Heat Transfer and Associated Effects in The Carbonization of Briquets

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ABSTRACT

Temperature-time patterns for the carbonization of coal-char briquets were computed with an electronic digital computer for various briquet sizes, film heat transfer coefficients and two shock heating methods - hot flue gas and hot fluidized solids. This represents solution of an unusual heat transfer problem wherein conductivity and specific heat are strong functions of temperature. Heating rate correlations evolved from the computed results permit extension of the data to conditions not included directly in the computations.

Combination of the thermal patterns with experimental briquet expansivity data yielded information on the relative magnitude of thermal stresses in briquets undergoing carbonization. Excessive stresses lead to deleterious briquet fracturing.

The assembled data supply the necessary background for estimation of operability limits for briquet carbonization by shock heating procedures and can be used to define physical conditions and dimensions in the design of carbonization units in formcoking processes.

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INTRODUCTION

The work reported here is part of a program aimed at the development of a continuous process for the production of formcoke suitable for blast furnace use. The potential advantages of such a process are lower investment costs/ton of coke, the ability to utilize the vast reserves of non-metallurgical grade coal, and the production of a product coke having uniform size and quality.

Experimental work carried out in these laboratories has shown that such a process can be developed based on briquetting followed by continuous coking of the briquets. The briquets are formulated from low temperature char, coal and a pitch binder. The briquetting aspects of this program will be discussed in subsequent papers. The present paper is concerned with the carbonization of the briquets and particularly with heat transfer problems associated with this process.

The briquets require very critical control in the carbonization process to yield acceptable formcoke. On the one hand, shock heating is necessary to prevent plastic deformation, and on the other, too severe shock heating causes fracturing of the briquets. Deformation and binding of briquets would cause inoperability in any continuous process and fracturing of the formcoke into small pieces would make it unacceptable for blast furnaces.

There are two immediate objectives of this work. One is the determination of the heating rates in briquets subjected to various methods of shock heating. These rates are required for the rational design of large scale carbonizing equipment. The other objective is to determine, by way of calculated thermal patterns within briquets undergoing carbonization, the relative magnitude of thermal stresses. Excessive thermal stresses are believed responsible for deleterious fracturing. Knowledge of these stresses produced under various conditions and methods of shock heating would be useful in the selection of the most favorable process for producing intact formcoke. Some empirical data, gathered from small scale laboratory experiments, outline the general thermal regime required for successful carbonization of briquets. The calculated temperature distribution within these briquets during carbonization can thus serve as a guide for selection of processes and equipment for large scale equipment. The general principle that will be adapted, as will be discussed later, is that the temperature gradient within a briquet undergoing carbonization shall be no greater than that corresponding to the operability limits prescribed by small scale work.

Attainment of both of the above objectives hinges upon solution of the problem of heat transfer to and through a briquet. This problem defies solution in a rigorous analytical form because both the thermal conductivity and the specific heat are strongly temperature dependent, as is established in a companion paper.

Therefore, recourse was had to an approximation method or numerical solution of the differential equations which involved use of an IBM 650 Digital Computer. The machine computations were carried out at the University of Pittsburgh Computing Center and were programmed to define the thermal pattern in a briquet at various times as a function of briquet size, film heat transfer coefficient, and two shock heating methods - with hot flue gas and with hot fluidized solids. Estimation of the film coefficient for a heating medium then allows selection of the appropriate heating pattern for the briquets. An empirical correlation was derived from the computed results which relates the rate of heating of briquets to all the important variables. With the law of squares for heated bodies, the correlation permits rapid extrapolation to many heating cases not directly covered in the computer program. The accuracy of the correlation is within 5%.

Dilatometer measurements were made to determine the magnitude of thermal expansion and contraction that occurs during carbonization of briquets. By coupling these data with the computed thermal patterns, the relative magnitude of thermal stresses can be estimated from the Timoshenko theory of elasticity for heated isotropic and elastic bodies.

Direct experimental data for the temperature rise of the center of a heated briquet are compared with the computed results in a few cases where a comparison can be made. Reasonable agreement with the comparable cases lends some degree of confidence to the other computed results. Many of the briquet heating cases investigated by machine computation cannot be easily examined experimentally on a small scale.

THE PROBLEM AND GENERAL PROPERTIES OF THE SOLUTIONS

The problem of heat conduction in carbonaceous materials has been attacked previously. Burke[1] et al. discussed some years ago mathematical relationships for the rate of heat conduction through coal undergoing carbonization. However, in order to arrive at an analytical solution, these authors treated the case that corresponded to the illegitimate assumption that the thermal diffusivity, (α), was independent of temperature. A constant α for carbonaceous materials cannot be assumed. The strong temperature dependence of thermal conductivity (k) and specific heat (c) has been shown in a companion paper. α is given by $\alpha = k/\rho c$ where ρ is the density. The non-constant conductivity of coal was also reported by Millard[2] who attempted solution of the Fourier heat-flow equation by use of an electrical analog technique. He could obtain agreement between calculated data and experimental thermal patterns in a coke oven only by injecting sizable heats-of-carbonization into the calculations.

The problem that concerns us is to define the temperature profile as a function of time within a spherical briquet undergoing carbonization, taking full account of the temperature dependence of the thermal parameters - the conductivity and specific heat. Two different methods of direct shock heating are considered, namely, with hot gas and hot fluidized solids.

At least in principle, the problem can be handled by solution of the Fourier heat conduction equation. The equation, in polar coordinates, for the general case of a sphere wherein the thermal diffusivity is temperature dependent, is

$$\left(\rho c + T\frac{d(\rho c)}{dt}\right)\frac{\partial T}{\partial t} = k\left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r}\frac{\partial T}{\partial r}\right) + \frac{dk}{dT}\left(\frac{\partial T}{\partial r}\right)^2 \qquad (1)$$

This equation must be solved with these boundary conditions:

$$T = T_1 \text{ at } t = o \text{ for all values of } r.$$

$$\text{and} \quad k\frac{dT}{dr} = h(T_o - T_1) \quad \text{at} \quad r = r_o \,. \qquad (2)$$

T_o, the ambient temperature of the heating medium surrounding the briquet, varies unless the heat content of the medium greatly exceeds that of the briquet. The variation of T_o with time can be derived from heat balance, yielding

$$dT_o = \frac{3h}{r_o M \rho c_o}(T_o - T_1)\,dt \qquad (3)$$

The above relation holds for continuous carbonization where concurrent flow of heating medium and briquets prevail. It also holds for batch carbonization where no temperature gradient exists within the heating medium.

It thus becomes evident, that solution of the heat flow equation (1), with the complex boundary conditions, as well as the non-constant parameters k and c, cannot be obtained by the usual analytical methods. A numerical method of solution is consequently necessary.

Although an analytical solution of the above equations cannot be obtained, certain interesting properties of the solutions follow from the form of equation (1) and the boundary conditions.

Let new variables be introduced, namely $X = r/r_o$, $t' = t/r_o^2$, and $h' = hr_o$. It can now be readily verified that the temperatures, as expressed in equations (1) and (2), become functions only of X, t', k, h', and M. It follows that the solution is a function only of X and t' if k, M, and hr_o are maintained constant. Consequently, an equivalent temperature profile is established within a briquet at corresponding values of the relative radius X at a time inversely proportional to the square of the radius of the briquet. This is a more generalized expression of the law of squares which has been previously discussed[2] and will become useful later.

NUMERICAL ANALYSIS AND SOLUTIONS

Before proceeding with the numerical analyses, it is necessary to establish the values of the parameters needed. These parameters are for briquets of Pittsburgh Seam coal and product char.

The thermal conductivity measured as a function of temperature for briquets is reported in the companion paper. The specific heat for briquets was obtained from the additive equation for the components thus,

$$C_{briq.} = 0.115\ C_{pitch} + 0.250\ C_{coal} + 0.635\ C_{char}.$$

where the numbers correspond to the weight fraction of the briquet components.

The specific heats of coal and char were taken from measurements given in the companion paper. The specific heat of pitch was taken from Hyman and Kay[3]. These data were adequate to cover the range from room temperature to 500°C. Above 500°C, it was assumed that the briquet was carbonized and the data of Terres[4] for char and coke was used.

Graphical representations of the specific heat and thermal conductivity as functions of temperature were reduced to algebraic expressions primarily for purposes of machine computation. The graphs were fitted to polynomial equations by a standard least-squares sub-routine used in the IBM 650 Digital Computer. The analytical expressions were found to be

$$C(T) = 2.14\times10^{-1} + 6.19\times10^{-4}T + 1.40\times10^{-6}T^2 + 4.36\times10^{-9}T^3 + 2.61\times10^{-12}T^4 \quad (4)$$

for the specific heat of briquets and

$$k(T) = 2.74\times10^{-1} + 5.28\times10^{-4}T + 4.57\times10^{-6}T^2 + 3.85\times10^{-9}T^3 + 4.91\times10^{-12}T^4 \quad (5)$$

for the thermal conductivity of briquets. T is expressed in °C.

The coefficients and exponents were stored in the computer memory section. The appropriate values of C(T) and k(T) could be determined by the machine whenever needed in the overall computations.

The measured density of raw briquets is 0.8 gm/cm^3. It was assumed not to change during carbonization. This assumption is acceptable since shrinkage compensates approximately for the loss in weight (volatilization) during carbonization.

Evaluation of the film coefficients is also explained in the companion paper. Values of 20 and 50 Btu/hr ft^2 F° were assigned for the computations on solids heating, to bracket expected values for heat transfer from fluidized solids to briquets. For the gas film heat transfer coefficient, 9.5 Btu/hr ft^2 F° was employed in the calculation of the heating rate of two-inch briquets by hot flue gas. This value derives from correlations by Gamson[5] et al. and by Wilke[6] et al. and corresponds to a flow rate of 375 lbs. gas/ft^2 hr. This is consistent with a physical situation in which a 15-ft. high shock heating zone, containing briquets, is injected with 2200°F flue gas and in which the briquet residence time is 80 minutes.

The problem of the rate of heating of briquets can be solved by application of numerical methods of analysis similar to the step methods described by Ingersoll[7]. In a generalized problem as complex as the one encountered here, hand calculations would become prohibitively long and tedious. Only the speed of modern computing machines allows one to consider attempting such numerical solutions. Machine computing time for a single set of conditions, a single heating case, was an hour and a half.

Initial attempts with the Digital Computer to solve the general numerical problem by applying "relaxation" operations to the step method[7] proved impractical. Programming the machine to make judicious predictions of temperature changes for small time intervals was difficult and it required too much time in working through many erroneous guesses before striking upon ones sufficiently correct. Therefore, a "guess-free" step method was developed to translate the numerical procedure into a form more suitable for machine computations.

To facilitate numerical solution of this problem, the physical process of heat transfer is artificially resolved into two distinct, sequential processes - first, isothermal flow of heat from one section of matter to another for a short time, and second, a resultant change in temperature of the section based upon its heat balance during the isothermal period. This artifice is most helpful in reducing the heat transfer problem into simple first order difference equations that are easily translated into the basic language of digital computation. In reality, the flow of heat and change of temperature are not sequential, as pictured here, but occur simultaneously, so that our solution of the problem is an approximate one, though of very close approximation. The numerical solution approaches the rigorous one as the increments of time and space that enter the computations are made smaller for if the increments become infinitesimals, the solution would be a true calculus integration of the differential equations. The use of an electronic digital computer, with its extremely rapid computation permits computation of a set of equations for a great number of very small time and space increments; thus, our solution is very nearly rigorous.

Definitions of symbolic terms used in the following calculations and discussions appear in the Appendix.

In this approximation method, a briquet is considered as being made up of ten concentric spherical layers having initial temperatures of ${}_1T_1$, ${}_1T_2 \cdots {}_1T_{10}$. The briquet is heated by hot gas of initial temperature ${}_1T_0$. For the duration of a short time interval, Δt, these temperatures are assumed constant while heat conduction proceeds, the driving force being differences between ${}_1T_0$, ${}_1T_1$ " ", T_{10}. The heat transferred is given by

$$q_{0,1} = \frac{({}_1T_0 - {}_1T_1)\,\Delta t}{\dfrac{\Delta r/2}{k({}_1T_1)\,a_1} + \dfrac{1}{h A_s}} \tag{6}$$

for the transfer from gas to the first layer, and by

$$q_{i,i+1} = \frac{k({}_1T_i)\,a_i\,({}_1T_i - {}_1T_{i+1})\,\Delta t}{\Delta r} \quad \text{for } i = 1 \cdots 10 \tag{7}$$

for the transfer from layer to layer. The balance of heat left in i'th layer at the end of a time interval is

$$\Delta q_i = q_{i-1,i} - q_{i,i+1} \tag{8}$$

which upon substitution of equations (6) and (7) leads to

$$\Delta q_0 = - q_{0,1} \tag{9}$$

for the gas since it can only lose heat. For the first layer, the heat balance is

$$\Delta q_1 = q_{0,1} - q_{1,2} = \frac{({}_1T_0 - {}_1T_1)\,\Delta t}{\dfrac{\Delta r/2}{k({}_1T_1)a_1} + \dfrac{1}{h a_0}} - \frac{k({}_1T_1)\,a_1({}_1T_1 - {}_1T_2)\,\Delta t}{\Delta r} \tag{10}$$

$$\Delta q_1 = B_0({}_1T_0 - {}_1T_1) - B_1({}_1T_1 - {}_1T_2)$$

where by definition

$$B_0 \equiv \frac{\Delta t}{\dfrac{\Delta r/2}{k({}_1T_1)\,a_1} + \dfrac{1}{k a_0}} \quad \text{and} \quad B_i \equiv \frac{k({}_1T_i)\,a_i\,\Delta t}{\Delta r} \quad \text{for } i = 1 \cdots 10. \tag{11}$$

For the remaining layers, the residual heat in each layer is

$$\Delta q_i = B_{i-1}({}_1T_{i-1} - {}_1T_i) - B_i({}_1T_i - {}_1T_{i+1}) \tag{12}$$

Equations (9) through (12) now give the balance of heat lost by the gas and gained by each layer during the arbitrary short time interval, Δt. Now, the temperatures of the gas and layers are allowed to change by virtue of the heat lost or gained so that

$$\Delta q_o = -m_o c_o ({}_1T_o - {}_2T_o) \tag{13}$$

and

$$\Delta q_i = m_i c ({}_2T_i - {}_1T_i) \tag{14}$$

Elimination of Δq_o from equations (9) and (13) and defining $A_o = M_o C_o$ yields

$$A_o ({}_1T_o - {}_2T_o) = B_o ({}_1T_o - {}_1T_1) \tag{15}$$

Elimination of Δq_i from equations (12) and (14) and defining $A_i = m_i c \; ({}_1T_i)$ yields

$$A_i ({}_2T_i - {}_1T_i) = B_{i-1} ({}_1T_{i-1} - {}_1T_i) - B_i ({}_1T_i - {}_1T_{i+1}) \tag{16}$$

Since the ${}_1T$ values are known from chosen initial conditions the ${}_2T$'s are the only unknowns involved in equations (15) and (16), both of which can be re-arranged to the form,

$$A_i \, {}_2T_i = B_{i-1} \, {}_1T_{i-1} - (B_{i-1} + B_i - A_i) \, {}_1T_i + B_i \, {}_1T_{i+1} \tag{17}$$

which is completely general if it is remembered that B_{i-1} does not exist when $i = o$ and that B_o has a different form than all the other B_i values (see equation (11)). Thus, the temperature of the gas, and of each layer in the briquet, at the end of the first time interval, are computed directly from equation (17). These end temperatures, $({}_2T_i)$, then become the initial temperatures, $({}_1T_i)$, for the next time interval, and the computations are repeated to determine the temperatures at the end of the second interval. Iteration of this procedure, for many time intervals, in the computer yields the temperature profile of the gas and the layers of the briquet as a function of time. Ten-second time intervals were used in computations for 2 and 3-inch briquets and one-second intervals for the 1-inch briquet.

Eight briquet heating cases were solved directly on the computer, covering variations of the following parameters, initial temperature of the heating medium, mass ratio of heating medium to briquets, film coefficient, and the briquet radius. The law of squares, mentioned earlier, can be used to apply the results to different size spheres by adjusting the value of h to maintain hr_o = constant. The cases studied are outlined in Table I.

The first four cases, involving high initial temperatures and a low value of h describe shock heating with hot gas. The specific heat and molecular weight of the heating medium in these cases was chosen to correspond to that of flue gas.

The other cases in Table I describe carbonization of briquets with hot fluidized solids, such as char.

The temperature distribution patterns solved for the eight programmed cases are shown in Figures 1 through 8. Figures 1 through 4 show the distribution obtained for shock heating with hot gas. Figures 5 through 8 show the distribution for the cases where a fluidized solid heat carrier is used for shock heating. These figures illustrate immediately the heating times involved in carbonization of different size briquets under various conditions.

The time scale in each case is given for either a 1, 2 or 3-inch briquet as noted in the particular figure. The conversion factor to convert the time scale to other briquet sizes by the law of squares is also noted on each figure.

The expected qualitative trends are clearly in evidence upon close examination of these figures. A faster rate of heating is observed, other things being equal, when 1) the shock heating temperature is increased, 2) the film coefficient becomes larger and 3) the briquets become smaller.

Some of these trends can be demonstrated more quantitatively by combining the salient features for several cases on individual plots. Figure 9, for example, shows the effect of briquet size on the rate of rise of the briquet center temperature with various values of h. The law of squares states that the rate of temperature rise is inversely proportional to the square of briquet radius when hr_o is constant. If h is held constant, the rate here does not decrease quite as rapidly. The rate, in this case, decreases roughly as the 1.75 power of the briquet radius. It is clear, that as h becomes very large, that the law of squares will again become valid. A very large value of h corresponds to the case in which the surface temperature is held equal to that of the heating medium. Conversely, as h becomes very small the temperature within the briquet will tend to become uniform at all points and the rate of temperature rise becomes inversely proportional to the first power of the briquet radius.

The effect of the value of the heat transfer coefficient on the rate of temperature rise of the surface and center temperatures for the case of a two-inch briquet may be seen in Figure 9. As the value of h increases beyond 50 Btu/hr ft^{2}F the rate of temperature rise tends to become independent of h.

The effect of the film coefficient on the time required for the briquet center to reach a given temperature is illustrated in Figure 10. The time required to reach temperature again becomes independent of h for large values.

Some experiments were conducted to observe the temperature rise at the briquet center for comparison with the theoretical behavior. The experiments were arranged so that the results could be compared with Cases IV through VIII where char was used as the heating medium. These computed cases were set up with a decreasing temperature of the char from an initial value of 1350°F to a final equilibrium temperature of 1110°F. The above temperature pattern (set up as representative of a continuous process) could not be conveniently reproduced in the laboratory.

The experiments were, therefore, conducted at a uniform 1200°F in the 8" fluidized sand bath. A thermocouple was inserted into the center of the briquet which was plunged into the sand bath and the temperature history was continuously recorded.

Measurements of this kind were made with 1", 2" and 3" diameter spherical briquets. The linear fluidizing velocity of the sand bath was maintained constant at 0.26 fps for 1 and 2-inch briquets. In order to check the effect of linear velocity a second and higher velocity of 0.45 fps was also employed for the 2-inch briquets. Since no effect of fluidizing velocity was found in this range, three-inch briquets were measured only at 0.45 fps.

The experimental measurements are compared with the calculated rate of temperature rise in Figure 9 for all three briquet sizes. The curves shown are the calculated curves for different values of h as parameter.

It should be remembered here that the work reported in the previous paper for aluminum spheres indicates that the correct value of h is in the neighborhood of 30 Btu/hr ft^2.

It is seen that in all cases the rate of temperature rise initially is greater than the calculated figures. This phenomenon is undoubtedly mainly due to a conduction thermocouple error. This was shown by the following experiment. The exposed extrusions of a thermocouple injected into the center of a 2" briquet was heated electrically to 1100°F. Another unheated couple was inserted also to the briquet center at a 90° angle to the former one. It was found that the heated thermocouple would read as much as 100°F above the unheated couple. This much thermocouple error is sufficient to bring about agreement between the lower temperature experimental points and a calculated curve expected for an h of 30 for 2" briquets, as can be seen from Figure 9.

As the temperature of the briquet rises the thermocouple error naturally would diminish quite rapidly both because of the smaller temperature differential and the increase in thermal conductivity of the briquet material.

The lowest value of h available from the calculations for the 1" sphere is 40. Extrapolation by the aid of the curve shown in Figure 10 to an h value of 30 shows that quite good agreement exists between theory and experiment after allowing for the initial thermocouple error.

It is also noted in the case of the two-inch briquet, that the effect of fluidizing velocity on the experimental rate of temperature rise is negligible. It is seen likewise, that good agreement between theory and experiment is obtained after the temperature rises above 300°C by assigning a lower than predicted value of h of the order of 20.

The agreement at higher temperatures becomes rather poor in the case of the three-inch briquet since one must assign a value below 13 to h to obtain agreement in this case.

The explanation of this higher temperature discrepancy is thought to lie in the retarding effect of volatile matter release on the penetration of heat through the surface of the briquet; i.e., effectively on the value of h. This effect was neglected in the calculations because of the added complexity it would have introduced. It should be noted, however, that the rate of volatile matter release per unit of briquet surface increases proportionately to the briquet radius, making it more serious for the larger briquets.

EMPIRICAL CORRELATIONS FOR HEATING RATES

It is desirable, if possible, to have available a simplified correlation encompassing the calculated results. If such a correlation can be derived it would simplify extrapolation to cases that were not directly considered and the application of the calculated rate of heating to many design problems.

A correlation was developed to fit the four cases, V through VIII, considered for solids heated briquets. These cases correspond, for a two-inch spherical briquet, to a range of values for h of 20 to 75 Btu/hr ft^2 F°.

The correlation is based on the use of the empirical equation

$$\frac{d\overline{T}}{dt} = K \; (T_s - \overline{T}) \tag{18}$$

$\overline{T}$ is approximately the mean briquet temperature and T_s is the temperature of the fluidized solids medium. $\overline{T}$ is exactly defined by the equation

$$\overline{T} = \overline{T_o} + Q/\overline{C} \tag{19}$$

$\overline{T_o}$ is the initial briquet temperature, Q is the amount of heat absorbed by the briquet and $\overline{C}$ is the mean specific heat of the briquet over the whole carbonization range. $\overline{T}$ would be exactly equal to the mean briquet temperature if the specific heat of the briquet were independent of temperature, which it is not.

It is clear that equation (18) in view of equation (19) can also be written as follows

$$\frac{dQ}{dt} = \overline{C} K (T_s - \overline{T}) \tag{20}$$

This equation is obviously fallacious since the exact equation is

$$\frac{dQ}{dt} = 4\pi r^2 h (T_s - T_1) \tag{21}$$

Where T_1 is the temperature of surface of the briquet.

If equation (20) is valid, it can only mean that the increase in the thermal conductivity of the briquet with temperature, is such that $\overline{T}$ follows, fortuitously, the relationship

$$\overline{T} = T_s - a (T_s - T_1) \tag{22}$$

The test for equation (18) is shown graphically in Figure 11 where the log (T_s - $\overline{T}$) is plotted against time. The points shown are derived from the computed results of Cases V through VIII. In the particular cases studied here, heat balance considerations give rise to the relationship

$$T_s - \overline{T} = T_o + 5.73 - 1.23\,\overline{T} \tag{23}$$

T_o is the initial temperature of the heating medium in degrees centigrade. The slope of the straight lines shown in Figure 11 are equal to K of equation (18) multiplied by 1.23.

It is clear that the correlation holds with adequate accuracy as noted by the linearity of the plots. The calculated slopes K'(= 1.23 K) are given for the different h values on the graph.

It now remains, to complete the correlation, to account for the variation of K with h and with briquet radius r. The variation with h, at constant r of one inch, is adequately expressed by the empirical equation

$$K = \frac{a h}{1 + b h} \tag{24}$$

where a = .00834, b = .0369, the time is in minutes and h has units of Btu/hr ft² F°.

The transposition of equation (24) to other briquet sizes is carried out readily by the law of squares. The final correlation is given below where r is in feet and t in minutes.

$$\frac{d\overline{T}}{dt} = \frac{6.93 \times 10^{-4}}{r^2} \left(\frac{h r}{1 + 0.443 h r} \right) (T_s - \overline{T}) \tag{25}$$

This equation fits the computer calculations shown in Figure 11 with an accuracy of 5%.

THERMAL STRESSES

Thermal stresses can arise during the coking operation as a result of the temperature distribution produced within the briquet combined with either a contraction or expansion of the briquet material. To provide a better understanding of the nature of the thermal stresses existing within the briquet, a brief dilatometer study was made of the thermal expansion and contraction characteristics of the briquet material.

The dilatometer used is simply an electrically heated vessel about 1 cm I.D. containing a 2 cm high sample. The sample supports a rod which is counterbalanced by a small weight attached to a string which presses over a pulley. The pulley is fitted with an indicating needle whose displacement can be calibrated in terms of linear expansion or contraction of the sample. Using a slow rate of heating, about 3 to 5 F° per minute, the sample is assumed to be at the same temperature as the container, and at essentially uniform temperature throughout.

The dilatometer studies were made on samples of briquets of material from Pittsburgh Seam coal, particularly from two of our West Virginia mines, the Arkwright and the Moundsville mines.

The results of two slow heating runs on material derived from Arkwright coal appear in Figure 12. In one case the sample was cut from a raw briquet and in the other case, loose mix (not briquetted) was used. The briquet sample contracted sharply at nominally 400 and 800°F, with an overall linear shrinkage of 9% upon calcination to 1500°F and subsequent cooling. The loose mix did not show as much shrinkage. This is probably a reflection of the less intimate contact of the particular ingredients in the mix. The coal and pitch may become coked as separate particles in the mix whereas they envelop or penetrate the char in the briquet making it one solid body upon coking.

Figure 13 shows the negative thermal expansion of a briquet sample of material from Moundsville coal. It had an overall shrinkage of 13.5% and exhibited an abrupt contraction at about 700 to 800°F as in the above Case...

Figure 14 shows the results of a run which is an attempt to simulate shock heating. The sample and container were set into the furnace at 1500°F which immediately dropped to ca. 1000°F, which is the shock heating temperature wanted. The furnace was maintained at this temperature for 20 minutes at which time the center of the sample was nearly at the same temperature as the wall (1000°F). The temperature was then raised to 1500°F. In this case the sharp contraction at about 800°F seen in Figure 1 was not evident, probably because the whole sample was not at that temperature at any one time.

It was hoped that use could be made of the above data with exact methods that are available for calculation of the thermal stresses developed within an isotropic and elastic body upon heating or cooling. The thermal stresses are a function of the temperature distribution within the body, the shape of the body, the coefficient of thermal expansion α, the modulus of elasticity E and Poissons number ν.

The tangential stress σ_t at a radial position r of a sphere of radius r_o is given by the following expression due to Timoshenko[8],

$$\sigma_t = \frac{\alpha E}{1-\nu}\left[\frac{2}{r_o^3}\int_0^{r_o} T r^2 dr + \frac{1}{r_o^3}\int_0^{r} T r^2 dr - T\right] \qquad (26)$$

The expression for the case of a hollow sphere with an inner radius a and an outer radius b is given by Timoshenko[8] as follows

$$\sigma_t = \frac{2\alpha E}{1-\nu}\left[\frac{2r^3+a^3}{2(b^3-a^3)r^3}\int_a^b Tr^2dr + \frac{1}{2r^3}\int_a^r Tr^2dr - \frac{1}{2}T\right] \quad (27)$$

The use of these expressions to calculate the exact magnitude of the stresses existing in briquets during coking is not possible. The main difficulty is that we are dealing with a material that is not homogeneous and that is changing in chemical and physical structure with time and temperature. Likewise, the physical parameters α, E, and ν are not known exactly. In fact, the above data show there is no constant α.

The briquets actually undergo shrinkage rather than expansion as the temperature rises due to the above mentioned physical changes. If we permit ourselves a rough approximation of the dilatometer results shown in Figure 24, the shrinkage may then be treated as linear with the temperature. Under such conditions the Timoshenko equation can be employed to calculate relative thermal stresses by treating the factor ($\alpha E/1-\nu$) as an unknown parameter for different coking conditions, but which is assumed to be constant.

The briquet mix remains in a plastic condition due to softening of the pitch and coal until a rigid coke bond is formed. Therefore, thermal stresses can only be set up within the rigid portion of the briquet, while the inner plastic region undergoes relaxation of any imposed stresses by flow into the rigid shell. The problem can therefore be handled by application of equation (27) for the case of a hollow sphere.

The application of this method requires that a more or less arbitrary decision be made relative to the temperature at which plasticity of the mix disappears. It has been assumed in what follows that the mix becomes rigid at 800°F. This may be in some error, but definition of the solidification temperature is not too important, however, since we are merely concerned with relative stresses.

The method adopted therefore was to compute the relative thermal stress over the coked portion of the briquet, i.e., over the shell where the temperature was 800°F and higher as a function of time, coking conditions and briquet size. For simplicity, the calculations were restricted to computing the tangential stress at the surface of the briquet only. Under these conditions, it can be shown that equation (27) reduces to

$$\sigma_t = \frac{2\alpha E}{1-\nu}\left[\frac{3}{2(1-c^3)}\int_c^1 Ty^2dy - \frac{1}{2}T\right] \quad (28)$$

where c = a/b and y = r/b. The computed temperature distribution patterns given in Figures 1 through 8 were employed with this equation to obtain the relative stress results discussed below.

The application of the Timoshenko equation to the calculation of thermal stresses can be readily criticized since the equations apply to an elastic body of constant chemical structure which is not the case here. It is clear, however, that in any case the thermal stresses are greater the sharper the temperature gradients within the body. The Timoshenko equations merely provides a convenient framework upon which to make a semi-quantitative evaluation of relative thermal gradients for different heating patterns.

To establish a background of comparison for determining which relative stresses can be expected to exceed the fracturing limits, a successful regime that has been worked out experimentally for shock carbonization of briquets without fracturing follows. Intact and non-deformed two-inch formcoke has been produced by shock heating in a fluidized sand bath, provided that the sand temperature was within the range of 900 to 1150°F. The proper regime for hot gas formcoking is difficult, if not nearly impossible, to investigate on a laboratory scale.

The calculated relative thermal stress in 2-inch briquets heated with gas is shown as a function of the initial gas temperature in Figure 15. In all cases the equilibrium temperature was maintained near 1000°F by selection of the quantity of gas. The maximum thermal stress increases as expected with initial gas temperature, but at a relatively low rate.

The thermal stress for char heated briquets as a function of briquet size, time and film coefficient is shown in Figure 16. The equilibrium temperature in all cases was constant at 1100°F. It is noted that the thermal stress is of the same order, or higher, than in the gas cases even where 2600°F gas was used. One may conclude, at least tentatively, from this that two-inch briquets may be successfully coked without fracturing even when 2600°F gas is used.

The other relationships in Figure 16 show the anticipated increase in thermal stress with increasing briquet size using a fixed value of h. The major increase in maximum stress is between the one and two-inch size with a relatively small increase between two and three inches. This complies with experimental findings, that 1" briquets survive the successful regime established for 2" briquets.

Experimentally, it is difficult to produce fracture-free 3" carbonized briquets by shock heating in fluidized sand. The slight increase in thermal stress in going from 2 to 3" briquets, as shown in Figure 16, must be critical.

Certain qualitative conclusions are signified by these results. It is readily seen from equation (28) that if the temperature distribution within a briquet is identical with respect to the relative radius y that the thermal stress should be identical and independent of briquet size. The law of squares states that the temperature distribution versus y will go through exactly the same sequence when plotted against the reduced time scale t/r_o^2 if hr_o is constant. Since the non-dependence of stress upon briquet size is not observed either experimentally or from the computed results (Figure 16) it can only be concluded that h does not decrease inversely with r. Actually, it is felt that h decreases less rapidly, and therefore, the thermal stress does increase with size.

ACKNOWLEDGEMENT

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LITERATURE CITED

1 Burke, S. P. and Others. "The Physics of Coal Carbonization". Am. Gas Assoc. Proc., 1930, p. 820 + p. 700 .A5p 1930.

2 Millard, D. J. "A Study of Temperature Conditions in a Coke Oven". J. Inst. of Fuel, 28, 345 (1955).

3 Hyman, D. and Kay, W. B., Ind. Eng. Chem., 41, 1764 (1949).

4 Terres, E. and Biederbeck, H. "Specific Heat of Char". Gas und Wasserfach, 71, 265-268, 297-302, 303-305, 338-345 (1928).

5 Gamson, B. W. and Others. "Correlation of Gas Film Coefficient". Trans. of the Am. Inst. of Chem. Engrs., 39, 1 (1943).

6 Wilke, C. R. and Hougen, O. A. "Correlation of Gas Film Coefficient". Trans. Am. Inst. Chem. Engrs., 41, 445 (1945).

7 Ingersoll, L. R. "Heat Conduction". Madison, Wisconsin University of Wisconsin Press, 1954.

8 Timoshenko, S. "Theory of Elasticity". New York, McGraw-Hill, 1934. QA 931 .T5.

APPENDIX

Definition of Symbolic Terms

${}_1T_o$	-	Temperature of hot gas or hot fluidized solids at the beginning of a specified time interval.
T_o	-	Ambient temperature of heating medium.
${}_1T_i$, $i = 1 \cdots n$	-	Temperatures of spherical layers in a briquet of n layers, at the beginning of a time interval. n^{th} layer is center.
${}_1T_c$	-	Temperature of hot gas or hot fluidized solids at the end of a specified time interval.
${}_2T_i$, $i = 1 \cdots n$	-	Temperatures of the briquet layers at the end of a specified time interval.
Δt	-	Time interval in seconds.
$q_{i,\ i+1}$	-	Quantity of heat transferred during a time interval from the i layer to the i + 1 layer or from fluid medium to the first layer in the briquet if i = o.
r	-	Radius in general.
Δr	-	Thickness of a briquet layer.
r_o	-	Radius of the solid spherical briquet.
a_o	-	Surface area of briquet.
a_i	-	Effective heat transfer area for transfer from the i-1 to the i layer. It is given by $a_i = 4\pi r_{i-1} r_i$.
ρ	-	Density of briquet material, assumed constant for the computer problem.
m_i	-	Mass of briquet layer, taken as $(a_i \rho \Delta r)$.
k(T)	-	Thermal conductivity of briquet material, a function of temperature.
c(T)	-	Specific heat of briquet material, a function of temperature.
h	-	Film heat transfer coefficient for transfer from gas or fluidized solids to the briquet.
n	-	Number of layers in the briquet.
α	-	$k/\rho c$, the thermal diffusivity. Also used for expansivity.
M	-	Mass ratio of heating medium/briquet.
N_u	-	Nusselt Number = $\frac{hr_o}{k}$

θ	-	$\alpha t/r_o^2$.
M_n	-	Roots of equation, $N_u = 1 - M_n \cot M_n$.
$\overline{T}$	-	Mean Briquet Temperature.
T_i	-	Initial Briquet Temperature.

All other symbols identified as used.

Table I

Formcoking Cases for Which the Thermal Patterns Were Solved

Case	Heating Medium	Initial Temp. °F of Medium	Equil. Temp. °F	Mass Ratio, Medium/Briquet	hr_o Btu/hr ft sec	$h \rightarrow$ Btu/hr ft^2 F° for Briquets of r_o of 1"	2"	3"
I	Gas	2200	705	0.58	.079	19.0	9.5*	6.3
II	Gas	2200	1000	1.24	"	"	" *	"
III	Gas	1800	1000	1.95	"	"	" *	"
IV	Gas	2600	1000	0.91	"	"	" *	"
V	Char	1350	1110	5.0	2.08	50.0*	25.0	16.7
VI	Char	1350	1110	5.0	4.16	100.0	50.0*	33.3
VII	Char	1350	1110	5.0	6.24	150.0	75.0	50.0*
VIII	Char	1350	1110	5.0	1.67	40.0	20.0*	13.3

* Identifies h and size used in machine computation of the case. Case also fits for the other two sizes given with the adjusted h as listed.

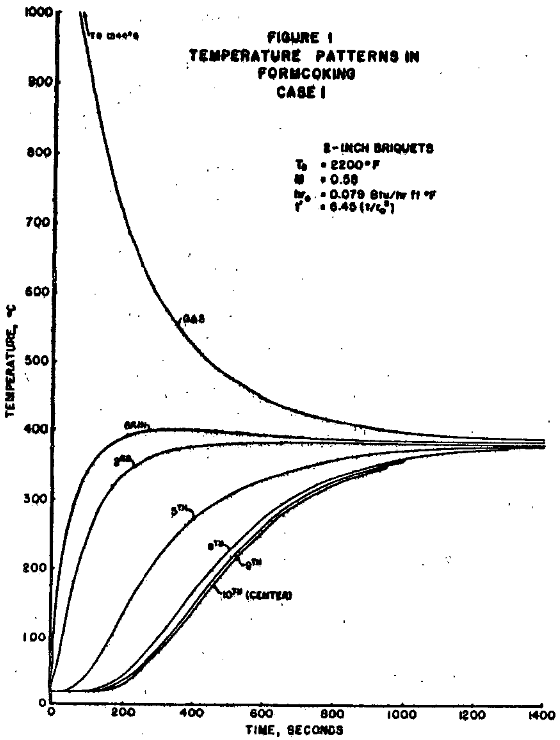

FIGURE 1
TEMPERATURE PATTERNS IN
FORMCOKING
CASE I

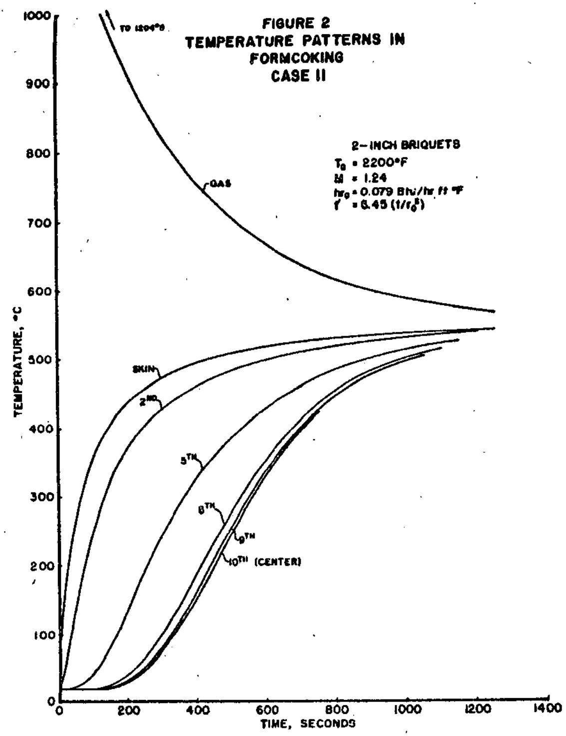

FIGURE 2
TEMPERATURE PATTERNS IN
FORMCOKING
CASE II

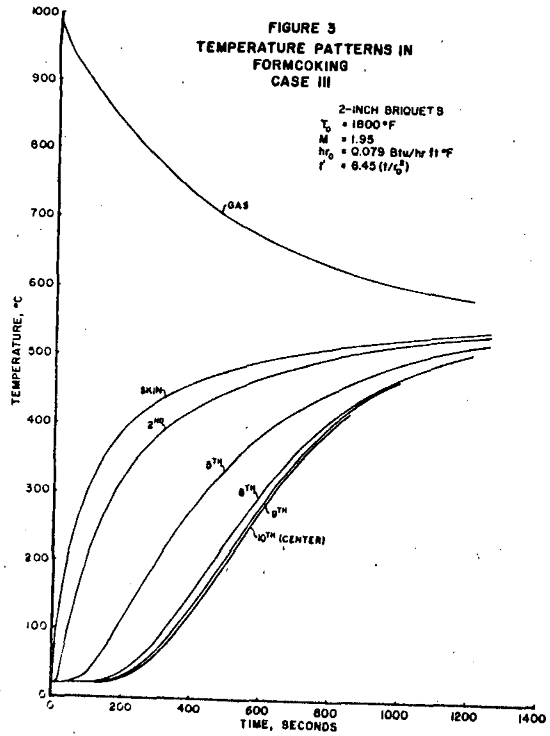

FIGURE 3
TEMPERATURE PATTERNS IN FORMCOKING
CASE III

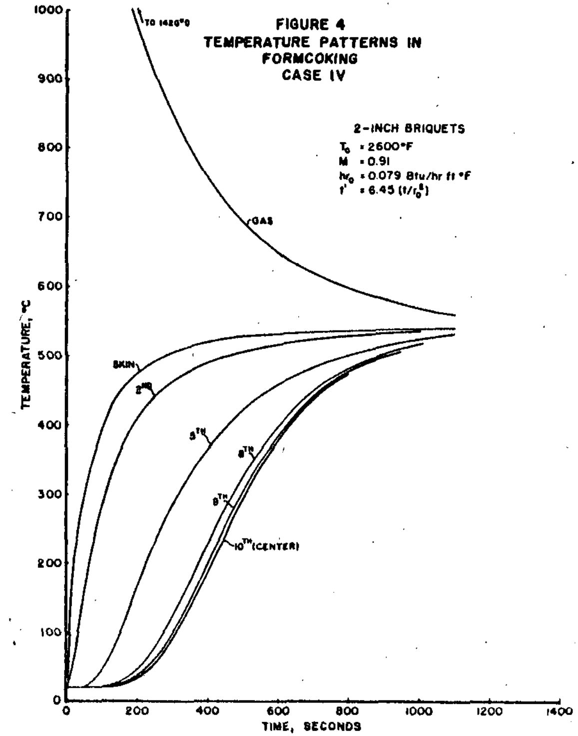

FIGURE 4
TEMPERATURE PATTERNS IN FORMCOKING
CASE IV

FIGURE 5
TEMPERATURE PATTERNS IN
FORMCOKING
CASE V

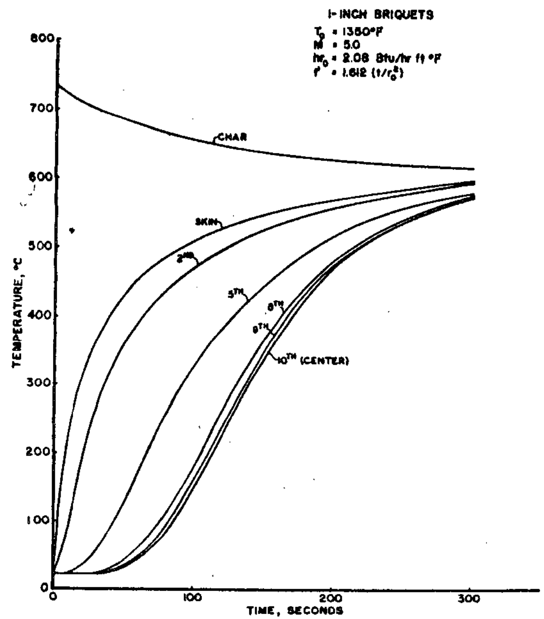

FIGURE 6
TEMPERATURE PATTERNS IN
FORMCOKING
CASE VI

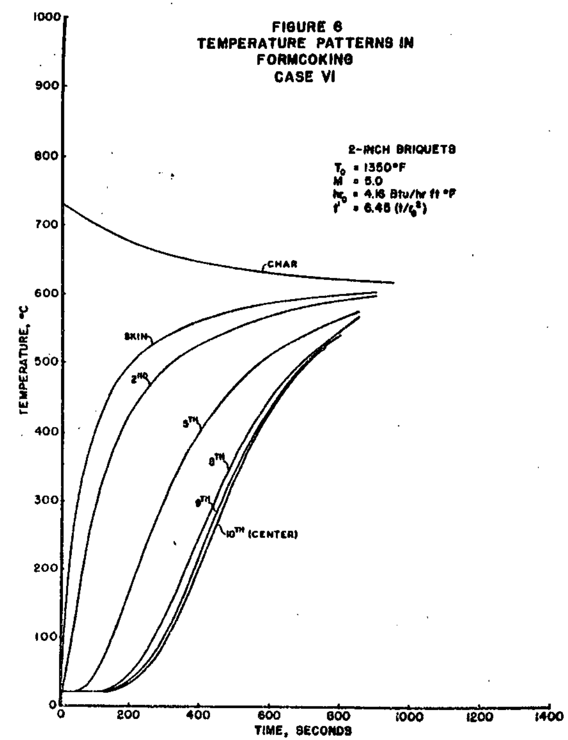

FIGURE 7
TEMPERATURE PATTERNS IN FORMCOKING
CASE VII

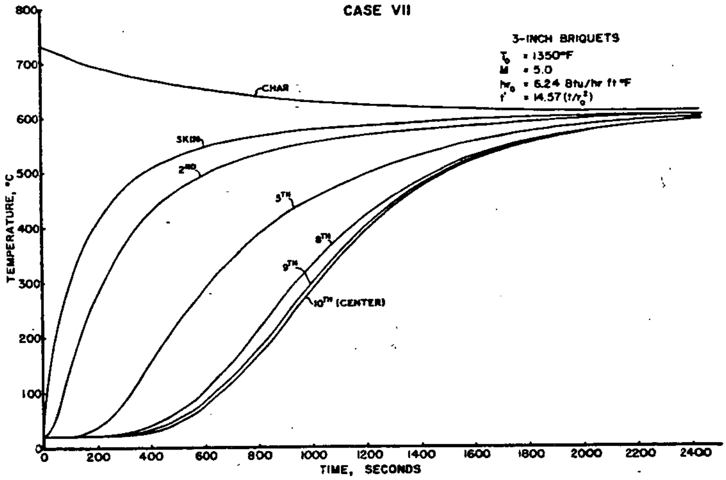

FIGURE 8
TEMPERATURE PATTERNS IN FORMCOKING
CASE VIII

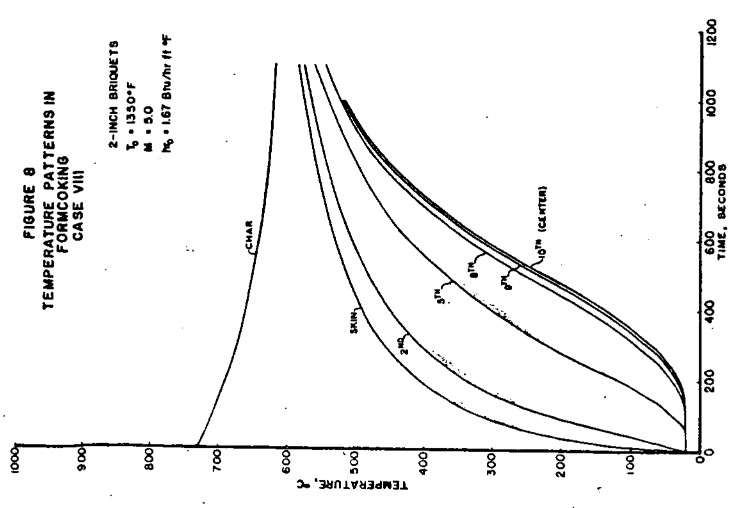

FIGURE 9

COMPARISON OF CALCULATED TEMPERATURE RISE OF BRIQUET CENTER WITH EXPERIMENTAL VALUES
EFFECT OF SIZE

EXPERIMENTAL POINT	FLUID VELC. fpm
□ 1" BRIQUET	0.26
○ 2" BRIQUET	0.26
△ 2" BRIQUET	0.45
⊖ 3" BRIQUET	0.45

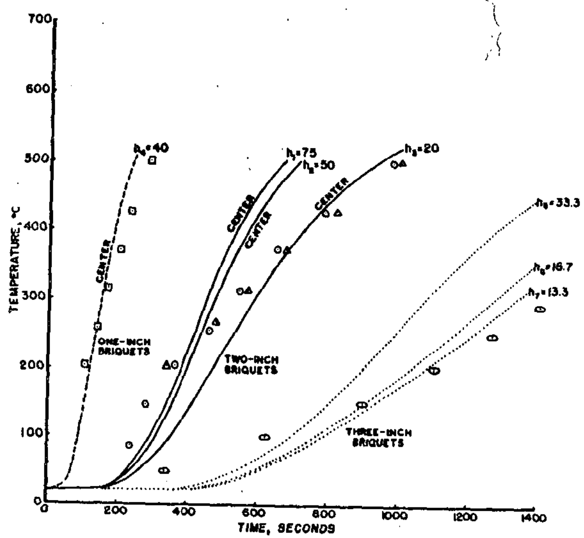

FIGURE 10

TIME REQUIRED FOR BRIQUET CENTER TO REACH A GIVEN TEMPERATURE AS A FUNCTION OF FILM COEFFICIENT AND SIZE

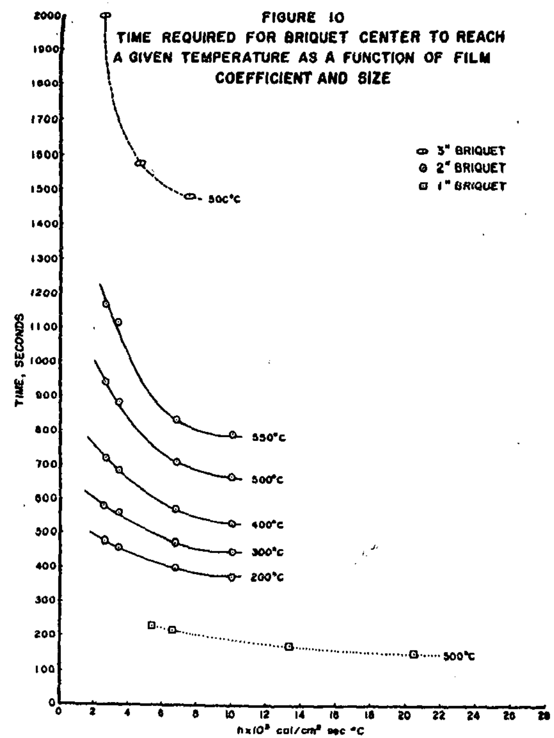

FIGURE 11

CORRELATION OF RATE OF HEATING OF BRIQUETS

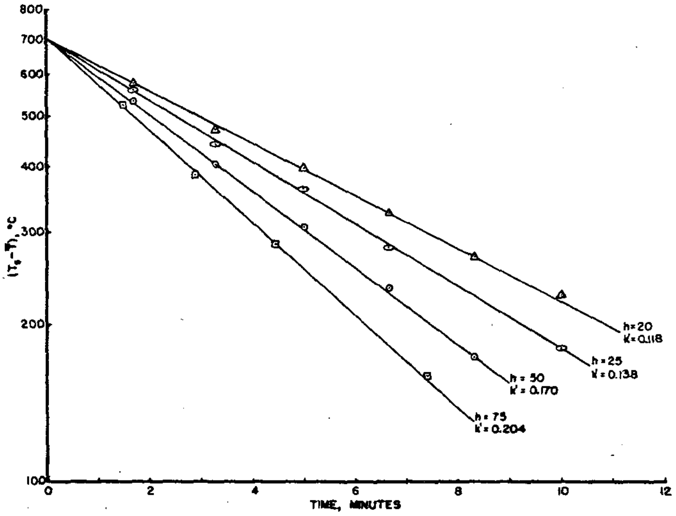

FIGURE 12

THERMAL CONTRACTION OF ARKWRIGHT BRIQUET
AND MIX, SLOW HEATING

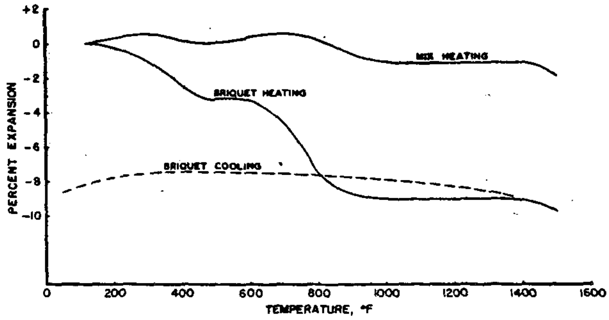

FIGURE 13

THERMAL CONTRACTION OF MOUNDSVILLE BRIQUET.
SLOW HEATING

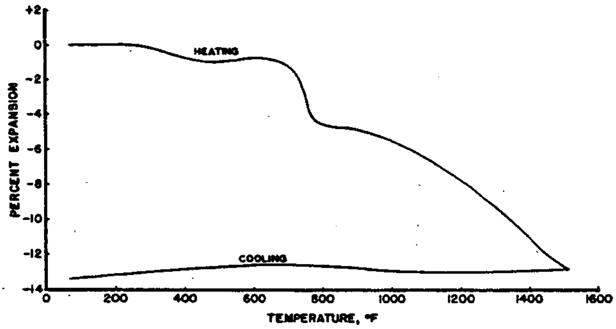

FIGURE 14

THERMAL CONTRACTION OF ARKWRIGHT BRIQUET.
SHOCK HEATING

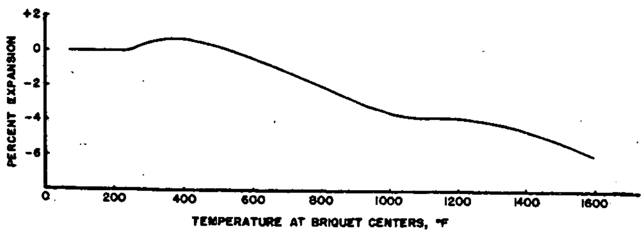

FIGURE 15

RELATIVE THERMAL STRESS IN GAS HEATED 2-INCH BRIQUET AS A FUNCTION OF TIME AND INITIAL GAS TEMPERATURE

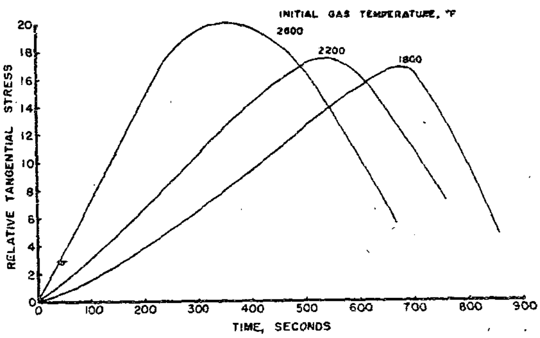

FIGURE 16

RELATIVE THERMAL STRESS IN CHAR HEATED BRIQUETS AS A FUNCTION OF TIME, BRIQUET SIZE AND h