WSRC-TR-2000-00427

Initiation Temperature for Runaway Tri-n-Butyl Phosphate/Nitric Acid Reaction

by
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INTEROFFICE MEMORANDUM

October 31, 2000 WSRC-TR-2000-00427-TL

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FROM: A. L. Blancett
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Transmittal Letter for WSRC-TR-2000-00427

Please find attached the technical report Initiation Temperature for Runaway Tri-n-Butyl Phosphate/Nitric Acid Reaction (WSRC-TR-2000-00427). This work was performed in response to a DNFSB concern about the margin of safety associated with the initiation of a runaway tri-n-butyl phosphate (TBP)/nitric acid reaction in a canyon tank. To address this concern, the initiation temperature for runaway reaction was measured as functions of nitric acid and dissolved solids concentrations and compared to the minimum initiation temperature (130°C) cited in the H-Canyon authorization basis. The experimental work demonstrated that the initiation temperature for TBP contacted with an aqueous solution containing no dissolved solids decreased with increasing acid concentration to a minimum of 137°C, at 14-15M nitric acid. The initiation temperatures for TBP contacted with nitric acid solutions containing 5, 10, and 20 wt% dissolved solids showed a small dependence on the salt concentration; however, the lowest temperatures were several degrees above the minimum valued for no dissolved solids. The slight lowering of the initiation temperature was attributed to the increased extraction of nitric acid due to the salting-out effect of the dissolved solids.

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Summary

During a review of the H-Canyon authorization basis, Defense Nuclear Facility Safety Board (DNFSB) staff members questioned the margin of safety associated with a postulated tri-n-butyl phosphate (TBP)/nitric acid runaway reaction due to the inadvertent heating of a canyon tank containing greater than 3000 lbs (1362 kg) of TBP. The margin of safety was partially based on experiments and calculations performed by the Actinide Technology Section (ATS) to support deletion of indication of tank agitation as a Safety Class System. In the technical basis for deletion of this system, ATS personnel conservatively calculated the equilibrium temperature distribution of a canyon tank containing TBP and nitric acid layers which were inadvertently heated by a steam jet left on following a transfer. The maximum calculated temperature (128°C) was compared to the minimum initiation temperature for a runaway reaction (greater than 130°C) documented by experimental work in the mid 1950's. In this work, the initiation temperature as a function of nitric acid concentration was measured for 0 and 20 wt% dissolved solids. The DNFSB staff members were concerned that data for 0 wt% dissolved solids were not conservative given the facts that data for 20 wt% dissolved solids show initiation temperatures at or below 130°C and H-Canyon solutions normally contained a small amount of dissolved solids.

To address the DNFSB concern, the initiation temperature for a runaway TBP/nitric acid reaction was measured as functions of the nitric acid and dissolved solids concentration of the aqueous phase in equilibrium with pure TBP. Initiation temperatures were measured using a Reactive System Screening Tool™ (RSST™), a nearly adiabatic calorimeter equipped with temperature and pressure monitoring capability. Initially, experiments were performed with the RSST™ open to atmospheric pressure; however, the self-heating rate was not sufficient for runaway reaction to occur. This observation is consistent with the result from previous studies which showed that adequate vessel venting is the first defense against a damaging runaway reaction.

To obtain a runaway TBP/nitric acid reaction, it was necessary to seal the RSST™ containment vessel at atmospheric pressure prior to the initiation of an experiment. Without adequate venting, self-heating from the oxidation of TBP degradation products was sufficient for runaway reaction to occur. The runaway reaction initiation temperature was defined by the time and corresponding temperature when a rapid increase in the vessel pressure was initially seen.

The runaway reaction initiation temperatures for TBP contacted with nitric acid solutions containing no dissolved solids were in good agreement with data from the 1950's. The initiation temperature gradually decreased with increasing aqueous phase nitric acid concentration due to the increase in the available oxidant (nitric acid) extracted by the TBP. The minimum initiation temperature, 137°C, measured at 14-15M nitric acid was consistent with previously measured values (132-137°C) at nominally 15.7M nitric acid. The initiation temperatures measured using TBP contacted with nitric acid solutions containing 5, 10, and 20 wt% dissolved solids showed a small dependence on the salt concentration; however, the lowest temperatures were several degrees above the minimum value for no dissolved solids. The slight lowering of the initiation temperature was attributed to the increased extraction of nitric acid due to the salting-out effect of the dissolved solids.

The results of the closed RSST™ experiments demonstrated that the initiation temperature for a runaway TBP/nitric acid reaction decreased with the amount of nitric acid extracted by the TBP. To illustrate this point, a correlation of the initiation temperature as a function of the extracted nitric acid concentration was developed by analyzing or estimating the amount of nitric acid extracted into the TBP samples used for each RSST™ experiment. When plotted, the initiation temperature decreased linearly with increasing nitric acid concentration. An increase in the TBP nitric acid concentration results in a faster reaction (oxidation) rate at a lower temperature which reduces the temperature where runaway reaction occurs. The correlation also illustrated that initiation temperatures measured previously using TBP contacted with an aqueous phase containing 8-10M nitric acid and 20 wt% sodium and/or potassium nitrate(Na/KNO_3) are 10-15°C below expected values based on a linear regression used to correlate the data.

RSST™ experiments were performed to look at the effect of other variables (nitrate salt and number of phases) on the initiation temperature for a runaway TBP/nitric acid reaction. Several experiments were performed in which the dissolved solids were changed from aluminum nitrate ($Al(NO_3)_3$) to $NaNO_3$, or KNO_3. No significant effect on the initiation temperature was seen. RSST™ experiments were also performed to evaluate the effect of additional phases (aqueous and solid) on the thermal behavior of the TBP samples. Neither the presence of the aqueous phase originally used to contact the TBP nor a small amount of undissolved solids in the aqueous phase had a significant effect on the runaway reaction initiation temperature. The only noticeable difference in thermal behavior was the extended time required to evaporate the aqueous phase prior to runaway reaction occurring.

Introduction

During a review of the H-Canyon Authorization Basis, Defense Nuclear Facility Safety Board (DNFSB) staff members questioned the margin of safety associated with a postulated tri-n-butyl phosphate (TBP)/nitric acid runaway reaction due to the inadvertent heating of a canyon tank containing greater than 3000 lbs (1362 kg) of TBP. The margin of safety was partially based on experiments and calculations performed by the Actinide Technology Section (ATS) to support deletion of indication of tank agitation as a Safety Class System. In the technical basis for deletion of this system, ATS personnel conservatively calculated the equilibrium temperature distribution of a canyon tank containing TBP and nitric acid layers which were inadvertently heated by a steam jet left on following a transfer.[1] The maximum calculated temperature (128°C) was compared to the minimum initiation temperature for a runaway reaction (greater than 130°C) measured by Colven in the mid 1950's.[2] In this work, the initiation temperature as a function of nitric acid concentration was measured for 0 and 20 wt% dissolved solids (see Figure 1). The DNFSB staff members were concerned that data for 0 wt% dissolved solids were not conservative given the facts that data for 20 wt% dissolved solids show initiation temperatures below 130°C and H-Canyon solutions normally contained a small amount of dissolved solids.

To address the DNFSB concern, the initiation temperature for a runaway TBP/nitric acid reaction was measured as functions of the nitric acid and dissolved metal nitrate salt concentrations of the aqueous phase in equilibrium with pure TBP. Only the organic phase was used for the experiments due to the cooling mechanism provided by water, nitric acid, and volatile components produced by the degradation of the TBP. Smith et. al.[3] showed that the forced evaporation of the volatile components by noncondensible product gases during the oxidation of TBP degradation products resulted in a cooling mechanism which more than balanced the heat from oxidation. As long as the TBP was in contact with an aqueous phase, water, the main coolant in the organic phase, was replenished by interfacial mixing by gas produced from oxidation in the aqueous phase. The results from Smith's experiments were applied to canyon evaporator operation just after shutdown when enough nitric acid-soluble organic material would be present in the aqueous phase to generate the bubbling required for mixing; however, Laurinat et. al.[1] showed that mixing in a canyon tank was sufficient to replenish water extracted by the TBP and runaway reaction would not occur. Although 7.5 and 30 vol% TBP diluted by a normal paraffin (n-paraffin) are used as solvents in H-Canyon,[4] only pure TBP was used for the runaway reaction experiments. Dilution of the TBP with the n-paraffin would only provide another volatile component of the solvent which must evaporate before runaway reaction occurs.

The dissolved solids used by Colven to measure the runaway reaction initiation temperatures for 20 wt% dissolved solids were either sodium or potassium nitrate ($NaNO_3$ or KNO_3) or a combination of the two salts.[2] For this study, aluminum nitrate ($Al(NO_3)_3$) was selected as the dissolved metal nitrate salt for the majority of the experiments for its ability to increase the extraction of nitric acid by a "salting-out effect." When a salting agent is added to the aqueous phase, extraction of nitric acid is enhanced by a combination of effects. The higher concentration of nitrate anions improves extraction by mass action. The activity of the nitric acid also increases due to complexation of water by aluminum which then becomes unavailable as "free solvent."[5] The effectiveness of $Al(NO_3)_3$ as a salting agent should be better than the monovalent cations based on the size of the hydrated ion and known hydration number (6 versus 4 for $NaNO_3$ and KNO_3).[6,7] Thompson [6] has demonstrated that $Al(NO_3)_3$ was a much better salting agent than $NaNO_3$ for nitric acid and selected lanthanide and actinide elements.

Experimental

Solution Preparation

Reagent grade TBP, nitric acid, and $Al(NO_3)_3$, $NaNO_3$, and KNO_3 salts were used to prepare the solutions for the runaway reaction experiments. Information concerning the reagent manufacturer, lot number, and purity is provided in Appendix A. The concentration and density of the nominally 70 wt% nitric acid used in the experiments were measured to ensure accurate dilutions were made during the preparation of the aqueous phase solutions for the experiments. The concentration and density measurements are summarized in Appendix A (see Tables A.1 and A.2, respectively).

The TBP used in the runaway reaction studies was prepared by contacting one volume (12 mL) of organic with 5 volumes (60 mL) of aqueous to ensure the maximum extraction of nitric acid. The aqueous solutions were prepared by transferring the target mass of the metal nitrate salt to a 200 mL beaker. The target masses of deionized water and nominally 70 wt% nitric acid were then added in succession. The mass of nitric acid required to prepare the diluted nitric acid solutions was calculated using nitric acid densities reported by Davis et. al.[9] at 25°C (Appendix A, Table A.3) and the measured concentration of the starting reagent. The temperature of the laboratory used to prepare the solutions was 25±5°C. Following the addition of all reagents, the metal nitrate salts were dissolved by stirring with a magnetic stir bar. For aqueous solutions containing metal nitrate salt concentrations approaching the solubility limit, it was necessary to slightly heat the solution in order to obtain complete dissolution. When heating was necessary, a watch glass containing water was placed on the beaker to slow evaporation. After dissolution, a disposable transfer pipette was used to rinse condensate from the bottom of the watch glass back into the beaker with an aliquot of the solution.

RSST™ Operation

The initiation temperatures for runaway TBP/nitric acid reactions were measured using a Reactive System Screening Tool™ (RSST™) manufactured by Fauske and Associates, Inc.[8] The RSST™ is a nearly adiabatic calorimeter equipped with temperature and pressure sensors to allow real time data monitoring and acquisition. A well insulated, 10 mL test cell is fitted with a small heater which allows heating of the contents at a controlled rate. The test cell is normally sealed within a high pressure containment vessel (see Figure 2) that serves as both a pressure simulator and a safety vessel; however, the TBP/nitric acid experiments were either performed at atmospheric pressure in a well vented system or the containment vessel was sealed at atmospheric pressure at the beginning of the experiment. The runaway reaction initiation temperature was determined for closed vessel experiments by monitoring the temperature of the TBP and pressure of the RSST™ safety vessel as functions of time.

To perform an RSST™ experiment, a 10 mL aliquot of TBP previously contacted with a nitric acid solution was transferred to a new RSST™ test cell. The mass of TBP was determined by difference using the premeasured mass of the test cell. A small magnetic stirrer was added to the test cell to provide stirring during the experiment. The RSST™ was then assembled and the experiment initiated by computer control. As noted above, RSST™ experiments were performed at atmospheric pressure using a well vented (open) safety vessel or after sealing the safety vessel at atmospheric pressure. Upon initiation of an experiment, the RSST™ control system increased the temperature of the TBP at nominally 1°C/min. The temperature of the TBP and the pressure inside the RSST™ (for closed system experiments) were recorded as functions of time by the data acquisition system. The RSST™ experiments were terminated when the temperature of the TBP reached 200°C by turning off the cell heater. The temperature/pressure data were then processed to generated plots of temperature versus time, pressure versus time, self-heating rate versus temperature, and rate of pressure change versus temperature which were used to evaluated the thermal stability of the TBP sample.

Extraction of Nitric Acid by TBP

After initiation of the RSST™ experiments, it became apparent that knowing the amount of nitric acid extracted by the TBP would be useful in correlating the runaway reaction initiation temperatures. To obtain these data, duplicate 1 mL samples of TBP were titrated with base to obtain the amount of nitric acid extracted during contact with the aqueous phase.

In order to obtain an estimate of the nitric acid extracted by TBP samples which were not analyzed, a series of extractions were preformed in which pure TBP was contacted with nitric acid solutions containing 5, 10, and 20 wt% $Al(NO_3)_3$. The nitric acid concentrations used for each concentration of $Al(NO_3)_3$ ranged from 4M to a concentration just below the point where crystallization was seen (12, 10, and 8M for 5, 10, and 20 wt% $Al(NO_3)_3$, respectively). The aqueous phase and TBP were prepared in the same manner as the solutions used for the RSST™ experiments. Three 1 mL samples of TBP were analyzed by titration to obtain the amount of nitric acid extracted. The data generated by these analyses were used to predict the amount of nitric acid extracted by the TBP used for the remainder of the RSST™ experiments.

Results and Discussion

Open RSST™ Experiments

The initial experiments to measure the initiation temperature for a runaway TBP/nitric acid reaction were performed with the RSST™ open to atmospheric pressure. This approach was used to model the well-vented tanks in F and H-Canyons without excessive conservatism. The energy released by the oxidation of TBP degradation products is a strong function of pressure. TBP degradation products such as butanol and butyl nitrate are volatile and their removal from the RSST™ test cell would limit the available energy release. A closed system which leads to increased pressure also inhibits the cooling mechanism provided by the forced evaporation of water and other volatile species from the TBP.[3]

Open RSST™ experiments were performed at 0 and 5 wt% dissolved solids ($Al(NO_3)_3$ and $NaNO_3$) using nitric acid concentrations ranging from 2 to 15M. A summary of the reagent masses used to prepare the aqueous and organic phases and resulting concentrations for each run is provided in Appendix B (see Table B.1). For the open system experiments, the self-heating rate from the oxidation of TBP degradation products was used to define the runaway reaction initiation temperature. The initiation temperature was defined as the temperature of the TBP when the self-heating rate diverged from the imposed heat-up rate of 1°C/min. The temperature profiles (i.e. temperature versus time data) and self-heating rates as a function of TBP temperature for the open system experiments are presented in Appendix C.

The self-heating rate curves generally reflected the imposed heat-up rate of 1°C/min until about 115-120°C when cooling from the evaporation of water and nitric acid from the TBP resulted in a noticeable decrease in the self-heating rate. Once water, the primary coolant evaporated, the self-heating rate increased substantially above 1°C/min; at that point, the initiation temperature was defined. The initiation temperatures measured in this manner are summarized in Table 1 as a function of the nitric acid and $Al(NO_3)_3/NaNO_3$ concentrations.

The runaway reaction initiation temperature should decrease as the nitric acid concentration of the aqueous phase (which has contacted the TBP) increases. This is consistent with the initiation temperatures measured by Colven [2] and would be expected since the nitric acid available to oxidize TBP degradation products increases with the nitric acid concentration of the aqueous phase (see Appendix A, Table A.3). However, the data presented in Table 1 are not in agreement with the expected behavior. The initiation temperature for runaway reaction is generally lower for TBP contacted with lower concentrations of nitric acid. Based on this observation, two (open system) RSST™ experiments were designed to determine if conditions approaching a runaway reaction actually occurred in the RSST™ test cell. In these experiments the TBP temperature was increased in a step-wise fashion until 200°C was reached. When the intermediate temperatures were attained, the RSST™ heater was shutdown to determine if the self-heating rate was sufficient for runaway reaction to occur. The temperature profiles and self-heating rates for the two experiments are shown on Figures 3 and 4.

Table 1 Initiation of Rapid Self-Heating for Open System Experiments

Run No.	Nitric Acid Concentration (moles/L)	$Al(NO_3)_3$ Concentration (wt%)	Initiation Temperature (°C)
TBP 0/2-1	2	0	123
TBP 0/8-1	8	0	130
TBP 0/15-1	15	0	134
TBP 5/4-1	4	5	125
TBP 5/4-2	4	5	131
TBP 5/4-3(1)	4	5	120
TBP 5/4-4(2)	4	5	124
TBP 5/6-1	6	5	137
TBP 5/12-1	12	5	135
TBP 5/12-2	12	5	134

(1) Initiation temperature was defined by the TBP temperature when the self-heating rate diverged from the achieved heat-up rate of approximately 0.35°C/min.
(2) $NaNO_3$ used as Dissolved Solid

The temperature profile for each RSST™ experiment shows that the temperature of the TBP began to decrease immediately after the heater was shutdown at each intermediate temperature. A self-heating rate sufficient for runaway reaction to occur in the RSST™ test cell was not attained. This observation reinforces the results of previous studies which have shown that adequate venting of vessels is the first defense against a damaging runaway reaction.[10] Fauske and Associates demonstrated that a vent area of 0.063 mm^2 per gram of TBP was sufficient to reduce the overpressure from a runaway reaction to less than 2 psi (13,789 Pa). The TBP used for the Fauske experiment was previously contacted with 15M nitric acid as a worst case condition.[11] The RSST™ used for the open system experiments was vented through a Whitey® ball valve (catalog no. SS-42F2) with a 3.2 mm orifice. The maximum mass of TBP used during an open system experiment was 11.04 g (see Appendix B, Table B.3) which corresponded to an aqueous phase containing 15M nitric acid. The calculated vent area is 0.73 mm^2 per gram of TBP; therefore, the RSST™ was a well vented vessel based on the work by Fauske and Associates and a runway reaction would not be expected to occur.

Closed RSST™ Experiments

To obtain a runway TBP/nitric acid reaction, it was necessary to seal the RSST™ safety vessel at atmospheric pressure prior to the initiation of an experiment. Without adequate venting, self-heating from the oxidation of TBP degradation products was sufficient for runaway reaction to occur. At the point of runaway, both rapid increases in the RSST™ safety vessel pressure and TBP temperature were seen. Measuring the initiation temperature for runaway reaction in a closed vessel like the RSST™ is consistent with the approached used by Colven.[2] In earlier experiments, Colven et. al.[12] used a sealed 1 L test vessel to measure the initiation temperature for spontaneous reaction in a two phase system containing TBP and highly concentrated (38-85 wt%) uranyl nitrate in dilute (1-4 wt%) nitric acid solution.

Closed RSST™ experiments were performed at 0, 5, 10, and 20 wt% dissolved solids ($Al(NO_3)_3$, $NaNO_3$, and KNO_3) using nitric acid concentrations ranging from 4 to 12M. A summary of the reagent masses used to prepare the aqueous and organic phases and resulting concentrations and mass of equilibrated TBP added to the RSST™ test cell for each run is provided in Appendix B (see Tables B.2 and B.4, respectively). The runaway reaction initiation temperature for the closed experiments was defined by the time period when a rapid increase in the pressure of the RSST™ safety vessel was initially seen. The procedure for defining the initiation temperature is illustrated on Figure 5. Using the pressure profile of the safety vessel (i.e. pressure versus time data), the time of the initial pressure spike is noted; the initiation temperature (or temperature range) is then determined from the corresponding temperature versus time data. In a majority of the experiments, the time of the initial pressure spike corresponded to a range of temperatures since the TBP temperature was rapidly increasing due to the excessive self-heating. When this behavior was seen, the average of the temperature range was designated the runaway reaction initiation temperature. Plots of the temperature and pressure profiles for each of the closed RSST™ experiments are presented in Appendix D. The results of this analysis for each successful experiment is summarized in Table 2.

The use of the rapid rise in the RSST™ safety vessel pressure to define the runaway reaction initiation temperature worked well except for experiments performed with TBP contacted with aqueous solutions containing high concentrations (13-15M) of nitric acid. In these experiments, a gradual increase in the system pressure, well before runaway reaction occurred, obscured the point of initiation. The increase in pressure can be attributed to the evaporation of both water and nitric acid. Evaporation of nitric acid extracted by the TBP is likely the key contributor to the initial pressure rise for these experiments. For TBP contacted with an aqueous solution containing 13-15M nitric acid, the extracted nitric acid approaches 5-6M (see Appendix A, Table A.3). To define the runaway reaction initiation temperature for these experiments, it was necessary to compare both the temperature and pressure profiles from the experiment to ensure that rapid increases in both temperature and pressure were occurring at the same time.

In order to compare the initiation temperatures for a runaway TBP/nitric acid reaction measured by Coven [2] and the data presented in Table 2, the initiation temperature as functions of nitric acid and dissolved solids concentrations for both data sets are plotted on Figure 6. Only the linear regression line for the Colven data at 0 wt% dissolved solids is shown to reduce the number of data points which facilitates the comparison. Inspection of the data on Figure 6 shows that there is good agreement between both data sets at 0 wt% dissolved solids with the initiation temperature gradually decreasing with increasing nitric acid concentration. The decrease in the initiation temperature is due to the increase in the available oxidant (nitric acid) extracted by the

Table 2 Runaway Reaction Initiation Temperature for Closed System Experiments

Run No.	Aqueous Concentration		Initiation Time (min)	Initiation Temp Range (°C)	Ave Initiation Temperature (°C)
	Nitric Acid (moles/L)	$Al(NO_3)_3$ (wt%)			
TBP 0/4-3	4.00	0	124	155-159	157
TBP 0/8-2	8.00	0	101-103	149-152	150.5
TBP 0/8-3(1)	8.00	0	162	151-155	153
TBP 0/10-1	10.00	0	127	143-145	144
TBP 0/12-1	12.00	0	132	139	139
TBP 0/13-1	13.00	0	153	141-143	142
TBP 0/14-1(2)	14.00	0	126.4	137	139.5
TBP 0/15-2	14.99	0	129.5	139	139
TBP 0/15-3	15.00	0	175	134-140	137
TBP 5/4-7	4.00	5.00	128	155-159	157
TBP 5/4-8	4.00	5.00	120	153-156	154.5
TBP 5/6-2	6.00	5.00	124	149-152	150.5
TBP 5/8-1	8.00	5.00	130	145-147	146
TBP 5/8-2(3)	8.00	5.02	108	147-149	148
TBP 5/10-1	10.00	5.00	137	143	143
TBP 5/12-3	11.99	5.00	138	139	139
TBP 5/12-4(4)	12.00	5.01	133	139-140	139.5
TBP 10/4-1	4.00	10.01	124	151-154	152.5
TBP 10/4-2(5)	4.00	10.00	130	155-156	155.5
TBP 10/6-1	6.00	10.01	112	148-151	149.5
TBP 10/8-1	8.00	10.01	111	146-148	147
TBP 10/8-2(3)	8.00	10.01	117	147	147
TBP 10/9-1	8.99	10.01	107	147-149	148
TBP 10/10-1	10.00	10.00	119	145-147	146
TBP 10/10-2	10.00	10.00	115	145-147	146
TBP 20/4-1	4.00	20.00	135	147-150	148.5
TBP 20/4-2	4.00	19.99	128	154-158	156
TBP 20/6-1	6.00	20.00	134	148-150	149
TBP 20/6-2	6.00	20.00	114	151-154	152.5
TBP 20/6-3	6.00	19.99	108	146-149	147.5
TBP 20/7-1	7.00	20.00	255	139-140	139.5
TBP 20/7-3	7.00	20.00	108	149-151	150
TBP 20/7-4	7.00	20.00	114	146-150	148
TBP 20/8-1	8.00	20.00	123	146-149	147.5

(1) Two Phase Experiment
(2) Initiation Temperature Based on Temperature Spike at 125.4 min
(3) $NaNO_3$ used as Dissolved Solid
(4) Three Phase Experiment
(5) KNO_3 used as Dissolved Solid

TBP. The minimum measured initiation temperature, 137°C, measured at 14-15M nitric acid is consistent with the values (132-137°C) measured by Colven at nominally 15.7M nitric acid. The initiation temperatures measured using TBP contacted with nitric acid solutions containing 5, 10, and 20 wt% dissolved solids show a small dependence on the salt concentration. This effect is more clearly seen on Figure 7 where linear regression lines were plotted instead of the actual data points.

Correlation of Initiation Temperature with Extracted Nitric Acid Concentration

The decrease in the runaway reaction initiation temperature with increasing dissolved solids content can be attributed to the increased extraction of nitric acid due to the salting-out effect. To illustrate this point, duplicate samples of the TBP used to perform a majority of the RSST™ experiments were analyzed for free acid to determine the amount of nitric acid which was extracted into the TBP. The results of these analyses and the corresponding runaway reaction initiation temperature are presented in Table 3.

To obtain an estimate of the nitric acid extracted by the TBP used in RSST™ experiments for which samples were not analyzed, a series of extractions were performed in which pure TBP was contacted with nitric acid solutions containing 5, 10, and 20 wt% $Al(NO_3)_3$. The reagent masses used to prepare the aqueous and organic phases and resulting concentrations and free acid analyses for triplicate samples of the organic phase are provided in Appendix E (see Tables E.1 and E.2, respectively). The free acid analyses were used to correlate the amount of nitric acid extracted into the organic phase with the concentrations of nitric acid and $Al(NO_3)_3$ in the aqueous phase. The correlations including data reported by Davis et. al.[9] for pure TBP contacted with various concentrations of pure nitric acid solution are presented on Figure 8. The data reported by Davis (see Appendix A, Table A.3) were based on experimentally determined values which were empirically smoothed to reduce scatter.

From inspection of Figure 8, one can see that the addition of $Al(NO_3)_3$ to the various nitric acid solutions did not have a measurable effect on the concentration of nitric acid in the organic phase until the aqueous phase contained 20 wt% $Al(NO_3)_3$. This is surprising given the small, but, measurable decrease in the runway reaction initiation temperature seen with TBP contacted with nitric acid solutions containing 5 and 10 wt% $Al(NO_3)_3$. It is possible that the analytical technique was not sensitive enough to resolve the difference between the amount of nitric acid extracted from the aqueous phase below 20 wt% $Al(NO_3)_3$. Since the nitric acid concentrations for the TBP contacted with acid solutions containing 5 and 10 wt% $Al(NO_3)_3$ differed little from the data reported by Davis, the smoothed data were used to estimate the concentration of nitric acid in the TBP samples contacted with aqueous phases containing 0, 5, and 10 wt% dissolved solids. For experiments performed with an aqueous phase containing 20 wt% $Al(NO_3)_3$, the measured values were used to estimate the amount of extracted nitric acid. The estimated concentrations and the corresponding runaway reaction initiation temperature are presented in Table 4.

Table 3 Nitric Acid Concentration in TBP Samples Used for RSST™ Experiments

Run No.	Aqueous Phase Nitric Acid (moles/L)	Aqueous Phase $Al(NO_3)_3$ (wt%)	Organic Phase Nitric Acid (moles/L)	Initiation Temperature (°C)
TBP 0/8-3	8.00	0	3.0810	153
TBP 0/10-1	10.00	0	3.5124	144
TBP 0/12-1	12.00	0	4.1521	139
TBP 0/13-1	13.00	0	4.5262	142
TBP 0/14-1	14.00	0	4.8299	139.5
TBP 5/4-8	4.00	5.00	2.3736	154.5
TBP 5/6-2	6.00	5.00	2.8337	150.5
TBP 5/8-2(1)	8.00	5.02	3.2057	148
TBP 10/4-1	4.00	10.01	2.4751	152.5
TBP 10/4-2(2)	4.00	10.00	2.0588	155.5
TBP 10/6-1	6.00	10.01	2.9746	149.5
TBP 10/8-1	8.00	10.01	3.4309	147
TBP 10/8-2(1)	8.00	10.01	3.2708	147
TBP 10/9-1	8.99	10.01	3.6747	148
TBP 10/10-1	10.00	10.00	3.8916	146
TBP 10/10-2	10.00	10.00	3.8933	146
TBP 20/4-2	4.00	19.99	2.8078	156
TBP 20/6-2	6.00	20.00	3.0770	152.5
TBP 20/6-3	6.00	19.99	3.2256	147.5
TBP 20/7-1	7.00	20.00	3.4274	139.5
TBP 20/7-3	7.00	20.00	3.6193	150
TBP 20/7-4	7.00	20.00	3.4772	148

(1) $NaNO_3$ used as Dissolved Solid
(2) KNO_3 used as Dissolved Solid

The Davis data and the measured values for TBP contacted with an aqueous phase containing 20 wt% $Al(NO_3)_3$ can also be used to estimate the concentration of nitric acid in the TBP samples used by Colven [2] to measure the initiation temperature for a runaway TBP/nitric acid reaction. Estimates for most of the Colven data and the corresponding runaway reaction initiation temperatures are presented in Table 5.

Table 4 Estimated Nitric Acid Concentration in TBP Samples Used for RSST™ Experiments

Run No.	Aqueous Phase Nitric Acid (moles/L)	Aqueous Phase $Al(NO_3)_3$ (wt%)	Organic Phase Nitric Acid (moles/L)	Initiation Temperature (°C)
TBP 0/4-3	4.00	0	2.330	157
TBP 0/8-2	8.00	0	3.370	150.5
TBP 0/15-2	14.99	0	5.784	139
TBP 0/15-3	15.00	0	5.790	137
TBP 5/4-7	4.00	5.00	2.330	157
TBP 5/8-1	8.00	5.00	3.370	146
TBP 5/10-1	10.00	5.00	3.820	143
TBP 5/12-3	11.99	5.00	4.37	139
TBP 5/12-4	12.00	5.01	4.37	139.5
TBP 20/4-1	4.00	20.00	2.76	148.5
TBP 20/6-1	6.00	20.00	3.14	149
TBP 20/8-1	8.00	20.00	3.70	147.5

Table 5 Estimated Organic Phase Nitric Acid Concentrations for Colven Data

Aqueous Phase Nitric Acid (moles/L)	Aqueous Phase $Al(NO_3)_3$ (wt%)	Est Organic Phase Nitric Acid (moles/L)	Initiation Temperature (°C)
3.9	0	2.294	161
4.2	0	2.398	158
5.1	0	2.678	156
6.0	0	2.920	155
6.9	0	3.128	151
8.1	0	3.392	149
8.3	0	3.436	151.5
8.6	0	3.502	150
8.8	0	3.546	148
10.0	0	3.700	142
10.0	0	3.700	144
10.0	0	3.700	148
15.7	0	N/A(1)	132
15.7	0	N/A(1)	136
15.7	0	N/A(1)	137
5.7	20	3.09	153
8.1	20	3.75(2)	131.5
9.6	20	N/A(1)	129

(1) Outside Bounds of Available Data
(2) Extrapolated Value Using Data at 8M Nitric Acid

The data from Tables 3, 4, and 5 were plotted on Figure 9 to show the initiation temperature for a runaway TBP/nitric acid reaction as a function of the nitric acid concentration in the organic phase. From Figure 9, one can generally see a linear decrease in the initiation temperature as the extracted nitric acid concentration increases. This behavior is not unexpected. The initiation temperature should decrease as the amount of oxidant (nitric acid) increases. The higher nitric acid concentration permits a faster reaction (oxidation) rate at a lower temperature which reduces the temperature where runaway reaction occurs.

The data plotted on Figure 9 also illustrates that the runaway reaction initiation temperatures measured by Colven [2] using TBP contacted with an aqueous phase containing 8-10M nitric acid and 20 wt% Na/KNO_3 are excessively low. An extrapolation of the data plotted on Figure 8 was used to estimate the extracted nitric acid concentration for one of the two Colven data points (8.1M nitric acid and 20 wt% Na/KNO_3). The measured initiation temperature for this experiment is approximately 15°C below the expected value based on the linear regression line used to correlate the data. One would also expect the initiation temperature for the Colven experiment performed using an aqueous phase nitric acid concentration of 9.6M to be approximately 10°C higher based on the experimental data.

Effect of Other Variables on Initiation Temperature

Several RSST™ experiments were performed to look at the effect of other variables (nitrate salt and number of phases) on the initiation temperature for a runaway TBP/nitric acid reaction. A baseline experiment was also performed in which an RSST™ run was made using pure TBP to ensure no exothermic behavior (from thermal decomposition products) was seen up to a temperature of 200°C. In this experiment (TBP 0/0-1), the TBP temperature increased at nominally 1°C/min until the termination of the experiment and no self-heating was seen. The temperature and pressure profiles for the experiment are included in Appendix D (see Figure D.1).

Since the dissolved solids used by Colven [2] to measure the initiation temperature for a runaway TBP/nitric acid reaction were either $NaNO_3$ or KNO_3, RSST™ experiments were performed for comparison using TBP contacted with nitric acid solutions containing both of these salts. Two RSST™ runs (TBP 5/8-2 and TBP 10/8-2) were performed using $NaNO_3$ and one (TBP 10/4-2) with KNO_3 as the dissolved solid. The runaway reaction initiation temperatures measured for these experiments were almost identical to the temperatures measured in experiments using the same nitric acid concentration and $Al(NO_3)_3$ as the dissolved solid (see Table 2). Apparently the salting effect of $Al(NO_3)_3$ is not significantly greater than the effect for $NaNO_3$ and KNO_3 at these concentrations of dissolved solids.

RSST™ experiments were also performed to evaluate the effect of additional phases (aqueous and solid) on the thermal behavior of the TBP samples. One experiment (TBP 0/8-3) was performed in which a 1 mL aliquot of the aqueous phase originally used to contact the TBP was also added to the RSST™ test cell. The presence of the aqueous phase had little effect on the runaway reaction initiation temperature. The measured value was approximately the same (153 versus 150.5°C) as the temperature measured during an RSST™ run (TBP 0/8-2) performed with just the organic phase contacted with an aqueous solution containing the same nitric acid and $Al(NO_3)_3$ concentrations. The only noticeable difference in thermal behavior was the extended time required to evaporate the aqueous phase prior to runaway reaction occurring. The temperature profiles which illustrate this point are contained in Appendix D (see Figures D.3 and D.4).

A second experiment was performed in which organic and aqueous phases and a small amount of solid $Al(NO_3)_3$ were added to the RSST™ test cell. In this experiment (TBP 5/12-4), a single seed crystal was added to the separated aqueous phase following contact with TBP. The seeded solution was placed in an ice bath to promote crystallization. Within a few minutes crystals had formed. The two phase mixture was removed from the ice bath and allowed to return to room temperature. A 1 mL aliquot of the mixture, including solid $Al(NO_3)_3$ crystals, was added to the RSST test cell with the organic phase. The presence of the aqueous and solid $Al(NO_3)_3$ phases had almost no effect on the runaway reaction initiation temperature. The initiation temperature was 139.5°C compared to a value of 139°C measured during an RSST™ run (TBP 5/12-3) using just the organic phase which had been contacted with an aqueous solution containing the same concentrations of nitric acid and $Al(NO_3)_3$. Like the two phase experiment, the only noticeable difference in the thermal behavior of the two experiments was the extended time required to evaporate the aqueous phase prior to the runaway reaction. The temperature profiles for the two experiments are presented in Appendix D (see Figures D.17 and D.18).

Nitrate Salt Solubility Limitations

The preparation of TBP samples for a number of RSST™ experiments was aborted due to the precipitation of the dissolved solids while contacting the aqueous and organic phases. The precipitation was attributed to the concentration of the salt by extraction of nitric acid and water into the TBP. Solubility data for $Al(NO_3)_3$ [13] (see Figure 10) show that nitric acid concentrations slightly greater than 8, 6, and 3M should result in the precipitation of $Al(NO_3)_3$ crystals from solutions containing 5, 10, and 20 wt% dissolved solids, respectively. Therefore, RSST™ experiments performed with more concentrated nitric acid solutions using these concentrations of $Al(NO_3)_3$ were actually supersaturated and would not be stable over a long period of time. Successful RSST™ experiments were performed with TBP contacted with aqueous phases containing 5, 10, and 20 wt% $Al(NO_3)_3$ in 12, 10, and 8M nitric acid, respectively. A number of unsuccessful attempts (see Appendix B, Table B.2) were made to perform RSST™ experiments using more concentrated nitric acid at 20 wt% dissolved solids by taking advantage of the increased solubility of KNO_3 compared to either $Al(NO_3)_3$ or $NaNO_3$ at high acid concentrations (see Figure 10). However, concentration of the KNO_3 during the extraction resulted in the formation of a precipitate during each experiment at this level of dissolved solids. This prevented the duplication of the experiments performed by Colven [2] using 20 wt% dissolved solids and nitric acid concentrations greater than 8M.

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Conclusions

An RSST™ was used to investigate the thermal stability of TBP contacted with an aqueous phase containing 2-15M nitric acid and 0 to 20 wt% dissolved solids. The initial experiments were performed with the RSST™ open to atmospheric pressure. In these experiments, the runaway reaction initiation temperature was defined as the temperature of the TBP when the self-heating rated diverged from the imposed heat-up rate of 1°C/min. However, the initiation temperatures measured in this manner were not consistent with the expected results showing a general increase with increasing aqueous phase nitric acid concentration. Based on this observation, RSST™ experiments were performed in which the TBP temperature was increased in a step-wise manner to determine if a runaway reaction occurred. The results from these experiments showed that the self-heating rate was not sufficient for runaway reaction to occur. This observation is consistent with the results from previous studies which showed that adequate venting of vessels is the first defense against a damaging runaway reaction.

To obtain a runaway TBP/nitric acid reaction, it was necessary to seal the RSST™ safety vessel at atmospheric pressure prior to the initiation of an experiment. Without adequate venting, self-heating from the oxidation of TBP degradation products was sufficient for runaway reaction to occur. At the point of runaway, both rapid increases in the RSST™ safety vessel pressure and TBP temperature were seen. The runaway reaction initiation temperature was defined by the time and corresponding temperature when a rapid increase in the pressure was initially seen. This procedure worked well except for experiments performed with TBP contacted with aqueous solutions containing high concentrations (13-15M) of nitric acid. In these experiments, the evaporation of water and nitric acid caused a gradual increase in pressure well before runaway reaction occurred. To define the runaway reaction initiation temperature, it was necessary to compare both temperature and pressure profiles to ensure that rapid increases in both temperature and pressure were occurring at the same time.

The runaway reaction initiation temperatures for TBP contacted with nitric acid solutions containing no dissolved solids were in good agreement with Colven's data.[2] The initiation temperature gradually decreased with increasing aqueous phase nitric acid concentration. The decrease in the initiation temperature was due to the increase in the available oxidant (nitric acid) extracted by the TBP. The minimum initiation temperature, 137°C, measured at 14-15M nitric acid was consistent with the values (132-137°C) measured by Colven at nominally 15.7M nitric acid. The initiation temperatures measured using TBP contacted with nitric acid solutions containing 5, 10, and 20 wt% dissolved solids showed a small dependence on the salt concentration; however, the lowest temperatures were several degrees above the minimum value for no dissolved solids. The slight lowering of the initiation temperature was attributed to the increased extraction of nitric acid due to the salting-out effect of the dissolved solids.

From the results of the closed RSST™ experiments, it was clear that the initiation temperature for a runaway TBP/nitric acid reaction decreased with increasing nitric acid concentration in the TBP. To illustrate this point the initiation temperature was correlated with the amount of nitric acid extracted into the organic phase. The extracted nitric acid concentration was either analyzed or estimated using published values or the results of separate experiments. An estimate of the nitric acid concentration in most of the TBP samples used by Colven [2] was obtained by the same procedure. When the runaway reaction initiation temperature was plotted as a function of the extracted nitric acid concentration, the temperature decreased linearly with increasing concentration. A higher nitric acid concentration in the TBP results in a faster reaction (oxidation) rate at a lower temperature which reduces the temperature where runaway reaction occurs. The correlation also illustrated that initiation temperatures measured by Colven using TBP contacted with an aqueous phase containing 8-10M nitric acid and 20 wt% Na/KNO_3 are excessively low. The measured initiation temperatures were 10-15°C below the expected values based on the linear regression line used to correlated the data.

A number of RSST™ experiments were performed to look at the effect of other variables (nitrate salt and number of phases) on the initiation temperature for a runaway TBP/nitric acid reaction. Experiments were performed in which the dissolved solids were changed from $Al(NO_3)_3$ to $NaNO_3$, or KNO_3. No significant effect on the initiation temperature was seen. RSST™ experiments were also performed to evaluate the effect of additional phases (aqueous and solid) on the thermal behavior of the TBP samples. Neither the presence of the aqueous phase originally used to contact the TBP nor a small amount of undissolved solids in the aqueous phase had a significant effect on the runaway reaction initiation temperature. The only noticeable difference in thermal behavior was the extended time required to evaporate the aqueous phase prior to runaway reaction occurring.

The preparation of TBP samples for a number of RSST™ experiments was aborted due to the precipitation of the dissolved solids while contacting the aqueous and organic phases. The precipitation was attributed to the concentration of the salt by extraction of nitric acid and water into the TBP. Solubility data for $Al(NO_3)_3$ showed that nitric acid concentrations slightly greater than 8, 6, and 3M should result in precipitation of $Al(NO_3)_3$ from solutions containing 5, 10, and 20 wt% dissolved solids, respectively. Therefore, RSST™ experiments performed with more concentrated nitric acid solutions using these concentrations of $Al(NO_3)_3$ were actually supersaturated and would not be stable over a long period of time.

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Figure 1 Colven Data – Initiation Temperature for Runaway TBP/Nitric Acid Reaction [2]

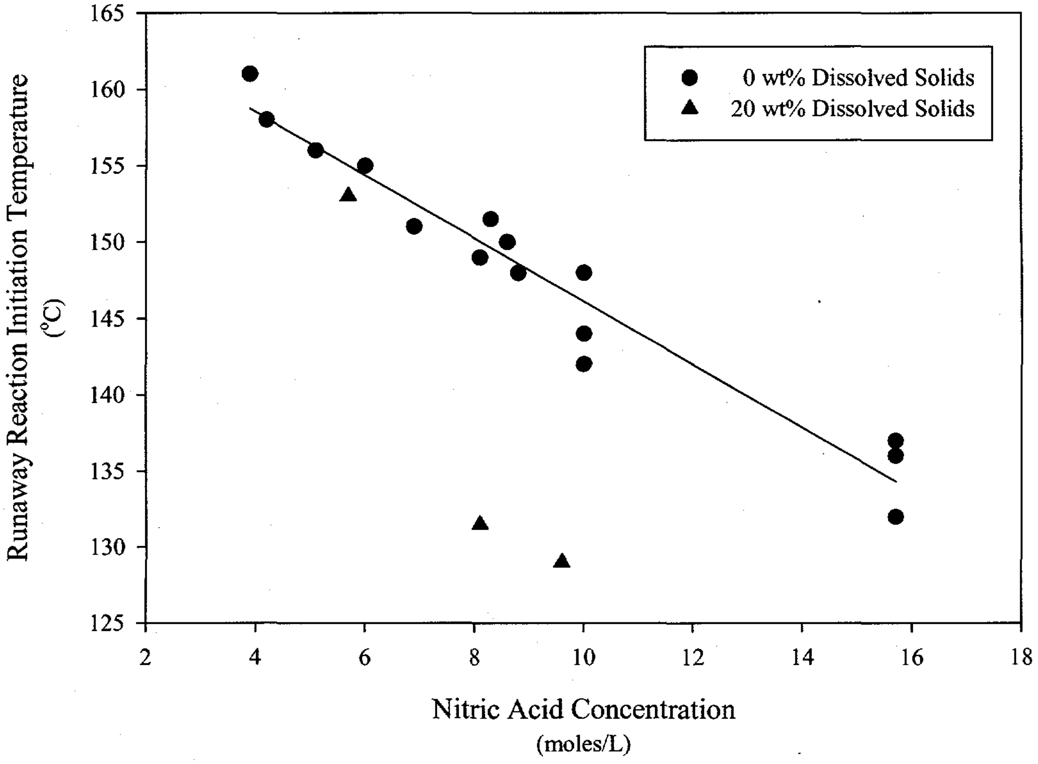

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Figure 2 RSST Pressure Vessel

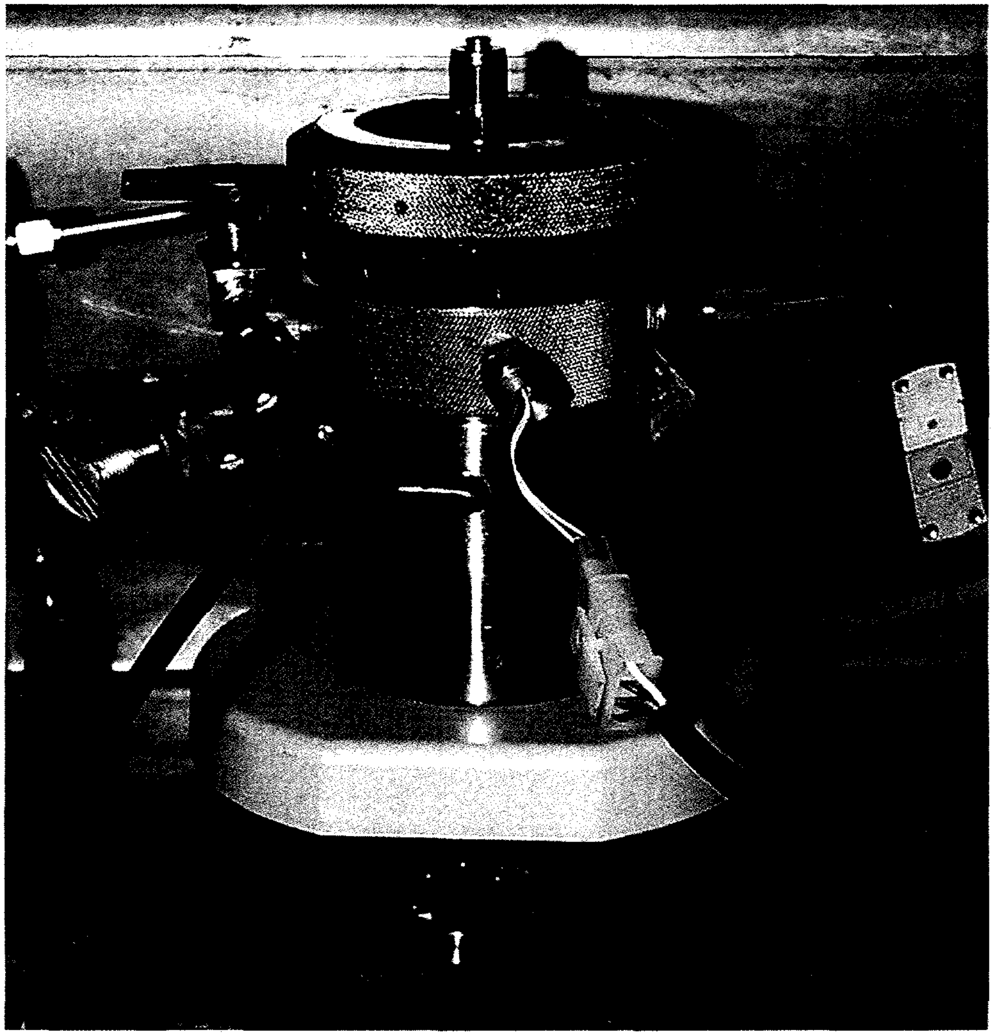

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Figure 3 Temperature Profile and Self-Heating Rate for Open System Run No. TBP 5/12-5

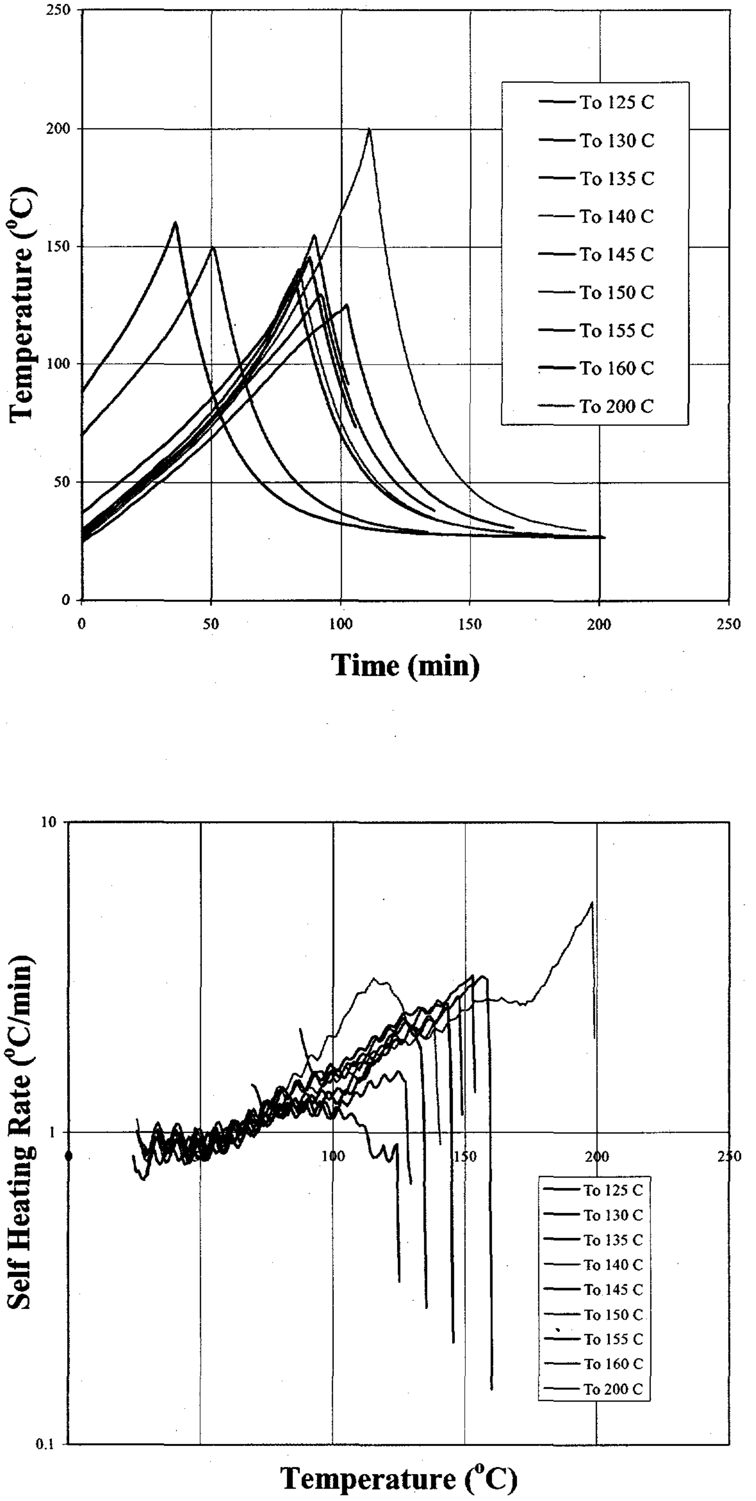

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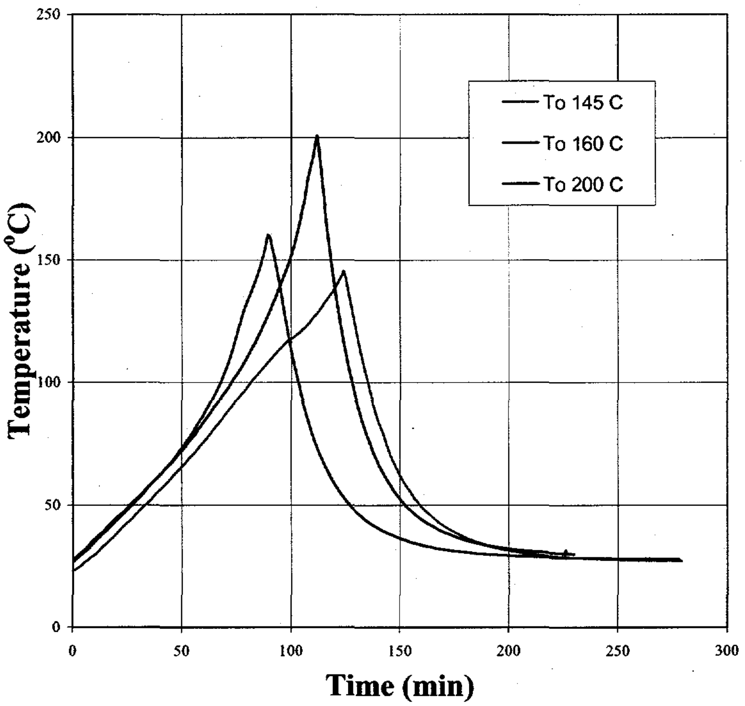
Figure 4 Temperature Profile and Self-Heating Rate for Open System Run No. TBP 5/12-6



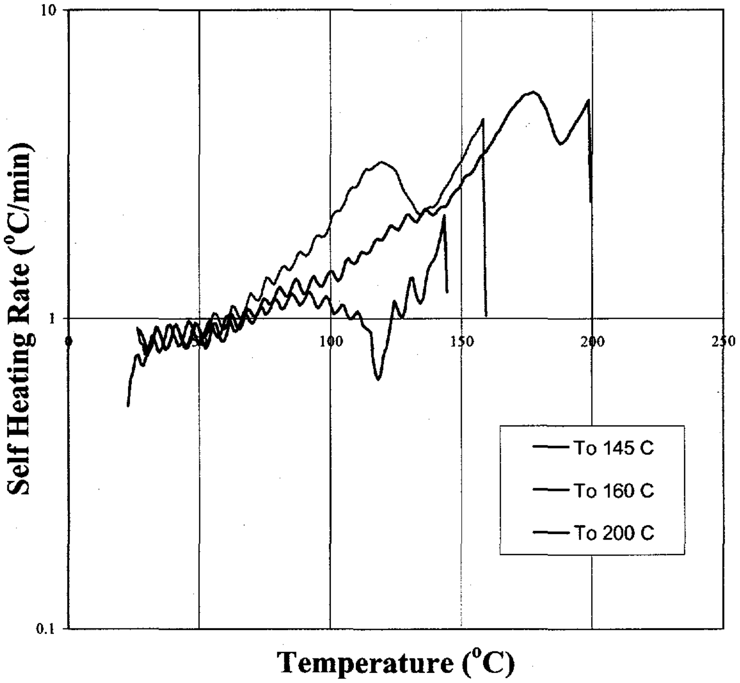


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Figure 5 Defining the Initiation Temperature for a Runaway TBP/Nitric Acid Reaction (Run No. TBP 0/8-3)

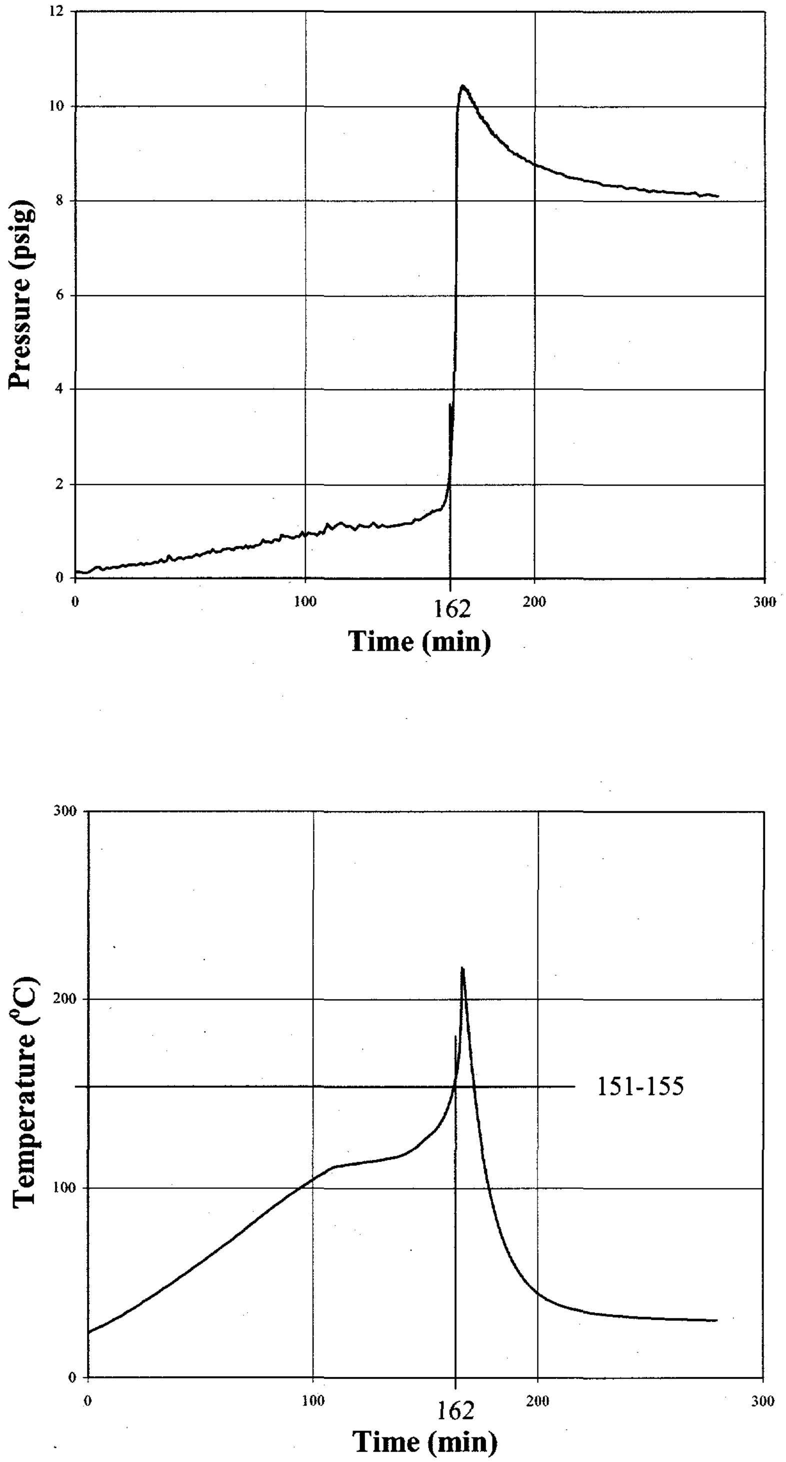

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Figure 6 Effect of Acid Concentration and Solids Content on the Initiation Temperature for a Runaway TBP/Nitric Acid

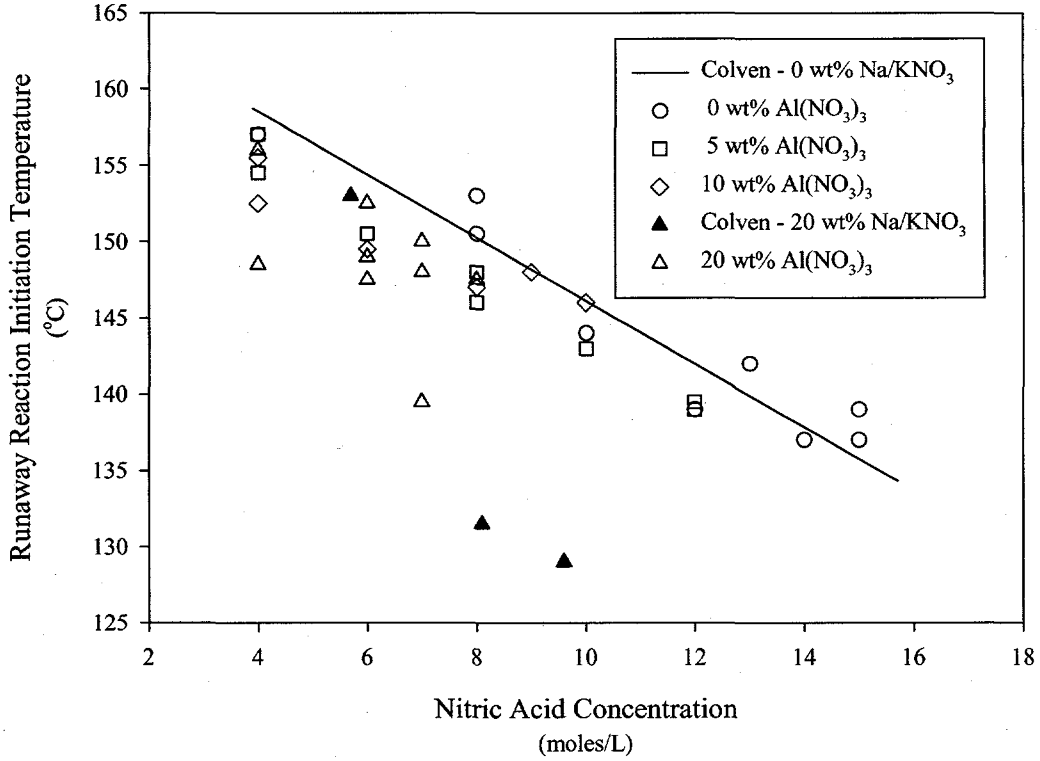

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Figure 7 Regression Analysis for Runaway TBP/Nitric Acid Initiation Temperature

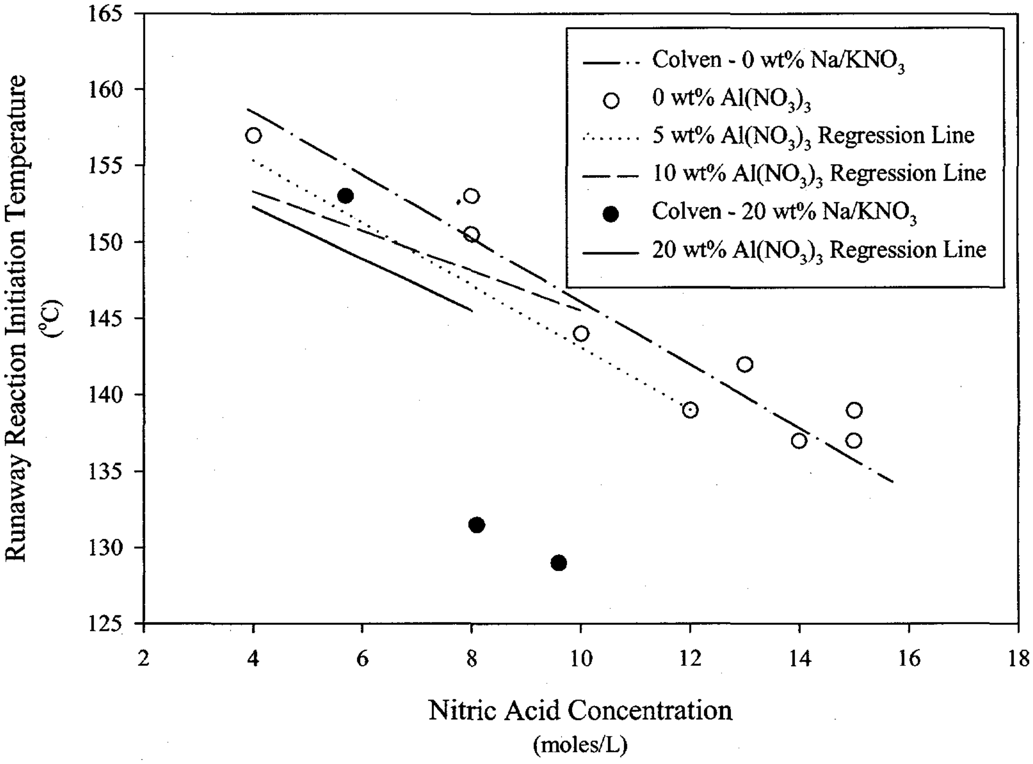

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Figure 8 Extraction of Nitric Acid into Pure TBP

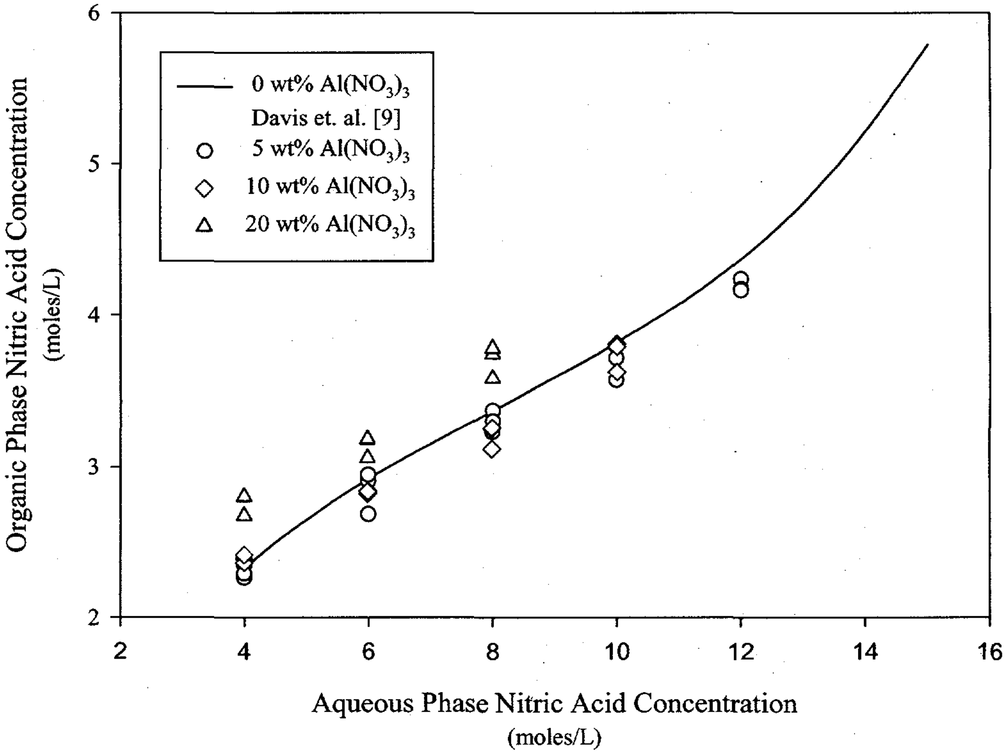

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Figure 9 Correlation of Runaway Reaction Initiation Temperature with Extracted Nitric Acid Concentration

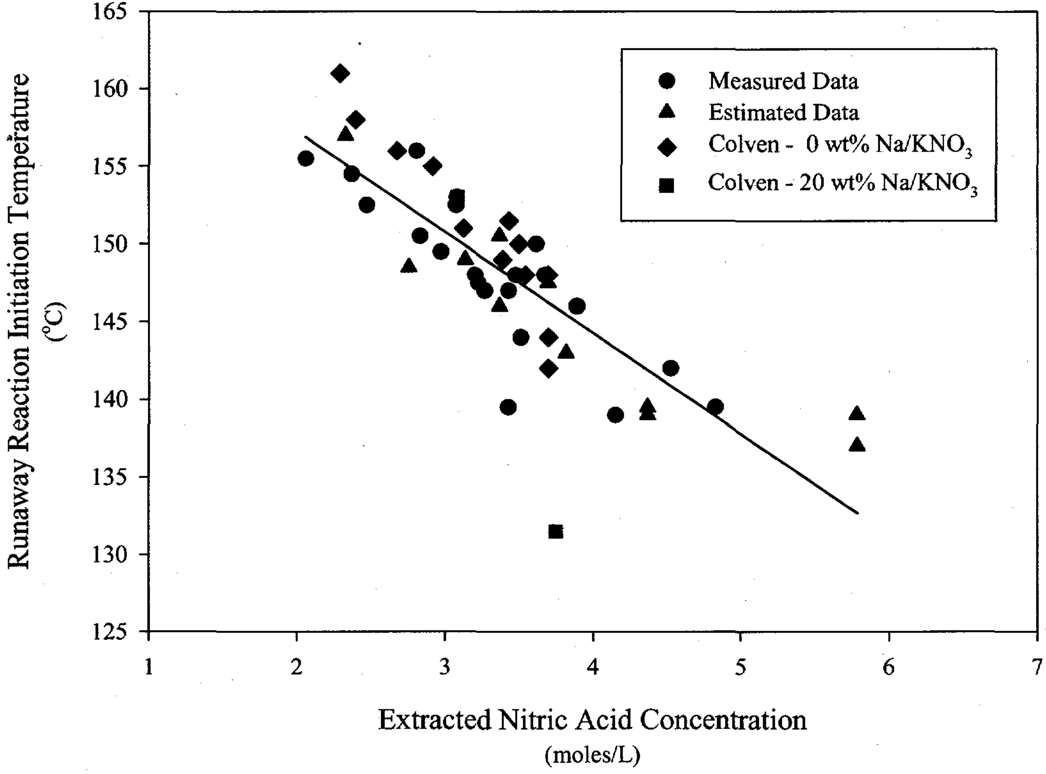

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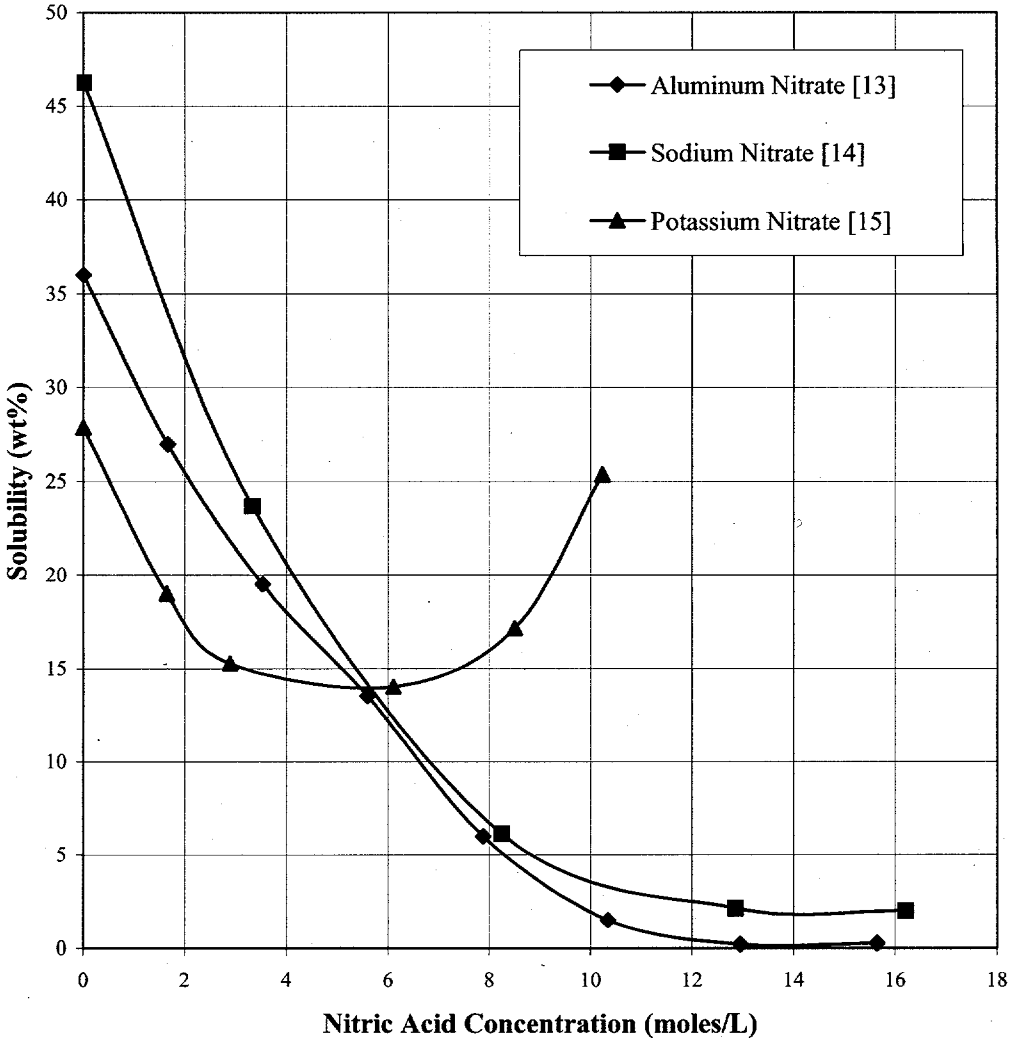
Figure 10 Solubility of Metal Nitrate Salts in Nitric Acid



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Appendix A Reagent Data and Properties

Reagents

The reagents used to prepare the solutions for the runaway TBP/nitric acid reaction initiation temperature measurements are described below.

Tributyl Phosphate
Manufacturer: Aldrich Chemical Company
Lot Number: 14628ER
Purity: 99+%

Nitric Acid (HNO_3)
Concentration: 69.7 wt%
Manufacturer: Fisher Chemicals
Lot Number: 993625

Aluminum Nitrate Crystals ($Al(NO_3)_3 \cdot 9H_2O$
Manufacturer: Fisher Chemicals
Lot Number: 990207
Assay: 98.1%

Sodium Nitrate ($NaNO_3$)
Manufacturer: Fisher Chemicals
Lot Number: 94164413
Assay: 100.1%

Potassium Nitrate (KNO_3)
Manufacturer: Mallinckrodt Specialty Chemicals Co.
Lot Number: 7028KLCM
Assay: Meets ACS Specification

Nitric Acid Concentration/Density

The concentration of the nitric acid used to prepare the aqueous phase solutions for the runaway reaction studies was measured by titration. The data from these measurements are summarized in Table A.1.

The density of the nitric acid was measured by transferring a 1 mL aliquot of solution using a calibrated pipette to a preweighed (tared) beaker. A new pipette tip was used for each of 10 measurements. The pipette tip was conditioned with the acid one time before making the transfer. The data from these measurements are given in Table A.2.

Table A.1 Actual Concentration of 70 wt% Nitric Acid

Sample Number	Nominal Concentration (wt% / M)	Measured Concentration (M)
1	70 / 15.7	15.2786
2	70 / 15.7	15.2948
3	70 / 15.7	15.1691
4	70 / 15.7	15.0881
5	70 / 15.7	15.1604
	Average	15.1982
	Standard Deviation	0.0869
	95% Confidence Limit	0.1079

Table A.2 Density of 70 wt% Nitric Acid

Sample Number	Nitric Acid Mass (g)	Nitric Acid Density(1) (g/mL)
1	1.4029	1.3934
2	1.4045	1.3950
3	1.4020	1.3925
4	1.4040	1.3945
5	1.4055	1.3960
6	1.4064	1.3969
7	1.4041	1.3946
8	1.4041	1.3946
9	1.4036	1.3941
10	1.4053	1.3950
	Average	1.3947
	Standard Deviation	0.0012
	95% Confidence Limit	0.0008

(1) Transfer Volume of Calibrated Pipette – 1.00683 ± 0.0015 mL

Distribution of Nitric Acid Between Aqueous and 100% TBP Phases

Data summarizing the distribution of nitric acid between the aqueous and 100% TBP phases are summarized in Table A.3. The data presented in the table were based on experimentally determined values which were empirically smoothed to reduce scatter.[9]

Table A.3 Distribution of Nitric Acid Between Aqueous and 100% TBP Phases

Aqueous Phase		Organic Phase			
Nitric Acid Conc. (moles/L)	Density 25°C (g/mL)	Nitric Acid Conc. (moles/L)	Water Conc. (moles/L)	TBP Conc. (moles/L)	Density 25°C (g/mL)
0.100	1.0002	0.032	3.59	3.420	0.9774
0.200	1.0034	0.105	3.58	3.411	0.9795
0.300	1.0066	0.201	3.57	3.396	0.9815
0.400	1.0098	0.304	3.54	3.383	0.9838
0.500	1.0131	0.409	3.52	3.367	0.9860
0.600	1.0164	0.513	3.47	3.356	0.9885
0.700	1.0196	0.617	3.43	3.344	0.9912
0.800	1.0229	0.709	3.39	3.331	0.9928
0.900	1.0263	0.796	3.35	3.320	0.9948
1.000	1.0296	0.870	3.32	3.312	0.9968
1.500	1.0462	1.185	3.08	3.282	1.0042
2.000	1.0627	1.480	2.76	2.257	1.0105
2.500	1.0792	1.733	2.50	3.234	1.0156
3.000	1.0955	1.950	2.30	3.213	1.0200
3.500	1.1116	2.150	2.12	3.191	1.0236
4.000	1.1276	2.330	1.95	3.172	1.0268
4.500	1.1432	2.500	1.79	3.153	1.0296
5.000	1.1586	2.650	1.65	3.136	1.0320
5.500	1.1738	2.790	1.52	3.120	1.0342
6.000	1.1886	2.920	1.40	3.105	1.0362
6.500	1.2032	3.040	1.31	3.090	1.0382
7.000	1.2174	3.150	1.25	3.076	1.0402
7.500	1.2313	3.260	1.22	3.059	1.0422
8.000	1.2449	3.370	1.20	3.043	1.0445
8.500	1.2581	3.480	1.20	3.026	1.0468
9.000	1.2710	3.590	1.20	3.009	1.0492
9.500	1.2835	3.700	1.22	2.991	1.0518
10.000	1.2957	3.820	1.24	2.970	1.0540
11.000	1.3189	4.070	1.31	2.926	1.0594
12.000	1.3406	4.370	1.41	2.872	1.0657
13.000	1.3608	4.740	1.53	2.808	1.0742
14.000	1.3795	5.220	1.69	2.723	1.0845
15.000	1.3965	5.790	2.00	2.608	1.0955

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Appendix B Preparation of TBP/Nitric Acid Solutions

The target concentrations and the amounts of materials used to prepare the aqueous and organic phases for each of the RSST™ experiments are provided in Table B.1 for open experiments and Table B.2 for closed experiments.

Table B.1 Preparation of Aqueous and Organic Phases for Open RSST™ Experiments

Run No.	Target Concentrations Nitric Acid (moles/L)	Target Concentrations $Al(NO_3)_3$ (wt%)	$Al(NO_3)_3 \cdot 9H_2O$ Mass (g)	Water Mass (g)	Nitric Acid Mass (g)	Actual Concentrations Nitric Acid (moles/L)	Actual Concentrations $Al(NO_3)_3$ (wt%)	TBP Mass (g)
TBP 0/2-1	2	0	0	52.683	11.097	2.00	0	11.513
TBP 0/8-1	8	0	0	30.362	44.367	8.00	0	12.010
TBP 0/15-1	15	0	0	0.648	83.198	15.00	0	12.014
TBP 5/4-1	4	5	6.274	42.793	23.010	4.11	4.94	11.483
TBP 5/4-2	4	5	6.299	42.796	22.193	4.00	5.02	12.022
TBP 5/4-3	4	5	6.296	42.771	22.202	4.00	5.02	11.584
TBP 5/4-4(1)	4	5	3.564	45.502	22.217	4.00	5.00	11.596
TBP 5/4-5	4	5	6.286	42.799	22.184	4.00	5.01	11.580
TBP 5/4-6	4	5	6.280	42.818	22.178	4.00	5.00	11.594
TBP 5/6-1	6	5	6.615	35.240	33.289	6.00	5.00	12.013
TBP 5/12-1	12	5	7.472	12.611	64.665	11.57	5.01	12.010
TBP 5/12-2	12	5	7.457	12.630	64.649	11.57	5.00	12.014

(1) $NaNO_3$ used as Dissolved Solid

Table B.2 Preparation of Aqueous and Organic Phases for Closed RSST™ Experiments

Run No.	Target Concentrations		$Al(NO_3)_3 \cdot 9H_2O$ Mass (g)	Water Mass (g)	Nitric Acid Mass (g)	Actual Concentrations		TBP Mass (g)
	Nitric Acid (moles/L)	$Al(NO_3)_3$ (wt%)				Nitric Acid (moles/L)	$Al(NO_3)_3$ (wt%)	
TBP 0/0-1	0	0	0	0	0	0	0	11.834
TBP 0/4-3	4	0	22.190	45.495	0	4.00	0	11.547
TBP 0/8-2	8	0	44.352	30.362	0	8.00	0	11.563
TBP 0/8-3(3)	8	0	44.364	30.364	0	8.00	0	11.498
TBP 0/10-1	10	0	55.438	22.322	0	10.00	0	11.508
TBP 0/12-1	12	0	66.610	13.922	0	12.00	0	11.532
TBP 0/13-1	13	0	72.213	9.592	0	13.00	0	11.509
TBP 0/14-1	14	0	77.680	5.162	0	14.00	0	11.526
TBP 0/15-2	15	0	83.172	0.680	0	14.99	0	11.575
TBP 0/15-3	15	0	83.159	0.646	0	15.00	0	11.525
TBP 5/4-7	4	5	22.181	42.802	6.274	4.00	5.00	11.580
TBP 5/4-8	4	5	22.190	42.782	6.279	4.00	5.00	11.536
TBP 5/6-2	6	5	33.283	35.232	6.617	6.00	5.00	11.536
TBP 5/8-1	8	5	44.353	27.369	6.926	8.00	5.00	11.508
TBP 5/8-2(1)	8	5	44.353	30.356	3.949	8.00	5.02	11.514
TBP 5/10-1	10	5	55.448	19.204	7.208	10.00	5.00	11.520
TBP 5/12-3	12	5	66.531	10.716	7.462	11.99	5.00	11.523
TBP 5/12-4(4)	12	5	66.532	10.694	7.469	12.00	5.01	11.536
TBP 10/4-1	4	10	22.205	39.769	13.268	4.00	10.01	11.534
TBP 10/4-2(2)	4	10	22.197	45.497	7.520	4.00	10.00	11.524
TBP 10/6-1	6	10	33.282	32.029	13.983	6.00	10.01	11.525

(1) $NaNO_3$ used as Dissolved Solid
(2) KNO3 used as Dissolved Solid
(3) Two Phase Experiment (Aqueous and Organic)
(4) Three Phase Experiment (Aqueous, Organic, and Solid $Al(NO_3)_3$)
(5) Precipitation Occurred

Table B.2 Continued

Run No.	Target Concentrations		$Al(NO_3)_3 \cdot 9H_2O$	Water	Nitric Acid	Actual Concentrations		TBP
	Nitric Acid (moles/L)	$Al(NO_3)_3$ (wt%)	Mass (g)	Mass (g)	Mass (g)	Nitric Acid (moles/L)	$Al(NO_3)_3$ (wt%)	Mass (g)
TBP 10/8-1	8	10	44.352	24.034	14.629	8.00	10.01	11.528
TBP 10/8-2(1)	8	10	44.366	30.350	8.309	8.00	10.01	11.541
TBP 10/9-1	9	10	49.894	19.953	14.941	8.99	10.01	11.518
TBP 10/10-1	10	10	55.440	15.754	15.216	10.00	10.00	11.536
TBP 10/10-2	10	10	55.480	15.734	15.224	10.00	10.00	11.509
TBP 20/4-1	4	20	22.188	32.619	29.797	4.00	20.00	11.512
TBP 20/4-2	4	20	22.186	32.633	29.791	4.00	19.99	11.545
TBP 20/4-3(2,5)	4	20	22.201	45.489	16.921	4.00	20.00	11.528
TBP 20/4-4(2,5)	4	20	22.643	45.510	19.920	4.06	22.62	11.518
TBP 20/6-1	6	20	33.264	24.493	31.413	6.00	20.00	11.528
TBP 20/6-2	6	20	33.265	24.498	31.419	6.00	20.00	11.549
TBP 20/6-3	6	20	33.279	24.499	31.404	6.00	19.99	11.524
TBP 20/7-1	7	20	38.806	20.352	32.166	7.00	20.00	11.535
TBP 20/7-2(5)	7	20	38.824	20.340	32.165	7.00	20.00	11.520
TBP 20/7-3	7	20	38.809	20.350	32.169	7.00	20.00	11.529
TBP 20/7-4	7	20	38.811	20.344	32.168	7.00	20.00	11.517
TBP 20/8-1	8	20	44.352	16.148	32.898	8.00	20.00	11.520
TBP 20/8-2(5)	8	20	44.354	16.130	32.889	8.00	20.00	11.530
TBP 20/8-3(2,5)	8	20	44.351	30.374	18.677	8.00	20.00	11.520
TBP 20/8-4(5)	8	20	44.398	16.162	32.892	8.00	19.98	11.514
TBP 20/10-1(2,5)	10	20	55.445	22.310	19.445	10.00	20.01	11.533
TBP 20/10-2(2,5)	10	20	110.899	44.613	38.873	10.00	20.00	11.523

(1) $NaNO_3$ used as Dissolved Solid
(2) KNO_3 used as Dissolved Solid
(3) Two Phase Experiment (Aqueous and Organic)
(4) Three Phase Experiment (Aqueous, Organic, and Solid $Al(NO_3)_3$)
(5) Precipitation Occurred

The mass of TBP used in each RSST™ experiment is provided in Table B.3 for open system experiments and Table B.4 for closed system experiments.

Table B.3 Mass of TBP Used for Open RSST™ Experiments

Run No.	Aqueous Phase Concentrations Nitric Acid (moles/L)	Al(NO_3)$_3$ (wt%)	TBP Added to RSST™ Test Cell (g)
TBP 0/2-1	2.00	0	10.21
TBP 0/8-1	8.00	0	10.48
TBP 0/15-1	15.00	0	11.03
TBP 5/4-1	4.11	4.94	10.40
TBP 5/4-2	4.00	5.02	10.37
TBP 5/4-3	4.00	5.02	10.38
TBP 5/4-4(1)	4.00	5.00	10.40
TBP 5/4-5	4.00	5.01	10.41
TBP 5/4-6	4.00	5.00	10.38
TBP 5/6-1	6.00	5.00	10.40
TBP 5/12-1	11.57	5.01	10.76
TBP 5/12-2	11.57	5.00	10.76

(1) $NaNO_3$ used as Dissolved Solid

Table B.4 Mass of TBP Used for Closed RSST™ Experiments

Run No.	Aqueous Phase Concentrations Nitric Acid (moles/L)	Al(NO_3)$_3$ (wt%)	TBP Added to RSST™ Test Cell (g)
TBP 0/0-1	0	0	9.65
TBP 0/4-3	4.00	0	10.40
TBP 0/8-2	8.00	0	10.54
TBP 0/8-3(1)	8.00	0	9.40
TBP 0/10-1	10.00	0	10.47
TBP 0/12-1	12.00	0	10.63
TBP 0/13-1	13.00	0	10.81
TBP 0/14-1	14.00	0	10.16
TBP 0/15-2	14.99	0	11.04
TBP 0/15-3	15.00	0	11.02

(1) Two Phase Experiment – Mass of Aqueous Phase was 1.24 g
(2) $NaNO_3$ used as Dissolved Solid
(3) Three Phase Experiment – Mass of Aqueous Phase was 1.30 g (Mass of Solids was not Measured)
(4) KNO_3 used as Dissolved Solid
(5) Precipitation Occurred

Table B.4 Continued

Run No.	Aqueous Phase Concentrations Nitric Acid (moles/L)	Aqueous Phase Concentrations $Al(NO_3)_3$ (wt%)	TBP Added to RSST™ Test Cell (g)
TBP 5/4-7	4.00	5.00	10.41
TBP 5/4-8	4.00	5.00	10.36
TBP 5/6-2	6.00	5.00	10.40
TBP 5/8-1	8.00	5.00	10.49
TBP 5/8-2(2)	8.00	5.02	10.43
TBP 5/10-1	10.00	5.00	10.60
TBP 5/12-3	11.99	5.00	10.81
TBP 5/12-4(3)	12.00	5.01	9.63
TBP 10/4-1	4.00	10.01	10.39
TBP 10/4-2(4)	4.00	10.00	10.35
TBP 10/6-1	6.00	10.01	10.41
TBP 10/8-1	8.00	10.01	10.54
TBP 10/8-2(2)	8.00	10.01	10.46
TBP 10/9-1	8.99	10.01	1049
TBP 10/10-1	10.00	10.00	10.66
TBP 10/10-2	10.00	10.00	10.65
TBP 20/4-1	4.00	20.00	10.43
TBP 20/4-2	4.00	19.99	10.37
TBP 20/4-3(4,5)	4.00	20.00	N/A
TBP 20/4-4(4,5)	4.06	22.62	B/A
TBP 20/6-1	6.00	20.00	10.53
TBP 20/6-2	6.00	20.00	10.46
TBP 20/6-3	6.00	19.99	10.46
TBP 20/7-1	7.00	20.00	10.49
TBP 20/7-2(5)	7.00	20.00	N/A
TBP 20/7-3	7.00	20.00	10.52
TBP 20/7-4	7.00	20.00	10.34
TBP 20/8-1	8.00	20.00	10.43
TBP 20/8-2(5)	8.00	20.00	N/A
TBP 20/8-3(4,5)	8.00	20.00	N/A
TBP 20/8-4(5)	8.00	19.98	N/A
TBP 20/10-1(4,5)	10.00	20.01	N/A
TBP 20/10-2(4,5)	10.00	20.00	N/A

(1) Two Phase Experiment – Mass of Aqueous Phase was 1.24 g
(2) $NaNO_3$ used as Dissolved Solid
(3) Three Phase Experiment – Mass of Aqueous Phase was 1.30 g (Mass of Solids was not Measured)
(4) KNO_3 used as Dissolved Solid
(5) Precipitation Occurred

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Appendix C Temperature Profiles and Self-Heating Rates for Open RSST™ Experiments

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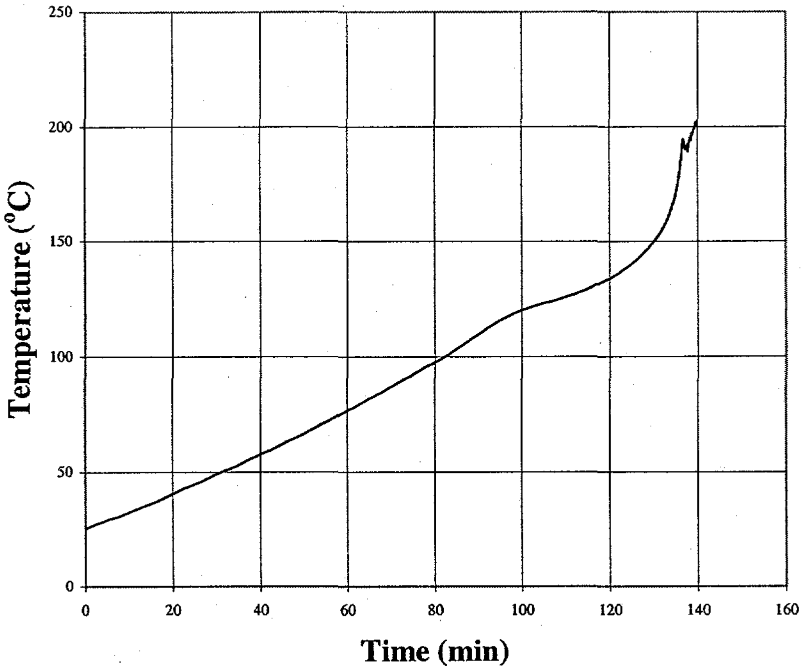
Figure C.1 Temperature Profile and Self-Heating Rate for Run No. TBP 5/12-1



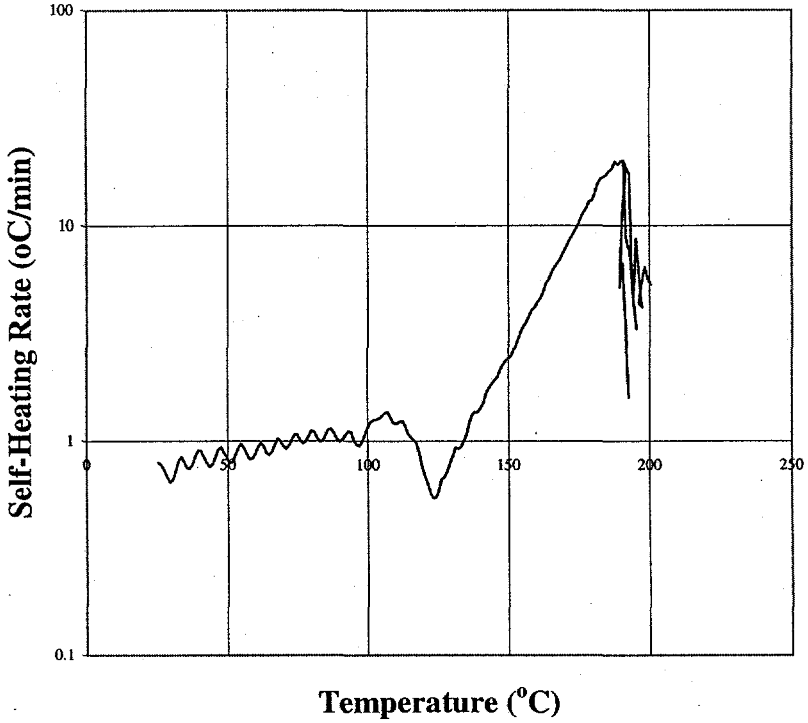
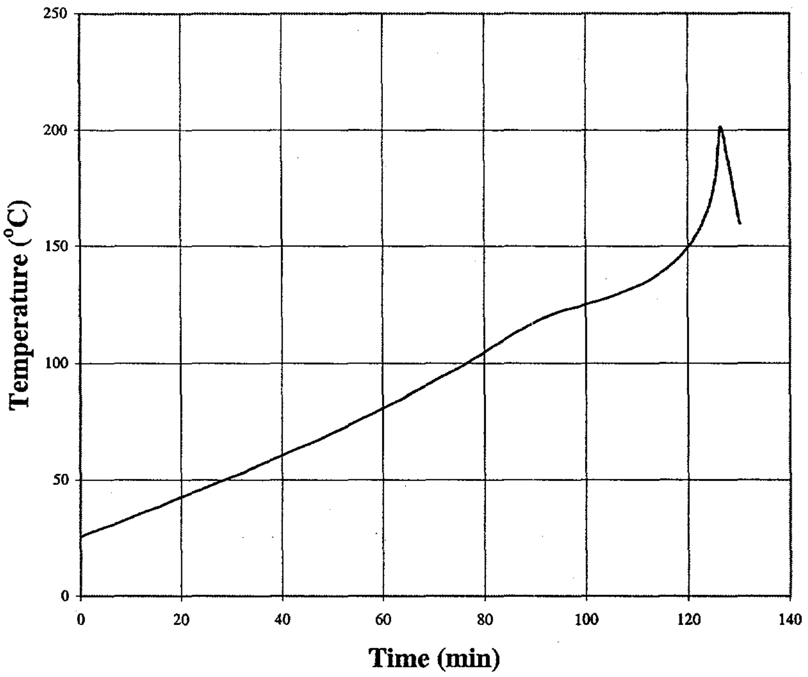


Figure C.2 Temperature Profile and Self-Heating Rate for Run No. TBP 5/12-2



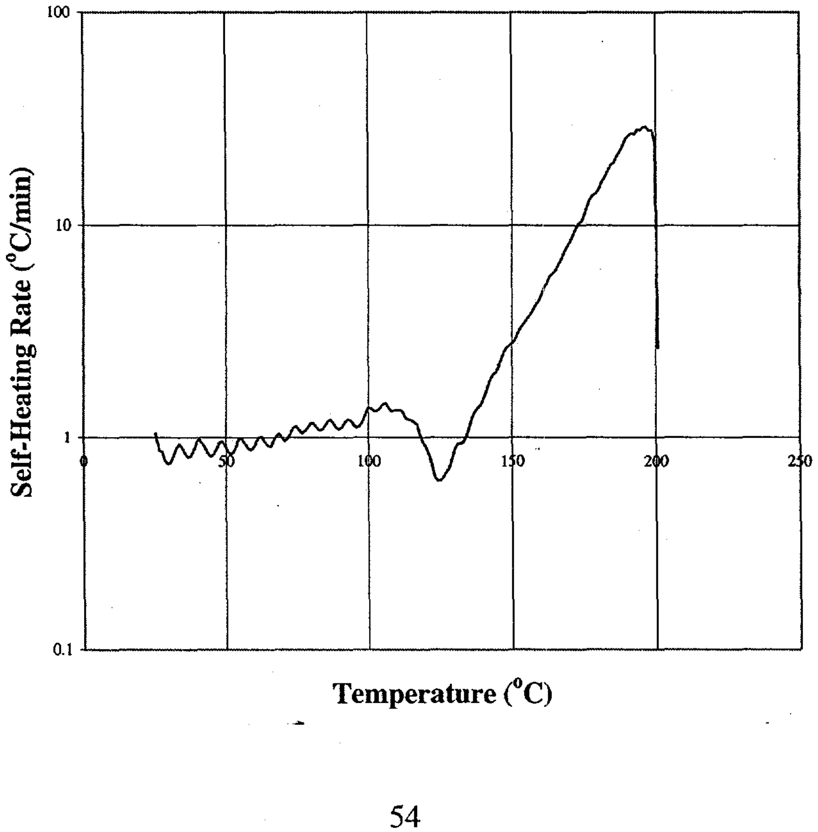


Figure C.3 Temperature Profile and Self-Heating Rate for Run No. TBP 5/4-1

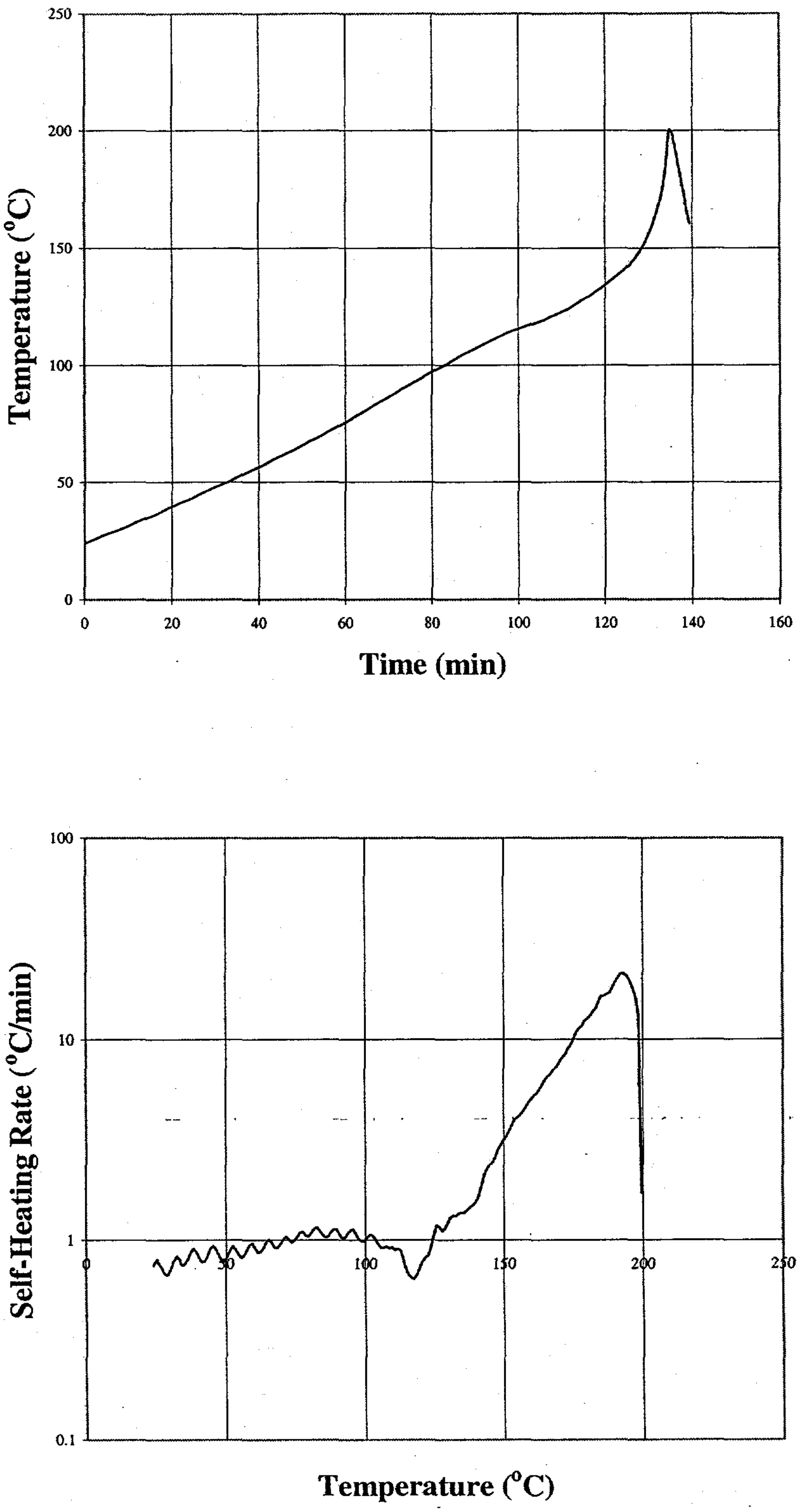
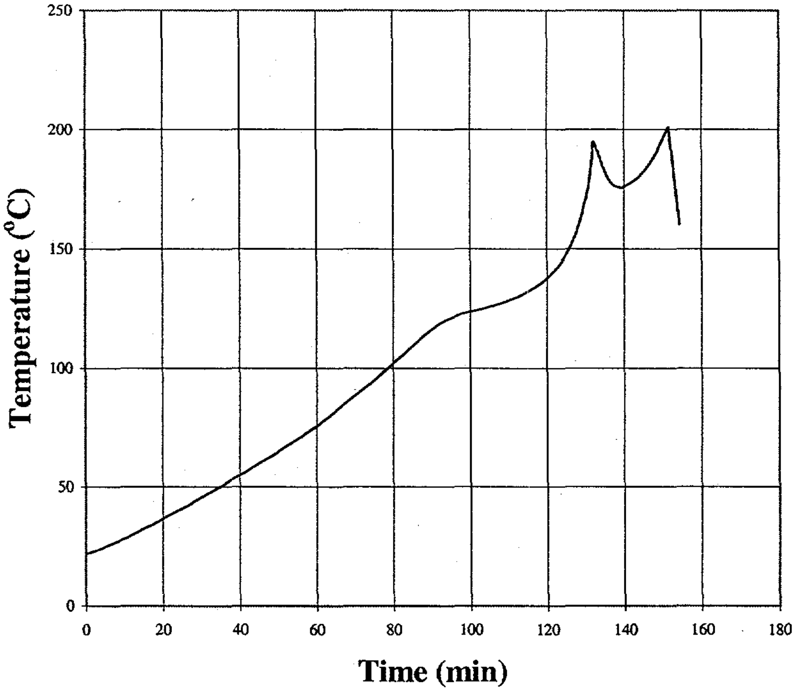


Figure C.4 Temperature Profile and Self-Heating Rate for Run No. TBP 0/15-1



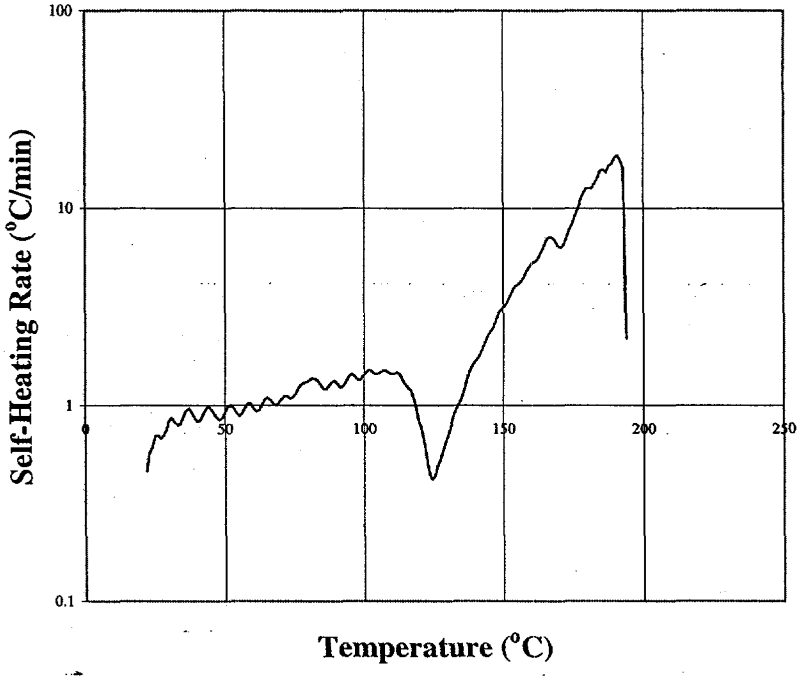


Figure C.5 Temperature Profile and Self-Heating Rate for Run No. TBP 5/6-1

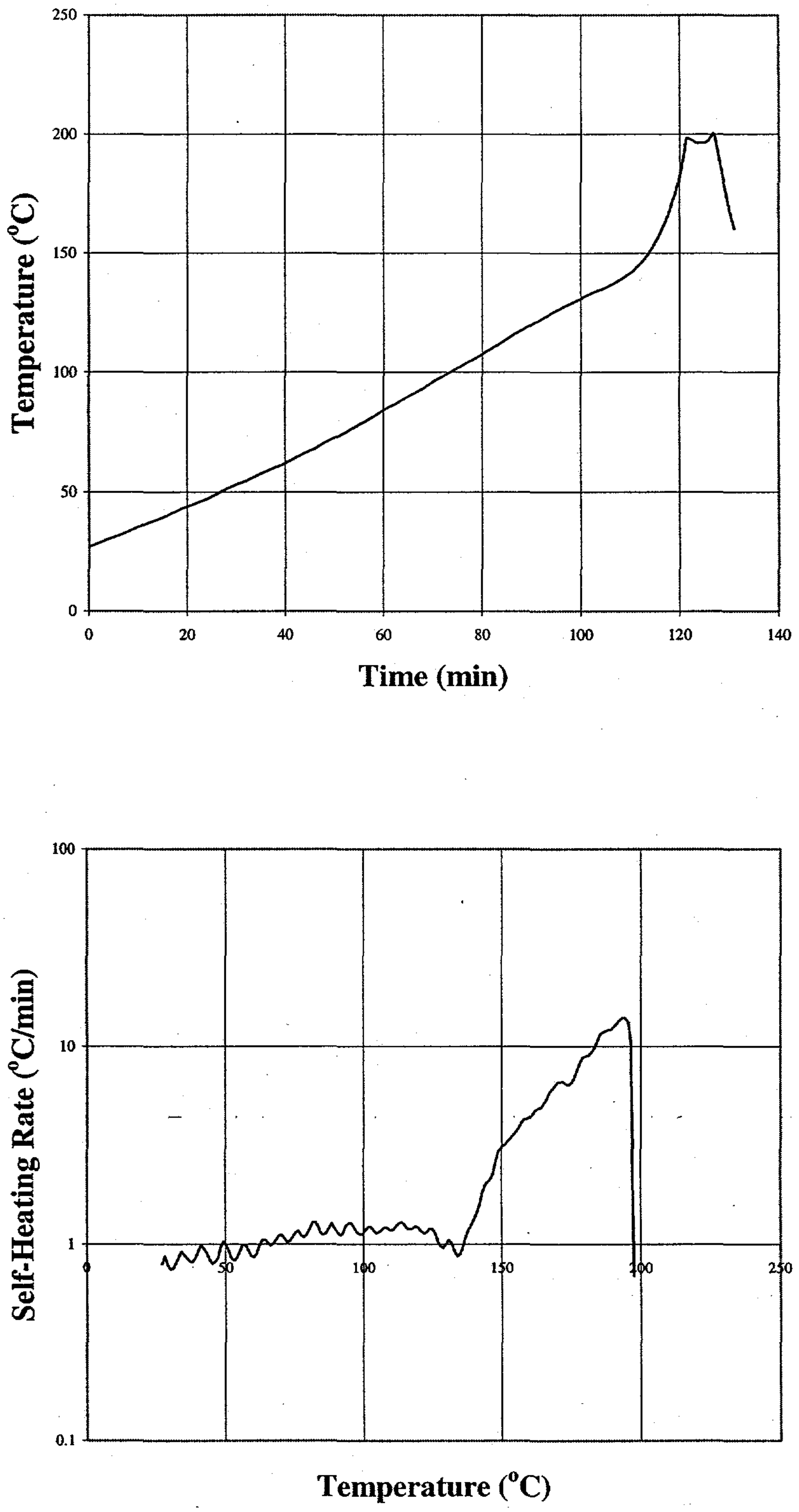
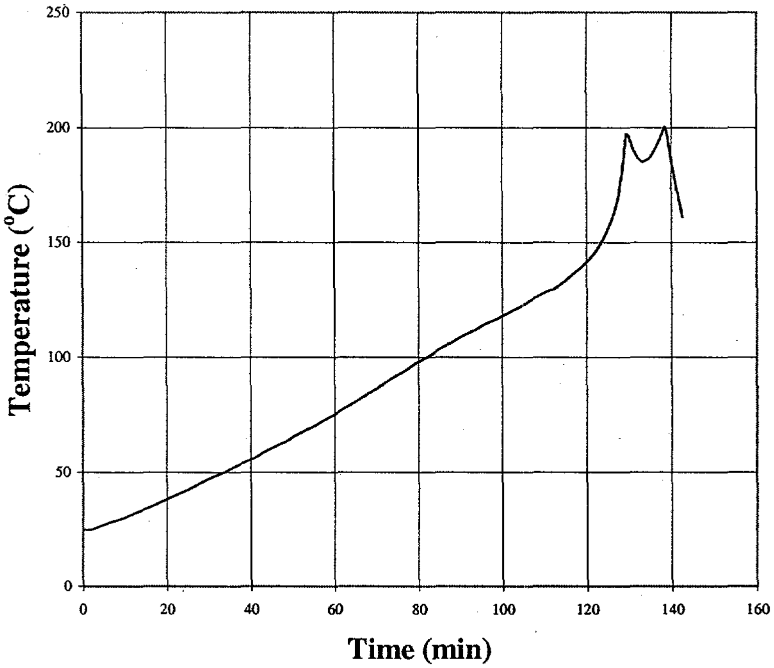


Figure C.6 Temperature Profile and Self-Heating Rate for Run No. TBP 5/4-2



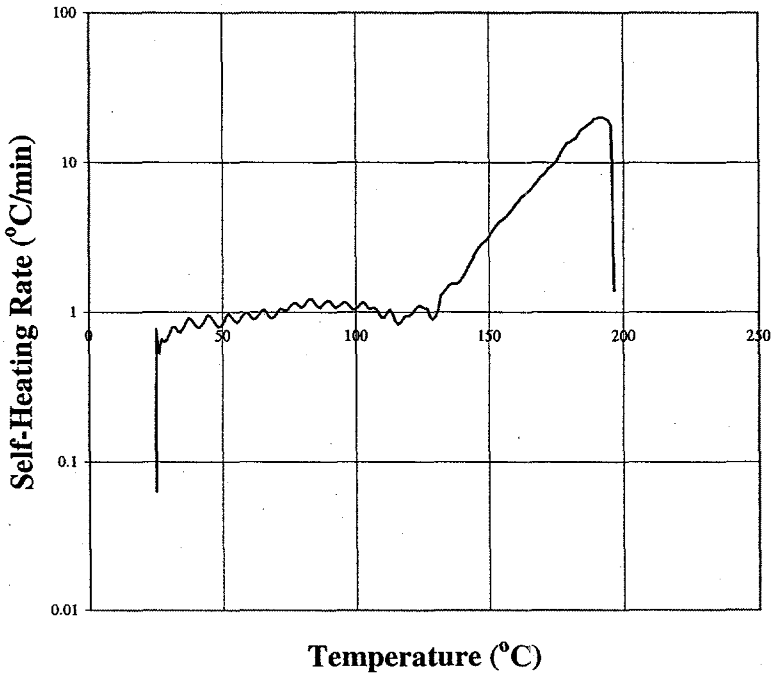
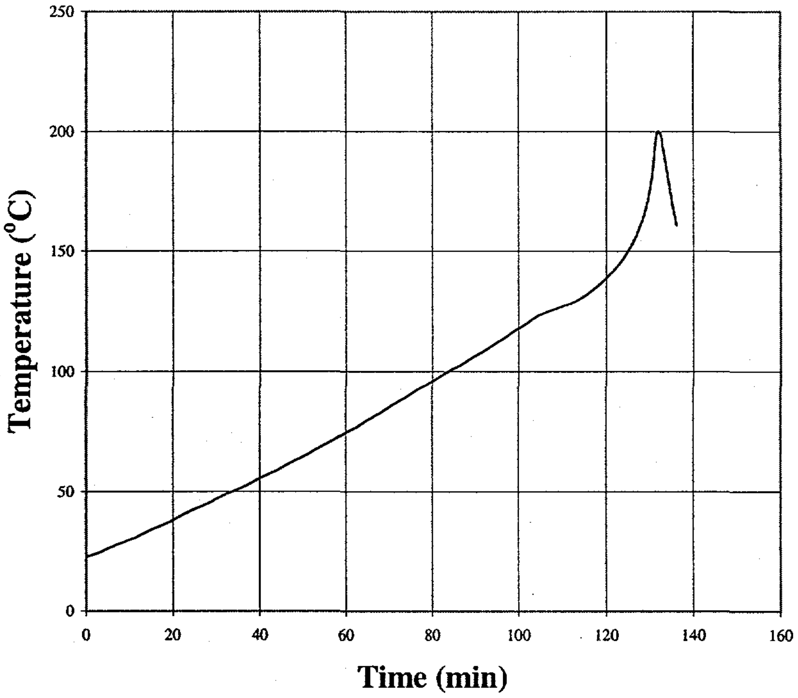


Figure C.7 Temperature Profile and Self-Heating Rate for Run No. TBP 0/8-1



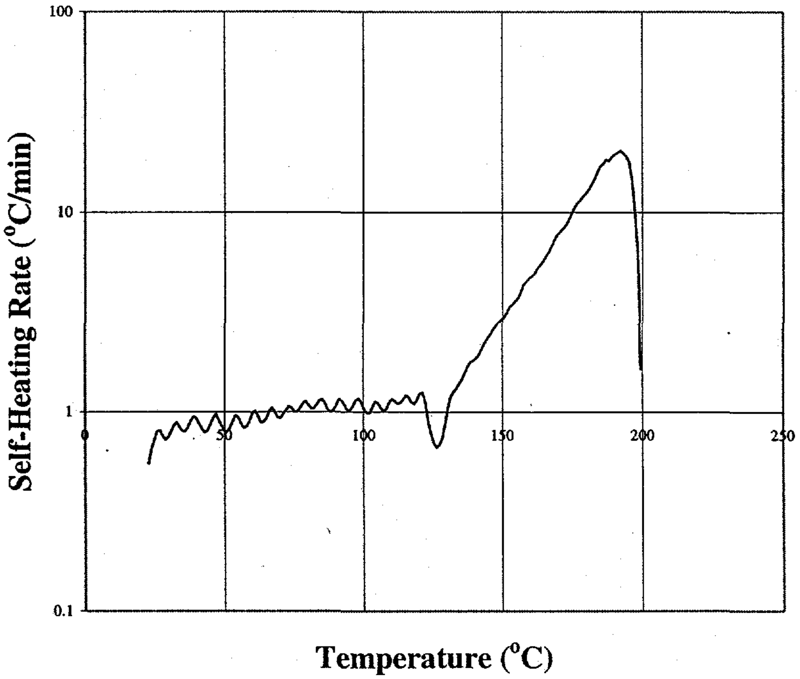
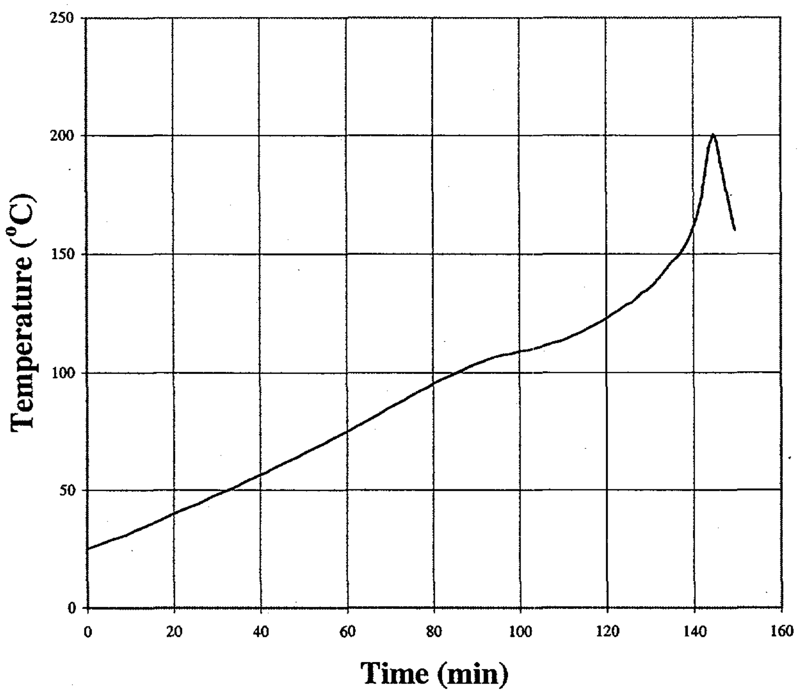


Figure C.8 Temperature Profile and Self-Heating Rate for Run No. TBP 0/2-1



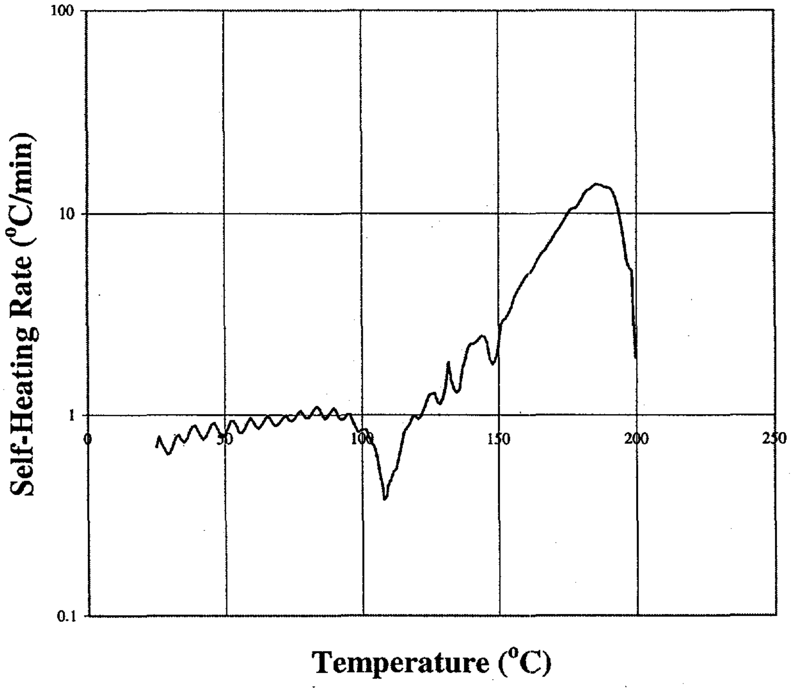
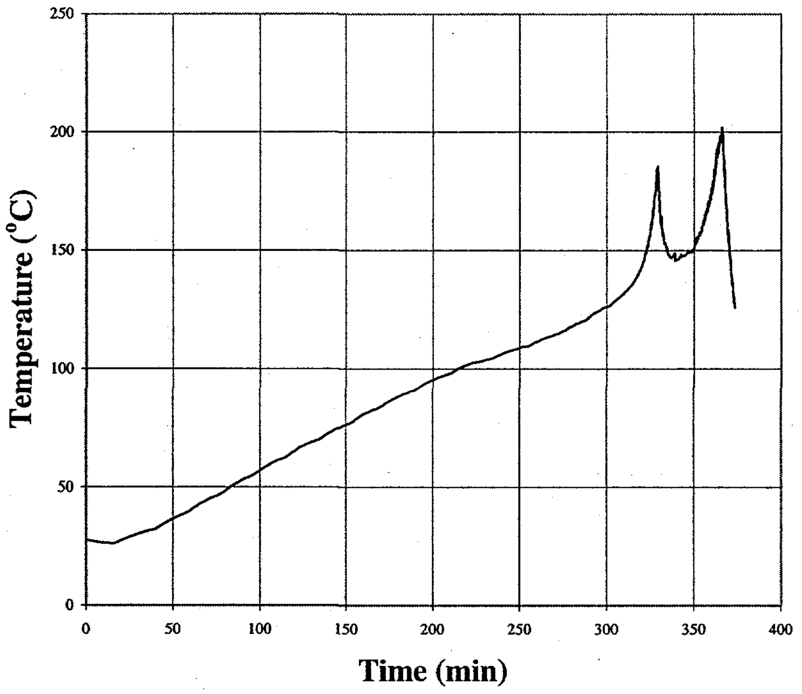


Figure C.9 Temperature Profile and Self-Heating Rate for Run No. TBP 5/4-3



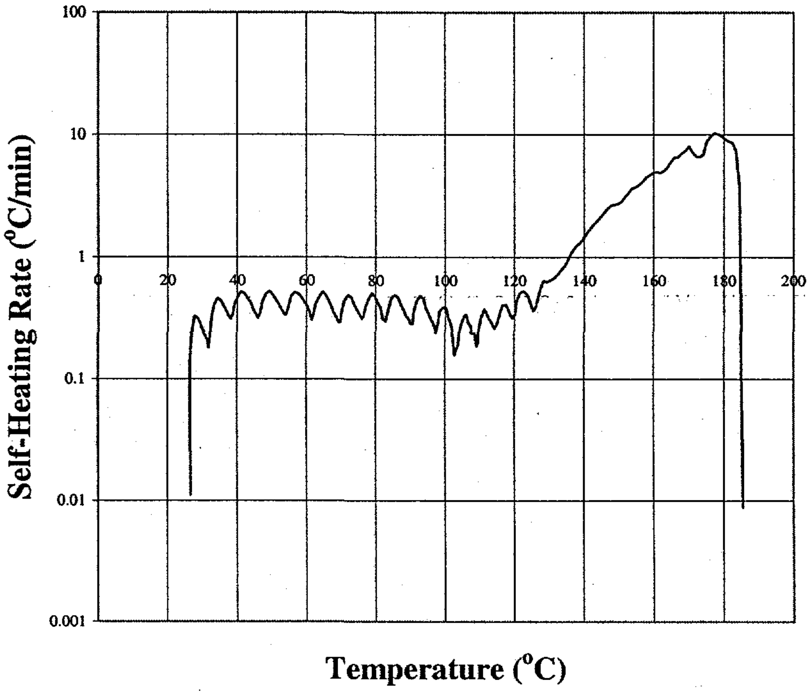
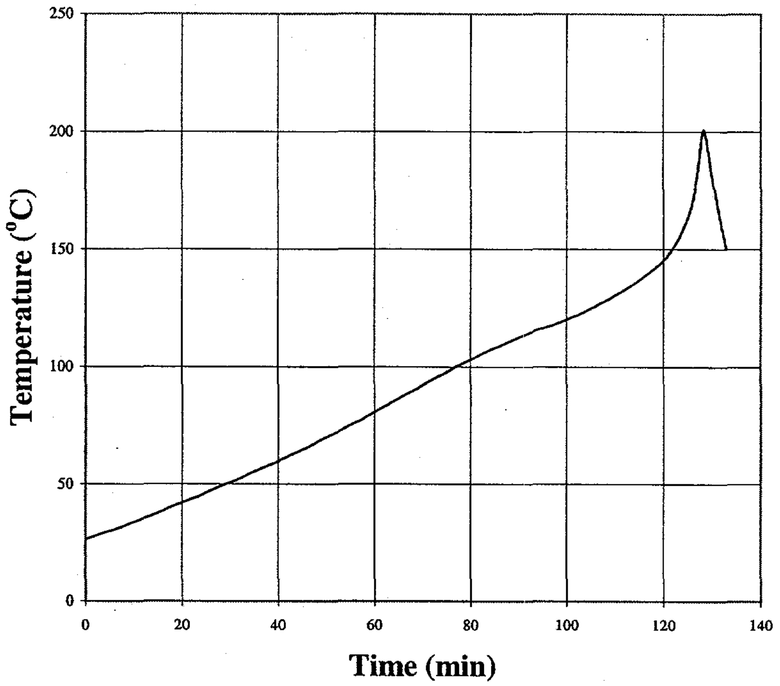
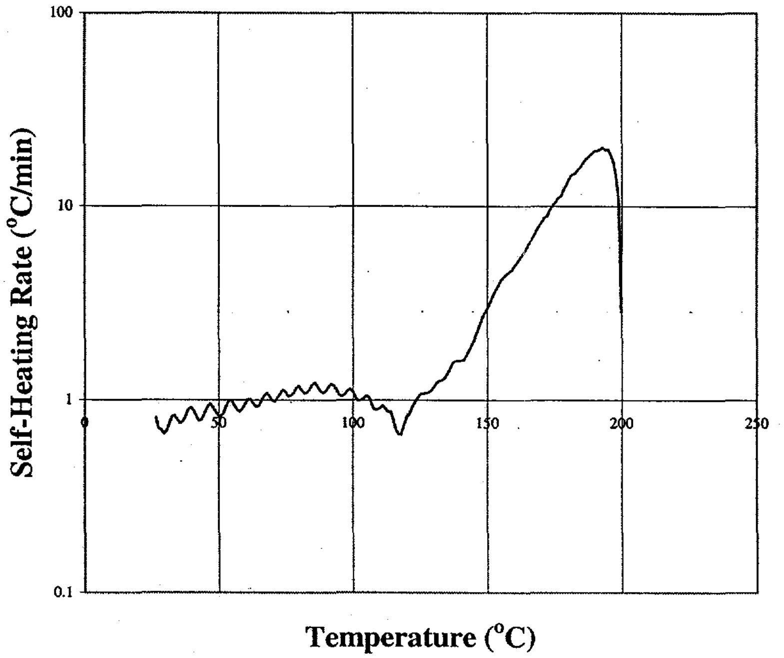


Figure C.10 Temperature Profile and Self-Heating Rate for Run No. TBP 5/4-4





Appendix D Temperature and Pressure Profiles for Closed RSST™ Experiments

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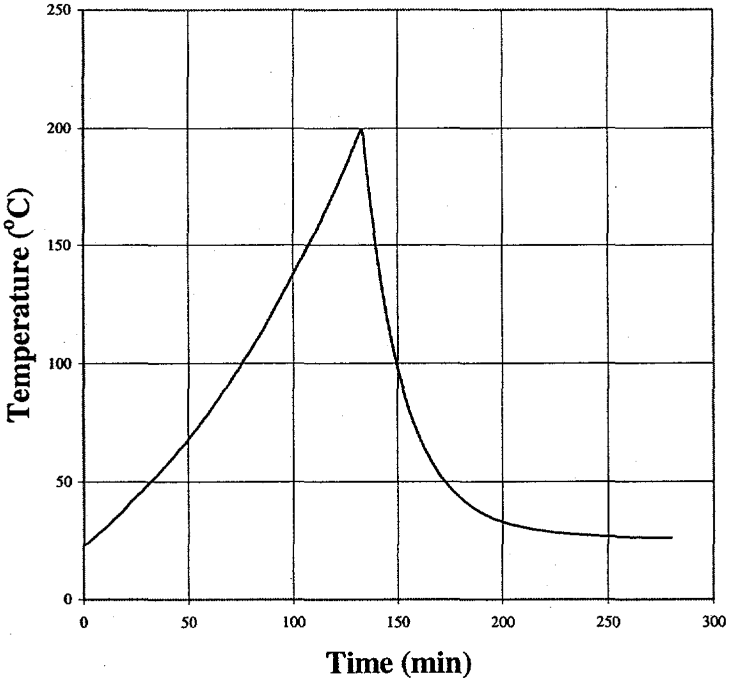
Figure D.1 Temperature and Pressure Profiles for Run No. TBP 0/0-1



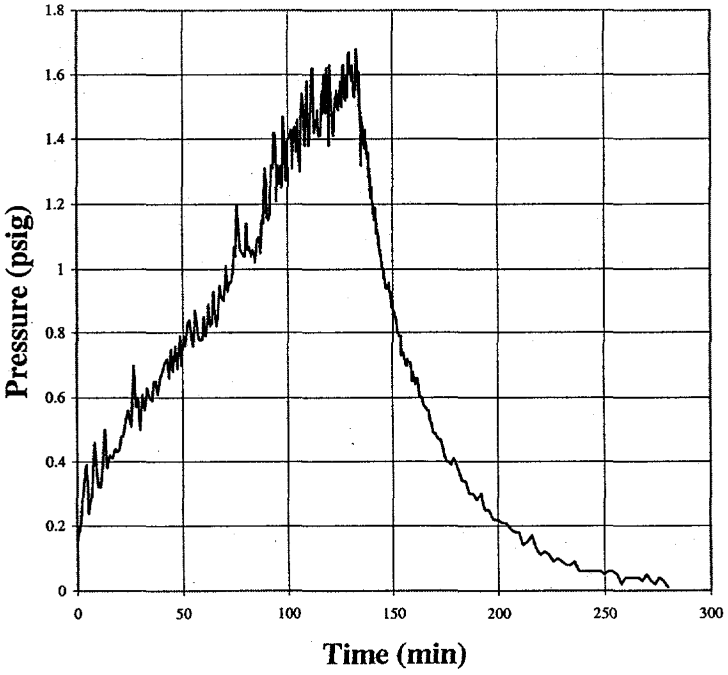
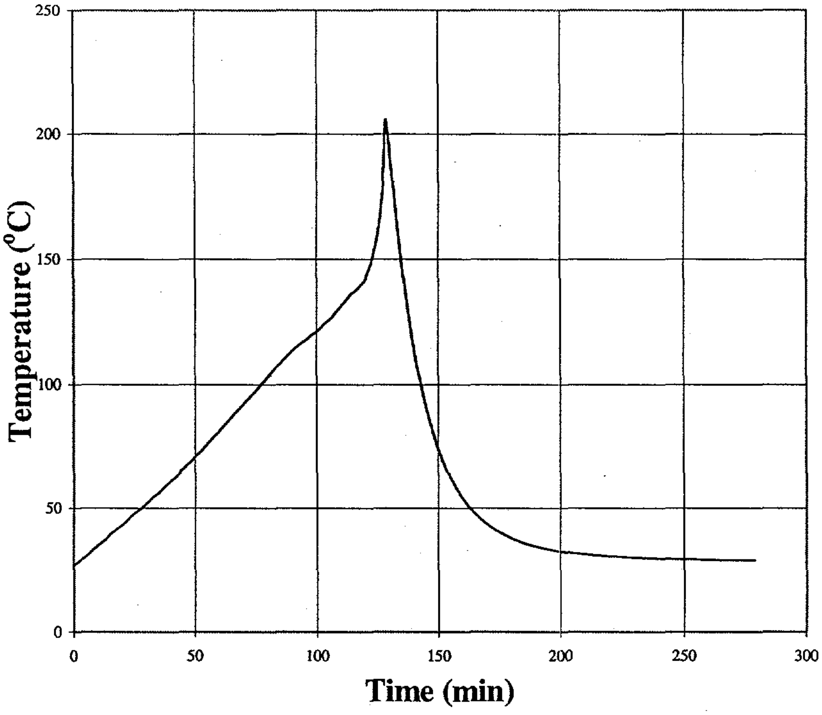


Figure D.2 Temperature and Pressure Profiles for Run No. TBP 0/4-3



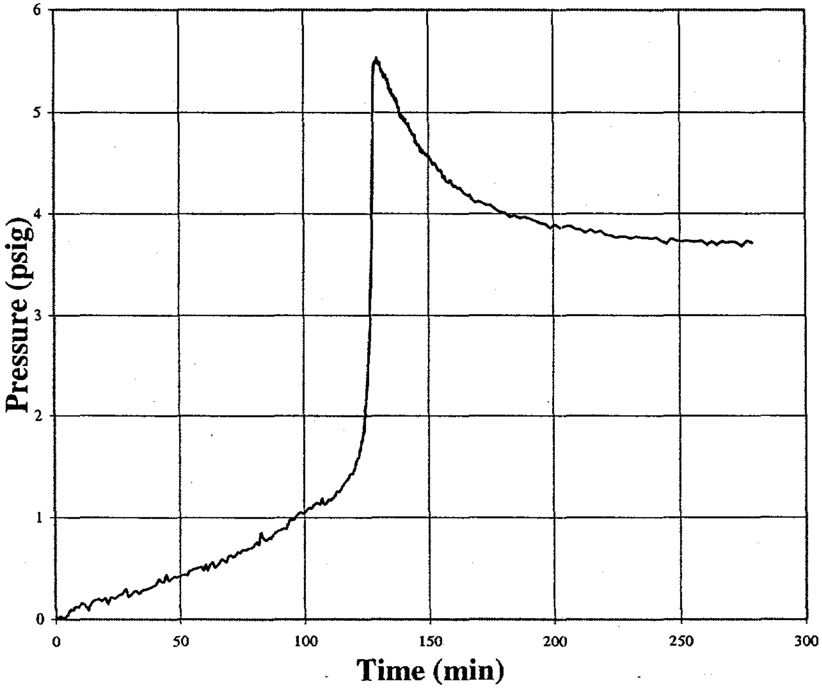
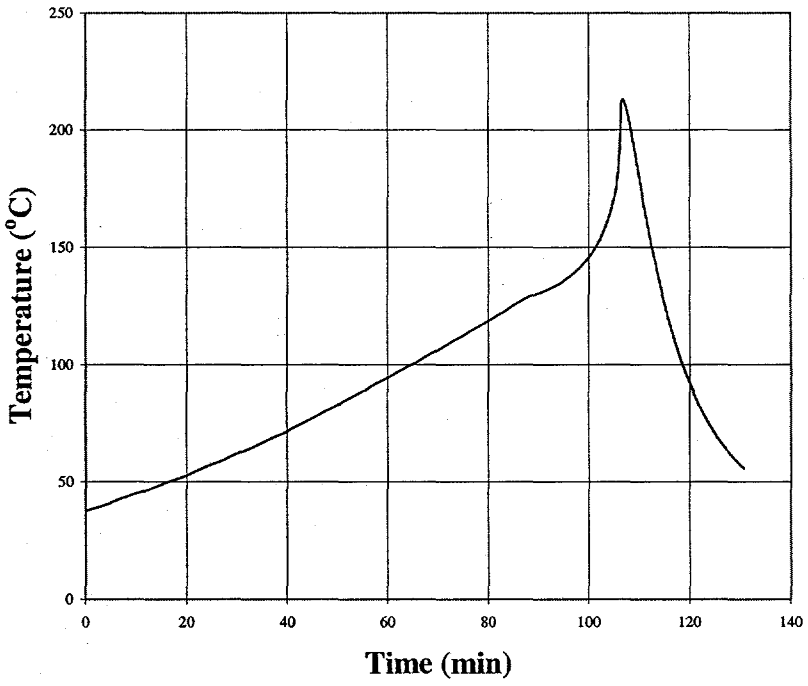


Figure D.3 Temperature and Pressure Profiles for Run No. TBP 0/8-2



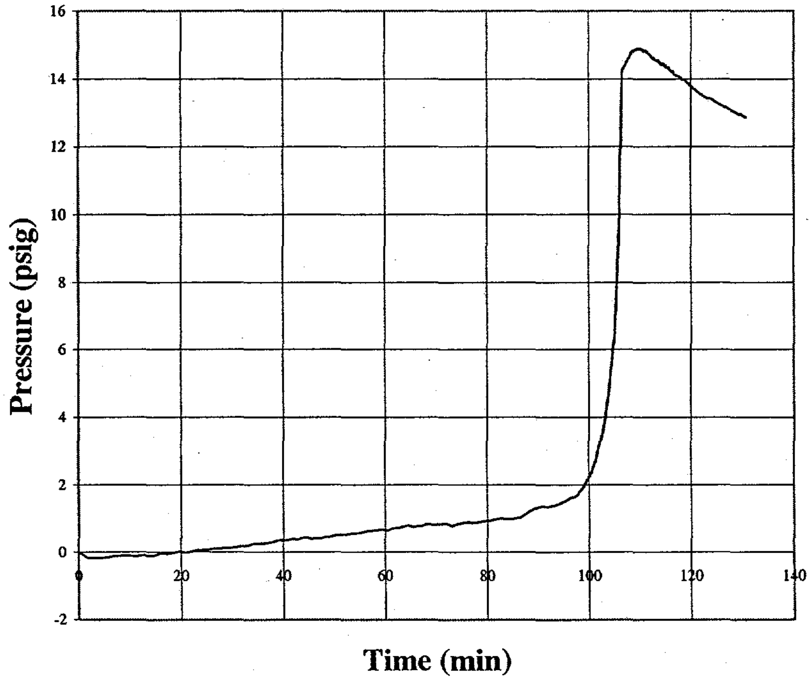
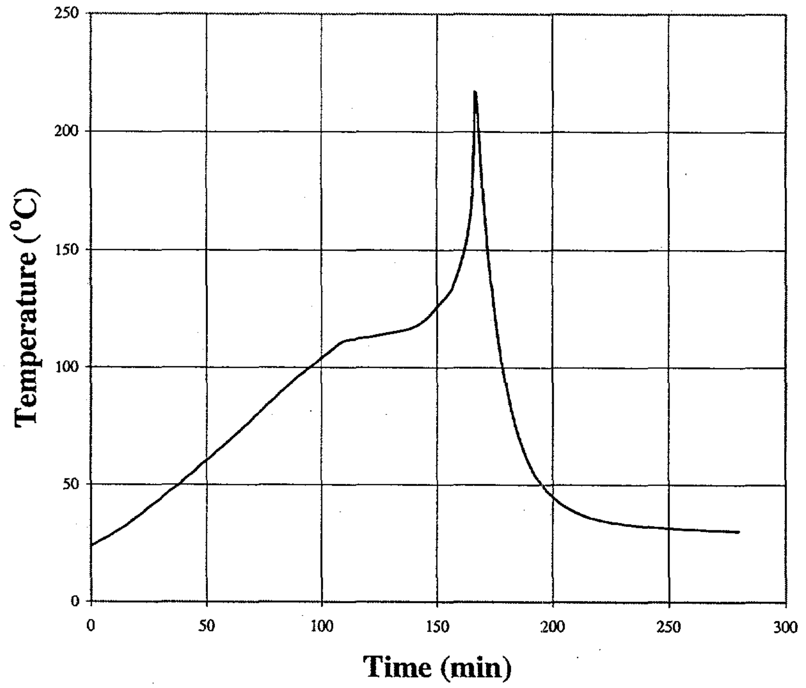


Figure D.4 Temperature and Pressure Profiles for Run No. TBP 0/8-3



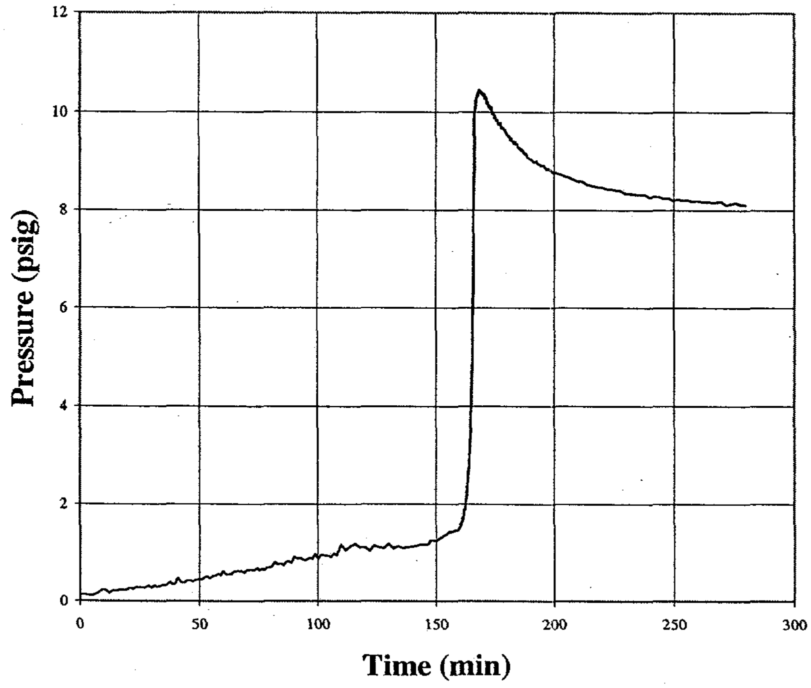


Figure D.5 Temperature and Pressure Profiles for Run No. TBP 0/10-1

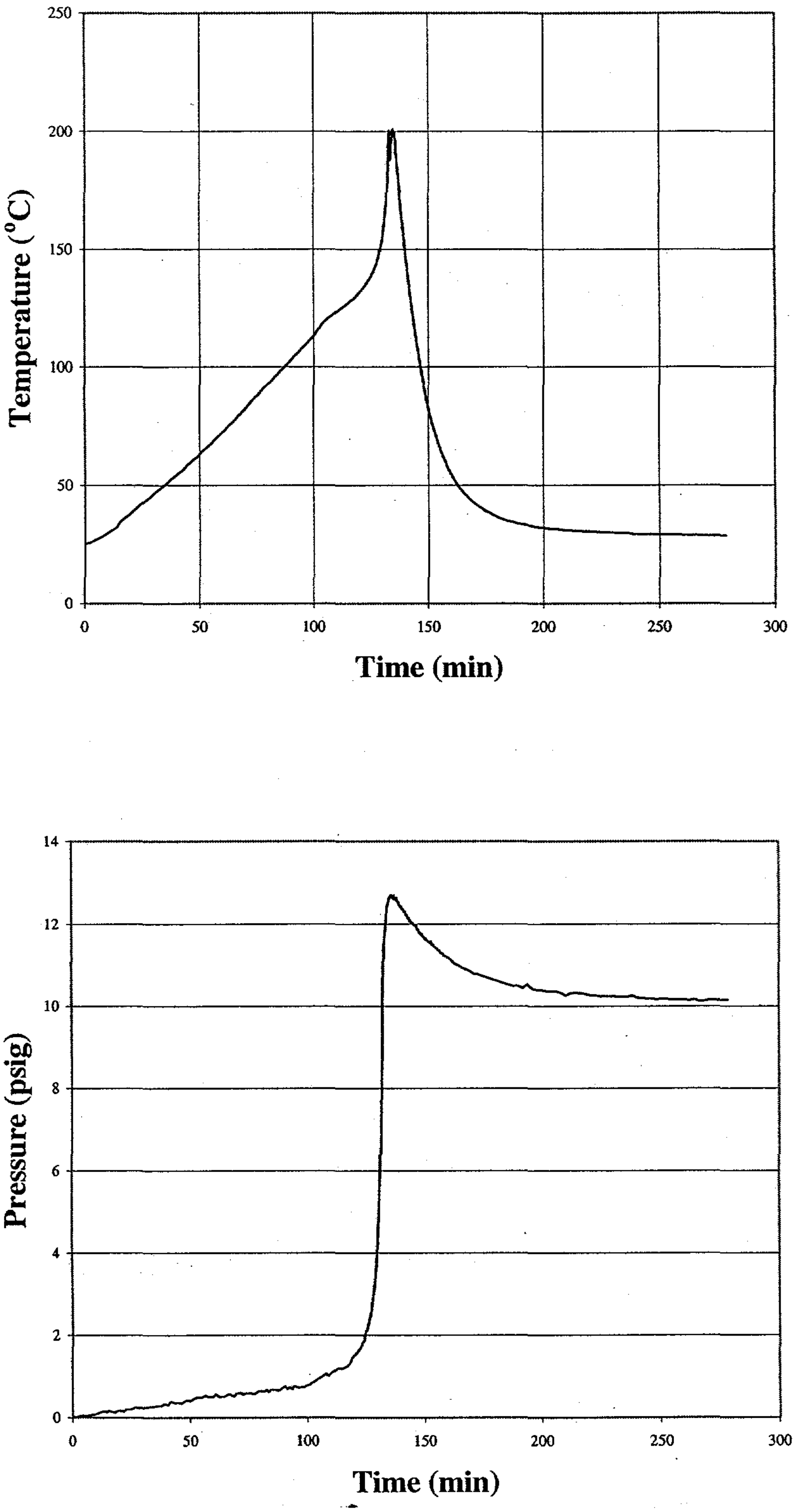
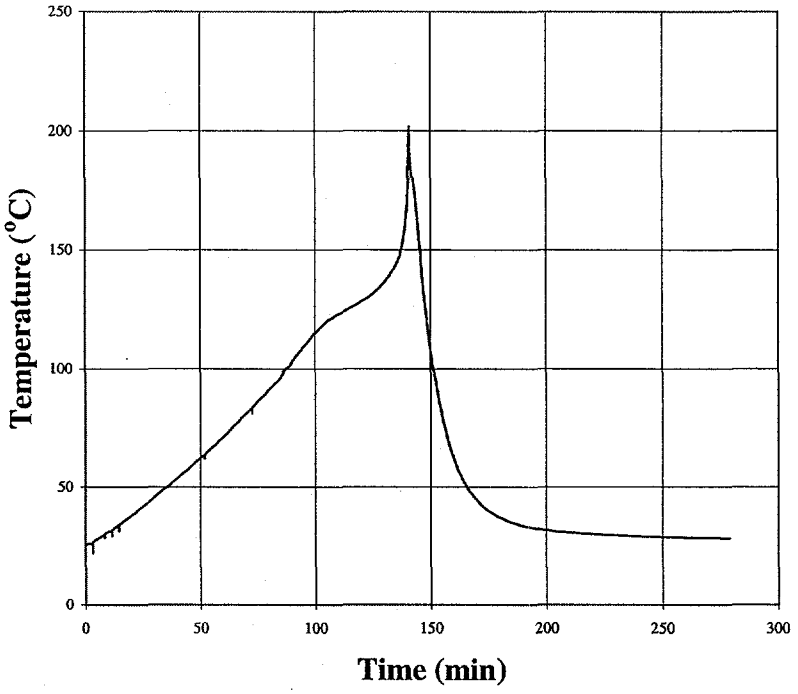
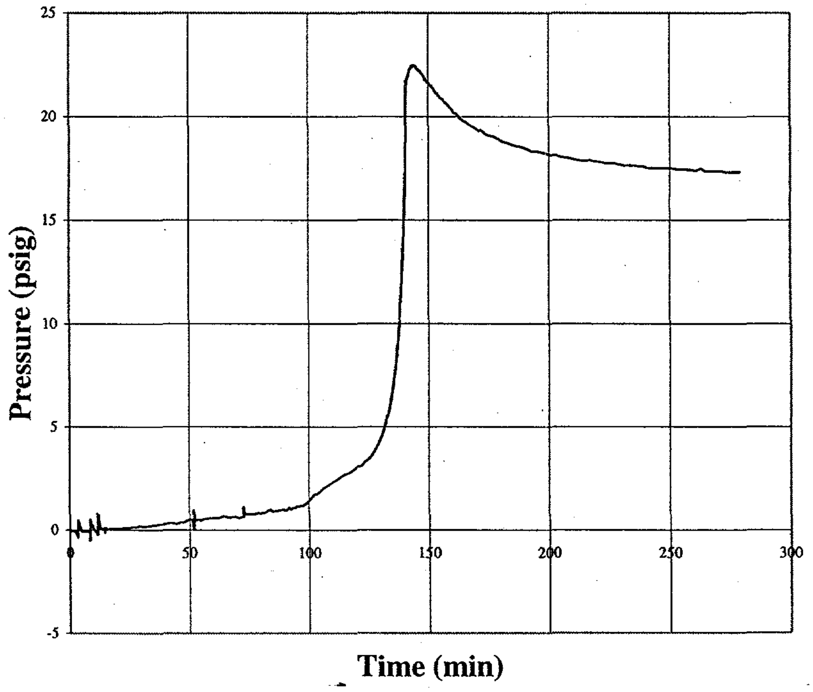


Figure D.6 Temperature and Pressure Profiles for Run No. TBP 0/12-1





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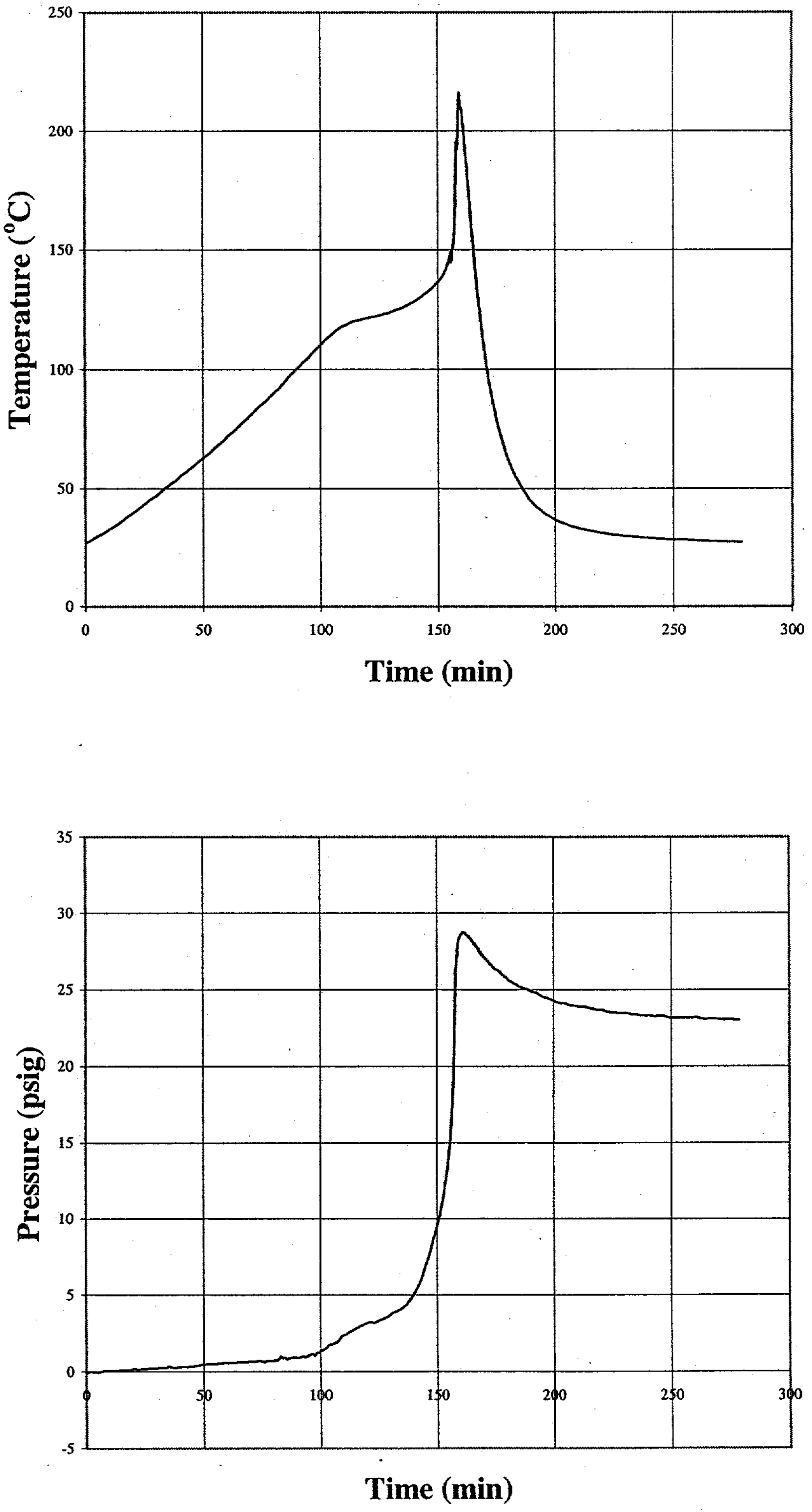
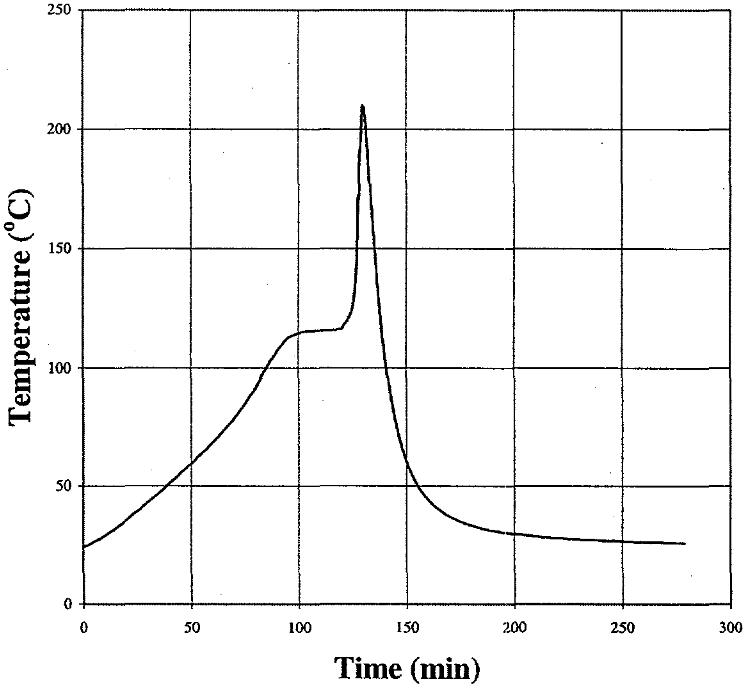


Figure D.8 Temperature and Pressure Profiles for Run No. TBP 0/14-1



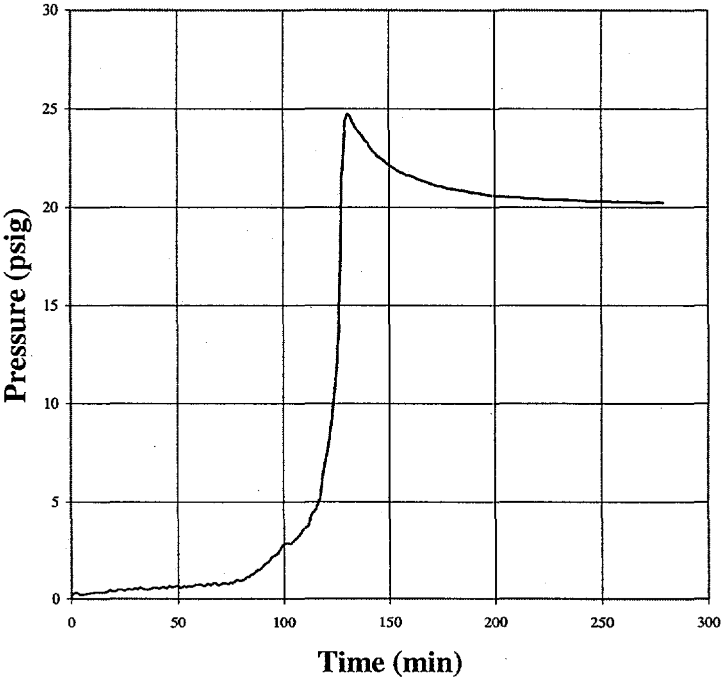
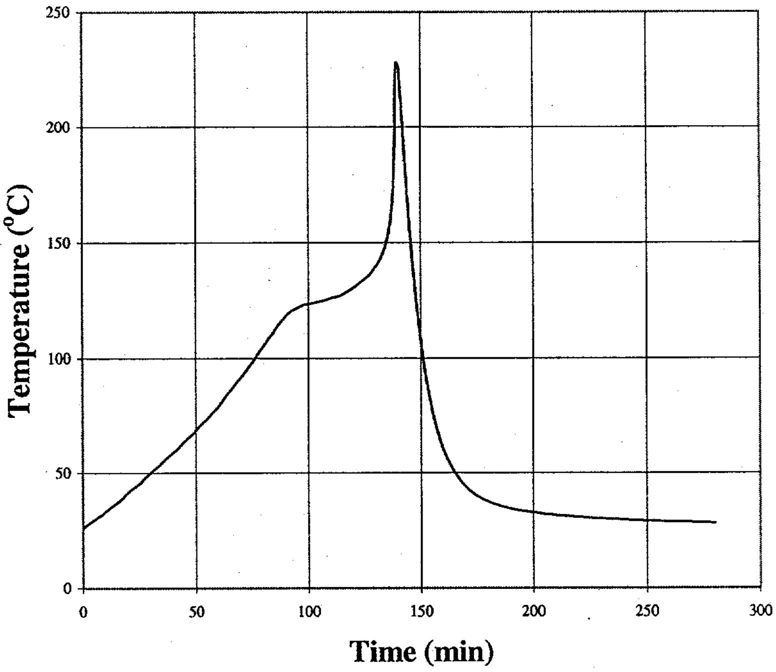


Figure D.9 Temperature and Pressure Profiles for Run No. TBP 0/15-2



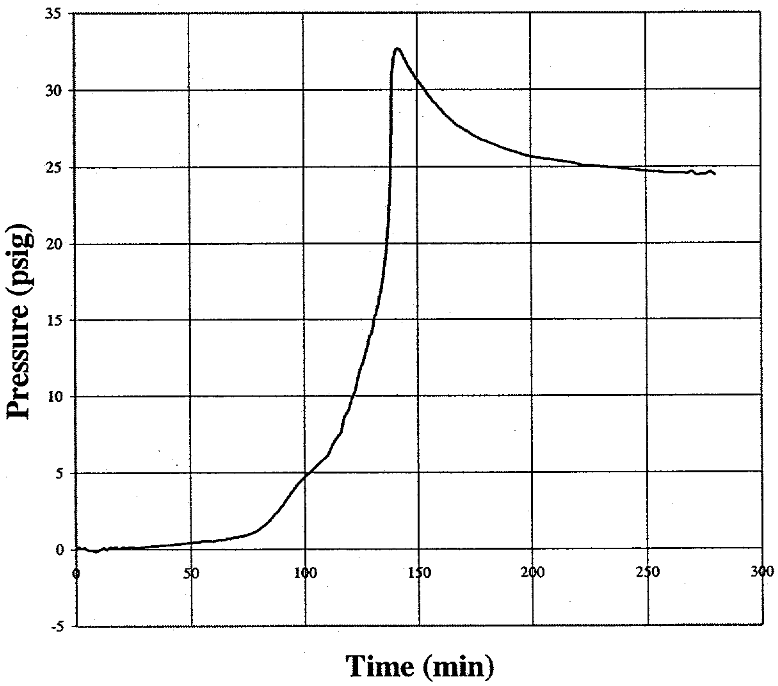
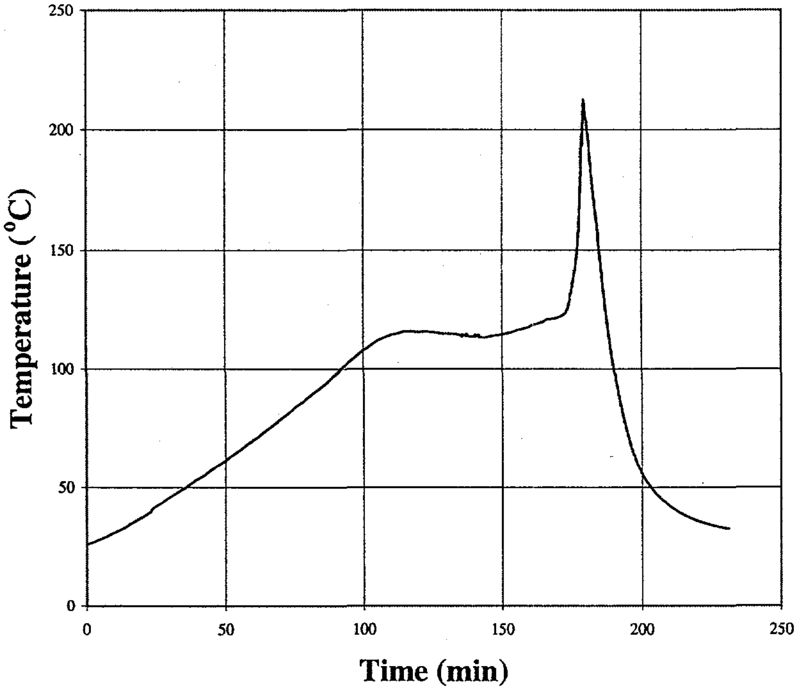


Figure D.10 Temperature and Pressure Profiles for Run No. TBP 0/15-3



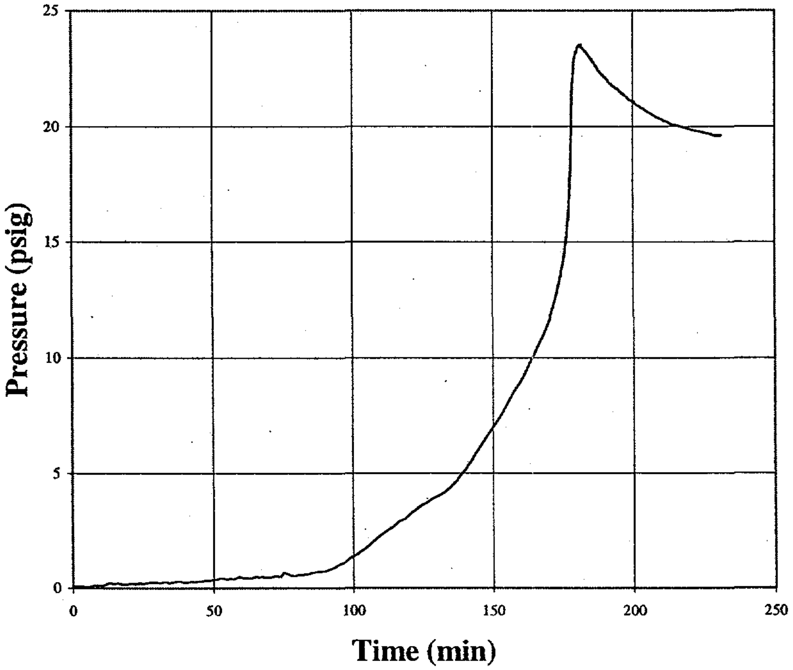


Figure D.11 Temperature and Pressure Profiles for Run No. TBP 5/4-7

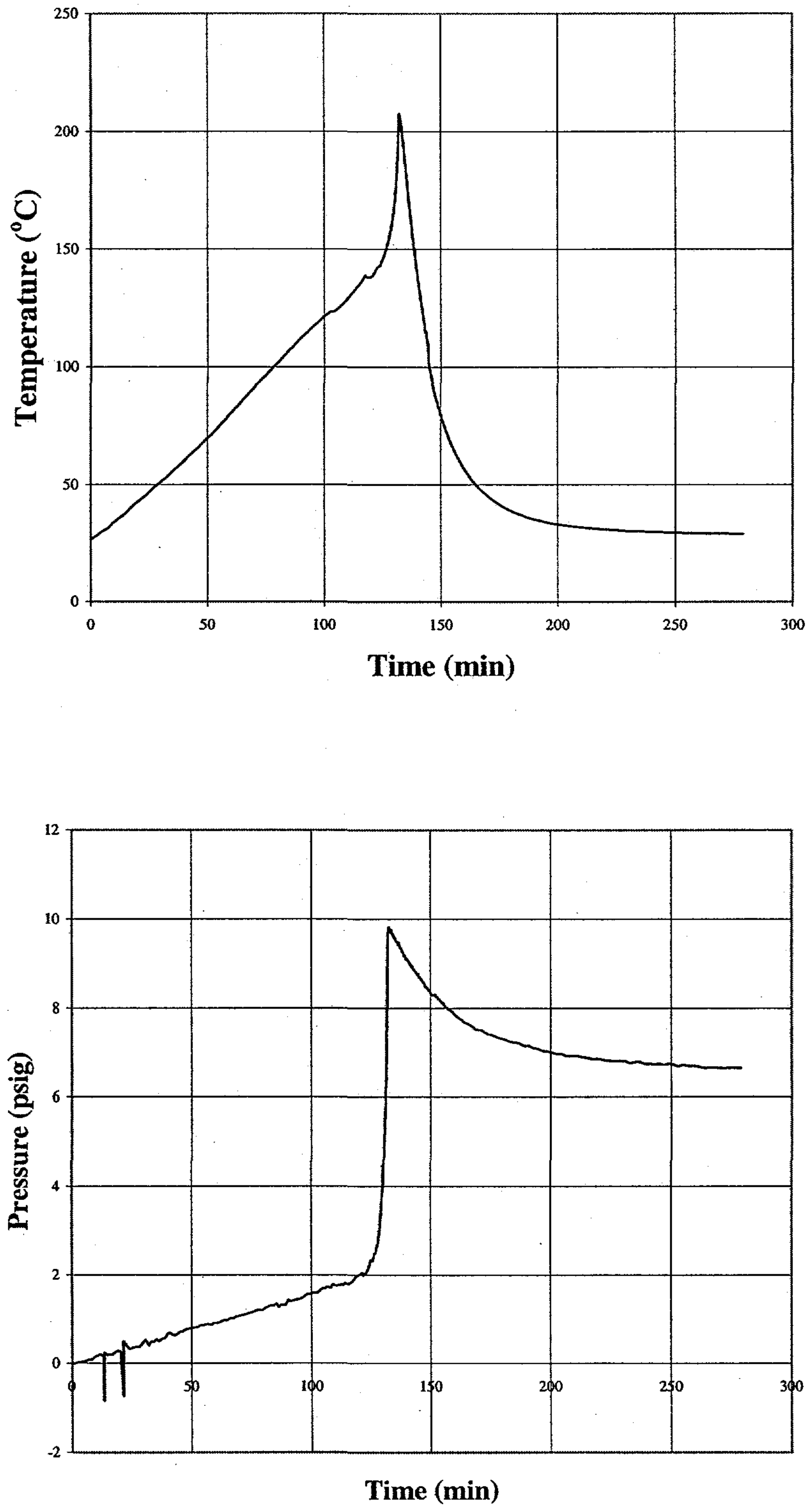
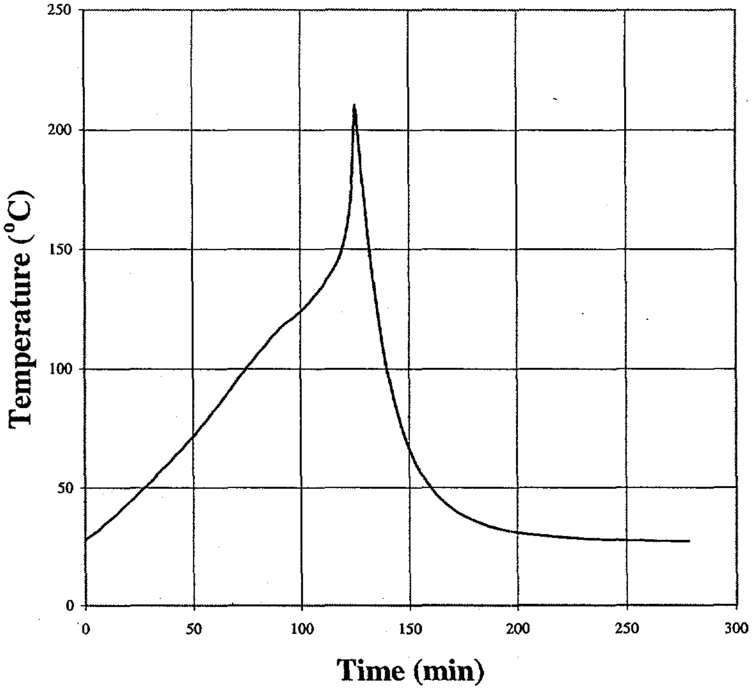


Figure D.12 Temperature and Pressure Profiles for Run No. TBP 5/4-8



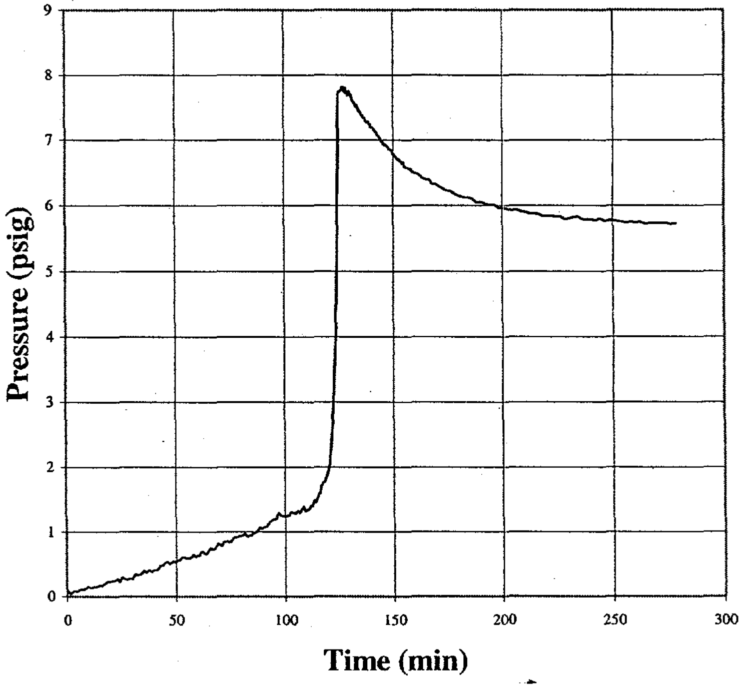
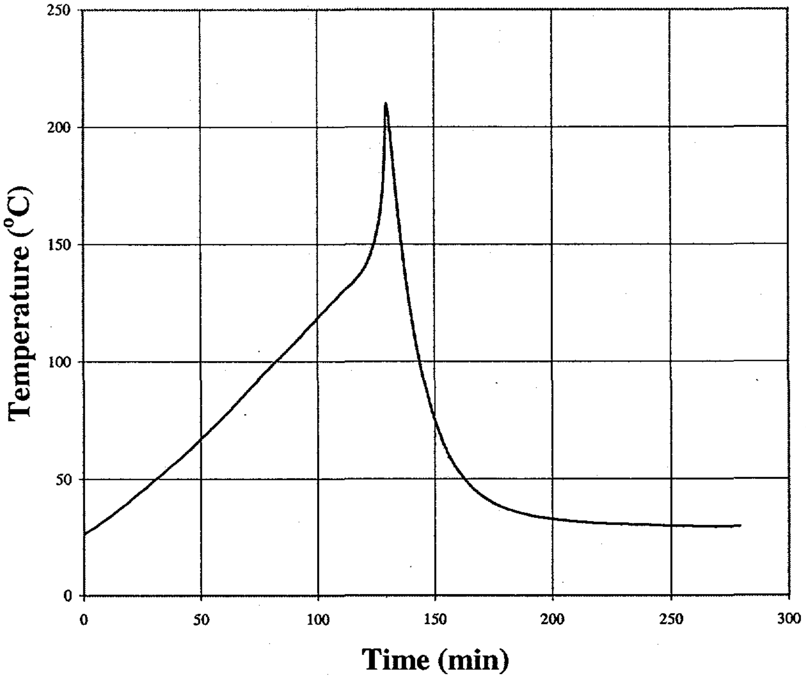


Figure D.13 Temperature and Pressure Profiles for Run No. TBP 5/6-2



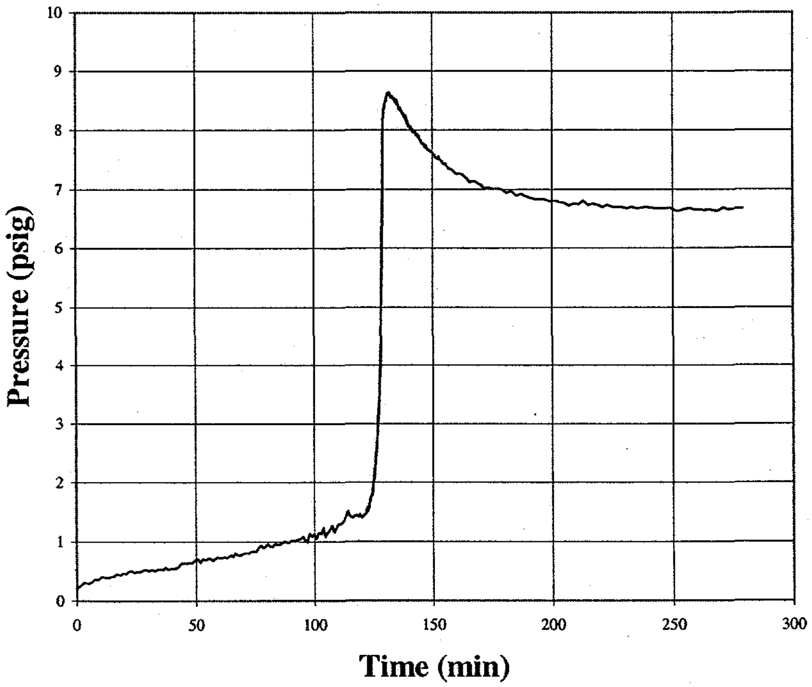
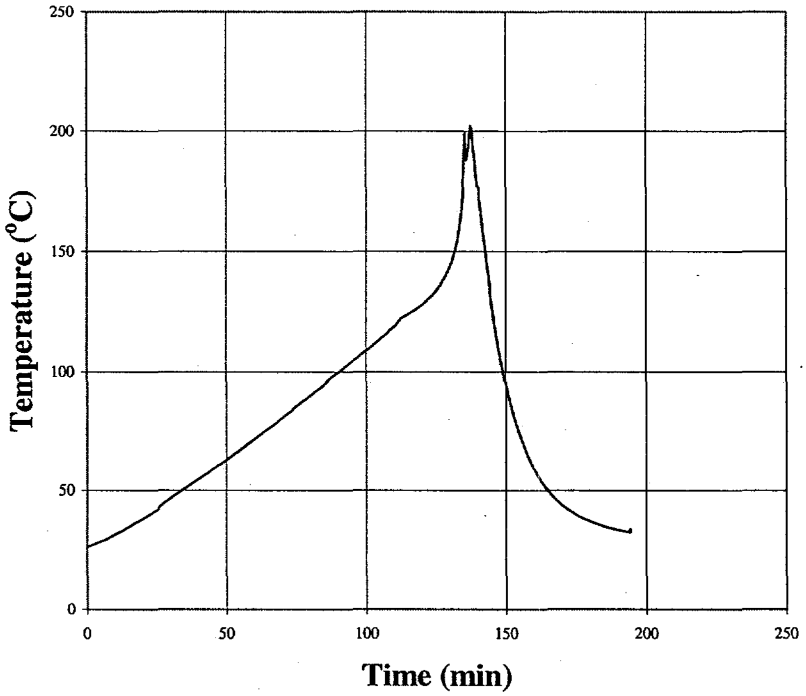


Figure D.14 Temperature and Pressure Profiles for Run No. TBP 5/8-1



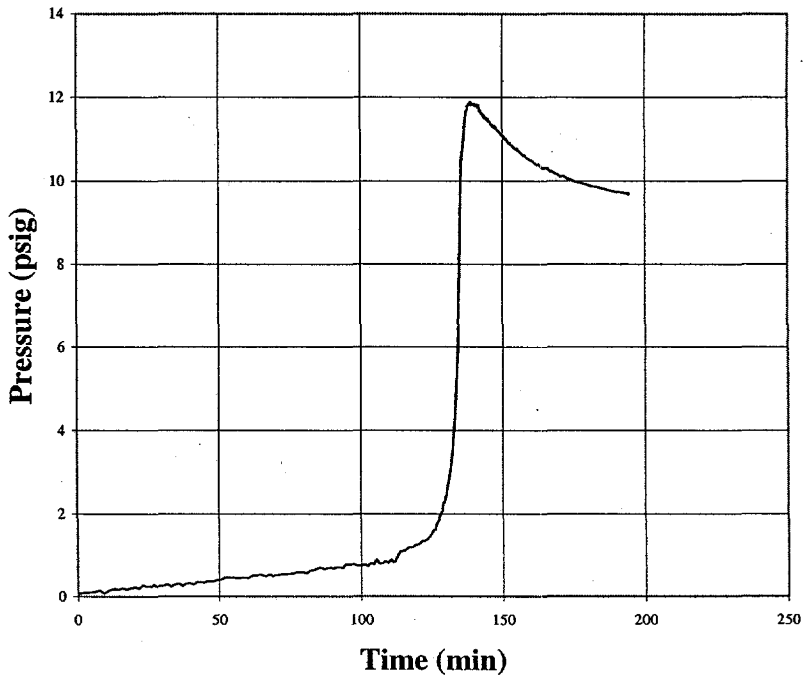
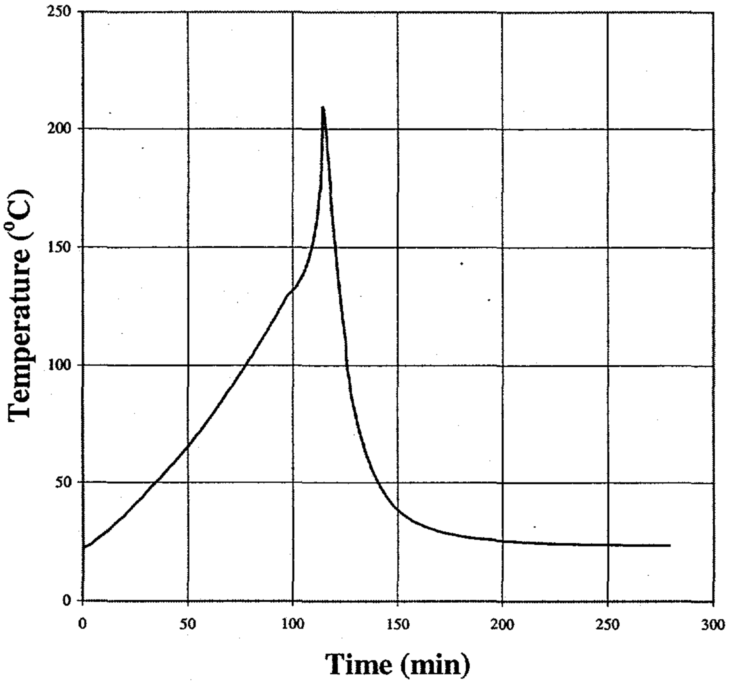


Figure D.15 Temperature and Pressure Profiles for Run No. TBP 5/8-2



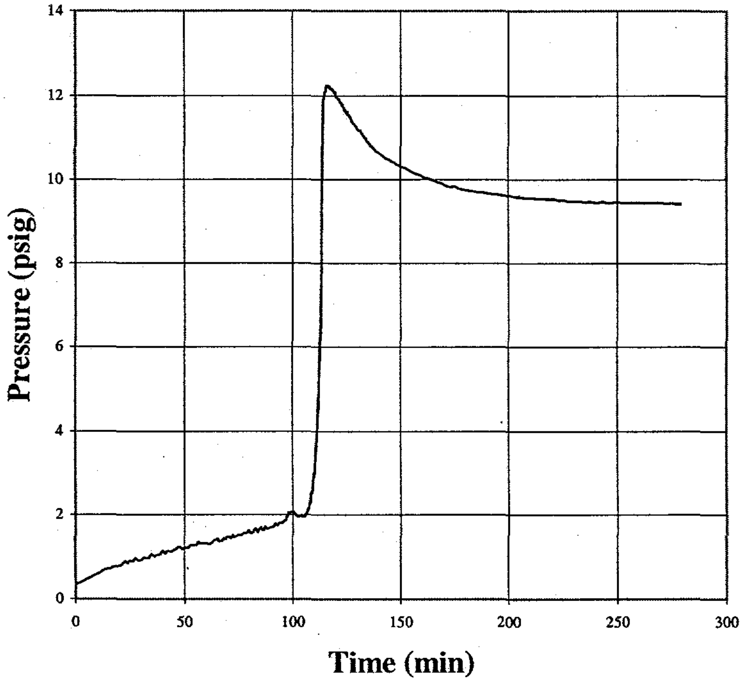
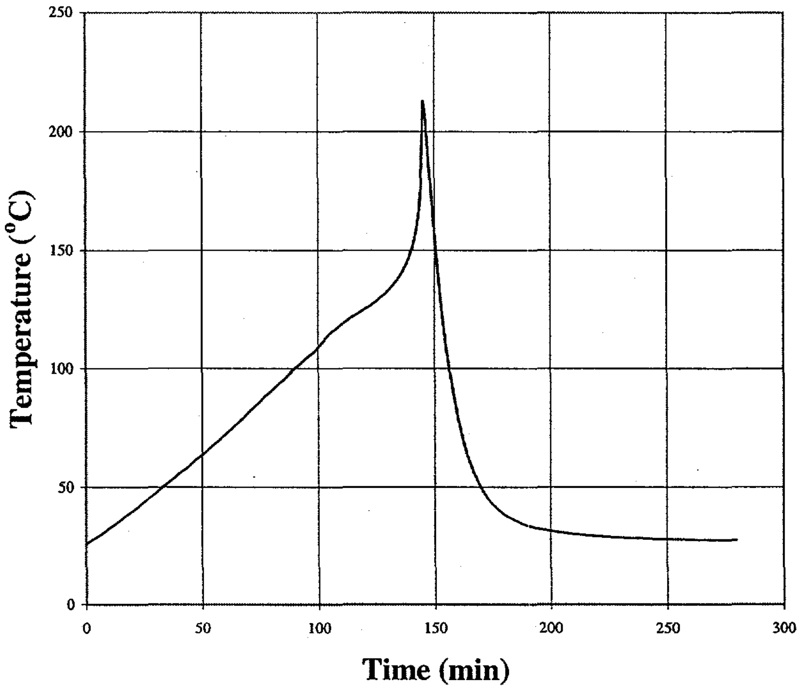


Figure D.16 Temperature and Pressure Profiles for Run No. TBP 5/10-1



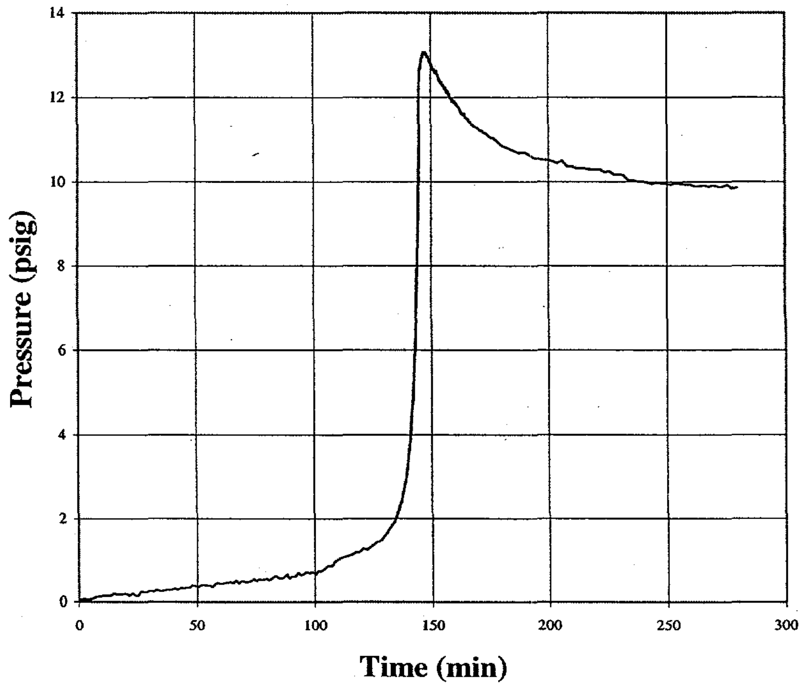
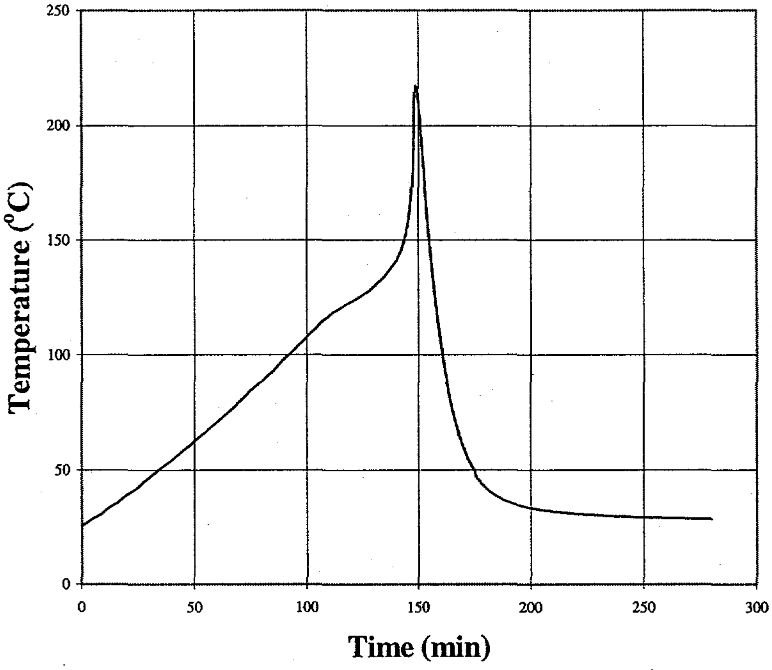


Figure D.17 Temperature and Pressure Profiles for Run No. TBP 5/12-3



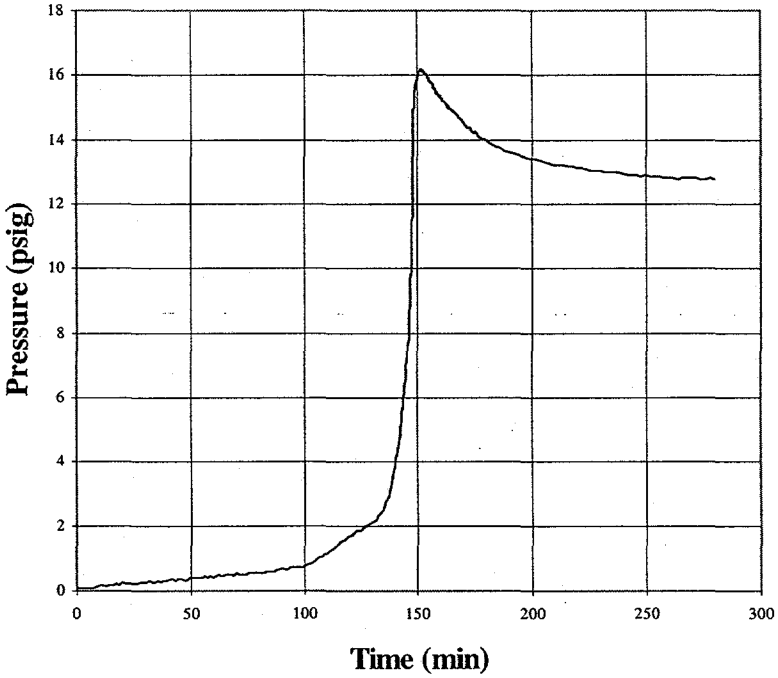
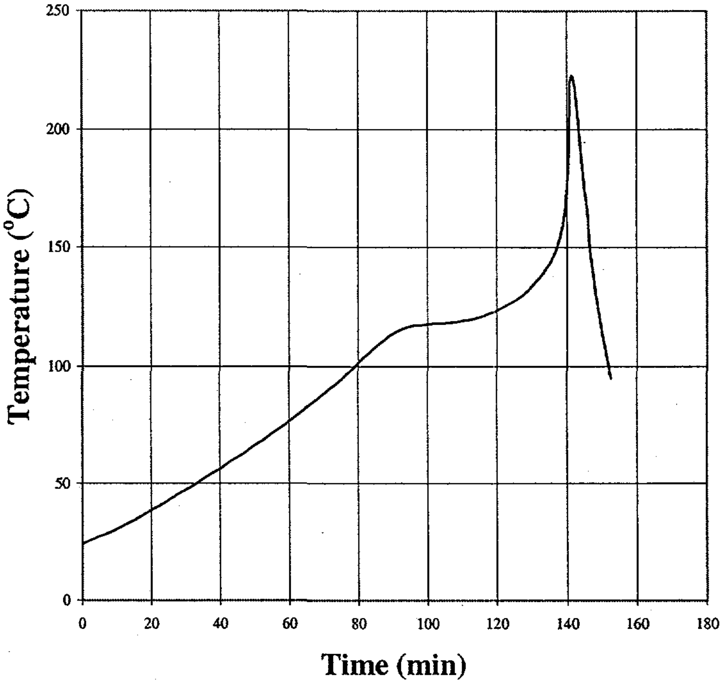


Figure D.18 Temperature and Pressure Profiles for Run No. TBP 5/12-4



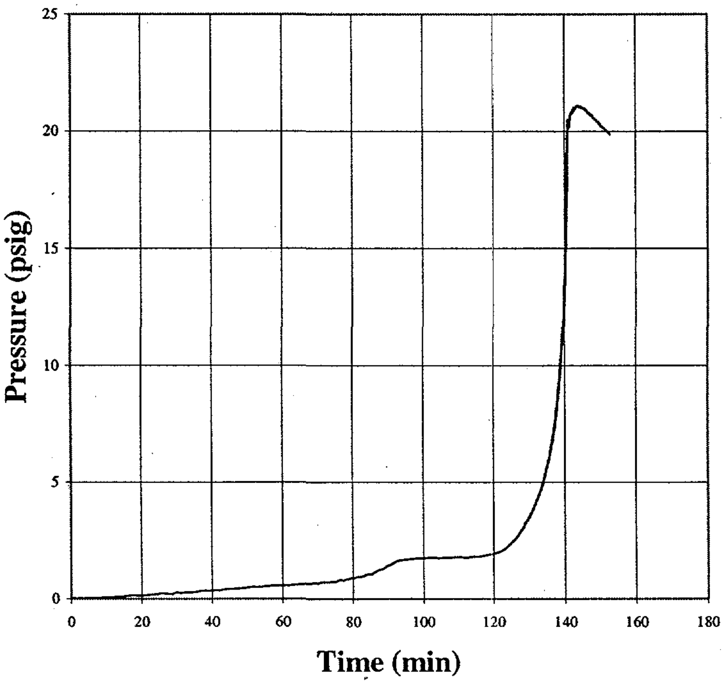
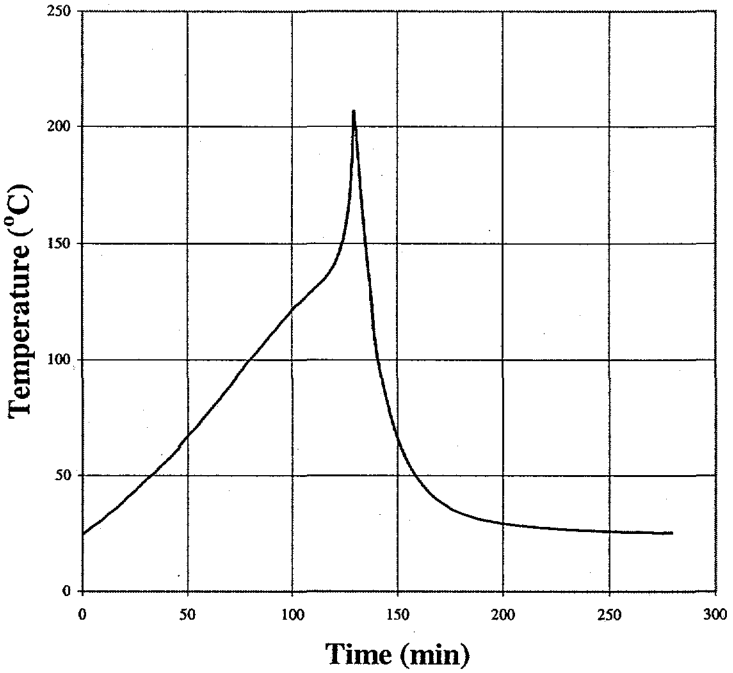


Figure D.19 Temperature and Pressure Profiles for Run No. TBP 10/4-1



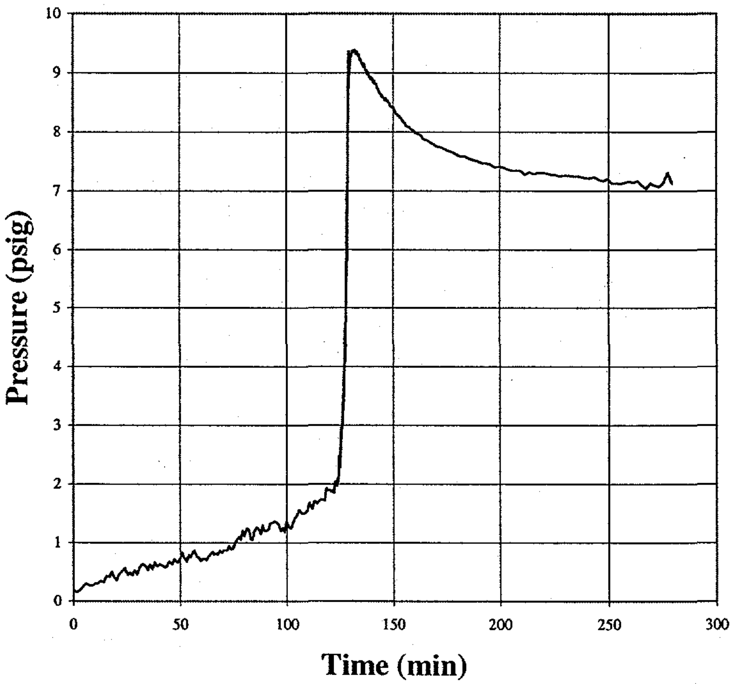
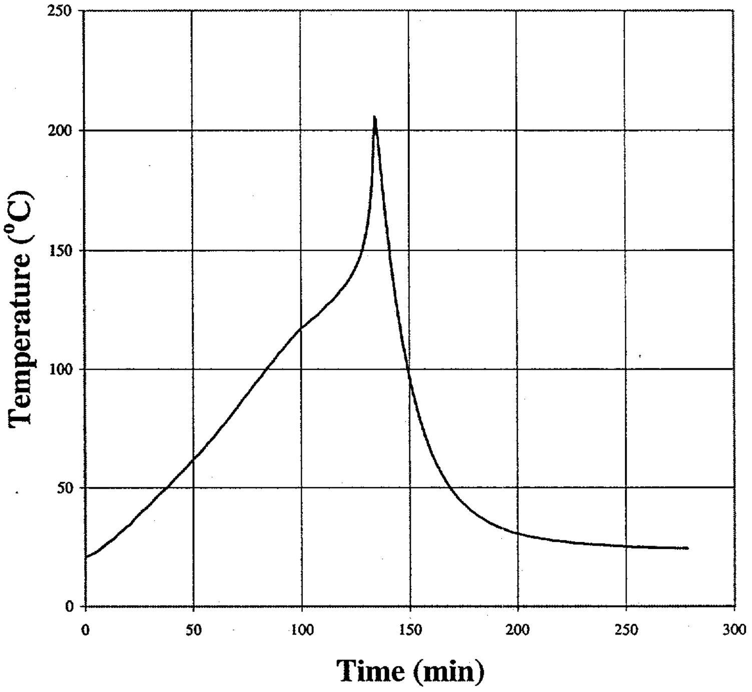


Figure D.20 Temperature and Pressure Profiles for Run No. TBP 10/4-2



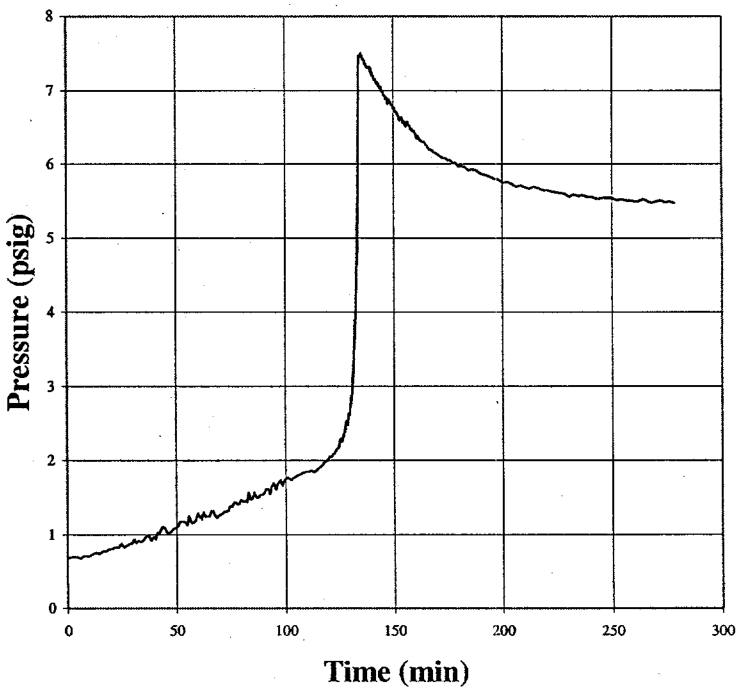


Figure D.21 Temperature and Pressure Profiles for Run No. TBP 10/6-1

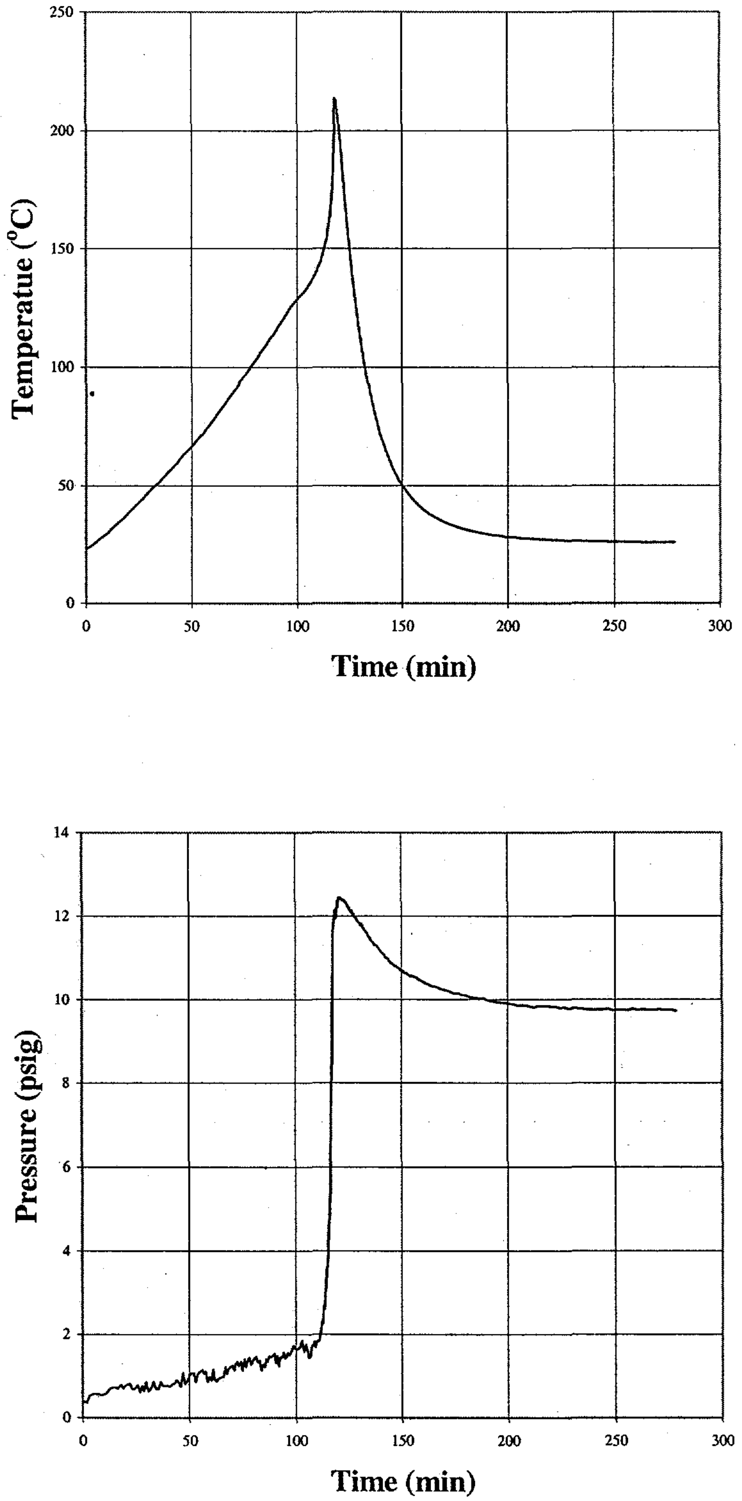
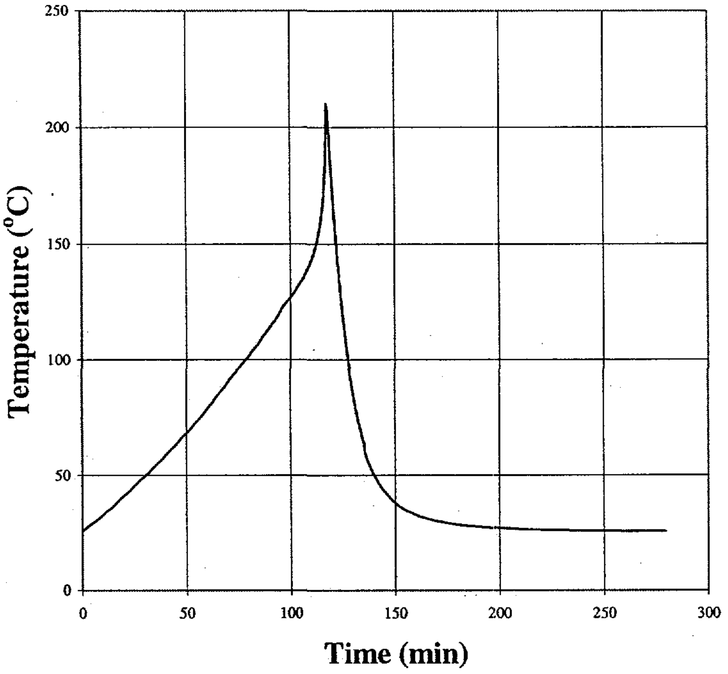


Figure D.22 Temperature and Pressure Profiles for Run No. TBP 10/8-1



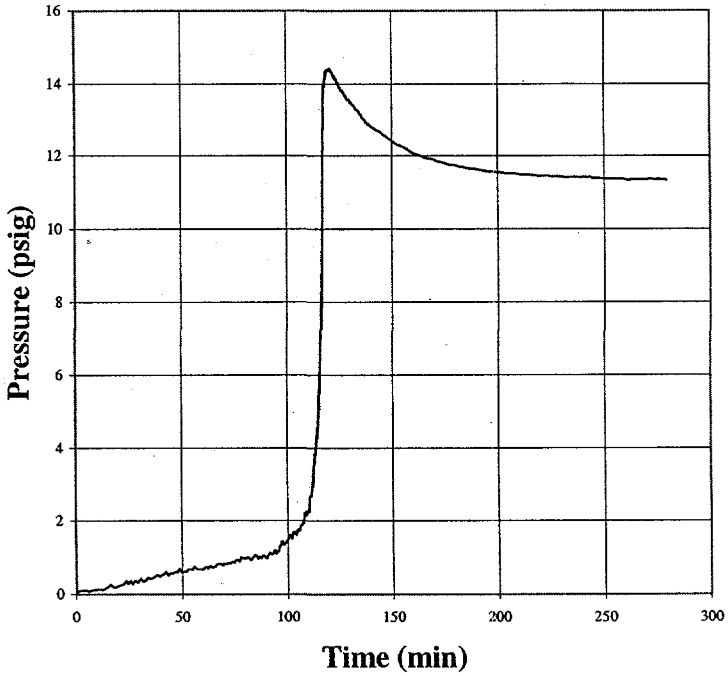
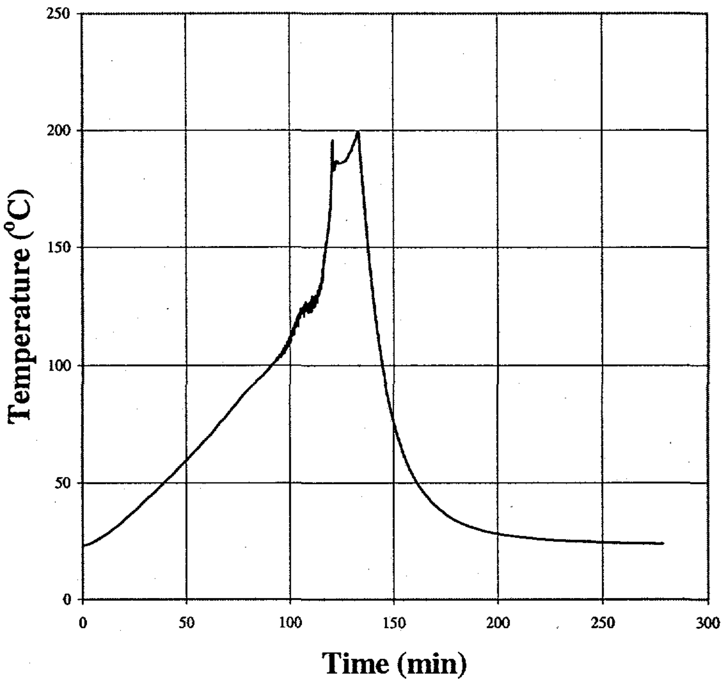


Figure D.23 Temperature and Pressure Profiles for Run No. TBP 10/8-2



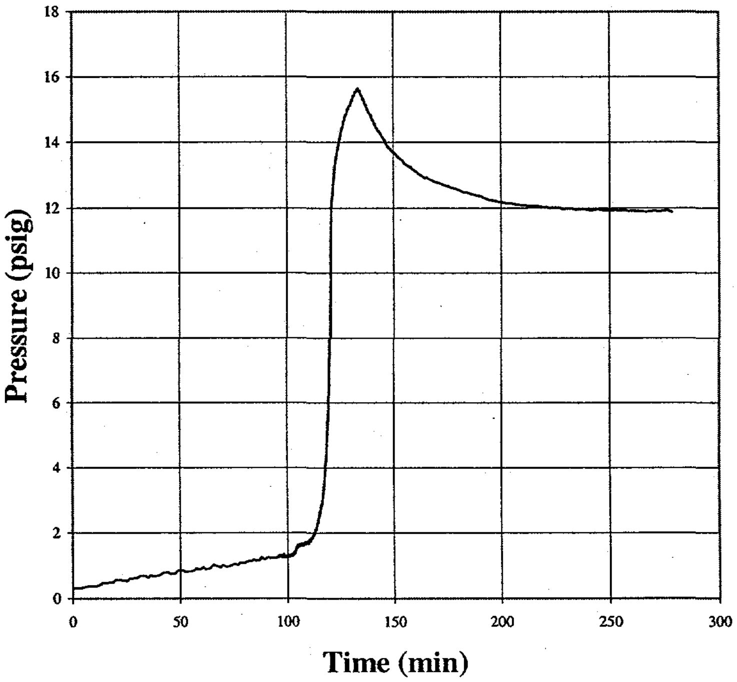
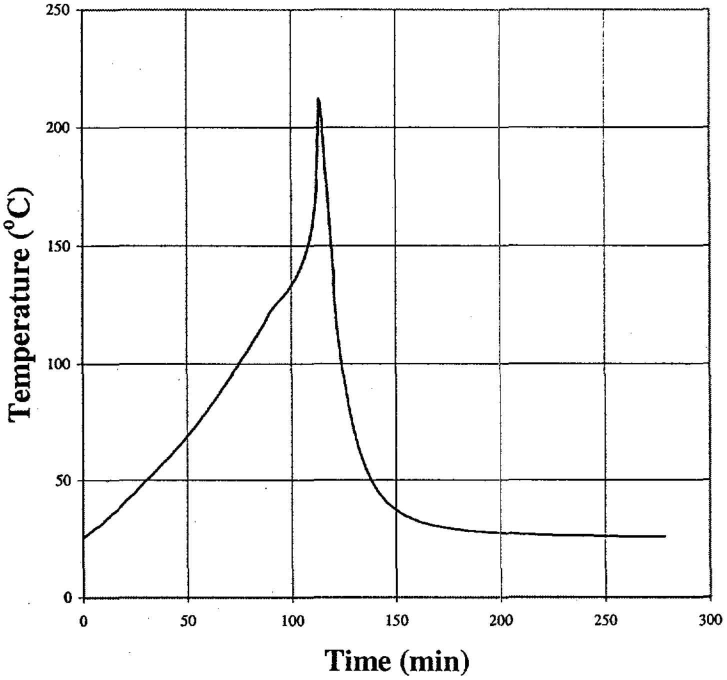


Figure D.24 Temperature and Pressure Profiles for Run No. TBP 10/9-1



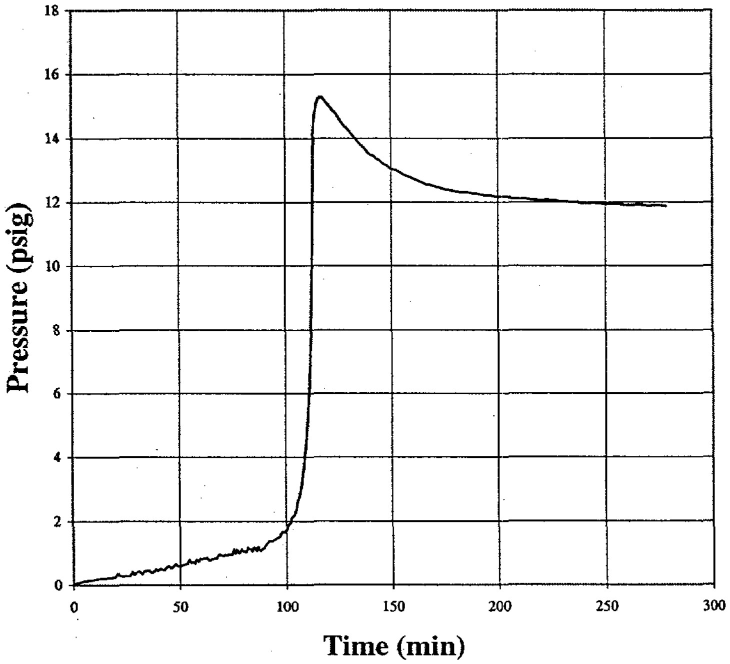
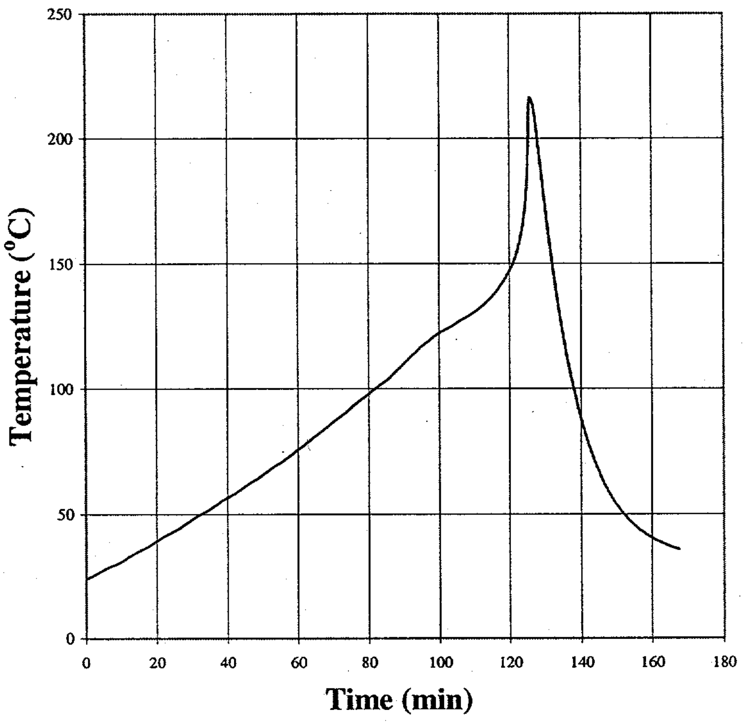


Figure D.25 Temperature and Pressure Profiles for Run No. TBP 10/10-1



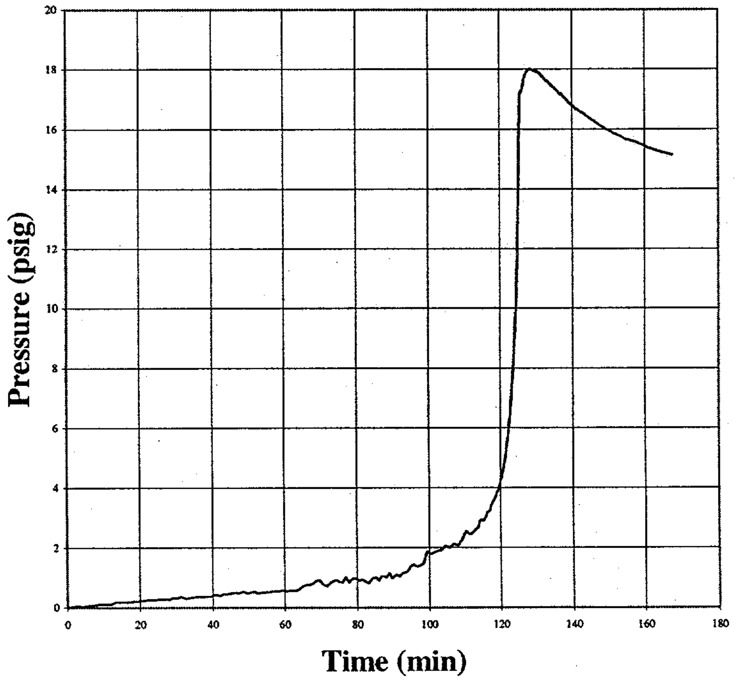
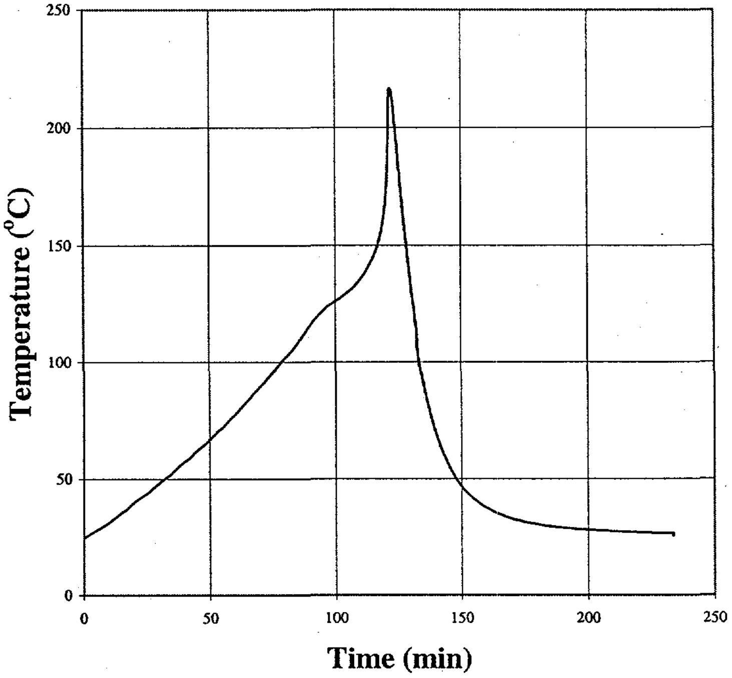


Figure D.26 Temperature and Pressure Profiles for Run No. TBP 10/10-2



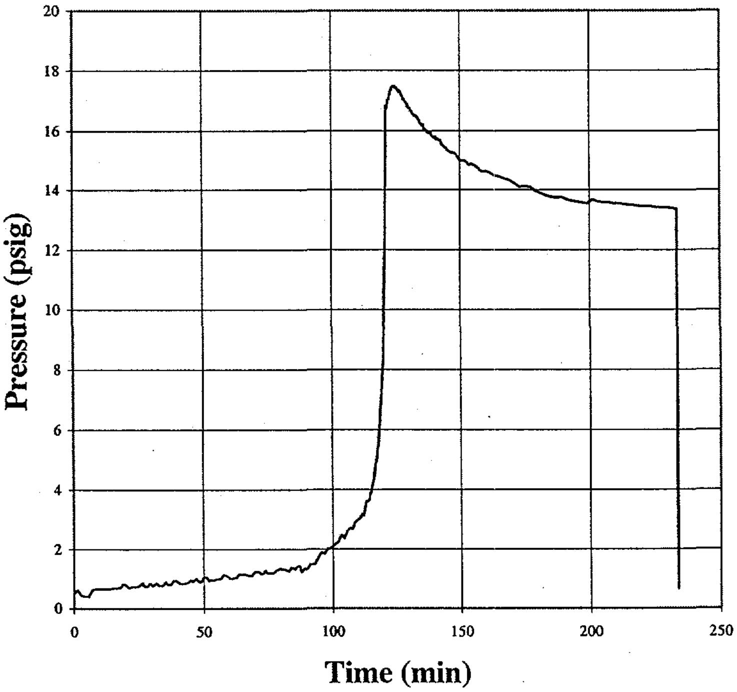
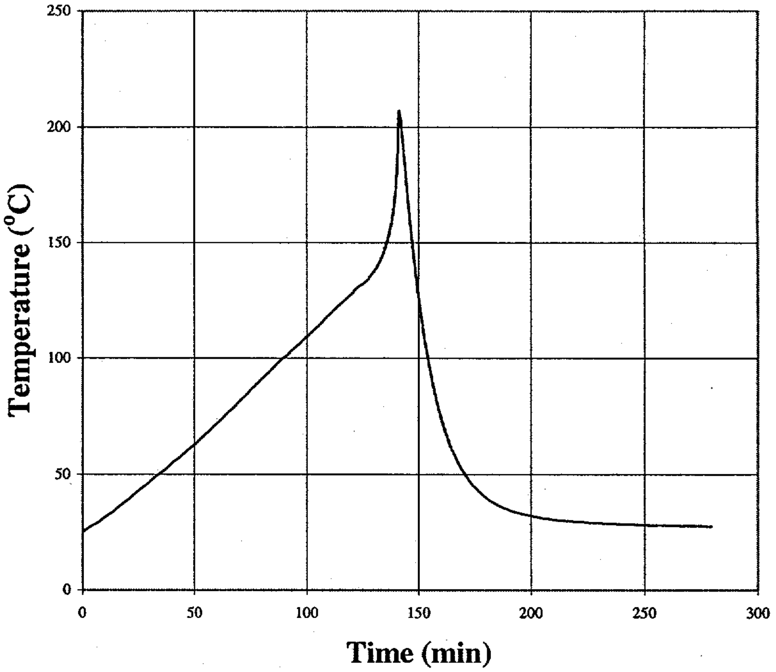


Figure D.27 Temperature and Pressure Profiles for Run No. TBP 20/4-1



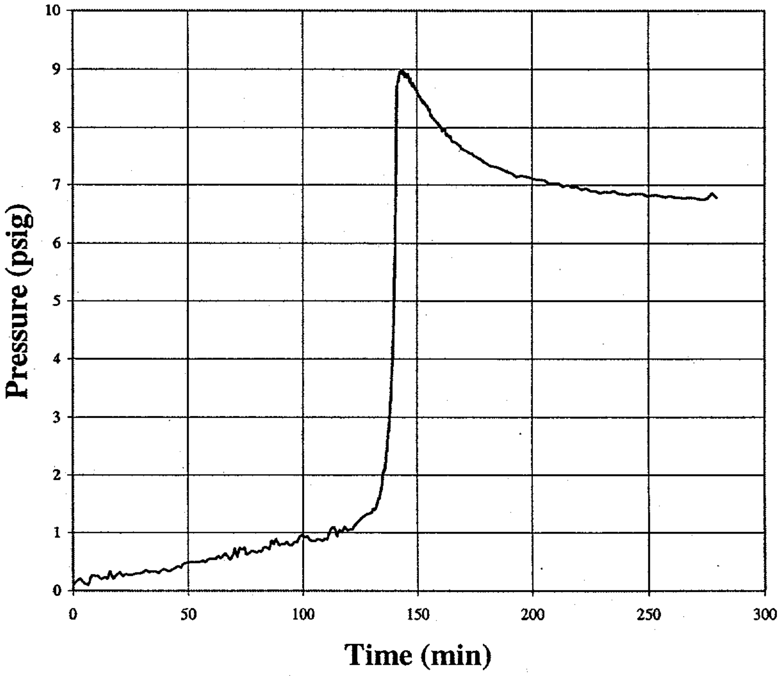


Figure D.28 Temperature and Pressure Profiles for Run No. TBP 20/4-2

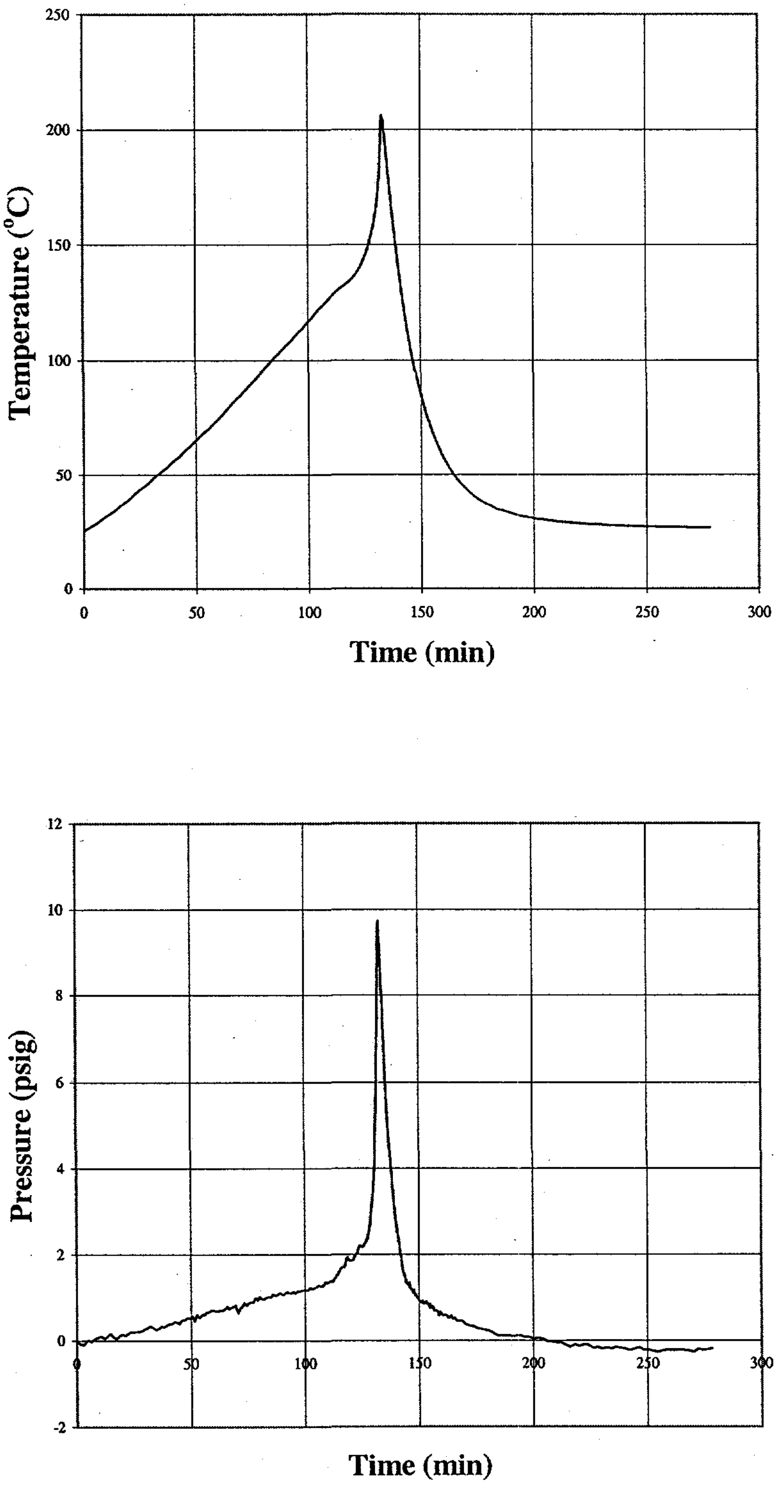
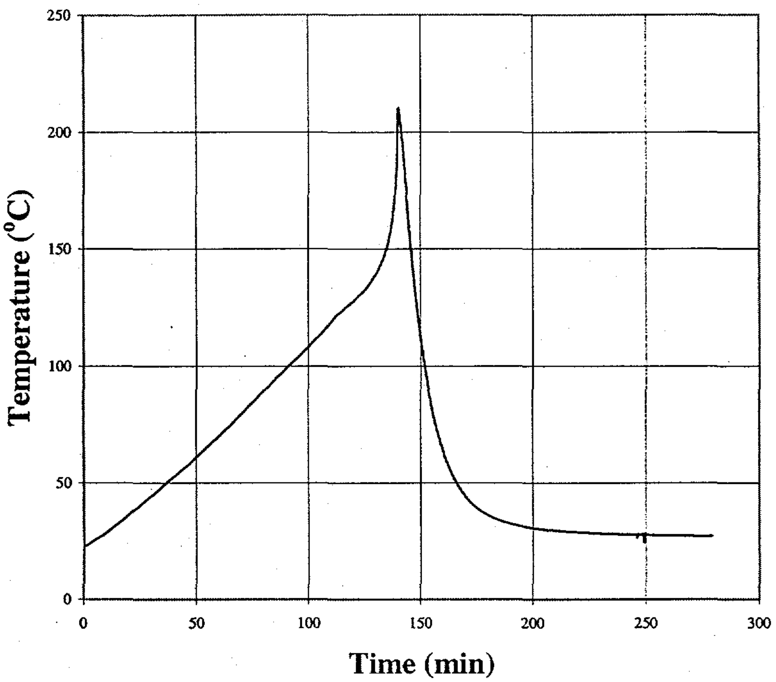


Figure D.29 Temperature and Pressure Profiles for Run No. TBP 10/6-1



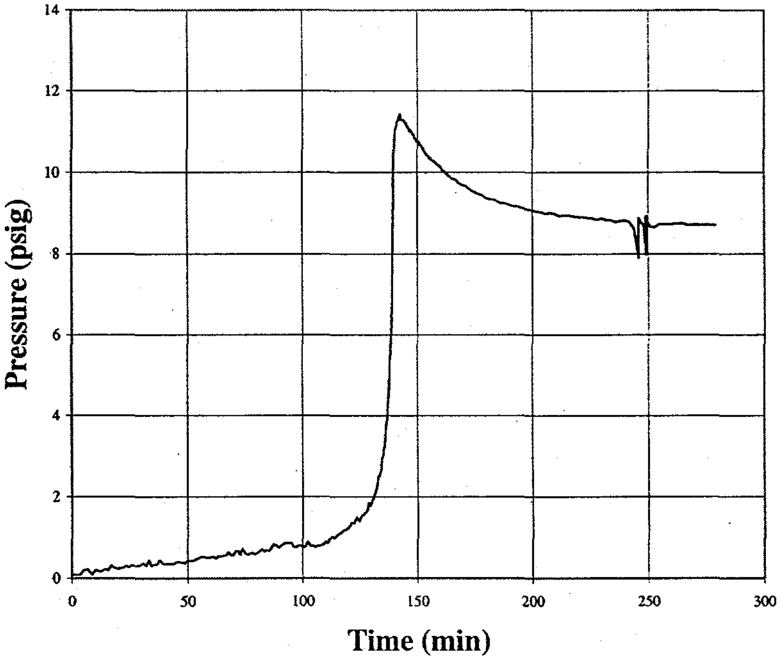


Figure D.30 Temperature and Pressure Profiles for Run No. TBP 10/6-2

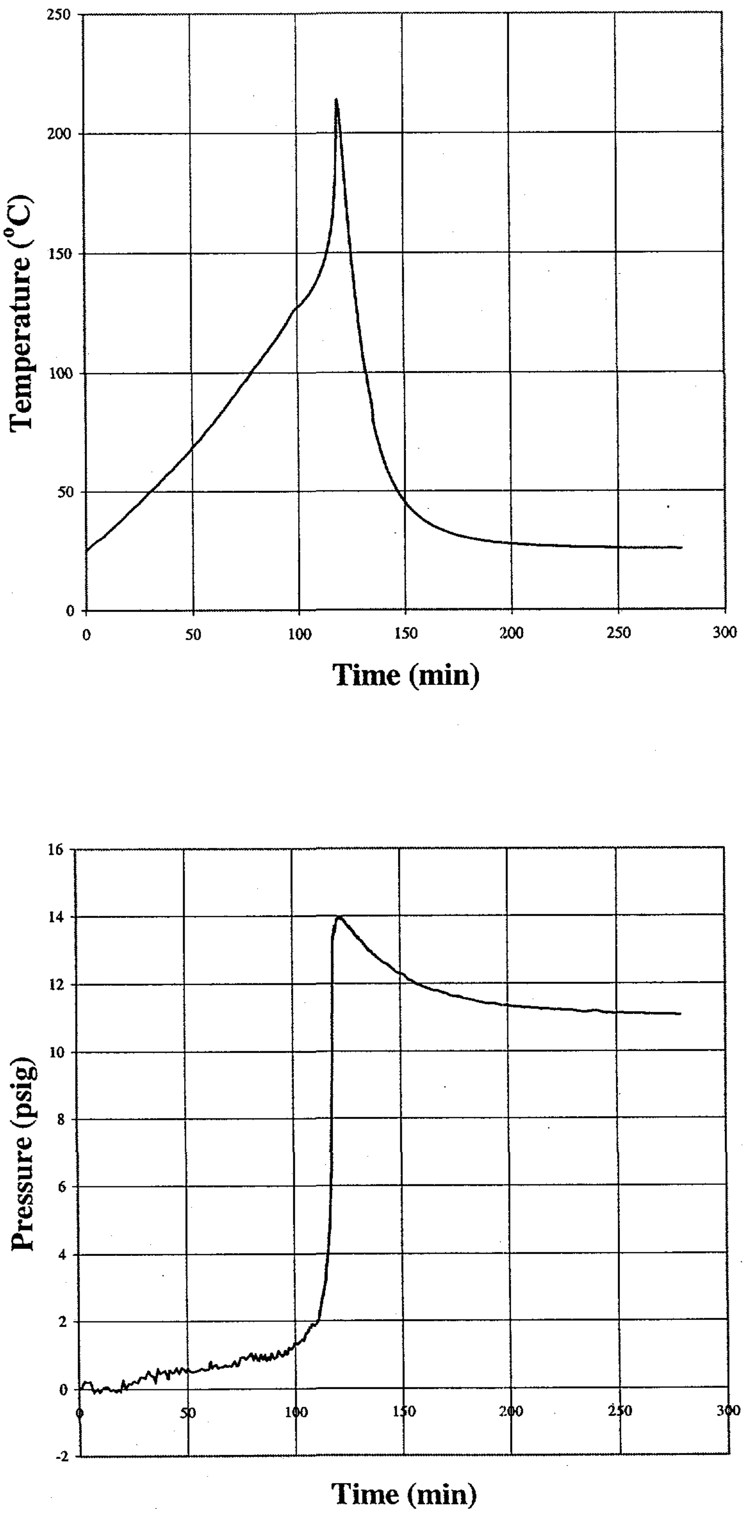
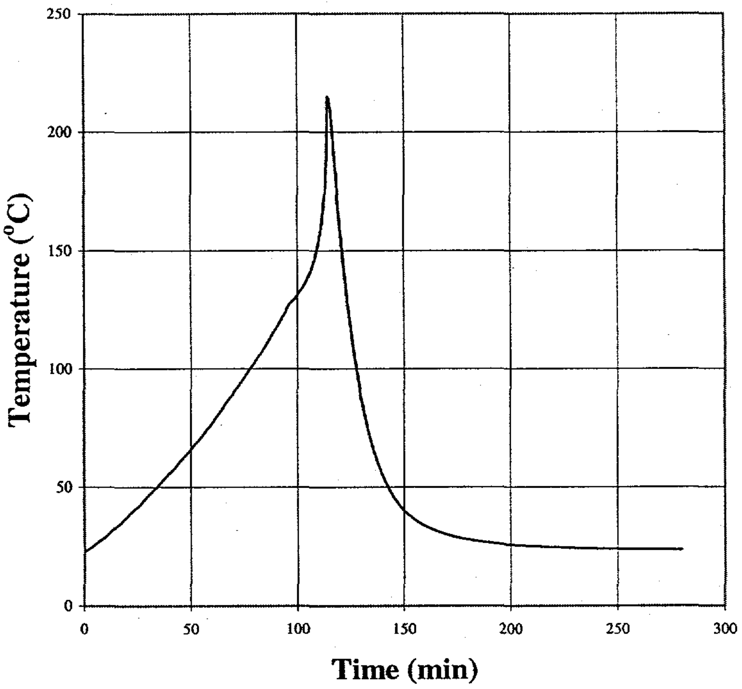


Figure D.31 Temperature and Pressure Profiles for Run No. TBP 10/6-3



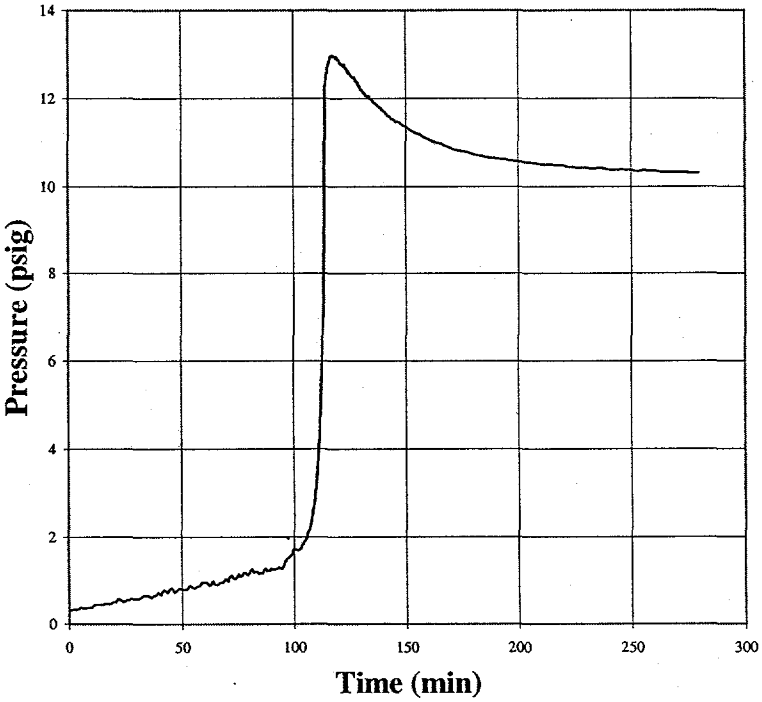
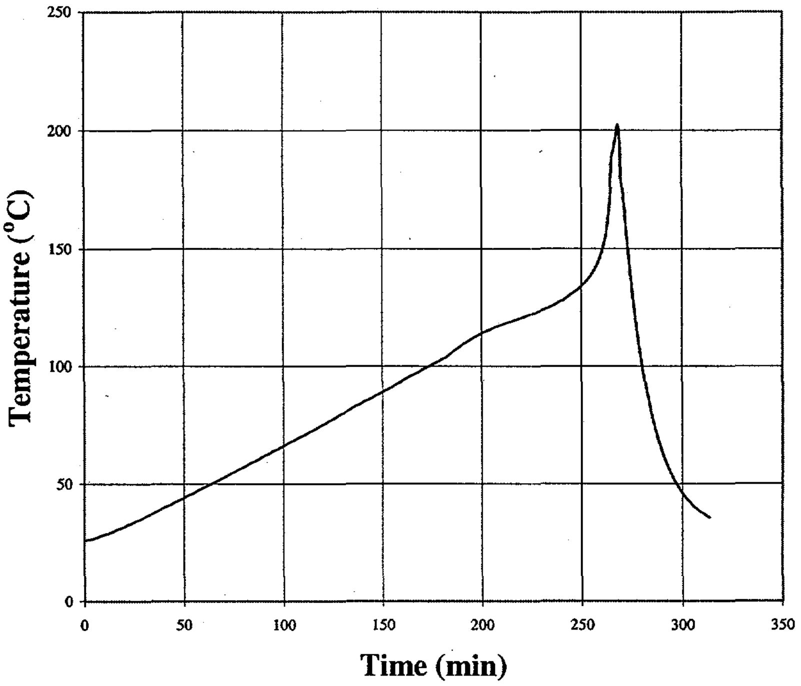


Figure D.32 Temperature and Pressure Profiles for Run No. TBP 20/7-1



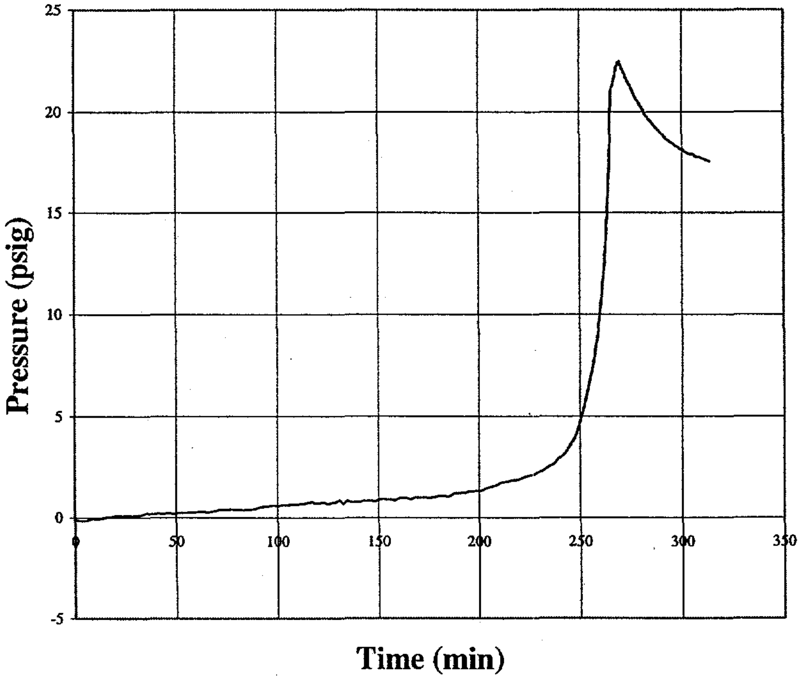
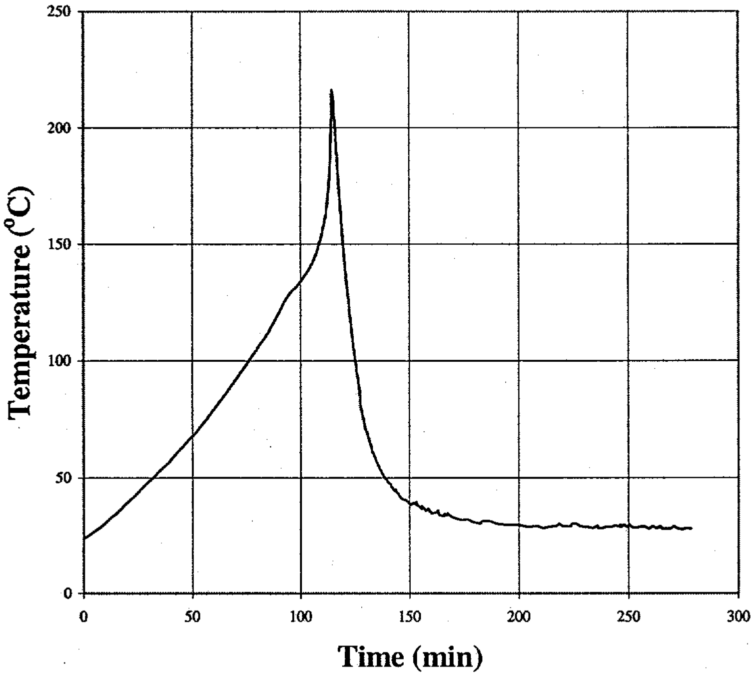


Figure D.33 Temperature and Pressure Profiles for Run No. TBP 20/7-3



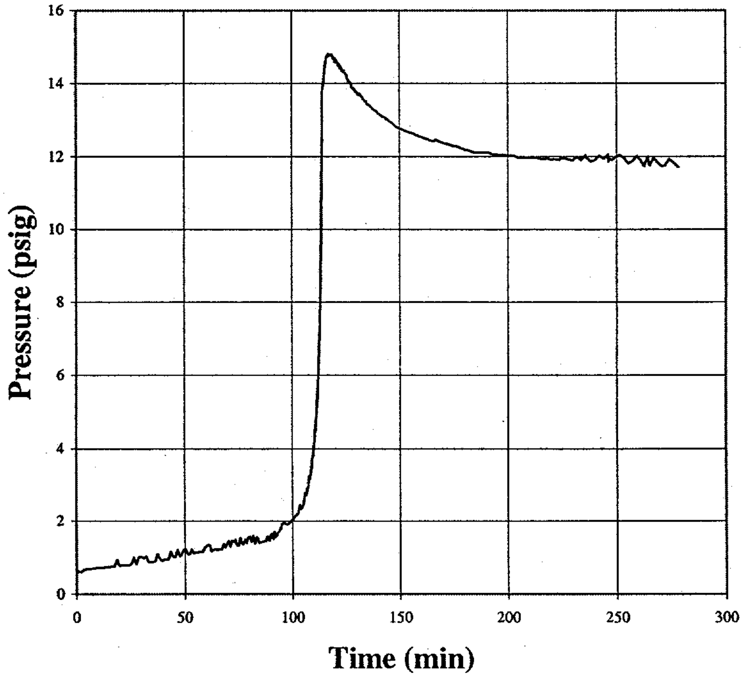
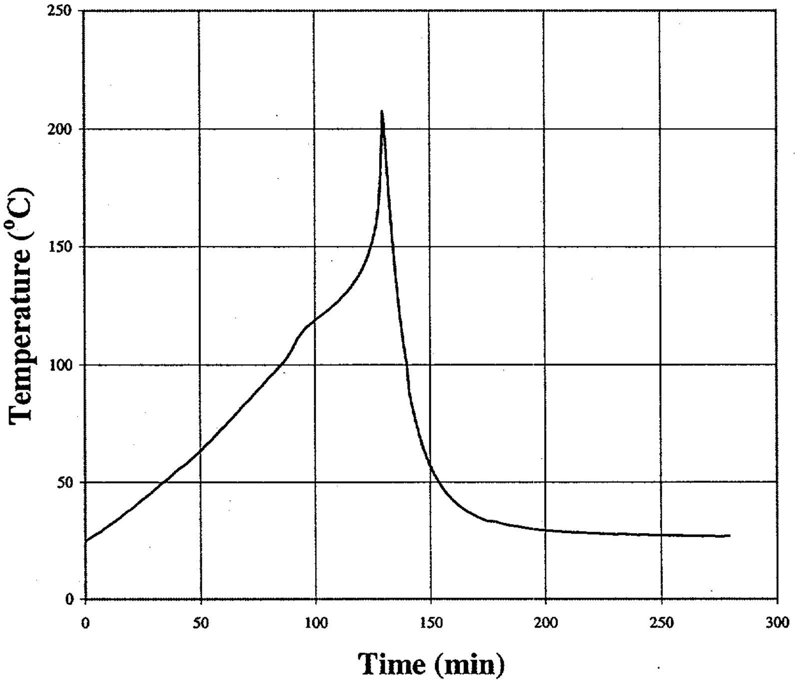


Figure D.34 Temperature and Pressure Profiles for Run No. TBP 20/8-1



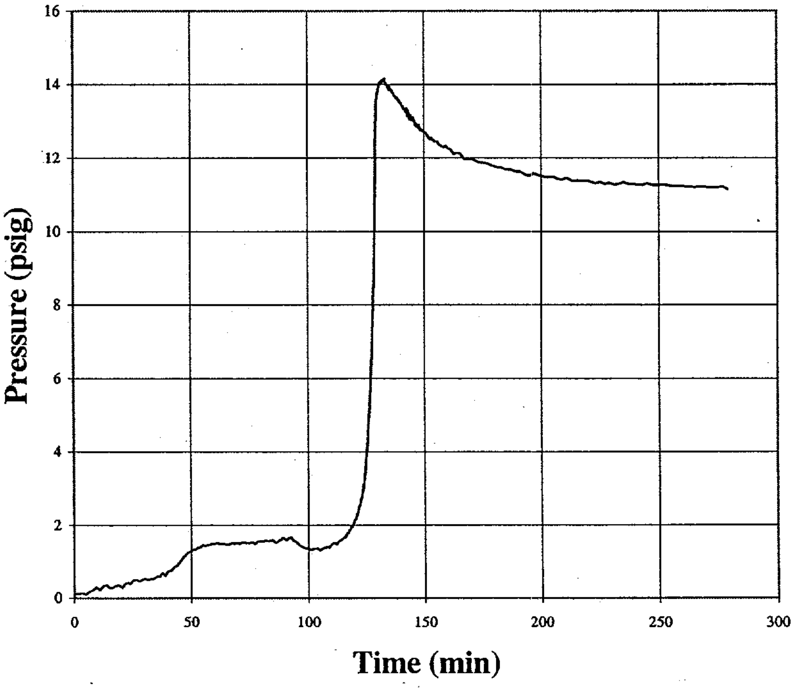
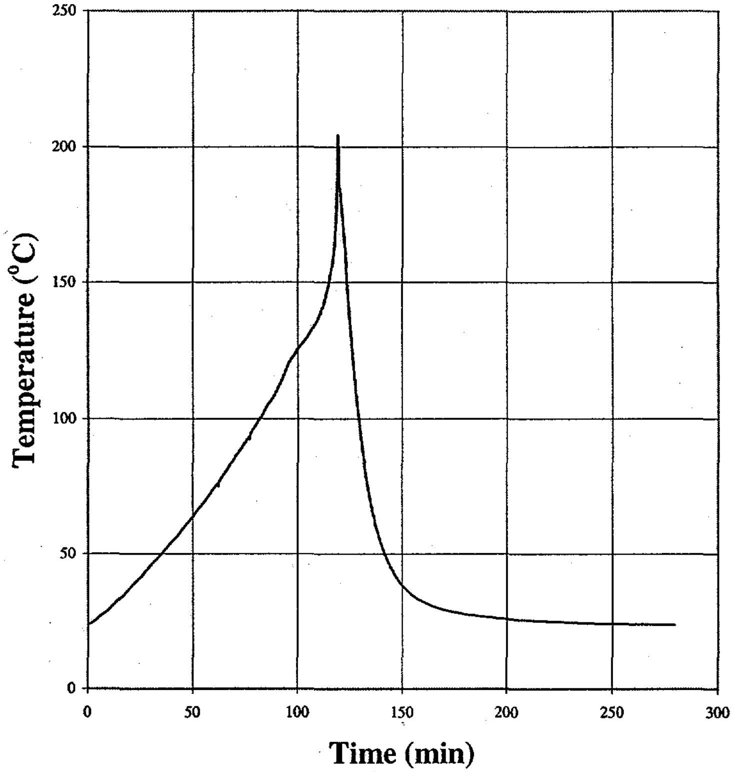
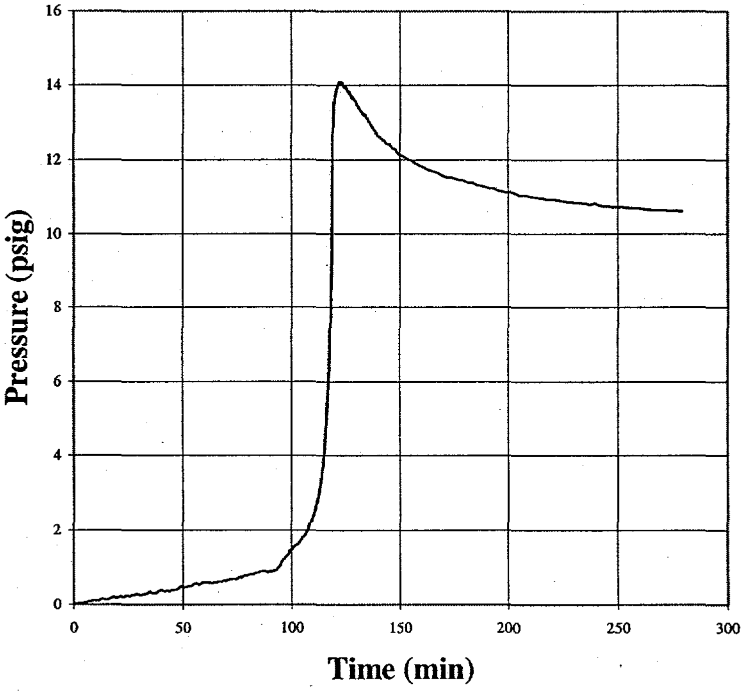


Figure D.35 Temperature and Pressure Profiles for Run No. TBP 20/7-4





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Appendix E Preparation of Solutions for Nitric Acid Extraction Measurements

The target concentrations and the amounts of materials used to prepare the aqueous and organic phases used to measure the extraction of nitric acid into pure TBP are provided in Table E.1.

Table E.1 Preparation of Aqueous and Organic Phases for Nitric Acid Extraction Measurements

Run No.	Target Concentrations		$Al(NO_3)_3 \cdot 9H_2O$	Water	Nitric Acid	Actual Concentrations		TBP
	Nitric Acid (moles/L)	$Al(NO_3)_3$ (wt%)	Mass (g)	Mass (g)	Mass (g)	Nitric Acid (moles/L)	$Al(NO_3)_3$ (wt%)	Mass (g)
TBPE 5/4	4	5	2.630	17.833	9.243	4.00	5.03	4.688
TBPE 5/6	6	5	2.765	14.679	13.876	6.00	5.01	4.598
TBPE 5/8	8	5	2.891	11.398	18.501	8.00	5.01	4.694
TBPE 5/10	10	5	3.019	8.020	23.113	9.99	5.02	4.708
TBPE 5/12	12	5	3.116	4.460	27.737	12.00	5.01	4.675
TBPE 10/4	4	10	5.530	16.573	9.249	4.00	10.01	4.674
TBPE 10/6	6	10	5.820	13.367	13.861	5.99	10.00	4.685
TBPE 10/8	8	10	6.092	10.029	18.481	7.99	10.00	4.698
TBPE 10/10	10	10	6.346	6.564	23.108	10.00	10.00	4.675
TBPE 20/4	4	20	12.418	13.613	9.254	4.00	19.98	4.673
TBPE 20/6	6	20	13.091	10.225	13.862	5.99	19.99	4.665
TBPE 20/8	8	20	13.705	6.730	18.493	8.00	19.99	4.670

Free acid analyses were used to measure the amount of nitric acid extracted into pure TBP following contact with a series of nitric acid solutions containing 5, 10, and 20 wt% $Al(NO_3)_3$. The actual concentrations of nitric acid and $Al(NO_3)_3$ in the aqueous phase and the concentration of nitric acid extracted into the TBP are provided in Table E.2.

Table E.2 Concentration of Nitric Acid Extracted into Pure TBP Contacted with Nitric Acid/$Al(NO_3)_3$ Solutions

Experiment No.	Aqueous Phase		Organic Phase
	Nitric Acid (moles/L)	$Al(NO_3)_3$ (wt%)	Nitric Acid (moles/L)
TBE 5/4-1	4.00	5.03	2.3484
TBE 5/4-2	4.00	5.03	2.2658
TBE 5/4-3	4.00	5.03	2.2930
TBPE 5/6-1	6.00	5.01	2.6862
TBPE 5/6-2	6.00	5.01	2.9042
TBPE 5/6-3	6.00	5.01	2.9470
TBPE 5/8-1	8.00	5.01	3.3696
TBPE 5/8-2	8.00	5.01	3.3013
TBPE 5/8-3	8.00	5.01	3.2319
TBPE 5/10-1	9.99	5.02	3.7953
TBPE 5/10-2	9.99	5.02	3.5708
TBPE 5/10-3	9.99	5.02	3.7174
TBPE 5/12-1	12.00	5.01	4.2390
TBPE 5/12-2	12.00	5.01	4.1739
TBPE 5/12-3	12.00	5.01	4.1656
TBPE 10/4-1	4.00	10.01	2.3893
TBPE 10/4-2	4.00	10.01	2.3652
TBPE 10/4-3	4.00	10.01	2.4177
TBPE 10/6-1	5.99	10.00	2.8213
TBPE 10/6-2	5.99	10.00	2.8391
TBPE 10/6-3	5.99	10.00	2.8346
TBPE 10/8-1	7.99	10.00	3.2527
TBPE 10/8-2	7.99	10.00	3.2578
TBPE 10/8-3	7.99	10.00	3.1182
TBPE 10/10-1	10.00	10.00	3.8084
TBPE 10/10-2	10.00	10.00	3.6243
TBPE 10/10-3	10.00	10.00	3.7924

Table E.2 Continued

Experiment No.	Aqueous Phase		Organic Phase
	Nitric Acid (moles/L)	$Al(NO_3)_3$ (wt%)	Nitric Acid (moles/L)
TBPE 20/4-1	4.00	19.98	2.7991
TBPE 20/4-2	4.00	19.98	2.8033
TBPE 20/4-3	4.00	19.98	2.6780
TBPE 20/6-1	5.99	19.99	3.0584
TBPE 20/6-2	5.99	19.99	3.1797
TBPE 20/6-3	5.99	19.99	3.1835
TBPE 20/8-1	8.00	19.99	3.7436
TBPE 20/8-2	8.00	19.99	3.5822
TBPE 20/8-3	8.00	19.99	3.7816

The average values for the nitric acid concentration in the organic phase for TBP contacted with aqueous phases containing 4.00, 5.99, and 8.00M nitric acid are 2.7601, 3.1405, and 3.7025M, respectively.