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SCIENCE DIRECT®
Energy 30 (2005) 1453–1468
ENERGY
www.elsevier.com/locate/energy

A general mathematical model of solid fuels pyrolysis

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Abstract

The aim of this work is to present and discuss a detailed kinetic model that describes the devolatilization process of solid fuels under pyrolysis conditions. The major reason for this interest in better understanding pyrolysis and combustion of coal, biomasses and solid fuels lies in the increasing concern for the environmental impact of large scale combustion processes. The common chemical and structural aspects of the different fuels are singled out and used as the starting point to define this mathematical model. The formation of light gases and liquid tars is the first step in the pyrolysis process. Particular attention is also devoted to the generality and flexibility of numerical and mathematical methods. Two major critical points are present inside this model: the first is related to the definition of the initial structure of the fuel and the second is constituted by the set of reference kinetic parameters of the different reactions. Several comparisons with experimental data are analysed and the molecular weight distributions of the tar from different coals evolved at different temperatures are also discussed.

1. Introduction

Coal devolatilisation is a process in which coal is treated at elevated temperatures to produce gases, *tar* and *char*, where *tar* is defined as the room-temperature condensable species formed during pyrolysis.

Devolatilisation processes play a very important role in coal combustion and it is generally agreed that the chemical differences among the different coals effect the combustion rates primarily through their devolatilisation behaviour. The extent of coal devolatilisation during pyrol-

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doi:10.1016/j.energy.2004.02.011

ysis has a strong effect also on char reactivity, since combustion reactions proceed on the active sites of residual hydrogen present in char. For these reasons, the prediction of pyrolysis behaviour, based on the properties of the different coals, is a fundamental feature in the modelling of coal combustion.

Models of coal devolatilisation moved from simple empirical expressions of total mass release, involving one or two rate expressions [1], to more complex descriptions of the chemical and physical processes. Nevertheless, simple models, like that developed by H. Kobayashi et al. [2], still have a relevant importance in computerized fluid dynamics-combustion simulations.

Gas formation is often related to the thermal decomposition of specific functional groups in coal, on the other hand, *tar* and *char* formation involve more complex reaction steps and the mechanistic modelling of *tar* formation has to be improved. The level of detail required in a model depends on its application: although simple ''weight loss'' models have often been employed, more sophisticated models are needed for a more accurate description.

Recent studies on the evolution of coal structure [3] during pyrolysis, based on solid state ^{13}C-NMR, XPS, TG-FTIR, GC-MS, have facilitated the extension of the capabilities of devolatilisation models to predict the composition of volatile matter with the time and the temperature.

Initially, C–C bond-cleavage reactions give rise to a mixture of different size fragments in the form of a melted material called *metaplast*. Light species are released as gases. Successive bond breaking leads to further gases and also to condensable species (*tar*) and to the formation of *char*. Secondary gases are formed during *char* condensation reactions. Finally, *tars* can crack in the gas phase forming soot and lighter gases.

This thermal decomposition of coal proceeds via the successive fragmentation of the different bridge types of chains connecting the fused aromatic ring clusters. In this process, existing bridges break and new shorter bridges are formed. Both Monte Carlo and percolation theory have been adopted to describe this process in a statistical way. By assuming a distribution of molecular weights of the base monomers, the amount of *tar*, extracts and *char* can be defined from the assumed distribution of oligomer size.

Pitt [4] first treated the coal as a mixture of a large number of species decomposing by parallel first order reactions with different activation energies. Similarly, Anthony et al. [5] proposed the distributed activation energy model (DAEM). The DISCHAIN model, distributed-energy chain statistics, used string statistics to predict the monomer production. These species are a source of volatile *tar* and they can also polymerise at chain ends forming *char*. This model includes also tar vaporisation as a multicomponent vapour-liquid equilibrium process. This flash distillation mechanism leads to the FLASCHAIN model [6]. Furthermore, Solomon et al. [7] combined the functional group (FG) model, used to describe the gas evolution, with the depolymerisation-vaporisation-cross-linking (DVC) algorithm in the FG-DVC model.

Coal dependent chemical structural parameters, deduced from solid state ^{13}C-NMR experiments, are the starting point for chemical percolation and devolatilization (CPD) model developed by Fletcher et al. [8]. The data are acquired by the extrapolation techniques of Solum et al. [9] and the obtained parameters are used to statistically describe the coal lattice. The size distribution of finite aromatic clusters is then described as constituted by several polyaromatic sites joined by intact bridges. These clusters are isolated from the remaining structure due to bond breaking. The detailed description of devolatilization process requires experimental data