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**Understanding Chemical Safety Instruments: Best Practices**

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**Keywords:** reactivity hazards, thermal stability, reaction calorimetry, adiabatic calorimetry, heat of reaction

## Abstract

Industry-standard thermal hazards screening is an effective and cost efficient tool to obtain the data required for the safe scale-up of new or altered chemical processes. Collected data can be used to characterize reaction kinetics, properly size process equipment (e.g. cooling systems, relief devices, condensers, knockout drums, etc.), understand decomposition or unwanted side reactions, guide the selection of safe processing conditions, and calculate many important process-related parameters (i.e. heat of reaction, moles of generated gas, self-accelerating decomposition or polymerization temperatures, and other). This paper illustrates several widely-used thermal hazard screening bench-scale techniques that lend themselves to quickly identifying reactive hazards while providing directly scalable data for chemical process or storage facility design. A case study is presented on a phenol formaldehyde process, which remains an active process in the industry as it relates to a wide variety of uses like ablation, abrasives, coatings, composites, wood bonding, and much more. Example data are presented from various instruments with discussion of how the data are analyzed keeping chemical process safety as a priority throughout the discussion. A further discussion is provided on selection of the appropriate tool based on the testing goals.

## 1. Introduction

This paper discusses three major categories of chemical process safety instruments used by Fauske & Associates, LLC (FAI) for characterizing thermally reactive materials: thermal stability/small scale screening instruments, reaction or isothermal calorimetry tools, and adiabatic calorimetry apparatuses. Combining the information collected from each of these instrument categories results in a comprehensive understanding of present hazards. The primary goal of screening or thermal stability testing is to quickly obtain an understanding of if and at what temperatures reactivity hazards exist. The data collected can quickly show heat flow or mass change data as a function of time and temperature. If a more advanced understanding of the primary, secondary, or decomposition reactions is desired, these instruments can be employed to determine kinetic parameters, or a wide variety of safe processing or storage conditions. Reaction or isothermal calorimeters can be used to complement the thermal stability data, but is a far more advanced technique and is typically used to guide the safe scale up of a new or altered chemical process. This type of calorimetry seeks to quantify the heat evolved and the rate of heat evolution from a chemical process reaction under desired conditions. Adiabatic calorimetry, on the other hand, is used to collect data for undesired runaway reactions that occur

due to some upset scenario (e.g. loss of cooling, fire exposure, reactant accumulation, overcharge, etc.). This data can be used for mitigation such as designing a relief system, or understanding when prevention is the only safe option (Figure 1).

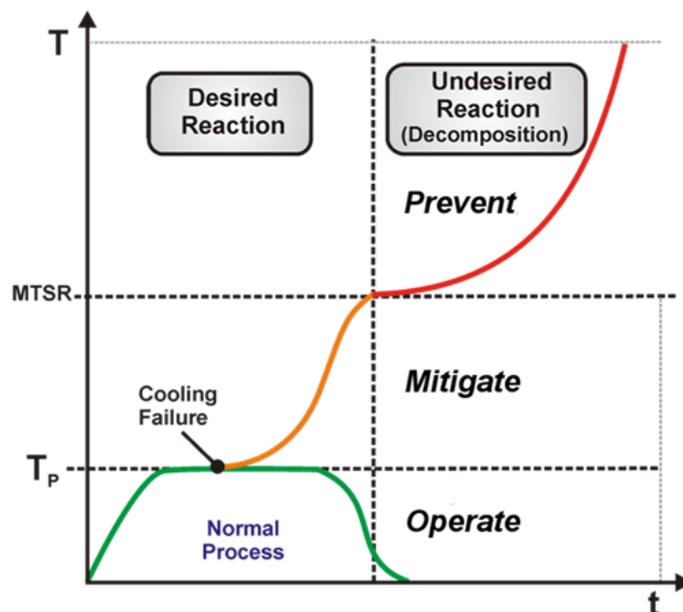


Figure 1 Temperature vs. Time Curve for Understanding Operation vs. Mitigation vs. Prevention

In order to better understand the differences between these categories of instruments and aid in selecting the right tool for the project goal, example phenol formaldehyde reaction data are provided. Over the years FAI has done substantial work characterizing the process safety aspect of phenol formaldehyde reactions.

Producing phenolic resin is a very old but still very active process in the industry. Today phenolic resins see a wide variety of uses such as ablation (heat shields), abrasives, coatings (can lining), composites, felt-bonding, foams, foundry (casting), friction, laminating (PCB), molding, proppants (fracking), refractory, rubber, substrate saturation (paper) and wood bonding (plywood, particle board). In 2001 the worldwide production of phenol formaldehyde resins was greater than  $4 \times 10^6$  metric tons.

There are two types of phenol formaldehyde resins. When the formaldehyde to phenol molar ratio is less than 1, a Novolac resin is formed. These resin reactions are typically acid catalyzed, react to completion, and the resulting product requires a separate crosslinking agent (typically hexamine) to produce the final resin. A Resole resin is formed when the formaldehyde to phenol molar ratio is greater than 1, typically 1 to 3. These reactions are base catalyzed and intentionally not reacted to completion. The Resole product carries pendent methylene hydroxy

moieties (that are not stable in acid) that allow the resin to be self-crosslinking at higher temperatures. It is these reactive groups that make the Resole version of this chemistry particularly hazardous due to this latent but elevated temperature activated reactivity. Figure 2 shows the basic structure of these two resins. This paper presents data collected from various thermal stability/screening, reaction calorimetry, and adiabatic calorimetry experiments.

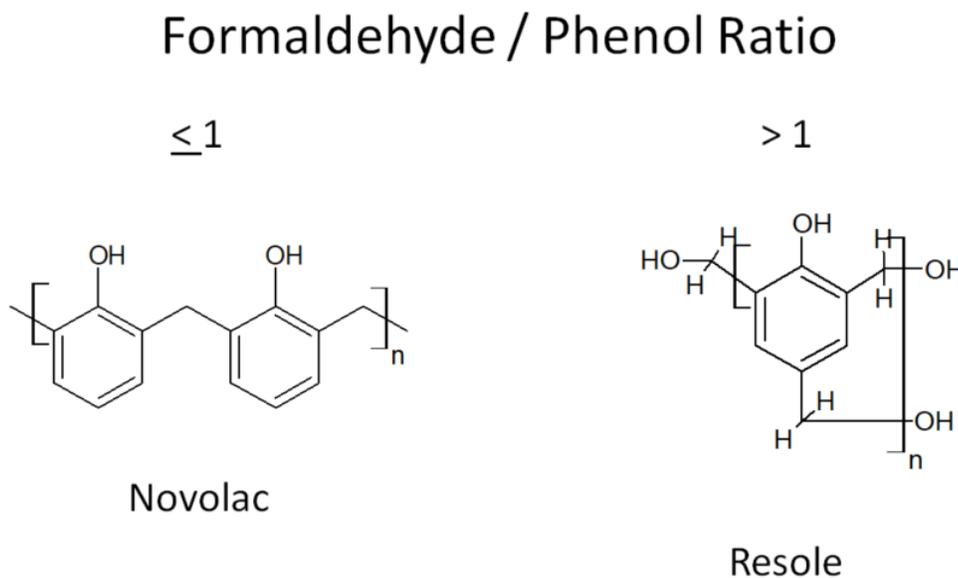


Figure 2      Novolac vs. Resole Resins

## 2. Process Safety Instrument Descriptions

### 2.1. Thermal Screening Instruments

#### 2.1.1. Test Overview

This type of testing involves exposing small samples (starting reagents, intermediates, final products, and samples of process streams) to temperature ramps or isothermal holds while measuring heat flow or change in mass as a function of time or temperature.

#### 2.1.2. Test Objectives

This type of testing is perfect for quickly screening a sample to determine if it has energetic potential, determining reaction kinetics, and calculating a variety of operating and storage parameters (e.g. Self-Accelerating Decomposition Temperature, Activation Energy, Time to Maximum Rate, Heat of Fusion, Melting Temperature, Heat Capacity, Heat of Reaction, etc.).

### 2.1.3. Specific Equipment Description

The primary thermal screening instruments used at FAI are the Differential Scanning Calorimeter (DSC) and the Thermogravimetric Analyzer (TGA) (which can be combined with the DSC). The DSC is a heat flow calorimeter capable of detecting both exothermic and endothermic reactions. This instrument operates differentially by measuring the heat flow difference between the sample container and a reference (inert) sample container; this difference in heat flow is then attributed to the sample. The DSC sample container is typically 10-40  $\mu\text{L}$  in volume and can be operated in a scanning mode (with a constant temperature ramp rate) or isothermally. The instrument can be run up to 500°C. It is typically operated in a closed cell fashion (i.e. the reactive mixture is entirely contained throughout the test) and the sole measured parameters are heat flow, time, and temperature. The TGA measures changes in sample mass as a function of temperature with high levels of sensitivity, and uses sample pans that are 50 to 100  $\mu\text{L}$  in volume. The TGA is capable of heating to 1400°C. The TGA can be combined with the DSC where it monitors mass, temperature, time, and heat flow. The TGA (simultaneous DSC-TGA) is an open cell test where the mass loss associated with decomposition or vaporization of test samples is measured. Table 1 summarizes advantages and disadvantages of these types of instruments to guide tool selection.



Table 1 Advantages and Disadvantages of Thermal Screening Instruments

<b>Advantages</b>	<b>Disadvantages</b>
<ul style="list-style-type: none"><li>- DSC and TGA testing are economical and quick</li><li>- The instruments are sensitive to even small changes in heat flow or mass (can measure mild and energetic reactions)</li><li>- Small sample size can be an advantage if sample quantities are limited or expensive</li><li>- Multiple materials of construction for material compatibility concerns</li><li>- Simple to operate</li></ul>	<ul style="list-style-type: none"><li>- No stirring capabilities</li><li>- No pressure measuring capabilities</li><li>- Cannot measure reactions that occur upon adding one component to another (only batch loaded reactions) or reactions that occur readily at room temperature</li><li>- It can be difficult to obtain a representative sample for complex mixtures</li></ul>

## 2.2. Reaction Calorimetry Instruments

### 2.2.1. *Test Overview*

This type of testing involves closely mimicking a desired process by maintaining temperature control on a bench scale in order to collect information on the heat (and off-gas) evolved and the rate of heat evolution from a chemical process. Mimicking the process could mean performing temperature control or ramps, pH control, controlled or all-in additions of various reagents or catalysts, etc., per the process procedures.

### 2.2.2. *Test Objectives*

This type of testing is essential for safely scaling up a chemical process in order to manage the energy or heat flux that the intended reaction produces. This is particularly the case when the chemical transformation is exothermic in nature. The data collected from this type of testing is useful for ensuring that the cooling capacity (whether from a jacket, a condenser, or a side loop heat exchanger) is sufficient for the projected heat flux rate. Furthermore, understanding the total energy potential due to the desired reaction is critical should the cooling system fail.

Data collected from reaction calorimetry experiments can also provide a unique window into the trajectory of the reaction. Processing parameters such as addition rate, reaction type (i.e. batch vs. semi-batch), temperature, mixing challenges, and reaction temperature can be studied in the reaction calorimetry instruments to guide scale up and provide recommendations for process improvement.

Simply put, the primary uses for reaction calorimetry data are: determining heat flux and heat of reaction for process scale up and cooling capacity requirements, collect data for kinetic evaluations on more complex systems, understanding safety implications for process changes (swapping solvents, changing addition rates, determining optimal process temperature, etc.), heat capacity determination, and projected adiabatic temperature rise.

### 2.2.3. Specific Equipment Description

The primary reaction calorimetry instruments used at FAI are the Mettler-Toledo RC1, the ChemiSens CPA202, and the Thermal Hazards Technology  $\mu$ RC. The RC1 is a heat flow calorimeter where the heat leaving or entering the reactor is characterized by  $U \cdot A \cdot (T_r - T_j)$  where  $U$  is the overall heat transfer coefficient,  $A$  is the area of heat transfer, and  $T_r$  and  $T_j$  are the temperature of the reactor and jacket, respectively. The temperatures are measured, the area of heat transfer is known by geometry, and the heat transfer coefficient is determined by calibration using an immersed calibration heater. The reactor primarily utilized is 500 mL in volume and made of borosilicate glass. The temperature range is -73 to 230°C, operates at ambient pressure, and agitation is completed using a magnetic drive. The inserts have a wide variety of material of construction. Automated reagent additions can be performed with integrated balances using positive displacement pumps or solenoid valves. Off gas can be measured using an integrated flow meter and pH control is possible.



The CPA202 is a heat flux calorimeter that provides a true heat flow signal without requiring calibration. The heat transfer surface is entirely through the bottom of the reactor via Peltier technology and is independent of the fluid heat transfer coefficient. The temperature range of this instrument is -50 to 200°C and the currently used version has pressure capabilities up to 100 bar. The volume of the reactor is 250 mL. Agitation is completed using a magnetic drive, and there is a variety of impellers and inserts. Additions can be performed against pressure using a syringe pump, and the reactor has the capability of being paired with a gas induction impeller and gas uptake rig for gas reactions. Both the RC1 and CPA202 can be operated isothermally or by undergoing temperature scans.

The  $\mu$ RC is a differential heat flow calorimeter that utilizes glass or metal (stainless steel or Hastelloy) vials that are approximately 1.5 mL in volume. The temperature range of the instrument is -5 to 150°C, and can work with pressures up to 10 bar. Modes of operation for this instrument include isothermal with steps, titration with an integrated syringe pump, scan and hold, and heat capacity determination. Table 2 summarizes advantages and disadvantages of these three types of instruments to guide tool selection.

Table 2 Advantages and Disadvantages of Reaction Calorimetry Instruments

<b>Advantages</b>	<b>Disadvantages</b>
<ul style="list-style-type: none"> <li>- Variety of temperature and pressure capabilities</li> <li>- Many options for material of construction for wetted parts</li> <li>- The RC1 and CPA202 have a variety of inserts to promote good mixing</li> <li>- Capable of pH monitoring in RC1 and CPA202</li> <li>- Gas reactions are easily studied in the CPA202</li> <li>- <math>\mu</math>RC is excellent for quickly measuring sample heat capacity and performing compatibility matrices</li> <li>- CPA202 (~40 mL) and <math>\mu</math>RC (~0.1 mL) required smaller minimum volumes for measuring reactions</li> <li>- Testing can be complex to closely follow a process procedures</li> </ul>	<ul style="list-style-type: none"> <li>- The <math>\mu</math>RC uses a magnetic stir plate and stir bar and the entire reaction vial is enclosed so it is difficult to understand if mixtures are well mixed or not</li> <li>- Difficult to add solids during a reaction in the CPA202 and impossible in the <math>\mu</math>RC</li> <li>- Difficult to collect qualitative observations in the CPA202 and impossible in the <math>\mu</math>RC</li> <li>- Requires more sample which can be an issue if materials are hard (or expensive) to source</li> <li>- The RC1 has a minimum volume for measuring reactions</li> <li>- The CPA202 sits in an isothermal bath so addition lines can be long making it difficult to add small quantities of materials</li> <li>- RC1 and CPA202 testing requires a skilled user</li> </ul>

## 2.3. Adiabatic Calorimetry Instruments

### 2.3.1. Test Overview

Adiabatic calorimetry experiments consist of simulating a process upset scenario (i.e. fire exposure, loss of cooling, overcharging of a reagent or catalyst, an all-in addition of a reagent, etc.) and measuring the full chemical potential achievable. This type of testing measures the total temperature and pressure (and thus the temperature and pressure rates) rises as a function of time for exothermic reactions. The collected data is representative of what a full scale vessel could experience when all the heat generated from the reaction remains within the sample.

A key parameter used to describe adiabatic calorimetry studies is the phi-factor ( $\phi$ ). The phi-factor is the ratio of the thermal inertia of the sample to the thermal inertia of the sample holder (i.e. how much heat is absorbed in heating the test cell vs. heating the sample). Low phi-factor experiments are ideal for direct scale up of the data as a correction is not needed (or is small) to account for the heat loss to the test cell. This maximizes the quality of the data

collected over the temperature rise by more closely simulating the phi-factor observed in a large scale process vessel.

### 2.3.2. Test Objectives

This type of testing is essential for safely scaling up a chemical process in order to ensure that the new or existing vessels to be used are equipped with the proper safety relief valves or rupture discs to mitigate the consequences of a process failure.

The temperature and pressure rise rates from low phi-factor experiments, as well as information on the flow regime are key parameters in designing or determining the adequacy of a relief system for ensuring overpressurization of a vessel does not occur for a given upset scenario.

In addition to relief system design, this type of data can be used to calculate a variety of parameters (e.g. self-accelerating decomposition temperature, adiabatic temperature rise, moles of noncondensable gas generated, temperature of no return, activation energy, time to maximum rate, heat of reaction, etc.).

### 2.3.3. Specific Equipment Description

FAI utilizes three adiabatic calorimeters: the Accelerating Rate Calorimeter (ARC), The Vent Sizing Package 2 (VSP2), and the Advanced Reactive System Screening Tool (ARSST). The ARC utilizes a 10 mL spherical test cell constructed of stainless steel, Hastelloy C, titanium, or tantalum. Typically ARC testing is conducted in a closed cell mode. Therefore, the pressure generated by a sample must be contained within the test cell. To accomplish this, ARC test cells use heavy walled test cells capable of withstanding pressures up to 3,000 psi or more (and the corresponding high temperatures). As a consequence, the phi-factor of the system is relatively high. The combined mass of the sample and the test cell are kept adiabatic, not just the sample itself. For this reason, care must be taken when applying this data to large scale hazard evaluations. The ARC can be run in two modes of operation: a heat-wait-search mode or an isothermal mode and is typically batch loaded. The ARCs used at FAI have no stirring capabilities and are primarily used for pure component testing. The data collected by the ARC is typically used in ways similar to that collected by the thermal stability/screening instruments.

The VSP2 is a low phi-factor adiabatic calorimeter capable of simulating abnormal process conditions using either an open or closed cell option. The test cells used are typically 110-120 mL in volume and have a wide variety of materials of construction and test cell configurations (e.g. baffles for immiscible solutions, dip tube for subsurface additions, a pluggable vent line for adding solids prior to performing a closed cell test, etc.). The test cell is

thin walled and very lightweight allowing the test to have a low phi-factor. The test cell is fitted with a guard heater (for maintaining adiabatic conditions) and auxiliary heater (for imposing a background heating rate or heating to a process temperature) and sits in a 4 liter containment vessel. For a normal test setup the reactions can be tracked to above 500°C and up to approximately 1,500 psi. A pressure control box is used to balance the pressure on the outside of the test cell with the pressure on the inside (for closed cell tests) so the thin walled cells do not rupture. Stirring is typically performed using a Super Magnetic Stirrer (capable of stirring up to 10,000 cps) but can also be performed using a mechanical overhead agitator. The VSP2 can be combined with auxiliary equipment such as an additional containment vessel, cooling coil, syringe pump, or piston to perform a wide variety of tests.

The ARSST is also a low phi-factor calorimeter used to obtain critical upset process design data. The ARSST typically utilizes a sample size of 5-10 grams in a lightweight glass test cell with a volume of approximately 10 mL. The test cell is outfitted with a belt heater (used to heat the sample through a preprogrammed temperature scan) and then installed in 350 mL containment vessel. The containment vessel and test cell are easily portable allowing for the entire test to be setup in an inert environment (via a glove box) or placed in a freezer prior to testing (for sub ambient starting temperatures). Tests are typically run using open test cell methodology. In this test configuration, the test cell is vented to the containment vessel. Volatilization of the test sample can partially be prevented by imposing an inert backpressure on the containment vessel. The standard ARSST vessel is capable of measuring up to 1,000 psig and the K type thermocouples submerged in the sample can read above 500°C. Table 3 discusses the key advantages and disadvantages of adiabatic calorimetry techniques.

Table 3 Advantages and Disadvantages of Adiabatic Calorimetry Instruments

<b>Advantages</b>	<b>Disadvantages</b>
<ul style="list-style-type: none"><li>- Variety of temperature and pressure capabilities</li><li>- Many options for material of construction for wetted parts</li><li>- Inherent safety features and instrument robustness aids operator safety</li><li>- The VSP2 cell has a variety of configurations for special test design</li><li>- Excellent mixing capabilities in the VSP2</li><li>- ARSST and VSP2 can be configured in a variety of ways for special test design like controlled additions</li><li>- The VSP2 can be run as an open or closed test</li><li>- Can track reactions to high temperatures and pressure to fully characterize reactivity</li><li>- VSP2 and ARSST are low phi-factor apparatuses that provide data which are directly scalable</li></ul>	<ul style="list-style-type: none"><li>- Very limited stirring capabilities in the ARC</li><li>- Mixing in the ARSST could be challenging for viscous mixtures or suspensions</li><li>- The ARC is primarily a closed cell test and the ARSST is primarily an open cell test</li><li>- It can be difficult to separate the desired vs. undesired reactions</li></ul>

#### **2.4. Key Differences Between Reaction and Adiabatic Calorimetry Data**

Collecting both reaction and adiabatic calorimetry data helps to completely characterize a chemical process by understanding its full reactive potential. Table 4 covers the common differences between the data collected from reaction and adiabatic calorimetry experiments.

Table 4

## Distinguishing Between the Data Collected from Reaction and Adiabatic Calorimetry Tests

Parameter	Reaction Calorimetry	Adiabatic Calorimetry
Primary Measured Parameter	Heat Flow	Temperature and Pressure Rise Rates
Primary Controlled Parameter	Temperature	Heat Flow Across Cell ( $\Delta Q=0$ )
Test Goal	Mimic the desired process	Mimic an upset scenario
Adiabatic Temperature Rise	Adiabatic temperature rise is inferred from heat associated with intended reaction	Adiabatic temperature rise is measured and may be higher than that determined in reaction calorimetry testing due to the potential to initiate secondary reactions
Heat of Reaction	Directly Measured by Integrating the Heat Flow Signal	Calculated from the Measured Adiabatic Temperature Rise – May be greater than that measured in the reaction calorimetry experiment due to also measuring secondary or undesired reactions
Data for Scale-Up	Used to determine the scaled required cooling capacity for the desired reaction  Can also use this data to guide optimal process procedures (ensuring safe scale up)	Used to quantify undesired reactions to understand mitigation strategies (e.g. relief system design or understanding quantities of potential noncondensable gas) or when an upset scenario must be prevented (i.e. unventable situations)  Can also use this data to characterize flow regimes for designing effluent handling systems
Instrument Robustness	Moderate to Low. These instruments are typically more expensive than their counterpart and require a skilled operator to safely perform without damaging the instrument, especially when processes are completely new and other thermal data is not available	High. These instruments have high temperature and pressure capabilities and can oftentimes be run unattended. The parts are designed to be easily replaceable and can handle a wide variety of corrosive and other extreme situations without harm to the operators

### 3. Phenol Formaldehyde Case Study

#### 3.1. Test Introduction

The wide assortment of uses for phenol formaldehyde resins and the latent heat present in the resole variety, makes this type of chemistry an interesting case study for examining the different types of process safety instruments. This case study will present thermal stability, reaction calorimetry, and adiabatic calorimetry data from a generic phenol formaldehyde process. The instruments used to collect the process safety data were the Mettler-Toledo RC1, the FAI VSP2, and the TA Instruments Q2000 DSC.

#### 3.2. Test Recipe

A generic phenol formaldehyde recipe was generated maintaining the formaldehyde to phenol ratio around 2.2 for a resole resin. The recipes used during testing were roughly the following (Table 5):

Table 5 Phenol Formaldehyde Test Recipe

Component	Composition (wt.%)
Phenol	31.5
37% Formaldehyde	44.1
Water	20.5
Catalyst (50% Sodium Hydroxide)	3.9

#### 3.3. Test Design

##### 3.3.1. *P-F Reaction Calorimetry Experiment*

For the reaction calorimetry experiment, the RC1 reactor was filled with phenol, formaldehyde, and water and heated to 50°C. The catalyst was then added to the reactor over 10 minutes and the mixture was stirred for 12 hours at a constant 50°C.

##### 3.3.2. *P-F Thermal Screening Experiment*

A sample was pulled from the final reaction mixture generated in the reaction calorimetry experiment and scanned at a rate of 2°C/min up to 400°C.

### 3.3.3. *P-F Adiabatic Calorimetry Experiment*

For the adiabatic calorimetry experiment, the VSP2 test cell was filled with phenol, formaldehyde, and water and heated to 50°C. The catalyst was then injected to the test cell and the reaction mixture was allowed to run away adiabatically.

## 3.4. Collected Data

### 3.4.1. *P-F Reaction Calorimetry Experiment*

The data collected from the RC1 experiment are available in Figure 3 (overall experiment) and Figure 4 (expanded plot). The signals plotted are reaction mass, heat flow, reactor temperature, and heat conversion vs. time.

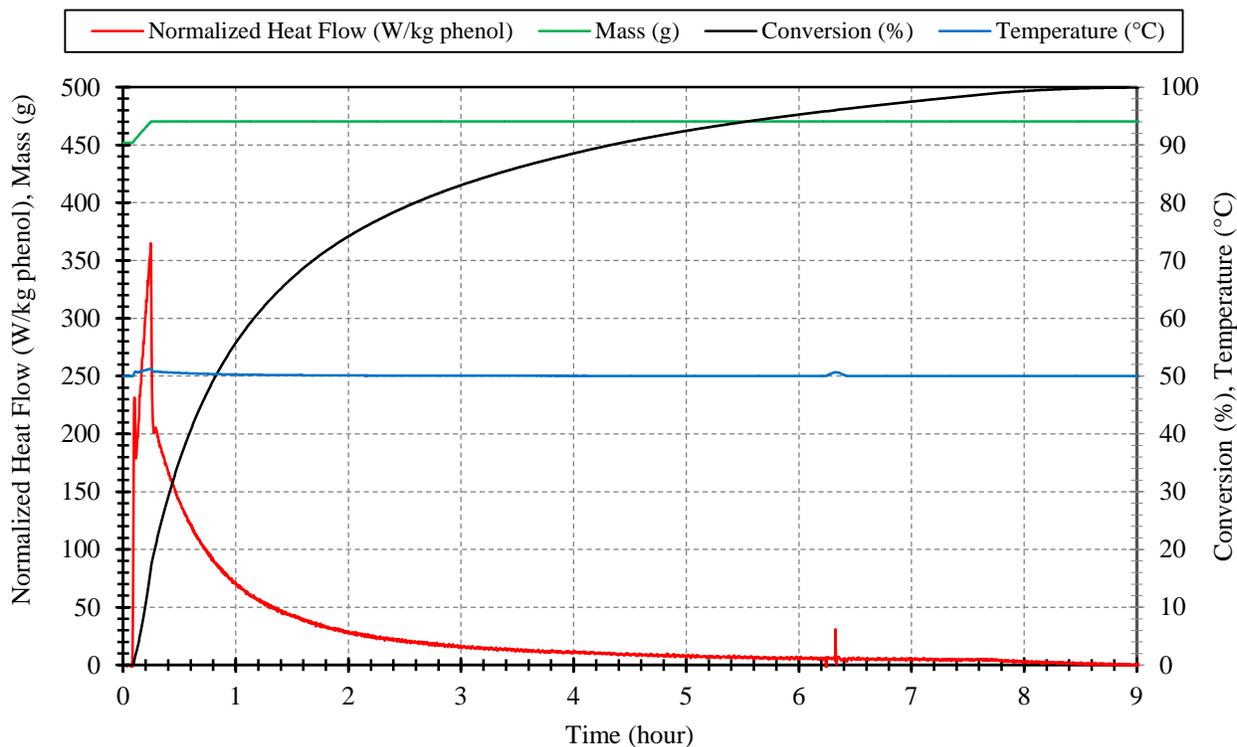


Figure 3 Overall Phenol Formaldehyde Experiment

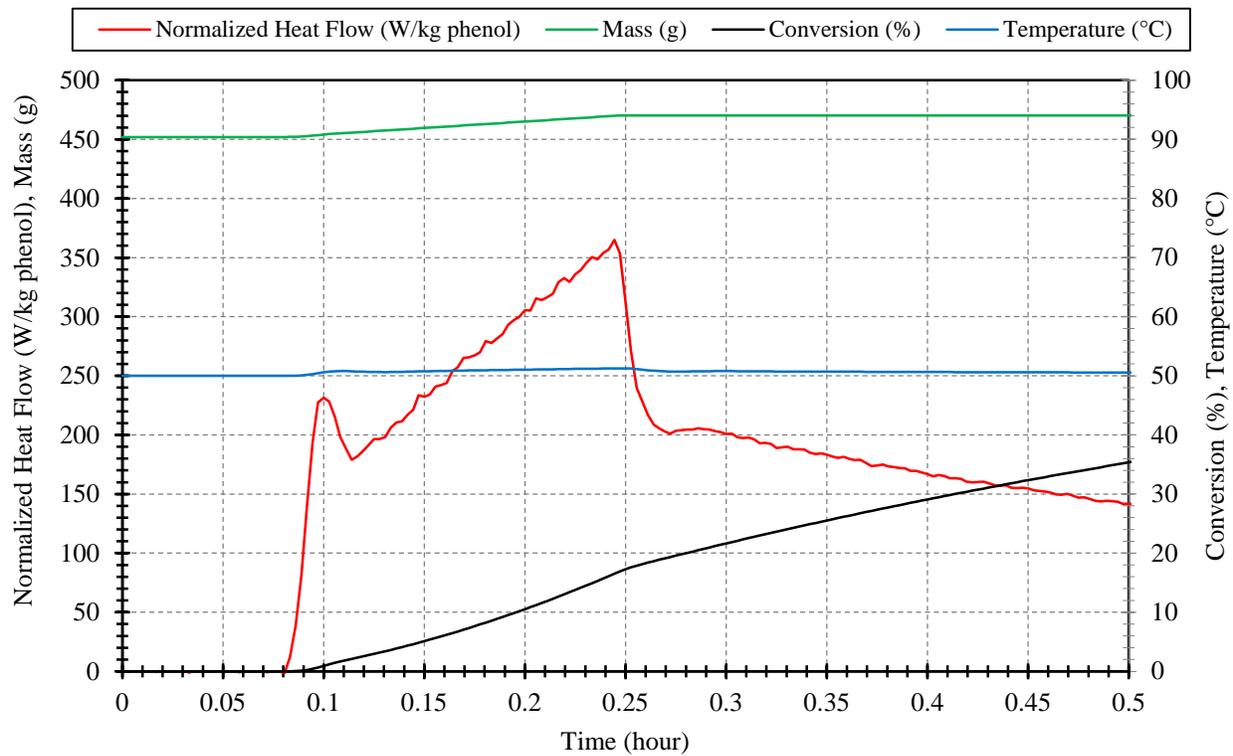


Figure 4 Expanded Phenol Formaldehyde Experiment

### 3.4.2. P-F Thermal Screening Experiment

The data collected from the DSC experiment on the post reaction mixture from the RC1 reaction are available in Figure 5 (heat flow vs. temperature).

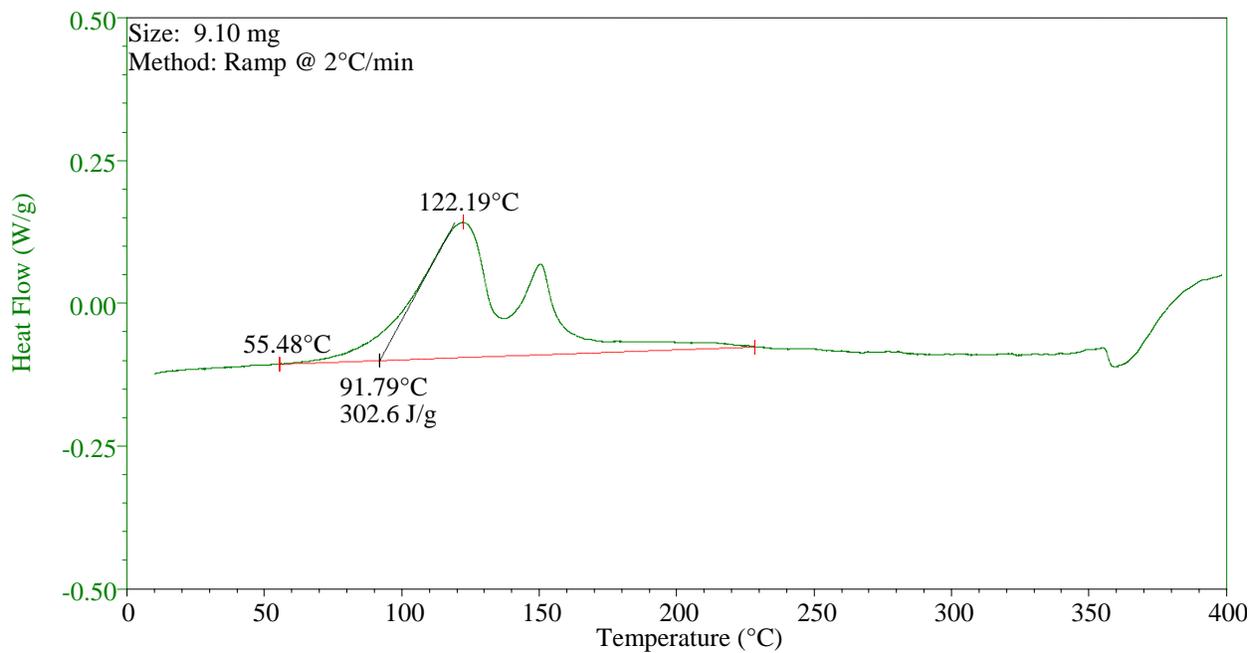


Figure 5 Thermal Screening of Post Reaction Mixture

### 3.4.3. *P-F Adiabatic Calorimetry Experiment*

The data collected from the VSP2 experiment are available in Figure 6 (temperature vs. time) and Figure 7 (temperature rise rate vs. temperature).

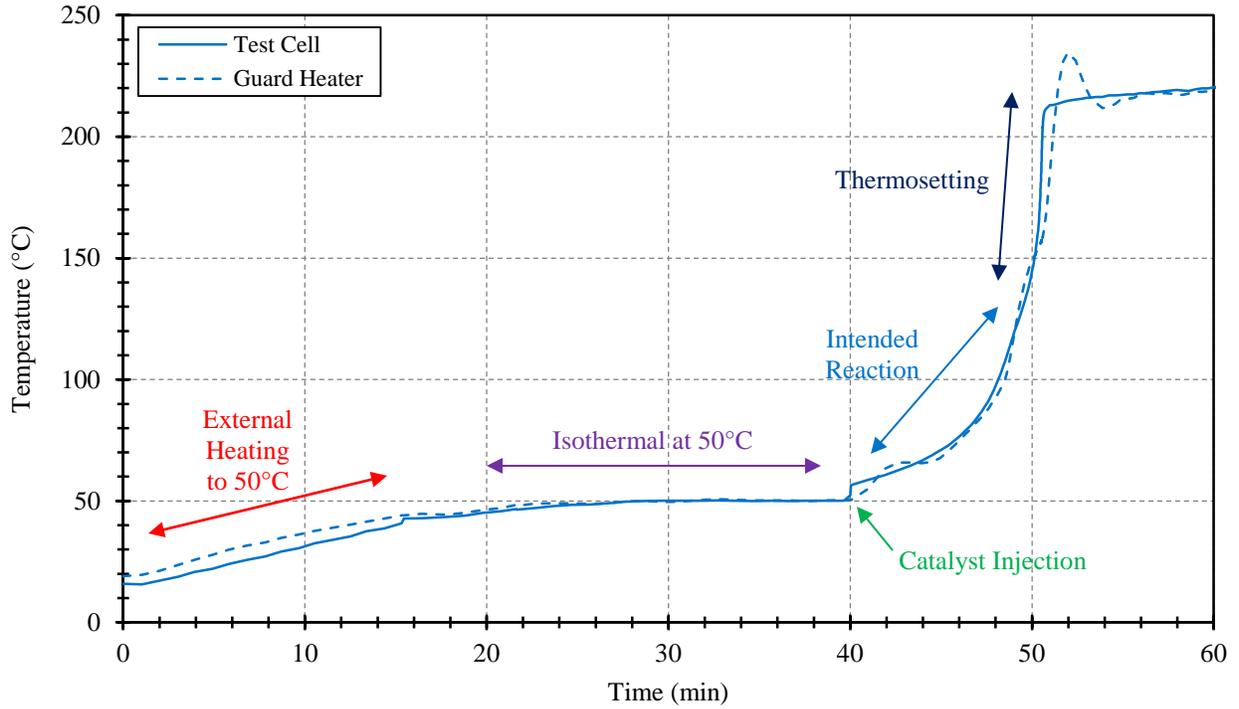


Figure 6 Temperature vs. Time for Adiabatic Runaway Reaction

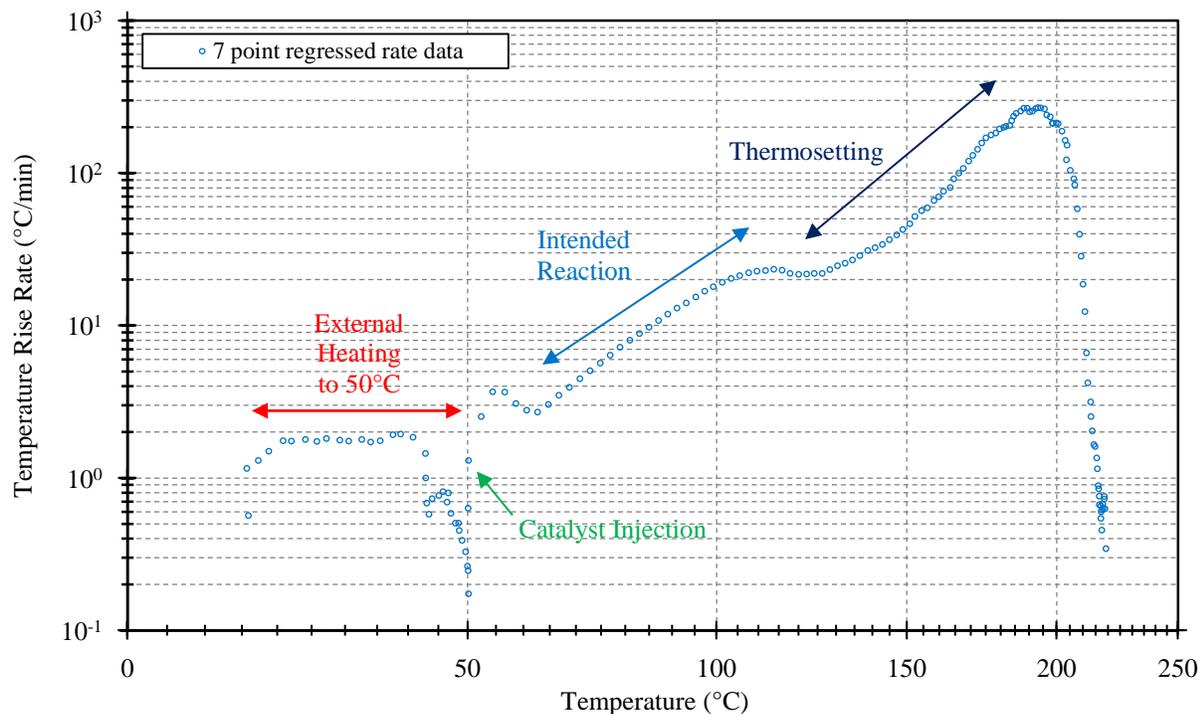


Figure 7 Temperature Rise Rate vs. Temperature for Adiabatic Runaway Reaction

#### 3.4.4. Reaction Calorimetry Results and Discussion

Figure 3 above shows the normalized (W/kg phenol) heat flux profile for a batch reaction at 50°C of this recipe initiated by a 10 minute addition of the catalyst. Figure 4 shows an expanded plot where the addition of the catalyst is clearly visible. Phenol is a weak acid while 50% sodium hydroxide is a strong base so the formation of sodium phenolate (the active species in the polycondensation) is a rapid and complete reaction. The sloped appearance of the heat flow profile during the catalyst addition is due to the growing rate of the polycondensation reaction underlying the addition limited kinetics of the phenol-caustic reaction (square-wave response).

The area under the heat flow ( $\dot{Q}$ , W) profile curve represents the total heat (Q, J) from the reaction. Integrating this signal yields a normalized heat of reaction of -902 kJ/kg phenol (Equation 1 divided by the mass of phenol). Dividing the total heat by the thermal mass (total reaction mass, m in kg, multiplied by the post reaction heat capacity,  $C_p$  in kJ/kg/K) as shown in Equation 2, calculates the theoretical temperature rise under adiabatic conditions due to the intended heat of reaction ( $\Delta T_{ad}$ ). For this recipe the calculated adiabatic temperature rise was +91°C.

$$Q = \int_{t_0}^{t_f} \dot{Q} dt \quad (1)$$

where

$$\begin{aligned} Q &= \text{heat (J)} \\ \dot{Q} &= \text{heat flow (W)} \\ t_f &= \text{time at end of reaction (s)} \\ t_0 &= \text{time at beginning of reaction (s)} \end{aligned}$$

$$\Delta T_{ad} = \frac{Q}{m C_p} \quad (2)$$

where

$$\begin{aligned} \Delta T_{ad} &= \text{calculated adiabatic temperature rise (}^\circ\text{C)} \\ m &= \text{total reactive mass (g)} \\ C_p &= \text{post reaction heat capacity (J/g/K)} \end{aligned}$$

This shows that even simply considering the intended heat of reaction, there is a large adiabatic potential. As the reaction is being completed at 50°C, a loss of cooling upset scenario could result in a temperature rise to 141°C. Considering that the dominating vapor component of this process is water, the vapor pressure could reach at least 371 kPa.

Outside of determining the reaction mass heat capacity, heat of reaction, and projected adiabatic temperature rise, the collected heat flux data can be useful for selecting large-scale process equipment.

Assuming the reaction was being scaled up to a 1,000 kg phenol recipe in a 5,000 liter reactor with a 1.75 m diameter, the heat transfer capabilities of various tanks and a condenser can be determined and compared to the heat flux profile of the reaction. The cooling capacity rate of some example process equipment can be calculated according to Equation 3.

$$\dot{Q}_c = U \cdot A \cdot \Delta T \quad (3)$$

where

$$\dot{Q}_c = \text{cooling capacity (W)}$$

U	=	heat transfer coefficient (~ 300 W/m <sup>2</sup> /K for a stirred glass reactor, ~500 W/m <sup>2</sup> /K for a stirred hastelloy reactor, and ~1000 W/m <sup>2</sup> /K for a stirred stainless steel reactor)
A	=	heat transfer area (m <sup>2</sup> )
ΔT	=	maximum temperature differential between the cooling fluid in the jacket and the reaction mixture (°C)

For this example, assume that the heat transfer area is 9 m<sup>2</sup> and the available maximum temperature differential is 50°C (assuming the cooling fluid is 0°C for the 50°C reaction temperature). This means that the available cooling capacity through the vessel jacket is 135 kW for the glass reactor, 225 kW for the hastelloy reactor, and 450 kW for the stainless steel reactor. Normalizing these values by the scaled phenol content (1,000 kg phenol), results in normalized cooling capacities of 135, 225 and 450 W/kg phenol, respectively. The same analysis could be completed for a condenser. Assume a condenser for the same size vessel has a heat removal capacity of 1,076 kg water/hr (672,236 W). This normalized cooling capacity limit by reflux for the 1,000 kg phenol recipe is 672 W/kg phenol.

Plotting the normalized cooling capacity lines against the normalized heat flow data collected from the reaction calorimetry experiment gives guidance as to what type of vessel the process can be run in. This is available in Figure 8. The proper selection of process equipment relies on the fact that the cooling capacity of the reactor and cooling jacket or condenser is greater than the reactive heat at a given addition rate.

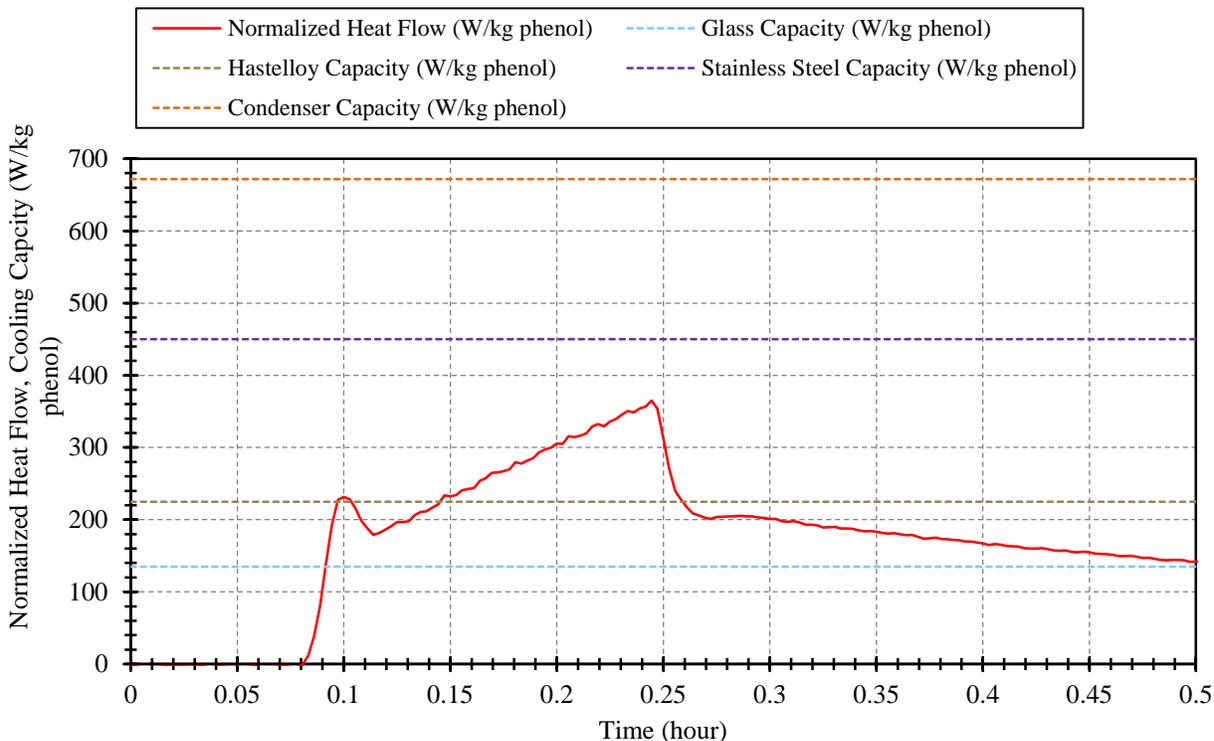


Figure 8 Phenol Formaldehyde Experiment: Catalyst Addition with Example Cooling Capacity Limits for Various Vessels and a Condenser

### 3.4.5. Thermal Screening Results and Discussion

Looking at the data collected from the DSC scan on the post reaction mixture (Figure 5), it is clear that there is substantial energy remaining in the final product. The results show latent crosslinking energy from the pendent methylene hydroxy groups in the Resole reaction mass. Taking the integrated energy from the scan, 302.6 J/g, and dividing by the heat capacity of the reaction mass tested (measured to be 3.1 J/g/K from the RC1 experiment) an additional +98°C adiabatic temperature rise potential is calculated. Adding this temperature rise to the measured value from the reaction calorimetry experiment, a total potential temperature rise of +189°C is calculated (a new corresponding water vapor pressure of 3284 kPa).

### 3.4.6. Adiabatic Calorimetry Results and Discussion

To confirm that the intended heat of reaction under loss of cooling conditions can raise the temperature of the reaction to a temperature where the latent crosslinking energy can be realized (and collect useful information necessary for a vent sizing evaluation), adiabatic calorimetry is needed. Figure 6 and Figure 7 show the same recipe run in the VSP2 adiabatic calorimeter.

In the VSP2, the reaction is initiated by injection of the catalyst at 50°C and proceeds under adiabatic conditions. Indeed, the VSP2 trace shows the intended reaction heat does carry the system into the temperature range where the crosslinking reaction occurs and further temperature rise is realized. Though not covered in this paper, the temperature rise rate and pressure rise rate data from such an experiment can be used to design a properly sized emergency relief vent for a plant reactor running this process. The measured adiabatic temperature rise (non phi-factor corrected) is approximately 169°C. Equation 4 depicts how to determine the adiabatic temperature rise from the VSP2 and Equation 5 shows the phi-factor correction.

$$\Delta T_{ad} = \phi (T_{max} - T_{onset}) \quad (4)$$

where

$$\begin{aligned} \Delta T_{ad} &= \text{adiabatic temperature rise (}^\circ\text{C)} \\ T_{max} &= \text{maximum temperature observed from adiabatic experiment (}^\circ\text{C)} \\ T_{onset} &= \text{starting temperature from adiabatic experiment (}^\circ\text{C)} \\ \phi &= \text{phi-factor (-)} \end{aligned}$$

$$\phi = \frac{C_{p,s} m_s + C_{p,b} m_b}{C_{p,s} m_s} \quad (5)$$

where

$$\begin{aligned} C_{p,s} &= \text{sample heat capacity (3.1 J/g/K)} \\ C_{p,b} &= \text{sample holder heat capacity (0.5 J/g/K)} \\ m_s &= \text{sample mass (74 g)} \\ m_b &= \text{sample holder mass (30 g)} \end{aligned}$$

For this experiment, the phi-factor is calculated to be 1.07. This indicates that the adiabatic temperature rise was 180°C.

The data collected from the VSP2 can also be used to determine the normalized measured heat of reaction using Equation 6. The results of this calculation indicate that the measured heat was greater than -1,888 kJ/kg phenol.

$$\Delta H_r = \frac{-\phi C_{p,s} \Delta T_{ad}}{m/m_t} \quad (6)$$

where

- $\Delta H_r$  = the heat of reaction (J/g phenol)  
 $\Delta T_{ad}$  = the adiabatic temperature rise ( $^{\circ}\text{C}$ )  
 $m/m_t$  = the mass fraction of limiting reagent (0.315 based on the mass of phenol)

### 3.5. Summary of Results

Table 6 provides a summary of the heat of reaction and adiabatic temperature rise results collected from the reaction calorimetry, thermal screening, and adiabatic calorimetry experiments.

Table 6 Summary of Results

Reaction	Reaction Calorimetry Results		Thermal Screening Results		Adiabatic Calorimetry Results	
	$-\Delta H_r$ (kJ/kg phenol)	$\Delta T_{ad}$ ( $^{\circ}\text{C}$ )	$-\Delta H_r$ (kJ/kg phenol)	$\Delta T_{ad}$ ( $^{\circ}\text{C}$ )	$-\Delta H_r$ (kJ/kg phenol)	$\Delta T_{ad}$ ( $^{\circ}\text{C}$ )
Batch Reaction (50 $^{\circ}\text{C}$ )	902	91	960	98	1,888	180

## 4. Conclusion

The difference in the results between the instruments is inherent to the instrument. The reaction calorimeter was capable of controlling the reaction allowing only the desired reaction to occur, hence overall lower heats of reaction and smaller adiabatic potential. The thermal screening tests show the addition heat leftover from the reaction calorimeter, and the adiabatic calorimetry shows the total thermal potential when the reaction cannot be controlled (a loss of cooling scenario) resulting in more heat and a higher temperature rise. It is invaluable to have both pieces of information to best prepare for how the desired process needs to be run and what could happen when an upset scenario occurs. From a process safety perspective, the information gathered and illustrated by these three instruments definitively shows how important it is to control the intended heat of reaction for this Resole phenol formaldehyde resin process. Not only is there plenty of intended reaction energy to deal with but there is also latent crosslinking energy waiting to be liberated should the reaction runaway. While these reactions are easy to control in a laboratory reaction calorimeter via jacket cooling, just how easy will it be to control with increased scale?

## 5. References

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