EMERGENCY RELIEF ADEQUACY FOR ACRYLIC POLYMERIZATION PROCESSES[1]

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Acrylic polymerizations are highly exothermic processes which must be carefully evaluated to ensure safe manufacture. In particular, failure to remove the heat of reaction can lead to runaway polymerizations, characterized by sudden and rapid increases in reaction rate, temperature, and pressure. If not adequately vented, runaway polymerizations can quickly lead to reactor overpressure, possible vessel rupture, and release of flammable or toxic materials.

Because of complex polymerization kinetics and the large number of industrial acrylic polymer processes, practical application of DIERS two-phase flow methodology for sizing reactor emergency vents required development of a computer model to simulate specific commercial polymerizations. This model is currently used to determine the emergency vent adequacy of reactors prior to manufacture of new resins in existing equipment, as well as to assist in design of new reactor systems. The purpose of this paper is to discuss practical application of DIERS technology for ensuring safe acrylic resin manufacture through use of computer simulation.

INTRODUCTION

Emergency relief systems are installed on process vessels to protect against the overpressure caused by runaway reactions and other upset events. Emergency relief system design has evolved over the last decade with the development of an understanding of the effects of two-phase flow on relief device capacity. Advances made by the original Design Institute for Emergency Relief Systems (DIERS), and the subsequent DIERS Users Group, have led to the development of recognized methods for the prediction of two-phase flow and a methodology for sizing relief devices under these flow conditions [1]. Most reported systems have been relatively simple first-order reactions or decompositions. In addition, with few exceptions, the practical applications have been limited to simple batch reactors, where overall composition is fixed throughout the batch. This paper discusses some of the difficulties in application of standard DIERS methodology to practical cases of commercial acrylic polymerization reactions and illustrates the value of computer simulation for proper application of the DIERS technology to emergency relief system design [2,3].

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[1] This is a preprint of an article published in Process Safety Progress, p. 71-77, 1999
www.interscience.wiley.com

Pressure build-up leading to emergency relief is caused either by the increasing vapor pressure of volatile species in the reaction mass during the course of an exothermic reaction ("high vapor pressure" system), or by the evolution of non-condensible gases through chemical decomposition or reaction ("gassy" system), or a combination of these two. The first of these systems is characterized by boiling of one or more ingredients upon venting of the reactor pressure, which serves to cool the remaining material in the reactor and limits further increases in temperature or pressure (reaction tempering). In the case of high vapor pressure systems, the specific volumetric flow rate required of the emergency relief system, and hence the required relief area, is proportional to the average heat release rate per unit mass during the venting process. For low vapor pressure systems, the critical parameter in determining the required vent area is the rate of non-condensible gas generation at relief conditions.

The DIERS research led to the development of calorimeters for direct determination of both the reaction type and the self-heat and/or gas generation rates [4,5] as a function of temperature for a fixed composition. These calorimeters are miniature batch reactors, allowing the programmed heat-up of a sample of mixed reactants under a superimposed inert gas pad. For high vapor pressure systems, the heat release rate during the venting process is taken as the average of the self-heat rates at relief and at temperature turnaround. These values can be obtained from tests run at both a high pad pressure to suppress boiling and at the relief pressure. For low pressure systems, the rate of gas evolution at relief is determined from the rate of pressure increase in the containment vessel. While calorimetric tests are important experimental tools, they must be used with a clear understanding of their limitations.

REACTOR SAFETY

Given the potential hazards of industrial polymerizations, a comprehensive resin Reactor Safety program has been implemented worldwide at all DuPont Performance Coatings resin manufacturing plants with the goal of achieving completely safe resin manufacturing [6]. One of the key activities of the Reactor Safety program is the mandatory, routine safety screening of all acrylic resin manufacturing formulas, prior to releasing these formulas for production in plant equipment [7]. Safety screening of acrylic resins includes checking the formula for inherent safety considerations, computer simulation to evaluate reaction exotherm and runaway reaction emergency vent sizing, and reaction calorimetry, as required. In all cases, no products may be produced in resin manufacturing equipment unless the Reactor Safety Group has conducted the required safety screening and issued written approval for manufacture.

ACRYLIC POLYMERIZATION SYSTEMS

The sizing of emergency vents for acrylic polymerizations and the determination of the adequacy of existing vent configurations to satisfactorily relieve a runaway reaction pose a significant challenge for the safety professional. Essentially all acrylic polymerizations utilize small amounts of one or more polymerization initiators to form primary free radicals through thermal decomposition. Polymer chains are then formed from monomer addition to these free radicals. When each primary radical adds a single monomer unit, it becomes a growing polymer chain. As the reaction proceeds, almost all of the polymerization involves addition to growing polymer chains, and only very little (1%) involves addition to primary radicals. Overall, polymerization kinetics are very complex, with a large number of side reactions and very fast reaction rates [8].

Most acrylic reactions are carried out in a solution of the volatile monomers in one or more solvents. The system vapor pressure is thus the sum of the individual solvent and monomer contributions. A number of factors makes these systems particularly challenging. First, the monomer component of the reacting mixture not only contributes significantly to the system vapor pressure, but is reacting and is thus being depleted as the polymerization proceeds. Secondly, the boiling point of the solution varies not only with system pressure, but with changing composition as the percent of polymer increases. Finally, the system viscosity increases significantly with time as the reaction proceeds.

Few commercial acrylic polymerizations are carried out in the batch mode used for many calorimeter tests, as discussed below. Not only must the specific process details be taken into account, but the use of two-phase DIERS methodology demands an accurate knowledge of the kinetics of the reaction system. It can be very misleading to assume that the maximum exotherm (peak relieving rate) occurs exactly at the relief pressure. A dynamic model is the only method we have found by which the DIERS two-phase flow technology can be realistically applied to commercial acrylic polymerization reactor systems.

Polymerization Processes

Batch Process. In the true batch process, monomers, initiators and solvents are charged to the reactor at ambient temperature and heated. External heating is stopped once the exotherm begins and the heat of reaction is removed by evaporative (reflux) cooling, cooling coils, cooling jacket, or similar means. This type of process is least preferred because there is little control over finished product properties and the risk of a severe runaway polymerization is high. It is considered the most hazardous type of acrylic process.

A variation of the batch process is the addition of initiator as a very rapid ("shot") feed to a solution of monomer and solvent held at its boiling point. This type of reaction is somewhat more controlled than the first, but still has very high runaway potential. Because the initiator solution is only a small percentage of the reaction mass, the temperature remains at the boiling point during the shot addition. Since no reactants have yet been converted up to that point, the reaction rate after the initiator addition is higher than if all reactants were heated together and had partially reacted at lower temperatures.

Semi-batch Process. A preferred process for acrylic polymerization is carried out in a batch reactor with the reactants fed in over relatively long periods of time to allow for a controlled exotherm and adequate removal of the heat of reaction. In these processes, either the initiator is fed into a monomer solution at its boiling point or both initiator and monomer solution are fed to the reactor as separate streams at fixed schedules while maintaining a boiling (reflux) condition in the reactor. The use of long feed schedules and adequate process control of feed rates and boil-up minimizes the potential for buildup of large quantities of unreacted reagent. The major runaway potential in these semi-batch processes is loss of external cooling with continued ingredient feed. Deviations in feed rates are also important.

Continuous Stirred-Tank Process (CSTR). In this variant of the semi-batch process, initiator and monomer solution streams are fed continuously to an agitated reactor maintained at reflux temperature while finished or semi-finished product is withdrawn at the same overall rate. Again, the continuous nature of the process serves to mitigate against buildup of unreacted monomer.

Potential Upset Conditions

Total and sustained loss of cooling, without any mitigating action on the part of operations, is considered the most hazardous, credible cause of a runaway polymerization for all of these processes. Other paths to a runaway condition include:

Operational error is always possible, particularly when certain steps in a batch involve manual weighing and addition of ingredients. Errors of this type can include such things as incorrect amounts of one or more ingredients, incorrect type of ingredient, or omission of one or more ingredients.

Control error, primarily in the semi-batch and CSTR processes, can also lead to a runaway condition. An incorrectly programmed rate of ingredient feed or feed system equipment failure can lead to a pooling of unreacted ingredients and a drop in reactor temperature - subsequent heating can result in a runaway condition. Poor temperature control during heat-up of a batch process can also present a hazard.

In some cases, combinations of these errors are considered as part of hazard evaluation methods. Other upset conditions leading to a runaway reaction are possible, such as loss of agitation, but are of lesser importance in routine safety screening analysis.

KINETIC MODEL

A dynamic tank model for free radical solution polymerization is used to simulate runaway behavior. The model combines material and enthalpy balances with multi-component free radical polymerization kinetics (initiation, propagation, chain transfer, diffusion-controlled termination) to predict the evolving polymer architecture and reactor performance. Arbitrary feed schedules and various temperature control options permit the simulation of a wide range of operating conditions; lab scale calorimeter and manufacturing processes are readily simulated. Thermodynamic and kinetic databases for reactants and a plant reactor equipment database facilitate the use of the model for routine safety evaluation of new formulations and/or operating conditions.

Several simulations are performed to ensure the safe manufacture of a resin prior to actual production. Simulation results of the proposed procedure determine if existing reactor cooling capabilities can safely remove the peak reaction exotherm. To mimic the sudden loss of cooling, runaway simulations in which the reactor becomes adiabatic at various times identify the worst case scenario. In these simulations, the predicted average exotherm during venting is used either to size the emergency relief for new reactor systems or to determine the relief system adequacy for new products in existing reactors, using established two-phase flow methods [9,10]. Homogeneous reactor venting and a 10% overpressure allowance are assumed for conservative screening analysis. To determine the start of emergency venting, reactor pressure is calculated from the batch temperature assuming an ideal solution for the non-polymeric species, with a Flory-Huggins based correction factor to account for the presence of polymer. A two-parameter Antoine equation is used for the pure component vapor pressures.

The model assumes that all polymerizations are the "high vapor pressure" type, that is, pressure build-up derives from increasing system temperature caused by the polymerization reaction. While the decomposition of the initiators used in this type of process generates either carbon dioxide or nitrogen, it is assumed that this contribution to reactor pressure is negligible. Calorimetric testing of each of the polymer reactions described in this paper confirmed that the gas generation rate from initiator decomposition was, at worst, slightly more than 3% of the total vapor generation rate. Calorimetric tests on many acrylic systems have shown the effect of reaction tempering to be relatively small, likely due to the relatively high viscosity of the solution at venting pressure.

It is also assumed that the "worst case" system failure is total loss of reactor cooling (reaction goes adiabatic) and that ingredient feeds continue. The model then calculates the “worst case” time for cooling to be lost and the time and conditions where relief pressure is exceeded and venting occurs. For batch processes, the “worst case” occurs after all ingredients are loaded and heated (time zero). For semi-batch processes, the worst case time can occur at the start of the batch or at some later time, depending on specific ingredients, feed schedules and processing conditions. We do not normally consider other major upset conditions (e.g.. ingredient mischarge or incorrect feed rate) occurring simultaneously with loss of cooling to be credible cases.

Figures 1 and 2 illustrate the temperature and pressure profiles due to a loss of cooling at 0, 50 and 100 minutes into a typical acrylic feed process, where initiator and monomer solutions are being fed simultaneously and uniformly into refluxing solvent over a 4 hour period. During normal operation, the reactor temperature decreases slowly with time as the percentage of polymer in the reactor increases. Loss of external cooling at the start of feeds (0 minutes) causes an immediate rapid rise in temperature. Loss of cooling at later times gives milder exotherms, reflecting the increasing quantity of reacted material in the reactor. As illustrated in Figure 2, the time that loss of cooling occurs can have a profound effect on the pressure profile during the runaway. Loss of cooling at the start of the feeds causes the pressure to rise sharply, exceeding the assumed Maximum Allowable Working Pressure (MAWP) of the reactor. Loss of cooling at 50 minutes will cause the relief device to open, but the final pressure will not exceed the MAWP. The final pressure from loss of cooling at 100 minutes will be below the relief pressure, and the runaway will be contained. Clearly, in this example, the “worst case” is loss of cooling at the start of the batch. The emergency relief vent must be adequately sized for this case in order to safely vent this pressure buildup, maintaining the reactor pressure below the MAWP.

APPLICATIONS

In this section, the kinetic model is applied to several different actual cases of batch and semi-batch acrylic solution polymerization. In each case we assume that the reactor is protected with a rupture disc opening at 50 psig. All calorimetric tests were run on a RSST Calorimeter by heating a sample of fixed composition at a specific temperature ramp rate. Since the RSST cannot be used to duplicate actual processing conditions for semi-batch or feed processes, all runs used the composition representing the total combined feeds with the results compared to the kinetic model simulating the same composition and heat-up rate. The differences between calorimetric results obtained in this way and the predicted results for actual semi-batch processes can be significant, requiring caution in the sizing of emergency relief vents.

Batch Process

Polymer A. This polymer consists of approximately 61% monomer dissolved in isopropyl alcohol and toluene, with an atmospheric boiling point of about 102°C.

Figure 3 compares the measured self-heat rate at 300 psig backpressure for this polymer with that calculated by the model, assuming that all ingredients are mixed at room temperature and heated adiabatically (standard batch process), in the same fashion as the calorimeter. These results show good agreement between the measured and predicted maximum self-heat rate, which is approximately 14.5°C/minute. At lower temperatures (<100°C) the reaction rate is slowed by the effect of polymerization inhibitors present in the calorimeter sample. Although the model represents this inhibition well, the effect is relatively unimportant, since all reactions of interest occurred at temperatures at which the inhibitor had been completely reacted. The inhibitor effect was found to some degree in all polymers studied.

In the actual manufacturing process, the initiator solution is added as a shot to a monomer/solvent mixture at its boiling point, and thus the reaction rates are higher than those realized when the initiator, monomers and solvents are heated together, as shown by the model results in Figure 3. The difference between the two, as explained earlier, is due to the partial reaction of the ingredients at lower temperatures during the heat-up process.

Figure 4 illustrates the temperature and pressure rise, as calculated by the model, for the "worst case" loss of cooling immediately after the initiator shot. The rate of temperature change at relief is 20.5°C/minute vs. a maximum of 29.7°C/minute just prior to the relief point. Pressure and temperature show no further rise after depletion of reactants, with a maximum pressure of 59.7 psig. Use of a higher relief pressure of 70-80 psig, if not in excess of the MAWP of the vessel, would allow the runaway to be fully contained.

In this simple bulk case, the measured peak self-heat rate of 14.5°C/minute is fortuitously close to the calculated value of 20.5°C/minute at the assumed vent pressure, and a reasonable value of emergency vent diameter can be obtained from calorimetric data.

Semi-batch Process

Polymer B. Polymer B is 82.3% monomer in amyl acetate solvent, with an atmospheric boiling point of 144°C. For this process the monomer and initiator solutions are fed simultaneously into refluxing solvent over a period of 180 minutes.

Figure 5 illustrates the temperature and pressure profiles for the "worst case" loss of cooling with the standard feed schedule. The "worst case" was found to be from loss of cooling 20 minutes after the start of the batch. After loss of cooling, the reaction rate initially accelerates, reflecting an increased rate of conversion of unreacted monomer already fed to the reactor. The maximum self-heat rate of 3.8°C/minute occurs shortly after loss of cooling, after which the temperature profile represents a combination of reaction of new monomer being fed to the process plus an increase in the overall monomer conversion in the reactor. As seen in Figure 5, the final pressure for this case barely reaches the relief pressure of 50 psig, at which point the reactants are virtually exhausted. The self-heat rate at the relief pressure is only 0.12°C/minute.

Figure 6 compares the self-heat rate predicted by the model for the combined feeds heated adiabatically from room temperature with calorimetric results for the same mixture. The maximum temperature rise rate for the mixed feeds is in excess of 1,000°C/minute. Again, fairly good agreement between the measured and predicted result is observed. The maximum self-heat rate of >1000°C/min measured for the combined feeds, though, is significantly higher than the value of 3.8°C/minute predicted for the continuous feed process. This is due to the higher monomer and initiator concentrations present in the batch model, illustrating the difficulty of directly using batch calorimetric results in sizing emergency relief vents for semi-batch processes.

This is shown more clearly in Figure 7, where the batch and semi-batch self-heat rates are compared. At the relief pressure of 50 psig (211°C), the batch process self-heat rate is over 1,000 times greater than that for the "worst case" semi-batch process, where the reaction takes place uniformly over a period of 180 minutes. If, therefore, an emergency relief system for this process were designed solely from calorimetric data at the relief pressure, the relief area would be overestimated by about the same factor.

Polymer C. Polymer C is 62.6% monomer in a mixed solvent of toluene and methyl ethyl ketone. In this case, a portion of the monomer/solvent charge is brought to reflux and the remaining monomer and most of the initiator is fed uniformly over 90 minutes. In the worst case shown in Figure 8, with loss of cooling at 10 minutes, the relief pressure of 50 psig is reached at about 40 minutes into the batch. At this point the self-heat rate is 1.6°C/minute, versus the maximum rate of 2.5°C/minute. The final stages of the process include a small solvent rinse at 90 minutes, followed by a final initiator feed to convert any remaining unreacted monomer. This final feed causes the temperature to reach a final peak of 200°C at about 110 minutes into the batch.

In order to best match the conditions during the first 90 minutes of the process, the overall composition corresponding to the initial monomer charge and the first monomer and initiator feeds was run in the calorimeter and compared with the model, as shown in Figure 9. Again, fairly good agreement between the calorimetric and predicted results are obtained, with a maximum self-heat rate of approximately 10°C/minute. This value is again significantly higher than the self-heat rate of 1.6°C/minute obtained from the semi-batch simulation. In addition, the final temperature reached in this case is about 140°C vs. a relief temperature of 160°C for the actual feed process, since the feed process is much more efficient in converting monomer and the presence of the second initiator feed. For this process, therefore, while the calorimetric data is in reasonable agreement with the model run under the same conditions, it is of little value in predicting the relief exotherm or determining an adequate vent diameter for the conditions of the actual process.

Polymer D. Polymer D is 50% monomer in a mixed solvent of isopropanol, toluene and ethyl acetate. The initiator solution is added in three stages - 25% of the total initiator is added as a shot to the monomer solution in the reactor, with the remainder added in two increments at 45 minutes and 120 minutes. A small solvent rinse follows the last initiator addition. The model indicates the worst case loss of cooling to be at the start of the batch, as shown in Figure 10. The initial charge of initiator solution is sufficient to react only about 1/3 of the monomer charge, and the pressure at the end of the first reaction stage is below the assumed relief pressure of 50 psig. The second initiator solution drives the monomer conversion to about 47%, and causes the system pressure to exceed the relief pressure of 50 psig. This is also the point of the highest self-heat rate.

This example illustrates the sensitivity of the required venting area to relief pressure in commercial polymerization processes. If, for example, the relief pressure was set at 30 psig, rather than 50 psig, the system would vent during the first exotherm, which is considerably less energetic than that occurring during the second initiator addition due to the lower reactor temperature. In addition, this process, with multiple shot additions of initiator, is very difficult to duplicate with a calorimeter to obtain experimental data for emergency vent sizing. In this case, computer simulation is required for reasonable determination of the emergency vent requirements.

SAFETY SCREENING

As discussed in the previous section, calorimetric data for maximum self-heat rates must be used with caution when sizing emergency vents for many typical commercial acrylic polymerization processes. Good agreement between calorimetric and predicted self-heat rates for batch processes is generally observed, however, confirming in many respects the complex kinetics incorporated into the computer model. For these reasons, routine safety screening of new acrylic resin processes prior to manufacture relies primarily on computer simulation. Calorimetric measurements are used to supplement the computer model, as needed, such as when good kinetic data are not available for new monomers.

Typical computer simulation results for determining emergency vent requirements for a runaway reaction of a semi-batch acrylic resin formula are shown in Figure 11. In this case, the required diameter for the emergency vent is shown for different relief pressures, as a function of the time loss of cooling occurs during the process, assuming a 10% overpressure. The emergency vent diameter requirement for this resin decreases when the runaway occurs later in the batch, due to higher monomer conversions and subsequent lower exotherms. In addition, the required emergency vent diameter also decreases as the relief pressure is increased, due to lower exotherms and higher venting rates at the higher relief pressures. In both cases, these results are often seen for many semi-batch resins, but always depend on the specifics of the resin formula. In general, vent areas calculated using two-phase homogenous venting are two to four times higher than vent areas assuming all-vapor venting.

SUMMARY

A wide range of commercial acrylic resin manufacturing processes have been reviewed. In each case, the use of an experimentally-validated computer simulation model of the complex reaction kinetics is vital in determining the reaction conditions throughout the process. With the model, it is possible to determine whether reactor pressure under various assumed upset conditions will exceed the relief pressure, the exotherm at emergency relief, and the required emergency vent area for two-phase flow. The quantitative use of RSST calorimetric data, other than to validate the model, is limited to those processes that exactly duplicate the batch conditions of the calorimetric test. In general, the use of calorimetric data for semi-batch or continuous feed processes will lead to significant oversizing of the relief system, requiring comparison with computer simulation to ensure reasonable emergency relief system design

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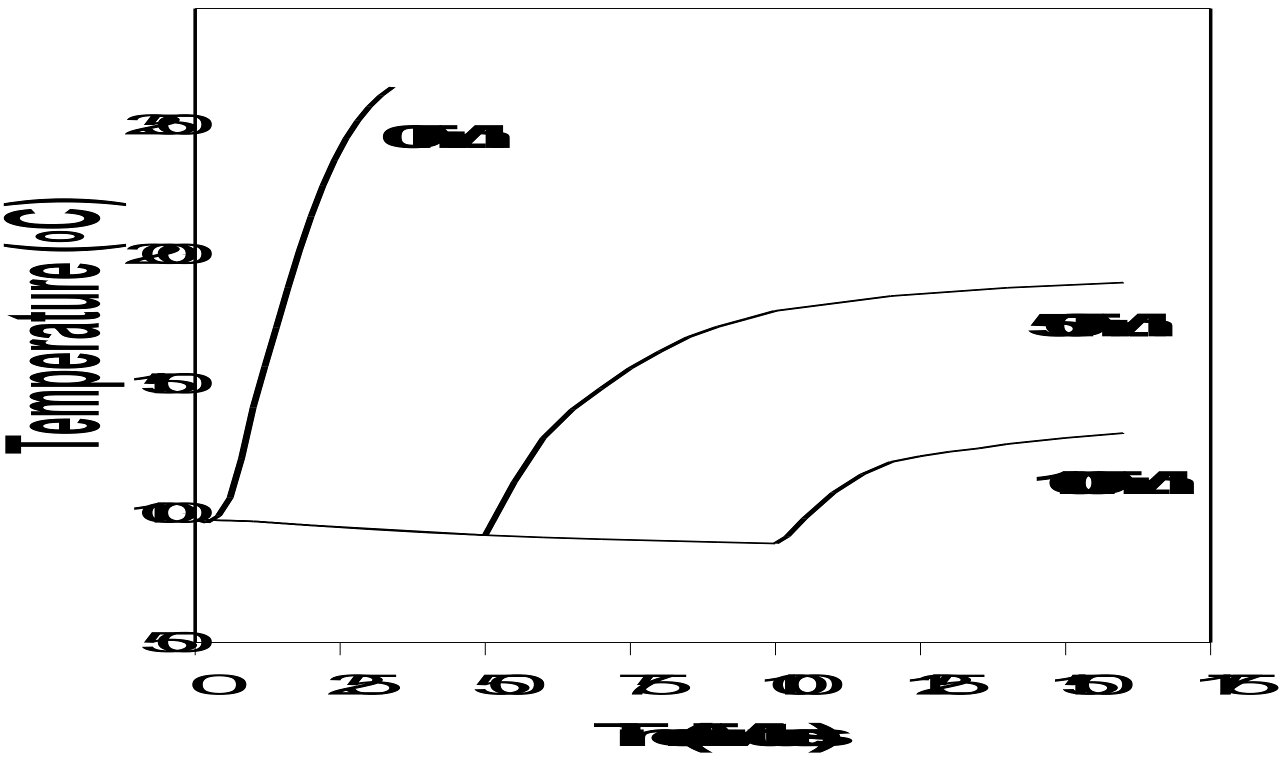
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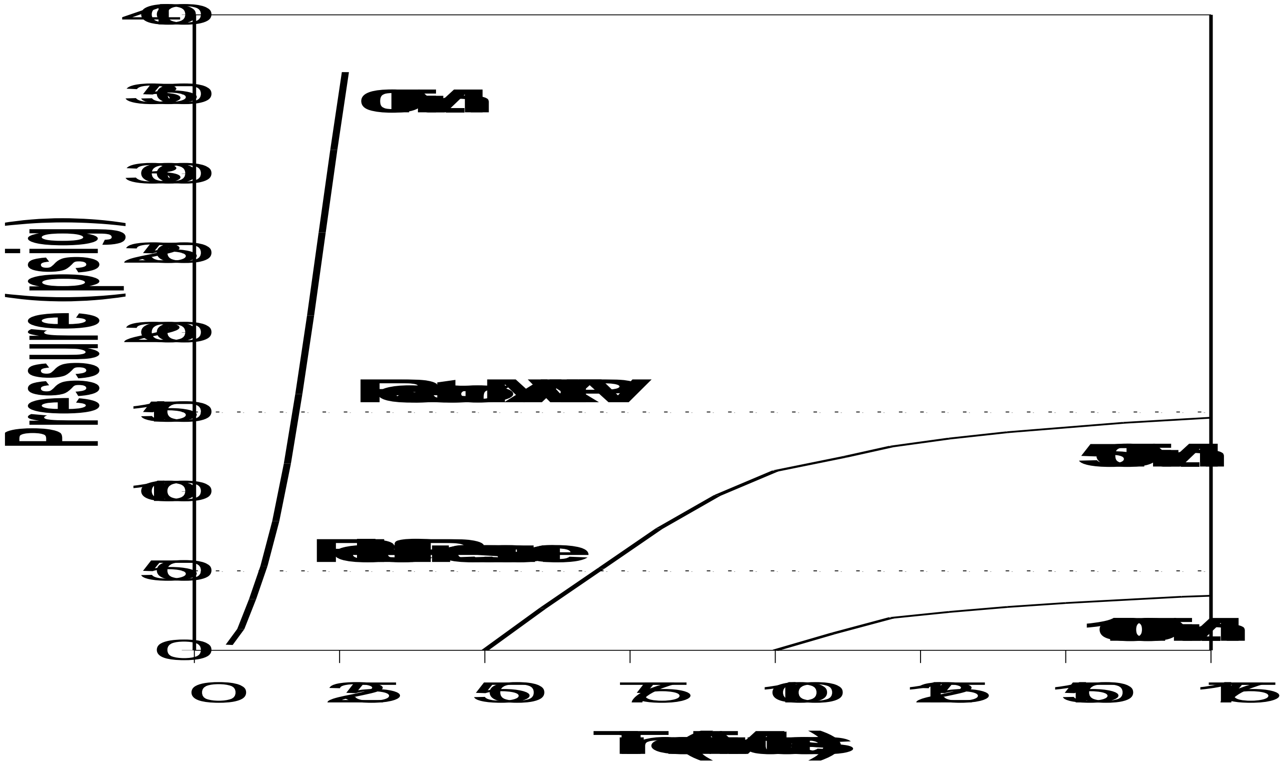
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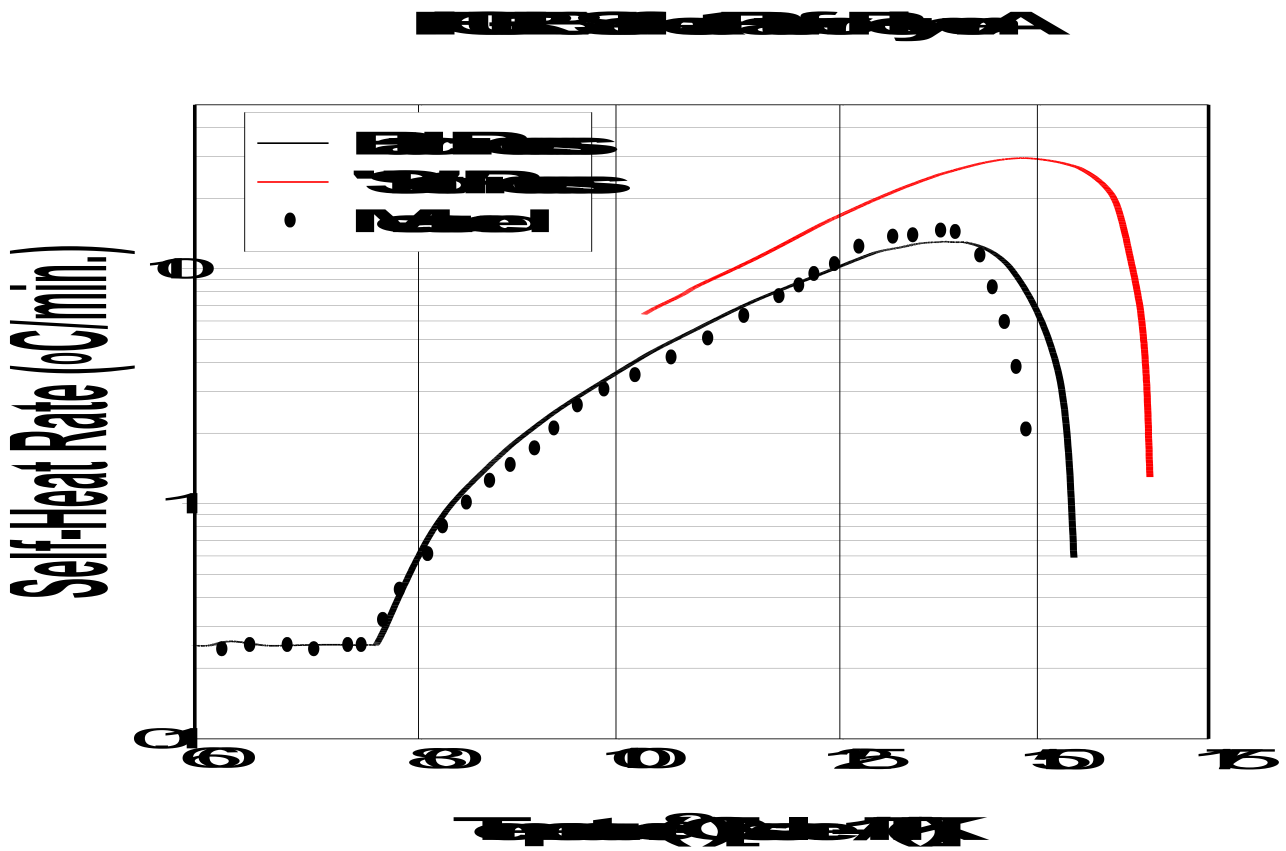
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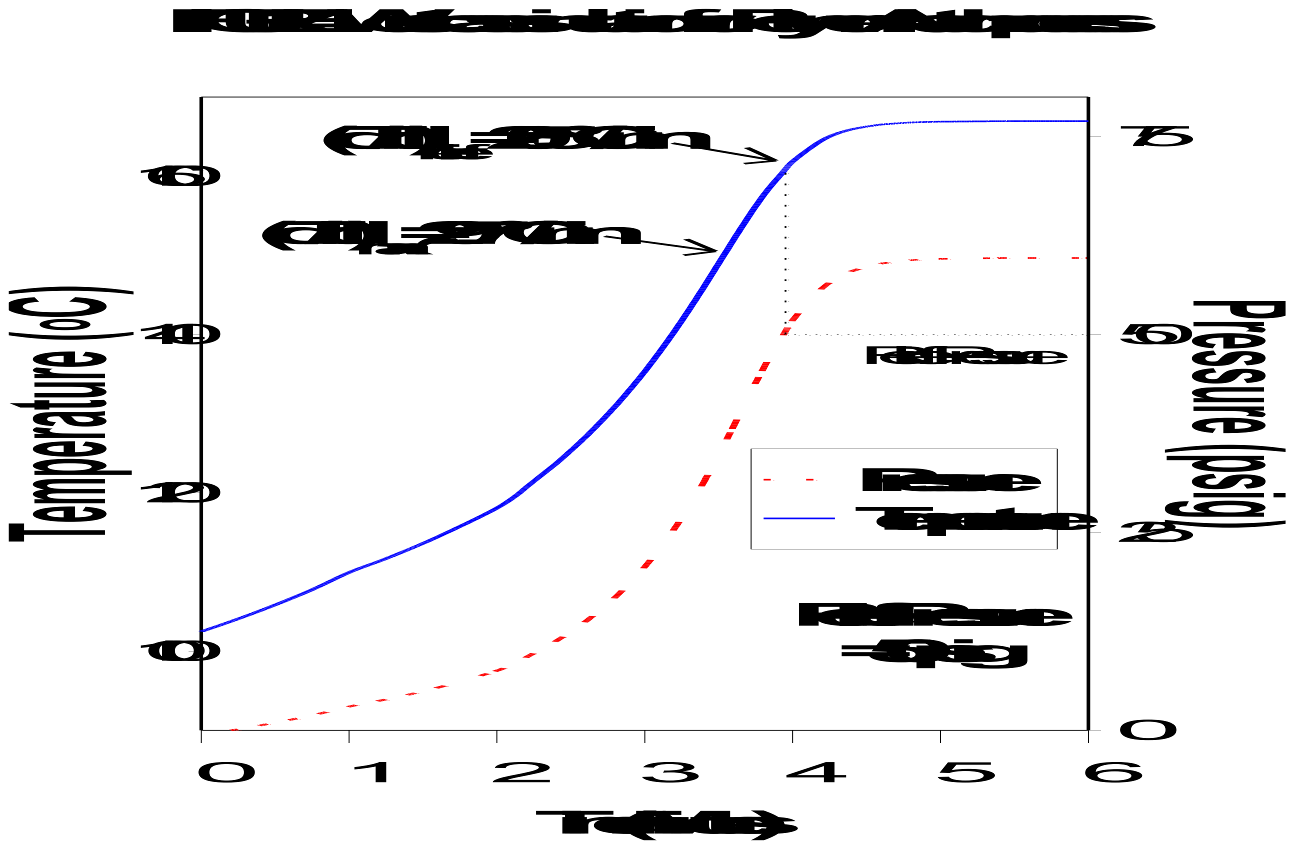
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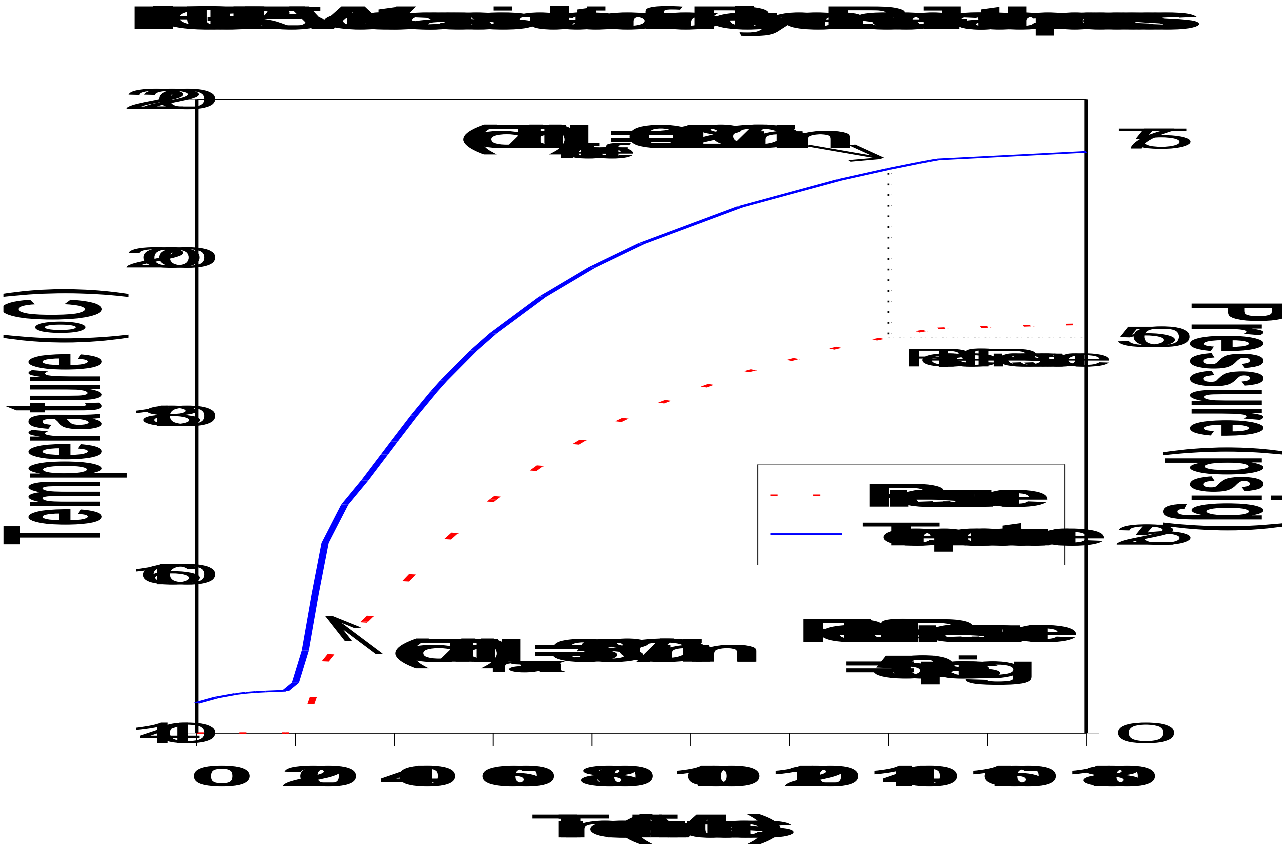
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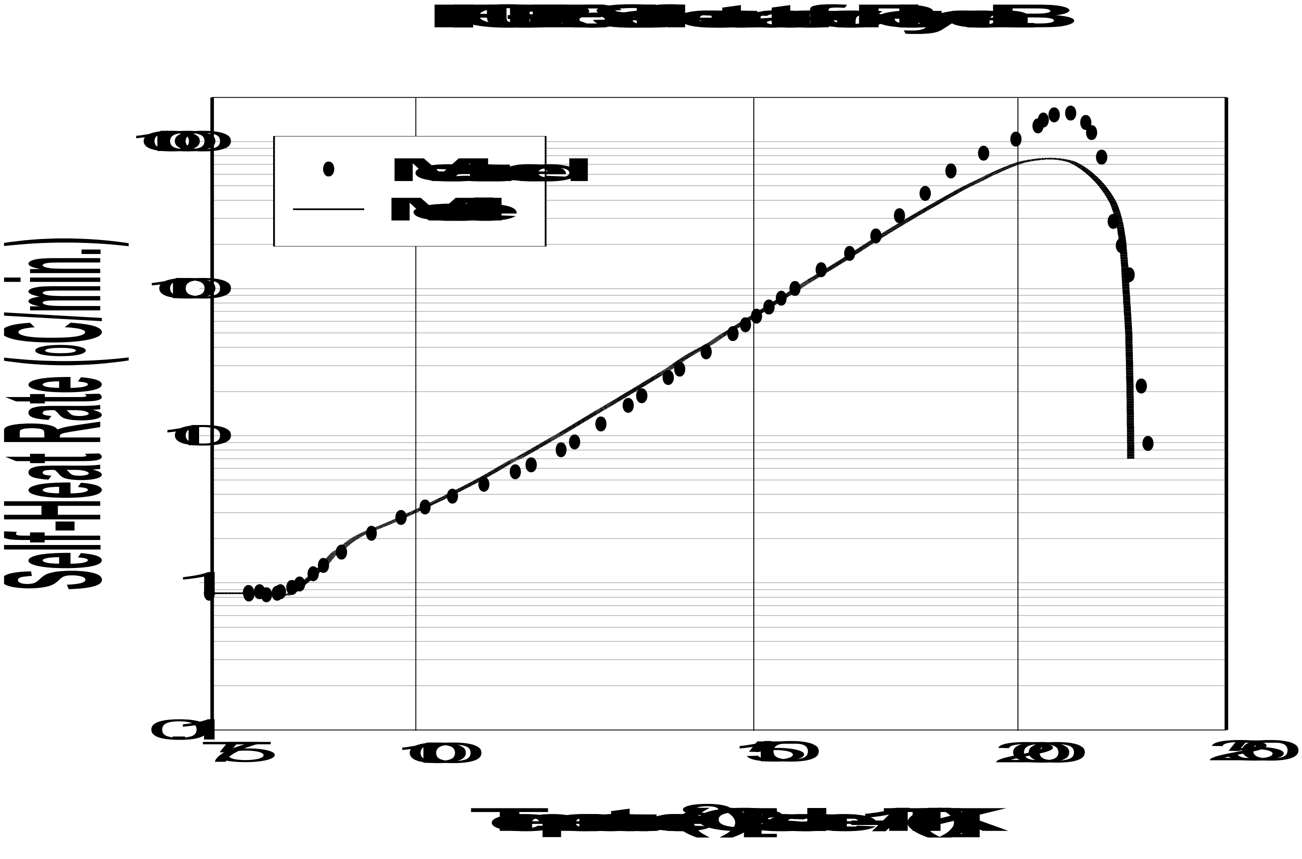
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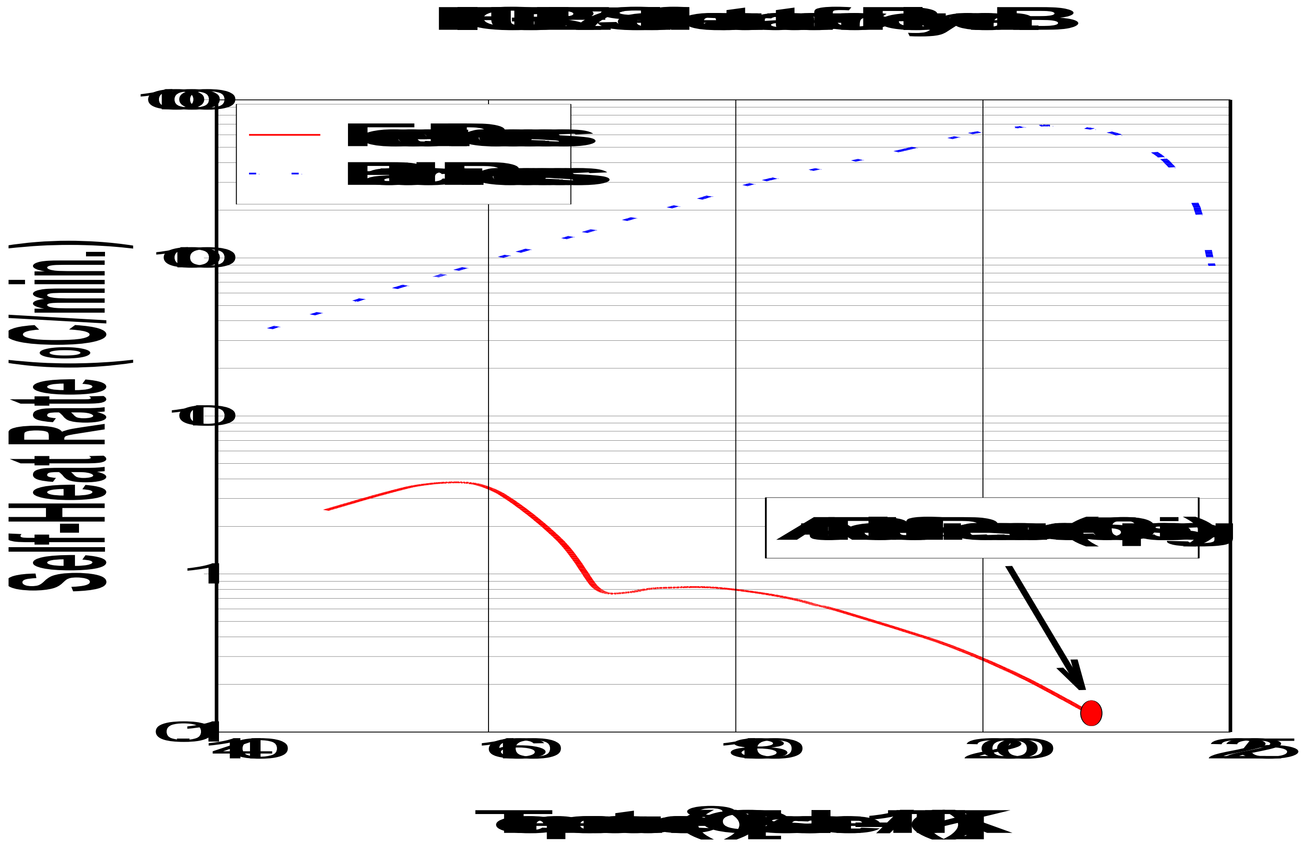
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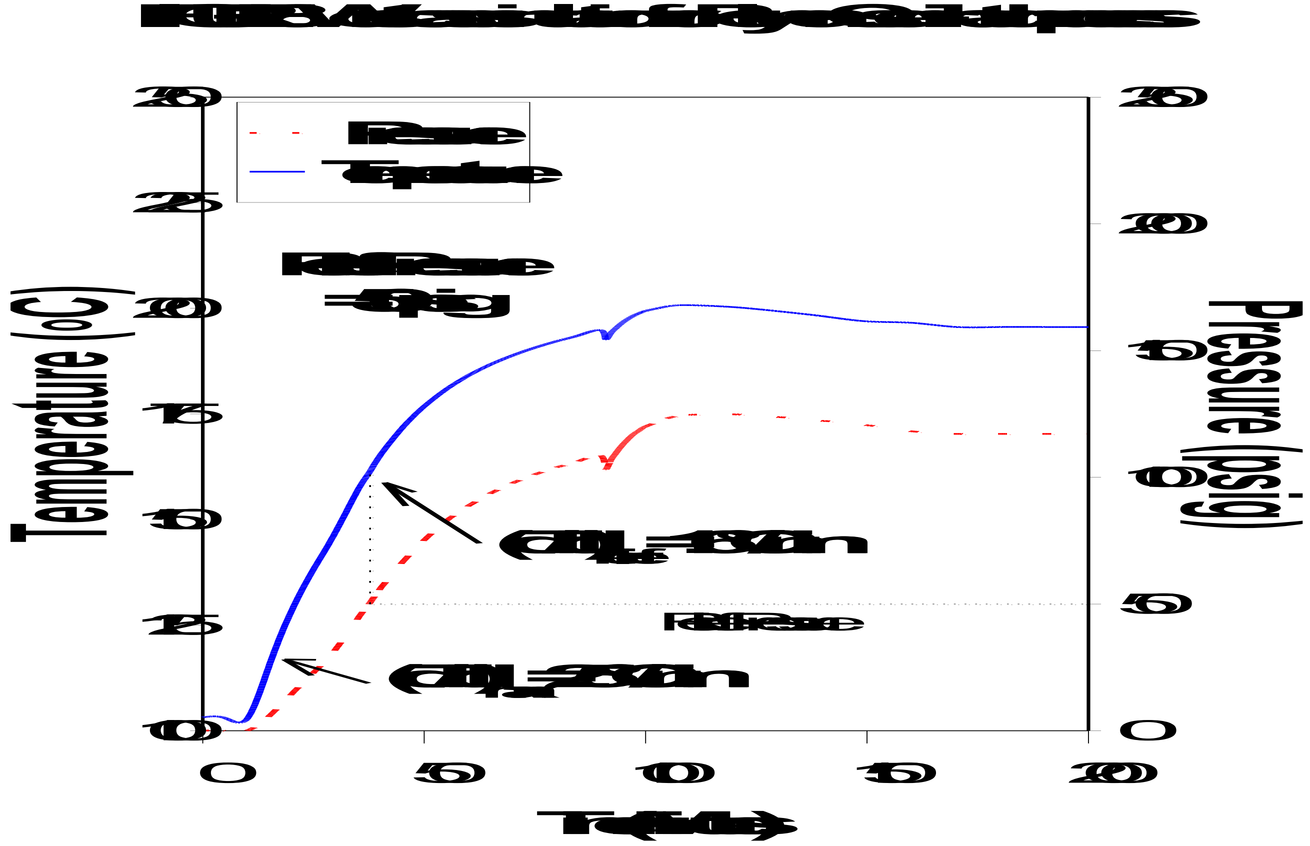
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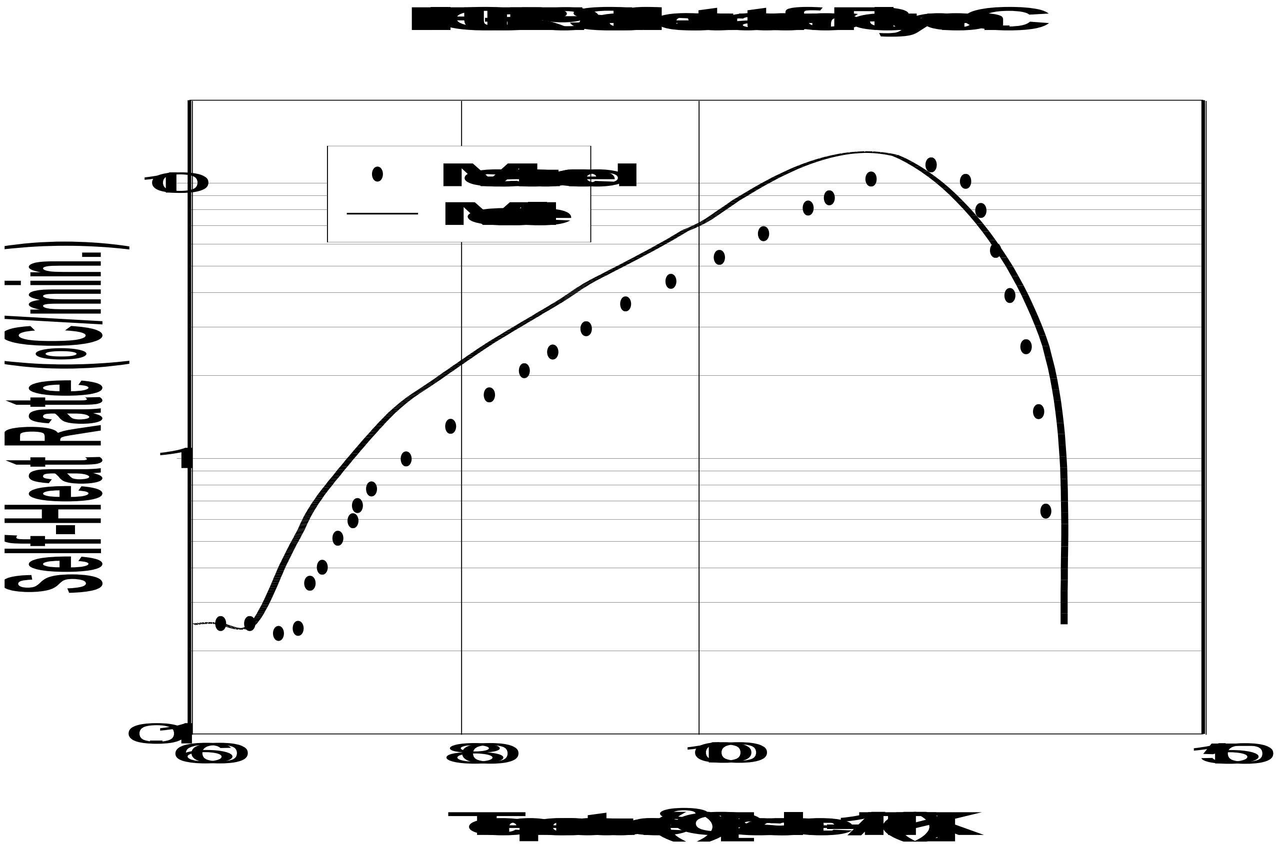
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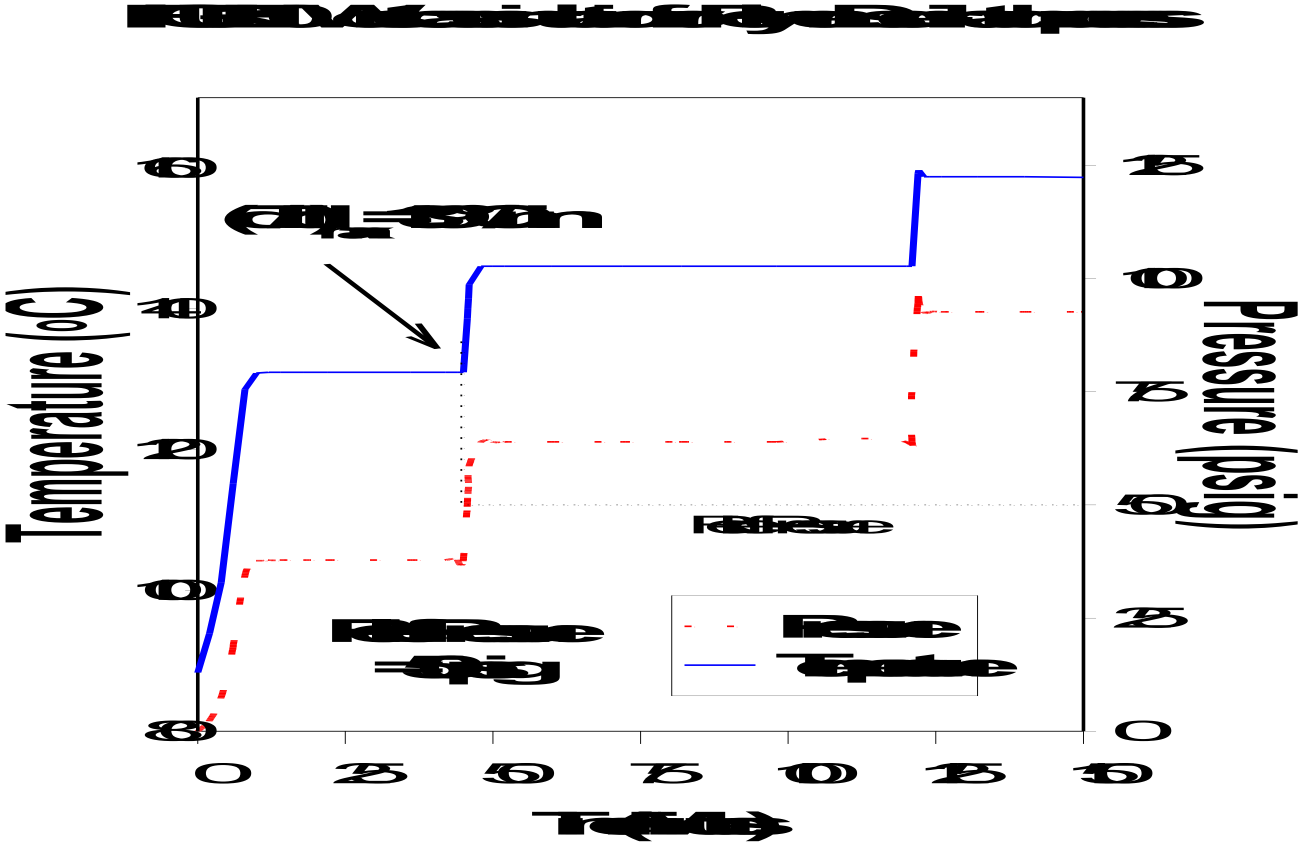
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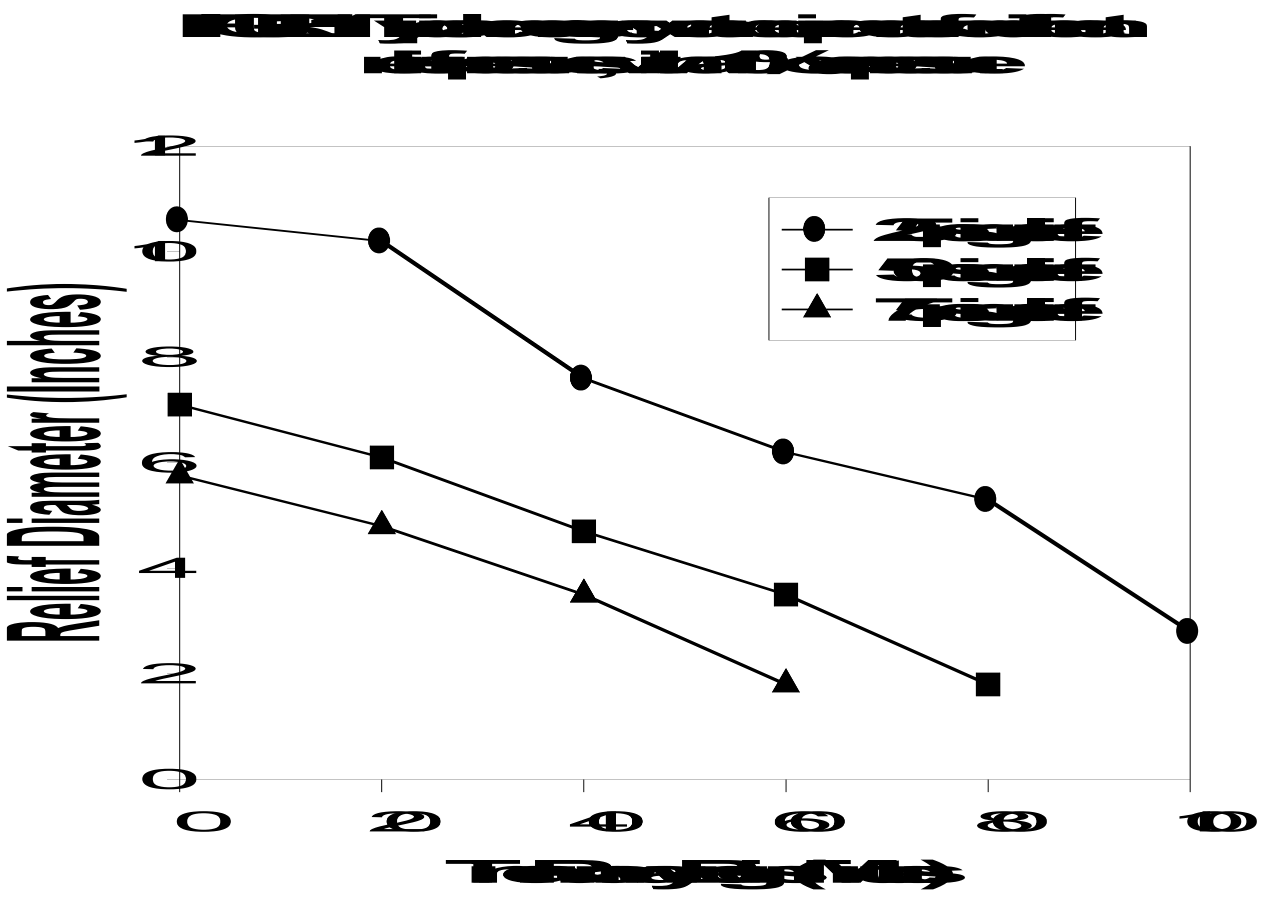
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