SECTION IV. TASK 4. APPLICATION OF INTEGRATED CODES

Objective

The objective of this task are to evaluate the integrated comprehensive codes for pulverized coal and fixed-bed reactors and to apply the codes to selected cases of interest to METC.

Task Outline

This task will be accomplished in two subtasks, one for the entrained-bed lasting 45 months and one for the fixed-bed lasting 36 months. Each of these subtasks will consists of three components: 1) Simulation of demonstration cases on BYU computers; 2) Implementation on a work station at AFR (the Sun workstation has been chosen); and 3) Simulation of demonstration cases on the workstation.

IV.A. SUBTASK 4.a. - APPLICATION OF GENERALIZED PULVERIZED COAL COMPREHENSIVE CODE

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Objective

Implement the comprehensive entrained-bed code developed in Task 3 at AFR. Simulate reactors of interest to METC.

Accomplishments

The FG/DVC model was successfully integrated with PCGC-2. The first generation code took 15 hours to run compared to less than 4 hours for running the PCGC-2 code alone. We analyzed the FG/DVC code to find ways of reducing the burden it placed on the combined code. A major area of investigation was to reduce the number of monomers in the model coal molecule created in the DVC routine. It was found that the number of monomers could safely be reduced by a factor of three without affecting the accuracy of the simulation. This change reduced the total CPU time for running the integrated code down to 6.5 hours. We examined reducing the number of calls to the FG/DVC subroutines. It was found that there were some redundant calls and we were able to further reduce the time to a little over four hours per simulation, in which the FG/DVC model takes less than 20% of the total time.

Plans

Continue work on improving the integrated model.

Integration of FG/DVC Model with PCGC-2

Work was undertaken during the fifth quarter to integrate AFR's FG/DVC model into PCGC-2. The FG/DVC had to be divided into submodels compatible with PCGC-2's requirements for input and output.

Work was undertaken during the Fifth Quarter to integrate AFR's FG-DVC model into the PCGC-2 code. The FG-DVC had to be divided into submodels compatible with PCGC-2's requirements for input and output. What the PCGC-2 currently needs from any single particle model is basically the total coal reaction rate (including devolatilization and oxidation), the coal off-gas production rate and the off-gas enthalpy rate. These parameters along with some other heat transfer parameters are calculated in the subroutine COAL2 in PCGC-2 and are then passed into the subroutine PSOLVE which uses a predictor-corrector method to update the mass and enthalpy of a coal particle at each time step. On the other hand, the FG-DVC model is capable of predicting the gas evolution (on the basis of individual functional groups), the tar formation and various coal properties during pyrolysis. However, the oxidation reaction is not included in the current FG-DVC model. Therefore, the FG-DVC model has been integrated into the PCGC-2 in the following manner:

(1) All the input data required by the FG-DVC model (including the coal composition file, the coal kinetic file and the coal polymer data file) are loaded at the beginning of the main routine named PCGC2.

(2) The subroutine POLYBD that sets up a coal polymer structure is called for each particle trajectory in the subroutine PSICT in the PCGC-2 due to the statistical nature of the Monte Carlo method used in the DVC model.

(3) All the subroutines that actually perform the FG-DVC calculations are called in the subroutine COAL2 of the PCGC-2 at each time step. The previous two-step devolatilization model is now replaced by the FG-DVC model. The functional group products and the tar yield are summed up to provide the pyrolysis rates as well as the off-gas enthalpy and the heat of oxidation required by the PCGC-2.

(4) The current oxidation model in the PCGC-2 is also implanted into the FG calculations to take care of the mass loss in each functional group pool due to oxidation.

(5) The calling of the FG-DVC routines is turned on at the onset of each particle trajectory, and is turned off when pyrolysis is completed. Beyond the end of pyrolysis, the oxidation becomes the only reaction associated with the coal particle.

(6) It should be noted that the PCGC-2 currently treats raw coal and char as two separate components whereas the FG-DVC model only deals with coal with a varying composition. During the integration of the two models, the difference in the concepts was circumvented by setting the char rate equal zero and thus making char a dummy variable to avoid an overall change in the code.

When the first successful simulation for the integrated PCGC-2 code with the combined FG-DVC model was made on Nov. 19, 1987, the total CPU time spent was about 15 hours as compared to less than 4 hours for running the PCGC-2 code alone. Obviously, most of the time was spent in the FG-DVC model, or more exactly, spent in the DVC subroutines where the Monte Carlo statistical method was employed to simulate the bond breaking, crosslinking and vaporization in a coal polymer sample. Therefore, it became our primary concern to reduce the CPU time spent in the FG-DVC model down to an acceptable level.

By using the profile tool (-p option) in the Sun workstation, we have been able to do a performance analysis on each simulation. The profile tool provides detailed information about the percentage of time spent in each subroutine or function; the number of calls made for each routine and the actual time used for each call, etc. In general, all the routines called in our simulations can be classified as one of the following three categories: (a) routines that belong to the original PCGC-2 code; (b) routines that belong to the FG-DVC model; and (c) the machine-related internal routines and functions. From the profile tables one can find out how the total CPU time is distributed in each routine and what are the time-consuming ones. For example, in the early simulations the DVC portion alone could spend as much as 70% of the total CPU time. It was also noted that the subroutine OLIGUP was the most time-consuming routine which updates oligomer records by searching through an oligomer chain each time a randomly chosen bond is broken or a crosslink is formed. The subroutine OLIGUP took as much as 50% of the total CPU time in the early simulations. Therefore, our efforts have been focused on reducing the CPU time spent in the DVC portion of the code.

The first modification made to reduce the time spent in the DVC routines was

to reduce the total number of monomers in the coal polymer sample. The original FG-DVC model uses 2100 - 2400 monomers to set up a coal sample, on which the Monte Carlo statistical calculations are performed to simulate the bond-breaking, crosslinking and vaporization processes during pyrolysis. It is thus not surprising that a lot of bookkeeping is required to keep track of the changing state of so many beads. In principle, a statistical method, such as the Monte Carlo method, requires a large ensemble to keep the accuracy and reproducibility of any calculations. Therefore, the feasibility of reducing the size of the ensemble depends on how much error could result from this approach. To check this out, we have carefully studied the effect of varying the size of the coal sample on the performance of the FG-DVC model. Both a bituminous coal and a lignite were tested. In each coal type there were three cases studied: (1) the original size of the coal sample, namely 2100 beads for bituminous and 2400 beads for lignite; (2) the total number of beads was reduced by a factor of 3 (referred to as R3 case hereafter); (3) the total number of beads was reduced by a factor of 6 (referred to as R6 case).

The DVC model provides a variety of coal properties during pyrolysis, such as tar yield, coal viscosity, volumetric swelling ratio, molecular distribution, etc. However, what is needed currently by the PCGC-2 simulations is the tar and gas yields and their rate during pyrolysis. The results of our study on the different cases and coal types showed excellent reproducibility and consistency as far as the tar yield as a function of time was concerned. Figure IV.A-1 presents the product yields for a bituminous coal under different cases, including tar, gas and pyridine soluble fractions. The upper portion of the figure represents the time-temperature history. Similar plots are presented in Fig. IV.A-2 for a lignite coal. It is shown in Fig. IV.A-1 and Fig. IV.A-2 that the tar and gas yields predicted by the DVC model using various sizes of the coal sample are very consistent. It is also noted that the amount of pyridine solubles and the coal viscosity did show a noticeable variation but became increasingly noisy when the size of the coal sample is reduced. Although these properties show fluctuations due to the reduced sample size, they are not the main concern in the integrated code because of the large number of particles being used in each simulation. The current version of PCGC-2 uses 50 particles with different trajectories to obtain averaged properties in a reactor. It implies that the random statistical errors caused by reducing the sample size may very well be alleviated by averaging over 50 particles. Therefore, it seems acceptable to reduce the size of the coal sample by at least a factor of 3 without losing accuracy in regard to the tar and gas yields. The saving of the CPU time by reducing the total number of monomers was remarkable. Take the R3 case

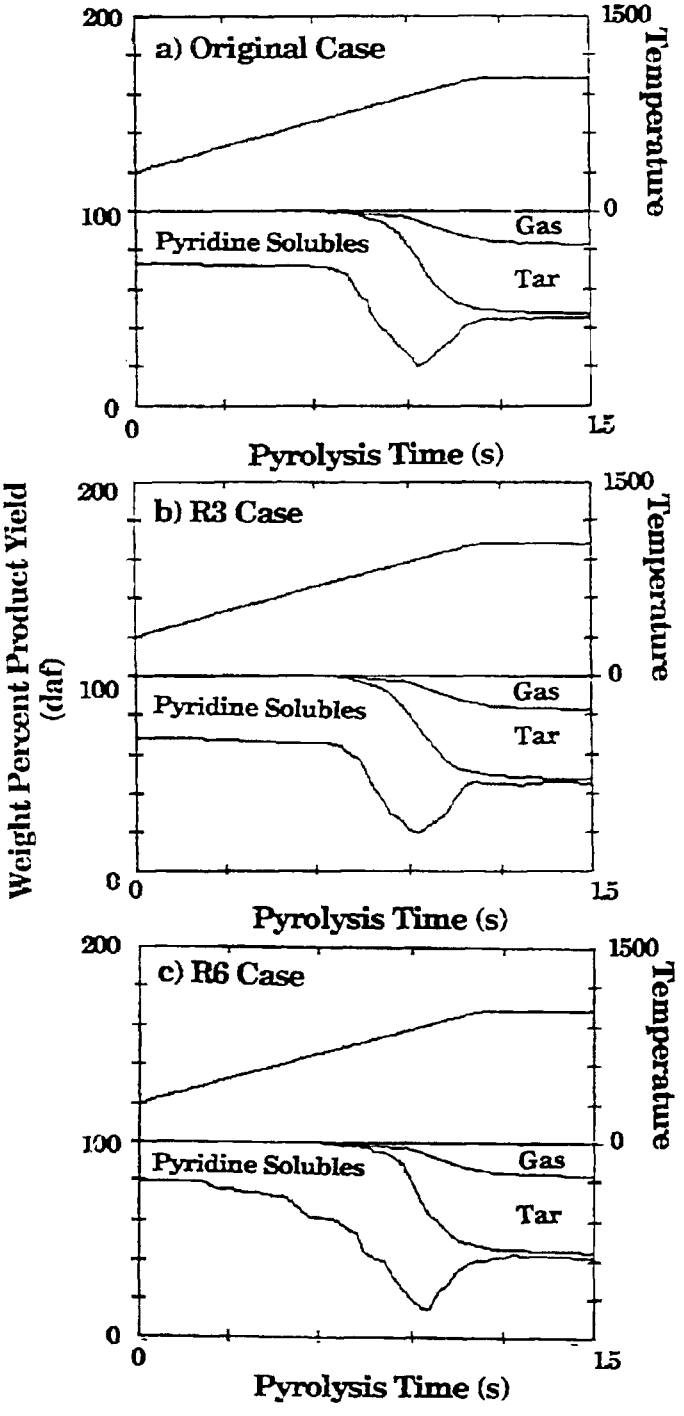

Figure IV.A-1. Product Yields for Bituminous Coal Under Various Sample Sizes.

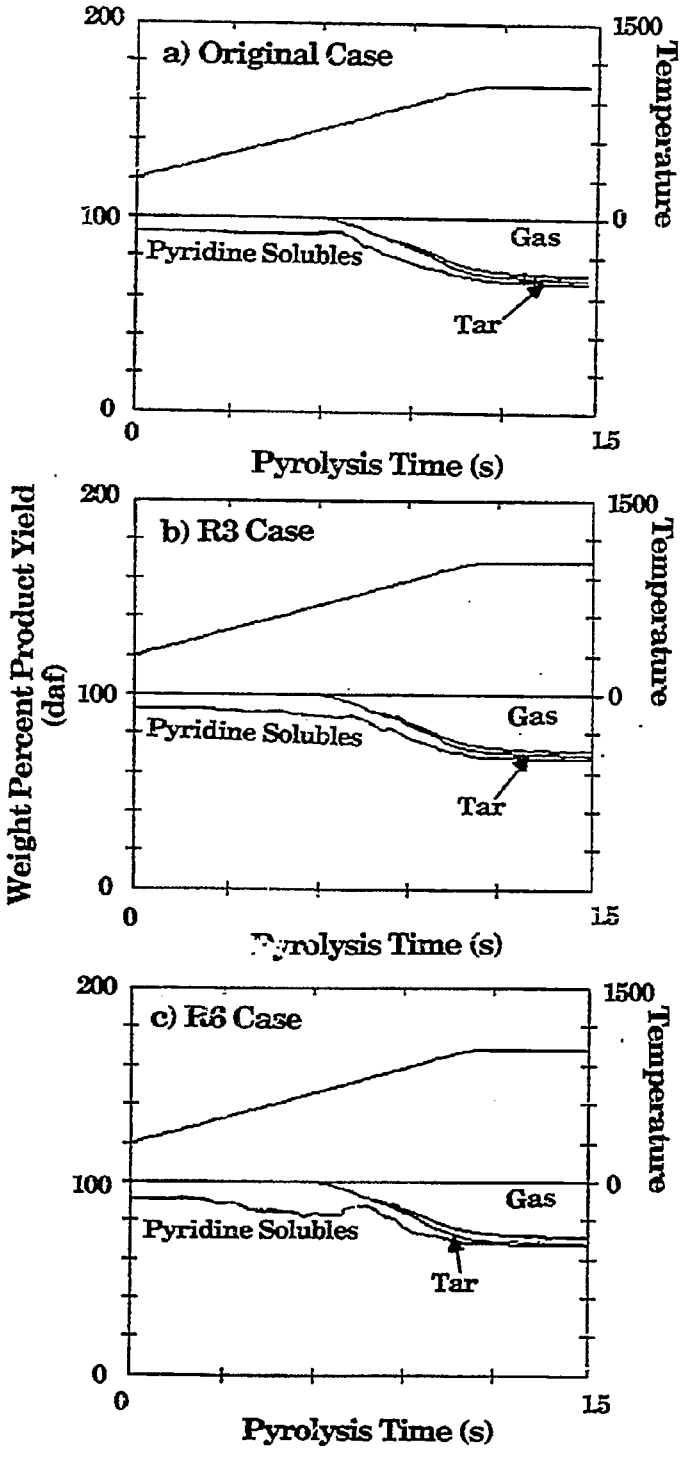

Figure IV.A-2. Product Yields for Lignite Under Various Sample Sizes.

for bituminous as an example, the total CPU time for running the integrated code was reduced to 6.5 hours in which the FG-DVC model took about 38% of the total time.

To further reduce the CPU time spent in the FG-DVC portion, we have made a second modification in the integrated code, which is to reduce the number of calls for the DVC routines. It was found in our study that the time step used in the PCGC-2 portion was too small compared to that used in the bare FG-DVC model. By using the debugger tool DBX at the Sun workstation, we were able to trace down the time step used at any point of time during the PCGC-2 simulations. The time step in the PCGC-2 is determinec and adjusted according to two factors: (a) the velocity of a particle by which it travels through the reactor and (b) tne rate of change in the particle enthalpy. It was observed that the time step in the PCGC-2 portion usually started with a value between 1.0E-4 to 1.0E-5 sec. determined by the particle velocity at the inlet and was often reduced even further when the enthalpy rate increased. On the other hand, the time step in the bare DVC model is determined by the heating rate of a particle. In our FG-DVC simulations, the DVC routines are called each time after the particle temperature is raised by 20 - 25 degrees. The average time step to call the DVC routines is around 0.025 sec.. However, when PCGC-2 and FG-DVC were first integrated together, the two portions shared the same time step determined by PCGC-2. At each time step, the FG-DVC routines are called once to update the mass fractions of evolved gases and tar. It is thus obvious that the time-consuming DVC routines may be called more frequently than necessary. The tar yield and its rate should only be updated according to the particle temperature change, not to the partic e velocity or other factors.

Based on the above reasoning, we investigated the profile tables of the integrated PCGC-2 simulations in which the shared time step was used. It was found from that the average number of calls for the DVC routines in each particle trajectory was 247. It is also noted that a typical number of DVC calls in the bare FG-DVC model is about 57 times for the whole pyrolysis. Therefore, a substantial saving of the CPU time can be made by choosing proper time steps for the DVC routines. This has been accomplished by two changes in the code. The first one was to skip e temperature range from room temperature to 500°C by setting up a proper initial time step so that the DVC routines would not be called within this range. This can be justified by the fact that there is virtually no tar and not much light gases evolved in this temperature range. The second change was to determine the time step during pyrolysis according to the particle heating rate. The allowed change in temperature between two consecutive calls of the DVC

routines was chosen to be 20 degrees. Then, the actual time step provided for the DVC routines is obtained from dividing this temperature span by the particle heating rate at that point of time.

The above-mentioned modifications made in the integrated code resulted in a significant saving of the total CPU time. Now, a typical run time for the integrated PCGC-2 simulations is reduced to a little over four hours, in which the FG-DVC model takes about 17% of the total CPU time or even less. The time-saving results are summarized in Tables IV.a-1 and IV.A-2. All the simulations were run at the Sun 3/260 workstation. Table IV.A-1 presents the results for the subroutine OLIGUP alone, which used to be the most time-consuming routine. It is worth mentioning that the actual time spent in OLIGUP for three cases is proportional to the square of the reduction factor, while the number of calls and the time per each call are both proportional to the reduction factor. Table IV.A-2 shows the partition of the CPU time in three portions: PCGC-2 routines, FG-DVC routines and the machine-related internal routines. For each portion, both actual time and the percent of the total time are listed. Moreover, the average time spent in the FG-DVC portion for each particle trajectory and the time ratio between the FG routines and the DVC routines are also included.

The changes which have been implemented thus provide an acceptable integrated code capable of predicting all of the particle chemistry which is presently required and those properties which have been considered for future improvements.

TABLE IV.A-1

TIME PROFILE FOR OLIGUP ROUTINE

COAL TYPE: Bituminous

Case	Total Number of calls for OLIGUP	ms/call	Percent of the Total CPU Time	Actual Time (sec)
Original	258787	13.54	15.2%	3538.0
R3	69621	4.38	3.0%	306.8
R6	32920	2.25	0.5%	78.6

COAL TYPE: Lignite

Case	Total Number of calls for OLIGUP	ms/call	Percent of the Total CPU Time	Actual Time (sec)
Original	424099	53.95	44.0%	22900.0
R3	142662	16.98	11.6%	2452.6
R6	71146	8.31	3.7%	590.2

TABLE IV.A-2

SUMMARIZED TIME PROFILE

COAL TYPE: Bituminous

Case	PCGC-2	FG-DVC	FG:DVC	Time in FG-DVC Per Particle	Internal	Total
Original (2100 beads)	3.3 hrs (50.4%)	2.32 hrs (35.5%)	3:10	27.93 sec	0.84 hr (12.8%)	6.46 hrs
R3 (700 beads)	2.94 hrs (69.1%)	44.5 min (17.4%)	3.24:1	10.8 sec	34 min (13.3%)	4.26 hrs
R6 (350 beads)	3.12 hrs (71.6%)	36.9 min (14.1%)	13.1:1	8.86 sec	35.4 min (13.5%)	4.36 hrs

COAL TYPE: Lignite

Case	PCGC-2	FG-DVC	FG:DVC	Time in FG-DVC Per Particle	Internal	Total
Original (2400 beads)	2.81 hrs (19.4%)	9.58 hrs (66.3%)	1:20.4	115.02 sec	2.04 hrs (14.1%)	14.46 hrs
R3 (800 beads)	3.32 hrs (56.5%)	1.71 hrs (29.1%)	1:2.93	20.51 sec	0.82 hrs (14%)	5.87 hrs
R6 (400 beads)	3.03 hrs (68.3%)	45.7 min (17.2%)	1:1.2	9.15 sec	38.0 min (14.3%)	4.43 hrs

IV.B. Subtask 4.b. - Application of Fixed-Bed Code

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Objective

Simulate coal conversion reactors of interest to METC.

Accomplishments

No work scheduled.

REFERENCES

Anthony, D.B. and Howard, J.B., AIChE J., 22, 625, (1976).

Baxter, L.L., "Condensed Phase Behavior in Combustion Environments," Ph.D. dissertation, Brigham Young University, Provo, UT, in preparation (1988).

Beittel, R., Gooch, J.P., Dismukes, E.B., and Muzio, L.J., "Studies of Sorbent Calcination and SO2-Sorbent Reactions in a Pilot-Scale Furnace," Paper No. 3c, 1st EPRI/EPA Symp. Dry SO_2 Simultan. SO_2/NO_x Control Technol., San Diego (Nov., 1984).

Best, P.E., Solomon, P.R., Serio, M.A., Suuberg, E.M., Mott, W.R., Jr., and Bassilakis, R., ACS Div. of Fuel Chem. Preprints, 32, (4), 138, (1987).

Bhattacharya, A., L. Salam, M.P. Dudukovic, and B. Joseph, "Experimental and Modelling Studies in Fixed-Bed Char Gasification", Ind. Eng. Chem. Process Des. Dev., 25, 988 (1986).

Bishop, M. and Ward, D.L., Fuel, 37, 191, (1958).

Bliek, A., van Poelje, W.M., van Swaaij, W.P.M., and van Beckum, F.P.H., AIChE J., 31, (10), 1666, (1985).

Carangelo, R.M., Solomon, P.R., and Gerson, D.J., Fuel, 66, 960, (1987).

Categen, B.M., Johnson, T.R., Payne, R., Moyeda, D.K., Sheldon, M.S., Li W. and Kindt G.S., "Effective Mixing Processes for SOx, Sorbent, and Coal Combustion Products", Final Report prepared for the Environmental Protection Agency, Contract No. 68-02-4205 (May 1987).

Cho, Y.S., "Modeling and Simulation of Lurgi-Type Gasifier," M.S. Thesis, Washington University, St. Louis, MO (1980).

Christensen, K.R., Rasband, M.W. and Smoot, L.D., "Revised Data Book: For Evaluation of Combustion and Gasification Models," Vol. II, Final Report prepared for U.S. DOE/METC, Contract No. DE-AC21-85MC22059, Brigham Young University, Provo, UT (October 1987).

Devanthan, N. and Saxena, S.C., Proceedings of the 2nd Annual Pittsburgh Coal Conference, Pittsburgh, PA, p. 605, (1985).

Devanthan, N. and Saxena, S.C., Ind. Eng. Chem. Res., 26, 548, (1987).

Drake, M.C., Pitz, R.W., Correa, S.M. and Lapp, M., "Nitric Oxide Formation for Thermal and Fuel-Bound Nitrogen Sources in a Turbulent Nonpremixed Syngas Flame," 20th Symposium (International) on Combustion, The Combustion Institute, 1983 (1984).

Drake, M.C., Correa, S.M., Pitz, R.W., Shyz, W. and Fenimore, C.P.,"Superequilibrium and Thermal Nitric Oxide Formation in Turbulent Diffusion Flames," Combust. Flame, 69, 347, (1987).

Ergun, S., "Fluid Flow Through Packed Columns," Chem. Eng. Prog., 48, 89 (1952).

Grant, D.M., Pugmire, R.J., Fletcher, T.H. and Kerstein, A.R., "A Chemical Model of Coal Devolatilization Using Percolation Lattice Statistics," in preparation (1988).

Gullett, B.K. and Bruce, K.R., "Pore Distribution Changes of Calcium-Based Sorbents Reacting with Sulfur Dioxide," AIChE Journal, 33, 1719 (1987).

Hedman, P.O., Smoot, L.D., Smith, P.J. and Blackham, A.U., "Entrained Flow Gasification at Elevated Pressure," Vol. I, Final Report prepared for U.S. DOE/METC, Contract No. DE-AC21-85MC22059, Brigham Young University, Provo, UT. (October 1987).

Jones, P.G., Lindsay, J.D., and Hedman, P.O., "Fluid Dynamic Measurements in a Simulated Entrained Flow Coal Combustor," Western States Section, The Combustion Institute, Stanford, California (Fall 1984).

Kamotani, Y. and Gerber, I. "Experiments on Confined Turbulent Jets in Cross Flow", Final Report prepared for the National Aeronautics and Space Administration, Report No. CR-2392 (March 1974).

Keffer, J.F. and Baines, W.O., "The Round Turbulent Jet in a Cross Wind," J. Fluid Mechanics, 15(4), 481-496 (1963).

Kobayashi, H., Howard, J.B., and Sarofim, A.F., Sixteenth Symposium (Int) on Combustion, The Combustion Institute, Pittsburgh, PA, p. 411, (1977).

Kobayashi, H., Howard, J.B. and Sarofim, A.F., "Coal Devolatilization at High Temperatures," 16th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA (1977).

Lindgren, E.R. and Pershing, D.W., "Fuel Rich Sulfur Capture in a Combustion Environment," Western States Section/Combustion Institute, Spring Meeting (1987).

Lindsay, J.D., Hedman, P.O., and Smith, P.J., "LDA Measurements in Simulated Gasifier Flows with Swirl," Proceedings of International Symposium on Laser-Doppler Velocimetry, Lisbon, Portugal (July, 1986).

Mason, E.A. and Malinauskas, A.P., "Gas Transport in Porous Media: The Dusty Gas Model", Chem. Eng. Monograph, **17**, Elsevier, Amsterdam, (1983).

Mason, E.A., Malinauskas, A.P., and Evans, III, R.B., J. Chem. Phys. **46**, 3, 199 (1967).

McLean, W.J., Hardesty, D.R. and Pohl, J.H., 18th Symp. (Int) on Combustion, The Combustion Institute, Pittsburgh, PA, 1239, (1981).

Midkiff, K.C., Altenkirch, R.A., and Peck, R.E., Combustion and Flame, **64**, 253, (1986).

Nenniger, R.D., Howard, J.B., and Sarofim, A.F., Proceedings of the 1983 Int. Conf. on Coal Sci., Pittsburgh, PA, 521, (Aug. 15-19, 1983).

Penner, S.S., "Coal Gasification: Direct Applications and Synthesis of Chemicals and Fuels," A Research Needs Assessment, prepared by the DOE Coal Gasification Research Needs (COGARN) Working Group, DOE/ER-0326, (1987).

Pershing, D.W. and Wendt, J.O.L., "Pulverized Coal Combustion: The Influence of Flame Temperature and Coal Composition on Thermal and Fuel NO_x" 16th Symposium (International on Combustion, The Combustion Institute, Pittsburgh, PA, 389 (1977).

Rossberg, M., "Experimental Results Concerning the Primary Reactions in the Combustion of Carbon", Z. Electrochem., 60, 952 (1956).

Sadakata, M., Y. Fujioka and D. Kunii, "Effects of Air Preheating on Emissions of NO, HCN and NH_3 form a two-Stage Combustion," 18th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 65, (1981).

Semerjian, H. and A. Varnos, "NO_x Formation in Premixed Turbulent Flames," 18th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 169, (1981).

Serio, M.A., Hamblen, D.G., Markham, J.R., and Solomon, P.R., Energy and Fuel, 1, 138, (1987).

Simons, G.A., Garman, A.R., and Boni, A.A., "The Kinetic Rate of SO_2 Sorption By CaO," AIChE J., 33, 211 (1987).

Smith, P.J. and Smoot, L.D., "Detailed Model for Practical Pulverized Coal Furnaces and Gasifiers," Second Annual Progress Report prepared for a Consortium of Government and Industrial Agencies, Brigham Young University, Provo, UT (May 31, 1987).

Smoot, L.D. and P.J. Smith, Coal Combustion and Gasification, Plenum Press, New York, NY (1985).

Solomon, P.R., Hamblen, D.G., Serio, M.A., Smoot, L.D. and Brewster, B.S., "Measurement and Modeling of Advanced Coal Conversion," Annual Report, Work Performed Under Contract No. DE-AC21-86MC23075 for U.S. Dept. of Energy, Morgantown Energy Technology Center (September 30, 1987).

Solomon, P.R., Serio, M.A., Carangelo, R.M. and Markham, J.R., "Very Rapid Coal Pyrolysis," Fuel, 65, 182-94, (1986).

Solomon, P.R. and Hamblen, D.G., Prog. Energy. Combust. Sci., 9, 323, (1983).

Solomon, P.R., Hamblen, D.G., Carangelo, R.M., Serio, M.A., and Deshpande, G.V., "A General Model of Coal Devolatilization", Energy and Fuel, submitted for publication (1988).

St. John, G.A., Buttrill, Jr., S.E., and Anbar, M., ACS Symposium SEries, 71, p. 223, (1978).

Stubington, J.F., Sumaryono, R., Fuel, 63, 1013, (1984).

Suuberg, E.M., Peters, W.A., and Howard, J.B., Ind. Eng. Chem. Process Des. Dev., 17, 37, (1978).

Suuberg, E.M., Peters, W.A., and Howard, J.B., Seventeenth Symposium (Int) on Combustion, The Combustion Institute, Pittsburgh, PA, 117, (1979).

Takagi, T. and Ogasawara, M., "A Study on Nitric Oxide Formation in Turbulent Diffusion Flames," 18th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1051, (1981).

Tang, S. and Churchill, S.W., "The Formation of Thermal and Fuel NO_x for Radiantly Stabilized Combustion," 18th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 73 (1981).

Thompson, D., Brown, T.D. and Beer, J.M., "Formation of NO in a Methane-Air Flame," 18th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 787 (1981).

Timothy, L.D., Froelich, D., Sarofim, A.F., and Beer, J.M., "Soot Formation and Burnout During the Combustion of Dispersed Pulverized Coal Particles", 21st Symp (Int) on Combustion, The Combustion Institute, Pittsburgh, PA, (1987).

Vorres, K.S., ACS Div. of Fuel Chem. Preprints, 32, (4), 221, (1987).

Webb, B.W., and Hedman, P.O., "LDV Measurements in a Simulated Entrained- Flow Coal Reactor," Proceedings of the Symposium on Engineering Applications of Laser Velocimetry, Fall ASME National Meeting, Phoenix, AZ (1982).

Whelan, J.K., Solomon, P.R., Deshpande, G.V., Carangelo, R.M., "Thermogravimetric Fourier Transform Infrared Spectroscopy (TG-FTIR)", Energy and Fuel, to be published, (1988).

Wornat, M.J., Sarofim, A.F., and Longwell, J.P., Energy and Fuels, 1, (5), 431, (1987).

Yoon, H., Wei J. and Denn, M.M., "A Model for Moving-Bed Coal Gasification Reactors," AIChE J., 24, 885 (1978).