Spontaneous Ignition of Styrene-Butadiene Rubber

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Synopsis

Laboratory experiments with small samples of styrene-butadiene rubber show a complex thermal history which suggests the presence of both endothermic and exothermic processes. The suggested mechanisms are shown to be qualitatively correct by computer simulation. Both the laboratory tests and two larger scale tests show that styrene-butadiene rubber of the present composition will not spontaneously ignite if its surroundings are held at a sufficiently low temperature below about 220°C (428°F).

INTRODUCTION

Whenever a complex polymer mixture is involved in a fire there are raised legitimate questions about its self-heating and potential spontaneous combustion. Styrene-butadiene rubber (SBR) is occasionally so involved. In fact the loss of a synthetic rubber factory in Hungary on September 18, 1965 (ref. 1) was traced to spontaneous combustion of the rubber in a mixing process which was presumably being operated at too high a temperature. Some laboratory experiments with this material indicated that there was little weight loss until a temperature of 380°C was reached.

Any material which is capable of an exothermic reaction, with or without atmospheric oxygen, can spontaneously ignite if appropriately insulated. If no atmospheric oxygen is required, any type of thermal insulation will do. This may consist of more (perhaps much more) of the same material, i.e., a bigger pile. If atmospheric oxygen is required the thermal insulation must be suitably porous. Piles of wood chips at a paper mill and piles of coal at a power station must be watched so as to be used before excess internal heat generation gives rise spontaneously to a fire.

SMALL SCALE TESTS

Like any complex process which depends upon chemical, thermal, and dynamic processes, freedom from spontaneous ignition must be determined by experience with the full scale procedures. However, much can be learned by laboratory scale tests if carefully performed. There are two laboratory methods of examining a material for self-heating leading to spontaneous ignition.

One method surrounds the material under study with a temperature controlled chamber which is electrically heated to the same temperature as the *center* of the sample. If the controller is of high precision, the sample has its surface exposed to surroundings at its central temperature and the experiment will proceed in the same manner as if it were perfectly insulated. Thus an internal exothermic reaction will raise the sample temperature and will lead to spontaneous ignition.

A second method is to test the material for self-heating by holding the sample in a constant temperature furnace and measuring the temperature difference between the sample center and edge. This second method indicates self-heating if the central temperature rises higher than the surrounding chamber. However, it will also detect an endothermic reaction if the central temperature remains lower than the ambient. The first method has been used at the National Bureau of Standards.[2] The second method was used in this study so that endothermic as well as exothermic reactions could be detected.

MATERIALS TESTED

The styrene-butadiene rubber as supplied by the manufacturer, The Goodyear Tire & Rubber Company, were 14 × 28 × 7 in. bales wrapped in polyethylene as they come off the production line. They included several types of Plioflex brand styrene-butadiene rubber having the average composition given in Table I.

The tests reported here were made on 7 cm cubes of this material cut from the bales. They were instrumented with a thermocouple as described in the next section, placed in a temperature controlled furnace and the central temperature rise was measured.

EXPERIMENTAL DETAILS

For a small sample as used here, the temperature difference between the center and edge at low temperatures may be very small so that care must be taken in the placement of the thermocouple wires.

An electric furnace of 10 × 12 × 25 cm inside dimension was used. To help spread the heat uniformly a loosely fitting 9 × 9 × 16 cm (a modified tin can) container was put inside and the samples were put, again loosely, inside the container. The thermal conduction time constant for the 7 cm cube of SBR was about 2 hr. Thus if a fraction of a degree temperature difference is to be reliably detected, it is necessary to hold the ambient (furnace) temperature constant to this same precision over periods long compared to 2 h.

The furnace available did not have the capability of control to a fraction of a degree. To make this precision possible an electronic temperature controller with time proportional anticipation of the final set temperature was used in the

TABLE I
Average Compositions of SBR

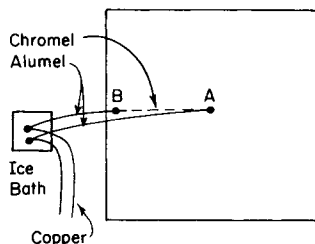|	
Volatile matter	0.26%
Ash	0.78%
Organic Acid	5.44%
Stabilizer-PPHR	0.90%
Oil	27.20%
Bound Styrene	23.50%
Mooney Viscosity, M/L-4' @ 100°C	47
Density	0.93 g/cm^3
Specific Heat	0.45 cal/g °C
Thermal Conductivity	4.29 × 10^{-4} cal/s cm °C
Thermal Diffusivity	1.04 × 10^{-3} cm^2/c

Fig. 1. Simple but poor thermocouple arrangement for the measurement of small temperature differences between points A and B.

furnace power supply with the temperature sensor (a cased platinum resistance wire) inside the inner chamber next to the sample under test.

To measure the temperature at the center of the sample may appear very simply accomplished by placing a thermocouple junction there. Since the temperature difference between the center and the edge is desired, a second temperature must be measured at the latter point. To avoid the necessity of very accurate thermocouple calibrations, the temperature difference should be measured directly by placing the "hot" junction of a thermocouple at the sample center and the "cold" junction at its edge.

If the thermocouple is placed as shown in Figure 1, the heat conduction along the wires decreases the temperature difference between the junctions at A and B. Furthermore, the lead wire from B causes the temperature of that junction to respond to the (small) ambient furnace temperature fluctuations. These problems are minimized by the use of the thermocouple arrangement in Figure 2. By laying the thermocouple wire in the form of a spiral, the wire conduction length is made so great as to cause a negligible temperature difference error. One could use the desired thermocouple material between the hot and cold junctions at A and B with the change to copper in (say) an ice bath or a change to copper as shown in Figure 2. Both methods were tried and the second was most free of unexplainable irregularities.

A block of SBR, 7 × 7 × 3.5 cm was placed on the work bench and No. 30 chromel, alumel thermocouple wires were carefully wound and placed on it as in Figure 2. A second identical block of SBR was placed on top of the first one making a 7 × 7 × 7 cm cube after being pressed together. This assembly requires some patience but is well worth the effort for accuracy of results. The temper-
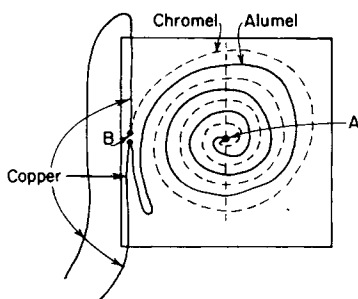

Fig. 2. Thermocouple arrangement for the accurate measurement of small temperature differences between points A and B.

ature difference was measured on a sensitive microvoltmeter. This instrument was also used as an amplifier, the output being recorded on a strip chart recorder.

THE TESTS

The test sample of SBR instrumented as described above was placed in the furnace, the temperature regulator was set at the desired test value, and the recorder was started. Since the furnace temperature rises many times faster than the SBR test samples, the recorded temperature difference between the center and the edge first becomes quite large negative (center temperature lower than the edge). As the furnace approaches the set temperature, the edge temperature becomes constant while the central temperature comes up to approximately the same value. Thus the temperature difference rises toward zero.

If at the furnace set temperature reactions in the SBR are exothermic, the central temperature will rise above that at the edge (the temperature difference becomes positive) by a sufficient amount to conduct the liberated reaction heat out of the sample. On the other hand, if the reactions are endothermic, the central temperature will stop rising at a temperature below that of the furnace (the temperature difference remains negative) so that the necessary reaction heat will be conducted in.

TEST RESULTS

Figure 3 shows in addition to a typical furnace temperature time curve three typical temperature records. At low furnace sample temperatures the center-edge temperature difference, after the initial transient, rises to a nearly constant *negative* value (see curve 204.9°C). At higher furnace temperatures, the temperature difference goes through its start up transient, rises to a *positive* value then falls to a *negative* value (see curve 261.0°C). At a still higher furnace
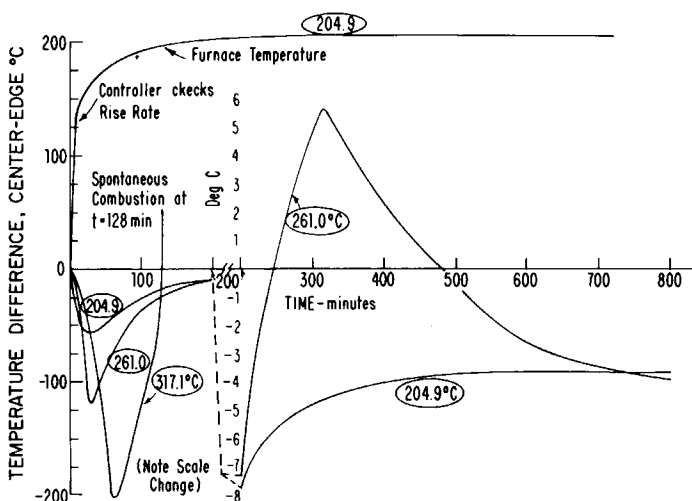

Fig. 3. Experimental heating curves of styrene-butadiene rubber at three furnace temperatures (shown ⬭). The upper curve is a typical furnace heating curve.
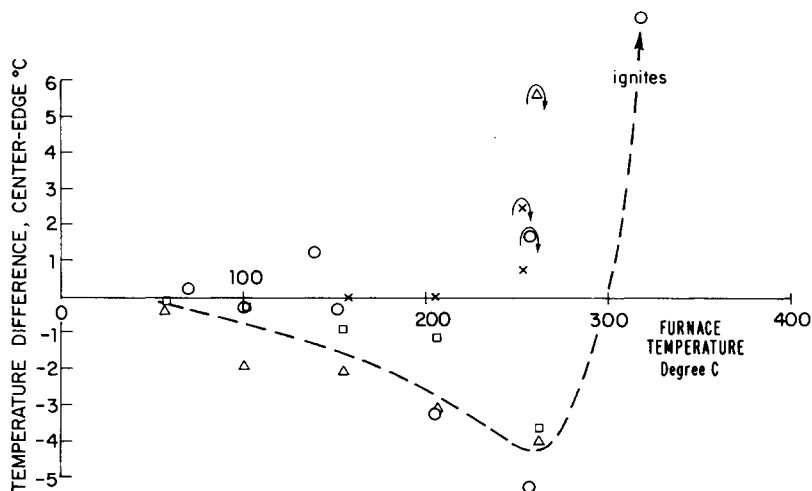
Fig. 4. Steady temperatures reached after about 800 minutes at various ambient furnace temperatures (⊙). Maximum positive transient temperatures, ⟨⊙⟩ . Temperatures of samples covered with polyethylene film (✕).

temperature, the initial transient is immediately followed by spontaneous combustion which burns out the whole center of the SBR sample (see curve 317.1°C).

All of the approximately steady final temperature differences are given in Figure 4. We note that at temperatures below about 250°C endothermic reaction(s) are indicated while at higher ambient temperatures exothermic reaction(s) are evident. The exothermic reaction rates grow exponentially with temperature such that for an experiment at 317°C, the 7 cm cube of SBR increased temperature uncontrollably and the cube burned up. Thus about 300°C is its spontaneous combustion temperature.

Figure 4 also shows the transient positive central temperature differences ⟨⊙⟩ for the several tests at about 250°C.

The crosses in Figure 4 at 157.3, 205.4, and 253.7°C were obtained by wrapping the sample in a polyethylene film during the test. This would reduce, perhaps suppress, evaporation. We note that for the two lower temperatures, the temperature difference between the center and edge of the sample is zero, indicating that all reactions are immeasurably slow (or exothermic and endothermic reactions exactly balance). At 253.7°C there is a small positive temperature difference. The higher transient temperature difference ⟨✕⟩ reached during this test indicates that either the vapor leaked* or there is some endothermic pyrolysis as well as evaporation.

If the reaction chemistry were simple—a single exothermic Arrhenius reaction, for example—the heat conduction equation with a heat liberation term could be solved and the solution fitted to the data of Figure 4. The fitting would serve to determine the effective heat of reaction, activation energy, and frequency factor. However, in the present case there must be more than one reaction and the reaction rate relation—a combination of a number of Arrhenius factors—is unknown.

The polyethylene wrapped tests were run for an entirely different purpose so no special attention was given to possible vapor leaks.

A hint of what is actually occurring is given by the points marked ⊙ near 260°C in Figure 4. These points are the first positive maximum for the cases like 261.0°C of Figure 3. This phenomenon of an initial positive maximum was not observed for furnace temperatures below 250°C (the positive ΔT point at 140°C is believed to be an error).

What is happening to cause these effects? These results can be explained by assuming one (or more) *exo*thermic reactions with high activation energy occurring throughout the sample. These reactions would be responsible for the spontaneous combustion at high furnace temperatures. At the same time one or more *endo*thermic reactions with a low activation energy are needed to explain the low furnace temperature results. But how can we account for the intermediate results where the exothermic reactions are at first effective but are then overpowered by the endothermic reactions thus resulting in an initial positive maximum?

The cause was suggested by the observation that a small amount of waxy substance condensed on the outside of the door of the furnace. This can be explained by assuming that the endothermic process is in fact the evaporation or endothermic pyrolysis of some material from the sample.

The easiest way to see what effect such a mechanism would have is to consider an experiment on a sample in which evaporation only could occur (i.e., no exothermic reactions). When such a sample is heated, the evaporation starts at the surface and a "wet-dry" front moves into the solid. The vapor moves from the front both out through the surface and deeper into the solid where it condenses.[3] Thus the early effect of the evaporation is to make the edge cooler and the center warmer than simple heat conduction alone. Later, however, when the wet-dry front has passed the edge thermocouple junctions the edge temperature rises and the central temperature falls until the evaporable material has been wholly removed.

Thus an exothermic reaction throughout the solid with an endothermic "evaporation" front would be expected to result in the observed effects.

ANALYSIS

An extensive review of thermal ignition theory up to 1971 has been written by Merzhanov and Averson.[4] A specific case has been studied more recently by Uehara, Uematsu, and Saito.[5] Neither of these studies discuss a case like the present in which the sample shows both endothermic and exothermic effects.

Because of the complex mixture of materials present in SBR, it does not warrant an attempt to develop a precise theory of heating along the lines suggested in order to adjust reaction constants for a good fit and thus to get effective reaction constants for this material. However, it does seem appropriate to develop sufficient theory to test the correctness of the above explanation.

For this purpose we consider a slab of material of thickness $2L$ and initial temperature T_0 whose surface temperature is raised at 1°C/min to a furnace temperature T_t and is then held constant. The heat condition equation is

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} + \frac{Q}{c\rho} \tag{1}$$

where

$$Q = Q_r A_r e^{-E_r/RT} \tag{2}$$

is the heat produced per unit volume per unit time by a single Arrhenius reaction.

At the same time an endothermic pyrolysis (evaporation) occurs at a front at a position δ below the surface. The pyrolysis at the front occurs at a rate dependent upon an Arrhenius pyrolysis reaction with activation energy E_v frequency factor A_v and has an endothermic heat of reaction of Q_v. Thus the boundary condition at the pyrolysis front is

$$-k\frac{\partial T_1}{\partial x} + k\frac{\partial T_2}{\partial x} = Q_v A_v e^{-E_v/RT_v} \tag{3}$$

where all terms are evaluated at the vaporization front and T_1 is the temperature in the solid between the surface and the front, while T_2 is the temperature of the solid between the front and the slab center.

Of course, as material is vaporized the wet-dry front moves away from the surface at a rate given by

$$Q_v \rho_v \frac{d\delta}{dt} = -k\frac{\partial T_1}{\partial x} + k\frac{\partial T_2}{\partial x} \tag{4}$$

The final boundary condition needed is at the center of the slab where by symmetry we will assume zero heat flow.

This one dimensional heat conduction problem was solved by computer using the constants given in Table II. Since the model is one dimensional, it is not an adequate representation of the actual three dimensional experiments. Therefore the constants were adjusted to test the hypothesis not for quantitative fit.

The results are shown in Figure 5 (see Appendix A for details). These results are indeed similar to the experimental results of Figure 3. They show that at low temperatures ($<200°C$), there is a small negative ΔT ($-1.6°C$ in 800 min at $200°C$ ambient temperature). At a higher tempeature $\Delta T(t)$ shows a positive maximum followed by a negative excursion, while at still higher temperatures (between $300-310°C$ in Fig. 5) there is spontaneous combustion.

Further work on the spontaneous ignition of organic mixtures should be made with mixtures of simpler materials so as to quantitatively clarify the thermal mechanisms proposed here.

LARGE SCALE TESTS

As manufactured, the styrene-butadiene rubber is made in $7 \times 14 \times 28$ in. bales and packed in large boxes. These boxes are stacked in railroad cars or a river barge for shipment or in a warehouse for storage awaiting shipment. As a check on the possibility of spontaneous combustion under these large scale conditions,

TABLE II
Constants Used in the Analysis

Same as in Table I with the addition of the following:
Exothermic reaction heat release rate $= Q_r A_r e^{-E_r/RT} = 2 \times 10^5 e^{-10^4/T}$ cal/s cm^3
Pyrolysis rate $= 0.25 e^{-4000/T_v}$ g/s cm^2
Heat of pyrolysis $Q_v = 70$ cal/g
Initial temperature $T_0 = 300°$K
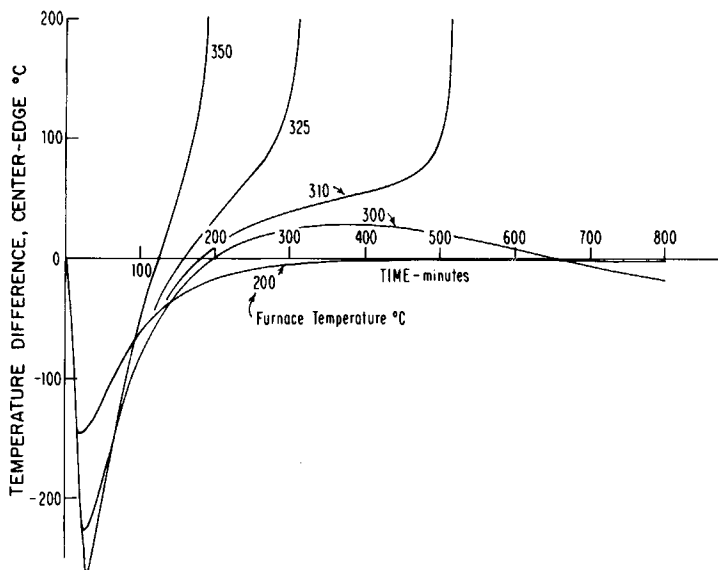Density of pyrolysable material $\rho_v = 0.093$ g/cm^3

Fig. 5. Computed thermal history of slab samples with thermal properties as listed in Tables I and II at various furnace temperatures.

several box configurations were instrumented with thermocouples as they were loaded and then set aside to "cool."

In one test, a large box was fitted with thermocouples as the Plioflex bales were loaded at 74°C (165°F). They were then placed outdoors in the sun. The central temperature fell in 14 days to the ambient temperature. The rate of temperature drop checked closely with that expected by simple heat conduction.

A second set of three tests were performed by in each case instrumenting a large box of Plioflex with thermocouples and placing it in a warehouse completely surrounded by other boxes. The original temperature as loaded would again have been about 74°C (165°F). Again the temperature fell continuously by heat conduction to the ambient temperature without any evidence of exothermic reactions.

CONCLUSIONS

(i) Styrene-butadiene rubber is sufficiently complex to support both endothermic and exothermic processes when heated.

(ii) At low temperatures [below about 220°C (428°F)], the endothermic processes dominate and cool the sample.

(iii) At high temperatures [above about 300°C (572°F)], the exothermic processes dominate and the material may spontaneously ignite.

(iv) At intermediate temperatures, a complex heating history occurs showing first a maximum temperature, then a minimum temperature and probably on a much longer time scale (days or longer) a second temperature rise.

(v) These effects are consistent with a single exothermic volumetric reaction of high activation energy and a single evaporation or pyrolysis endothermic reaction of low activation energy as shown by computer simulation.

(vi) Some large scale experiments (1 to 3 m cubes) confirm that at low initial

temperatures [below 80°C (176°F)], the material cools to ambient without any evidence of internal exothermic or endothermic reactions. This is consistent with the laboratory results on small samples.

APPENDIX A

Heat conduction in a slab with an exothermic volume reaction and an endothermic pyrolysis front.

A slab of thickness $2L$ conducts heat with constant thermal conductivity k and constant thermal diffusivity α. Assume that an exothermic reaction proceeds at rate $A_r e^{-E_r/RT}$ and has a heat of reaction Q_r. Simultaneously a fraction of the material of density ρ_v is subject to pyrolytic gasification at the rate of $A_v e^{-E_v/RT_v}$ per unit area of the pyrolysis front whose temperature is T_v and absorbs heat at the rate of Q_v per unit mass pyrolyzed.

The surface temperature of the slab will be raised at the rate $(dT/dt)^0$ for the first τ sec and held constant thereafter. If there were no internal reactions, heat conduction would raise the internal temperature, rapidly near the surface, slowly at the center until the whole slab reached $\tau (dT/dt)^0$ above the ambient temperature.

If there was an added exothermic reaction only, the internal slab temperature would rise faster than for conduction alone, and would rise to a temperature sufficiently above the surface temperature to conduct the reaction heat out. A runaway rise in central temperature implies spontaneous ignition.

If on the other hand there was an added endothermic pyrolysis front, the slab temperature would rise everywhere but pyrolysis would start at the surface and progress inward as the pyrolyzed gases escape through the surface. Thus after an initial period the slab consists of a fully pyrolyzed region "1" at the surface, separated by a pyrolysing surface from a central region "2" of virgin material. Because of the endothermic nature of the pyrolysis, the central region is cooler than the surface by sufficient to conduct in the pyrolysis heat. In the following analysis both reactions occur along with heat conduction.

The temperatures in both regions are described by

$$\frac{\partial T_i}{\partial T} = \alpha \frac{\partial^2 T_i}{\partial x^2} + \frac{Q_r}{c\rho}, \quad i = 1,2 \tag{5}$$

At the slab surface the boundary condition is

$$T_1(t,0) = \begin{cases} \left(\dfrac{dT}{dt}\right)^0 t, & 0 < t < \tau \\[2ex] \left(\dfrac{dT}{dt}\right)^0 \tau, & \tau < t \end{cases} \tag{6}$$

At the slab center

$$\frac{\partial T_2}{\partial x} = 0 \quad \text{for all } t \tag{7}$$

At the pyrolysis front

$$-k \left.\frac{\partial T_1}{\partial x}\right|^f + k \left.\frac{\partial T_2}{\partial x}\right|^f = Q_v \rho_v \frac{d\delta}{dt} = Q_v A_v e^{-E_v/RT_v} \tag{8}$$

and

$$T_1 = T_2 \quad \text{for all } t \tag{9}$$

The first and last terms of eq. (8) together with (9) serve as the required boundary conditions for eq. (5) at each time while the second term of eq. (8) gives the rate of movement of the pyrolysis front.

All of the above equations were expressed in finite difference form and solved for the thermal data of Table II on 36 points from the surface to the center spaced 1 mm apart. The infinite rate of change encountered at the beginning if the pyrolysis front starts from the surface is avoided, not unrealistically, by starting the front at 1 mm below the surface (some pyrolysis, perhaps evaporation, would occur at the surface during specimen preparation).
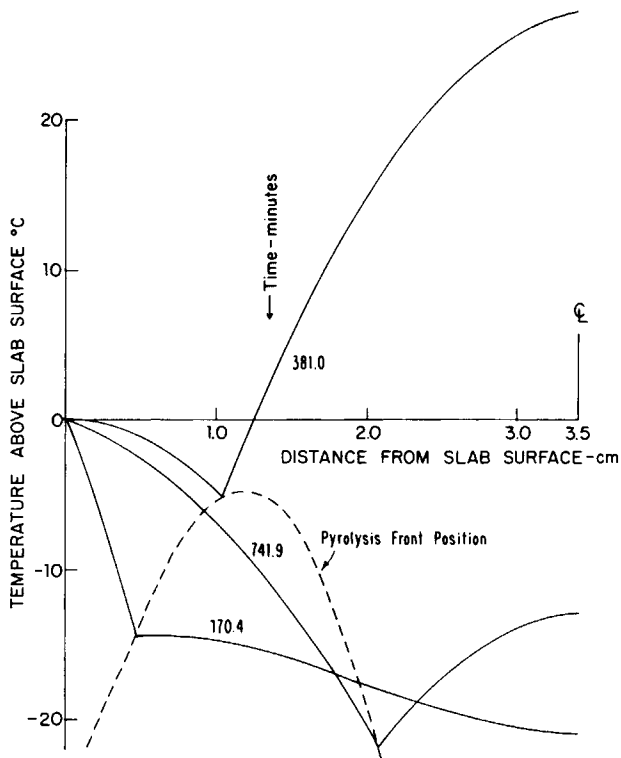
Fig. 6. Temperature distribution through a slab of pyrolyzing, reacting material at three different times: 170.4, 381.0, and 741.9 min; furnace temperature 300°C.

Computations were made for various surface temperatures, i.e., various heating times τ. The temperature difference between the slab center, thermocouple A, Figure 1 and thermocouple B (taken as placed 2 mm below the surface) is shown in Figure 5.

A large scale graph of events in the slab interior at various times for the furnace temperature of 300°C is shown as Figure 6. This graph shows how the temperature of the pyrolysis (evaporation) front changes as the front moves inward and thus causes the central temperature to fall below the surface temperature after first passing through a positive maximum.

APPENDIX B: LIST OF SYMBOLS

A_r frequency factor of the exothermic reaction
A_v frequency factor of the pyrolysis reaction
E_r activation energy of the exothermic reaction
E_v activation energy of the pyrolysis reaction
k thermal conductivity (cal/s cm °C)
L half thickness of slab (cm)
Q heat production rate (cal cm^3 s)
Q_r heat of exothermic reaction (cal/g)
Q_v heat of endothermic pyrolysis reaction (cal/g)
R gas constant (cal/g mol °C)
T temperature (°C)
T_0 initial temperature
T_1 temperature of slab material between surface and pyrolysis front
T_2 temperature of slab material between pyrolysis front and center
T_v temperature of pyrolysis front

ΔT temperature of sample center above its edge (defined as 2 mm below the surface)

x Slab coordinate in from surface (cm)

α thermal diffusivity (cm^2/s)

δ position of pyrolysis front below surface (cm)

ρ_v density of pyrolysable fraction of sample (g/cm^3)

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