Chapter 1

INTRODUCTION

During the last decade, developments of both experimental and theoretical nature have advanced our knowledge of coal pyrolysis to a degree that justifies a systematic exposition on the subject. Noteworthy among experimental advances and refinements have been the design of equipment for rapid but controlled heating and the analysis and characterization of pyrolysis products by chromatographic and spectroscopic measurements. Modeling advances worth mentioning include the estimation of rate parameters by group additivity techniques, improved capabilities for numerical handling of complex reaction systems and improved understanding of the coupling between mass transfer and chemical reactions.

Despite the aforementioned advances, the bulk of available information is of experimental and descriptive nature while the understanding of fundamental mechanisms remains largely qualitative. In surveying and summarizing experimental information, we have been selective rather than exhaustive, emphasizing studies involving broad and controlled variation of experimental conditions. The discussion of experimental results and kinetic models has concentrated on fundamental issues such as reaction mechanisms and interaction between reactions and mass transfer. This choice of subject matter clearly reflects the personal interests of the author.

Early pyrolysis research was concentrated on coal carbonization, i.e. slow heating of dense coal samples, conditions pertaining to coke making. By contrast, recent work has emphasized rapid heating of dilute coal samples which has been amply termed "flash pyrolysis". Behind this shift in emphasis have been the desire to elucidate the role of pyrolysis in combustion and gasification and the possibility of applying pyrolysis to convert coal to liquid fuels or chemicals. The material in this monograph is mainly addressed to pyrolysis under conditions of rapid heating.

Chapters 2 and 3 are devoted to the chemistry of pyrolysis. In Chapter 2, recent spectroscopic and wet chemical information is utilized to describe coal's structure in terms of functional groups. Since most of the experimental data concern coal derived liquids, extrapolation to solid coal involves considerable uncertainty. However tentative it may be, this extrapolation is necessary for mechanistic analysis of pyrolysis. Having established or postulated the pertinent functional groups, it is possible to identify with considerable confidence the important elementary thermal reactions. Basic organic chemistry and kinetic studies with model compounds, provide a firm basis for this purpose. Chapter 3 contains a survey of the energetically favored elementary reactions and discusses techniques for estimating their rate parameters. The estimation techniques are illustrated with numerous examples. However, a number of elementary reactions defy estimation by these established predictive techniques. This is the case, for example, with reactions which are limited by diffusion in the condensed phase.

The bulk of experimental results are presented in Chapter 4. The data consist of the yield of various pyrolysis products as a function of temperature and pyrolysis time under conditions that minimize the influence of heat and mass transfer limitations. A brief discussion of commercial process development efforts is also included in this chapter. Chapter 5 is devoted specifically to heat and mass transfer limitations as manifested by the dependence of product yields on pressure and particle size. Although the chapter contains experimental and modeling results, the modeling part is limited to delineating conditions under which transport phenomena become important.

In the presentation of experimental results in chapters 4 and 5, a distinction is made between softening coals, primarily high volatile bituminous, and nonsoftening coals e.g. subbituminous or lignites. This rudimentary distinction does not do justice to the variety of composition and properties within each of the two categories. However, it is a point of departure and has particular significance relative to the evolution of porous structure and plastic properties both of which strongly influence mass transfer rates.

Chapter 6 contains a survey of kinetic models of pyrolysis with emphasis on underlying assumptions rather than mathematical details. A brief discussion is also given about the ability of each model to describe experimental data. This ability does not by itself imply the validity of the underlying assumptions. Product yields are smooth and gently sloping functions of operating conditions, that could be fitted by many phenomenological models with reasonable kinetic form, provided the rate parameters are in each case suitably adjusted. Quite often the scatter in the data masks subtle distinctions between alternative models. Phenomenological models have reached a maturity that allows their application to coal combustion or gasification. By contrast, the one or two detailed chemical models discussed in this chapter are still at a stage of flux and are not ripe for practical applications.

The final Chapter, 7, contains a brief survey of experimental data and modeling work on hydropyrolysis, the heating of coal in a hydrogen atmosphere. This variant of pyrolysis is receiving increased attention as one of the most promising routes to chemicals from coal.