Fuel Processing Technology 126 (2014) 513–520

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

A generalized correlation for coal devolatilization kinetics at high temperature

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ARTICLE INFO

Article history:
Received 21 March 2014
Received in revised form 4 June 2014
Accepted 5 June 2014
Available online 22 June 2014

Keywords:
Coal pyrolysis
Decomposition kinetics
Activation energy
Combustion
CFD model

ABSTRACT

The optimization of thermochemical (combustion, gasification, pyrolysis, oxyfiring) systems requires a comprehensive model, able to simulate conventional and innovative plants, for achieving the high levels of efficiency and low pollutant emissions required by the current applications. A devolatilization model is the basis of these processes and should be sufficiently simple and accurate to be implemented in commercial codes for simulating large scale plants. Kinetic parameters should be validated in qualified tests under severe thermal conditions and for coals of different ranks. In this work the experimental data from the isothermal plug flow reactor of IFRF (with temperatures up to 1673 K and heating rates on the order of 10^4 K/s), previously uniformed and organized in the solid fuel database SFDB, are elaborated to obtain the kinetic parameters according to a modified version of the single first order reaction model. The effective thermal history of the particles is estimated by simulating the devolatilization tests with a CFD model. A generalized correlation is obtained between the kinetic parameters and coal properties, preferably among those routinely reported in standard analyses. Finally, a practical and useful predictive tool is provided for studying the devolatilization of pulverized coal.

1. Introduction

The renewed scientific and technological interest in coal has to face the high levels of efficiency and low pollutant emissions required by the current applications. To this purpose the process and plant optimization are recommended and should be performed with tools able to simulate conventional as well as innovative systems, and predict the parameters of coals of different origins and properties. The devolatilization is the first step in all the thermochemical processes (combustion, pyrolysis, gasification, oxyfiring), and influences the overall reactions of the fuel inside the reactor. A devolatilization model is thus the basis of comprehensive codes, such as computational fluid dynamic (CFD) models, for studying the coal combustion in pilot and large size plants, optimizing the reactor and operating conditions, predicting the formation of pollutants and their precursors (some examples can be found in [1–7]). The devolatilization models in the literature spread from simple approaches (single, parallel, multistep, or distributed kinetic models [8–12]), generally applied to specific coals and operating ranges, to complex structural models (such as Flashchain [13], CPD [14], and FG-DVC [15]), including also thermal and mass transfers and thus potentially applicable to wide ranges of coal composition and operating conditions.

It is important to provide model parameters validated with experimental tests under the severe thermal conditions (high temperature and heating rate) encountered in full scale plants. Parameters validated under mild conditions can give rough predictions if applied in extremely different conditions. As a matter of fact, the use of high temperature and heating rate tests requires a qualification of the equipment and experimental procedure to give a reliable basis for model validation. The estimation of the effective thermal history of the samples is crucial for avoiding errors due to heat transfer limitations.

Due to the variety in coal origin and composition, and the effect of the operating conditions on the devolatilization parameters (such as kinetics), a large number of uniform experiments are recommended to validate model parameters and correlations. The data used in this work derived from the pyrolysis tests carried out in the same experimental apparatus, the Isothermal Plug Flow Reactor (IPFR), that allows severe thermal conditions to be achieved. Conversions, kinetics and other specific test parameters can be obtained for several fuels under proven procedures that give uniform and reliable data [16].

The IPFR data on different fuels were previously uniformed and organized in the Solid Fuel DataBase (SFDB) of IFRF [17,18]. A selection of the coal devolatilization data is done in this work to elaborate the kinetics with a simple devolatilization model. The kinetic model adopted here is a modification of the Single First Order Reaction model, that guarantees simplicity and accuracy. Because of the low computational effort required, it can be directly included in CFD simulations of a large

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http://dx.doi.org/10.1016/j.fuproc.2014.06.008
0378-3820/

combustion plant. The aim of the work is to validate a correlation between the kinetic parameters (at high temperature and heating rate) and coal properties, preferably among those routinely reported in standard coal analyses.

2. Experimental section

2.1. Description of the isothermal plug flow reactor

A detailed description of the geometrical, operating and diagnostic parameters of the new asset of the IPFR in the site of Livorno (Italy) can be found in [16,19,20]. It is a drop tube (4.5 m total length × 0.15 m inner diameter, see Fig. 1) with the heating system formed of the electrical resistances (globally 54 kW) located on the walls, and the hot gasses coming from the 60 kW burner located at the top section of the reactor. The solid fuel particles are pneumatically injected with a primary gas through a feeding probe inserted at different heights through one of the 19 ports available along the tube. The material is sieved and samples of size fractions comprised in the range 40–100 μm are studied. The solid flow rate is maintained constant (100 g/h). The gaseous environment (pure nitrogen for devolatilization tests, though the secondary gas can be formed of adjustable mixtures of $N_2/O_2/CO_2$) and reactor temperature (up to 1670 K) can be programmed. The particle residence time is estimated between 15 and 1500 ms, and heating rate between 10^4 and 10^5 K/s [21]. The solid residue and gaseous products are quenched and sampled in the collection probe for online and offline analyses. The ash content of the solid residue is then compared to that of the parent coal for calculating the conversion with the ash tracer method.

2.2. The solid fuel database SFDB and data mining

The SFDB is basically formed of 4 interconnected lists: facilities, procedures, fuels and experiments. The first two lists describe the reactors and procedures used to study the solid fuels (see previous subsection and documents cited therein). The fuel list contains the fuel name, classification, fundamental (ultimate, proximate, heating value, and particle size) and advanced characteristics (ash analysis, morphological and physical properties, structural parameters, and fusion temperatures, when available) from the Solid Fuel Laboratory (SF-Lab). The experiment list links the fuel data to the test conditions (nominal thermal history and gas concentration) and results (conversion).

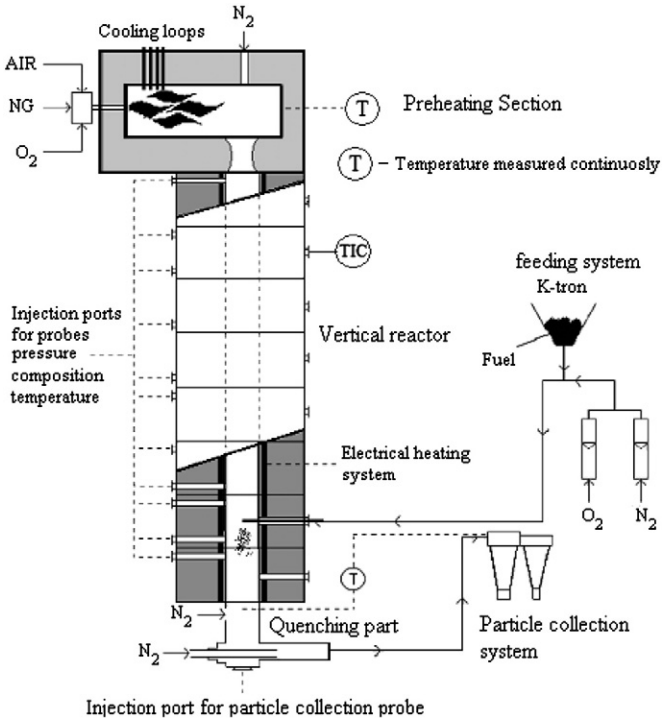

Fig. 1. Scheme of the Isothermal Plug Flow Reactor of IFRF.

So far, the SFDB contains more than 800 tests (devolatilization, char oxidation and nitrogen partitioning) of 270 fuels (mostly coals, some biomasses, respective chars and some blends of the parent fuels). All the tests have been carried out in the IPFR. The data set used in this study is formed of a selection of the data from the SFDB with the following characteristics:

- coals;
- complete set of fundamental (ultimate and proximate) analyses for each coal;
- devolatilization tests; and
- sufficient number of experimental results for each coal.

Each experimental result is defined by a value of the nominal particle residence time, calculated on the basis of the reactor length and the actual conditions, the nominal reactor temperature and the devolatilization conversion. Table 1 contains the selected 20 coals (specified by their names and the identification number within the SFDB) and their properties. The ash content varies from 3.7 to 18.5 %wt (dry basis) and the Low Heating Value (LHV) from 21.5 to 33.1 MJ/kg. Fig. 2 shows the coals in the Van Krevelen diagram. The Hydrogen-to-Carbon (H/C) mass ratio ranges between 0.40 and 0.83 and the Volatile Matter-to-Fixed Carbon (VM/FC) ratio between 0.26 and 1.07. Most coals studied here have an Oxygen-to-Carbon (O/C) ratio in the range 0.09–0.22, while a small group of low rank coals can be observed in the separate zone of 0.36–0.48. The data in Table 1 are grouped in type ST and MT, the former referring to data from devolatilization tests at a single reactor temperature, the latter at two or more temperatures.

3. Description of the methodological approach

As stated in the introduction, the aim of this work is to validate a correlation for the kinetics of devolatilization at high heating rate and temperature for a significant number of coals. The basic step is to adopt a kinetic model with characteristics of simplicity and sufficient accuracy. It is required that it will be able to:

- calculate the devolatilization conversion under different temperatures and reaction times; and
- predict different final conversions at different temperatures.

The latter point is indeed important as the volatile yield V depends strongly on the thermal history of the fuel during the devolatilization [22–24]. The simplest and most used kinetic approach is the Single First Order Reaction (SFOR) model:

$$\frac{dV}{dt} = A \cdot e^{-E/RT_P} \cdot \left(V_f - V\right) \tag{1}$$

where t is the time, T_P the absolute temperature of the particle, R the ideal gas constant and $V$is the volatile yield. It requires two parameters (the pre-exponential factor A and exponential factor E) and the final volatile yield V_f. The main assumption of this approach is that the devolatilization occurs in a single step according to a first order law. The approximation obtained with the SFOR model is not generally acceptable [2,10,23]. Furthermore, the adoption of SFOR parameters for temperatures higher than those used for validating the kinetic parameters can give inaccurate predictions of the coal devolatilization. This is mainly due to the fact that the parameter V_f is assumed constant, commonly corresponding to the value of VM from the proximate analysis, that is evaluated at the standard temperature T_{st} of 1223 K for coals, and thus the model will predict the same final conversion under different thermal conditions.