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HETEROGENEOUS CHEMICAL KINETICS BY GAS EFFLUENT ANALYSIS - THE UNZIPPING OF PARAFORM

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EXTRACTION METALLURGY RESEARCH SECTION

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INTRODUCTION

Heterogeneous chemical reactions of the type:

$$S_1 + G_1 \rightleftarrows S_2 + G_2$$

are involved in many of the major chemical and metallurgical processes which support the economy of Canada. When S_1 represents iron ore, G_1 carbon monoxide, S_2 iron metal and G_2 carbon dioxide, the equation describes the primary reaction occurring in a blast furnace for the production of iron. When S_1 represents limestone, S_2 represents CaO, and G_2 represents CO_2, the equation relates to the burning of lime in the manufacture of CaO for the making of slag or plaster. It is well established (1-3) that this type of reaction occurs at a sharply defined interface between the solid reactant and the product. The observed rate of reaction varies with the area of the interface (4). Usual methods of relating the observed rate of reaction to the area of the interface, or to the weight of sample, are based on the unreacted-core shrinking model.

The rate of reaction may be controlled by processes occurring in the interface (2), or by heat or mass transfer (6, 7) through a product layer. It has been suggested that a model combining both heat and mass transfer is often required (5).

Many of the arguments for and against certain models are predicated on the assumption that the shrinking core model is valid and predictable from relationships such as (2, 8):

$$f = 1 - (1 - \alpha)^{1/3} \qquad [1]$$

where f is the fractional movement of an interface or the equivalent, $(\text{weight})^{2/3}$, in a spherical particle that has decomposed to a fraction α.

The experimental evidence is heavily weighted to acceptance of relationships such as that shown in Equation [1], because they seem to be reasonably effective in resolving many of the observed experimental results.

To test the validity of the shrinking core model, a series of experiments were initiated in which there was no residue that might interfere with the transfer either of heat or mass to or from the interface. It was hoped that the exact change in the geometry of the interface might be observed and related precisely to the measured reaction rate.

EXPERIMENTAL

Materials and Their Preparation

Ammonium bicarbonate, ammonium carbonate, ammonium carbamate, anthracene, napthalene, paradichlorobenzene and paraform were used in initial experiments. Because of multiple stages in some decompositions, or because of purification and handling problems, the list of experimental materials was reduced to paradichlorobenzene and paraform. The volatilization of paradichlorobenzene is a simple sublimation process, whereas the unzipping of paraform to its monomer is the equivalent of an inorganic chemical reaction in which a solid reactant is converted to a gaseous product.

Resublimed paradichlorobenzene was used as purchased, without further purification. The paraform was dehydrated at 100°C. for 48 hours. X-ray analyses of the material indicated that it was alpha-polyoxymethylene $[HO.(CH_2O)_n.H]$. The value of n is normally in the 100-300 range, and the formaldehyde content of the material is usually between 99.7 and 99.9 percent (9). When alpha-polyoxymethylene is depolymerized in the temperature range below 140°C., only monomeric formaldehyde gas is obtained (10). The unzipping of the polymer occurs at its exposed end-groups so that the rate of depolymerization is proportional to their number (11). When alpha-polyoxymethylene was depolymerized at temperatures below 140°C., there was a small fluffy residue. Because this represented only 0.4 percent of the original weight and did not appear to interfere with the reaction in any way, its presence was ignored in treating the results.

Because paradichlorobenzene flows freely under pressure, no attempts were made to sieve-size it before it was made into pellets. The alpha-polyoxymethylene was sieve-sized into the following micron size fractions: 37-43, 43-53, 53-62, 62-74, 74-88, 88-104, 104-125, 125-147, and 147-208. Both materials were kept in closed containers until they were used to prepare pellets of 1/4 inch in both height and diameter under pressures of 100,000 psig.

Apparatus and Procedure

A schematic diagram of the apparatus is shown in Fig. 1. The pelletized sample was supported (Fig. 2) on the bare junction of a Pt-Pt/10% Rh thermocouple which permitted a reliable measurement of the temperature at the reaction interface. This was normally in the range of 10 to 20°C. below that of the furnace in which it was supported. The evolved formaldehyde or paradichlorobenzene gas was swept from the pellet into a Gow-Mac tungsten-filament thermal conductivity cell by a stream of helium monitored with a Mathieson flow meter. The emf. signals representing pellet temperature, gas flow, current to the filaments, and output from the thermal conductivity cell, were digitized and printed on paper tape. A Hewlett-Packard digital voltmeter was used for the gas-flow and current signals, and an Infotronics integrator was used to monitor the temperature and gas- analysis signals. From the paper tape, data were selected and punched together with a computer program on 8 level ASCII tape. A Datacom teletype unit connected with a General Electric Time Sharing computer was used to resolve the data. It was usual to have, within twenty minutes, the results of experiments that lasted up to twenty hours.

RESULTS AND DISCUSSION

Normalization of Observed Reaction Rates

In the first group of experiments, pellets of both paradichlorobenzene and alpha-polyoxymethylene were prepared and examined after various periods of reaction. The freshly prepared pellets of both materials were smooth and shiny, with sharply defined corners. As decomposition progressed, the general form of the pellet was retained although the edges became slightly rounded. The paradichlorobenzene pellets remained smooth, because of material flow during preparation of the pellet. The alpha-polyoxymethylene pellets developed roughness equivalent to the particle size of the material from which they had been prepared. It was evident, from visual observations, that although the initial surface areas of pellets of both materials were essentially the same, the area presented by the roughened surface of the alpha-polyoxymethylene pellet was greater at all stages during its decomposition, than it had been initially.

In the next group of experiments, three pellets of alpha-polyoxymethylene were heated in a 50 $cm.^3 min.^{-1}$ stream of helium in the 15/16-inch diameter reaction vessel. The pellet temperatures, as measured by their supporting thermocouple, were 96 ± 1°C., 105 ± 1°C. and 114 ± 1°C., respectively.

In an experiment of this type, the partial pressure of formaldehyde in the helium carrier gas is the observed rate of reaction (12, 13). The observed rate of reaction was calculated by multiplying the number of counts obtained in a 100-second period by the calibration factor of 9.10×10^{-6} $mg.cm.^{-2} min.^{-1} count^{-1}$. The results of the three experiments are shown by the curves in Fig. 3. If there were no changes in surface roughness and no decrease in the area of the reaction interface, one would expect the reaction rate to increase rapidly at the beginning of an experiment and to remain constant throughout the reaction. When geometric changes occur, the data must be normalized to determine the true reaction rate per unit of interfacial area.

The usual method of normalizing the observed reaction rate is based on the shrinking core model (2, 14). This model was used to calculate the factor by which the observed reaction rate should be multiplied to obtain the true reaction rate per unit of surface area of a cylindrical pellet. The variation of the factor with the fraction of decomposition is shown by curve D, Fig. 4. The calculation was made on the assumption that there was no change, during decomposition, in the surface roughness of a cylindrical pellet which was initially 1/4 inch in both height and diameter (the curve is identical for a smooth sphere of the same dimensions). When attempts were made to use curve D to normalize the experimental results, it was evident that the relationship was not applicable. The correction curve that would be required to normalize the data from all of the experiments is that shown by the broken curve, E. From the difference in the position and shape of these two curves, it is evident that changes in surface roughness must cause a substantial change in the shape of the normalization curve. To check the validity of the shape of curve E, the data for curve A (Fig. 3) were corrected for a 25% increase in surface roughness as the pellet passes through 10% decomposition. This accommodates to the observation that the pellet is smooth initially and that a small amount of reaction is necessary before roughness is fully developed. The revised curve is represented by the circles superimposed on curve E, Fig. 4. The excellent agreement of the predicted relationship with that required experimentally for normalization indicates the importance of surface roughness in influencing the observed rate of reaction. As a corollary, it illustrates the inadequacy of a simple model based on a smooth interface covering a shrinking core.

The Influence of Particle Size on the Reaction Rate

In the previous section, it was shown that during the depolymerization of a pelletized sample of powder, the pellet develops a surface roughness which represents the size of the particles from which it was pressed. Although earlier experiments by Ingraham and Marier (14) had shown that the reaction rate for calcite decomposition was independent of particle size, this conclusion was re-examined by making a series of experiments with pellets prepared from different size fractions of alpha-polyoxymethylene. The results of experiments at 100°C. in a 50 $cm.^3 min.^{-1}$ flow of helium are shown in Fig. 5. Within experimental scatter, the results show that the reaction rate, and hence the interfacial area, is independent of particle size.

This experimental conclusion may be supported by a simple argument (Fig. 6) based on a cross-sectional view of two interfaces, one having an exposure of seven particles in an interfacial length of L, and another with an exposure of three particles in the same length. In each case the length of the cross section of exposed interface is the sum of the distances around the semicircles. For the seven semicircles the distance is $7\pi L/14$, and for the three semicircles it is $3\pi L/6$ or $\pi L/2$ in each case. The argument is also valid in three dimensions. It was concluded from this, and from the experimental evidence, that the weathered interfacial area of a pellet remains constant, irrespective of the size of the powder particles from which it is constructed.

It will be recognized that the foregoing conclusions are valid only when a powder compact is studied in a flowing gas that permits the interstices between the particles to remain filled with reaction product gas. It is not valid for experiments under reduced pressure, when each particle behaves individually because of rapid removal of the product gases from the interior of the pellet.

The Influence of Carrier Gas Flow-Rate on Reaction Rate

To assess the possibility that the reaction rate at the surface of the pellet might be influenced by diffusion of the product gas though a stagnant layer of gas on the pellet surface, the rate of depolymerization of alpha-polyoxymethylene was examined at gas flows of from 25 $cm.^3 min.^{-1}$ to 150 $cm.^3 min.^{-1}$ (linear flows from 0.1 to 0.6 $cm.sec.^{-1}$). The results are shown in Fig. 7, which indicates that at flow rates greater than 0.3 $cm.sec.^{-1}$ there is no significant effect of carrier gas flow on the reaction rate.

The Effect of Temperature on Reaction Rate - Isothermal Experiments

In Fig. 3, the effect of temperature change on the reaction rate of alpha-polyoxymethylene was shown for three typical isothermal experiments. When the observed rates were normalized for changes in surface roughness and geometry, the reaction rate per unit of interfacial area was constant throughout the reaction as shown in Fig. 8. The linear relationships are characteristic and are usually obtained within ±5% scatter over the range from 10 to 85% reaction. When the logarithm of the reaction rate at a variety of temperatures was plotted against the reciprocal of absolute temperature, the Arrhenius plot in Fig. 9 was obtained. The figure includes the results for the normalized runs A, B and C from Figs. 3 and 8, and for the peak values of the rate from a series of additional experiments. The relationship is linear and is represented by the least-square regression equation:

$$\ln \text{rate} = 32.587 - 12{,}172/T \qquad [2]$$

The corresponding exponential rate equation is:

$$\text{rate } (\text{mg.cm.}^{-2}\text{min.}^{-1}) = 1.432 \times 10^{14} \exp(-24{,}100/RT) \qquad [3]$$

The activation energy governing the change in rate with a change in temperature is 24.1 kcal.mole^{-1}

Iwasa and Imoto (15) have also studied the kinetics of depolymerization of alpha-polyoxymethylene. From experiments in which the rate of depolymerization was measured by following the rate of increase of formaldehyde pressure in a closed container, they calculated a pre-exponential factor of 1.8 x 10^{10} and an activation energy of 27.1 kcal.mole^{-1}. As one might expect, both activation energies are substantially larger than the 18 kcal.mole^{-1} heat of depolymerization measured by Galiazzo, et al. (16). There is a significant inconsistency between these more recent measurements of the energies involved in depolymerization, and the earlier work of Kern and Cherdron (17) in which it is suggested that depolymerization at temperatures near 100°C. gives an activation energy of about 10 kcal.mole^{-1} for the removal of end groups from a polymer chain. They calculated that during autoxidation of the polymer at about 170°C., the activation energy is about 14.5 kcal.mole^{-1}. Similarly at 270°C., when the polymer is depolymerized and decomposed to methanol, water, methane, etc., the calculated activation energy was about 28 kcal.mole^{-1}.

The Effect of Temperature on Reaction Rate - Non-Isothermal Experiments

One of the most attractive features of experiments done by gas effluent analysis is their amenability to automation (12). It is possible to use modern gas-analysis equipment to do very precise experiments at low temperatures where heat and mass transport are not rate-controlling factors. The experiments can be arranged to gather a large amount of data, which when analyzed with computer programs, can provide highly reliable results.

In the earlier discussion of normalization of observed reaction rates to eliminate the effects of geometry change, mention was made of the fact that the partial pressure of the decomposition product in the carrier gas is the reaction rate (12). If one also assumes that the rate of reaction at a specified temperature is the same whether that temperature is constant or increasing or decreasing slowly (18), then gas effluent analysis experiments offer a very convenient method of directly relating changes in reaction rate to changes in temperature.

As a test of the application of the non-isothermal approach (12) to determining activation energy, a series of programmed heating-rate experiments was done with pellets of alpha-polyoxymethylene. The pellets were heated at rates from as slow as 1/12°C.min.$^{-1}$ to as rapid as 2°C.min.$^{-1}$. The duration of the experiments varied from about 30 hours to about 2 hours. Heating rates were programmed with an F & M programmed controller in which the original driving motor was replaced by one with one-sixth of the speed (1/30 rpm.). The results of a series of five experiments were indistinguishable over the range of decomposition from $\alpha = 0.10$ to $\alpha = 0.85$. A typical run is shown on an Arrhenius plot in Fig. 10. The relationship is linear, as shown in Fig. 9 for isothermal experiments. The points inserted at the top and bottom of the line are taken from the isothermal curve in Fig. 8. The agreement of the data from the isothermal and non-isothermal experimental methods indicates that the more rapid non-isothermal method may be used as a valid substitute for a more tedious series of isothermal experiments. It is significant that the non-isothermal procedure reproduces the results of the classical isothermal method. The non-isothermal procedure also provides a very effective and rapid method for detecting any stages in a reaction by observation of changes in the slope of the Arrhenius line.

The Effect of Partial Pressures of Formaldehyde

The effect of small partial pressures of formaldehyde in the helium carrier gas was not examined in these experiments. From previous experimental work in the

$CaCO_3$-CaO system, where adsorption in a product layer is not involved (14), it was shown that the effect is directly proportional to the difference between the equilibrium partial pressure (p_e) and the ambient partial pressure (p). The factor by which the rate may be expected to decrease (4) can be calculated from:

$$(p_e - p)/p_e \qquad [4]$$

When Iwasa and Imoto (15) studied the kinetics of depolymerizing alpha-polyoxymethylene, they found that this relationship, raised to the power 1.6, was suitable for correlating the effect of formaldehyde back-pressures. Because of the approximate method they selected for normalizing the changing geometry of their sample, it is probable that some of the effects they attributed to changing pressure might be ascribed to geometry changes.

MODEL OF DEPOLYMERIZATION REACTION

In the previous sections it has been shown that the observed rate of depolymerization of a single pellet of alpha-polyoxymethylene is a function of:

(a) the size and roughness,
(b) the carrier gas flow-rate over it,
(c) the temperature,
(d) the partial pressure of formaldehyde around the pellet.

When these functions are expressed mathematically and combined, a model of the depolymerization process can be constructed. The model has the following form:

$$x = k\, f_1 . f_2 . f_3 . f_4 ,$$

in which x = the amount of alpha-polyoxymethylene depolymerized per minute
f_1 = the function of geometry
f_2 = the function of carrier gas flow rate
f_3 = the temperature function
f_4 = the back-pressure function
k = the proportionality constant.

For simplicity, and as a parallel to industrial metallurgical practice, it is presumed that the paraform is available as solid quarter-inch lumps. For estimating grinding costs, it is assumed that the material has about the same hardness as a typical sulphide ore.

In the following sections, each of these variables will be examined individually and a series of computer-produced tables will be used to illustrate the effects of the variables. The decomposition rate at 100°C. is used as the basis for comparison. A standard flow condition of 16 $cm.^3 min.^{-1}$ was used with cylindrical pellets which were 1/4 inch in both height and diameter.

The Effect of Pellet Size and Roughness on the Rate of Depolymerization

When a cylindrical pellet of alpha-polyoxymethylene is depolymerized it decreases in size, while maintaining the same form. Its surface roughness is increased to a maximum at about 10% decomposition. The decrease in size is governed by the basic law that the interface must move at a constant rate at a constant temperature. The rate of interface movement may be obtained by dividing the rate of reaction per unit of interfacial area by the density of the pellet. When this calculation is made for a pellet at 100°C., in a 50 $cm.^3 min.^{-1}$ flow of helium containing no back-pressure of formaldehyde, the results obtained are shown in Table I.

The Effect of Carrier Gas Flow-Rate on the Rate of Depolymerization

The effect of carrier gas flow-rate on the rate of depolymerization was shown in Fig. 7. After the data were analyzed mathematically, Table II was prepared. showing a rate factor of unity for a linear flow of 12 $cm.min.^{-1}$. When the flow is decreased to 4 $cm.min.^{-1}$, the rate is decreased to 53% of the original value, whereas when the flow is increased to 40 $cm.min.^{-1}$, the rate is only increased by 5.3%.

The Effect of Temperature on the Rate of Depolymerization

When the rate-controlling step of a reaction has an activation energy of about 25 $kcal.mole^{-1}$, the rate is approximately doubled for each increase of 10°C. in the reaction temperature. Calculations of the reaction rate made from Equation [3] are shown in Table III. When the rate at 100°C. is used as the basis for comparison, it is evident that a decrease of 20°C. brings about an 85% reduction in the reaction rate. When the temperature is increased by 40°C., the rate is increased by a factor of 23. It is evident that the rate of depolymerization is very sensitive to temperature changes.

The Effect of Back-Pressure of Formaldehyde

Although not defined in the present work, this effect has been sufficiently well established in other systems to warrant including a prediction of its effect. The predictions are based on Equation [4] and are shown in Table IV for pellet temperatures of 100, 110 and 120°C. At 120°C., the effect of a specific partial pressure of formaldehyde in the carrier gas is less than that at 110 or 100°C., respectively, because the rate of depolymerization is more rapid at the higher temperature. At 120°C. the rate is only decreased by 30% when one-third of the carrier gas is formaldehyde, whereas at 100°C., under the same conditions, the rate of depolymerization would be decreased by about 89%.

The method of using the model to predict the expected amount of formaldehyde production under specified conditions is illustrated by the following example. All of the variables are presumed to be independent. From the earlier discussion it is evident that when a single quarter-inch pellet of alpha-polyoxymethylene is heated in a 50 $\text{cm.}^3\text{min.}^{-1}$ (12 cm.min.^{-1}) stream of pure helium, the rate of formaldehyde production is 1.237 mg.min.^{-1} (0.976 $\text{mg.cm.}^{-2}\text{min.}^{-1}$ multiplied by surface area of 1.267 cm.^2). When the rate of helium flow is increased to 40 cm.min.^{-1}, that rate must be multiplied by the factor 1.053 from Table II. If, in addition, the pellet temperature were increased to 120°C., the rate would be increased again by a factor of 5.251, from Table III. At 120°C., if a back-pressure of 23% of formaldehyde were used in the helium, then the rate would be reduced by a factor of 0.799.

Thus, the model predicts that a single pellet, at 120°C., in a flow of 40 cm.min.^{-1} containing a back-pressure of 23% formaldehyde, would decompose at a rate of

$$1.237 \times 1.053 \times 5.251 \times 0.799 = 5.465 \text{ mg.min.}^{-1} \qquad [5]$$

Presuming no mutual interference, the rate of formaldehyde production from a dozen pellets would be twelve times that shown in Equation [5].

There are other interesting applications of the model. In Table III, the rate of production of formaldehyde is shown to increase rapidly with increasing temperature. In Table I it is shown to decrease rapidly with decreasing pellet size. The model can be used to predict the rate at which the temperature must be increased to produce a constant flow of formaldehyde from a pellet which is diminishing in size. The product of the two factors should remain equal to about 1.0. For example, after two hours, Table I shows that the rate of decomposition of a single pellet has been reduced by a factor of 0.676. In Table III, it is evident that the rate could be increased by a corresponding amount by a temperature increase to 105°C. Similarly, after 3.5 hours of reaction, the rate of depolymerization of the smaller pellet could be restored to its original value by a temperature increase to about 110°C. The foregoing manipulations from the tables illustrate the method. A more sophisticated program of temperature increase may be obtained from simultaneous computer solution of the equations used to produce each table.

It will be recognized that the foregoing is similar to the problem which one might encounter in attempting to maintain a steady flow of either SO_2 or CO from the oxidation of sulphur, a sulphide mineral, or coke.

Economics of Increasing the Rate of Formaldehyde Production

In the foregoing sections, the effects of each of the variables on the rate of formaldehyde production from 1/4-inch platform pellets have been examined. It is evident, from the results, that the principal factors which affect the rate of depolymerization are geometry of the pellet, pellet temperature, and the partial pressure of formaldehyde in the carrier gas. Because the latter can be controlled by the rate of flow of the carrier gas, which by itself does not alter the rate of the reaction, there are only two significant variables which control the rate of a slow depolymerization reaction. They are the temperature and the size of the pellet.

If a hypothetical process is assumed, it is possible to use simple linear models (19) to determine the minimum cost for increasing the rate of formaldehyde production by changes in both the temperature and the size of the paraformaldehyde aggregates. One such hypothetical process is shown schematically in Fig. 11. It is assumed that a carrier gas is circulated through a bed of pellets. The size of the pellets is open to prior selection. The bed is heated uniformly, either by gas or by electricity. When the evolved formaldehyde gas is passed into the reactor, it is presumed to be completely consumed, with the result that the returning carrier gas is barren of formaldehyde. If the cost of heating one ton of pellets through 1°C. is x_1 and the cost of reducing the size of the pellets by half is x_2, then the minimum cost of increasing the production by a factor of, say, $M = 10$, may be calculated from the equation:

$$\text{Cost (dollars/ton)} = x_1 n_1 + x_2 n_2 \qquad [6]$$

in which n_1 and n_2 are respectively the number of degrees of temperature increase and the number of multiples of size decrease (e.g., $n_2 = 1$ is the equivalent of reducing the pellet size from 1/4 to 1/8 inch in height and diameter; $n_2 = 2$ would be a reduction to 1/16 inch in height and diameter).

Certain constraints are required on the economic model. If f_1 is the factor by which n_1 units of temperature increase the rate, and f_2 is the factor by which n_2 units of reduction increase the rate, then

$$f_1 \cdot f_2 = M \text{ (where M is the multiple; 10 in this case)}$$

Similarly, if it is assumed (to a good first approximation) that over short ranges the rate of reaction increases linearly with temperature and with the number of units of size reduction, then

$$f_1 = n_1 k_1 \text{ and } f_2 = n_2 k_2$$

Substitution in Equation [5] gives the relationship:

$$\text{Cost} = x_1 n_1 + M/(n_1 k_1 k_2) \qquad [7]$$

From the data already established, $k_1 = 0.3$ and $k_2 = 2.0$. On the basis of gas heating, x_1 is 0.0040 cents per ton.degree, and for heating by electricity it is

0.014 cents per ton•degree. When the size reduction is done on a high tonnage basis, x_2 is 0.03 cents per ton•multiple, and when done on a low tonnage basis it is 0.06 cents per ton•multiple.

The four combinations of factors have been programmed to determine the conditions for the minimum cost to increase the production of formaldehyde by a factor of ten. The results are shown in Table V to VIII. From Table V, it is evident that the rate may be increased by a factor of ten, at minimum cost of 8.9 cents per ton, by increasing the temperature by 11°C. and by reducing the size by 1.5 multiples (from 1/4 inch to 3/32 inch). When gas heating is used along with only a small-tonnage grinding plant, the minimum cost is 12.6 cents per ton. This may be achieved by increasing the temperature by 16°C. and using the pellets after reducing them to 1/8 inch (6 mesh).

When electrical heating is used (at $1.40 per million BTU, as contrasted to $0.40 for gas), the minimum cost is 16.7 cents for increasing the temperature by 6°C. and reducing the size to 1/32 inch (20 mesh) in a high-tonnage grinding plant. In contrast, a temperature increase of about 8.5°C., with a size reduction to 1/16 inch (10 mesh), would be required to minimize the cost when electrical heating was used to heat the product obtained from a small-tonnage grinding plant.

CONCLUSIONS

When pelletized samples of alpha-polyoxymethylene are depolymerized, it is necessary to introduce a surface roughness factor into the data normalization procedure to obtain a correct resolution of the data. It seems likely that this factor would also be required in any application of the shrinkage core model in which an interfacial roughness develops during a reaction.

The most significant factors in determining the rate of unzipping polyoxymethylene are the particle size, temperature, and the partial pressure of product gas in the sweep gas. The latter is most significant at low temperatures.

A mathematical model for the unzipping of polyoxymethylene is applicable in concept to the burning of pelletized solid fuels (20) and to sublimation processes.

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TABLE I

CHANGE IN OBSERVED RATE OF FORMALDEHYDE EVOLUTION AT 100 DEG CENT. AS THE PELLET SIZE DECREASES WITH TIME.

TIME (HRS)	DIST (CM)	FRACT. DECOMP.	NORMALIZATION	FACTOR
.00	.000	.000	1.250	.800
.25	.010	.093	1.010	.990
.50	.020	.179	1.005	.995
.75	.030	.260	1.056	.947
1.00	.040	.335	1.120	.893
1.25	.050	.405	1.210	.826
1.50	.060	.470	1.290	.775
2.00	.081	.585	1.480	.676
2.50	.101	.682	1.730	.578
3.00	.121	.763	2.050	.488
3.50	.141	.829	2.430	.412

TABLE II

```
THIS PROGRAM CALCULATES THE EFFECT OF CHANGES IN
THE FLOW OF HELIUM ON THE REACTION RATE FOR AN
EXPERIMENT DONE AT 100 DEGREES CENTIGRADE

  FLOW            RATE               FACTOR
(CM/MIN)     (MG/SQ.CM-SEC)

   4              .504                .521
   8              .877                .906
  12              .946                .977
  16              .970               1.002
  20              .981               1.013
  24              .987               1.020
  28              .991               1.024
  32              .993               1.026
  36              .995               1.028
  40              .996               1.029
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TABLE III

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THIS PROGRAM CALCULATES THE REACTION RATE PER UNIT OF
SURFACE AREA AT 100 DEGREES CENTIGRADE, AND THE FACTOR
BY WHICH THE RATE IS CHANGED AT OTHER TEMPERATURES.

  TEMP               RATE                 FACTOR
 (DEG C)       (MG/SQ.CM-MIN)

   80                .154                   .158
   85                .249                   .255
   90                .398                   .407
   95                .627                   .642
  100                .976                   .999
  105               1.503                  1.538
  110               2.288                  2.341
  115               3.444                  3.524
  120               5.132                  5.251
  125               7.571                  7.747
  130              11.061                 11.318
  135              16.011                 16.384
  140              22.970                 23.504
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TABLE IV

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THIS PROGRAM SHOWS THE EFFECT OF FORMALDEHYDE FLOW ON
THE REACTION RATE WHEN THE HELIUM FLOW IS 50 CC/MIN.


    FLOW     PARTIAL PRESS.    TEMP.    FACTOR
  (CC/MIN)       (ATM)        (DEG C)

     0           .000           100     1.000
     1           .020           100      .948
     2           .038           100      .897
     3           .057           100      .848
     4           .074           100      .802
     5           .091           100      .757
    10           .167           100      .554
    15           .231           100      .382
    20           .286           100      .235
    25           .333           100      .108
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THIS PROGRAM SHOWS THE EFFECT OF FORMALDEHYDE FLOW ON
THE REACTION RATE WHEN THE HELIUM FLOW IS 50 CC/MIN.


    FLOW     PARTIAL PRESS.    TEMP.    FACTOR
  (CC/MIN)       (ATM)        (DEG C)

     0           .000           110     1.000
     1           .020           110      .970
     2           .038           110      .942
     3           .057           110      .915
     4           .074           110      .888
     5           .091           110      .863
    10           .167           110      .749
    15           .231           110      .652
    20           .286           110      .570
    25           .333           110      .498
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THIS PROGRAM SHOWS THE EFFECT OF FORMALDEHYDE FLOW ON
THE REACTION RATE WHEN THE HELIUM FLOW IS 50 CC/MIN.


    FLOW     PARTIAL PRESS.    TEMP.    FACTOR
  (CC/MIN)       (ATM)        (DEG C)

     0           .000           120     1.000
     1           .020           120      .983
     2           .038           120      .966
     3           .057           120      .951
     4           .074           120      .935
     5           .091           120      .921
    10           .167           120      .85
    15           .231           120      .799
    20           .286           120      .751
    25           .333           120      .709
```

TABLE V

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THIS PROGRAM CALCULATES THE MINIMUM COST OF INCREASING
THE RATE OF FORMALDEHYDE PRODUCTION BY A FACTOR OF TEN
BY INCREASING TEMPERATURE AND REDUCING PELLET SIZE.
CALCULATIONS ARE BASED ON GAS HEATING WITH HIGH-TONNAGE
GRINDING COSTS.


    TEMP INCR           SIZE DECR          COST
   (DEG CENT)          (MULTIPLES)      (CENTS/TON)

        5                  3.3             12.0
        6                  2.8             10.7
        7                  2.4              9.9
        8                  2.1              9.4
        9                  1.9              9.2
       10                  1.7              9.0
       11                  1.5              8.9
       12                  1.4              9.0
       13                  1.3              9.0
       14                  1.2              9.2
       15                  1.1              9.3
```

TABLE VI

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THIS PROGRAM CALCULATES THE MINIMUM COST OF INCREASING
THE RATE OF FORMALDEHYDE PRODUCTION BY A FACTOR OF TEN
BY INCREASING TEMPERATURE AND REDUCING PELLET SIZE.
CALCULATIONS ARE BASED ON GAS HEATING WITH LOW-TONNAGE
GRINDING COSTS.


    TEMP INCR           SIZE DECR          COST
   (DEG CENT)          (MULTIPLES)      (CENTS/TON)

       10                  1.7             14.0
       11                  1.5             13.5
       12                  1.4             13.1
       13                  1.3             12.9
       14                  1.2             12.7
       15                  1.1             12.7
       16                  1.0             12.6
       17                  1.0             12.7
       18                   .9             12.8
       19                   .9             12.9
       20                   .8             13.0
```

TABLE VII

```
THIS PROGRAM CALCULATES THE MINIMUM COST OF INCREASING
THE RATE OF FORMALDEHYDE PRODUCTION BY A FACTOR OF TEN
BY INCREASING TEMPERATURE AND REDUCING PELLET SIZE.
CALCULATIONS ARE BASED ON ELECTRICAL HEATING WITH HIGH
TONNAGE GRINDING COSTS.

  TEMP INCR             SIZE DECR             COST
 (DEG CENT)            (MULTIPLES)        (CENTS/TON)

      1                   16.7               51.4
      2                    8.3               27.8
      3                    5.6               20.9
      4                    4.2               18.1
      5                    3.3               17.0
      6                    2.8               16.7
      7                    2.4               16.9
      8                    2.1               17.4
      9                    1.9               18.2
     10                    1.7               19.0
```

TABLE VIII

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THIS PROGRAM CALCULATES THE MINIMUM COST OF INCREASING
THE RATE OF FORMALDEHYDE PRODUCTION BY A FACTOR OF TEN
BY INCREASING TEMPERATURE AND REDUCING PELLET SIZE.
CALCULATIONS ARE BASED ON ELECTRICAL HEATING WITH LOW
TONNAGE GRINDING COSTS.

  TEMP INCR             SIZE DECR             COST
 (DEG CENT)            (MULTIPLES)        (CENTS/TON)

      3                    5.6               37.5
      4                    4.2               30.6
      5                    3.3               27.0
      6                    2.8               25.1
      7                    2.4               24.1
      8                    2.1               23.7
      9                    1.9               23.7
     10                    1.7               24.0
     11                    1.5               24.5
     12                    1.4               25.1
     13                    1.3               25.9
```

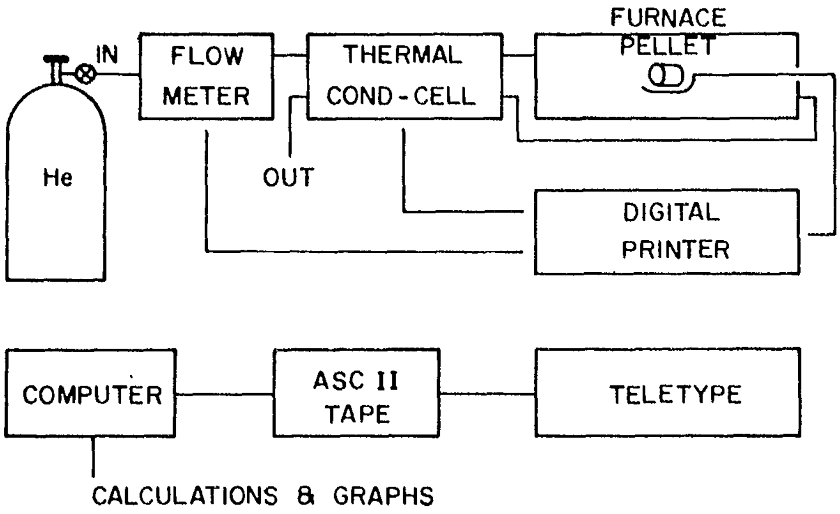

FIG 1 SCHEMATIC DIAGRAM OF APPARATUS

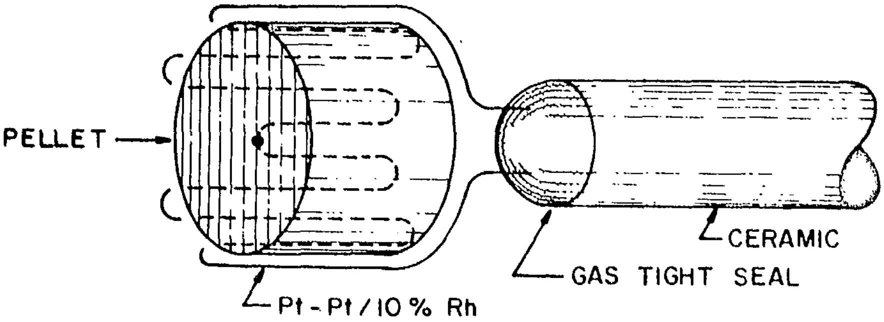

FIG 2 THERMOCOUPLE SUPPORT FOR PELLET

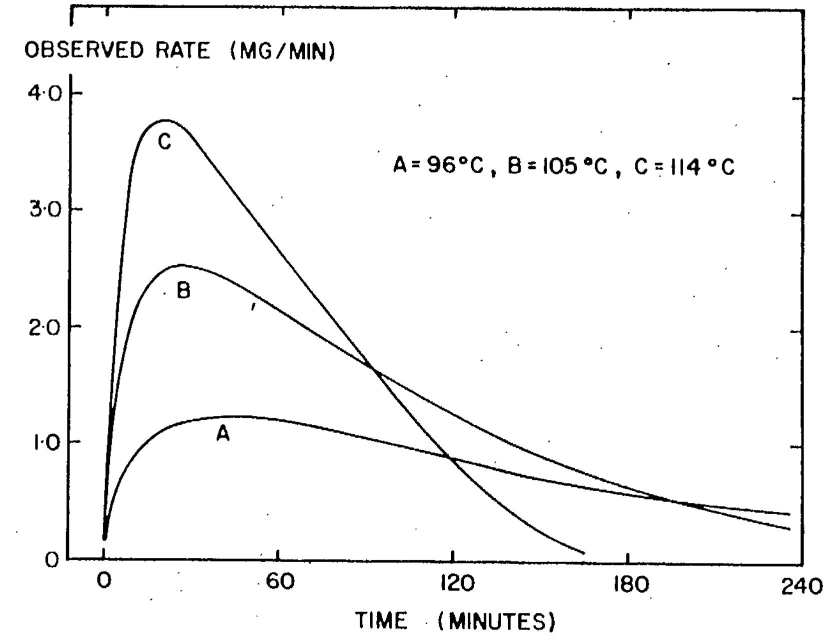

FIG 3 RATE DATA FOR THE DECOMPOSITION OF ALPHA-POLYOXYMETHYLENE

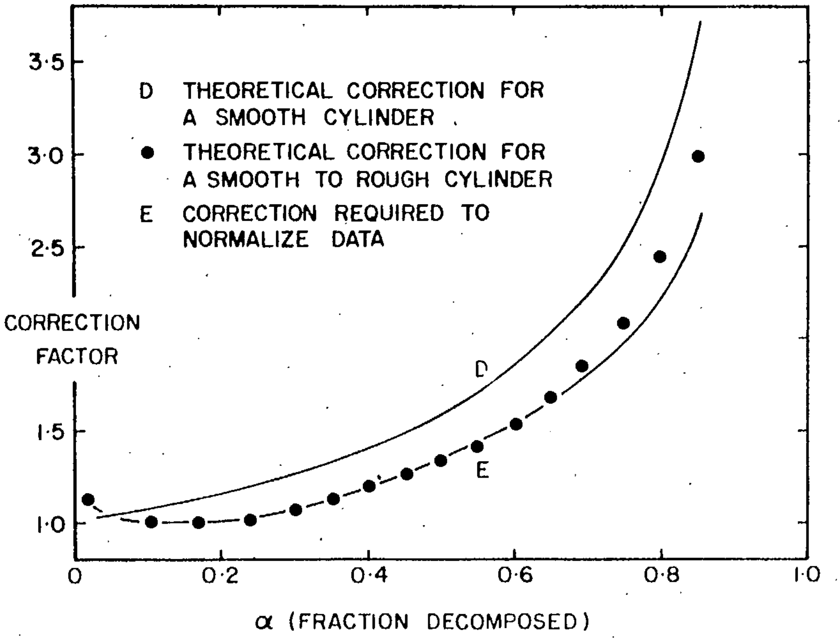

FIG 4 VARIATION OF NORMALIZATION FACTOR WITH FRACTION OF DECOMPOSITION

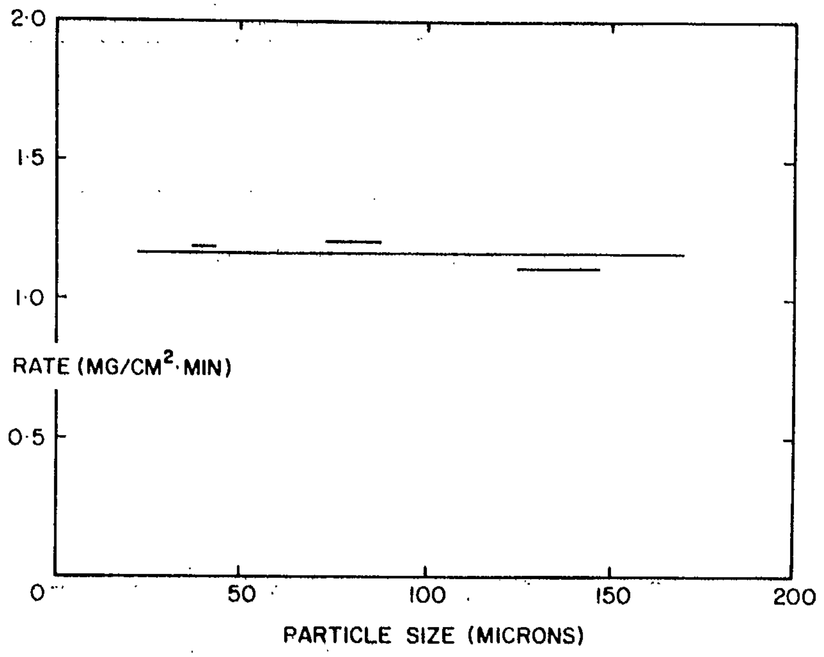

FIG 5 EFFECT OF PARTICLE SIZE IN THE PELLET ON THE RATE OF DEPOLYMERIZATION

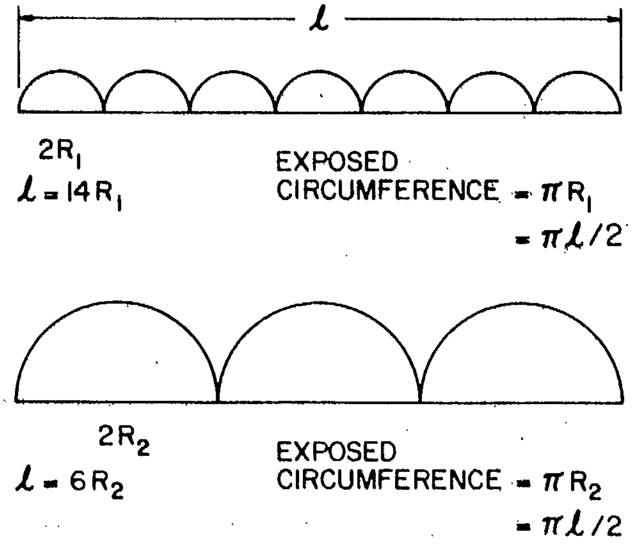

FIG 6 SURFACE ROUGHNESS AS A FUNCTION OF PARTICLE SIZE

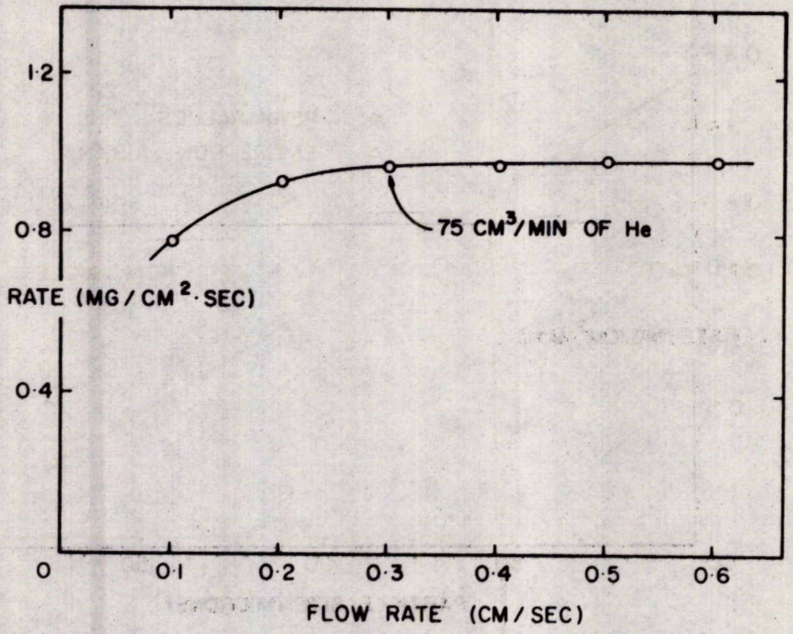

FIG 7 VARIATION OF DEPOLYMERIZATION RATE WITH RATE OF GAS FLOW

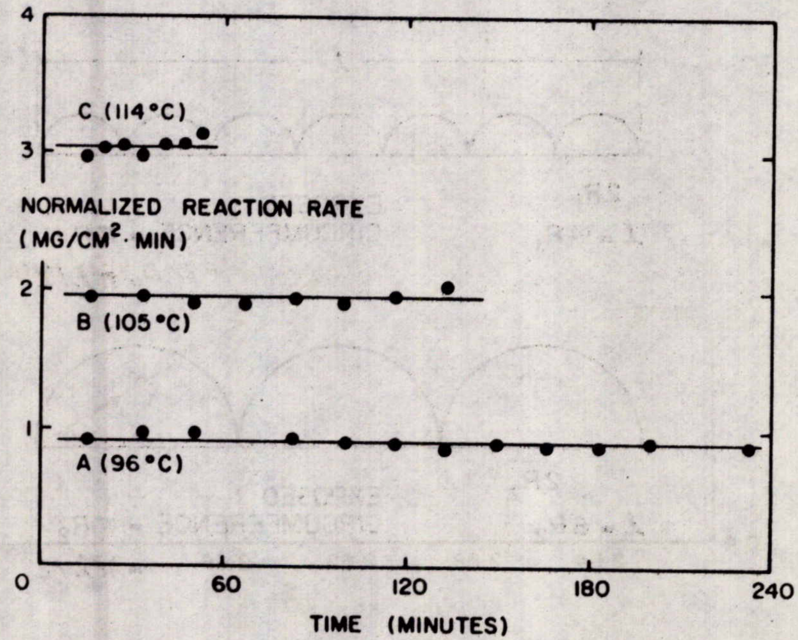

FIG 8 EFFECT OF TEMPERATURE CHANGE ON NORMALIZED REACTION RATE

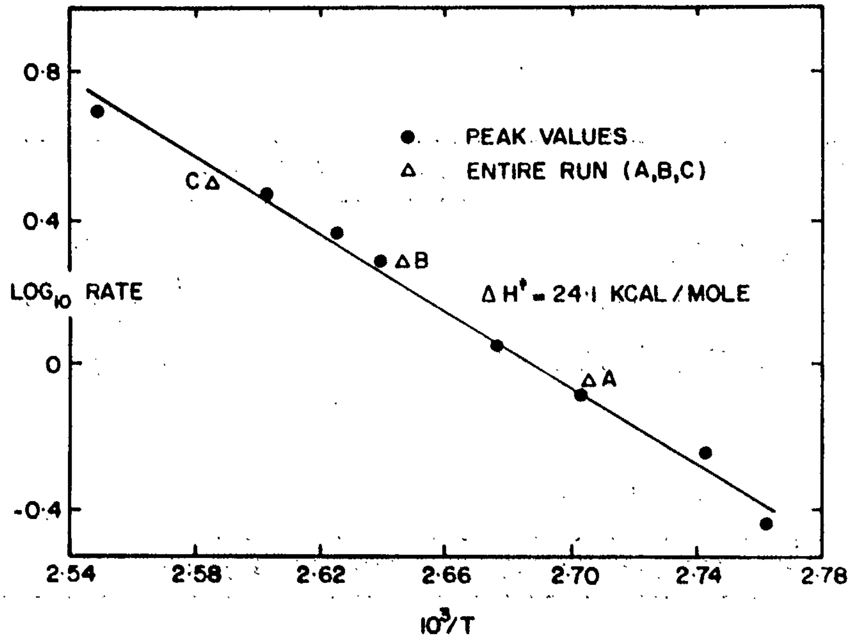

FIG 9 ARRHENIUS RELATIONSHIP FOR ISOTHERMAL EXPERIMENTS

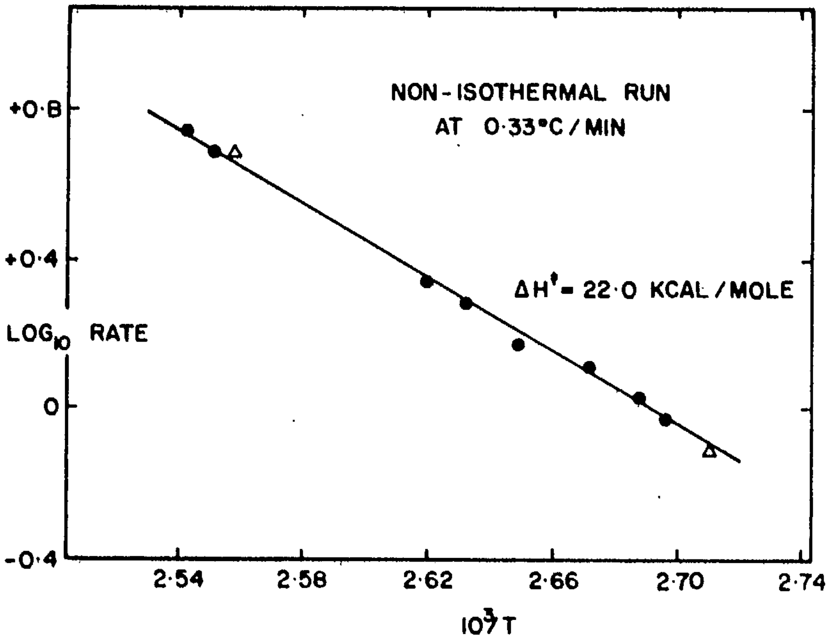

FIG 10 ARRHENIUS RELATIONSHIP FOR NON-ISOTHERMAL EXPERIMENTS

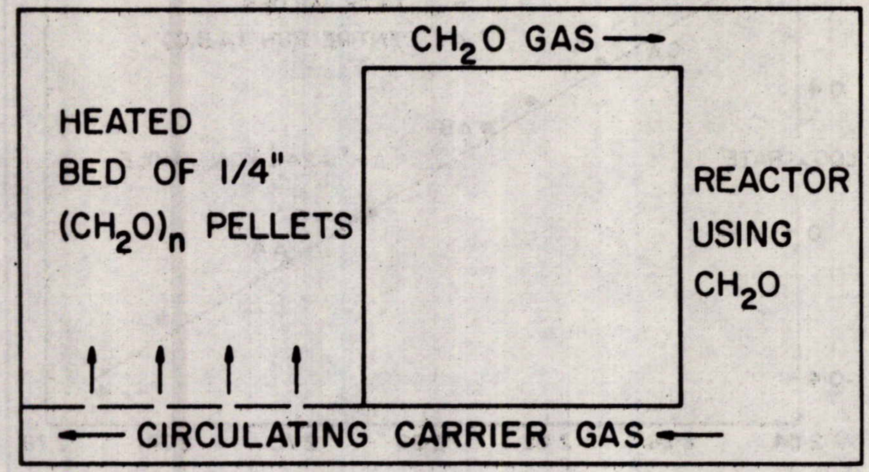

FIG 11 HYPOTHETICAL DEPOLYMERIZATION PROCESS FOR MODELLING