MASTER

ADDITION OF DEVOLATILIZATION
EQUATIONS TO SYNTHANE COMPUTERIZED
MATHEMATICAL MODEL

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I. ABSTRACT

Six approaches to devolatilization modeling have been reviewed. Two have been selected for further evaluation - the Vand-type model of Anthony and Howard and the diffusion model of Russel et al. The first of these treats particles under kinetic control only. The second includes some mass transfer control along with kinetic control. Behavior of particles in the SYNTHANE process appears to be in the transition region between kinetic and mass transfer control. Work during the next quarter will focus on the temperature history of average particles in the carbonizer of the SYNTHANE process and on the methods by which the two devolatilization models chosen will be used to describe conversion in the SYNTHANE carbonizer.

II. INTRODUCTION

The Pittsburgh Energy Technology Center (PETC) has been actively involved during the past six years in developing the SYNTHANE coal gasification process. SYNTHANE is one of a half-dozen second generation processes for the conversion of coal to high-BTU pipeline gas, which have received developmental support from the Department of Energy.

An important element of the SYNTHANE developmental program is the construction of a mathematical model which simulates the process and which can be used to optimize, scale up and design the process. To date, the development of this model has progressed to the point where the material and enthalpy balances around the PDU gasifier and the rate of conversion in the fluid bed region of this reactor can be calculated and analyzed. (1) Unfortunately, the model in its present form does not include fundamental relationships by which the rate of conversion of the coal falling through the carbonizer of the reactor can be calculated and analyzed. This region is a most important one, for it is there that all of the higher hydrocarbons (including tar) and organic trace pollutants (such as phenol and ammonia) are produced.

The purpose of the present project is to develop from the literature a procedure for modeling the carbonizer of the PDU, to test the procedure on the runs already analyzed by the SYNTHANE mathematical model (1), and to analyze a set of PDU runs where no fluid bed was maintained in the gasifier region of the PDU reactor.

III. REVIEW OF DEVOLATILIZATION MODELS

The recent review by Anthony and Howard (2) of coal devolatilization provides a firm basis for reviewing models for the devolatilization of coal particles of small enough size that particle-size effects are negligible. For lignites, this includes particles up to 1000 μm in diameter (3), while for bituminous coals only particles up to 150 μm in diameter are included (2). Sub-bituminous coals logically should fall in between these two extremes.

Five approaches are identified by Anthony⁽²⁾ and Suuberg⁽³⁾ for modeling the rate of devolatilization of small coal particles. These are

- a. simple nth-order models, which many authors have concluded are inadequate;
- b. Vand-type model, which assumes a large number of independent, parallel first-order rate equations all having the same pre-exponential constant but different activation energies;
- c. general lumped-parameter models, proposed by Kobayashi, Reidelbach and Summerfield, and Stickler et al⁽⁴⁾, which use two or several consecutive, parallel, or competitive reactions;
- d. Jüntgen and Van Heek model, a definitive model which assumes a constant heating rate and a separate first-order rate equation for each evolved species;
- e. Suuberg model, another definitive model, which assumes a series of sixteen solid species, each of which decomposes by first-order kinetics to one of five gaseous products.

Anthony and Howard (2), Overturf, Kayihan and Reklaitis (5) and others recommend using the Vand-type model for predicting the devolatilization yield from small coal particles, because it is relatively simple but has sufficient complexity to fit available data with reasonable accuracy.

For coal particles above the critical size of 150 μm for bituminous coal and 1000 μm for lignite, mass transfer effects must be considered in modeling the rate of devolatilization (2). A recent study by Russel, Saville and Greene (6) describes a model which includes bulk flow, diffusion, and a single first-order chemical reaction as steps in the overall devolatilization process for larger particles; instantaneous heatup to an isothermal state is assumed, however. This model is considerably more complex than the Vand-type model, which would tend to make it more difficult to use. However, Russel et al. provide a comprehensive set of both instantaneous and integrated performance (yield) figures, which should allow one to bypass considerable complex computation in using this model.

Several investigators have incorporated devolatilization kinetic equations into their models for coal conversion reactors of the fixed-bed or moving-bed type. Borowiec et al.⁽⁷⁾ and Yoon, Wei and Denn (8) have used the simple first-order model to predict the yield of devolatilized products from moving bed reactors used, respectively, in the Simplex and Lurgi processes.

Campbell (9) has taken the Jüntgen and Van Heek model to correlate data from the pyrolysis of a 50 to 60 g sample of Poland Seam coal (1680 to 3350 μm in diameter). This kinetic model is to be used in the modeling of the in situ gasification process being developed by Lawrence Livermore Laboratory.

Models of entrained bed gasifiers incorporating devolatilization kinetic equations are also under development. Russel et al. (6) have developed their devolatilization model with this type of gasifier in mind, but they have yet to include it in a gasifier model. Ubhayakar, Stickler and Gannon (10) have used the devolatilization equations of Stickler et al. (4) in their entrained bed gasifier model. Schneyer, Brownell, Henline and Blake (11) have recently reported on their work to develop an extremely fundamental set of reactor models, in which they are building Suuberg's devolatilization kinetic equations into the model for the entrained bed gasifier.

Finally, fluid bed gasifier models, which include kinetic equations for devolatilization are also being explored. Overturf et al. (5), in modeling a multiple-bed coal pyrolysis system, have used the Vand-type devolatilization kinetic equations, as mentioned earlier. The Vand-type equations are also used by Borghi, Sarofim and Beer (12) to describe the rate of devolatilization at the surface of coal particles in fluid bed combustors. Like Russel et al. (6), Borghi et al. have developed a complex model for the rate of combustion of a single particle only and have yet to integrate these results into a full reactor model.

In all of the reactor models mentioned in the last three paragraphs and also in the complex particle models of Russel et al. (6) and Borghi et al. (12) material and energy balances are used along with rate expressions to develop a description of the composition and temperature profile throughout the reactor or particle. Several of these reactor models in addition take into account a range of particle sizes and particle residence times -- particularly those of Overturf et al. (5) and Ubhayakar et al. (10).

IV. APPROACH OF THIS STUDY

In this study the amount of devolatilization of coal particles falling through the carbonizer of the SYNTHANE PDU gasifier will be predicted using calculated particle temperature profiles along the carbonizer, and both the Vand-type devolatilization kinetic equations (2) and those of Russel et al.(6). Initially, particles having a uniform particle size, equal to the average particle size of the coal being fed, will be examined.

The runs, from which devolatilization data will be drawn for comparison with model predictions, will be the same 35 Montana Runs examined by Pukanic et al.(1) in a previous study. Comparative data will be obtained from unpublished records (13) and original data files at the Pittsburgh Energy Technology Center.

Use of both types of kinetic expressions will be examined, because the average particle size of the subbituminous Montana coal fed to the PDU lies in the range of 300 - 400 μm (13). This particle size is estimated to be near the boundary between chemical and mass transfer control of the rate of devolatilization.

V. WORK PLAN FOR NEXT QUARTER

Having assembled and analyzed the pertinent literature references on the modeling of devolatilization during this quarter, the project staff will expand from one (the Principal Investigator) to two (the Principal Investigator and a graduate research assistant) during the next quarter. The temperature profile of the gas and particles along the carbonizer will be computed and the approach to the prediction of solid conversion to gas by devolatilization, using both chemical control and mass transfer control expressions, will be developed.

VI. TRAVEL

The Principal Investigator made the following visits during the quarter:

November 6, 1979, Omaha, Nebraska; Northern Natural Gas Company; Nebraska Section of the American Institute of Chemical Engineers to speak on the modeling of fluid bed coal gasifiers.

November 7, 1979, Chicago, Illinois; Institute of Gas Technology to talk with Donald Fleming and William Bodle on gasifier modeling.

November 12-16, 1979, Miami Beach, Florida; 71st Annual Meeting of the American Institute of Chemical Engineers to support the presentation of the gasifier modeling work at the Pittsburgh Energy Technology Center and to attend other presentations on coal conversion development projects and modeling.

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