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Devolatilization kinetics of woody biomass at short residence times and high heating rates and peak temperatures

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HIGHLIGHTS

- High peak temperature (1405–1667 K) and heating rate (10^5 K s^{-1}) devolatilization.
- CFD aided particle history tracking.
- Significantly faster devolatilization kinetics than suggested in the literature.
- Shown to significantly change the predicted ignition distance in pilot scale.
- Partial conversion experiments with residence times below 0.1 s.

ARTICLE INFO

ABSTRACT

This work combines experimental and computational fluid dynamics (CFD) results to derive global kinetics for biomass (pine wood) devolatilization during heating rates on the order of 10^5 K s^{-1}, bulk flow peak temperatures between 1405 and 1667 K, and particle residence times below 0.1 s. Experiments were conducted on a laboratory laminar entrained flow reactor (LFR) using solid fuel feed rates on the order of 10–20 mg h^{-1}. Employing a simple single step first order (SFOR) mechanism with an Arrhenius type rate expression, the best fit of the pyrolysis kinetics was found to be: $A = 18.9 \times 10^3$ s^{-1}, $E_a = 21\,305$ J mol^{-1}. The accuracy of the derived global kinetics was supported by comparing predictions to experimental results from a 15 kW furnace. The work emphasizes the importance of characterizing the temperature history of the biomass particles when deriving pyrolysis kinetics. The present results indicate faster kinetics than found in the literature, leading to predicted residence times required for full conversion one order of magnitude lower than when compared to thermogravimetric analysis (TGA) derived kinetics.

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1. Introduction

Pulverized biomass combustion is of interest in both the academic community and for industrial application. The ability to achieve high thermal throughputs and high electrical and thermal efficiencies makes the technology appealing in the replacement of fossil fuel based facilities.

Biomass being primarily cellulose, hemicellulose, and lignin is less thermally stable than coal due to the high number of readily breakable bonds compared to the more complex coal structures. This results in high quantities of volatile matter which changes the ignition and primary heat release mechanisms compared to coal.

Being able to describe the devolatilization process is important in biomass combustion modeling due to the high content of volatile matter. Devolatilization and pyrolysis studies have been extensively reported in the literature for low heating rates between 5 and 80 K min^{-1} and long residence times using simple global first order models [1–14]. Only a few studies attempt to determine devolatilization kinetics at higher heating rates, i.e. on the order of > 100 K s^{-1} [15,16], using variations of thermogravimetric apparatuses. Extrapolation of the low heating rate studies to pulverized fuel firing, characterized by high heating rates and temperatures, is

difficult due to the changes in devolatilization kinetics with heating rate [17–19]. Also the ratio between tar, char, and gases is known to be influenced by the temperature [18,20].

Alternative equipment such as captive sample set-ups [21–23] allow for experimens to be carried out at higher heating rates, typically on the order of 1000 K s^{-1}. However, the thermal inertia of the heating elements in these kind of set-ups makes it difficult to study partial conversion for small particles.

In general; achieving high heating rates and peak temperatures, typically come at the cost of the loss of control of particle residence time [24,25], particle temperature history [26–30], and the ability to close the sample mass balance [31], making it difficult to derive kinetics.

A number of studies using high heating rate and/or high temperature together with short residence times have been published. However, many of these rely on one of the following assumptions: (1) the particle temperature equals the adiabatic flame temperature or the temperature of the isothermal reactor wall [26]; (2) the particle temperature follows the gas phase temperature [27], or (3) the particle temperature is calculated from a simple heat balance based on the properties of the parent fuel and assumptions on the expected particle trajectory [28]. Experimentally determined particle temperatures would be preferable, but difficulties in covering the entire temperature range have been reported as a limitation [29].

One concern often encountered is the lack of a sufficiently accurate model of the bulk flow, which is necessary in order to describe the reaction environment to which the entraining particles are subjected [32,33]. The short residence times required for biomass devolatilization make it difficult to examine the dynamics of the process. The development of the bulk flow and the conversion of the fuel particles are strongly coupled processes, thus, being able to mathematically describe and relate both phases are of equal importance to pyrolysis modeling [34].

Brown et al. [33] employed a laminar entrained flow reactor, thus achieving peak heating rates on the order of 10^4 K s^{-1}. The particle and gas flow was simulated by CFD thus significantly improving the energy balance comparing to similar studies. However, the particle modeling it self was decoupled and processed in a separate procedure using the information on particle temperature and time from the CFD results. They also concluded how particles around 50 μm are well within the kinetically limiting regime and thus accurate predictions on the pyrolysis will in terms influence on e.g. full-scale flame simulations.

Simone et al. [24] conducted a detailed CFD aided investigation on the devolatilization of cacao shells using a drop tube furnace at peak temperatures of 873–1073 K. Applying a first order single step mechanism, they concluded that a single set of kinetic parameters struggled to describe the pyrolysis adequately, even at the relatively low peak temperatures. To accommodate the observed model deviations from the experimental results, they divided the kinetic model into a low and high temperature regime, each with its own set of kinetic parameters.

The objective of this work was to determine wood pyrolysis kinetics at high heating rates aided by computational fluid dynamic simulations of the particle property histories (temperature, mass loss, and residence time). Combining simulation results with high temperature, high heating rate experiments at low residence times (partial devolatilization) allows for the derivation of devolatilization kinetics. This study includes the following work:

- Employment of a laboratory scale laminar flow reactor heated by an understoichiometric CH_4/H_2-pilot flame with heating rates on the order of 10^5 K s^{-1} and peak temperatures of 1405–1667 K at residence times below 0.1 s.

- Introduction of dilute solid particle feed, effectively studying single particle behavior.
- Determination of the local conditions in the laminar flow reactor by the use of computational fluid dynamics (CFD) simulations, thereby providing detailed temperature histories of the particles.
- Evaluation of the derived devolatilization kinetics using measurements and CFD simuluation results of a 15 kW furnace.

2. Fuel characterization and experimental

The same fuel (pine wood) was used throughout the study. This section presents the fuel characterization and the experimental set-ups.

2.1. The fuel

In this study, the main emphasis has been on low ash content woody fuels. This represents the type of fuel that is commonly used for suspension fired combustion with 100% biomass, i.e. high quality fuels without bark and soil containments. The fuel was a commercial wood pellet made from Norwegian pine. Proximate and ultimate analyses are presented in Table 1. The volatile fraction is based on the DS/EN15148:09 standard. This or similar standards are widely used [35]. It is, however, commonly recognized that the low heating rates and low temperatures used in the standard do not provide a true measure of the extent of pyrolysis taking place at higher heating rates and temperatures [35]. To determine a more accurate measure of the volatile fraction representative of suspension fired boiler conditions, we calculate the values based on a solid phase tracer method.

The wood pellets were crushed and subsequently treated in a rotating cutter mill with laboratory accuracy screens attached for specific size classification. The resulting wood dust was analyzed by two dimensional image analysis using a Netzsch CamSizer XT. The obtained particle size distributions (PSD) are shown in Fig. 1.

As is common for many biomass fuels, the particles were characterized by high aspect ratios. This study aims to incorporate the derived kinetics into larger CFD systems. It is therefore desirable to be able to describe the particles in a single dimension. Selected methods describing characteristic lengths of oddly shaped

Table 1
Proximate and ultimate analysis of the parent pine wood fuel. Fuel treatment prior to analysis has been carried out according to CEN/TS 14780:05.

Species	Method	Unit		
HHV	EN 14918:10	MJ kg^{-1}, dry	20.58	±0.12
LVH	EN 14918:10		19.23	–
Moisture	EN 14774-1:09	wt.%, dry	4.0	–
Ash	DS/EN 14775:09	wt.%, dry	0.2	±0.2
Volatiles[a]	DS/EN 15148:09		82.4	±1.6
C	CEN/TS 15104:11	wt.%, dry	51.1	±1.5
H			6.2	±0.2
N			<0.20	–
S	CEN/TS 151289:11	mg kg^{-1}, dry	60	±30
Cl	CEN/TS 15289:11		160	±20
Ca	CEN/TS 15290:06		950	±60
Mg			140	±10
K			480	±30
Na			95	±10
P			52	±8
Si			<200	–
Al			32	–
Fe			26	±5
Ti			<5.0	–

[a] The volatile determination has been carried out according to current standards. The result is not true for high temperature, high heating rate application [35].