

# MODELING PYROLYSIS BEHAVIOR FOR INTERNATIONAL COALS

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## INTRODUCTION

Pyrolysis (devolatilization) is the initial step in most coal conversion processes, accounting for up to 60% of the initial weight loss from the coal. It is also the process that is most dependent on the organic properties of the coal, and is important because of its influence on the subsequent conversion process. The modeling of coal pyrolysis has progressed from simple, single equation kinetic models for overall weight loss to fairly complex “network” models. These models approximate coal as a polymeric structure and provide more detailed predictions of pyrolysis behavior than is possible with the simpler models. Professor Eric Suuberg has been involved for many years in the study of coal devolatilization modeling, pyrolysis kinetics, tar formation and vaporization, crosslinking reactions, network structure, thermochemistry of pyrolysis reactions, and char gasification and combustion reactivity [1-14]. All of the network model development efforts have greatly benefited from this body of work.

A total of three network coal devolatilization models have been developed, [15-19], which have various capabilities for predicting coal thermal decomposition under practical conditions. These coal devolatilization models are: (1) the Functional Group – Depolymerization, Vaporization, Crosslinking (FG-DVC) model [15-17], (2) the Chemical Percolation Devolatilization (CPD) model [18]; and the FLASHCHAIN model [19]. A common feature of the original versions of these models is that they required a large set of data inputs, including kinetic parameters, coal composition files, and additional parameters describing the coal polymeric structure. These input data could be generated on the basis of experimental measurements for each coal of interest, although this limited predictions to coals that had been studied. Alternatively, some investigators have tried to correlate the devolatilization properties to the coal types using simpler models. For instance, Ko *et al.* [20] and Neavel *et al.* [21] have developed methods for predicting the upper bound of tar yields,  $X_{tar}$ , from coal elemental compositions. Recently, successful efforts were made to retain the predictive capabilities of the network models, but with the ability to use ultimate analysis or comparable data to generate the input files. Niksa has developed a correlation method for the FLASHCHAIN model which predicts volatile yields in pyrolysis from ultimate analysis data [22-24]. A similar approach was used by Zhao *et al.* [25] to correlate the input parameter files for the FG-DVC model, while Fletcher and coworkers have used NMR data to correlate input parameters for their CPD model [26].

This paper briefly describes the historical development of one of the network models, the FG-DVC model [15-17], and how its development was influenced by the work of Professor Eric Suuberg. FG-DVC is a network coal devolatilization model which can predict, in addition to the tar and total volatile yields, the yields of individual gas species, the tar molecular weight distribution, and the char fluidity. It has also been coupled with a char reactivity model which incorporates the effect of thermally induced annealing on char reactivity. This model was primarily validated using data for North American coals and is now being extended to a range of international coals. This paper also discusses the progress of these efforts, along with the status and future prospects for coal devolatilization modeling activities in various parts of the world.

## BACKGROUND ON FG-DVC MODEL

Coal has a very complicated organic structure, which is essentially a mixture of an aromatic matrix, side chain components, and some loose fragments. The thermal decomposition of the coal structure involves many parallel and competitive processes. In modeling these processes, FG-DVC uses two submodels. The FG model simulates the thermal evolution of various functional groups and the DVC model predicts the depolymerization, vaporization and crosslinking processes occurring in the coal polymer network. In the FG submodel, the gas evolution from functional group precursors is modeled with parallel first order reactions and a distributed activation energy (DAE) formulation is used to reflect the diversity of coal structures. In his doctoral thesis work at Massachusetts Institute of Technology [1,2,9] and in his academic work at the Carnegie-Mellon University [3,4,7], Prof. Suuberg and his colleagues pioneered the development of pyrolysis models which track individual species from coal using DAE kinetic models. These methods were adapted by researchers at Advanced Fuel Research, Inc. (AFR) for coal and related materials in the development of the FG-DVC model. More recently, Professor Suuberg collaborated with AFR on a major review of pyrolysis experiments, kinetic rates and mechanisms, which summarized the progress in these areas and attempted to resolve the remaining controversies in the choices of kinetic rates and models [14].

The thermal evolution of the coal polymer matrix is modeled with a network model [16], which consists of nodes and the connections between them. The nodes represent the polymer clusters and there are two types of connections between them, i.e., weak and strong bonds and initial crosslinks. At elevated temperatures, there is a competition between bond breaking and crosslinking reactions, and the properties of the network are fully determined by these two competing processes through percolation theory calculations [27]. In the case of coal, crosslinking in the DVC subroutine is computed by assuming that this event is correlated with CO<sub>2</sub> and CH<sub>4</sub> evolutions predicted in the FG subroutine. The yield of rapidly released CO<sub>2</sub> (which is related to coal rank and weathering) is the factor that controls the thermosetting or thermoplastic behavior of coals, an observation that was first made by Suuberg and coworkers [5]. For coals which exhibit thermoplastic behavior, the fluidity is assumed to be limited by the cross-linking associated with the evolution of methyl groups [15-17].

The most important property of the network is the molecular weight distribution of the clusters. The heavy molecules remain in the condensed phase to become char, while the light ones evaporate to become tar. The model originally used the tar vapor pressure law of Unger and Suuberg [7], which was later modified by Suuberg *et al.* [4], and more recently improved by Fletcher *et al.* [26]. The tar rate is further limited by internal transport, which is assumed to be controlled by the evolution rate of gas species and the light tar [15]. This mechanism enables the model to predict the pressure variation of the tar yields.

A char reactivity model was developed as a submodel of FG-DVC [28]. The reactivity model can predict intrinsic reactivity based on correlations with char hydrogen content, coal oxygen content, and coal mineral content. A random pore model and a volumetric model are used for high rank and low rank coals, respectively, in order to predict variations of intrinsic reactivity with burnoff. In the pore diffusion regime, the model uses the Thiele modulus to calculate the reaction rate as a function of the intrinsic rate and char structural properties. The model includes the effects of thermal annealing on reducing the intrinsic char reactivity and also benefits from the work of Suuberg in this area [13].

The FG-DVC model was validated for the eight Argonne Premium coals [29] using measurements of pyrolysis kinetics from TG-FTIR analysis, solvent extraction and solvent swelling to measure extractables and the initial crosslink density, Gieseler plastometer

experiments to measure fluidity, pyrolysis-FIMS to measure the tar molecular weight distribution, and ultimate analysis to determine the elemental compositions (C, H, N, S, O) [17]. The large number of experimental inputs allowed the development of a model which can make detailed predictions of coal devolatilization under various conditions of temperature, pressure, and heating rate.

A correlation method was subsequently developed which allows the FG-DVC model to be used for untested coals by providing an interpolation between the input files of known coals based on the coal elemental analysis [25]. The interpolation mesh is composed of nine coals: six from the Argonne Premium Coal Sample Program, and three from the Penn State Sample Bank (PSOC 1474, PSOC 1448, and PSOC 1521). Extensive experimental studies were carried out on these reference coals and the model input parameters are well established. With this scheme, any of the FG-DVC input parameters can be interpolated for an untested coal when its elemental composition is known.

## RECENT DEVELOPMENTS IN MODELING OF COAL DEVOLATILIZATION

There are several recent developments and remaining challenges in the area of modeling coal devolatilization. Because of the globalization of coal markets, there is growing interest in predicting the pyrolysis behavior for a wide variety of coals from all over the world. Recent work at AFR has extended the range of FG-DVC model application to include South American, Japanese, Australian, South African, Indonesian, European, and Chinese coals [30]. Niksa has developed his FLASHCHAIN model to be applicable for a wide range of coal types [22-24]. This model has been recently incorporated into the EPRI NO<sub>x</sub>-LOI predictor. In this expert system, the FLASHCHAIN model provides the underlying basis for predicting NO<sub>x</sub> formation and unburned carbon formation (LOI) in a power plant by calibration against a known coal [31]. Since the partitioning of nitrogen species in pyrolysis has an important influence on NO<sub>x</sub> formation in combustion, this aspect of devolatilization modeling has recently received increased attention [31-33].

For the same reasons, there has been increased interest in the incorporation of network devolatilization models into Comprehensive Fluid Dynamic (CFD) codes. Until recently, all of the commercial CFD codes incorporated relatively simple coal devolatilization models. The FG-DVC model has been integrated with research CFD codes, such as the Brigham Young University (BYU) PCGC-2 code and the DOE MFIX fluidized bed code [34,35]. The CPD model was recently integrated with the commercial FLUENT code [36], and the preliminary integration of FG-DVC with a CFD code has been accomplished at the University of Leeds [37]. AFR has also developed a streamlined version of the FG-DVC model which facilitates the integration process [38]. This version involves running the complete model outside the main CFD code and using it to define a set of coefficients that relate individual product evolution to a reference process (e.g., weight loss) over a prescribed range of conditions. AFR is also exploring artificial neural network (ANN) models for coal devolatilization which may result in another streamlined model [39]. In addition, a larger particle devolatilization version of FG-DVC has been developed for use as a submodel in fixed and fluidized bed systems [40].

Matthews *et al.* [41] have devised a molecular modeling approach to coal devolatilization which appears to be successful in predicting the general features of the mass loss and chemical structural changes for vitrinite samples heated in a drop tube. Work on molecular modeling of coal is also underway in Japan [42,43], although so far it has only been used to predict drying and coal/solvent interactions. Finally, coal devolatilization models are being adapted to predict related phenomena, such as coal liquefaction [44] and coal maturation [45].

## CONCLUSIONS

During the past decade, the modeling of coal devolatilization has progressed from simple 1 or 2 step models to relatively complex network models. These models approximate coal as a polymeric structure and have demonstrated good predictive capability for a wide range of coal types and experimental conditions. There are three major network model development efforts, all of which have benefited from Professor Suuberg's work on coal macromolecular structure, crosslinking behavior, modeling of pyrolysis kinetics, tar vaporization behavior, and the effects of pyrolysis on intrinsic char reactivity.

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