

## SCALE UP ASPECTS OF PHENOL-FORMALDEHYDE REACTIONS

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Over the years Fauske & Associates, LLC (FAI) has done much work characterizing the process safety aspect of phenol-formaldehyde reactions on behalf of several customers. We recently presented a paper at Scientific Update's 2013 International Conference on the Scale Up of Chemical Processes held in La Jolla, Ca July 15-17, titled "Analyzing Phenol-Formaldehyde Resin Reactions for Safe Process Scale Up." We present here some highlights of this paper.

Producing phenolic resin is a very old but still active industry. Von Bayer first reported the polycondensation of phenol with aldehydes in 1872. In 1902 Blumer had the first industrial process producing shellac from a phenol formaldehyde reaction. Baekeland made the first thermosetting plastic in 1909. 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).

There are two types of phenol formaldehyde resins. When the formaldehyde to phenol ratio is less than 1 a Novolac resin is formed. These resin reactions are 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 ratio is greater than 1, typically 1 to 3. These reactions are based catalyzed and intentionally not reacted to completion. The Resole product carries pendent methylene hydroxy moieties (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.

We will use Reaction Calorimetry, Differential Scanning Calorimetry (DSC) and Adiabatic Calorimetry to characterize the energies involved in a generic Resole recipe. Our example generic recipe has a formaldehyde to phenol ratio of 2.2 and is 31% wt phenol, 21% water, 4% catalyst (50% aq. sodium hydroxide) with the aldehyde source being 50% aq. formaldehyde (44% wt).

Figure 1 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 2 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 profile curve represents the total heat of our batch reaction and integrating yields a normalized heat of reaction of -902 kJ/kg phenol. Dividing the total heat by the thermal mass (mass x heat capacity) calculates the theoretical temperature rise under adiabatic conditions due to the intended heat of reaction. For this recipe the calculated adiabatic temperature rise was +91°C.

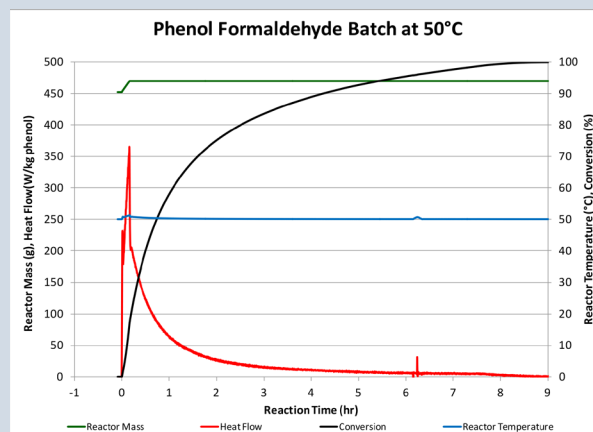


Figure 1

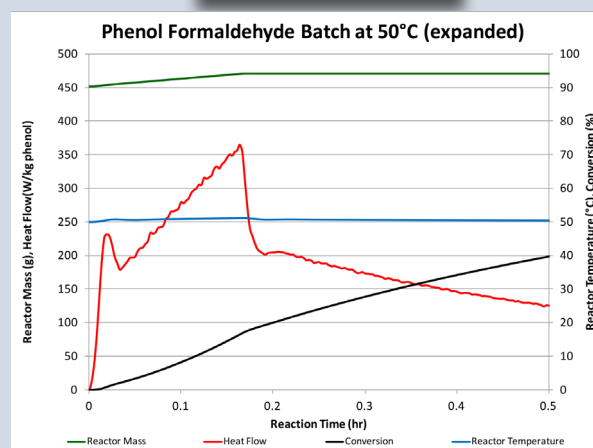


Figure 2

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So here, just from the intended heat of reaction, we see a large adiabatic potential as from 50°C a loss of cooling scenario could result in a temperature rise to 141°C where the vapor pressure of water would be 54 psig. But, that's not all of the story. If we take the reaction product from the batch reaction at 50°C and look at it in the DSC we see the scan shown in Figure 3.

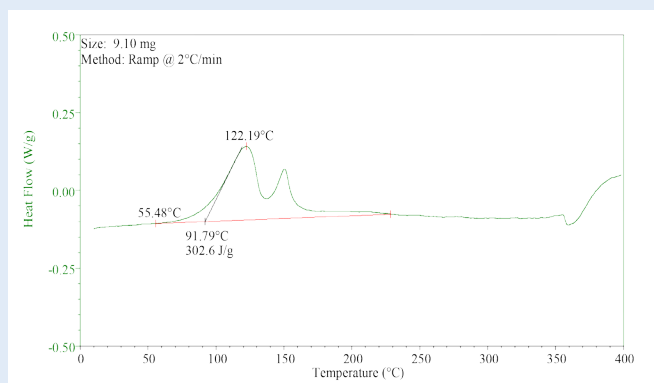


Figure 3

In the DSC scan we see the 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 (3.1 J/g°C) we calculate an additional +98°C adiabatic temperature rise potential. Adding this higher temperature activated energy to our previous intended reaction energy totals a temperature rise +189°C!

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, adiabatic calorimetry is needed. Figure 4 shows the same recipe run in the VSP2™ adiabatic calorimeter.

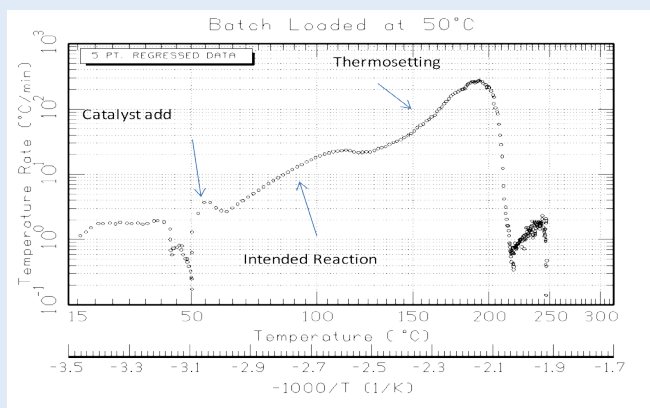


Figure 4

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 article, the temperature rise rate and pressure rise rate data from such an experiment can be used to design a proper vent size for plant reactor for this process. The information gathered and illustrated by these three instruments definitively shows how important it is to control the intended heat of reaction in 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 is it to control with scale?

In our Fall 2013 *Process Safety News* we will explore some simple calculations to show how these thermal challenges offered by the phenol formaldehyde process are handled with scale.

Reaction Calorimetry was performed in a Mettler-Toledo RC1, Differential Scanning Calorimetry in a TA Instruments Q2000 and Adiabatic Calorimetry in a FAI VSP2™.

If you have process scale up concerns or reaction calorimetry needs, please contact Don Knoechel at [knoechel@fauske.com](mailto:knoechel@fauske.com) or 630-887-5251 to discuss your process.