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PROGRAMMED TEMPERATURE GASIFICATION STUDY

Final Report, October 1, 1979—November 30, 1980

By
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M. P. Gardner
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November 30, 1980

Work Performed Under Contract No. AC21-79MC11630

TRW
Defense and Space Systems Group
Redondo Beach, California

U. S. DEPARTMENT OF ENERGY

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ABSTRACT

An experimental, modeling and conceptual engineering analysis study has been performed to assess the feasibility of TRW's Programmed Temperature Gasification (PTG) concept for carbonizing caking coals without severe agglomeration. The concept involves control of carbonizing heating rate to maintain metaplast concentration at a level equal to or slightly below that which causes agglomeration. The experimental studies required the construction of a novel programmed temperature, elevated pressure, hot stage video microscope for observation of coal particle changes during heating. This system was used to develop a minimum-time heating schedule capable of carbonizing the coal at elevated pressures in the presence of hydrogen without severe agglomeration. Isothermal fixed heating rate data for a series of coals were subsequently used to calibrate and verify the mathematical model for the PTG process. These results showed good correlation between experimental data and mathematical predictions. Commercial application of the PTG concept to batch, moving bed and fluid bed processing schemes was then evaluated. Based on the calibrated model programmed temperature gasification of the coal without severe agglomeration could be carried out on a commercial batch reaction in 4 to 12 minutes. The next step in development of the PTG concept for commercial application would require testing on a bench scale (3-inch diameter) gasifier coupled with a full commercial assessment to determine size and cost of various gasification units.

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1. INTRODUCTION

Although several fixed-bed gasification processes are commercially operable today, the use of strongly caking coals characteristic of bituminous deposits in the Eastern United States, seems to require reduced throughput with a potential adverse effect on process economics. One potential factor which would affect thoughput is the aggomeration of coal during the carbonization process, which could impede solids and gas flow.

Although other factors occurring in the lower bed zones such as the limitations imposed by the reactivity of coke or char or the relationship of gas velocity to solids carryover would reduce throughput, a problem amenable to solution with current technology is that of agglomeration during carbonization. TRW believes that a process modification to promote devolatilization by adjusting the temperature-time distribution of coal in the top part of the bed, could potentially improve reactor throughput and process economics.

When a caking coal is heated beyond about 400°C (752°F) in a reducing atmosphere, it passes through a plastic state, producing a viscous liquid or metaplast capable of coalescing and binding individual coal particles into an indivisible mass. Subsequent decomposition of the metaplast produces volatile matter and a semicoke residue that eventually undergoes further carbonization to yield a dry coke or char.

When substantial concentrations of metaplast are present, individual coal particles in contact with one another will agglomerate and also attach themselves to a reactor wall. This agglomeration reduces bed permeability to gas flow and impedes solids flow through the reactor, the net effect being a markedly reduced coal throughput rate and, in severe cases, a complete setting up of the coal bed in the reactor.

Several approaches have been used in the past to accommodate caking coals in a gasification process:

- Operating the reactor in the entrained flow mode to minimize the contact of coal particles with one another or reactor walls

- Chemical pretreatment of coal, e.g., partial oxidation, to nullify the caking tendency

- The use of stirrers in fixed-bed reactors to break up incident agglomeration.

The first technique noted above is not applicable to gasification in fixed-bed reactors, and chemical pretreatment generally involves a separate reactor, greatly increasing costs. Oxidative pretreatment also renders the coal less reactive when undergoing subsequent gasification reactions and reduces gasification efficiency by removing hydrogen in the form of water. Stirrers will function satisfactorily with weakly caking coals as long as the bed diameter is not too large, however stirring at several levels with high torque is required for strongly caking coals.

TRW's Programmed Temperature Gasification (PTG) concept involves control of the coal's heating rate in the top portion of the bed to maintain the metaplast concentration at a level equal to or just below the critical level causing agglomeration. Maintaining the metaplast concentration at this level allows devolatilization to proceed at the highest rate consistent with avoidance of caking.

This document is a report of the work conducted under sponsorship of the Department of Energy to experimentally assess the validity of the programmed temperature gasification concept for carbonizing caking coals without severe agglomeration.

This assessment consisted of the: (1) evaluation of the effects of gasification reaction parameters on the agglomeration of caking coals, (2) definition of minimum time heating schedules (MTHS) under selected sets of reaction conditions for carbonizing caking coals without agglomeration, and (3) improvement or further development of a predictive model for PTG. Evaluation of gasification parameter effects on coal agglomeration and definition of minimum time carbonization schedules were performed using a specially designed elevated pressure, hot stage reactor for visually observing coal swelling and agglomeration or the lack of agglomeration under variable heating rate schedules. Coal sample mass changes observed under isothermal and variable heating rate schedules were used to evaluate metaplast formation/decomposition kinetic rate constants and to refine TRW's predictive model for PTG. In addition to the principal experimental studies with the hot stage reactor, differential thermal analysis and thermal gravimetric analysis were performed with different caking coals to define enthalpies of reaction, phase changes and weight loss occurring during PTG.

The programmed temperature gasification (PTG) concept is presented in Section 2 with the hot stage system described in Section 3. Parametric studies of the agglomeration process are discussed in Section 4 with the minimum time heating schedule development prescribed in Section 5. The PTG model refinement is set forth in Section 6. Application of the PTG concept to commercial gasifiers is discussed in Section 7 and Section 8 presents recommendations for further development of this concept.

2. PROGRAMMED TEMPERATURE GASIFICATION CONCEPT

The PTG concept for rapid coal carbonization without agglomeration is based upon the metaplast theory. This theory postulates that, upon heating a caking coal, a portion of the coal decomposes to a metastable plastic (metaplast) substance. This metaplast further decomposes to form semi-coke and gaseous products. The reaction sequence is as follows:

$$P \rightarrow M$$

$$M \rightarrow S + G_1$$

$$S \rightarrow C + G_2$$

where

P = parent metaplast forming material in coal

M = sticky substance, metaplast

S = semi-coke, non-stick solid

G_1 = primary gaseous decompositions products

G_2 = secondary gaseous products

C = carbon

Fitzgerald(1) and Chermin and Van Krevelen(2) have used this theory to obtain a quantitative interpretation of fluidity and plasticity behavior of coal. First-order kinetics, typical for solid cracking reactions, have been assumed for these reactions.

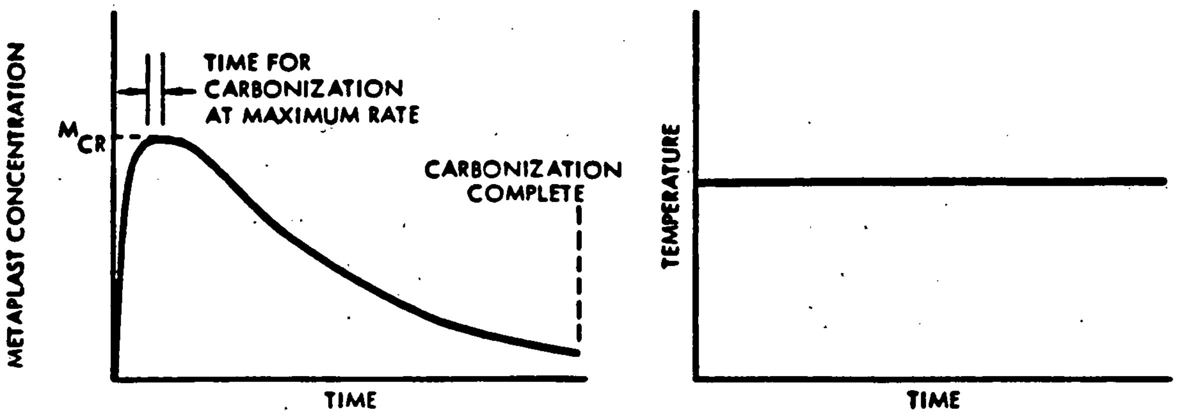
The PTG model postulates that the presence of metaplast on coal particles causes caking or agglomeration during carbonization and to avoid caking, the metaplast concentration must be maintained below some critical level. One way to avoid caking is to carbonize using a uniformly increasing temperature schedule where the peak metaplast concentration remains below the critical value. However, this results in prohibitively long carbonization times and correspondingly low gasifier throughput rates.

TRW's approach is to heat the coal at a rate that is fast enough to maintain the metaplast concentration at the highest possible value while still maintaining it below the critical value. Ideally, the metaplast concentration would be maintained just below the critical value throughout carbonization.

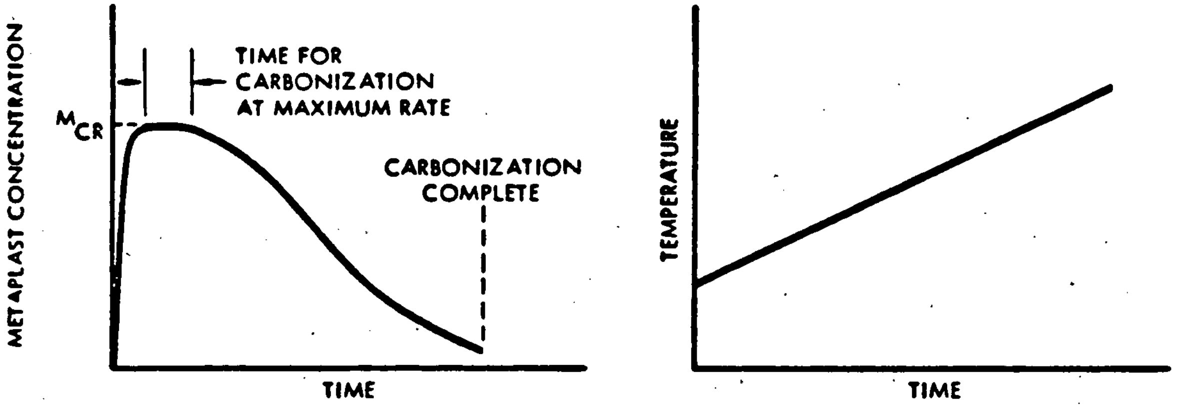
The advantage of this concept is illustrated in Figure 1 which shows three temperature-time curves during carbonization and the corresponding variations of metaplast concentration. In Figure 1a carbonization is occurring at a constant temperature, and the peak metaplast concentration is just below the critical value. When the peak metaplast concentration occurs, carbonization is proceeding at the maximum allowable rate; at all other times the carbonization rate is well below the maximum allowable rate.

In Figure 1b carbonization is occurring while temperature is being increased at a constant rate, and the peak metaplast concentration is maintained for a slightly longer time. However, when the metaplast concentration is significantly less than the critical value, carbonization is occurring at a rate significantly below the optimum value.

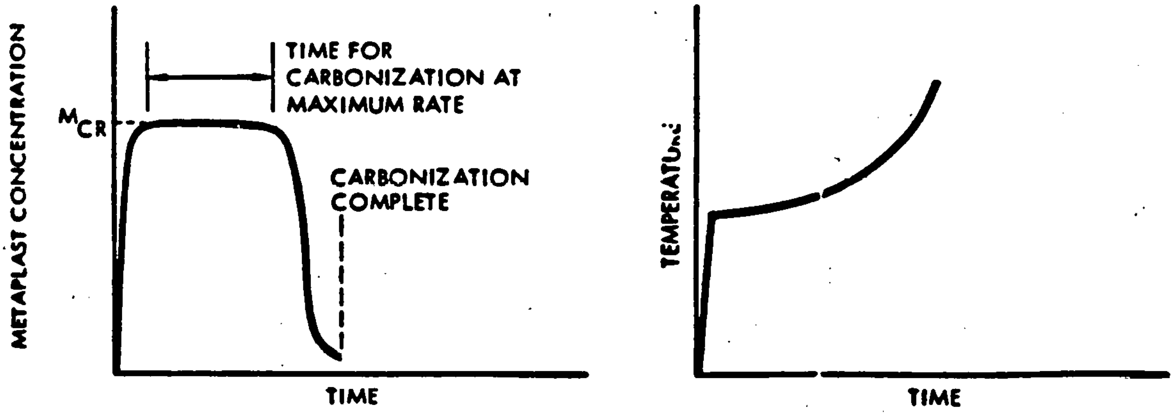
TRW's approach is illustrated by Figure 1c. The coal is rapidly heated to achieve the critical metaplast concentration as quickly as possible. The coal is held at constant temperature for a short time and then heated at a continuously increasing rate to maintain the metaplast concentration as near to the critical value as possible. Finally, the metaplast concentration falls when all the coal has been carbonized. In contrast to the approaches shown in Figures 1a and 1b, the TRW approach permits carbonization to proceed at the optimum rate during the entire carbonization period.



(a) CARBONIZATION AT CONSTANT TEMPERATURE



(b) CARBONIZATION WITH UNIFORMLY INCREASING TEMPERATURE



(c) TRW APPROACH: TEMPERATURE PROFILE ADJUSTED TO MAINTAIN CARBONIZATION RATE AT MAXIMUM VALUE WITHOUT AGGLOMERATION

Figure 1. Comparison of Carbonization with Three Temperature-Time Profiles

3. EXPERIMENTAL SYSTEM

Two experimental systems were employed for the generation of data used in this program. An elevated pressure, hot stage video microscope system was designed and constructed specifically for use in this study. It is capable of observing the physical behavior of coal under variable heating rates of 0-100°C/min (650°C maximum) at pressures from atmospheric to 350 psig in hydrogen and nitrogen atmospheres. The second system consisted of a Burrell furnace equipped with a quartz tube and nitrogen purge system. This was used for determination of isothermal weight loss and agglomeration data for selected coals in which visual observation was not necessary.

3.1 HOT STAGE REACTOR

3.1.1 Pressure Vessel and Hot Stage

The hot stage reactor assembly consisted of two major components: the hot stage block upon which the sample was heated and the pressure vessel into which the hot stage block was mounted. The pressure vessel was constructed of a flanged 6-inch diameter schedule 40, 304 stainless steel pipe. A single 3-inch diameter saddle flange, located midway on the pressure vessel, held a quartz window view port with a spray ring which allowed visual observation of the hot stage block during heating without significant fogging. Electrical conductors, thermocouples and gas lines entered the vessel through the blind flange on the right end of the pressure vessel (Figure 2a), while access to the hot stage block for sample manipulation was obtained through a hinged blind flange assembly on the opposite end.

The copper hot stage block (Figure 2b) was heated by five, 3/8-inch diameter, 500-watt resistive cartridge heaters and equipped with a removable deep dish sample tray etched with a millimeter reference grid for sample size determination during reaction. Hot gas of selected composition could be directed over the surface of the sample tray by passage through gas channels drilled in the hot stage body which terminate into a sweep gas slot milled above the sample tray. Separate channels were also located within the block for cooling gas to permit rapid quench of a sample after completion of reaction. Thermocouple wells were provided at key locations

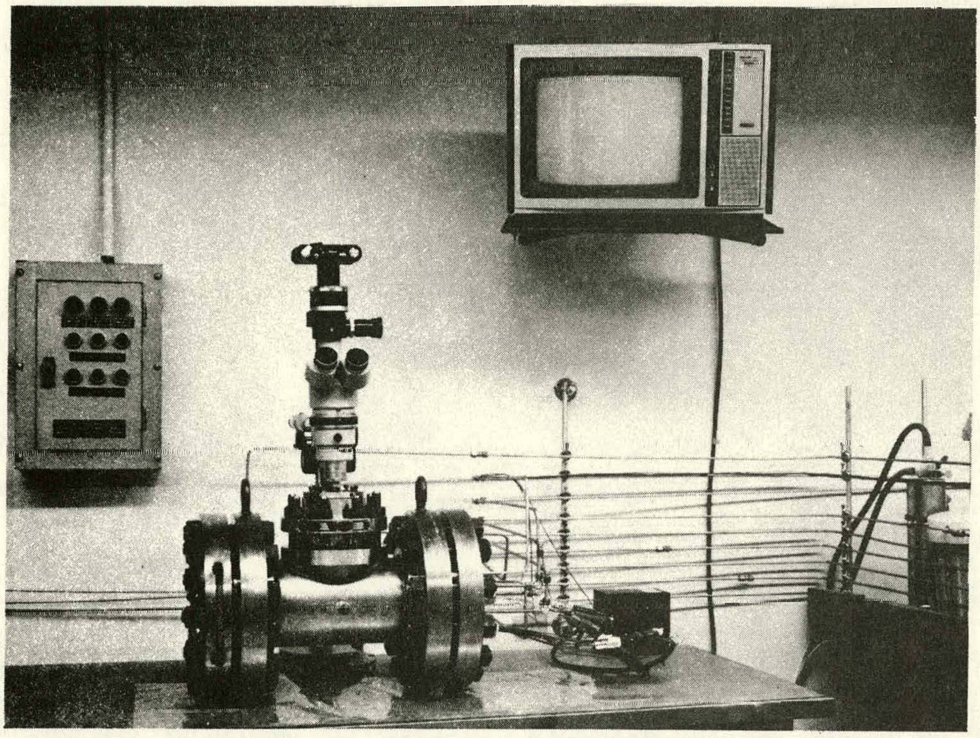


Figure 2a. Pressure Vessel

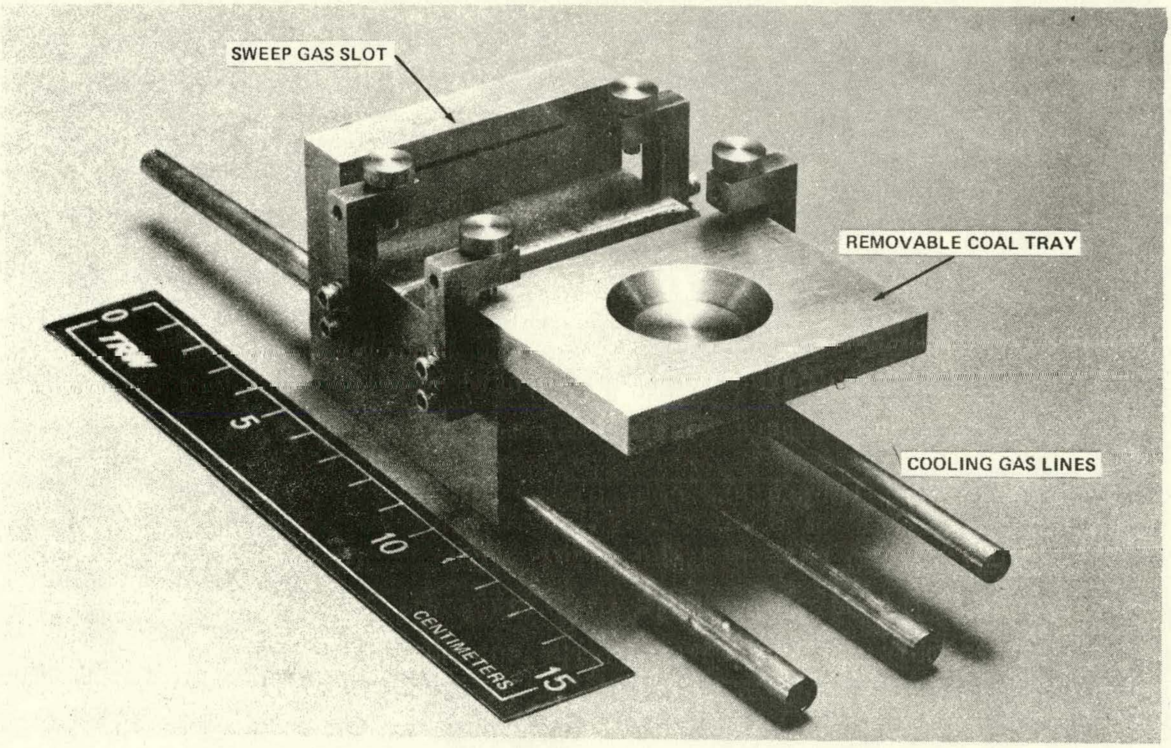


Figure 2b. Hot Stage

within the sample tray and block. The current hot stage reactor assembly can subject a 150 mg coal sample to pressures from vacuum to 350 psig and temperatures to 650°C at heating rates of up to 100°C/min.

3.1.2 Hot Stage Temperature Control

Hot stage temperature control was maintained with a Data Trak model 73211 microprocessor based programmer coupled to a 63911 process controller which allowed preprogramming of a complete heating rate schedule for the hot stage block. Programs were generated by straight line segments that fit the desired temperature profile and allowed up to 51 setpoint changes at durations of 1-1999 seconds, minutes or hours. The process controller was a general purpose two mode, proportional band plus reset, unit with manual setpointing adjusted through a 10 turn 1000 ohm potentiometer. This controller drives an external 40 watt solid state relay (SSR) which switched 230 Vac to the resistive cartridge heaters imbedded in the hot stage block. Sheathed Omega chromel-alumel thermocouples were used for monitoring hot stage temperature at selected locations within the block and sample tray. The feedback control signal was provided by a thermocouple located in the middle of the hot stage block. Temperature control could be maintained to within ±5°C of desired setpoint.

3.1.3 Video Data Acquisition System

Visual data of coal particle changes under magnification as a function of coal temperature and time were collected with a Nikon SMZ-10 microscope coupled to a closed circuit color television camera (Figure 3). The Nikon SMZ-10 was a 6:1 zoom stereo microscope equipped with a trinocular head to which was mounted a 35 mm still frame camera. An auxiliary phototube directed an image of the hot stage sample tray surface to the vidicon tube of the television camera allowing video image magnifications of 1 to 50X using the microscope zoom capability. Coaxial illumination was provided by a fiber optic light ring mounted on the microscope body. If desired, a double iris diaphragm attachment could extend the depth of field allowing simultaneous focus for both the top and bottom of large or thick samples. Video data were recorded on a JVC HR-6700 1/2-inch format tape recorder featuring slow motion; freeze frame and up to six hour recording capability. Critical video tape segments were analyzed for changes in

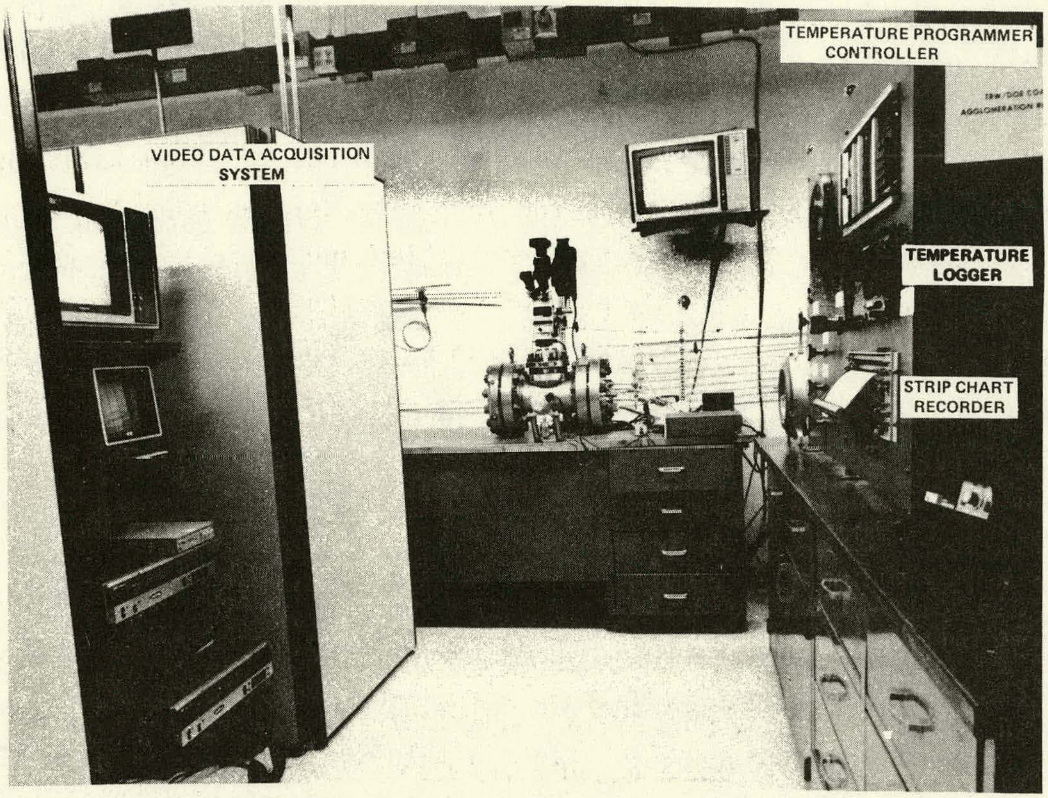


Figure 3. Hot Stage Reactor System

movement such as swelling, contraction, or position shifts with a Sony SVM-1010 Video Motion analyzer which was capable of indefinite still frame or frame advance in 1/7 or 1/15 of normal speed in forward or reverse direction. Clock time in hours, minutes, seconds and date information was presented on video tape and the Videotek 15-inch screen color monitors by a Vicon V240T date-time generator. This configuration permitted direct observation of coal sample changes with time which was synchronized to a temperature logger and strip chart recorder for direct time-temperature correlation.

3.2 SYSTEM OPERATION

Prior to experimental testing on coal samples, the hot stage was calibrated for sample temperature versus setpoint for the selected operating pressures of 0, 100, 200 and 300 psig. Temperature accuracy was determined using pure material melting points. Agreement with book value melting points was within ±5°C.

A typical experimental test with an agglomerative coal consisted of sample loading, system pumpdown to remove air, followed by backfilling with the desired gas, usually nitrogen or a hydrogen-nitrogen mixture. The system was brought up to desired pressure with a purge gas flow maintained through the spray ring to prevent fogging. The desired heating schedule was programmed into the temperature controller and strip chart, while temperature logger and video time readouts were synchronized. Microscope illumination intensity, color balance and focus were then adjusted, the video recorder activated, and the heating schedule initiated. From this point forward, all data were recorded automatically without operator assistance, unless visual observations through the binocular eyepiece were desired.

3.3 OVEN EXPERIMENTAL SETUP

Figure 4 shows the test configuration for the isothermal oven experiments conducted for the purpose of calibrating the PTG model. This system consisted of a Burrell furnace equipped with a 1-inch diameter quartz tube holding a ceramic boat with up to 0.5 gram of coal. In these tests the oven, purged by a flow of nitrogen, was preheated to a selected temperature. The boat was then placed in the oven tube for a preselected time period.

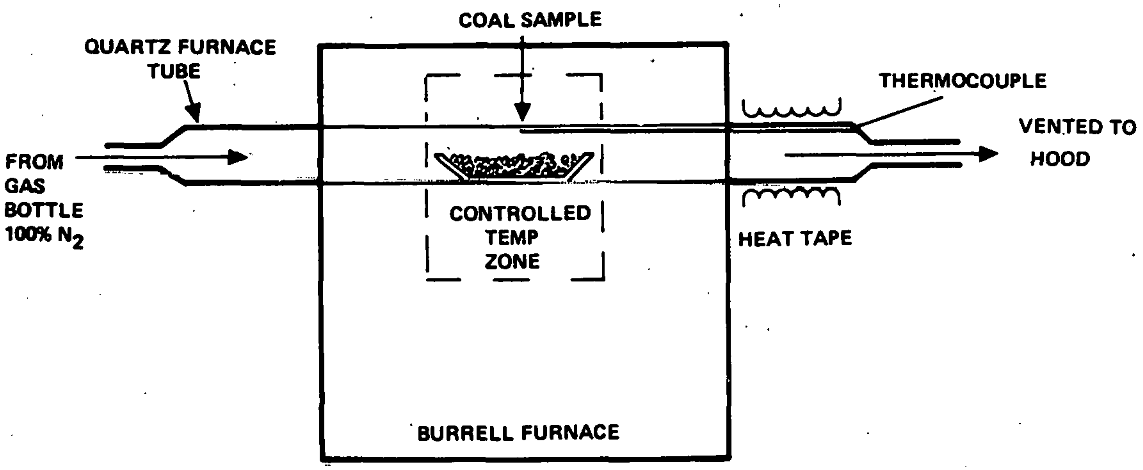


Figure 4. Experimental Setup for Oven Tests

Temperature was monitored by a thermocouple located over the boat. The time was measured after initial temperature equilibrium. Temperature was controlled to within ±5°C.

3.4 COALS STUDIED

Four coals were obtained from the Pennsylvania State University coal bank for use in this study. Two were high volatile A bituminous coals; Pittsburgh No. 8 (PSOC-293) and Pennsylvania B (PSOC-337), one was a high volatile B bituminous, Illinois No. 6 (PSOC-282) and one was subbituminous A, Upper Block (PSOC-181). Data on these coals are presented in Appendix A. Most work was conducted with the two high volatile A bituminous coals since agglomeration is most severe in coals of this rank.

4. COAL CARBONIZATION STUDIES

The unique capabilities of the hot stage video microscope enable observation of coal particles under magnification during the entire carbonization process. The purpose of the carbonization studies was to utilize this capability to (1) determine the temperature range over which selected coals undergo agglomeration, (2) observe the physical behavior of coal particles during carbonization and, (3) assess the effects of variable heating rate, gas composition and pressure on the carbonization process.

4.1 DETERMINATION OF AGGLOMERATION RANGE

Physical changes in coal particles during heating were assumed to indicate that the coal had entered the plastic or agglomerating regime where the metaplast concentration meets or exceeds the critical level. To ensure that the observed physical changes in coal particles viewed and recorded through the video microscope during heat-up were depicting the agglomeration process, a series of tests was conducted in which the observed changes were compared to the final agglomerate state of the coal after cooldown. The highly agglomerative coal Pittsburg No. 8 (PSOC-293) was used for this correlation. As seen in Table 1, the video microscope observations correlate well in qualitative sense with the final agglomerative state of the coal.

Agglomeration was measured by inverting the sample tray, estimating the fraction of coal which falls out and removing the remaining coal from the tray with a spatula. Five degrees of agglomeration could be qualitatively estimated in this manner:

N (None): All particles fall off the inverted tray, free-flowing particles.

S (Slight): Only a few particles stick to the tray, easily removed from the tray.

M (Medium Hard): More than 2/3 of the particles fall off the tray. Some particles stick to the tray and each other. Easily broken up by spatula.

Table 1. Correlation of Observed Changes During Heating with Final State of Agglomeration for Pittsburgh #8 (PSOC-293)

Run Number	Heating Schedule*	Observations Through Video Microscope	Final State of Agglomeration
6	Ramp to 310°C in 5.4 minutes	No observed changes in sample	N (no agglomeration) ∿6% weight loss
23	Ramp to 420°C in 11.5 minutes	Some movement - no swelling or bubbling observed	S (slight agglomeration) 14.2% weight loss
43	Ramp to 606°C in 66.6 minutes	Moderate bubbling and swelling	H (hard agglomeration) 26.2% weight loss
25	Ramp to 530°C in 7 minutes	Severe bubbling and swelling	V (very hard agglomeration) 30.2% weight loss

*All tests were conducted in 100% N_2 at atmospheric pressure except Run #23 (100 psig).

H (Hard):	Just a few particles fall off the tray. Moderately difficult to remove with spatula.
V (Very Hard):	All particles stick to the tray. Must be scraped off with spatula. Difficult to remove.

At 310°C no physical changes in the coal were observed and indeed the coal was not agglomerated after cooldown. At 420°C some particle movement was noted, but no rounding or bubbling was observed. The cooled material was only slightly agglomerated. A slow heating ramp to 606°C produced rounding with moderate swelling and contracting of individual particles. Some bubbling was observed as volatiles broke through the coal particle surface. On cooldown the coal sample was a hard agglomerate. Finally, a fast heating ramp to 530°C produced rapid movement of particles with severe rounding, swelling and bubbling, allowing the individual particles to assume spherical shapes as rapid devolatilization occurred. The final product was severely agglomerated.

The temperature at which movement of the coal particles was first observed was considered here as the agglomeration temperature of the coal. The agglomeration range of the coal was the temperature from initial particle movement to the point at which the coal sample ceased to exhibit any further change. The time duration of agglomeration was a function of the rate at which the coal was heated. The agglomeration temperature and range were measured for two major agglomerative coals, Pittsburgh #8 (PSOC-293) and Pennsylvania B (PSOC-337), at different pressures, gas compositions and heating rates. These data are summarized in Table 2. In general the agglomeration temperature did not vary extensively for the coals at reaction conditions studied. The lowest agglomeration temperature was 353°C for PSOC-337 small particle size, 76°C/minute heating rate, 0 psig in 100% nitrogen. The highest agglomeration temperature was 504°C for PSOC-337 large particle size at 76°C/minute, 100 psig in 100% nitrogen. The average agglomeration temperature for all tests listed in Table 2 was 412°C with an average agglomeration temperature range of 412 to 562°C.

Table 2. Summary of Data Collected for Coal Agglomeration Range and Temperature Determination

Run Number	Coal Type/ Size*	Pressure (psig)	Atmosphere (% N_2)**	Heating Plate (^oC min^{-1})	Maximum Temperature (^oC)	Agglomeration Range (^oC)	State of Agglomeration	Sample Weight Loss (%)
43	Pittsburgh #8/S	0	100	10	610	438-453	H	26.2
44	Pittsburgh #8/S	107	100	10	662	392-500	V	32.8
45	Pittsburgh #8/S	203	100	10	642	415-544	V	25.9
46	Pittsburgh #8/S	302	100	10	653	414-638	V	26.5
47	Pittsburgh #8/L	0	100	10	612	462-612	H	15.5
48	Pittsburgh #8/L	105	100	10	610	415-610	H	17.3
49	Pittsburgh #8/L	305	100	10	650	410-650	H	17.7
51	Pittsburg #8/S	0	70	10	600	452-567	M	29.6
50	Pittsburg #8/S	109	70	10	620	422-497	H	32.9
54	Pittsburgh #8/S	0	100	5	650	397-638	H	31.1
55	Pittsburgh #8/S	202	100	5	575	391-483	H	25.2
53	Pittsburgh #8/S	301	100	5	630	397-603	H	30.65
25	Pittsburgh #8/S	0	100	76	530	403-520	V	30.24
27	Illinois #6/S	0	100	76	560	386-518	S	24.21
28	Pennsylvania B/S	0	100	76	552	353-539	V	33.54
33	Pittsburgh #8/L	105	100	76	556	358-553	V	14.6
37	Pennsylvania B/4	101	100	76	626	504-626	V	13.4

*Small -32 +42 mesh
Large -8 +10 mesh

**Balance Hydrogen

4.2 ANALYSIS OF PHYSICAL BEHAVIOR OF COAL

The most frequently observed physical changes in coal particles during severe agglomeration usually progressed through several distinct steps:

Temperature Range 25° to 400°C

Step 1 — No particle movement. Inertinite macerals deposit charcoal like black powder on tray surface at approximately 270°C.

Temperature Range 400° to 500°C

Step 2 — Slight particle movement. One or several particles shift position quickly.

Step 3 — More particles shift position. Some particles begin to lose sharp edges.

Step 4 — Continued rounding of some particles. A few particles begin to swell with slow rocking movement.

Step 5 — Particles begin to alternatively swell then shrink as gas bubbles form and break within the particles. Many particles begin to fuse together at this point.

Step 6 — All previous particle identity is lost. Individual particles assume spherical shapes while agglomerate particles melt into indivisible mass.

Temperature Range 500° to 650°C+

Step 7 — Bubbling slows down and particle movement stops. Coal particles are fully agglomerated.

A series of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) tests were conducted on all four coals at two heating rates in an effort to correlate the physical changes described above with sample weight loss and endothermic reactivity enthalpy. In addition, these data were used to help identify the major maceral constituents responsible for agglomeration. The TGA and corresponding DTA scans are presented in Appendix B. In general, the region of maximum weight change in the TGA scan corresponds to the region of maximum endothermic reactivity for each coal tested. In Table 3 the temperature ranges over which these changes were noted are listed along with the agglomeration range measured in the hot stage reactor. In every case the region of maximum particle agglomeration corresponded to the regions of maximum weight change and endothermicity.

Table 3. Comparison of Temperature Ranges of Maximum Change for TGA, DTA and Hot Stage Data

Coal Type/ Reaction Conditions(1)	TGA(2) Temperature Range (°C)	DTA(3) Temperature Range (°C)	Hot Stage Tests Agglomeration Range (°C)
Pittsburgh #8 76°C/min	440-590	10-560	403-520
Pennsylvania B 76°C/min	460-610	410-560	353-539
Pittsburgh #8 10°C/min	410-590	410-600	438-544
Pennsylvania B 10°C/min	410-540	440-635	353-539
Illinois #6 10°C/min	420-530	420-595	None observed
Upper Block 10°C/min	410-560	435-575	None observed

(1) Conducted in 100% N_2

(2) Temperature range over region of maximum loss in weight

(3) Temperature range over maximum endothermic reaction

This correlation is exemplified in Figure 5 where photomicrographs of the coal particles corresponding to the temperature ranges of interest are added to the TGA and DTA curves. The major phases of agglomeration can be observed in these views taken at 40X magnification in the hot stage reactor. Initial weight loss to about 400^{0}C caused by moisture and surface condensed volatiles corresponds to step 1 with no physical changes in the coal noted. The DTA curve shows a sharp endotherm at 140^{0}C because of moisture loss. From 400^{0} to 500^{0}C weight loss increases substantially as the particles go through rapid devolatilization described in steps 2 through 6. Maximum endothermic reaction occurs in this region. Past 500^{0}C substantial weight loss still occurs after coal particles reach the fully agglomerated state described in Phase 7 and some endothermic changes are still observed in this region.

Although extensive dilatometer tests have been conducted on a wide variety of coals by Chermin and Van Krevelen(2) the video data collected with the hot stage reactor allowed a unique opportunity to analyze individual particle changes as a function of temperature and weight loss when coupled with TGA information. A two-dimensional surface area analysis of selected coal particles in microphotographs taken from the video data was conducted and is presented in Figure 6. The data are presented as normalized two-dimensional particle surface area (ratio of area at temperature to initial particle area) versus particle temperature. These surface area data are only in the x-y plane. No information was obtained for particle changes in the vertical z direction, hence, these data cannot yield a total particle volume change. Note from these data, most particles underwent maximum swelling in the 440^{0} to 500^{0}C range before obtaining their final size between 500^{0} to 580^{0}C. All but two of the particles showed a net reduction in two-dimensional surface area. Maximum particle swelling of nearly 70% and shrinkage of 65% were measured. These normalized surface area data were replotted in Figure 7 as a function of percent carbonization (ratio of weight loss at temperature to final weight loss at 800^{0}C) of the total sample to determine at what stage during the carbonization process these particle changes took place. In the first one-third of carbonization (35%) little or no particle changes occurred. Between 35 and 65% maximum swelling was observed. The particles attained their final configuration at

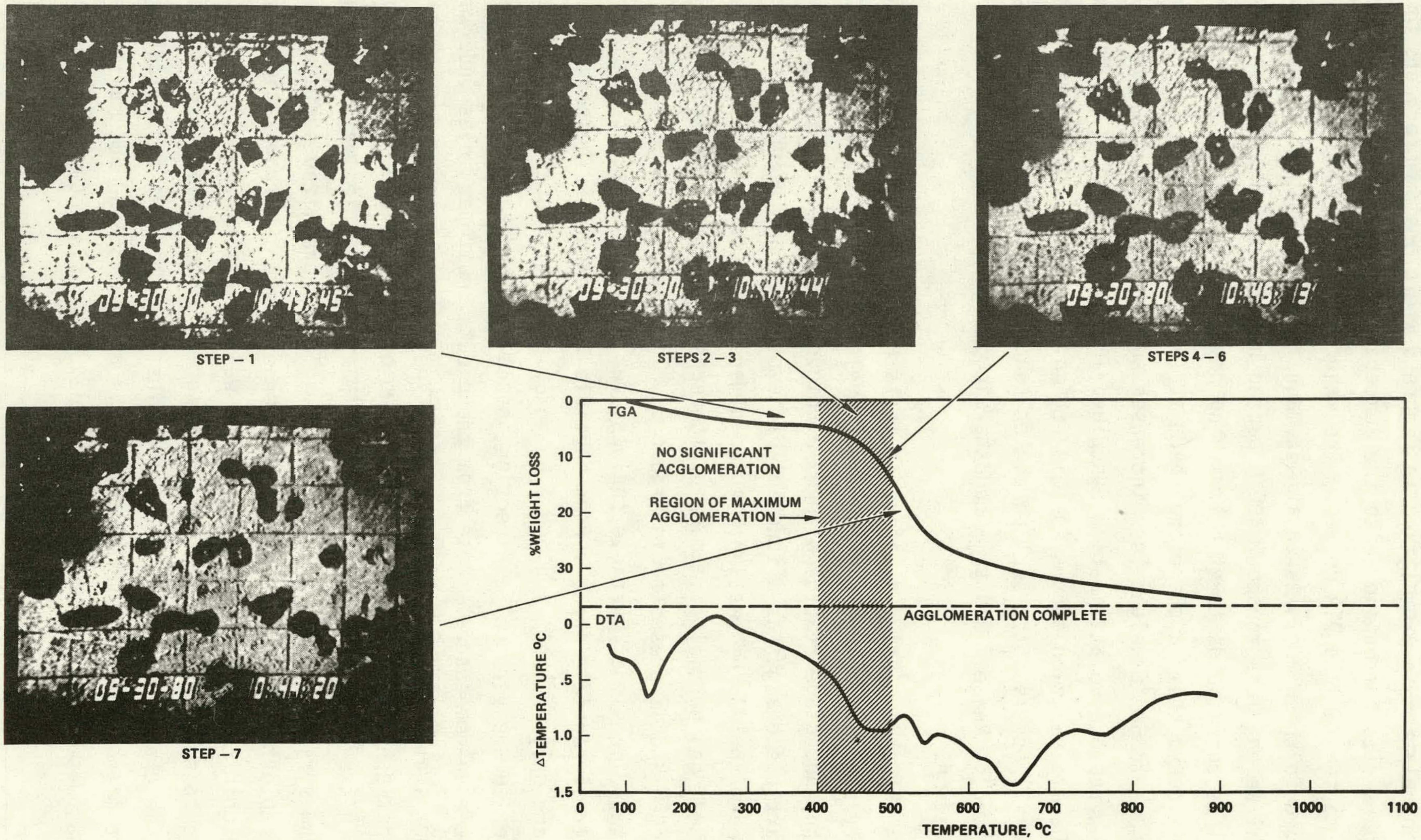


Figure 5. Correlation of Video Microphotographs of Agglomeration with TGA and DTA Tests

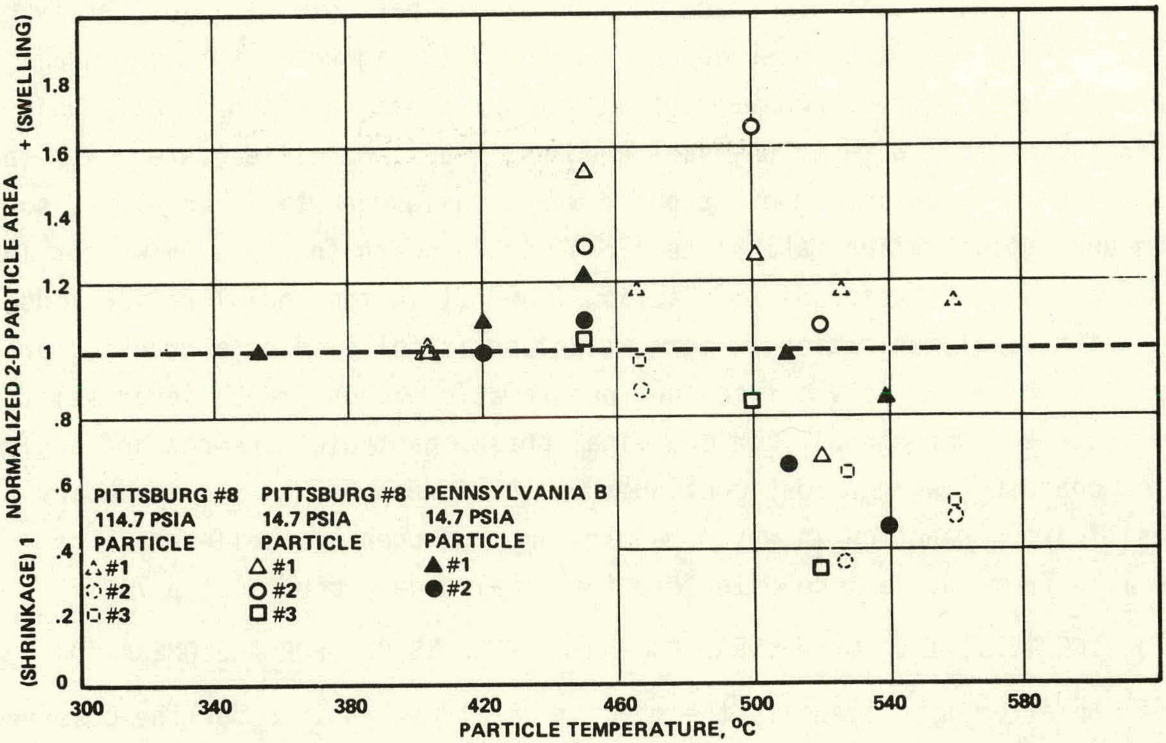


Figure 6. Correlation of Particle Size Changes with Temperature

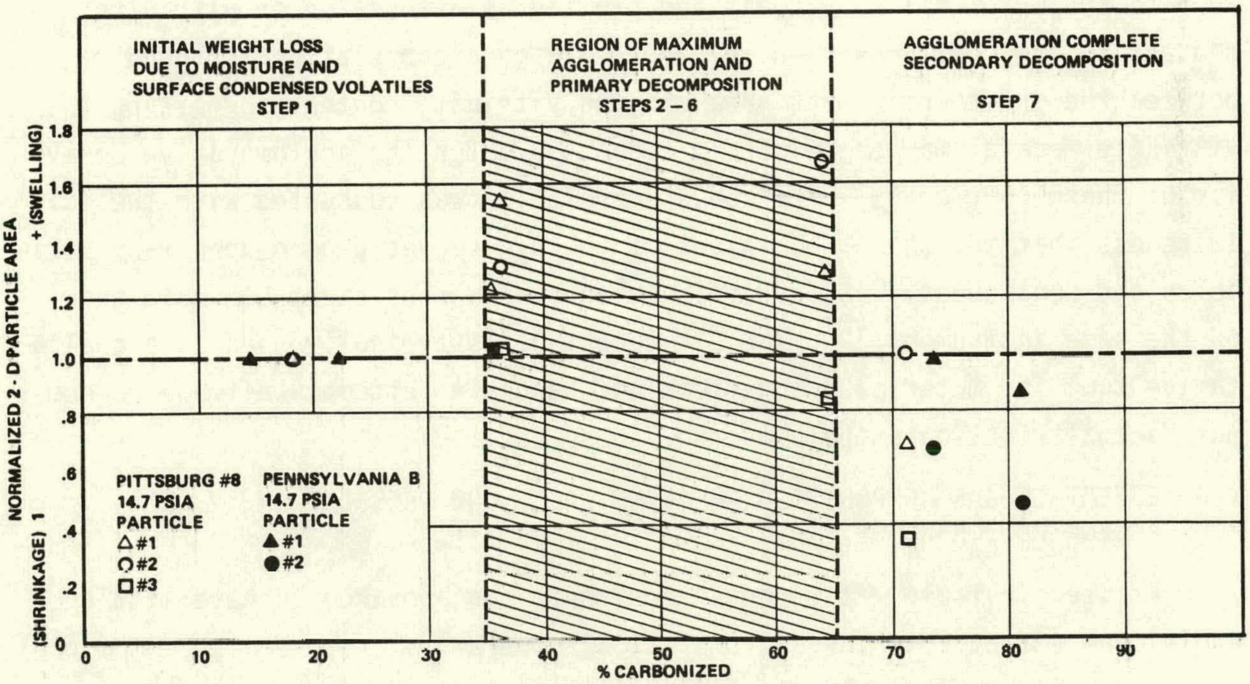


Figure 7. Correlation of Particle Size Changes with Percent Carbonization

70 to 80% carbonization. These data on single particle behavior verify on a microscale what was observed and presented in Figure 5, that the coal carbonization process consists of an initial phase in which a small weight loss is recorded with no physical changes in coal particles (step 1). This is followed by an intermediate phase where maximum particle movement, swelling and agglomeration take place along with a sharp increase in weight loss. This behavior corresponds to reaction I and II in the agglomeration model in which depolymerization to form metaplast is followed by a cracking process in which tar is vaporized and nonaromatic groups are believed split off (steps 2 through 6). In the final phase, particle movement and agglomeration cease but weight loss continues which corresponds to the secondary gasification reaction in which methane and hydrogen are believed to be evolved from the semi-coke to form the final coke product (step 7).

4.3 IDENTIFICATION OF MACERAL COMPONENT RESPONSIBLE FOR AGGLOMERATION

An attempt to identify the major maceral responsible for the observed agglomeration in the hot stage reactor was made. The endothermic peak areas were computed from the DTA scans in the region of maximum endothermicity 400^0 to 600^0C for all four coals and plotted as a function of vitrinite content in the coal. As seen in Figure 8 a good correlation is found between the endothermic peak area and the vitrinite content suggesting the vitrinite maceral may be primarily responsible for the agglomerative behavior of these four coals. The above correlation was conducted with the full awareness that the shape and extent of the DTA curves depend upon many variables and consequently it is difficult to obtain consistent DTA data even on the same instrument.(3) The DTA technique is typically used as a qualitative tool for material identification, hence, no attempt was made to compute actual reaction enthalpies from these data.

4.4 EFFECT OF GAS COMPOSITION, HEATING RATE, AND PRESSURE ON AGGLOMERATION RANGE

As seen in Table 2 the presence of hydrogen appeared to have little additional effect upon the agglomeration temperature or severity of the coal agglomeration process. Similarly, the agglomeration temperature was not affected by the rate of heating although the severity of agglomeration was greater for faster heating rates.

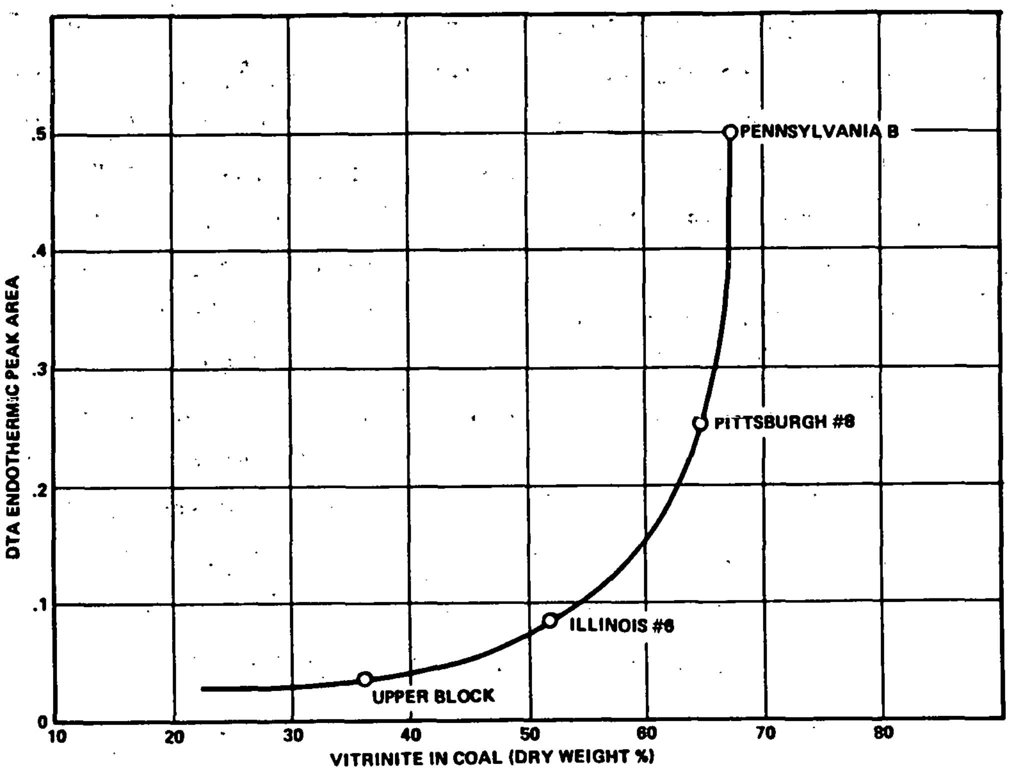


Figure 8. Correlation of Endothermic Peak Area with Vitrinite Content of Coal

The effect of pressure on the carbonization process was studied with Pittsburg No. 8 coal (PSOC-293). The temperature range over which this coal remained in its plastic or agglomerating phase appeared dependent upon the pressure at which the carbonization was carried out in the hot stage reactor. A plot of the agglomeration temperature range versus the reaction pressure for two heating rates and two particle sizes is shown in Figure 9. Higher pressure appeared to induce a greater agglomeration range while a twofold change in heating rate did not appear to effect this dependency. The smaller size coal particles went through a minimum in agglomeration temperature range at 100 psig while the large particles followed a linear dependence.

This observed dependence on pressure is probably a combination of both mass and heat transport limitations within the coal sample. D.B. Anthony et al.(4) has developed an approximate model for the effect of secondary reactions on yields of volatiles which shows that a net reduction in total volatiles yield is obtained with increasing pressure. This result implies that increased pressure inhibits the rate of volatiles release extending the period of time over which the volatiles remain in contact with the coal.

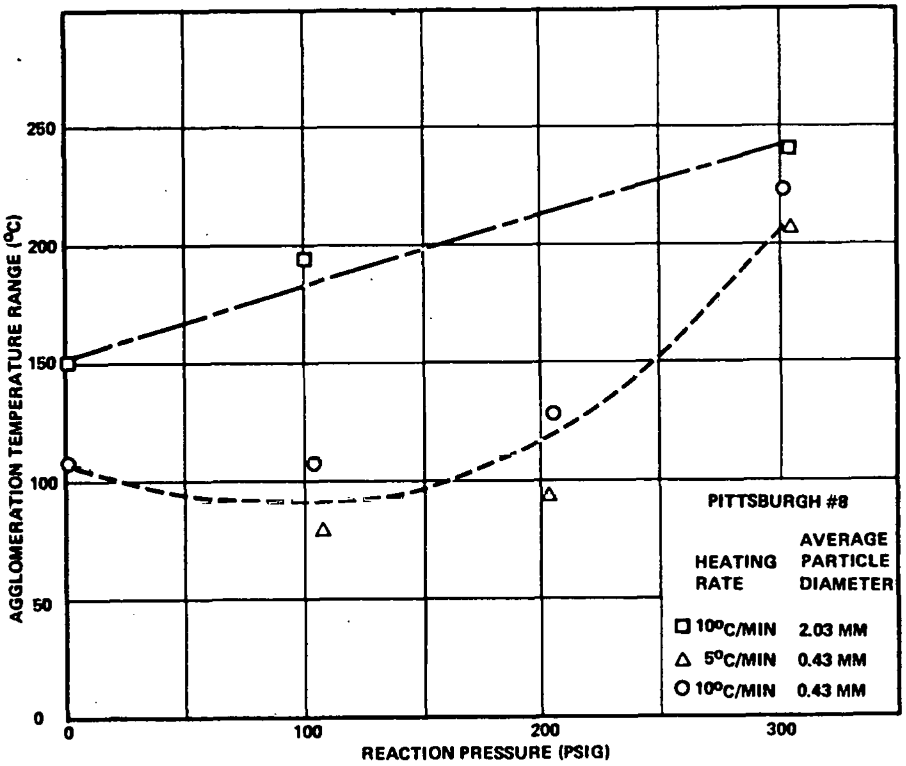


Figure 9. Dependence of Coal Agglomeration Range on Inert Gas Pressure

Additionally, Lewellen's(5) bubble transport model for volatiles flow in plastic coals assumes that the plasticity of the agglomerating coal is directly proportional to the concentration of the metaplastic material formed by pyrolysis and released into the bubble phase at a mass transfer controlled rate. Consequently, a slower volatiles release rate keeps the coal in its plastic or agglomerating condition over an extended temperature range. A possible physical description of this process assumes that increased inert gas pressure inhibits the mass transport rate of volatiles leaving the coal particles by closing off the microporous structure of the coal in this plastic phase. Regions of high pressure gas must now expand against increased viscous forces as well as higher external pressure in order to leave the particle surface and, hence, higher temperatures are required to force the devolatilization.

The differences in agglomeration range between the large and small coal particles may be tied to heat transfer limitations within the large particles. A detailed analysis of heat transfer in the hot stage reactor was conducted and is presented in Section 6.5.3. This analysis revealed that a substantial temperature gradient is imposed upon the large particles due to nonuniform heating in the hot stage. The gradient is small for the smaller particles. In a qualitative sense this accounts for the somewhat greater temperature ranges over which agglomeration occurred for the large particles since higher hot stage temperatures are required to overcome the temperature gradient in the coal. The effect of pressure on the temperature gradient was determined (Section 6.5.3) as minimal for both small and large coal particles.

In addition to the differences in agglomeration range between the large and small coal particles there also exists a substantial difference in the total weight loss between the two particle sizes. Average weight loss for the large 1.68 to 2.38 mm particles was 15.7% compared with 29.0% for the small 0.35 to 0.50 mm particles. This may again be explained by heat transfer limitations within the large particles. W. Peters(6) provided an empirical equation to explain the dependence of the volatiles release rate from coal on the particle diameter assuming internal heat transfer controlled devolatilization, which is probably true for the large particles in the hot stage reactor. The equation for particles of 0.25 mm to 2.0 mm diameter is:

$$dV/dt = \frac{0.03\ (Ta - 330)}{d^{0.26}}$$

where

Ta = external coal temperature, ^{o}C

d = particle diameter, mm

V = volatiles lost from particle to t

t = time, s

This equation describes the propagation of an evaporation front through the particle with the rate of volatiles release controlled by the overall temperature gradient. In Table 4 the ratio of dV/dt (small particles) to dV/dt (large particles) is compared to the weight loss ratios of the small and large particle samples computed from the data in Table 2. Note the numerical values compare favorably for all three sets of data supporting the

Table 4. Comparison of Theoretical and Experimental Weight Loss

Average Particle Diameter (d, mm)	Reaction Pressure (psig)	Final Coal Temperature (Ta, ^{o}C)	Experimental Weight Loss (W %)	Calculated Weight Loss* (dW/dt)	**Experimental Weight Loss Ratio** $\left(\frac{W_s}{W_L}\right)$	Calculated Weight Loss Ratio $\left(\frac{dW_s/dt}{dW_L/dt}\right)$
0.425	0	610	26.2	10.5	**1.69**	1.50
2.03	0	612	15.5	7.0		
0.425	107	662	32.8	12.5	1.89	1.79
2.03	105	610	17.3	7.0		
0.425	302	653	26.5	12.1	1.50	1.51
2.03	305	650	17.7	8.0		

$$*dW/dt = \frac{0.03\ (Ta - 330)}{d^{0.26}}$$

argument that internal heat transfer is governing volatiles release for the large particles in the hot stage reactor.

This conclusion is further supported by the isothermal oven tests conducted in the Burrell furnace for PTG model calibration (Section 6.4). In these tests the coal samples were heated uniformly in a boat configuration (Figure 4) with a low nitrogen gas purge directed over the sample surface. These data show no differences in weight loss between the large and small particle coal.

Thus, the weight loss variations between the large and small coal particles observed in the hot stage reactor tests may be a consequence of the method of heating. This proves to be an important factor when considering various methods of coal pyrolysis in large scale reactors and cannot be ignored if bench or pilot scale reactors are designed for demonstration of the PTG concept.

5. MINIMUM TIME HEATING SCHEDULE DEVELOPMENT

As described in Section 2 verification of the programmed temperature gasification concept depends on the ability to develop a heating schedule which will heat the coal at a rate fast enough to maintain the metaplast concentration at the highest possible value while keeping it just below the critical level to prevent severe agglomeration. This would be the minimum time heating schedule for a coal. The purpose of this phase of the laboratory effort was to develop a minimum time heating schedule for the highly agglomerative coals Pittsburgh No. 8 (PSOC-293) and Pennsylvania B (PSOC-337) and, thus, to verify the PTG concept for the reaction conditions studied.

This minimum time heating schedule was developed for small coal particle samples in the hot stage reactor at 0, 100, 200, and 300 psig in both 100% N_2 and 30% H_2/70% N_2 environments. It was decided that the simplest heating profile possible, consisting of not more than three ramps and three isothermal periods, should be used since a complex heating schedule could probably not be duplicated in larger scale fixed-bed gasifiers. Hence, the heating schedule would consist of the following:

1) An initial fast ramp to just below the agglomeration temperature of the coal, T_2
2) Near isothermal condition at T_2 for fixed time
3) Slow ramp up through agglomeration zone, T_3
4) Moderate ramp up past agglomeration zone, T_4
5) Isothermal at that temperature for short time
6) Cooldown

The initial approach to determining a minimum time heating schedule for these coals was to obtain a successful nonoptimized heating profile and then selectively reduce the times for isothermal and slow ramp heating. The process was continued until the minimum time heating schedule (MTHS) for carbonization without severe agglomeration was attained. Several iterations were required to optimize the initial heating profile. This resulted in a reduction of the total time for carbonization without severe agglomeration from approximately 130 minutes for the initial heating schedule to 45 minutes for the minimum time heating schedule.

The experimentally determined minimum time heating schedule applicable to the pressure and gas conditions stated above is shown in Figure 10 and consisted of the following:

1) Fast ramp to 390°C in 8 minutes (T_2 = 390°C)
2) Near isothermal at 410°C for 15 minutes
3) Slow ramp to 470°C in 12 minutes (T_3 = 470°C)
4) Moderate ramp to 610°C in 10 minutes (T_4 = 610°C)
5) Isothermal at 610°C for 4 minutes
6) Cooldown

This heating schedule produced only moderate agglomeration in PSOC-293 and PSOC-337 at 300 psig in 100% N_2 and 30% H_2 gas environments. Illinois No. 6 coal (PSOC-282) was nonagglomerating under those conditions. A heating schedule was considered successful if it produced a final product which was not "V" or very hard agglomerate as defined by the physical tests described in Section 4, and whose sample weight loss exceed the 65% carbonized limit (21.5% weight loss). As seen in Figure 10, the coal is 36% carbonized midway between T_2 and T_3, reaches 59% carbonization near T_3 and finishes at 83% carbonization at T_4. From Figure 7 it can be seen that the coal is essentially out of the agglomeration range shortly past T_3.

In Table 5 the MTHS described above is compared with the other heating schedules conducted in the hot stage reactor and Burrell furnace. Note the time required for carbonization to produce a moderate agglomerate is only 45 minutes using the MTHS with a 24 to 75% improvement in time over the other three heating schedules which produce hard or very hard agglomerates.

Increased pressure had a negative effect on the success of a heating schedule for preventing agglomeration. The heating schedule defined above worked for 300 psig and, thus, worked for all pressures below 300 psig. However, a 36-minute heating schedule was developed for atmospheric pressure which was not successful at 100 psig or higher. The longer agglomeration ranges associated with higher pressures (Figure 9) may force the tailoring of the minimum time heating schedule to the pressure at which the fixed bed gasification system operates.

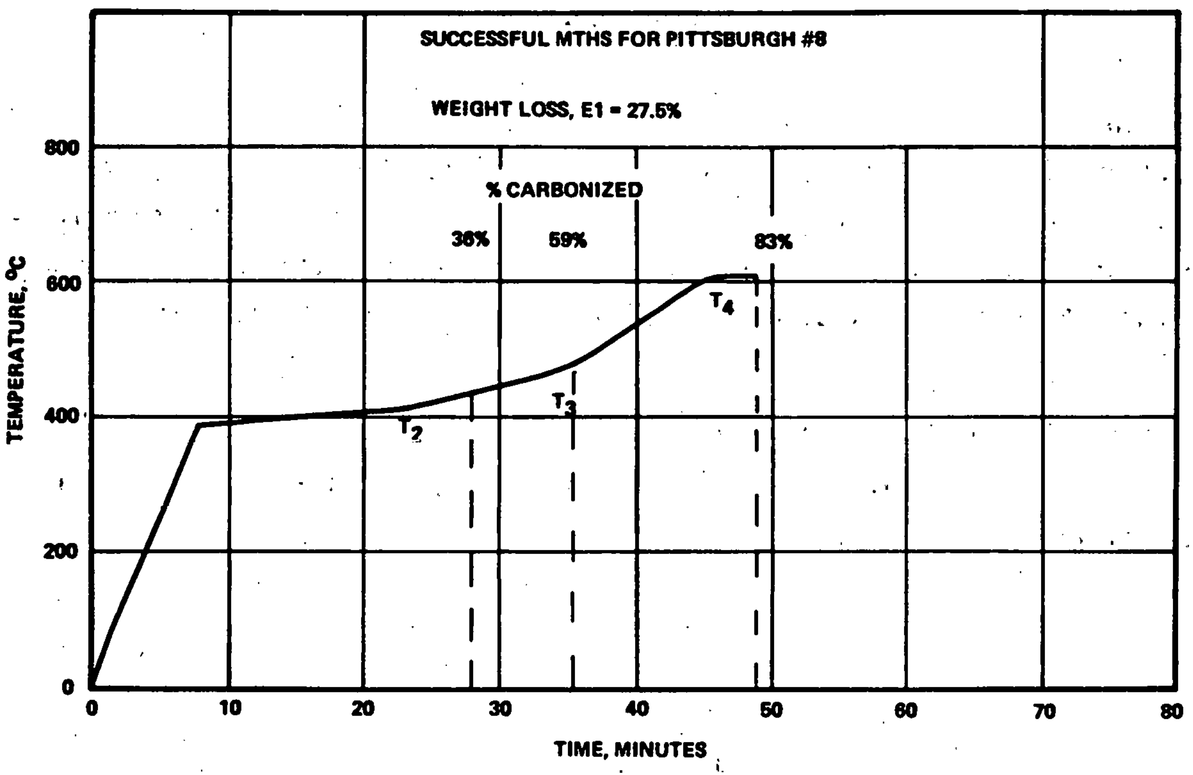


Figure 10. Temperature-Time Curve for Experimentally Determined Minimum Time Heating Schedule

Table 5. Comparison of MTHS to Ramp and Isothermal Heating

Heating Schedule	Maximum Temperature Obtained (°C)	Time to Temperature (min)	Weight Loss (%)	State of Agglomeration	Improvement in Time (%)
MTHS*	610	45	27.5	M	--
Ramp 10°C/min	645	59	26.5	V	24
Ramp 5°C/min	625	105	30.7	H	57
Isothermal**	430	180	21.8	H	75

*Described in text

**Conducted in Burrell furnace, all others in hot stage reactor

6. PTG MODEL REFINEMENT

In this section the mathematical formulation of the programmed temperature gasification model is presented. Experimental data from the oven tests are used to calibrate the model for prediction of the agglomerative behavior of the coal. These predictions are checked against the remainder of the TRW oven and hot stage data plus the results of Harrison and Dulhunty.(7)

6.1 MATHEMATICAL DESCRIPTION OF THE METAPLAST THEORY

The rates of metaplast formation and decomposition can be represented quantitatively as follows:

$$\frac{dP}{dt} = - k_1 P \qquad (1)$$

$$\frac{dM}{dt} = k_1 P - k_2 M \qquad (2)$$

where:

P = amount of metaplast forming material in coal expressed as fraction of original coal

M = amount of metaplast expressed as fraction of original coal

t = time (min)

k_1, k_2 = reaction rate constants (min^{-1})

The reaction rate constants are assumed to have Arrhenius-type dependencies on temperature, or:

$$k_i = k_{i0} \exp [- (E_i/RT)] \qquad (3)$$

where:

k_{i0} = frequency factor for reaction i (min^{-1})

E_i = activation energy of reaction i (kcal/mole)

R = gas constant (kcal/mole ^oK)

T = absolute temperature (^oK)

Table 6 lists estimates from several sources of the activation energies for the two reactions. The estimates suggest that E_2 equals 50 ±8 kcal/mole and that E_1 is between 50 and 70 kcal/mole.

6.2 RELATIONSHIP BETWEEN METAPLAST THEORY AND COAL AGGLOMERATION

The PTG model associates agglomeration tendency with the maximum metaplast concentration experienced during any given heating schedule. Thus, to examine the behavior of the model, the maximum metaplast concentration for isothermal heating was calculated. The effect of other heating schedules can then be inferred.

For the isothermal case, the maximum metaplast concentration and the time required to reach the maximum can be obtained from the analytical solution of Equations (1) and (2) for the initial conditions:

$$M = 0 \text{ and } P = P_o \text{ at } t = 0$$

The resulting expressions are:

$$\frac{M_{max}}{P_o} = \left(\frac{k_1}{k_2}\right)^{k_2/(k_2 - k_1)} \qquad (4)$$

Table 6. Estimates of Activation Energy for Metaplast Forming and Decomposing Reactions

Source	Method	Activation Energy (kcal/mole)
Fitzgerald(1)	Fluidity - time relationships	$E_2 = 50$
Fitzgerald(1)	Fluidity - time relationships	$E_1 = E_2$
Fitzgerald(8)	Elastic properties of coal in plastic state	$E_2 = 50 \pm 8$
Kirov, Stephens(9)	Geisler plasticity versus time	$E_1 = 70$
Kirov, Stephens(9)	Geisler plasticity versus time	$E_2 = 54$
Kirov, Stephens(9)	Bond energy of average C-C bond in mineral oil	$50 < E_2 < 60$

$$t_{max} = \frac{\ln(k_2/k_1)}{(k_2 - k_1)} = \frac{1}{\text{log mean }(k_1, k_2)} \quad (5)$$

where:

M_{max} = maximum metaplast formed

t_{max} = time required to reach maximum.

The trends in metaplast formation and decay for various values of k_2/k_1 are shown in Figure 11a. As indicated in the figure, M_{max} increases as k_2/k_1 decreases. Because previous data (Table 6) indicate that E_2 is less than E_1, increasing temperature will result in decreasing k_2/k_1 and increasing maximum metaplast. Equation (5) shows that t_{max} decreases with increasing temperature. Thus, maximum metaplast, maximum fluidity, and severity of agglomeration should increase with increasing temperature, while the time required to reach these conditions should decrease.

The severity of agglomeration for near-isothermal heating was examined by Coalcon(10). Their observations showed increasing severity of agglomeration with increasing temperature as predicted by the model. Isothermal fluidity has been measured by Van Krevelen(11) and the results are shown in Figure 11b. The trend of increasing maximum fluidity with increasing temperature is also qualitatively consistent with model predictions, although the rapidity of the initial fluidity increase shown in Figure 11b may not be explainable by the metaplast theory alone. However, the model predictions for isothermal heating are generally consistent with agglomeration and fluidity observations if E_1 is larger than E_2.

Harrison and Dulhunty(7) observed the severity of agglomeration as a function of ramp heating rate for five different coals. In all cases they found that the severity of agglomeration increased with increased heating rate. Because increasing the heating rate is equivalent to increasing the temperature at which maximum metaplast concentrations are reached, the model predictions are consistent with these observations if E_1 is greater than E_2. Changes in Geisler fluidity for ramp heating have been observed by Kirov and Stephens(9), Van Krevelen(11), and Lloyd et al(12). As for isothermal heating, the trends observed for maximum fluidity are consistent

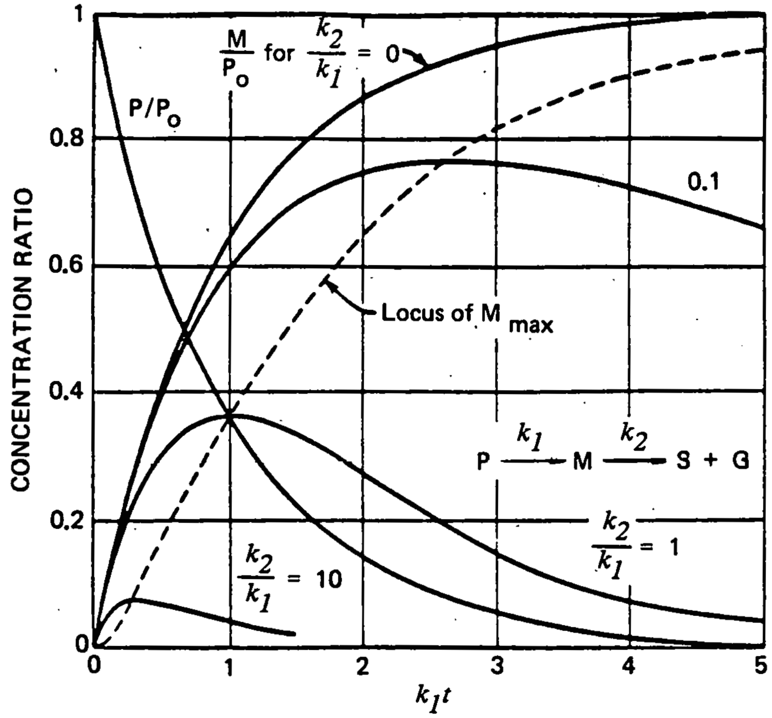


Figure 11a. Variation of Metaplast with Time for Isothermal Case

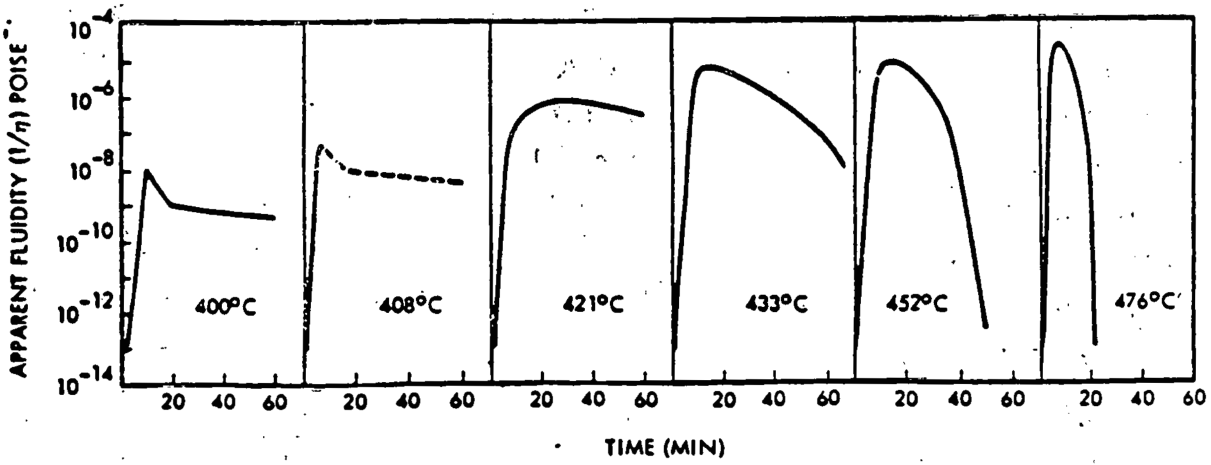


Figure 11b. Gieseler Curves at Constant Temperatures (Medium Volatile Bituminous Coal, 24% Volatile Matter)

with the theoretical variation of maximum metaplast concentration, but the initial rapid increase in fluidity is probably not explainable by the metaplast theory alone.

The effect of particle size on coal pyrolysis behavior has been examined by Anthony and Howard(4). Although different investigators have observed changes in coal pyrolysis behavior with particle size, Anthony and Howard show these effects to reflect heat transfer limitations rather than intrinsic changes in the coal's behavior as observed in this study (Section 4.3). In other words, the temperature of larger coal particles responds more slowly to changes in the temperature of their environment than does the temperature of small particles, so the effective heating rate for large particles is often smaller than the indicated or measured heating rate for a given experiment. Heat transfer from gas to the particle is often the limiting factor.

For the most part, agglomeration and fluidity have been measured in inert atmospheres although the Coalcon data include a few observations in a hydrogen atmosphere. The interest here is limited to reducing atmospheres, and no clear effect of the surrounding atmosphere has been observed. Van Krevelen and Kirov and Stephens speculate that metaplast may be stabilized by the addition of hydrogen. However, whether this saturation with hydrogen will lead to increased or reduced "stickiness", or agglomeration tendency, is not clear. The results of this study indicate that hydrogen has little effect on agglomeration (Section 4.3). Also, the effect of pressure on agglomeration and fluidity has not been extensively investigated. The work presented in this study shows some pressure effect on the agglomeration range of the coal exists.

Different coals have different agglomeration behavior. This can be quantitatively incorporated into the metaplast model by attributing different amounts of metaplast parent material (P_0) to different coals. Petrographic studies of coal by Kirov and Stephens and Van Krevelen show some evidence that the vitrinite and fusinite macerals of coal may be the metaplast precursors and, thus, may be responsible for caking. The work presented in this report (Section 4.2.1) tends to support this conclusion.

6.3 SENSITIVITY OF MODEL PREDICTIONS TO ITS FREE PARAMETERS

As discussed in Section 6.2, setting E_1 greater than E_2 leads to qualitative agreement between the metaplast theory and observed agglomeration behavior. Based on this observation and the data in Table 6, E_1 and E_2 have been set equal to 70 and 50 kcal/mole, respectively. Having established values for E_1 and E_2, two degrees of freedom remain in the PTG model. These can be removed by specifying the temperature at which k_1 equals k_2, and a value for either k_{10} or k_{20}. The approach adopted was to examine the sensitivity of model predictions to both of these specifications to identify the constraint with the least influence on model predictions. This value was then fixed, and the remaining free parameter was varied to find the value that results in the best agreement between the PTG model and the experimental data.

In selecting a measure of model sensitivity to these specifications, it should be recalled that the ultimate objective of the data interpretation is to select a critical metaplast concentration below which the coal bed in the gasifier will not agglomerate. Furthermore, a basic tenet of the PTG model is that the critical metaplast concentration is independent of the carbonization temperature profile, that is, the same critical metaplast concentration applies for isothermal carbonization, varying temperature carbonization, or any combination of these two conditions. Thus, the measure of model sensitivity used in this analysis should reflect a comparison between predicted maximum metaplast concentrations for a varying temperature carbonization and an isothermal carbonization. The selected sensitivity parameter ϕ is the ratio of predicted maximum metaplast concentration for a constantly increasing temperature profile (ramp heating) to the predicted maximum metaplast concentration for isothermal carbonization. In selecting specific temperature profiles for this sensitivity analysis, we noted from the experimental data that the results from isothermal carbonization at 700°K were similar (but not the same) to results from ramp heating at 10°C/minute. Thus, these two temperature-time histories were selected for the sensitivity analysis.

To carry out the sensitivity analysis, values for the sensitivity parameter ϕ were calculated for different values of the temperature at which k_1 equals k_2 and for different values of k_{10}. The actual values selected for these parameters and the calculation results are given in Table 7. In selecting these values, we noted that Van Krevelen concluded from his pyrolysis data that k_1 equaled k_2 at 527°C. Also, the values for k_{10} were selected so that model predictions of the time required to reach the maximum metaplast concentration roughly agreed with the times actually required to reach agglomeration in the isothermal experiments at 427°C. These experimental agglomeration times ranged between 5 and 30 minutes.

Table 7 shows that ϕ is insensitive to the value selected for the temperature at which k_1 equals k_2. Thus, this parameter was fixed at 800°K, and k_{10} was varied to obtain the best fit between model predictions and experimental data. This refinement of the model to provide the best fit with the experimental data is discussed in detail in Section 6.5.1.

It should be noted that the computed value for the maximum metaplast concentration is sensitive to the value of the temperature at which k_1 equals k_2. However, this sensitivity is not significant because, although M_{max} can be interpreted physically, it is used in the PTG model mainly as a mathematical discriminator between temperature profiles that cause caking and those that do not. The value of this critical metaplast concentration is unimportant as long as it adequately discriminates for all practical temperature profiles. The ultimate test of the model is whether such a calculated value of metaplast concentration exists.

Table 7. Model Predictions for Various Values of the Temperature at Which k_1 Equals k_2 and k_{10}

Temperature For $k_1 = k_2$ (°C)	k_{10} (min^{-1} x 10^{-20})	Isothermal Heating at 700°K		ϕ (See Text)
		M_{max}	t_{max} (min)	
527	3.8	0.115	6.6	1.39
527	2.0	0.115	13.0	1.61
485	3.9	0.191	10.0	1.40
485	2.0	0.191	20.0	1.58

6.4 EXPERIMENTAL DATA

TRW obtained experimental agglomeration data using two types of test apparatus, oven and hot stage reactor, which were described in Section 3. Table 8 summarizes the oven data for a Pittsburgh #8 coal and Table 9 summarizes the data for three other coals. Pittsburgh #8 coal was tested in two size ranges: -8, +10 mesh and -32, +42 mesh, and agglomeration behavior was essentially the same for both coal size ranges. Pennsylvania B coal behaved similarly to the Pittsburgh #8. Illinois #6 had considerably less agglomeration tendency, while Upper Block coal was nonagglomerating. Table 10 summarizes the hot-stage reactor data used for model refinement, and includes a brief description of the time-temperature history of each run. A more detailed history is given in Appendix C. In addition to the TRW data, the agglomeration behavior reported by Harrison and Dulhunty(7) was also used in the PTG model development.

6.5 DATA ANALYSIS

6.5.1 Selection of Best Value for k_{10}

The PTG profile as shown in Figure 1C has an isothermal and a controlled heating portion. Therefore, the model was calibrated on isothermal and ramp heating data to determine the best value for k_{10}. Other constants had already been set as discussed in Section 6.3.

All the hot-stage reactor runs with ramp heating rate were used in calibration. All the oven data, where state of agglomeration changed between consecutive (either in time or temperature) runs, were selected. Logical analysis lead to the selection of a base value of k_{10}. Model predictions were then made for the base value and for the base value ±40%.

The base value was selected on the following bases:

- The state of agglomeration at 427°C is between S and H at 5 minutes (runs A-11 and A-12); it reaches H at 30 minutes, and stays at H for up to 180 minutes (runs A13 to A17). Thus, the computed maximum metaplast at 427°C corresponds to a state of agglomeration of H. The maximum value was probably reached between 5 and 30 minutes (closer to 5 minutes than 30).

Table 8. Oven Agglomeration Data for Pittsburgh #8 Coal

Run No.	Temperature (oC)	Particle Size	Time (minutes)	State of Agglomeration	Weight Loss (%)
A1	371	Small	15	N	6.4
A2	371	Small	60	N	7.5
A3	371	Small	180	N	9.1
A4	399	Small	15	N	7.1
A5	399	Large	20	S	8.6
A6	399	Small	30	S	14.2
A7	399	Small	60	S	12.0
A8	399	Large	60	S	11.7
A9	399	Small	180	S	16.4
A10	399	Small	240	S	16.0
A11	427	Small	5	S	9.3
A12	427	Large	5	M	9.5
A13	427	Small	30	H	19.2
A14	427	Large	30	H	18.0
A15	427	Small	60	H	20.3
A16	427	Small	180	H	21.8
A17	427	Large	180	H	20.4
A18	454	Small	5	V	15.5
A19	510	Small	5	V	25.1
A20	510	Large	5	V	29.3
A21	510	Small	15	V	26.6
A22	510	Large	15	V	25.4
A23	510	Small	60	V	27.1
A24	510	Large	60	V	26.3

N = None
S = Slight
M = Medium Hard
H = Hard
V = Very Hard

Table 9. Oven Agglomeration Data for Three Coals

Run No.	Temperature (°C)	Time (minutes)	State of Agglomeration(1)	Weight Loss (%)
Coal A(2)				
B1	371	15	N	5.3
B2	371	60	N	6.2
B3	371	180	N	10.5
B4	399	15	N	8.2
B5	399	30	S	10.4
B6	399	60	S	11.0
B7	399	180	S	16.6
B8	399	240	S	18.5
B9	427	5	S	8.2
B10	427	30	H	10.4
B11	427	60	H	18.5
B12	427	180	H	20.7
B13	454	5	V	13.3
B14	510	5	V	24.9
B15	510	15	V	26.0
B16	510	60	V	27.1
Coal B				
C1	399	5	N	10.3
C2	399	60	N	16.6
C3	454	5	N	18.6
C4	454	60	N	23.9
C5	510	5	S	24.8
C6	510	15	S	27.1
C7	510	60	H	28.5
Coal C				
D1	510	60	N	33.1

(1) See Section 4.1

(2) Coal A = PSOC-337 (Pennsylvania B)
Coal B = PSOC-282 (Illinois #6)
Coal C = PSOC-181 (Upper Block)

Table 10. Hot-Stage Reactor Data

Run No.	Particle Size	Pressure (psig)	Atmosphere %N_2	State of Agglomeration	Weight Loss (%)	Comments
10	Small	111	100	H	28.0	About 5°C/min ramp
21	Small	104	90*	H	26.3	449°C isotherm for 10 minutes, followed by 25°C/min ramp
23	Small	105	100	S	14.3	Isothermal at 423°C
24	Small	105	100	M	27.2	415°C isotherm for 20 minutes, then 10°C/min ramp
28	Small	0	100	V	33.5	64°C/minute ramp, PSOC-337 Coal
29	Small	0	100	S	27.6	Similar to 24 with longer isothermal period
38	Large	0	100	S	22.8	435°C isothermal for 25 minutes followed by 11°C/min ramp
39	Small	0	100	M	29.0	432°C isotherm for 7 minutes then 10°C/min ramp
40	Large	0	100	S	24.4	Same Heating Schedule as Run 39
43	Small	0	100	H	26.2	9.1°C/min ramp
44	Small	106.5	100	V	32.8	11.1°C/min ramp
45	Small	202.5	100	V	25.9	11.2°C/min ramp
46	Small	301.5	100	V	26.5	10.5°C/min ramp
47	Large	0	100	H	15.5	9.36°C/min ramp
48	Large	104.5	100	H	17.3	9.1°C/min ramp
49	Large	304.5	100	H	17.7	10.0°C/min ramp

*10% H_2

- At 454°C the state of agglomeration reaches V in 5 minutes (run A18). From the 427°C deductions and activation energies of 50 and 70 kcal/g/mole, the maximum metaplast concentration at 454°C must have been reached between 1 and 6 minutes (this corresponds to 20% of the 5 to 30 minute range at 427°C). Therefore, the computed maximum metaplast at 454°C should be reached in about 5 minutes and it should correspond to a state of agglomeration V.

- State of agglomeration for runs 43-49 changes from H to V, and these runs were made with an approximately 10°C/minute ramp.

Model predictions consistent with these observations were obtained by setting $k_{10} = 3.841 \times 10^{20}$ min^{-1}. This value corresponds to setting the time required to reach the maximum metaplast concentration at 427°C equal to 6.75 minutes. Predictions for this base value of k_{10} and for ±40% of base are compared to the experimental observations in Figure 12.

For k_{10} equal to 60% of the base value, the lines of demarcation between H and V and between S and H are not clearly defined. In this case, two H observations and two S observations are in the wrong zone. In the base case, only one S observation is in the wrong zone, and even that observation is on the boundary. This observation of S, corresponding to run A-11 (at 427°C and 5 minutes), can be compared to run A-12 (at 427°C and 5 minutes) with observation of M. It is obvious that one of these two observations is going to be in the wrong zone. For k_{10} equal to 1.4 of base case, again only one S observation is in the wrong zone. But four observations ranging from S, M, and H are at the same metaplast level and on the boundary between S and H.

Overall the base value of k_{10} seems best. A 40% higher value is almost as good and a 40% lower value is clearly worse.

6.5.2 Comparison of Model Predictions to Observations

With the calibrated model, predictions for all the TRW runs were made. The agglomeration data from different coals can be interpreted by determining the value of parent metaplast forming material, P_0, in different coals.

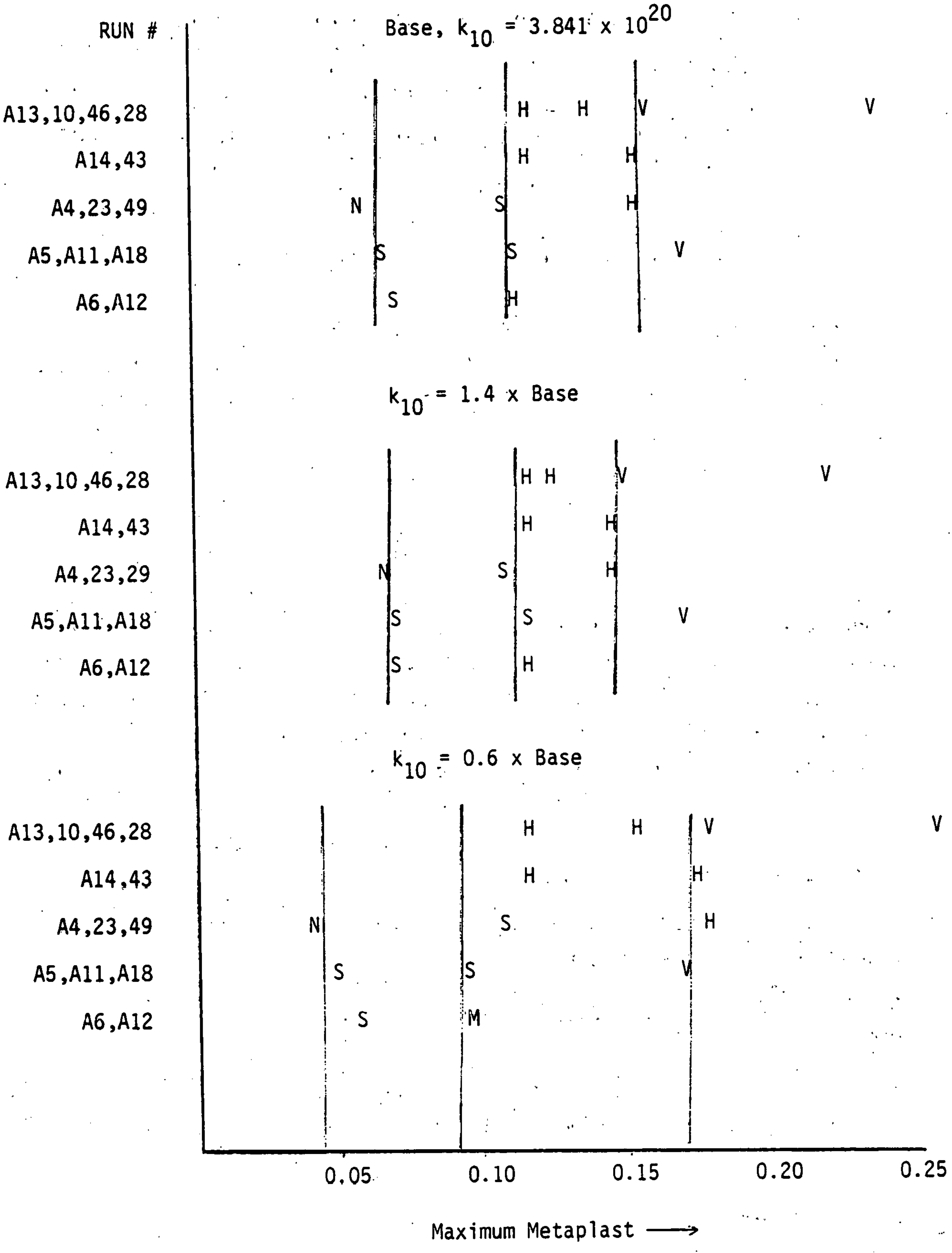


Figure 12. Summary of Model Calibration

TRW evaluated four coals, and the following three relationships between P_o were noted after examining the data.

- The behavior of Pennsylvania B coal (Coal A) is very similar to the behavior of Pittsburgh #8 coal

$$P_o \text{ for Coal A} = P_o \text{ for Pittsburgh \#8} \tag{6}$$

- Oven data at 510°C for Illinois #6 (Coal B) coal ranges from S to H. Because the times for all of the 510°C data are sufficient for the maximum metaplast concentration to have been reached, this level must correspond to the boundary between S and H. This conclusion allows specifying P_o for this coal as:

$$P_o \text{ for Coal B} = 0.364 \times P_o \text{ for Pittsburgh \#8} \tag{7}$$

- Upper Block coal (Coal C) is essentially a nonagglomerating coal. Assigning the value of P_o for this coal equal to 0.15 P_o for Pittsburgh #8 sets the one observation for Coal C at 510°C in the nonagglomerating zone.

$$P_o \text{ for Coal C} = 0.15 \times P_o \text{ for Pittsburgh \#8} \tag{8}$$

Metaplast model predictions for all the TRW data are shown in Table 11 and Figure 13. Because one free model parameter was set from the only data point available for Coal C, there is no way to check the model predictions for this coal. Consequently, this data point was excluded from Table 11 and Figure 13.

Sixty-four data points are shown in Figure 13. These cover three different coals, two different experimental setups, two different particle sizes, four pressure levels, two different atmospheres, and an uncounted number of temperature-time histories. The four agglomeration levels of N, S, H, and V have a definite range of associated calculated maximum metaplast levels. Overall, three observations of S are in the wrong zone and one observation of H is in the wrong zone. Only three model parameters (two for P_o and k_{10}) are adjusted to achieve these predictions. Thus, it is

Table 11. Comparison of Observations to Model Predictions

Run No.	Observation	Maximum Metaplast	Run No.	Observation	Maximum Metaplast	Run No.	Observation	Maximum Metaplast
10	H	0.136	A1	N	0.009	B1	N	0.009
21	H	0.127	A2	N	0.027	B2	N	0.027
23	S	0.109	A3	N	0.040	B3	N	0.040
28	V	0.236	A4	N	0.057	B4	N	0.057
24	M	0.135	A5	S	0.065	B5	S	0.071
29	S	0.119	A6	S	0.071	B6	S	0.072
38	S	0.111	A7	S	0.072	B7	S	0.072
39	M	0.122	A8	S	0.072	B8	S	0.072
40	S	0.122	A9	S	0.072	B9	S	0.113
43	H	0.156	A10	S	0.072	B10	H	0.116
44	V	0.163	A11	S	0.113	B11	H	0.116
45	V	0.164	A12	H	0.113	B12	H	0.116
46	V	0.160	A13	H	0.116	B13	V	0.173
47	H	0.157	A14	H	0.116	B14	V	0.319
48	H	0.156	A15	H	0.116	B15	V	0.319
49	H	0.158	A16	H	0.116	B16	V	0.319
			A17	H	0.116	C4	N	0.063
			A18	V	0.173	C5	S	0.116
			A19*	V	0.319	C6	S	0.116
			C1	N	0.013	C7	H	0.116
			C2	N	0.026			
			C3	N	0.063			

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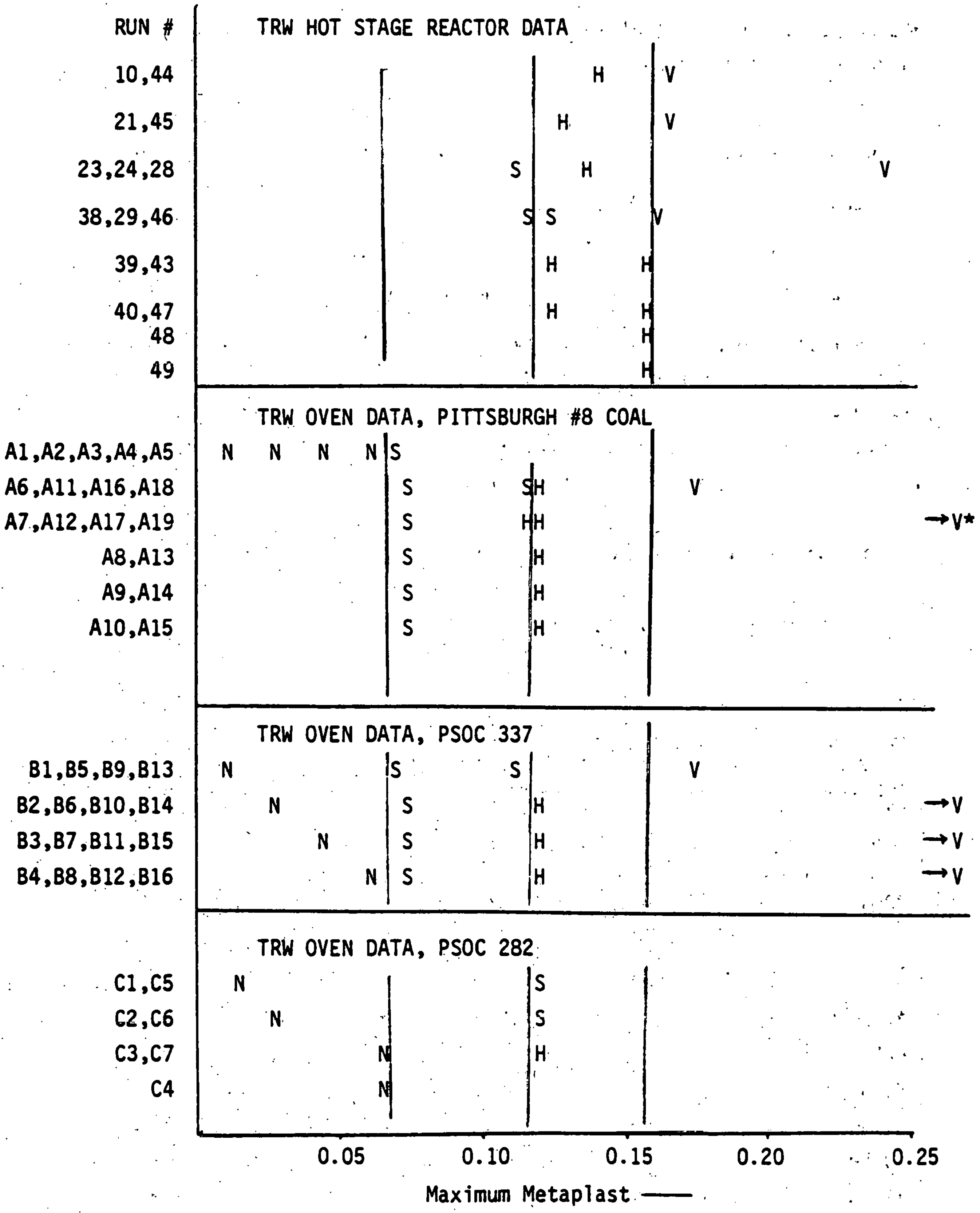
*Prediction and observations for A20-A24 are same as A19



*Six data points

Figure 13. Metaplast Model Predictions for TRW Data

reasonable to conclude that the agreement between the experimental data and the model predictions is excellent.

The different agglomeration zones can be defined as follows:

Very Hard (V)		Maximum Metaplast	>0.160
Hard (H)	0.115<	Maximum Metaplast	<0.160
Slight (S)	0.064<	Maximum Metaplast	<0.115
None (N)	0.064>	Maximum Metaplast	

Harrison and Dulhunty(7) observed agglomeration behavior of five different coals at nine different heating rates. Metaplast model predictions were made for their heating rates. Three of the five coals tested were essentially nonagglomerating. Because the model requires setting one constant, P_o, for each coal, the predictions for these three coals could obviously be made to fit the data. These three coals were not evaluated. For the two caking coals the model predictions are shown in Table 12.

Table 12. Comparison of Metaplast Model Predictions with Harrison, Dulhunty(7) Data

Time for 550°C Increase	Coal #4		Coal #5	
	Observation	Maximum Metaplast	Observation	Maximum Metaplast
4 min	Very Strongly Coherent	0.187	Very Strongly Coherent	0.273
20 min	Strongly Coherent	0.137	Very Strongly Coherent	0.200
1-1/2 hr	Strongly Coherent	0.098	Very Strongly Coherent	0.143
3-1/2 hr	Strongly Coherent	0.080	Strongly Coherent	0.117
6-1/2 hr	Medium Coherent	0.067	Strongly Coherent	0.098
32 hr	Medium Coherent	0.046	Medium Coherent	0.067
64 hr	Slightly Coherent	0.038	Medium Coherent	0.056
99 hr	Noncoherent	0.034	Slightly Coherent	0.050
144 hr	Noncoherent	0.031	Very Slightly Coherent	0.045

For Coal #4 the top medium coherent observation was matched to the top medium coherent observation for Coal #5 by specifying:

$$P_o \text{ (Coal \#4)} = 0.684 \times P_o \text{ (Coal \#5)}$$

The lines of demarcation between various states of agglomeration could then be inferred as:

Very strongly coherent: Maximum metaplast > 0.14
0.08 < Strongly coherent < 0.14
0.038 < Slightly coherent < 0.046
Noncoherent < 0.038.

With these boundaries only two observations (99 and 144 hr) for Coal #5 would be in the wrong zone. Thus, out of a total of 18 observations, the agreement between the agglomeration behavior for the two coals obtained by specifying only one model parameter is excellent. This agreement lends further support to the validity of the PTG model.

6.5.3 Degree of Uncertainty Associated with Model Predictions

The PTG model will ultimately be used to predict the time-temperature profile for the commercial implementation of the concept. The total time required to complete PTG is of commercial significance; therefore, the uncertainty associated with model predictions was examined for its effects on the total time required.

Re-evaluating the model calibration, it was estimated that the uncertainty associated with the value of k_{10} is approximately +30% and -20%. This translates into an uncertainty in the time required for carbonization of +30% and -20%.

In the experimental configurations, there is an uncertainty associated with the measured temperature. For oven experiments, this uncertainty is $\pm 5^{\circ}C$, resulting from variations in oven temperature control. Because of the physical setup the coal temperature is expected to be very close to the oven temperature. Based on a total of 47 experiments, the uncertainty (assuming normal distribution of errors) is $\pm 0.73^{\circ}C$. The corresponding uncertainty in carbonization time is ±4.7%.

For the hot-stage reactor, the copper plate temperature is measured. Because the coal particles see the hot plate on one side and the cool pressure vessel and microscope on the other side, there is an uncertainty associated with the coal temperature. To determine the order of magnitude of this uncertainty the heat transfer from a hot flat copper plate to a single layer of coal particles was calculated. These calculations determined the difference between the measured temperature of the copper plate and the coal temperature. The calculations are summarized in Appendix D.

Based on these calculations, the best theoretical estimate for the temperature difference is about 10^oC for 32-mesh particles. This temperature difference between the copper plate and coal temperature changes with the temperature of the copper plate, size of coal particle, and the operating pressure. Theoretical estimates of these various cases are listed in Table 13. Note that because of the heat transfer limitations, the measured and actual heating rates are different, for example, at 10^oC/min measured rate, the actual heating rate at 0 psig is 9.5^oC/min for 32-mesh particles, but only 8.63^oC/min for the larger particles.

Because heat transfer terms are neglected in the calculations, the actual temperature error in the hot-stage reactor is expected to be less than 10^oC. To assess the effect of this uncertainty, model predictions were calculated assuming a 10^oC lag and a 5^oC lag (and corresponding changes in ramp heating rate). These model predictions are compared to the no-lag calculations in Table 14. Using the lines of demarcation between various states of agglomeration already determined (Figure 12), the number of observations in the wrong zone is two for no lag, two for 5^oC lag, and three for 10^oC lag. Also, runs 29 and 40 are in the wrong zone for all three cases. Overall, it seems that not accounting for a possible temperature lag within the hot-stage reactor has no significant effect on the model parameters already determined.

Considering all three sources of uncertainty, the overall uncertainty for model predictions is +20 to -30% on the time required for PTG. This degree of uncertainty associated with model predictions could be reduced by model refinements. Potential model improvements were analyzed. However, any model improvement effort does not seem justified at this time. The potential improvements are discussed in Appendix E.

Table 13. Steady-State Temperature Response

Measured Condition (psig)	Small (32-42 Mesh) Particles			Large (B-10 Mesh) Particles		
	Temperature of 427°C	Temperature of 457°C	Ramp Heating at 10°C/min	Temperature of 457°C	Temperature of 487°C	Ramp Heating at 10°C/min
0	418°C	446.2°C	9.5°C/min	425°C	450.7°C	8.63°C/min
100	419.2°C	447.8°C	9.54°C/min	428.4°C	454.6°C	8.74°C/min
200	419.5°C	448.2°C	9.56°C/min	429.2°C	455.5°C	8.78°C/min
300	419.6°C	448.3°C	9.58°C/min	429.5°C	455.8°C	8.78°C/min

Table 14. Model Predictions Versus Observations Including Temperature Lag Correction for Hot Stage

Run No.	Observed Stage of Agglomeration	Maximum Metaplast		
		No Lag	Lag = 5°C	Lag = 10°C
10	H	0.136	0.137	0.135
21	H	0.127	0.130	0.139
23	S	0.109	0.101	0.096
24	M	0.135	0.150	0.145
28	V	0.236	0.227	0.227
29	S	0.119	0.132	0.134
38	S	0.111	0.100	0.144
39	M	0.122	0.130	0.137
40	S	0.122	0.141	0.151
43	H	0.156	0.156	0.154
44	V	0.163	0.163	0.162
45	V	0.164	0.164	0.161
46	V	0.160	0.160	0.159
47	H	0.157	0.156	0.152
48	H	0.156	0.151	0.151
49	H	0.158	0.156	0.155

7. COMMERCIAL PTG CONCEPTS

The commercial Programmed Temperature Gasification concept involves three steps:

1) Rapid heat-up to a predetermined temperature
2) Isothermal period of predetermined duration
3) Controlled heat-up from the isothermal temperature to a temperature beyond the agglomeration range.

The isothermal temperature, the duration of the isothermal period, and the required controlled heating rate are determined by the PTG theory.

The PTG treatment schedule may be accommodated in a batch mode or in a continuous mode. The batch processing can follow a minimum time heating schedule. However, in the continuous mode gas-solid flow considerations will require a compromised heating schedule. The total time required for batch processing includes charging and discharging time in addition to treatment time. Overall evaluation including all these factors has not been completed. Preliminary evaluation of required residence time, flow rate, etc., is discussed in this section.

7.1 PTG IN A BATCH PROCESSING VESSEL

Figure 14 shows a conceptual diagram for a batch PTG system. Two or more parallel batch processing vessels are required to provide a continuous feed to the gasifier. The treatment could be carried out in a modified lock-hopper, as shown in Figure 15. PTG vessel size is determined by the gasifier coal requirement, the number of parallel PTG vessels, and the time required for PTG.

In the batch operating mode, coal is fed to the PTG vessel, and a controlled flow rate of gas is initiated. The temperature of the gas is controlled by mixing gasifier raw gas with recycled pyrolysis gas. The gas temperature is controlled so that the coal in the vessel follows the PTG profile. In this mode both the gas flow rate and its temperature can be independently controlled. Therefore, the coal temperature can be controlled at the minimum time schedule.

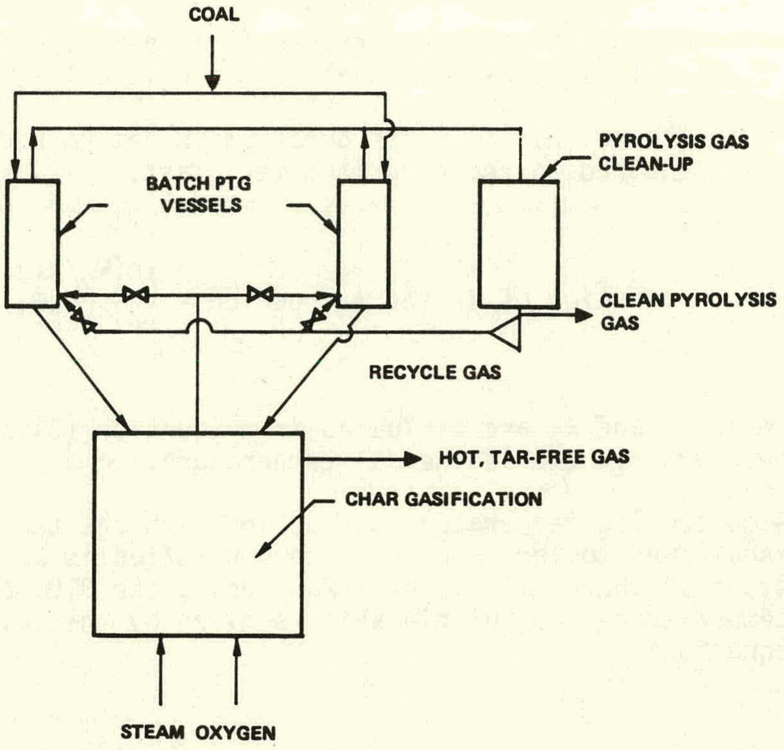


Figure 14. PTG — Batch Processing Vessel

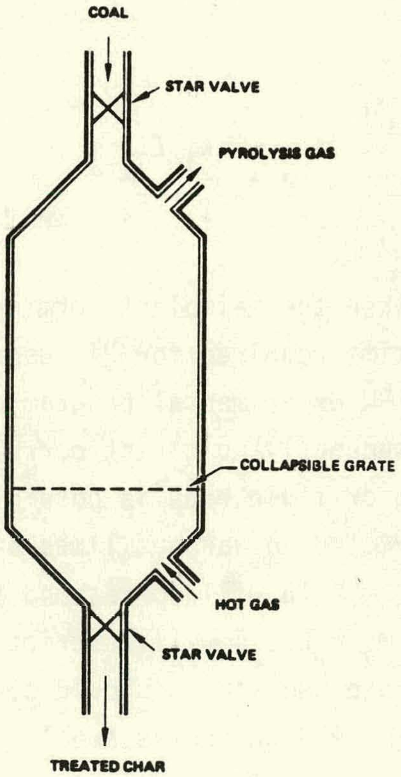


Figure 15. Modified Lock-Hopper for Batch PTG

The minimum time PTG schedule can be described as follows:

1) A rapid heat-up to a temperature (T_1) where the maximum isothermal metaplast is equal to the critical metaplast.

2) An isothermal period whose duration is determined by the time required to reach maximum metaplast:

$$\tau_2 = \text{duration of isothermal period} = \frac{\ln(k_2/k_1)}{(k_2 - k_1)} \tag{9}$$

where k_1 and k_2 are evaluated from Equation (3) at temperature τ_1, the isothermal temperature.

3) A controlled temperature period in which the temperature is allowed to increase while concentration is kept constant at the critical level M_c. Using the PTG model, the temperature-time relationship is given by the following equation:

$$a(t - \tau_2) = \exp\left(\frac{E_1}{RT_1}\right) - \exp\left(\frac{E_1}{RT}\right) \tag{10}$$

where:

$$a = \frac{k_{10}E_1}{E_1 - E_2}$$

The PTG is complete when the metaplast forming material, P, has essentially disappeared. The time required for PTG depends very strongly on the critical metaplast. The TRW experimental program was restricted to small laboratory equipment; consequently no direct correlation to commercial operation in either moving or fluid beds is possible. However, the metaplast amount will be restricted to various lines of demarcation as shown in Figure 13. Thus, using $M_c = 0.16$ will correspond to the state of agglomeration of hard. Similarly, $M_c = 0.115$ will restrict the state of agglomeration to slight. One of these two states should correspond to commercial operation. The minimum-time PTG schedules are listed in Table 15. Both of these schedules look promising for commercial operation. The residence

Table 15. Theoretical Minimum Time PTG Schedule

	Schedule to Stay Just Below Very Hard Agglomerate (V)		Schedule to Stay at Slight (S) State of Agglomeration	
Critical Metaplast	0.160		0.115	
Isothermal Temperature	447°C		427°C	
Isothermal Period	2.1 minutes		6.6 minutes	
Controlled Profile:	Time (min)	Temperature (°C)	Time (min)	Temperature (°C)
1. Fast ramp to T_2	2.1	447	6.6	427
	2.19	448	6.97	428
	2.27	449	7.31	429
2. Near isothermal	2.48	452	8.20	432
	2.74	457	9.30	437
	3.07	467	10.61	447
3. Slow ramp to T_3	3.23	477	11.25	457
4. Moderate ramp to T_4	3.41	552	11.88	502
			11.92	552

time in a Lurgi gasifier is about 1 hour. Therefore, 12 minutes to treat an agglomerating coal seems reasonable. If a state of agglomeration of hard is found to be acceptable in the treatment vessels, the treatment time would be less than 4 minutes.

7.2 PTG IN A MOVING BED

PTG may be carried out in the top portion of a moving bed gasifier using the flow scheme shown in Figure 16. Coal feed to the gasifier enters via lock-hoppers into a holding vessel. Gas bypassing the PTG bed carries coal to the PTG bed via dense phase transport. The incoming coal is heated to the isothermal PTG temperature during the dense phase transport. Both the transport gas and gas passing up the PTG bed leave the gasifier as dirty pyrolysis gas, while tar-free hot gas is withdrawn from the char gasification section. In this flow configuration the dirty pyrolysis gas would be at the PTG isothermal temperature.

Various gas flow rates and temperatures were estimated using a study by Fluor(13) on the design of a dry-bottom Lurgi:

Basis: 100 lb of Eastern Coal
Total Raw Gas Production: 345 lb wet

(1) Hot Clean Gas Production: 95 lb @ 1075°F
(2) Dirty Pyrolysis Gas: 250 lb @ 800°F
(3) Gas Flow through PTG Bed: 50 lb
(4) Transport Gas Flow: 200 lb

Streams designated as 1, 2, 3, and 4 are as shown in Figure 16.

Another way to achieve essentially the same temperature-time profile is shown in Figure 17. The temperature profile of coal and gas is also shown in Figure 17. Various gas flow rates in this case are as follows:

Basis: 100 lb of Eastern Coal
Total Raw Gas Production: 345 lb wet

(1) Hot Clean Gas Production: 255 lb @ 1075°F
(2) Dirty Pyrolysis Gas: 90 lb @ 300°F
(3) Gas Flow through PTG Bed: 50 lb
(4) Bypass Flow around PTG: 40 lb

These streams are indicated in Figure 17.

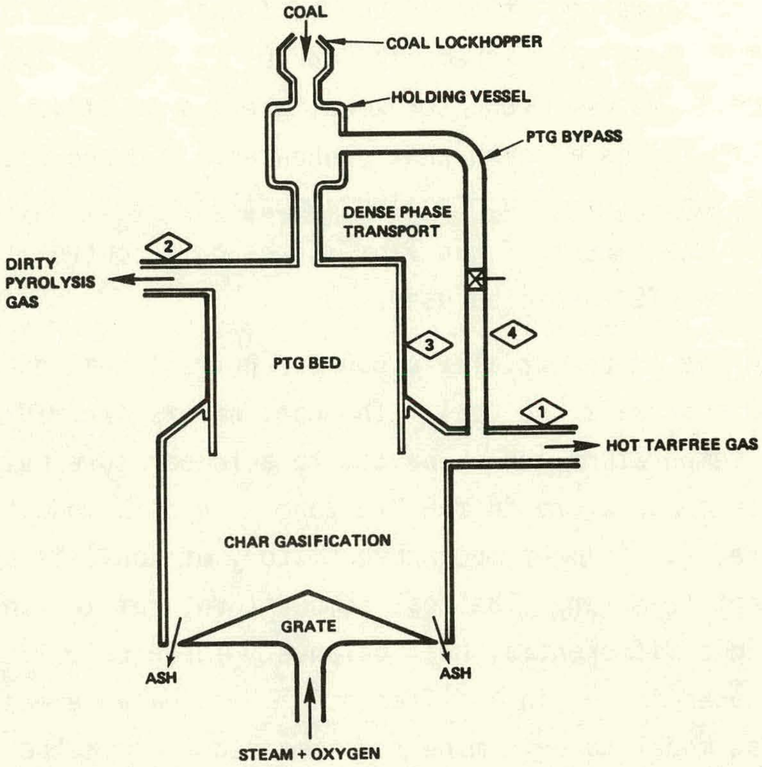


Figure 16. PTG in a Moving Bed, Concept I

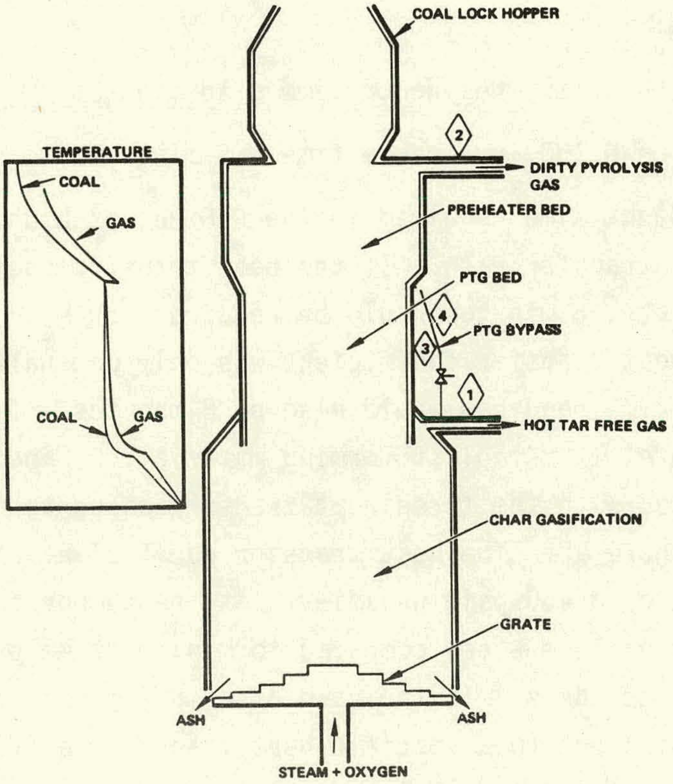


Figure 17. PTG in a Moving Bed, Concept II

A major difference between Concepts I and II is the operation of the coal preheater zone. The scheme in Concept II (Figure 17) represents a counter-current type of preheater zone, whereas the flow scheme of Concept I (Figure 16) is a co-current preheater. PTG bed operation is the same in both concepts. A controlled amount of gas flows through the PTG bed. Because the amount of gas flow is the only control, an approximation to minimum time PTG has to be used.

The PTG bed is essentially a counter-current heat exchanger. Hot gas flows upward and heats the coal. The coal enters the PTG zone at the isothermal PTG temperature and is heated to a temperature well beyond the agglomeration temperature in the PTG zone. In this mode the rate at which coal is heated (the time-temperature history of coal) is determined by the gas-solid heat transfer. The coal temperature profile can be calculated by performing a differential heat balance. These calculations are summarized in Appendix F. This differential heat balance was combined with the metaplast model to determine the time required in the PTG bed. Using the best estimates of the gas-solid heat transfer coefficient for a 450-psig gasifier (Appendix F), the following residence time is required in the PTG bed:

For $M_c = 0.115$, residence time = 16 minutes

$M_c = 0.160$, residence time = 5 minutes.

The residence time required in the PTG bed is highly dependent on the gas-solid heat transfer rate. If the heat transfer coefficient was twice the best estimate, 8 minutes would be required for $M_c = 0.16$. On the other hand, if the heat transfer coefficient was only one-half the best estimate, the residence time required would also be 8 minutes. The variation of coal temperature, T, metaplast forming material, P, and metaplast, M, with time is compared with the three heat transfer cases to the minimum time schedule in Figure 18. The heat transfer coefficient of 20 Btu/hr-ft^2 was estimated for a 450-psig gasifier. As the temperature profile becomes either steeper or less steep compared to minimum time profile, the total time required increases. In the case of a moving bed, the minimum time profile is equivalent to a specific heat transfer coefficient (or gas/solid flow ratio), and the time required for PTG increases on either side of this optimum.

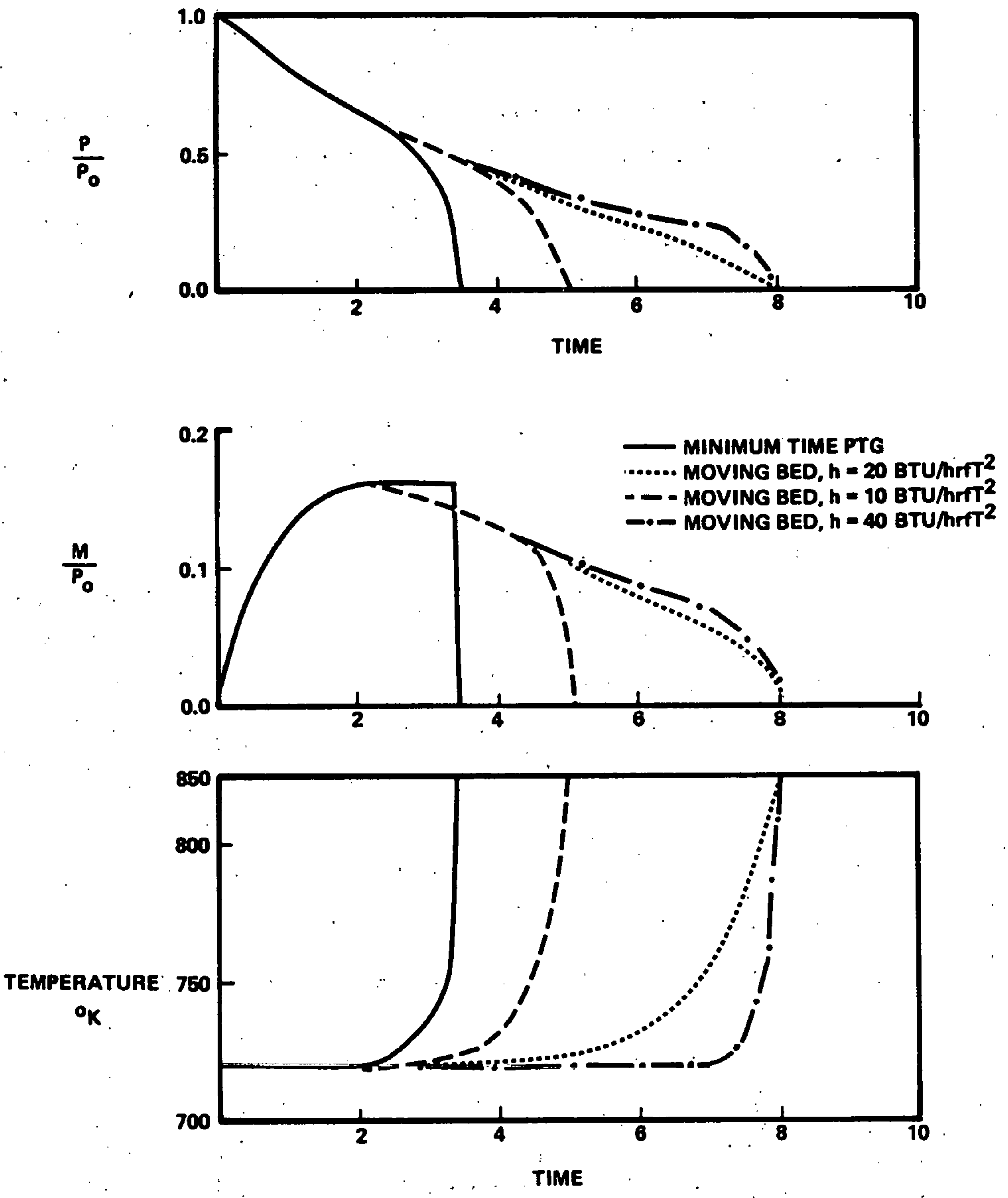


Figure 18. Comparison of Theoretical Minimum Time PTG to Moving Bed PTG

7.3 PTG IN A FLUID BED

PTG can also be carried out in multiple fluid beds of increasing temperature as shown in Figure 19. The residence time in each fluid bed may be controlled to obtain the closest approximation to minimum time PTG.

However, in the case of fluid beds there is another possible approach. There is considerable attrition in a fluid bed. Also, a fluid bed can handle a larger proportion of sticky particles as evident from agglomerating bed gasifiers. These properties of a fluid bed can be used effectively by operating the fluid bed in the middle of the agglomeration range while using a long enough residence time so that most of the bed material is nonsticky char. This approach was used by Colaluca(14) in the Tri-gas process where Pittsburgh #8 coal was successfully gasified by operating the fluid bed at 493°C (920°F) with a 1-hour residence time. According to the PTG model, a nonsticky char is obtained within 1 minute. Thus, at the Tri-gas operating condition, 98.3% or most of the fluid bed material is a nonagglomerating char.

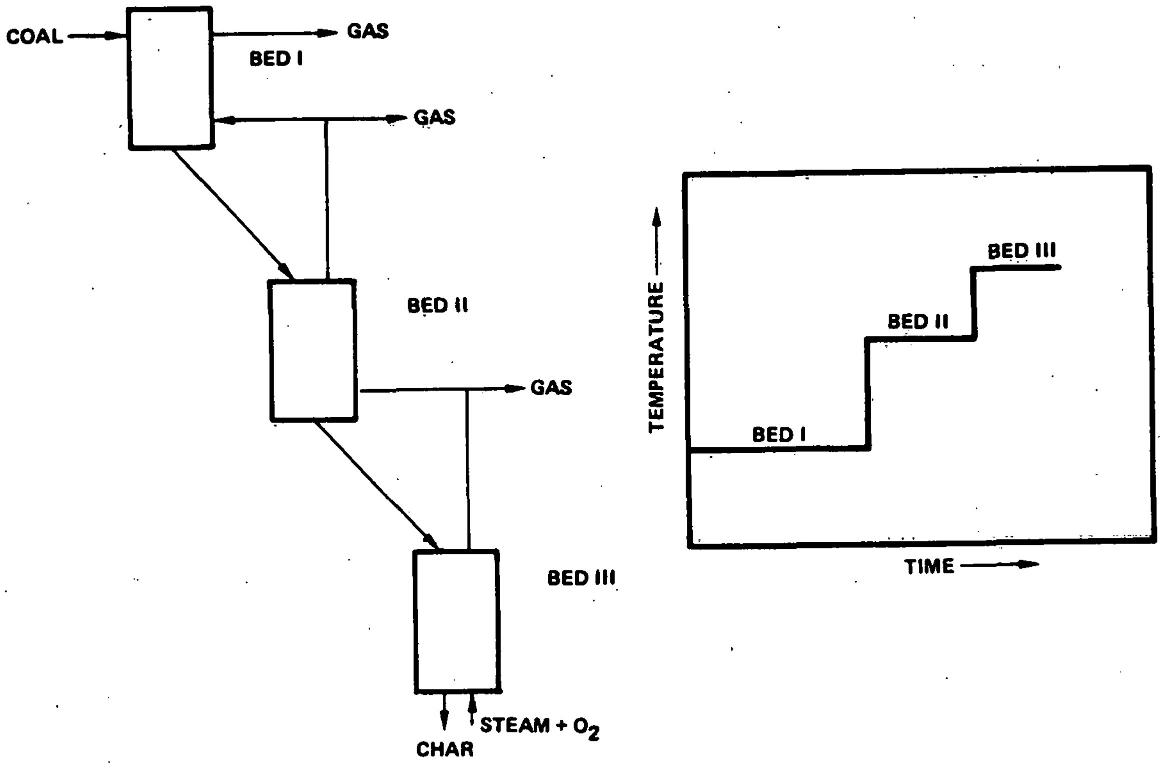


Figure 19. PTG in a Fluid Bed

8. CONCLUSIONS AND RECOMMENDATIONS

Certain conclusions have been drawn and a specific recommendation is made based on the results of this study.

8.1 CONCLUSIONS

- The TRW experimental program has essentially confirmed the soundness of the PTG concept.
- The qualitative observations of state of agglomeration can be quantitatively predicted by the PTG model.
- The simple PTG model seems to account for variations in states of agglomeration from nonagglomerated to very hard agglomerates.
- Various potential shortcomings and improvements of the PTG model were identified (Appendix D). However, the present data can be adequately represented by the simple model, and no adjustments to the mathematical model appear warranted at this time.
- Data from one other source, Dulhanty and Harrison(7), were adequately represented by the model as calibrated by TRW data.
- TRW experiments were conducted in small scale equipment; consequently the observed states of agglomeration cannot be directly translated to operating criteria for either a moving bed or a fluid bed gasifier.
- Commercial PTG concepts were evaluated. Using a conservative state of agglomeration (slight), PTG may be conducted in a batch mode in 12 minutes. However, if more optimistic projections hold, the time required would be only 4 minutes.
- Commercial PTG may be carried out in the top portion of a moving bed gasifier. Specifying a conservative state of agglomeration (slight), the time required for PTG will be about 15 minutes for a gasifier operating at 450 psig. At the optimistic state of agglomeration the time required is 5 minutes. However, heat transfer upsets could increase the time required from 5 minutes to between 8 and 9 minutes.

8.2 RECOMMENDATION

The following recommendation for future work is based on our concern for making the PTG concept widely available. Pressurized moving bed gasifiers are commercially available now, but these gasifiers have difficulty using largest U.S. coal resources. Using the PTG concept in combination with moving bed gasification could broaden the use of the most abundant resource in commercially proven gasifiers.

During the next level of development the PTG model should be employed in combination with bench scale sized experimentation for the purposes of assessing the PTG concept at the next level of development. The model as developed in this work can be utilized to develop time-temperature profile envelopes for coals of interest. The envelopes can be utilized to develop a reduced experimental matrix for subsequent additional concept and model verification. The experimental phase of the effort should employ a larger diameter reactor and increased particle size to more effectively assess this concept on a more reasonable engineering scale. Once the model refinement has been accomplished to reduce current variability and concept demonstration achieved with larger scale experiments, commercial assessment of the PTG concept for a variety of commercial concepts could be made. This assessment would specify operating requirements and determine the size and cost of various units designed for commercial operation.

APPENDIX A

ANALYSIS OF COALS USED IN PTG STUDY

SEAM NAME	PITTSBURGH PSOC-293	COUNTRY	U.S.A.
APPARENT RANK	HIGH VOLATILE A BITUMINOUS (HVAB)	STATE	PENNSYLVANIA

CHEMICAL DATA 1

PROXIMATE ANALYSIS	AS REC'D	DRY	DAF	DMMF (PARR)	DMMF (PARR-G)	DMMF (DIR MM)
% MOISTURE	1.82					
% ASH	8.54	8.70				
% VOLATILE MATTER	36.11	36.78	40.28	39.43	39.36	39.31
% FIXED CARBON	53.53	54.52	59.72	60.57	60.64	60.69

CALORIFIC VALUE (GROSS BTU/LB)	DRY	AS REC'D MOIST.	EQUIL. MOIST.
MM-FREE, DIRECT	15252	14943	14588
MM-CONTAINING	13743	13493	13204
MM-FREE (PARR)	15241	14932	14577
MM-FREE (MOD.P)	15271	14922	14567
BEST MM FREE		14943	14588
NET CV, DMMF BTU/LB	14765		
ASH-FREE	15053		

MOTT-SPOONER DIFFERENCE =

ASSOCIATED ANALYSES	DRY	MMF
% EQUILIBRIUM MOISTURE	3.92	4.38
% TOTAL SULFUR	1.95	

RANK CALCULATIONS

APPARENT RANK (AS REC'D MOIST)	HIGH VOLATILE A BITUMINOUS (HVAB)
ASTM RANK (EQUIL. MOIST.)	HIGH VOLATILE A BITUMINOUS (HVAB)
REFLECTANCE RANK CATEGORY	HIGH VOLATILE A BITUMINOUS (HVAB)
INTERNATIONAL RANK	
AS REC'D MOIST.	630
EQUIL. MOIST.	730
REPORTED RANK	

SEAM NAME	PITTSBURGH PSOC-293	COUNTRY	U.S.A.
APPARENT RANK	HIGH VOLATILE A BITUMINOUS (HVAB)	STATE	PENNSYLVANIA

CHEMICAL DATA 2

ULTIMATE ANALYSIS	AS REC'D	DRY	DAF	DMMF(PARR)
				(10.47 %MM)
% ASH	8.54	8.70		
% CARBON	76.58	78.00	85.43	87.12
% HYDROGEN	4.62*	4.71	5.16	5.26
% NITROGEN	2.02	2.06	2.26	2.30
% SULFUR	1.91	1.95	2.14	
% CHLORINE	0.04	0.05	0.05	0.05
% OXYGEN(DIFF)	4.45*	4.54	4.97	5.27

SULFUR FORMS	% PYRITIC	% SULFATIC	% ORGANIC	% TOTAL
DRY	1.29	0.01	0.65	1.95
DAF	1.41	0.01	0.71	2.14
OPTICAL				

ELEMENTAL ANALYSIS	DRY	DMMF(MOD.P)	DMMF(DIR.)
		(10.46%MM)	(10.35%MM)
% CARBON	77.87	86.97	86.86
% HYDROGEN	4.57	5.11	5.10
% NITROGEN	2.06	2.30	2.30
% ORGANIC SULFUR	0.65	0.73	0.73
% OXYGEN(DIFF)	4.50	4.86	4.97
% CHLORINE	0.05	0.05	0.05
% MINERAL MATTER (INCLUDES 2.41 % FES2)	10.35		

ATOM RATIOS (DMMF)	PARR	MOD.PAR	DIRECT
ATOMIC H/C	0.725	0.705	0.705
ATOMIC O/C	0.045	0.047	0.043

MISC. CHEMICAL DATA	DRY	OF DMMF COAL	OF DMMF OXYGEN
% O AS COOH			
% O AS OH			
% S AS SO4, IN ASH			
% CARBONATE AS CO2			
% CHLORINE	0.09		

INFRA-RED ANALYSIS

(*)-EXCLUDES MOISTURE

SEAM NAME PITTSBURGH PSOC-293 COUNTRY U.S.A.
APPARENT RANK HIGH VOLATILE A BITUMINOUS (HVAB) STATE PENNSYLVANIA

PETROGRAPHIC DATA

MACERAL COMPOSITION

	DRY VOLUME %	DMMF VOLUME %	DRY WEIGHT %
VITRINITE (CALC.)	75.9	80.2	70.9
INERTINITE	14.5	15.3	14.9
LIPTINITE	4.3	4.5	3.7
MINERAL MATTER	5.3		10.5
VITRINOIDS			
VITRINITE	69.2	73.1	64.6
PSEUDOVITRINITE	6.7	7.1	6.3
FUSINITE	4.5	4.8	4.9
SEMI-FUSINITE	2.5	2.6	2.5
MACRINITE	1.8	1.9	1.8
MICRINITE	5.7	6.0	5.7
SCLEROTINITE	0.0	0.0	0.0
SPORINITE	4.0	4.2	3.5
CUTINITE	0.0	0.0	0.0
EXINITE (ANAL)			
RESINITE	0.3	0.3	0.2
EXUDATINITE	0.0	0.0	0.0
FLUORINITE	0.0	0.0	0.0
BITUMINITE	0.0	0.0	0.0
ALGINITE	0.0	0.0	0.0
LIPTODETRINITE	0.0	0.0	0.0
MINERAL MATTER(ANAL)			
INERTINITE			
LIPTINITE			

REFLECTANCE DATA (%, IN OIL)	HIGH	LOW	RANGE	MEAN MAX	STAND.DEV.
VITRINITE	0.89	0.71	0.18	0.81	
PSEUDOVITRINITE	0.00	0.88		0.93	
VITRINOIDS			0.00		

SEAM NAME	PENNSYLVANIA B PSOC-337	COUNTRY	U.S.A.
APPARENT RANK	HIGH VOLATILE A BITUMINOUS (HVAB)	STATE	PENNSYLVANIA

CHEMICAL DATA 1

PROXIMATE ANALYSIS	AS REC'D	DRY	DAF	DMMF (PARR)	DMMF (PARR-G)	DMMF (DIR MM)
% MOISTURE	2.28					
% ASH	8.32	9.51				
% VOLATILE MATTER	34.19	34.99	38.24	37.47	37.33	
% FIXED CARBON	55.21	56.50	61.76	62.53	62.67	

CALORIFIC VALUE (GROSS BTU/LB)	DRY	AS REC'D MOIST.	EQUIL. MOIST.
MM-FREE,DIRECT			
MM-CONTAINING	13884	13567	
MM-FREE (PARR)	15345	14957	
MM-FREE (MOD.P)	15380	14953	
BEST MM FREE		14953	
NET CV, DMMF BTU/LB	14833		
ASH-FREE	15175		

MOTT-SPOONER DIFFERENCE =

ASSOCIATED ANALYSES	DRY	MMF
% EQUILIBRIUM MOISTURE		
% TOTAL SULFUR	1.48	

RANK CALCULATIONS

APPARENT RANK (AS REC'D MOIST)	HIGH VOLATILE A BITUMINOUS (HVAB)
ASTM RANK (EQUIL. MOIST.)	
REFLECTANCE RANK CATEGORY	HIGH VOLATILE A BITUMINOUS (HVAB)
INTERNATIONAL RANK	
AS REC'D MOIST.	630
EQUIL. MOIST.	
REPORTED RANK	HIGH VOLATILE A BITUMINOUS (HVAB)

SEAM NAME	PENNSYLVANIA B PSOC-337	COUNTRY	U.S.A.
APPARENT RANK	HIGH VOLATILE A BITUMINOUS (HVAB)	STATE	PENNSYLVANIA

CHEMICAL DATA 2

ULTIMATE ANALYSIS	AS REC'D	DRY	DAF	DMMF(PARR)
				(10.00 %MM)
% ASH	8.32	8.51		
% CARBON	75.86	77.63	84.85	86.26
% HYDROGEN	5.19*	5.31	5.80	5.90
% NITROGEN	1.42	1.45	1.58	1.61
% SULFUR	1.45	1.48	1.62	
% CHLORINE	0.02	0.03	0.03	0.03
% OXYGEN(DIFF)	5.47*	5.60	6.12	6.20

SULFUR FORMS	% PYRITIC	% SULFATIC	% ORGANIC	% TOTAL
DRY	0.83	0.01	0.64	1.48
DAF	0.91	0.01	0.70	1.62
OPTICAL				

ELEMENTAL ANALYSIS	DRY	DMMF(MOD.P)	DMMF(DIR.)
		(10.02%MM)	(%MM)
% CARBON	77.51	86.14	
% HYDROGEN	5.18	5.76	
% NITROGEN	1.45	1.61	
% ORGANIC SULFUR	0.64	0.71	
% OXYGEN(DIFF)	5.20	5.76	
% CHLORINE	0.03	0.03	
% MINERAL MATTER	10.02		

(INCLUDES 1.55 % FES2)

ATOM RATIOS (DMMF)	PARR	MOD.PAR	DIRECT
ATOMIC H/C	0.822	0.803	
ATOMIC O/C	0.054	0.056	

MISC. CHEMICAL DATA	DRY	OF DMMF COAL	OF DMMF OXYGEN
% O AS COOH			
% O AS OH			
% S AS SO4, IN ASH			
% CARBONATE AS CO2			
% CHLORINE	0.05		

INFRA-RED ANALYSIS

(*)-EXCLUDES MOISTURE

SEAM NAME PENNSYLVANIA B PSOC-337
APPARENT RANK HIGH VOLATILE A BITUMINOUS (HVAB)

COUNTRY U.S.A.
STATE PENNSYLVANIA

PETROGRAPHIC DATA

MACERAL COMPOSITION

	DRY VOLUME %	DMMF VOLUME %	DRY WEIGHT %
VITRINITE (CALC.)	71.3	75.1	67.8
INERTINITE	8.0	8.4	8.3
LIPTINITE	15.6	16.4	13.9
MINERAL MATTER	5.1		10.0
VITRINOIDS			
VITRINITE	70.2	74.0	66.8
PSEUDOVITRINITE	1.0	1.1	1.0
FUSINITE	1.7	1.8	1.9
SEMI-FUSINITE	2.7	2.8	2.7
MACRINITE	1.3	1.4	1.4
MICRINITE	2.3	2.4	2.3
SCLEROTINITE	0.0	0.0	0.0
SPORINITE	13.6	14.3	12.1
CUTINITE	0.0	0.0	0.0
EXINITE (ANAL)			
RESINITE	1.9	2.0	1.7
EXUDATINITE	0.0	0.0	0.0
FLUORINITE	0.0	0.0	0.0
BITUMINITE	0.0	0.0	0.0
ALGINITE	0.1	0.1	0.1
LIPTODETRINITE	0.0	0.0	0.0
MINERAL MATTER(ANAL)			
INERTINITE			
LIPTINITE			

REFLECTANCE DATA (%,IN OIL)	HIGH	LOW	RANGE	MEAN MAX	STAND.DEV.
VITRINITE	0.94	0.78	0.16	0.89	
PSEUDOVITRINITE			0.00		
VITRINOIDS			0.00		

SEAM NAME	ILLINOIS #6 PSOC-282	COUNTRY	U.S.A.
APPARENT RANK	HIGH VOLATILE B BITUMINOUS (HVBV)	STATE	ILLINOIS

CHEMICAL DATA 1

PROXIMATE ANALYSIS	AS REC'D	DRY	DAF	DMMF (PARR)	DMMF (PARR-G)	DMMF (DIR MM)
% MOISTURE	7.65					
% ASH	9.37	10.15				
% VOLATILE MATTER	33.56	36.34	40.45	39.63	39.24	39.54
% FIXED CARBON	49.42	53.51	59.55	60.37	60.76	60.46

CALORIFIC VALUE (GROSS BTU/LB)	DRY	AS REC'D MOIST.	EQUIL. MOIST.
MM-FREE, DIRECT	14760	13493	
MM-CONTAINING	13056	12057	
MM-FREE (PARR)	14710	13449	
MM-FREE (MOD.P)	14777	13468	
BEST MM FREE		13493	
NET CV, DMMF BTU/LB	14222		
ASH-FREE	14531		

MOTT-SPOONER DIFFERENCE =

ASSOCIATED ANALYSES	DRY	MMF
% EQUILIBRIUM MOISTURE		
% TOTAL SULFUR	1.35	

RANK CALCULATIONS

APPARENT RANK (AS REC'D MOIST)	HIGH VOLATILE B BITUMINOUS (HVBV)
ASTM RANK (EQUIL. MOIST.)	
REFLECTANCE RANK CATEGORY	HIGH VOLATILE B BITUMINOUS (HVBV)
INTERNATIONAL RANK	
AS REC'D MOIST.	630
EQUIL. MOIST.	
REPORTED RANK	

SEAM NAME ILLINOIS #6 PSOC-282 COUNTRY U.S.A.
APPARENT RANK HIGH VOLATILE B BITUMINOUS (HVBV) STATE ILLINOIS

CHEMICAL DATA 2

ULTIMATE ANALYSIS	AS REC'D	DRY	DAF	DMMF (PARR)
				(11.70 %MM)
% ASH	9.37	10.15		
% CARBON	67.61	73.21	81.48	82.91
% HYDROGEN	4.73*	5.12	5.70	5.80
% NITROGEN	1.93	2.09	2.33	2.37
% SULFUR	1.25	1.35	1.50	
% CHLORINE	0.21	0.22	0.25	0.25
% OXYGEN (DIFF)	7.24*	7.85	8.77	8.69

SULFUR FORMS	% PYRITIC	% SULFATIC	% ORGANIC	% TOTAL
DRY	0.64	0.00	0.71	1.35
DAF	0.71	0.00	0.79	1.50
OPTICAL				

ELEMENTAL ANALYSIS	DRY	DMMF (MOD.P)	DMMF (DIR.)
		(11.88%MM)	(11.78%MM)
% CARBON	73.19	83.06	82.96
% HYDROGEN	4.98	5.65	5.64
% NITROGEN	2.09	2.37	2.37
% ORGANIC SULFUR	0.71	0.81	0.80
% OXYGEN (DIFF)	7.26	7.89	8.00
% CHLORINE	0.22	0.25	0.26
% MINERAL MATTER (INCLUDES 1.20 % FES2)	11.78		

ATOM RATIOS (DMMF)	PARR	MOD.PAR	DIRECT
ATOMIC H/C	0.840	0.816	0.816
ATOMIC O/C	0.079	0.081	0.072

MISC. CHEMICAL DATA	DRY	OF DMMF COAL	OF DMMF OXYGEN
% O AS COOH			
% O AS OH			
% S AS SO4,IN ASH			
% CARBONATE AS CO2	0.08		
% CHLORINE	0.45		

INFRA-RED ANALYSIS

(*)-EXCLUDES MOISTURE

SEAM NAME ILLINOIS #6 PSOC-282
APPARENT RANK HIGH VOLATILE B BITUMINOUS (HVBV)

COUNTRY U.S.A.
STATE ILLINOIS

PETROGRAPHIC DATA

MACERAL COMPOSITION

	DRY VOLUME %	DMMF VOLUME %	DRY WEIGHT %
VITRINITE (CALC.)	72.4	77.0	67.1
INERTINITE	16.4	17.5	16.8
LIPTINITE	5.1	5.4	4.3
MINERAL MATTER	6.0		11.7
VITRINOIDS			
VITRINITE	55.5	59.0	51.4
PSEUDOVITRINITE	16.9	18.0	15.7
FUSINITE	5.6	6.0	6.0
SEMI-FUSINITE	5.2	5.5	5.2
MACRINITE	0.0	0.0	0.0
MICRINITE	5.6	6.0	5.6
SCLEROTINITE	0.0	0.0	0.0
SPORINITE	3.9	4.2	3.4
CUTINITE	0.0	0.0	0.0
EXINITE (ANAL)			
RESINITE	1.1	1.2	1.0
EXUDATINITE	0.0	0.0	0.0
FLUORINITE	0.0	0.0	0.0
BITUMINITE	0.0	0.0	0.0
ALGINITE	0.0	0.0	0.0
LIPTODETRINITE	0.0	0.0	0.0
MINERAL MATTER(ANAL)			
INERTINITE			
LIPTINITE			

REFLECTANCE DATA (%,IN OIL)	HIGH	LOW	RANGE	MEAN MAX	STAND.DEV.
VITRINITE	0.69	0.48	0.21	0.58	
PSEUDOVITRINITE	0.76	0.54	0.22	0.63	
VITRINOIDS			0.00		

SEAM NAME	UPPER BLOCK PSOC-181	COUNTRY	U.S.A.
APPARENT RANK	SUBBITUMINOUS A (SUBA)	STATE	INDIANA

CHEMICAL DATA 1

PROXIMATE ANALYSIS	AS REC'D	DRY	DAF	DMMF (PARR)	DMMF (PARR-G)	DMMF (DIR MM)
% MOISTURE	15.24					
% ASH	6.64	7.83				
% VOLATILE MATTER	33.16	39.12	42.44	41.94	41.68	
% FIXED CARBON	44.96	53.04	57.55	58.06	58.32	

CALORIFIC VALUE (GROSS BTU/LB)	DRY	AS REC'D MOIST.	EQUIL. MOIST.
MM-FREE,DIRECT*			
MM-CONTAINING	12509	10603	
MM-FREE (PARR)	13681	11428	
MM-FREE (MOD.P)	13729	11439	
BEST MM FREE		11439	
NET CV, DMMF BTU/LB	13246		
ASH-FREE	13572		

MOTT-SPOONER DIFFERENCE = 241.

ASSOCIATED ANALYSES	DRY	MMF
% EQUILIBRIUM MOISTURE		
% TOTAL SULFUR	0.58	

RANK CALCULATIONS

APPARENT RANK (AS REC'D MOIST)	SUBBITUMINOUS A (SUBA)
ASTM RANK (EQUIL. MOIST.)	
REFLECTANCE RANK CATEGORY	HIGH VOLATILE C BITUMINOUS (HVCB)
INTERNATIONAL RANK	
AS REC'D MOIST.	
EQUIL. MOIST.	
REPORTED RANK	

SEAM NAME UPPER BLOCK PSOC-181
APPARENT RANK SUBBITUMINOUS A (SUBA)

COUNTRY U.S.A.
STATE INDIANA

CHEMICAL DATA 2

ULTIMATE ANALYSIS	AS REC'D	DRY	DAF	DMMF(PARR)
				(8.78 %MM)
% ASH	6.64	7.83		
% CARBON	60.37	71.22	77.27	78.07
% HYDROGEN	4.03*	4.75	5.15	5.21
% NITROGEN	0.82	0.97	1.05	1.06
% SULFUR	0.49	0.58	0.63	
% CHLORINE	0.06	0.07	0.08	0.08
% OXYGEN(DIFF)	12.35*	14.58	15.82	15.59

SULFUR FORMS	% PYRITIC	% SULFATIC	% ORGANIC	% TOTAL
DRY	0.04	0.00	0.54	0.58
DAF	0.04	0.00	0.59	0.63
OPTICAL				

ELEMENTAL ANALYSIS	DRY	DMMF(MOD.P)	DMMF(DIR.)
		(8.90%MM)	(%MM)
% CARBON	71.11	78.06	
% HYDROGEN	4.65	5.10	
% NITROGEN	0.97	1.06	
% ORGANIC SULFUR	0.54	0.59	
% OXYGEN(DIFF)	13.83	15.11	
% CHLORINE	0.07	0.08	
% MINERAL MATTER (INCLUDES 0.07 % FES2)	8.90		

ATOM RATIOS (DMMF)	PARR	MOD.PAR	DIRECT
ATOMIC H/C	0.801	0.785	
ATOMIC O/C	0.150	0.160	

MISC. CHEMICAL DATA	DRY	OF DMMF COAL	OF DMMF OXYGEN
% O AS COOH			
% O AS OH			
% S AS SO4,IN ASH			
% CARBONATE AS CO2			
% CHLORINE	0.14		

INFRA-RED ANALYSIS

(*)-EXCLUDES MOISTURE

SEAM NAME UPPER BLOCK PSOC-181
APPARENT RANK SUBBITUMINOUS A (SUBA)

COUNTRY U.S.A.
STATE INDIANA

PETROGRAPHIC DATA

MACERAL COMPOSITION

	DRY VOLUME %	DMMF VOLUME %	DRY WEIGHT %
VITRINITE (CALC.)	36.4	38.1	36.0
INERTINITE	23.4	24.5	25.2
LIPTINITE	35.7	37.4	30.1
MINERAL MATTER	4.4		8.8
VITRINOIDS			
VITRINITE	36.4	38.1	36.0
PSEUDOVITRINITE	0.0	0.0	0.0
FUSINITE	8.5	8.9	9.3
SEMI-FUSINITE	2.9	3.0	3.0
MACRINITE	3.7	3.9	4.0
MICRINITE	8.3	8.7	8.8
SCLEROTINITE	0.0	0.0	0.0
SPORINITE	33.0	34.5	27.8
CUTINITE	1.2	1.3	1.0
EXINITE (ANAL)			
RESINITE	1.0	1.0	0.8
EXUDATINITE	0.0	0.0	0.0
FLUORINITE	0.0	0.0	0.0
BITUMINITE	0.0	0.0	0.0
ALGINITE	0.6	0.6	0.5
LIPTODETRINITE	0.0	0.0	0.0
MINERAL MATTER(ANAL)			
INERTINITE			
LIPTINITE			

REFLECTANCE DATA (%,IN OIL)	HIGH	LOW	RANGE	MEAN MAX	STAND.DEV.
VITRINITE	0.65	0.43	0.22	0.52	
PSEUDOVITRINITE			0.00		
VITRINOIDS			0.00		

APPENDIX B

TGA/DTA DATA

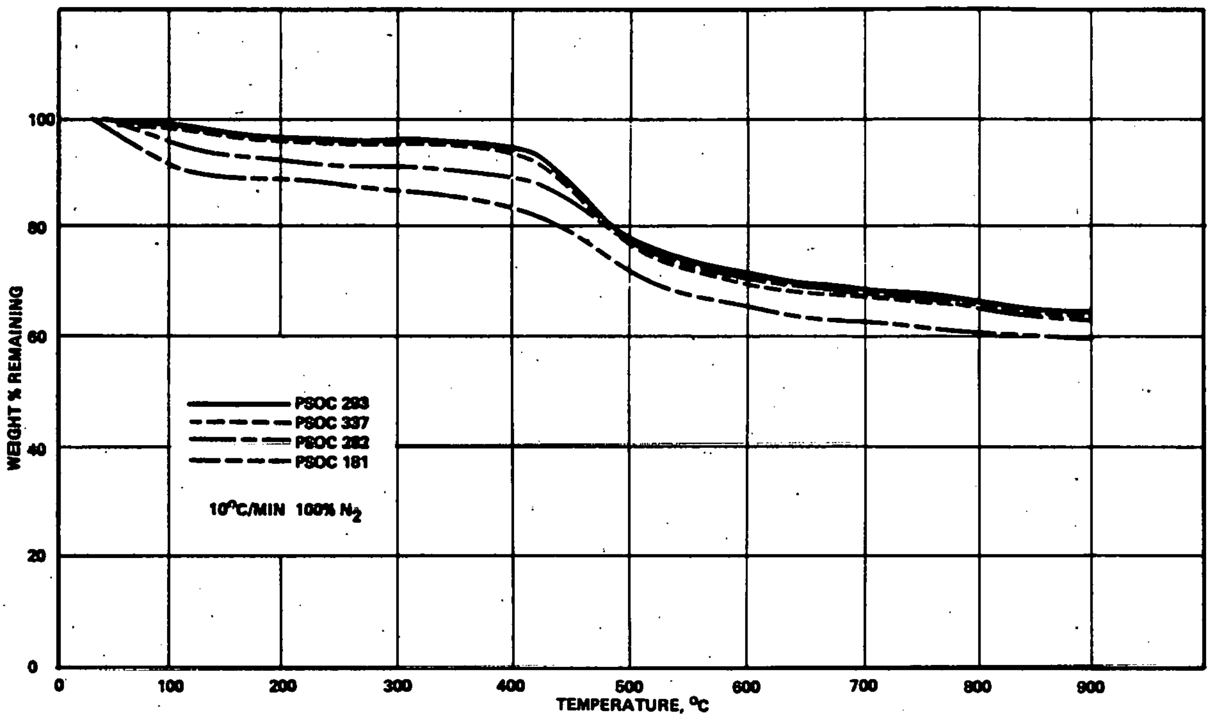


Figure B-1. TGA Analysis Data

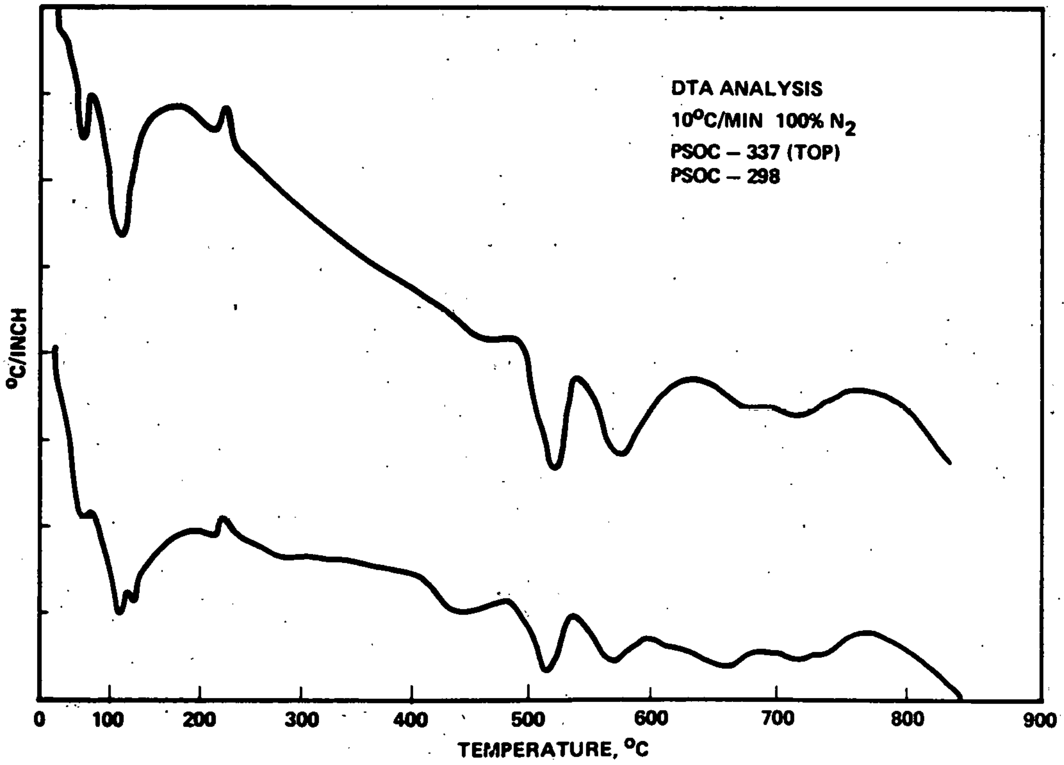


Figure B-2. DTA Data for PSOC 293 and 337 Coal

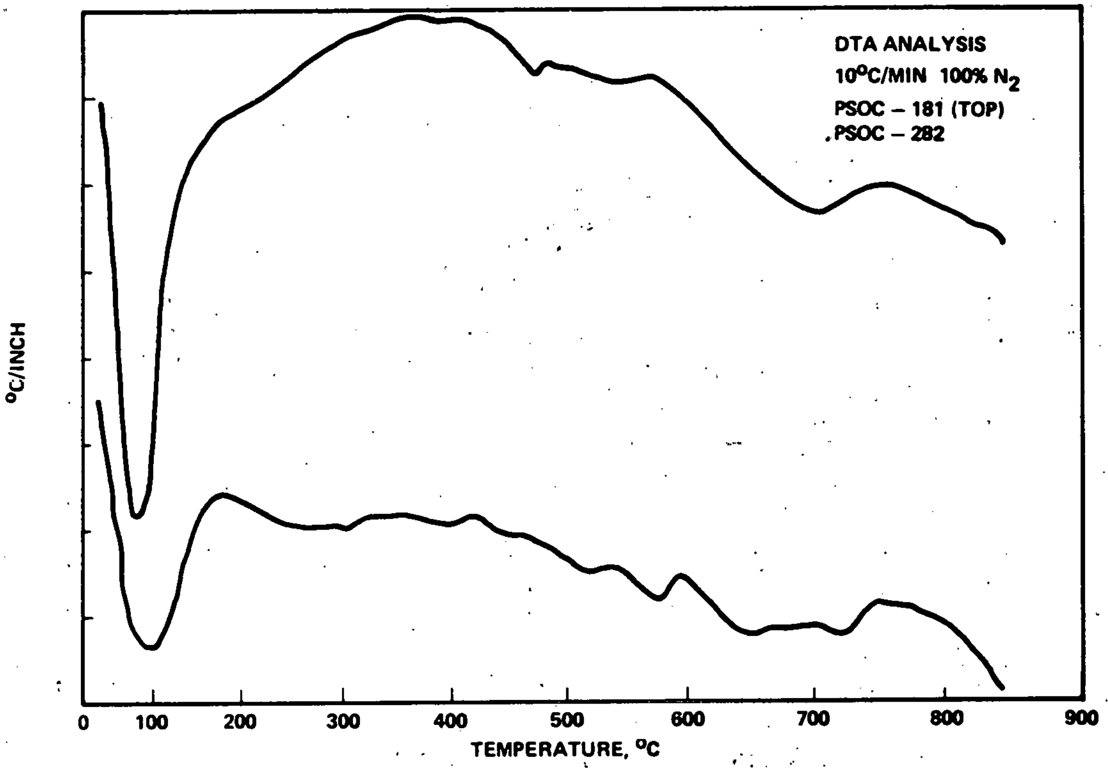


Figure B-3. DTA Data for PSOC 282 and 181 Coal

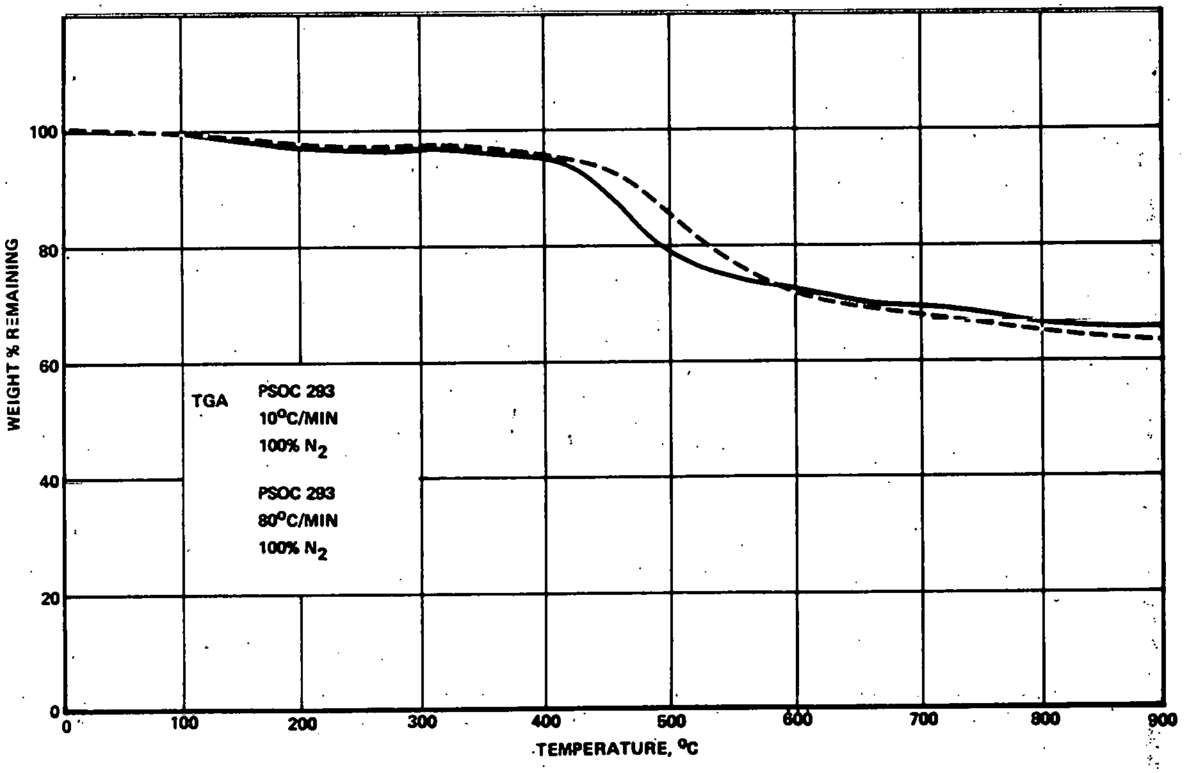


Figure B-4. TGA Data for PSOC 293 at Two Heating Rates

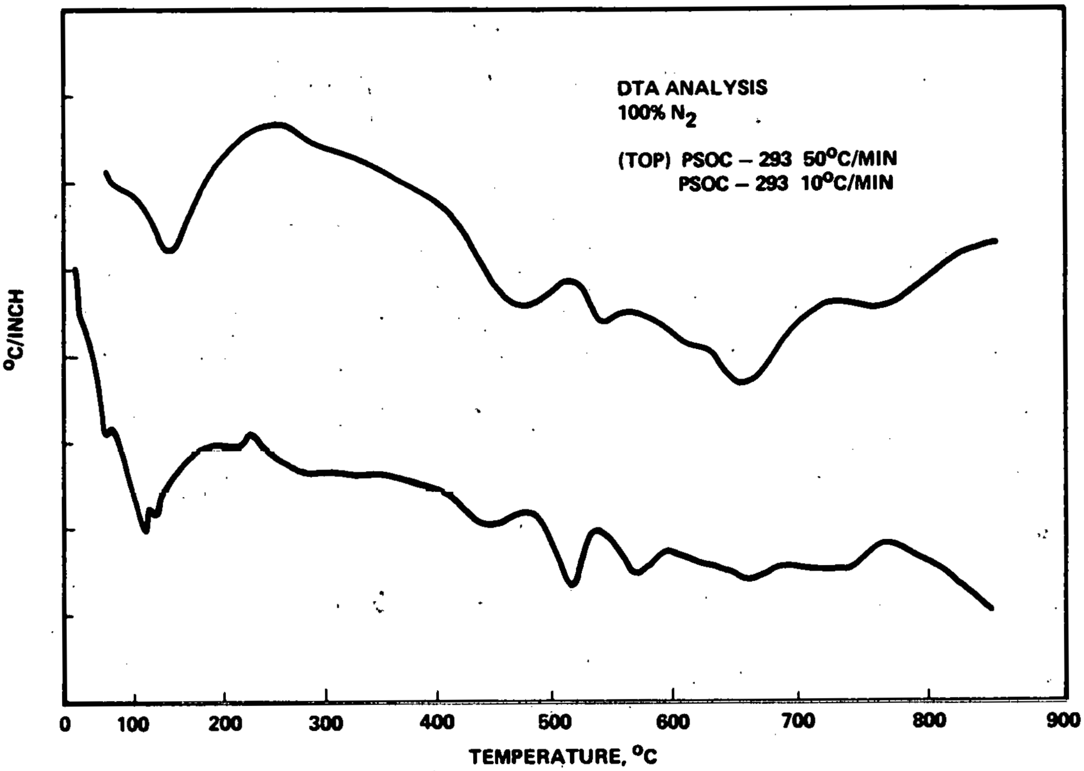


Figure B-5. DTA Data for PSOC 293 at Two Heating Rates

APPENDIX C

TIME-TEMPERATURE PROFILES FOR HOT STAGE REACTOR DATA USED IN MODEL CALIBRATION

In the hot-stage reactor runs, the measured time-temperature profiles were recorded on strip charts. All the recorded data shows that no significant changes take place in coal below about 337°C (650K). The following significant (temperature above 650K) time-temperature profiles for various hot-stage reactor runs were taken from the strip charts:

Run #10: 4.9°C/minute ramp

Run #21: 3.643°C/minute up to 449°C, then a 32.417°C/minute ramp

Run #23: 423°C isothermal run for about 190 minutes

Run #24: 1.143°C/minute up to 415°C, then a 9.933°C/minute ramp

Run #28: 64°C/minute ramp

Run #29: 1.864°C/minute ramp up to 410°C, 13 minute isothermal period,
5°C/minute for 2 minutes, then a
8°C/minute ramp

Run #38: 2°C/minute up to 435°C,
0.2°C/minute for 16 minutes, then a
9.667°C/minute ramp

Run #39: 4 minute isothermal at 391°C,
6.833°C/minute for 6 minutes,
isothermal for 5 minutes, then a
10°C/minute ramp

Run #40: Same as Run #39

Run #43: 9.091°C/minute ramp

Run #44: 11.111°C/minute ramp

Run #45: 11.217°C/minute ramp

Run #46: 10.526°C/minute ramp

Run #47: 9.364°C/minute ramp

Run #48: 9.083°C/minute ramp

Run #49: 10.0°C/minute ramp

APPENDIX D

HEAT TRANSFER IN HOT STAGE REACTOR

The essential geometry of the hot-stage reactor is shown in Figure D-1. The major modes of heat transfer to the coal are:

1. Conduction by direct contact with copper plate
2. Natural convection from a plate to the coal
3. Radiation from a copper plate to the coal
4. Radiation from the coal to the pressure vessel
5. Forced convection from the purge gas to the coal.

The heat transfer rates for each of these modes were evaluated and the net response of the coal was determined.

1. <u>Conduction by Direct Contact</u>. There are few points of contact between the coal and the copper plate (only one for a sphere). Heat transfer by this mode has been determined by McAdams(15) to be significant only in the case of contact between high conductivity solids, such as metal to metal.

2. <u>Natural Convection from Plate to Coal</u>. There are three regimes of natural convection:

- Pure conduction by gas trapped between coal and plate
- Laminar natural convection
- Turbulant natural convection.

The controlling regime is determined by the value of the dimensionless number Grashoff X Prandtl. The regime limiting value is 10^4, that is below a value of 10^4 for the dimensionless number regime 1 controls. The following expression relating the dimensionless number to a temperature driving force and a characteristic length was taken from the ASHRAE Handbook(1).

$$Gr \times Pr = 1.6 \times 10^6 L^3 (\Delta t) \quad (1)$$

where

L = characteristic length, 1/2 the diameter for a sphere, ft

Δt = temperature difference, ^oF.

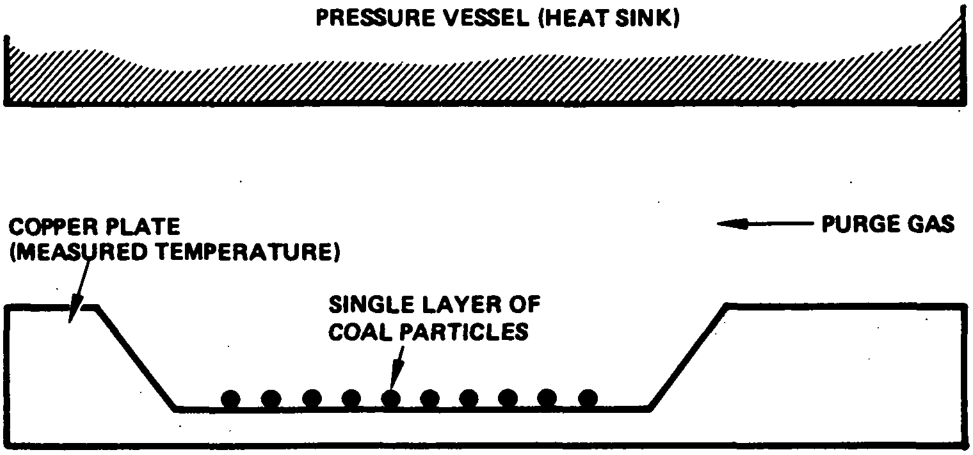


Figure D-1. Coal in a Hot-Stage Reactor

One of the hot-stage reactor runs, run #23, was an isothermal run. Comparing the weight loss from this run to the oven data, the maximum value of Δt was estimated at 40^{0}F.

For small particles,

$$L = \frac{1}{2 \times 42 \times 12} \text{ ft} \tag{2}$$

and for large particles,

$$L = \frac{1}{2 \times 10 \times 12} \text{ ft} \tag{3}$$

Substituting expressions (2) and (3) into (1) results in the following values for the dimensionless number:

$$\begin{aligned} Gr \times Pr &= 0.0025 \text{ for small particles} \\ &= 4.63 \quad \text{for large particles.} \end{aligned}$$

Based on this, regime 1 is the controlling regime and the equivalent heat transfer coefficient as given by McAdams is:

$$h_2 = \frac{k}{(D/2)}$$

where

k = thermal conductivity of gas, Btu/hr ft^{o}F

D = particle diameter, in ft.

3. Radiation from a Plate to a Coal Particle. This radiation flux can be expressed as follows:

$$q_3 = rEA\ (T_1^4 - T_2^4) \tag{5}$$

where

r = Stefan-Boltzman constant, 1.713 x 10^{-9} Btu/(hr ft^2 $^{o}R^4$)

E = effective emissivity; for a hot copper plate the emissivity is 0.57 and for the coal it is 0.8 (McAdams). The effective emissivity for this combination is 0.5

A = effective area including view factor, $\pi/4\ D^2$, ft^2

T_1 = copper plate temprature, ^{o}R

T_2 = coal temperature, ^{o}R

4. Radiation from a Coal Particle to the Pressure Vessel. This radiation heat flow can be expressed as:

$$q_4 = rEA\ (T_3^4 - T_2^4) \tag{6}$$

where

r = Stefan-Boltzman constant

EA = evaluated as above, $\pi/8\ D^2$, ft^2

T_3 = temperature of the pressure vessel, ^{o}R

T_2 = coal temperature, ^{o}R

5. Forced Convection from the Purge Gas to the Coal. This is a small heat flow, about 1/2% of total; consequently, this heat flow is negligible.

The heat balance around the individual coal particle may be written as:

$$\frac{\Pi}{6} D^3 pC \frac{dT_2}{dt} = q_1 + q_2 + q_3 + q_4 + q_5 \tag{7}$$

The heat gain of the individual particle = net heat flow to particle. Substituting the expressions for q_1 to q_5 determined above in Equation (7) yields the following:

$$60 \times \frac{\Pi}{6} D^3 \; pC \frac{dT_2}{dt} = 2k\Pi D \; (T_1 - T_2) + r \frac{\Pi}{8} D^2 \; (T_1^4 + T_3^4 - 2T_2^4) \tag{8}$$

where

D = particle diameter, ft

p = particle density, 80 lb/ft^3 for coal

C = coal heat capacity, 0.3 Btu/lb ^oR

T_2 = coal temperature, ^oR

t = time, min

k = gas thermal conductivity, Btu/hr ft ^oR

T_1 = copper plate temperature (measured), ^oR

r = Stefan-Boltzman constant, Btu/hr ft^3 $^oR^4$

T_3 = temperature of pressure vessel, ^oR

The steady-state response is determined by the right-hand side of Equation (8). A characteristic coefficient may be defined as:

$$B = \frac{2K\Pi D}{r \frac{\Pi}{8} D^2} = \frac{16K}{rD} \tag{9}$$

where B has the units $^oR^3$.

When Equation (9) is substituted into Equation (8), a simplified steady-state equation is obtained:

$$B\ (T_1 - T_2) + T_1^4 + T_3^4 - 2T_2^4 = 0 \qquad (10)$$

B is a function of thermal conductivity, k, and particle diameter, D, and thermal conductivity is a function of pressure. Consequently B and the steady-state coal temperature depend on pressure and particle size. Note that, if it is of no interest to look at the coal as it is being heated, the coal dish could be covered by a hot plate, $T_3 \rightarrow T_1$; consequently, $T_2 \rightarrow T_1$ and the heat transfer factors become less important.

Values of B are listed in Table D-1 as a function of pressure and particle size. A response time may be defined by examining the transient equation as follows:

$$T = \frac{10\pi\ D^3\ pC}{2k\pi D} = \frac{5D^2\ pC}{K}$$

The response time, T, will change with pressure and particle size. The response time is listed in Table D-2 as a function of pressure and particle size. Considering the values of T, the response time is fairly small and transient effects may be neglected. However the steady-state effects on coal temperature and heating rate should be included.

Examination of TRW agglomeration data show 700K → 730K as the agglomeration range. The steady-state coal temperature for these values of measured temperature are listed in Table D-3. The effective heating rate for a 10^{0}C/min measured heating rate is also shown in Table D-3. Note the large difference between the actual coal temperatures for large and small particles and the large difference between the effective heating rates of small and large particles.

In summary, the major modes of heat transfer within the hot-stage reactor were calculated. The effect of heat transfer on measured versus actual coal temperature was determined. The best estimate of coal temperature and its heating rate is summarized in Table D-3 as a function of measured conditions.

Table D-1. Variation of B (K^3) with Pressure and Particle Size

Pressure (psig)	Particle Size	
	42 Mesh	10 Mesh
0	2.3×10^{10}	5.5×10^{9}
100	2.76×10^{10}	6.6×10^{9}
200	2.89×10^{10}	6.9×10^{9}
300	2.95×10^{10}	7.0×10^{9}

Table D-2. Variation of T (Minutes) with Pressure and Particle Size

Pressure (psig)	Particle Size	
	42 Mesh	10 Mesh
0	0.0166	0.07
100	0.014	0.06
200	0.013	0.055
300	0.012	0.054

Table D-3. Steady-State Coal Temperature Response

Measured Condition	Small (32-42 Mesh) Particles			Large (8-10 Mesh) Particles		
	Temperature of 700°K	Temperature of 730°K	Ramp Heating at 10°C/min	Temperature of 730°K	Temperature of 760°K	Ramp Heating at 10°C/min
0	691	719.4	9.5	698	723.9	8.63
100	692.4	721	9.54	701.6	727.8	8.74
200	692.7	721.4	9.56	702.4	728.7	8.78
300	692.8	721.5	9.58	702.7	729.0	8.78

APPENDIX E

POTENTIAL IMPROVEMENTS TO THE PTG MODEL

Before considering potential improvement to the PTG model, it is instructive to consider the physical changes that take place during coking. (Coking and caking are often used interchangeably in the literature.) The following description is taken from Given(17).

> "All coals are porous and have a large surface area (100-300 m^2/gm), nearly all of which represents the walls of the very fine pores. When a coal is heated to about 400°C chemical decomposition becomes active, and tarry substances are released into the pores inside the particles with bituminous (coking) coals. These substances cannot readily escape because of the small diameter of the pores and their pore entrances, and so during their residence inside the particles they act as boundary lubricants for colloidal micelles, making the particles behave like a very viscous (non-Newtonian) liquid, so that they agglomerate.
>
> The porosity of coals goes through a minimum in the upper part of the bituminous range of rank, and it is here that swelling and caking go through a maximum.
>
> With anthracites, insufficient tarry material is formed to act in this way. With lower rank coals, there is a considerably greater proportion of large pores, and so the copious quantities of tarry substances can escape too rapidly to give the particles fluidity. Consequently neither with anthracties nor with sub-bituminous coals does agglomeration occur.
>
> This qualitative description has never been firmly established by experimental proof, nor has any alternate view. Nevertheless it has always seemed to me to be plausible and to provide an easily visualized physical model of real phenomena.
>
> On further heating the tarry substances evaporate and/or decompose, so that the fluid mass re-solidifies. This final phase of the coking process is analogous to the curing of a thermosetting resin such as bakelite or a glyptal."

An independent confirmation of this general physical picture was obtained by Kirov and Stephen(9) and Dryden and Pankhurst(18) who measured the amount of chloroform extract as a function of heating time for various coals. They observed a rapid increase in the extract yield on heating to the caking temperatures, followed by a rapid decrease on heating beyond the caking range. The peaks and valleys in the chloroform extract yield lead the rapid increases and decreases in fluidity. The metaplast may be considered to be analogous to the chloroform extract, which, in turn, is the tarry sticky substance formed by initial decomposition of coal. The kinetic study by Kirov and Stephen also conforms that the formation of the metaplast precedes any decomposition to gaseous products.

The metaplast model as described by Van Krevelen(11) can be considered to describe the formation of a sticky tarry substance that blocks the pores of coal on heating. If the metaplast is uniformly distributed throughout coal, and, if the degree of swelling is small, then the Van Krevelen model approximates the concentration of sticky plasticizer by M. Therefore, the maximum value reached by M is related to severity of agglomeration.

After understanding the phenomena mathematically described by the model, the physical changes not adequately described can be outlined. The following is a discussion of physical phenomena not adequatley described by the model and the changes required to satisfactorily describe the phenomena.

1) Effect of volatiles released during pyrolysis and their subsequent effect, namely swelling. This swelling can lead to higher interparticle pressure and more severe agglomeration.
2) Effect of particle size and pressure on agglomeration.
3) Effect of carbonization in the presence of hydrogen.

If any of the above described phenomena are important contributors to the severity of agglomeration, the PTG model in its present form will not be adequate. Possible additions to the model required to relate swelling to agglomeration include:

- Kinetic description of volatiles formation from coal
- Rate of escape of volatile from inside the particle through pores partially blocked by metaplast

- Relate the kinetics of formation and escape volatiles into the intraparticle and interparticle pressure build-up
- Relate the pressure and the amount of metaplast to degree of agglomeration.

A mathematical description that includes all these factors will be considerably more complicated than the simple metaplast model. Although rigorous mathematical analysis was not performed, the simple metaplast model seems equivalent to the complex model if the amount of metaplast is more unimportant that interparticle pressure in determining severity of agglomeration.

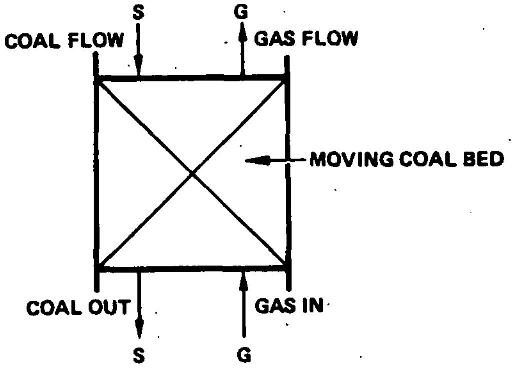
The present PTG model does not include any effect of particle size. The parameter, M, in the model is approximately proportional to the amount of metaplast per unit volume. If the particle size has a significant effect on the degree of agglomeration, and if smaller particles agglomerate more readily than larger ones, the critical variable may be the amount of metaplast per unit outside surface area. Thus, a simple mathematical modification will account for this change.

Because no gas-solid or gas-metaplast reactions are included in the PTG model, any changes in agglomeration with pyrolysis atmosphere are not included in the present model. At present, there is no conclusive evidence to show the effect of different atmospheres on agglomeration. However, if future data indicate a need for modification, these changes can be adequately accounted for by proposing parallel reactions between gaseous components such as H_2 or O_2 and metaplast M, or metaplast forming material P.

APPENDIX F

TEMPERATURE PROFILE OF SOLIDS IN A MOVING BED PTG

In a moving bed gasifier, coal moves counter-currently to the hot gas generated in the gasifier. The physical configuration for a moving bed gasifier is shown in the following figure:



where S denotes the flow of the solid in and out of the bed and G denotes the gas flow. The temperature profile of coal in the PTG bed is of interest here. In this PTG temperature range, the gas evolution is small and the heat requirements of the coal pyrolysis reactions are small. These effects were, therefore, neglected in the following analysis. The temperature profile in the moving bed PTG can be calculated by performing a differential heat balance. The nomenclature used in this analysis:

A = external heat transfer area of coal particles, ft^2/lb

C = heat capacity, Btu/lb^oF

G = gas flow rate through the programmed temperature section of the bed, lb/hr

h = gas-to-solid heat transfer coefficient, $Btu/hrft^{2o}F$

S = coal flow rate, lb/hr

t = residence time of coal, hr

T = temperature at time t, ^oF

The subscripts used are:

c = coal

g = gas

1,2 = as defined by Equations (3) and (4) below

a = ratio of gas-solid heat capacity, defined by Equation (5)

b = ratio of total residence time to system characteristic time, defined by Equation (6).

For the programmed temperature gasification, the gas and solid flow rates, their heat capacity, and the external heat transfer areas were assumed to remain constant. Under this condition the solid heat balance and overall heat balance result in the following differential equations.

$$\frac{dTc}{dt} = \frac{hA}{Cc}(tg - Tc) \tag{1}$$

$$\frac{dTc}{dTg} = \frac{GCg}{SCc} \tag{2}$$

If the total residence in the bed is τ the boundary conditions can be specified as:

$$Tc(\tau) = T_1 \tag{3}$$

$$Tg(\tau) = T_2 \tag{4}$$

Two characteristic ratios may be defined as:

$$a = \frac{SCc}{GCg} \tag{5}$$

$$b = \frac{hA\tau}{Cc} \tag{6}$$

Equations (1) and (2) were solved with boundary conditions (3) and (4) giving the following equation for Tc:

$$Tc = \frac{(T_2 - aT_1)}{(1 - a)} + \frac{(T_2 - T_1)}{(a - 1)} \exp [(a - 1) B (\frac{t}{\tau} - 1)] \qquad (7)$$

and for a = 1

$$Tc = T_1 + b (T_2 - T_1) (\frac{t}{\tau} - 1) \qquad (8)$$

Numerical Calculations

The time-temperature profiles of the moving bed were calculated based on the following assumptions:

- Temperature corresponding to isothermal period of PTG is 625K.
- Rapid heat-up to 625K is obtained in a small, controlled bed heater. This rapid heat-up period was excluded from this set of calculations.
- Total coal residence in isothermal and controlled temperature period is 40 minutes.
- Temperature of coal at bed exit is 825K. This temperature is beyond the plastic range.
- Heat-transfer coefficient was assumed to be 20 $Btu/hrft^2{}^oF$. This coefficient is typical for a 30-atm gasifier. The value was estimated from typical coefficients given by Perry's Handbook[19] (3rd edition, page 480) and the variation of h with pressure given by McAdams (3rd edition, page 295).
- Heat capacity of coal is 0.3 Btu/lb^oF. This is a typical value taken from Perry (3rd edition, page 235).
- Temperature of gas entering the PTG zone is 995K. This is a typical temperature for a Lurgi gasifier.
- External surface area of coal particles was estimated by assuming coal particles to be 1/2-inch diameter spheres.

Based on the above assumptions, the following numerical values were obtained:

T_1 = 825K

T_2 = 995K

a = 1.85 (required to yield 625^{0}K as bed inlet temperature)

b = 53.333

τ = 40/60 hours.

The resulting temperature profile is:

$$Tc = 625 + 170 \exp \left[0.85 \times 53.333 \times \left(\frac{t}{\tau} - 1\right)\right]$$

This temperature profile is shown in Figure F-1.

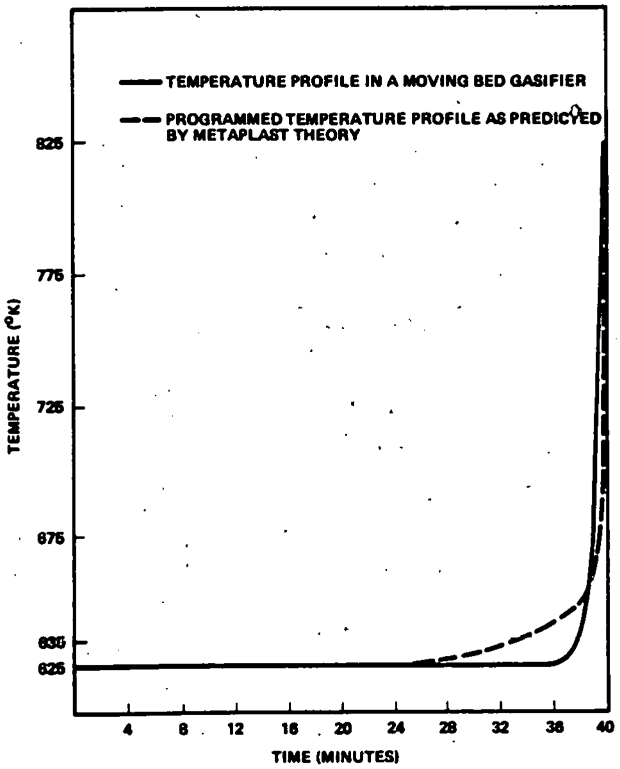


Figure F-1. Comparison of Theoretical Programmed Temperature Gasification Profile to Temperature Profile in a Moving Bed Gasifier

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