K runs, respectively. Composition of volatiles was calculated from the proximate and ultimate analysis and their oxidation was represented by a 2-step scheme, the first step considering oxidation of volatiles to CO and the second step oxidation of CO to CO₂. The Eddy Dissipation Model was used to treat the turbulence-chemistry interaction, even though as mentioned earlier, the runs were performed nearly in absence of O₂. Radiation was taken into account through the P1 radiation model.
and Weighted Sum of Gray Gases Model for the spectral properties.
A stationary solver was used to solve the equations using a second order discretization scheme and the SIMPLE algorithm for the pressure-velocity coupling. The steadiness of the solution with iteration was checked for convergence. All residuals were well below $10^{-4}$.

**Results**

Figure 2a shows the particle tracks colored by their diameter; it can be observed that particles experience different paths and trajectories, resulting in a particle cloud. Thus the following considerations can be made.

1. Particles will have different residence times at a specific reactor length $y$ (i.e. distance between feeding and sampling probe) as shown in Figure 2b;
2. The average particle residence time can be different from the one evaluated preliminary using the flue gas velocity, as shown in Figure 2b;
3. Particles will have different particle temperatures at a specific reactor length $y$ (i.e. distance between feeding and sampling probe) as shown in Figure 2c.
4. Particles are likely to be at a temperature lower than the reactor one for the residence times using for sampling during the devolutilization runs, i.e. 0.05-0.25 s, as shown in Figure 2c.

![Figure 2. Cloud of particles: (a) particle tracks, (b) particle residence time at the experimental reactor lengths and (c) particle thermal histories. $T_R=1173K$.](image)
The above considerations suggest to revise the standard procedure to derive kinetics from EFRs, according to which particles are taken to be at a temperature equal to the reactor one (i.e. $T_p=T_R$), so that Eq. 2 can be easily integrated using experimental data on conversion vs time, i.e. $(X,t)$ to get values of the kinetic constant $k$. Experiments at different temperatures will allow deriving $k$ at different temperatures and hence Arrhenius parameters ($A$, $E$).

Two CFD-aided procedures are suggested (see Figure 3). In the first procedure (SFOR), residence times $t$ are evaluated from CFD performed in non-reactive conditions and used to compute kinetics by assuming $T_p=T_R$. Once $A$, $E$ are evaluated, they are inserted in the CFD model in reactive conditions, so that $t$ values are updated; in this manner new $(A, E)$ parameters can be calculated. In the second procedure (SFOR-HR), the information on the particle thermal histories are used to evaluate an average heating rate, $HR$. In Eq. 2, the particle temperature is assumed to be linearly dependent on the residence time $T_p=T_0+HR \cdot t$, where $T_0$ is the feeding temperature; this allows integrating analytically Eq. 2, to obtain $(A, E)$ from experimental conversions. Also this procedure is iterative. Table 2 reports heating rate $HR$ and kinetic parameters as evaluated for this latter method after 1, 2 or 3 iterations. It can be noticed that 2 iterations are sufficient to get final data. Experimental conversions are compared to those predicted with the SFOR and SFOR-HR models at different iterations in Figure 4. Experimental horizontal bars are calculated from the uncertainty on the sampling probe position whereas vertical bars from uncertainty on ash content. Error bars on the predicted data represent variance on residence time and volatile matter content of the cloud of particles.

Table 2. Kinetic parameters and heating rate for SFOR-HR at different iterations.

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<thead>
<tr>
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<th>Iter n.1</th>
<th>Iter n.2</th>
<th>Iter n.3</th>
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<tbody>
<tr>
<td>HR (K/s)</td>
<td>12900</td>
<td>16600</td>
<td>17000</td>
</tr>
<tr>
<td>$E$ (J/mol)</td>
<td>8.59e+6</td>
<td>6.23e+7</td>
<td>6.23e+7</td>
</tr>
<tr>
<td>$A$ (1/s)</td>
<td>31.4</td>
<td>18.46</td>
<td>18.47</td>
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Figure 3. Procedure to derive kinetics.
The SFOR model systematically under-predicts conversion: the reason is that the error minimization procedure is based on a temperature of the particle equal to the reactor one, hence higher than the true particle temperature at most of the sampling locations. Thus the calculated kinetic parameters are somewhat weaker, resulting in a strong underestimation of conversion. The simple assumption of linear dependence of temperature on residence time (SFOR-HR) strongly improves the matching with experimental data.

**Conclusions**
A CFD-aided iterative procedure has been suggested to derive devolatilization kinetics from a pilot-scale EFRs; particle residence time and heating rates are computed from the CFD model and the particle temperature is assumed to be linearly dependent on the residence time. This was found to largely improve the conversion predictions. The analysis of the cloud of particles can be used to evaluate uncertainties in predictions and kinetic parameters.

**References**