Evaluation of Reaction Hazards for a Wiped-Film Evaporator

Harold Johnstone
Dow Chemical Company
2301 N. Brazosport Blvd.
Freeport TX 77541

Phone: (979) 238-9758
Email: HMJOHNSTONE@dow.com

ABSTRACT

A production plant desired to increase its capacity by raising the operating temperature of a wiped film evaporator (WFE) unit. The WFE separates a high-boiling product (taken overhead) from a heavy tar stream (taken out the bottom). Both the product and the tars will begin to decompose at temperatures near the operating temperature of the WFE. The plant's Management of Change procedure required a consideration of reactivity hazards before making the proposed change in operating temperature. This paper will describe the experimental work that was done with ARC and Setaram C-80 instruments on plant samples and the estimation of decomposition kinetic parameters that was done using Thermal Safety software from Cheminform, Ltd. The results of this hazard evaluation allowed the plant personnel to make an informed decision about the proposed operating change.

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Harold Johnstone
The Dow Chemical Company
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Problem Statement

A production plant within The Dow Chemical Company desired to increase the operating temperature of a wiped-film evaporator unit in order to increase its throughput. As a part of Dow's Management of Change procedures, a hazard evaluation was requested to determine whether the proposed process change was safe to implement.

Background

The subject unit operation involves the separation of a volatile liquid from a non-volatile residue under vacuum at high temperature in a wiped-film evaporator (WFE). Figure 1 is a schematic diagram of the WFE. Both the overhead stream and the bottoms stream are sold as products, so it is important to minimize degradation. The WFE is well-suited for this separation since it promotes good heat and mass transfer with a low residence time. The feed is distributed onto the wall as a thin film. The high ratio of heat transfer surface to feed mass provides rapid heating by the hot oil jacket. As the film of liquid flows downward, it is agitated by the rotating wiper blades which have a very close clearance to the wall. This agitation increases the mass transfer of the volatile component. The overhead section is equipped with a demister to eliminate entrainment of heavy components. The bottoms stream falls into a cooled storage tank to provide immediate quenching of the hot liquid.

The feed typically enters at about 50 degrees C (Celsius). Hot oil is supplied at 294 C and exits the jacket at 289 C. The overheads stream is typically 199 C at 4 mm Hg pressure. The bottoms stream exits at 250 C and 15-20 mm Hg. It was desired to increase the feedrate to the WFE which required a corresponding increase in the flowrate and temperature of the hot oil supply. It was estimated that this change would raise the bottoms temperature to approximately 260 C.

The proposed higher bottoms temperature created concern about possible decomposition based on the results of previous reactive chemicals testing in an ARC (Accelerating Rate Calorimeter). It was known that decomposition of this material could lead to the formation of solids and non-condensable gases with possible equipment plugging and over-pressurization. Figure 2 is a schematic diagram of an ARC instrument. Typically, a sample is loaded into the ten milliliter sample sphere at ambient temperature and pressure and connected to the instrument. A thermocouple

Figure 1
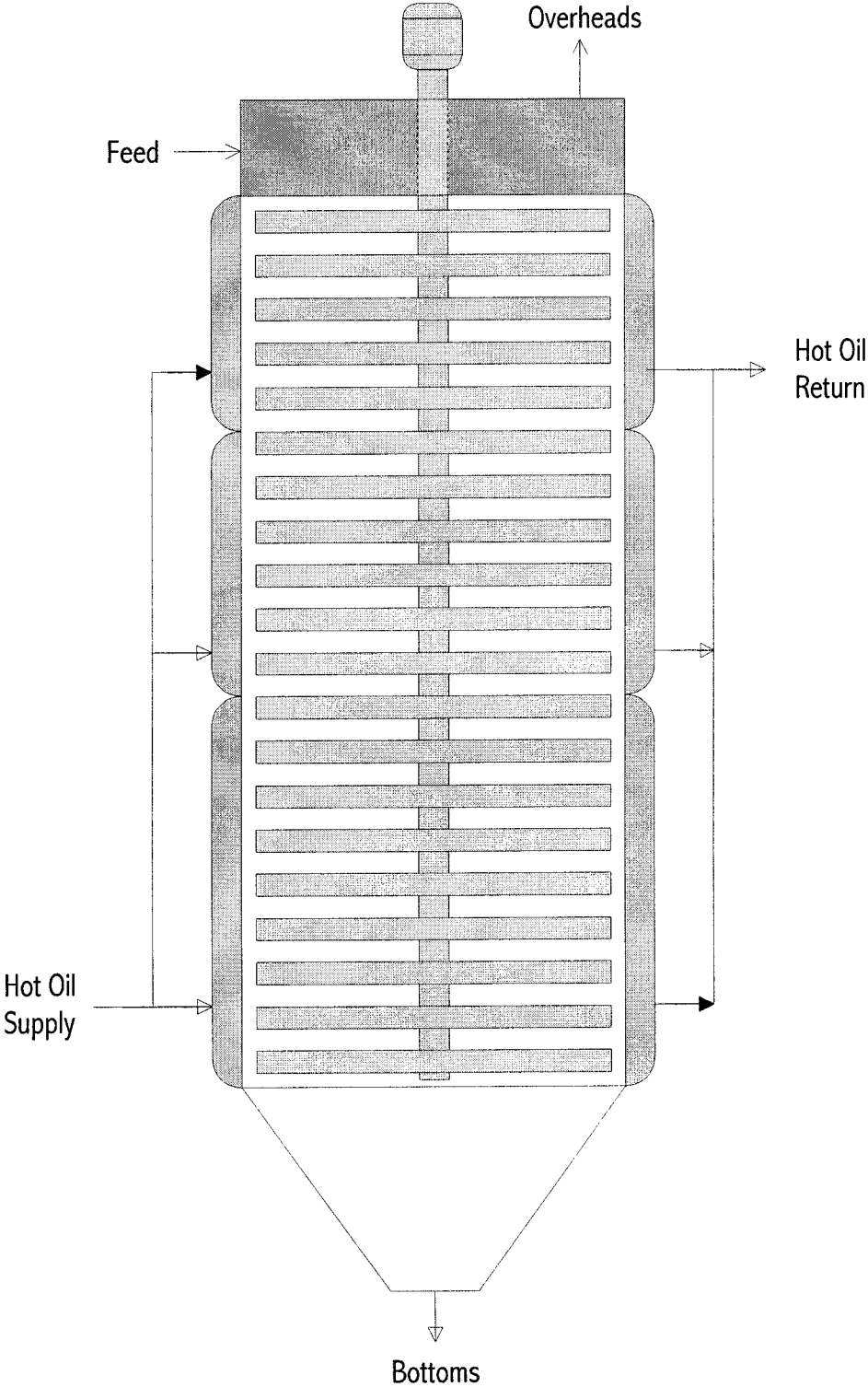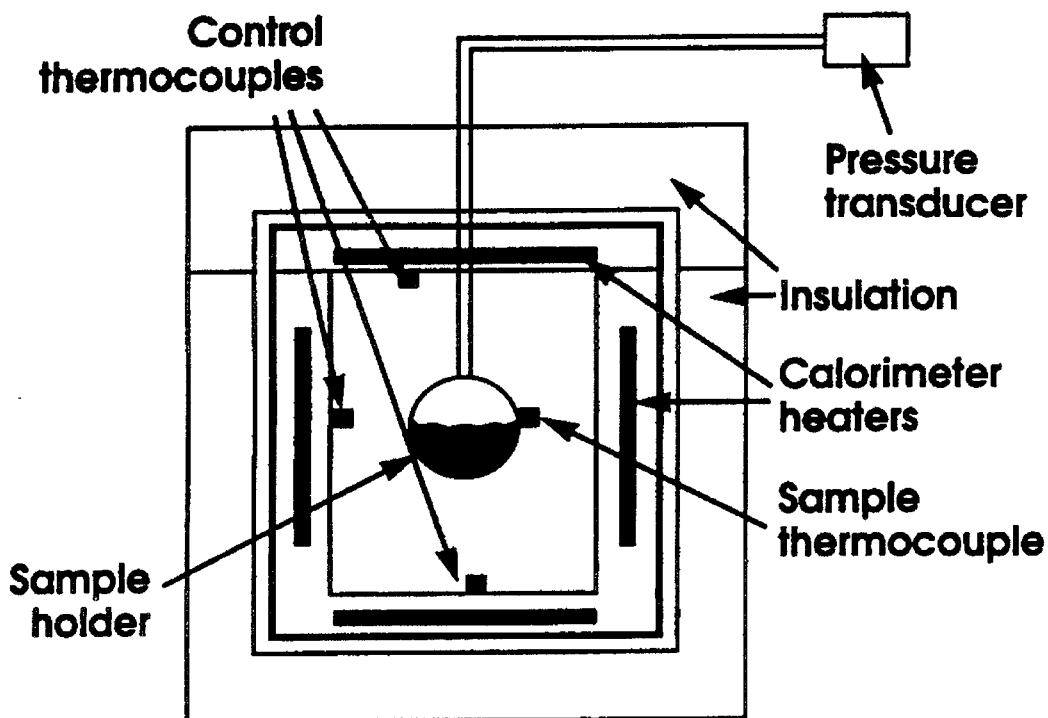## Wiped-Film Evaporator Schematic Diagram

Figure 2
Accelerating Rate Calorimeter Schematic Diagram

ARC™ CALORIMETER ASSEMBLY

on the outside of the sphere measures the sample temperature. A small tubing line through the lid of the calorimeter connects to a pressure transducer. Normally, the radiant heater in the bottom of the calorimeter heats the sample in steps of five degrees C. After each "heat" step, the instrument "waits" ten minutes for thermal equilibrium to be re-established. It then commences a "search" period during which it monitors the sample for any signs of self-heating (detection limit of 0.02 degrees C/minute). If no self-heating is detected, then another heat step is taken, and the sequence repeats itself until the specified end temperature is reached or self-heating is detected. If self-heating is detected, the controller declares an exotherm and switches to adiabatic mode. In this mode, the heating elements in the walls of the calorimeter are controlled so that the temperature of the surroundings matches the sample temperature to keep it adiabatic. These heaters can maintain an adiabatic environment up to sample self-heating rates of 12 degrees C per minute. Figure 3 shows the heat rate versus temperature plot from an ARC test on a material typical of the WFE bottoms stream. It can be seen that exothermic activity is indicated in the normal temperature range of operation.

Figure 3
ARC Heat Rate vs. Temperature for WFE Bottoms Stream Sample
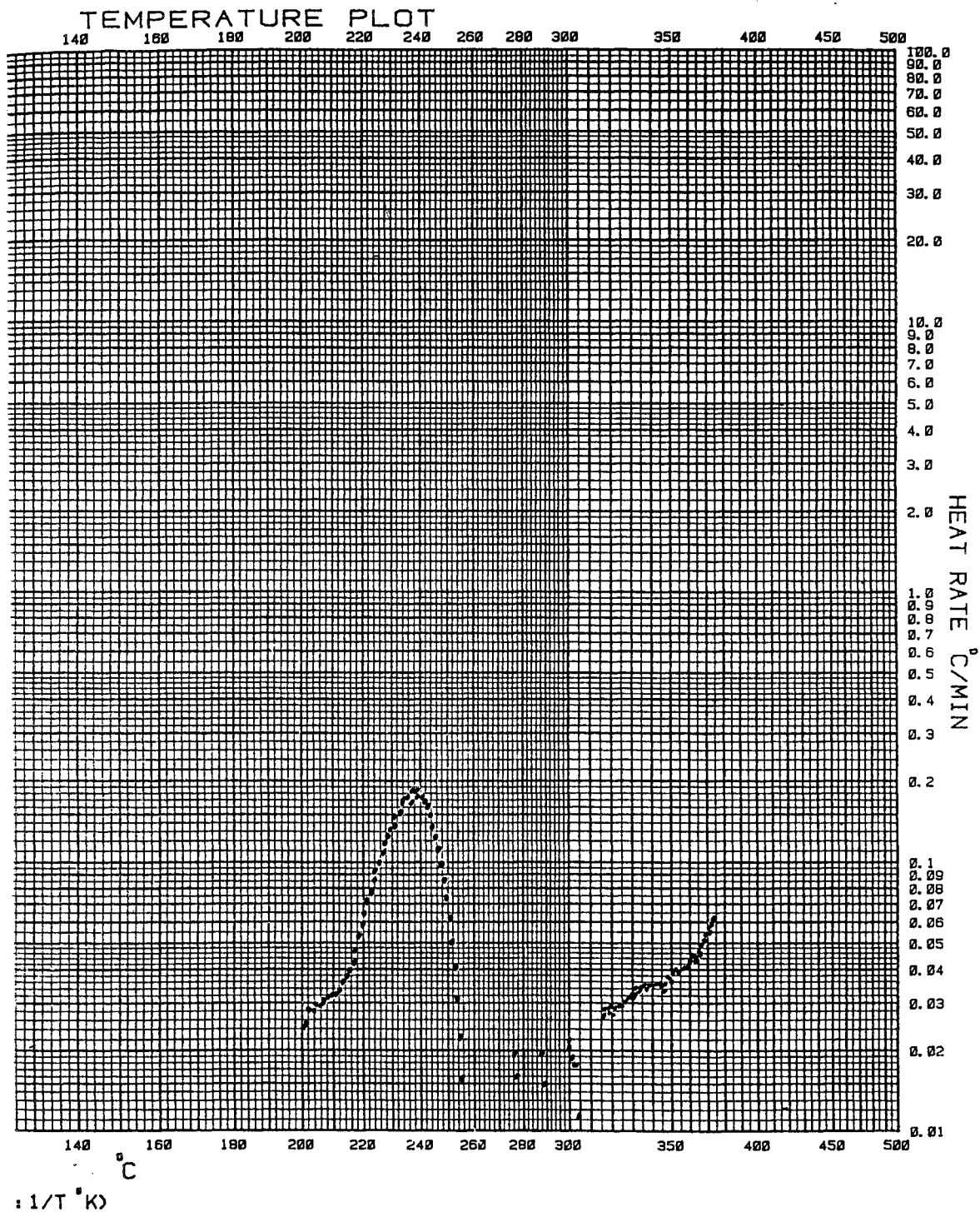
Experimental

Since this original ARC data had been generated several years ago, a repeat test was done using a current bottoms sample from the plant. Figure 4 shows that the result was very similar to the previous one. In this new ARC test, the heat-wait-search algorithm required 1114 minutes before an exotherm was declared at 196 degrees C.

Figure 4
ARC Heat Rate vs. Temperature for New WFE Bottoms Stream Sample
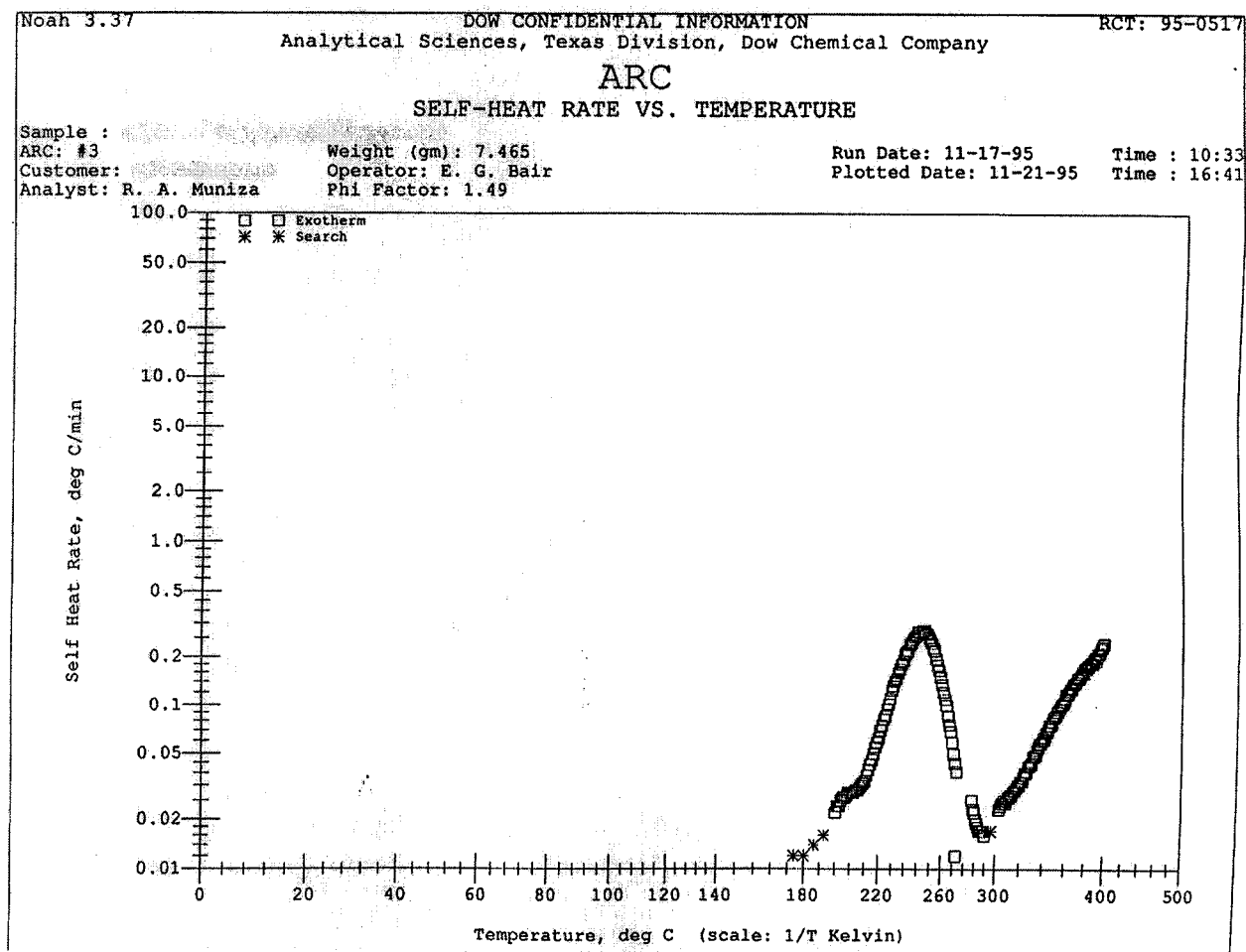
In order to examine the impact of heat history, another ARC test was run on the fresh sample, but the heat-wait-search algorithm was bypassed. The sample was heated directly to a temperature of 210 degrees C and then switched into normal operation, whereupon the instrument immediately declared an exotherm. This "jump-start" approach required only 236 minutes to reach 210 degrees C. Figure 5 shows the dramatic difference which this procedure made on the heat rate versus temperature. In neither case was significant pressure generated early in the reaction.

Figure 5
"Jump-Started" ARC Heat Rate vs. Temperature for New WFE Bottoms Stream Sample
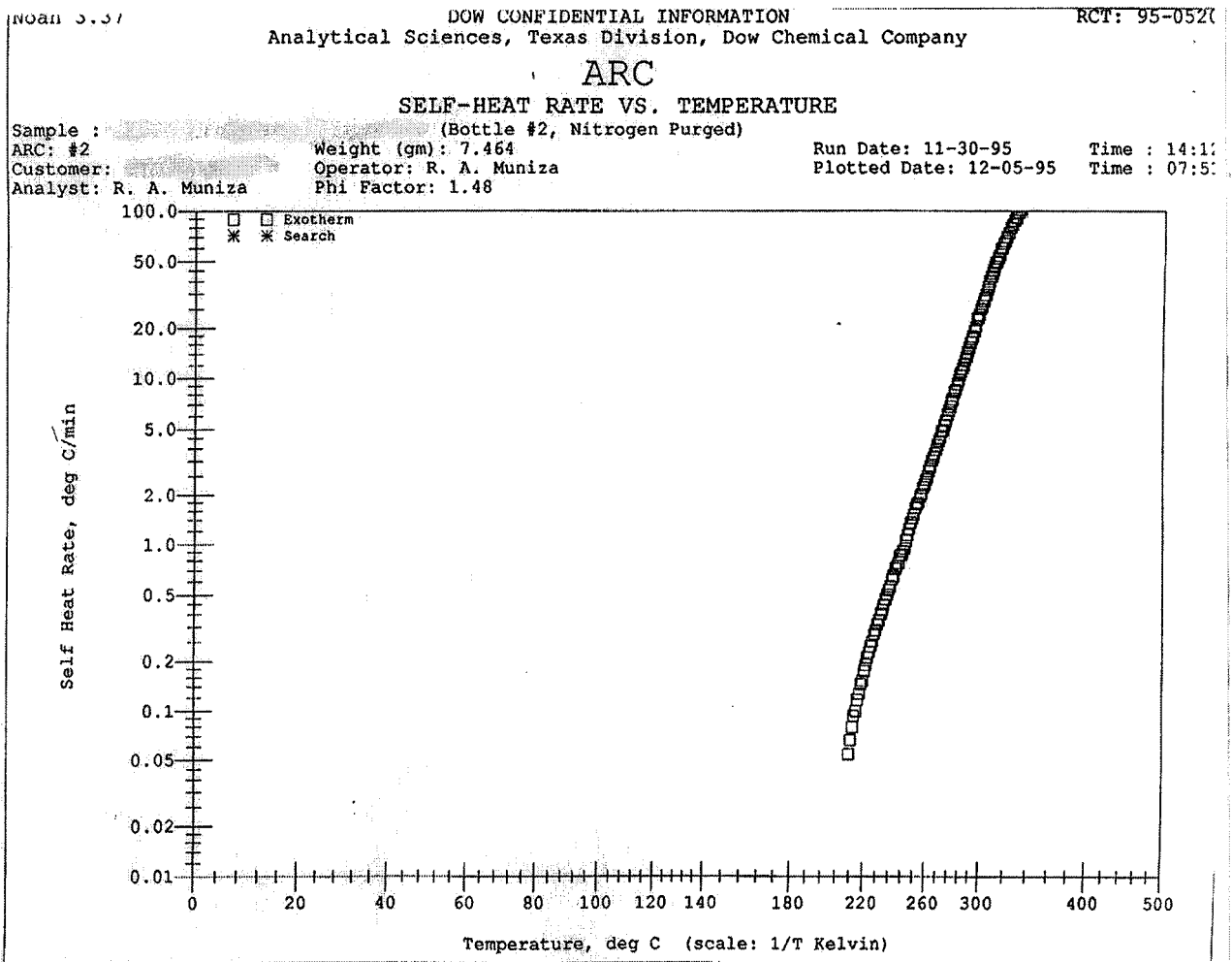
Since the jump-started ARC still created a much longer heat history in the sample than the actual process (30-120 seconds residence time in the WFE), a different type of test was needed. A Setaram C-80 isothermal calorimeter was used to run tests at three different temperatures. Figure 6 is a schematic diagram of the C-80 with its dual chamber for the reference cell and sample test cell, each surrounded by a device for measuring heat flux.

Figure 6
Schematic Diagram of the Setaram C-80 Isothermal Calorimeter

rear (reference)   front (measure)

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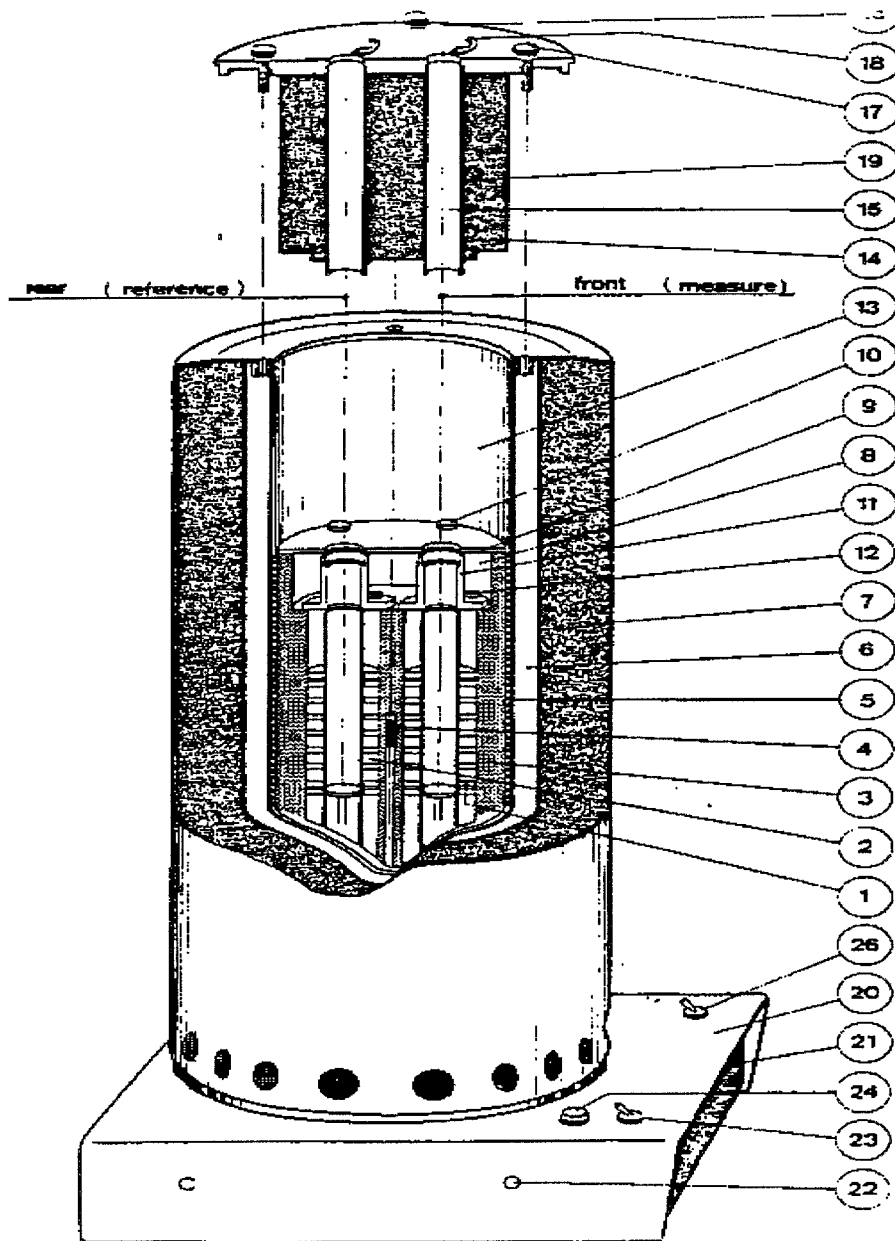15
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FIG . 2
partial side view

C

The general procedure for the C-80 experiments was to preheat the system to the desired temperature and then inject a one gram sample of the WFE bottoms stream into the test cell. Due to the relatively small mass of the sample compared to the mass of the test cell and calorimeter, the sample was very quickly heated with very little disturbance to the test temperature. Heat flux data were collected to monitor reaction rates at three different temperatures versus time in order to estimate kinetic parameters. Figure 7 illustrates the results of these experiments.
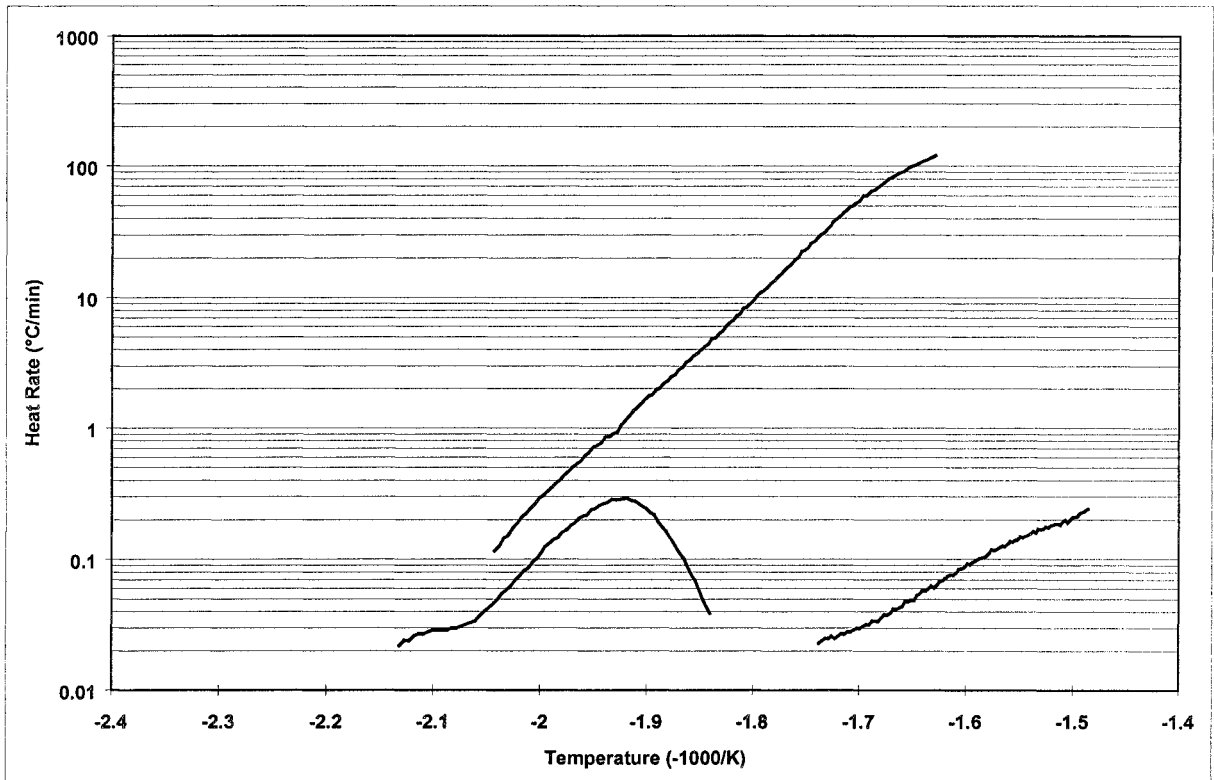
Figure 7

Isothermal Calorimetry of Wiped Film Evaporator Bottoms (Ambient Injections)
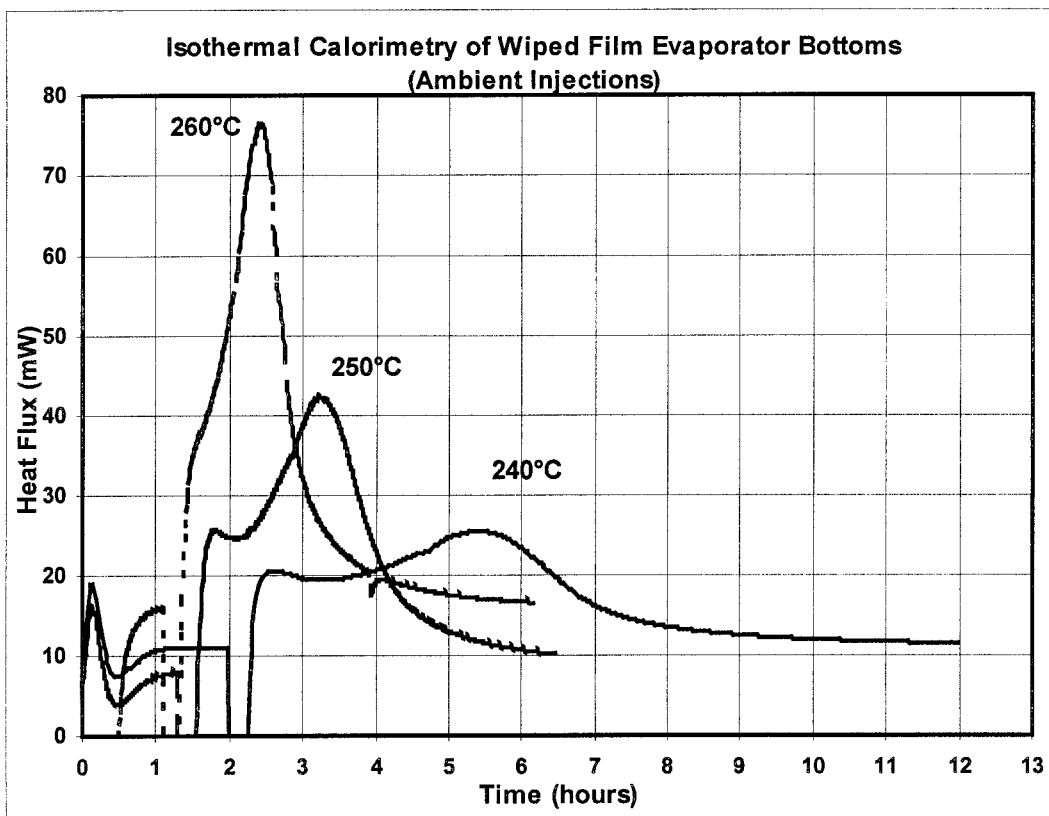
Data Interpretation

Figure 8 shows an overlay of the two new ARC experiments in this study. At any temperature, the jump-started ARC run has a significantly higher reaction rate. This is due to the greater concentration of reactive species still available after the faster pre-heat compared to the normal heat-wait-search method. The initial slopes appear to be parallel, as expected, since the reaction (and activation energy) is the same in each case. Extrapolation of the jump-started exotherm curve back to the detection limit of 0.02 degrees C, would indicate an earlier observed onset temperature for this experiment, also.

Figure 8
Comparison of New ARC Runs

In Figures 3 and 4 (old and new regular ARC runs), it can be seen that there is more than one reaction occurring. In Figure 5 (jump-started ARC), these reactions run together, but they can be distinguished again in Figure 7 (C-80 experiments). In the C-80 experiments, the first reaction appears to follow an Arrhenius N-order type model as it decays exponentially from an initial maximum rate. The second reaction is somewhat convoluted with the first one, but appears to be auto-catalytic in nature as it has a symmetrical shape which builds to a maximum rate.

Figure 9 illustrates a simple preliminary analysis of the C-80 data. The percentage of decomposition which has occurred at any given time is estimated as the cumulative fraction at that time of the total integrated heat generation. It appears that extrapolation of these curves back to the actual residence time of the WFE (less than two minutes) would indicate much less than 1% decomposition. In order to better quantify the amount of decomposition and allow predictions for other temperatures (especially for higher temperatures where the experimentation becomes more difficult), the kinetic parameters were estimated from the C-80 data.

Figure 9
Percent of Decomposition Reaction Completed vs. Time in the C-80
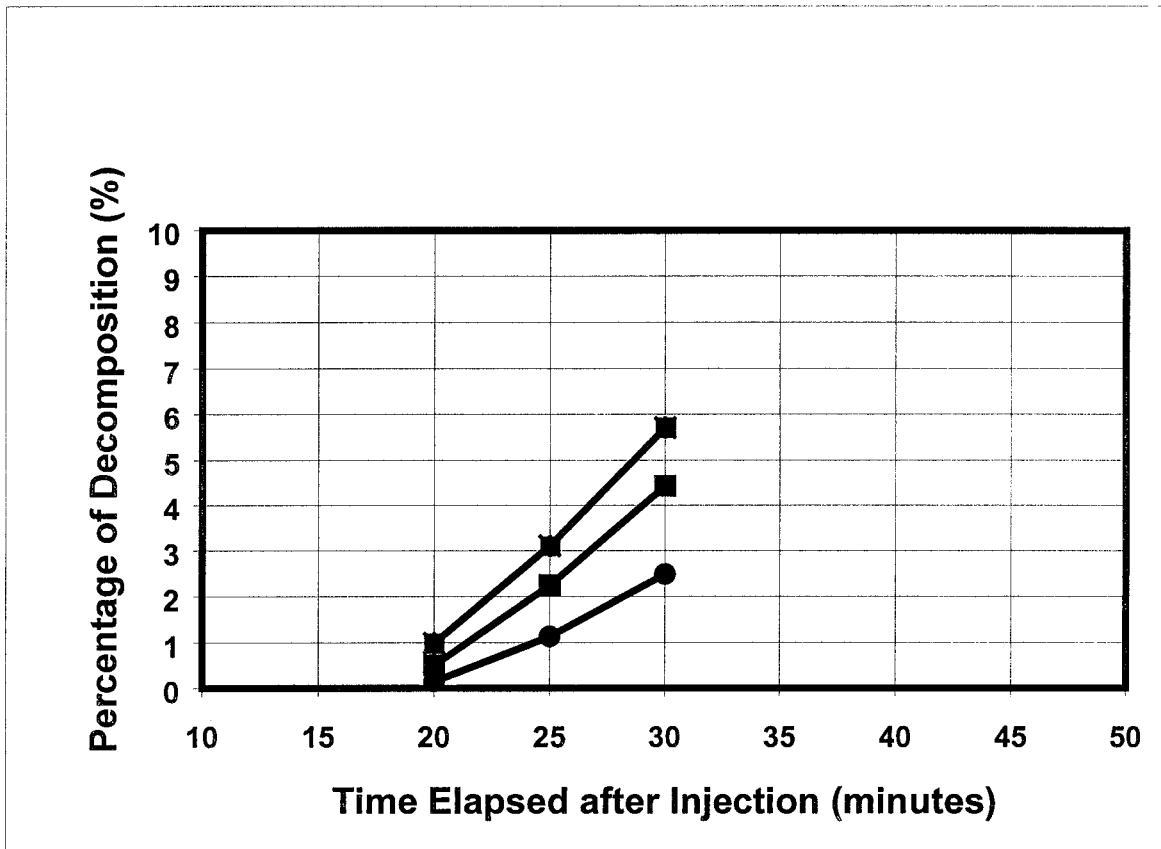

Modeling to Estimate Kinetic Parameters

A pair of programs from Cheminform St. Petersburg, Ltd. was used to do the kinetic parameter estimation. The first program, TDPro (Thermoanalytical Data Processing), uses a Text File Converter to transform the data from the C-80 into the proper format and units for further processing.

Processing in TDPro involves several steps. The first step involves cutting away extraneous data. The only data which are kept are those from the time the power reading has recovered fully from the sample injection until the end of the experiment where the power reading has returned to baseline. This step is illustrated in Figure 10 where the data between the two marks are saved.
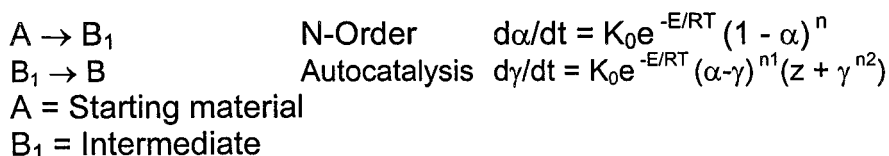
Figure 10

Data Processing in TDPro

DSC, mW   Temperature, C
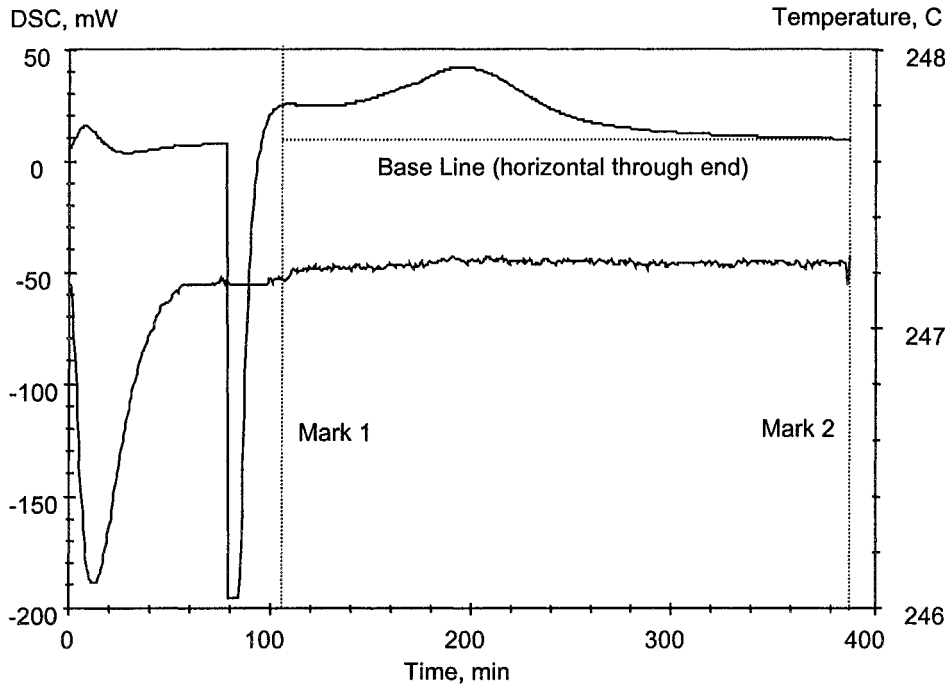
The next step corrects the time axis so that the first saved datapoint corresponds to zero time. Then a baseline is constructed and subtracted to leave only the power due to the observed reactions. A horizontal baseline from the end is used since it is assumed that under isothermal conditions the power returns to the baseline value. This is also illustrated in Figure 10. Finally, the data are deconvoluted to account for the time constant of the instrument. The results are then saved for kinetic parameter estimation.

The parameter estimation was done with a program called ForK (Formal Kinetics). Because the WFE bottoms stream is a complex mixture, little a priori knowledge was available about the reactions. Fortunately, no detailed stoichiometry is required. ForK allows the user to choose from a variety of built-in kinetic models. It can handle multiple reactions in series or parallel. As mentioned previously, it appeared from inspection of the experimental data that at least two reactions were occurring in the temperature range of interest. Therefore, the kinetic scheme chosen was for two consecutive reactions. The first was an N-order Arrhenius type reaction and the second was autocatalytic. The model was thus represented as follows:

Consecutive reactions $A \rightarrow B_1 \rightarrow B$

$A \rightarrow B_1$ N-Order $d\alpha/dt = K_0 e^{-E/RT} (1 - \alpha)^n$

$B_1 \rightarrow B$ Autocatalysis $d\gamma/dt = K_0 e^{-E/RT} (\alpha - \gamma)^{n1} (z + \gamma^{n2})$

A = Starting material

B_1 = Intermediate

B = Product
α = conversion of A
K_0 = pre-exponential factor, sec^{-1}
E = activation energy, kJ/mol
R = gas constant, kJ/mol degrees K
T = temperature, degrees K
n, n1, n2 = reaction order (or pseudo order)
γ = conversion of B_1
z = autocatalytic constant

ForK provides initial default values for the kinetic parameters. The user can edit these parameter values while viewing a graph which plots the model against the experimental data. An optimization routine can then be utilized which allows ForK to adjust all parameters within user-specified ranges in order to minimize the error between the model and the experimental data (integral and/or derivative responses). Two datasets were used to make the initial parameter estimates (experiments at 237 and 247 C). The third dataset (257 C) was then added to check the fit of the model data. Finally, all three datasets were used together in the optimization routine to fine-tune the parameter estimates. The results are shown in Figures 11 and 12.

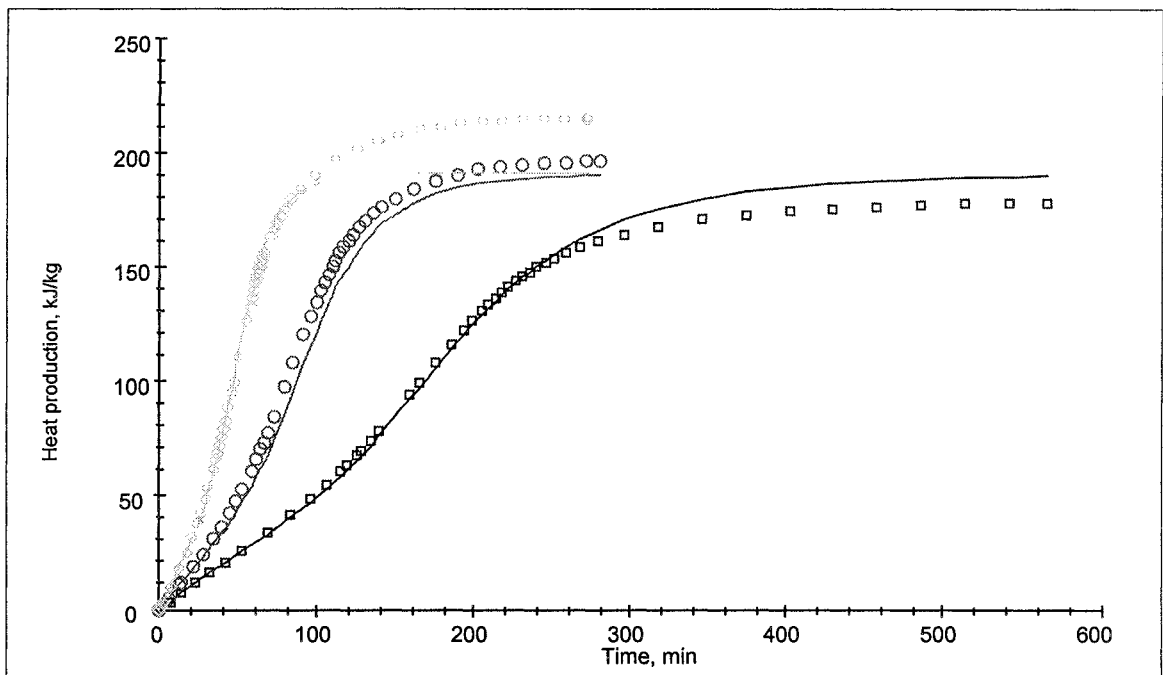Figure 11
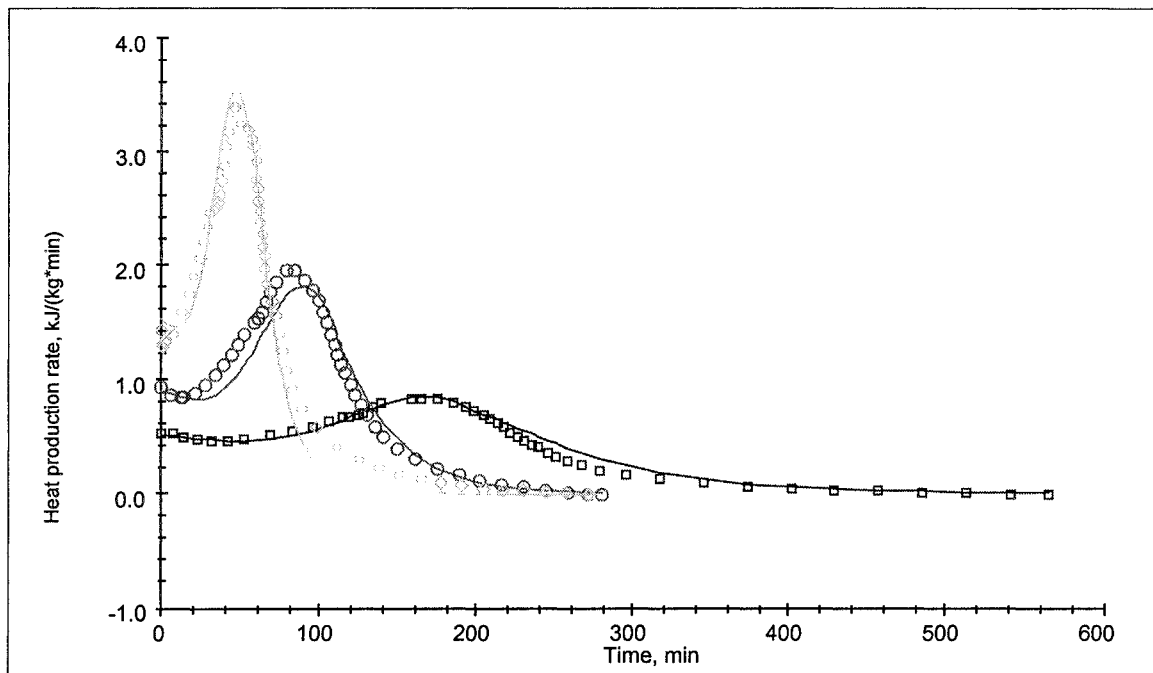Fit of Kinetic Model to Integral Heat Production

Figure 12
Fit of Kinetic Model to Heat Production Rate

Although the fit is not perfect at any of the three temperatures, it was considered to be close enough (particularly at times near zero which are most relevant to the WFE). The parameter estimates of the model are summarized in Table 1.

Table 1
Kinetic Parameter Estimates for WFE Bottoms Material

A → B1

Stage type: N-Order
Equation: $d\alpha/dt = K_0 e^{-E/RT} (1 - \alpha)^n$

Parameter	Units	Value
ln(k0)	ln(1/sec)	19.7408
E	kJ/mol	121.2509
n	-	0.4240
Q	kJ/kg	59.1009

B1 → B

Stage type: Autocatalysis
Equation: $d\gamma/dt = K_0 e^{-E/RT} (\alpha-\gamma)^{n1}(z + \gamma^{n2})$

Parameter	Units	Value
ln(k0)	ln(1/sec)	33.7264
E	kJ/mol	177.5648
n1	-	1.1576
n2	-	0.6393
z	-	0.0170
Q	kJ/kg	132.1758

The kinetic model was now ready to be used in the simulation module of ForK to quantify the amount of degradation that might occur in the WFE at various temperatures.

Simulation for Predictions at Proposed Plant Conditions

The ForK simulation module offers a choice of three heat exchange modes for simulating various types of homogeneous systems: general (user specifies heat transfer characteristics), adiabatic, or forced temperature. Since the temperature profile on the process side of the WFE was unknown, it was difficult to implement the general mode. Adiabatic was not a good choice since the WFE transfers heat very effectively. Forced heating mode was selected using the bottoms temperature as the temperature for the simulation. This is equivalent to assuming that the feed instantaneously heats to the bottoms temperature upon entering the WFE. This should give a conservative result since the material will actually spend part of its residence time heating from the feed temperature to the bottoms temperature. Thus, the amount of actual degradation should be less than that predicted by ForK.

A base case was run at 250 C (representing the current maximum bottoms temperature in the plant WFE). Cases were also run at 260 and 270 C (proposed new maximum operating temperatures for the WFE). Table 2 summarizes the results by showing how much degradation or yield loss occurs versus time and temperature as measured by conversion of component A (starting feed material).

Table 2
Effect of Bottoms Temperature on Degradation
(% Decomposition of Feed Heavy Fraction)

Time		Temperature	
(Minutes)	250 C	260 C	270 C
0.7	1.2	2.1	3.4
1.7	3.0	5.0	8.2
2.7	4.8	6.5	13.0

Conclusions

1. Consideration of residence time and sample heat history is crucial to the correct interpretation of thermoanalytical data. Failure to recognize the consumption of reactive species prior to the detected onset temperature in an ARC or other adiabatic device can lead to non-conservative estimates of onset temperature, maximum self-heat rates, adiabatic temperature rise, and the potential for runaway reactions.

2. Isothermal calorimetry and kinetic modeling are useful tools for studying potential decomposition reactions, especially in processes involving high temperatures and short residence times.
3. The low amounts of conversion (yield loss) at short residence times in the plant's wiped film evaporator were considered to be acceptable even at temperatures up to 270 C. Since there was not a significant amount of gas or solids generated at these low conversions, the proposed change in operating conditions was considered safe.

Acknowledgments