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Vent Sizing for the Phenol + Formaldehyde Reaction

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Abstract:

The manufacture of phenolic resins is subject to a relatively high frequency of runaway reaction incidents. This unfavourable record may be explained by the process chemistry and operating conditions. Two consecutive reactions are involved, and the second reaction may not be properly controlled by the "controlling" reactant injection or the process conditions. The reaction exothermic potential is significant, and high pressure may be generated by vapour pressure under runaway reaction conditions. The reactors are equipped with an emergency relief vent. The present vent design is based on the DIERS methodology. The generally accepted worst case scenario is the loss of cooling once the reaction is initiated, under conditions of maximum reactant accumulation. This method of vent design is explained, and its application to the manufacture of phenolic resins is presented with more details. A comprehensive example of vent design calculation is given.

Introduction

Phenolic resins are manufactured by the reaction of phenols and aldehydes in the presence of a catalyst under various operating conditions. The resins obtained by the reaction of phenol and formaldehyde are the most common phenolic resins in the chemical industry. The phenol + formaldehyde reaction is also frequently used in the synthesis of very different products which are not phenolic resins. However, Phenol−Formaldehyde resins (PF resins) are the most important product obtained by this reaction. In 2003, the consumption of 37 wt % formaldehyde solution was of 4.3 million metric tons in the USA and 24 million metric tons worldwide, of which 11.8% to 16.5% were used for the manufacture of phenol−formaldehyde resins.

PF resins are used as adhesive for binding wood-particule boards, fiber boards, plywood, nonwoven textiles, and insulation materials. In the United States where the building of wooden houses is particularly appreciated, the use of PF resins is widespread. Other uses of PF resins are in foundry mould binders, moulding materials, adhesives for papers, and water-based paints, as well as the manufacture of high-tech high-temperature resistant composite materials. The earliest commercial synthetic resin, with the commercial name Bakelite, is a phenol−formaldehyde resin.

Recently, however, occupational safety considerations draw public attention to the toxic properties of Formaldehyde, a human carcinogen (2004 IARC group 1), also a gen-toxic, an irritant, an asthmagen, and a skin sensitizer. Phenol is also a highly toxic material. The presence of PF resins everywhere is a concern. Hopefully the reactants, phenol and formaldehyde, are no longer present in PF resins.

Numerous runaway reaction accidents are known in the manufacture of phenol−formaldehyde resins, leading most of the time to the complete destruction of the production plants. It is generally the case for the worst credible scenario, leading to the most severe consequences. A frequently cited enquiry published in the UK by the HSE[1] shows that in the period 1962−1987, 134 accidents involving a runaway reaction in a batch or semibatch process occurred in the UK of which 64 were related to polymerization reactions, of which 13 were due to the phenol + formaldehyde reaction alone. An information booklet published by the British Plastic Federation (BPF)[2] on this reaction helped to reduce the frequency of these accidents. The process deviations "by introduction" or "by loss of cooling" leading to a loss of control of the synthesis reaction, and the reaction mixture "high vapour system" behaviour, make the reactor protection by an emergency relief vent quite effective. However the vent sizing calculations must take into account the reaction mixture gelation under runaway reaction conditions. The reactor must be emptied before the reaction mixture gelation. This makes this process quite interesting by a process safety point of view.

Process Chemistry

Phenolic resins are obtained by the reaction of an aldehyde and a phenol in the presence of a catalyst. Formaldehyde is the most frequent aldehyde used in the manufacture of phenolic resins. Different phenols are used: alkyl phenols, cresols, *tert*-butylphenols, octylphenol, xylenols, resorcinol. Phenol is the most frequently employed for the manufacture of PF resins. The different catalysts used, the different possible phenol-to-formaldehyde mole ratios, and the various possible operating conditions for the manufacture of PF resins give very different products for a wide range of applications. Two types of PF resins may be distinguished: Novolac or Novolak resins and Resoles.

Novolac resins are obtained with a formaldehyde-to-phenol mole ratio *R* lower than 1, frequently between 0.5 and 0.8, using an acid catalyst.

Acid catalysts are said to be more active than alkaline catalysts because they allow the phenol + formaldehyde

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(1) Barton, J. A.; Nolan, P. F. "Incidents in the chemical industry due to thermal runaway chemical reactions", Conference on chemical hazards, London Press Center (IBC), 5−6. December, 1989.

(2) "Guidelines for the safe Production of Phenolic resins", The British Plastics Federation, Thermosetting Materials Group, 1979.

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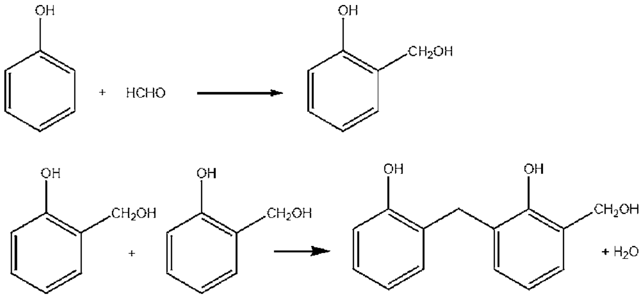

Figure 1. **Phenol + Formaldehyde reaction giving up a Novolac resin. Scheme 1, above, methylolation reaction. Scheme 2, below, polycondensation reaction**

polycondensation reaction where formaldehyde gives a methylene bridge between two consecutive phenol rings in o, o′, or p positions and water to take place directly. (See the reaction schemes in Figure 1.) The acid catalysts used are sulfuric, formic, oxalic, phosphoric, or *p*-toluenesulfonic acids. A pH of 0.5 to 1.5 is obtained, allowing a fast condensation reaction. Hydrochloric acid could also theoretically be used. However, under certain conditions, hydrochloric acid may react with formaldehyde to form bis-chloromethylether, $ClCH_2{-}O{-}CH_2Cl$, which is a well-known carcinogen. Therefore, hydrochloric acid should not be used as a catalyst for this reaction. Chlorosulfonic acids may allow the methylolation of phenol in the meta position but should never be used for the same reason. Due to their low formaldehyde-to-phenol mole ratio, Novolacs present a low degree of cross-linking and are used as thermoplastics or photoresists.

High ortho Novolacs are obtained using metal salts, i.e., calcium, magnesium, or zinc acetate, as catalyst to achieve a pH of 4 to 7 allowing a high proportion of o and o′ condensation on phenol, leaving the p position free.

Resoles are obtained with a formaldehyde-to-phenol mole ratio R greater than 1, between 1 and 3 and most frequently between 1.2 and 2.0, using alkaline catalysts.

Alkaline catalysts are said to be less active than acid catalysts because they allow us to obtain the methylolated phenol alone if the process temperature does not exceed 60 °C. The catalysts used are caustic soda, potassium hydroxide, lithium hydroxide, barium hydroxide, calcium hydroxide, ammonium hydroxide, and primary amines. Ammonium hydroxide is said to be a more active catalyst, compared to the other alkaline catalysts, allowing us to obtain directly the formation of methylene bridges between the phenol rings.[2] The formaldehyde + phenol reaction in the presence of ammonium hydroxide should proceed like the reaction carried out using acid catalysts.

Due to the excess of formaldehyde with respect to phenol, formaldehyde may react in more than one position ortho or para on the phenol ring allowing the polycondensation reaction to proceed with a high degree of cross-linking. (See the reaction schemes in Figure 2.) The polycondensation reaction proceeds through the formation of methylene bridges. The formation of ether bridges between two methylol groups is said to occur only in specific conditions and to produce a much lower exotherm than the condensation reaction through the formation of methylene bridges. Under runaway reaction conditions, the etherification reaction may be neglected.

The production of resoles accounts for the largest percentage of PF resin production and for the highest rate of runaway reaction accidents. However, it is difficult to determine if the manufacture of Resoles is more dangerous than the manufacture of Novolacs.

Overview of Process Conditions

Reactants Used. Pure molten phenol may be used as a reactant for the manufacture of PF resins. The use of phenol aqueous solutions allows the storage of phenol under ambient temperature.

Formaldehyde may be used as 37% or 50% aqueous solutions containing methanol as a stabilizer. The 50% formaldehyde solution is best produced on site. Remote delivery of this solution would allow the precipitation of a solid on cooling, which would not react under normal process conditions. To obtain a reactive 50% formaldehyde solution to carry out laboratory experiments, *para*-formaldehyde is best dissolved in water at the proper concentration before use. The 37% formaldehyde solution, stabilized with methanol, may be transported and stored without any detrimental effect on its reactivity for the manufacture of PF resins. Solid *para*-formaldehyde may be employed to reduce the recipe initial water content. *para*-Formaldehyde may depolymerize at 60−65 °C and then react with phenol.

Expected Heat of Reaction. The heat of reaction of formaldehyde with phenol is reasonably well-known. According to the BPF booklet,[2] the heat of reaction is

$$\Delta H_R = -17.2 \text{ kJ/mol of HCHO reacting to a } {-CH_2OH} \text{ methylol group.}$$

$$\Delta H_R = -90 \text{ kJ/mol of HCHO reacting to a } {-CH_2-} \text{ methylene bridge.}$$

Reference 2 also suggests that the heat of reaction for ammonia catalysed resins would be between $\Delta H_R = -66$ kJ/mol and −71.5 kJ/mol. However the author had the opportunity to measure the heat of reaction of an ammonia-catalysed resin and found it close to the generally accepted value of $\Delta H_R = -90$ kJ/mol.

Earlier data given by Brode[3] concerning the heat of reaction of an acid-catalysed phenol−formaldehyde condensation, suggest that $\Delta H_R = -98.3$ kJ/mol at low formaldehyde-to-phenol mole ratio and that $\Delta H_R = -82$ kJ/mol at a formaldehyde-to-phenol mole ratio of 1. A heat of reaction of $\Delta H_R = -20$ kJ/mol was also mentioned for the methylolation reaction, deduced from combustion data.

Booth et al.[4] said that the heat of reaction was

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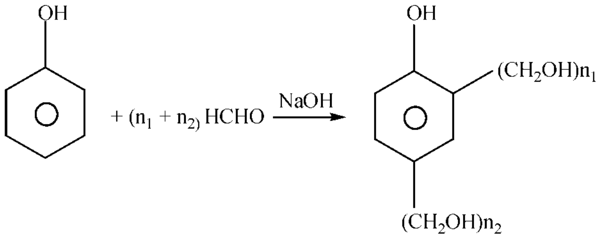
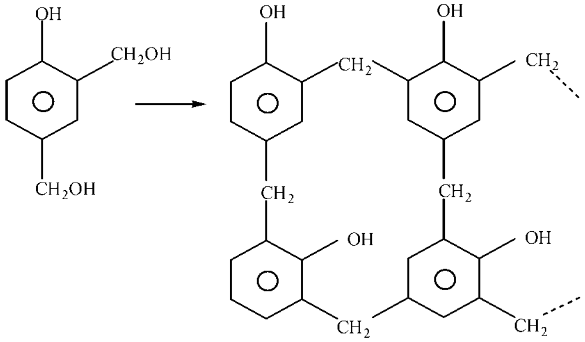
(3) Brode, L. G. Phenolic Resins. *Kirk Othmer Encyclopedia of Chemical Technology*; John Wiley: New York, 1982; Vol. 17, pp 384−416.

(4) Booth, A. D.; Karmarkar, M.; Knight, K.; Potter, R. C. L. Design of emergency venting system for phenolic resin reactors. *Trans. IChemE* **1980**, *58*, 75−90.



Scheme 1 : Methylolation reaction



Scheme 2 : Polycondensation reaction giving-up one molecule of water per methylene bridge

Figure 2. **Phenol + Formaldehyde reaction giving up a Resole resin. Scheme 1: Methylolation reaction. Scheme 2: Polycondensation reaction giving up one molecule of water per methylene bridge**

$\Delta H_R = -17.2$ kJ/mol of HCHO reacting to a $-CH_2OH$ methylol group.

$\Delta H_R = -91$ kJ/mol ofHCHO reacting to a $-CH_2-$ methylene bridge.

One may suggest that the optimum heat of reaction is not always obtained under runaway reaction conditions and that some steric hindering may lower the measured heat of reaction for high formaldehyde-to-phenol mole ratios.

Reaction Mixture Specific Heat. The reaction mixture specific heat is an important parameter when pseudo-adiabatic calorimetric determinations are used to study the runaway polycondensation reaction. This specific heat is necessary to calculate the experiment thermal inertia or ϕ factor, to characterize the deviation of experimental conditions from true adiabatic conditions:[5]

$$\phi = \frac{\sum mC_P(\text{sample} + \text{test cell})}{mC_P(\text{sample alone})}$$

The ϕ factor is estimated under ambient temperature conditions or at the reaction onset temperature, as the reaction mixture specific heat is not known at the current temperature under runaway reaction conditions.

A reaction mixture specific heat of $C_P = 0.7$ kcal/kg/°C $= 2.926$ kJ/kg/°C is suggested in ref 6. This data are quite representative for the liquid initial reaction mixture of many recipes. Determinations of C_P using a reaction calorimeter confirm this order of magnitude for the normal process temperature. The C_P of the final cross-linked solid resin obtained in a runaway reaction may be different.

Estimation of the Reaction Adiabatic Temperature Rise, Adiabatic Final Temperature and Possible Final Pressure for PF Resins. The prediction of the possible adiabatic temperature rise, adiabatic final temperature, and final pressure, in the case of runaway polycondensation is of great interest, to detect the recipes which may generate a pressure exceeding the reactor maximum allowable pressure, in the case of a runaway reaction. The estimated adiabatic final temperature and final pressure may not be obtained because the reaction did not reach completion or because the conversion ratio when the loss of control of the reaction occurred was not negligible. However this estimate may be considered as a worst case scenario as long as the final cross-linked resin does not decompose and generate noncondensable decomposition gases. Should this occur, the final pressure in a closed vessel cannot be predicted. The circumstances where these most unfavourable circumstances might occur are the runaway polymerization of a PF resin with a formaldehyde-to-phenol mole ratio of 3 and a limited amount of water introduced in the recipe.

Assuming the reaction proceeds until a resin cross-linked by methylene bridges is obtained, the estimated adiabatic temperature rise is

$$\Delta T_{ad} = \frac{n_{HCHO} * \Delta H_R}{m_0 * C_P}$$

In this relation, n_{HCHO} is the number of mole of formaldehyde charged to the reactor, ΔH_R is the heat of reaction per mole of formaldehyde reacting to a methylene bridge (kJ·mol^{-1}),

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(5) Townsend, D. I.; Tou, J. C. Thermal hazard evaluation by an accelerating rate calorimeter. *Thermochim. Acta* **1980**, *37*, 1−30.

(6) Leung, J. C.; Fauske, H. k.; Fisher, H. G. Thermal runaway reactions in a low thermal inertia apparatus. *Thermochim. Acta* **1986**, *104*, 13.

m_0 is the reactor inventory or the mass of reactants, catalyst, and water charged (kg), C_P is the initial reaction mixture specific heat (kJ·kg^{-1}·°C^{-1}). ΔT_{ad} is the corresponding possible adiabatic temperature rise (°C). Replacing ΔH_{R} and C_P by the relevant data, the relation turns to

$$\Delta T_{\mathrm{ad}} = \frac{n_{\mathrm{HCHO}} * 90\ \mathrm{kJ{\cdot}mol^{-1}}}{m_0 * 2.926\ \mathrm{kJ{\cdot}kg^{-1}{\cdot}{}^{\circ}C^{-1}}}$$

The estimated adiabatic final temperature is

$$T_{\mathrm{Fad}} = T_0 + \Delta T_{\mathrm{ad}}$$

where T_0 is the reaction initial or onset temperature and T_{Fad} the runaway reaction adiabatic final temperature.

The vessel possible final pressure as well as the pressure during the course of the runaway reaction as measured in a pseudo-adiabatic calorimeter like the Vent Sizing Package is the vapour pressure of water. The water present is either the water charged to the reactor according to the process recipe or the water produced by the polycondensation reaction. The influence of the methanol present as a stabilizer in formaldehyde aqueous solutions is often negligible. This pressure does not depend on the vessel filling ratio. The water vapour pressure may be estimated by the following equation:

$$P_{\mathrm{F}} = \left(\frac{T}{100}\right)^4$$

where T is the temperature (°C) and P_{F} is the final vapour pressure, i.e., the water vapour pressure (bar abs).

Example: We consider the resole recipe discussed in our previous paper on the phenol + formaldehyde runaway reaction.[7] In the recipe considered, the charge of formaldehyde was 44 400 mol, the vessel total inventory was 6168 kg, the expected adiabatic temperature rise was

$$\Delta T_{\mathrm{ad}} = \frac{n_{\mathrm{HCHO}} * 90\ \mathrm{kJ/mol}}{m_0 * 2.926\ \mathrm{kJ/kg/{}^{\circ}C}} = \frac{44\,400 * 90}{6168 * 2.926} = 221.41\ {}^{\circ}\mathrm{C}$$

The runaway reaction onset temperature was $T_0 = 60$ °C. The expected final temperature was

$$T_{\mathrm{Fad}} = 60\ {}^{\circ}\mathrm{C} + 221.41\ {}^{\circ}\mathrm{C} = 281.41\ {}^{\circ}\mathrm{C}$$

The potential final pressure was

$$P_{\mathrm{F}} = \left(\frac{281.41}{100}\right)^4 = 62.71\ \mathrm{bar\ abs} = 61.71\ \mathrm{barG}$$

This potential final pressure is far above the current reactor pressure resistance. Therefore, prevention and mitigation measures are necessary to reduce the probability of a worst case scenario or mitigate the consequences of a runaway reaction initiation. This recipe needs to be studied on an experimental basis to compare the above prediction with the corresponding experimental results and obtain the data necessary to protect the reaction vessel by an emergency relief vent.

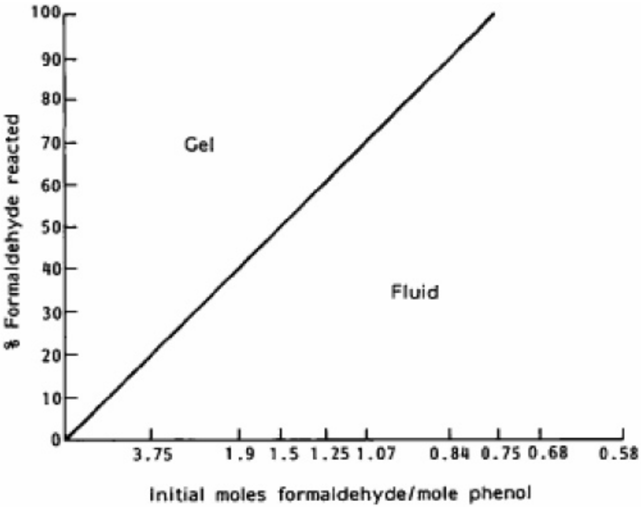

Figure 3. **Influence of initial raw material ratio and percentage formaldehyde reacted on gelation, given by Booth et al.[4,7]**

Reaction Mixture Gelation. With increasing conversion ratio of the phenol + formaldehyde polycondensation reaction, the reaction mixture viscosity increases and finally gelation occurs. When this occurs, the reaction self-heat rate increases significantly. This phenomenon is known as the "gel effect" in the field of polymerization reactions.

The consequences of the reaction mixture gelation are a significant reduction of the reactor cooling capacity and the fact that the reaction vessel can no longer be emptied. When venting is considered for the reactor protection for a runaway reaction case, the reaction conversion ratio on gelation is an important piece of information. This information is available in refs 2 and 4 for the phenol + formaldehyde reaction. The gel point is specified as a function of the recipe formaldehyde-to-phenol mole ratio, by the percentage of formaldehyde reacted to a methylene bridge (see Figure 3). The current formaldehyde conversion ratio is estimated by the percentage of the total reaction heat obtained, assuming that the polycondensation reaction readily occurs. This method of prediction is considered to be reasonable for runaway reaction conditions.

Different Types of Process to Manufacture PF Resins. Different types of processes are known to manufacture PF resins. Continuous processes are described for the manufacture of Novolac resins[3] where phenol, formaldehyde, and the catalyst are continuously fed to two reactors in series. The resin solution is concentrated in the process vacuum section before crystallization by cooling.

Resoles are manufactured in batch or semibatch processes operated under atmospheric pressure or under vacuum conditions. In batch processes, the reactants, phenol and formaldehyde, the catalyst, and water are charged to a stirred reactor under ambient temperature, and the reaction mixture temperature is raised to 60−80 °C to initiate the reaction. Upon reaction initiation, cooling is applied to control the reaction mixture temperature rise or keep the temperature constant. Cooling is applied through a jacket, cooling coils in the reaction mixture, an external heat exchanger, or a condenser for atmospheric processes. If the reaction vessel pressure is allowed to rise above the atmospheric pressure,

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(7) Gustin, J. L.; Fillion, J.; Treand, G.; El Biyaali, K. The phenol + formaldehyde runaway reaction. Vent sizing for reactor protection. *J. Loss Prev. Process Ind.* **1993**, *6* (2), 103−113.

the reaction mixture temperature will rise above the atmospheric boiling point of water allowing a higher reaction rate. The process may be operated under a vacuum to control the reaction mixture temperature by evaporative cooling and possibly increase the batch concentration. In batch processes, the rate of reaction and the reaction exotherm are controlled by the catalyst concentration present in the reaction mixture. A double charge of catalyst would increase the reaction rate and exotherm. The catalyst may be introduced in several successive aliquots to reduce runaway reaction hazards upon reaction initiation. Under constant temperature conditions, the reaction rate slows down with the reaction mixture conversion ratio and may be increased by the introduction of a further catalyst aliquot.

Resoles are also manufactured in semibatch processes where phenol, water, and the catalyst (caustic soda) are charged to the reactor. The reaction mixture temperature is set to 60 °C, and a formaldehyde solution is fed continuously to the reactor under temperature control by cooling. Finally the reaction mixture is held at 60 °C during 1 or 2 h to allow the reaction to reach completion. This type of process is suitable to obtain a methylolated phenol with limited methylene bridge formation. However, if the process temperature is allowed to rise above 60 °C, the polycondensation reaction is obtained to some extent causing an increase in the reaction exotherm and reaction mixture viscosity.

Runaway Reaction Scenarios. As pointed out by J. A. Barton and P. F. Nolan,[1] a high rate of runaway reaction accidents is recorded in batch or semibatch polymerisation processes and in the manufacture of PF resins. The consequences of the accidents are severe, consisting of the violent rupture of the reaction vessel or loss of containment, with emission of a toxic release of PF resin and unreacted toxic materials, phenol and formaldehyde. The reactor inventory may also polymerize in the equipment which must then be replaced or rebuilt. If the runaway reaction final temperature is greater than the formaldehyde autoignition temperature (AIT = 300 °C) the release may self-ignite in an air atmosphere, due to the emission of hot unreacted formaldehyde.

The process deviations which may cause a runaway reaction incident in the manufacture of PF resins are as follows:

In batch processes, a loss of cooling after the reaction initiation, a loss of vacuum in the vacuum processes, an undetected excess of catalyst charged to the reactor, too high a process temperature.

In semibatch processes, the catalyst not charged before the introduction of the controlling reactant (formaldehyde) and introduced later, a loss of cooling during the continuous introduction of the controlling reactant, the accumulation of unreacted controlling reactant in the reaction mixture.

The causes of the controlling reactant accumulation in semibatch processes are as follows:

Too low a process temperature, too fast a rate of the controlling reactant introduction, not enough catalyst or no catalyst at all charged to the reactor, the agitator not running and started later when a large amount of unreacted formaldehyde is present.

One may also point out that if the temperature is too high in a PF resin semibatch process, the reaction may well change from the methylolation below 60 °C to the polycondensation reaction above 60 °C, allowing the heat of reaction to increase by a factor of 5.23 whilst the heat-exchange capacity is reduced by the reaction mixture increasing in viscosity.

It is generally considered that semibatch processes are safer than total batch processes because the latter operate under total reactant accumulation conditions. On this basis, recommendations are issued to switch from total batch to semibatch process conditions. However, one may point out that the process conditions are very different in batch and semibatch processes and the controlling parameters are quite effective in both processes. Batch processes are probably more productive than semibatch processes, and the resin obtained may be different in the two different processes.

The methods to prevent runaway reaction accidents include prevention and mitigation measures. Prevention measures rely on a good understanding of the process conditions and control parameters. They should be applied with high reliability to exclude any mistake on the process charges, catalyst, process temperature, rate of the controlling reactant introduction, agitation, and cooling capacity. The selection of the possible scenarios for a runaway reaction in the manufacture of PF resins always reaches the conclusion that a loss of the cooling capacity when the reaction is initiated is an acceptable worst case scenario. In total batch processes, this may occur on reaction initiation when the reactant accumulation is maximum. In semibatch processes, the worst case may consider the conditions of maximum controlling reactant (formaldehyde) accumulation which may be determined using reaction calorimeter experiments. In the semibatch resole process described in ref 7, the worst case scenario was the omission of the catalyst charge before the introduction of formaldehyde and the introduction of caustic soda in a subsequent process step, whereas the whole formaldehyde charge was present and unreacted in the reactor. This scenario is equivalent to a loss of cooling when the reaction is initiated under total accumulation conditions.

The above discussion leads us to the conclusion that the correct commonly accepted worst case scenario for a runaway reaction in PF resin manufacture is a loss of cooling after the reaction initiation, under the condition of maximum possible formaldehyde accumulation. The other possible causes of runaway reaction incidents, consisting of errors or maloperations, are best controlled by instrumental interlocks.

Vent Sizing for the Phenol + Formaldehyde Reaction

The protection of reactors for the runaway reaction case by an emergency relief system is widely accepted in the manufacture of PF resins. The other possible methods such as catalyst killing, reaction quenching, or dumping of the reaction mixture through the bottom valve are not considered as reliable options.

Catalyst neutralisation by injection of an acid to neutralise the base-catalyzed resole reaction mixture may not be effective because acids may well catalyze the polycondensation reaction.

Quenching of the reaction by injection of cold water to the reactor would require the use of a low reactor filling ratio and of a high push pressure, to quickly transfer the necessary amount of water to the reactor.

Dumping of the reaction mixture to a quench tank would require a very large bottom valve to obtain a reasonable transfer time. The vessel pressure would only be released when the reactor is empty. The long emptying time would allow the reaction mixture viscosity to rise and to reach gelation and the bottom valve plugging. Therefore top venting is the preferred method. The only venting device suitable for this reaction is a rupture disk. The required vent area is so large that pressure safety valves would not meet the venting requirement and could be plugged by polymers. Vent sizing is achieved using the DIERS methodology.

DIERS Methodology Applied to the Phenol + Formaldehyde Reaction. The Design Institute for Emergency Relief Systems (DIERS) is an AIChE working party devoted to the design of emergency relief systems for the control and mitigation of runaway reactions in vessels. The DIERS methodology takes into account the occurrence of a two-phase release during venting of runaway reactions. The liquid carry-over during venting may significantly reduce the vent capacity compared to the all-vapour venting hypothesis. See the DIERS Project Manual.[8]

The DIERS methodology includes the following steps:

- Choice of the worst case scenario,

- Characterization of the reaction system behaviour. Three types of reaction systems are considered: high vapour systems, gassy reactions, and hybrid systems.

- Determination of the relevant experimental data. The data required depends on the type of reaction system considered.

- Choice of the relevant vent sizing method and of the two-phase flow calculation method.

As pointed out earlier, the worst case scenario considered for the manufacture of PF resins is the loss of cooling upon reaction initiation for batch processes or under conditions of maximum formaldehyde accumulation for semibatch processes.

The PF reaction mixture is a "high vapour system"; i.e., the vessel pressure is vapour pressure only, and we know that it is the vapour pressure of water. The "high vapour systems" are said to be tempered. This means that if the pressure is controlled by an emergency relief vent, the temperature is also controlled through the vapor−liquid equilibrium and the chemical reactions do not accelerate any longer. This type of reaction system is most favourable for the reactor protection by an emergency relief vent.

The experimental data required for vent sizing for "high vapour systems" is the "Heat rate versus Temperature" curve and the "Vapour pressure versus Temperature" curve of the runaway reaction, obtained under pseudoadiabatic conditions in the VSP or a similar experimental setup. VSP is short for Vent Sizing Package, the DIERS bench scale apparatus, allowing us to achieve low thermal inertia experimental conditions. The experiment initial conditions and thermal inertia must best represent the worst case scenario initiation conditions, to avoid any complex correction calculations. The VSP experiments allow us both to characterize the reaction system behaviour and to obtain the relevant experimental data.

J. C. Leung's Formula To Determine the Ideal Vent Size for "High Vapour Systems".[9,10] Assuming vessel homogeneous behaviour, i.e., constant heat production rate $\dot{q}$, specific heat C_P, enthalpy of vaporization h_{fg}, and volume change on vaporization v_{fg}, through the reaction mixture and constant volatility so that the Clapeyron equation applies

$$h_{fg} = T^* v_{fg} {}^* \frac{\mathrm{d}P}{\mathrm{d}T}$$

The required vent two-phase mass flowrate W is obtained using Leung's equation for high vapour systems:[9,10]

$$W = \frac{m_0\, \dot{q}}{\left[\left(\frac{V}{m_0} T \frac{\mathrm{d}P}{\mathrm{d}T}\right)^{1/2} + (C_P \Delta T)^{1/2}\right]^2}$$

The adiabatic specific heat production rate by the reaction mixture during the vent actuation $\dot{q}$ is

$$\dot{q} = \frac{1}{2} C_P \phi \left[\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\mathrm{S}} + \left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\mathrm{Max}}\right]$$

In the above relations, ϕ is the VSP experiment thermal inertia:

$$\phi = \frac{\sum m C_P(\text{sample + test cell})}{m C_P(\text{sample alone})}$$

$(\mathrm{d}T/\mathrm{d}t)_{\mathrm{S}}$ is the experimental self-heat rate measured at T_{S}, the temperature at which the reaction mixture vapour pressure is equal to the vent actuation pressure P_{S}.

$(\mathrm{d}T/\mathrm{d}t)_{\mathrm{Max}}$ is the experimental self-heat rate measured at T_{Max}, the temperature at which the reaction mixture vapour pressure is equal to P_{Max}, the maximum pressure allowed in the reaction vessel.

In the above relation, the experimental self-heat rates are corrected to adiabatic conditions using the zero-order correction described by Townsend and Tou.[5]

V is the reaction vessel overall volume.

m_0 is the reaction vessel initial inventory.

$\mathrm{d}P/\mathrm{d}T$ is the slope of the reaction mixture vapour pressure curve.

$\Delta T = T_{\mathrm{Max}} - T_{\mathrm{S}}$ is the temperature rise corresponding to the pressure rise $\Delta P = P_{\mathrm{Max}} - P_{\mathrm{S}}$.

The ideal vent area A_0 is then obtained by the relation:

$$A_0 = \frac{W}{G_0}$$

where G_0 is the two-phase flashing mass-flux through an

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[8] Emergency Relief System Design Using the DIERS Technology, The Design Institute for Emergency Relief Systems (DIERS) Project Manual. ISBN 0-8169-0568−1, 1992.

[9] Leung, J. C. Chemical Process Relief System Design Seminar, Saint Etienne Mining School (France), April 9−11, 2003.

[10] Leung, J. C. Simplified vent sizing equations for emergency relief requirements in reactors and storage vessels. *AIChE J.* **1986**, *32* (10), 1622−1634.

ideal nozzle. The venting of high vapour systems will produce flashing flows. The ideal vent area A_0 is the area of a rupture disk without any downstream vent line, assumed to be a frictionless ideal nozzle. As the two-phase vent release must be collected, a downstream vent line is necessary to send the release to a quench tank. The downstream vent line head losses will induce a reduction of the two-phase flashing mass flux G with respect to the ideal nozzle mass flux G_0. The required vent area A is increased accordingly to restore the necessary venting capacity.

$$A = \frac{W}{G}$$

The two-phase ideal nozzle flashing mass flux G_0 and the reduced vent line flashing mass flux G are obtained using J. C. Leung's omega method.

J. C. Leung's Omega Method To Determine the Two-Phase Ideal Mass Flux for Turbulent Flashing Flows in Nozzle.[9,11] A two-phase flow of liquid and vapour is a compressible fluid and as such may present choked flow conditions. The two-phase discharge in a frictionless nozzle is assumed to be isentropic. In Leung's omega method an equation of state is defined for the two-phase fluid where the parameter ω is similar to a compressibility:

$$\frac{v}{v_0} = \omega\left(\frac{P_0}{P} - 1\right) + 1$$

In this equation of state, v is the two-phase fluid specific volume and P the local pressure. v_0 and P_0 are the specific volume and pressure in a reference state. The omega parameter must be defined somewhere in the flow and preferably in the stagnation conditions, i.e., in the vessel conditions when the emergency relief vent is actuated. According to Leung,

$$\omega = \alpha_0 + \rho_0 C_P T_0 P_0 \left(\frac{v_{fg0}}{h_{fg0}}\right)^2$$

where α_0 is the average void fraction in the vessel on vent actuation, and ρ_0, the two-phase specific mass under stagnation conditions.

$$\rho_0 = \frac{m_0}{V}$$

Applying the Clapeyron equation, another expression of omega is obtained which may be easily determined from experimental data obtained in the VSP:

$$\omega = \alpha_0 + \rho_0 C_P T_0 P_0 \left(\frac{1}{T\frac{\mathrm{d}P}{\mathrm{d}T}}\right)^2$$

The isentropic discharged critical mass flux in an ideal nozzle is

$$G = \left[\frac{-1}{(\mathrm{d}v/\mathrm{d}P)_S}\right]^{1/2}$$

By substitution of the equation of state in this critical mass flux equation, the choking conditions are obtained. The critical pressure ratio $\eta_C = P_C/P_0$ is obtained by solving the following equation:

$$\eta_C{}^2 + (\omega^2 - 2\omega)(1 - \eta_C)^2 + 2\omega^2 \ln \eta_C + 2\omega^2(1 - \eta_C) = 0$$

The nondimensional critical mass flux $G_C{}^*$ is

$$G_C^* = \frac{G_C}{\sqrt{P_0\rho_0}} = \frac{\eta_C}{\sqrt{\omega}}$$

The critical mass flux may also be obtained from a more general relation valid for choked and unchoked conditions:

$$G^* = \frac{\{-2[\omega \ln\eta + (\omega - 1)(1 - \eta)]\}^{1/2}}{\omega\left(\frac{1}{\eta} - 1\right) + 1}$$

where $\eta = P_b/P_0$ is the ratio of the superimposed back-pressure to the stagnation pressure.

The choking conditions as a function of ω are obtained from the isentropic correlation given by Leung[9,11] and reproduced in Figure 4. The determination of G_C and η_C using Figure 4 does not require any computational effort once the value of ω is known. As shown by Figure 4, the critical flow conditions for flashing flows with $\omega \geq 10$ are obtained if the back-pressure does not exceed 80% of the absolute stagnation pressure P_0.

J. C. Leung's Omega Method To Determine the Two-Phase Mass Flux for Turbulent Flashing Flows in Vent Lines.[9,12] The vent line is schematically represented on Figure 5. On this figure, P_0, T_0, ρ_0 are the vessel stagnation conditions, and P_1 is the nozzle pressure. P_2 is the exit pipe pressure; this is not the superimposed back pressure. The change of elevation between the vent line inlet and outlet is characterized by a flow inclination factor Fi.

$$Fi = \frac{\rho_0 g H}{\left(4f\frac{L}{D}\right)P_0}$$

where $4f(L/D)$ is the pipe equivalent resistance, $H = L \cos \theta$ the positive change of elevation between the vent line inlet and outlet, ρ_0 is the stagnation two-phase specific mass, P_0 is the stagnation pressure, and g is the gravity constant. f is the two-phase friction factor. According to Wallis,[13] $f = 0.005$.

The flashing two-phase flow in the vent line is assumed to be isenthalpic and represented by the Homogeneous Equilibrium Model (HEM). Using the equation of state of Leung's omega method,

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(11) Leung, J. C. A generalized correlation for One-Component Homogeneous Equilibrium Flashing Choked Flow. *AIChE J.* **1986**, *32* (10), 1743.

(12) Leung, J. C.; Epstein, M. The discharge of two-phase flashing flow from an inclined duct. *J. Heat Transfer* **1990**, *112* (2), 524.

(13) Wallis, G. B. *One dimensional two-phase flow*; McGraw-Hill: New-York, 1969.

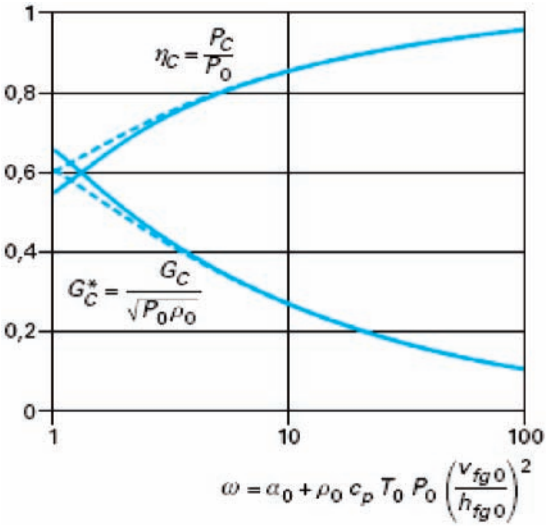

Figure 4. **Generalized HEM correlation for flashing flow through a perfect nozzle. Given by J. C. Leung.[9]**

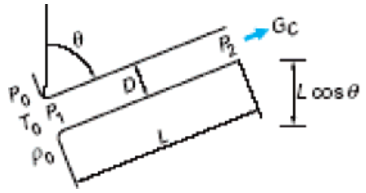

Figure 5. **Schematic representation of an inclined vent line as described by Leung.[9]**

$$\frac{v}{v_0} = \omega\left(\frac{P_0}{P} - 1\right) + 1$$

Defining the dimensionless variables

$$\eta_1 = \frac{P_1}{P_0}; \eta_2 = \frac{P_2}{P_0}; G^* = \frac{G}{\sqrt{P_0 \rho_0}}$$

the following system of equation is solved:

Frictionless inlet flow conditions

$$G^* = \frac{\{-2[\omega \ln \eta_1 + (\omega - 1)(1 - \eta_1)]\}^{1/2}}{\omega\left(\frac{1}{\eta_1} - 1\right) + 1}$$

Momentum equation

$$-4f\frac{L}{D} = \int_{\eta_1}^{\eta_2} \frac{[(1-\omega)\eta^2 + \omega\eta]\left(1 - G^{*2}\frac{\omega}{\eta^2}\right) \mathrm{d}\eta}{\frac{G^{*2}}{2}[(1-\omega)\eta + \omega]^2 + \eta^2 Fi}$$

Exit choking conditions

$$G_C^* = \frac{\eta_2 C}{\sqrt{\omega}}$$

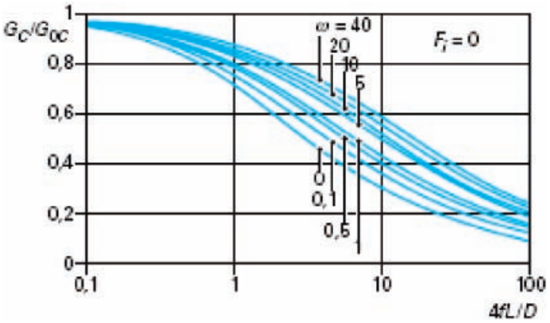

Figure 6. **Critical turbulent flow discharge through an horizontal vent line ($Fi = 0$) Flow reduction factor as a function of the equivalent pipe resistance. $\omega \geq 1$ for flashing flows, according to Leung.[9]**

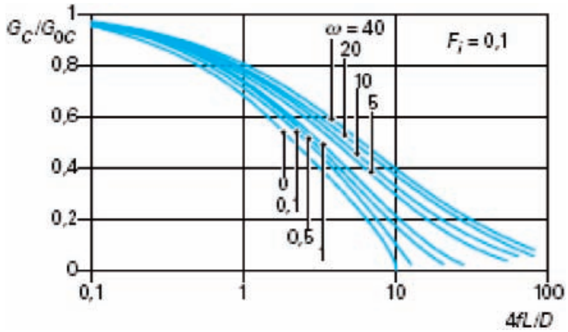

Figure 7. **Critical turbulent flow discharge through an inclined vent line ($Fi = 0.1$) Flow reduction factor as a function of the equivalent pipe resistance. $\omega \geq 1$ for flashing flows, according to Leung.[9]**

The solution obtained by Leung[9] is represented in Figure 6 for a horizontal vent line ($Fi = 0$) and in Figure 7 for an inclined vent line with $Fi = 0.1$. The flow reduction factor G_C/G_{0C} to be applied to a critical flow discharge from a vent line is given as a function of the line equivalent flow resistance and ω parameter in Figures 6 and 7. Graphic interpolation is necessary for different values of ω and Fi. Once the flow reduction factor is obtained, the revised vent area is estimated by

$$A = A_0 \frac{G_{0C}}{G_C}$$

The line exit critical pressure ratio P_{2C}/P_0 is given as a function of the flow reduction factor G_C/G_{0C} by the relation

$$\frac{P_{2C}}{P_0} = \frac{P_C}{P_0}\left(\frac{G_C}{G_{0C}}\right)$$

If the flow is not choked, a flow reduction factor G/G_C is applied to the exit mass flux. This flow reduction factor is obtained as a function of the pressure ratio G_C/G_{0C} for different values of $\omega \geq 1$ for flashing flows in Figure 8.

Practical Application of the Vent Sizing Method to a Phenol−Formaldehyde Resin Process. A phenol−formaldehyde Resole process is considered in which the formaldehyde-to-phenol mole ratio was $F/P = 1.85$. The recipe initial water concentration was 28.6 wt %. The catalyst concentration was 0.5 wt % caustic soda. According to the Booth et al. correlation,[4] the reaction mixture gelation should occur when 40% of the total heat of reaction, including the methylolation step and the polycondensation step, is obtained. The recipe considered was studied using a VSP experiment representing the loss of cooling scenario. In this VSP experiment, the reactants phenol and formaldehyde aqueous

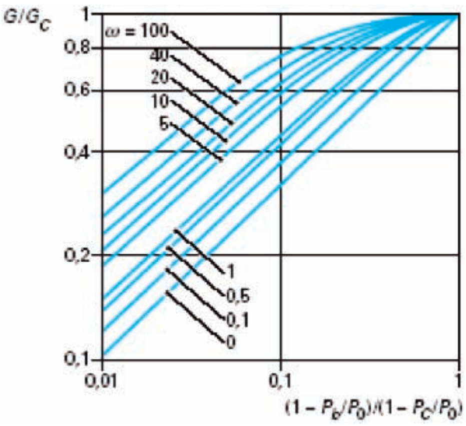

Figure 8. **Influence of the superimposed back-pressure at the vent line exit when the flow is subcritical. Flow reduction factor G/G_C as a function of the pressure ratio $[1 - P_b/P_0]/[1 - P_C/P_0]$ for different values of ω. $\omega \geq 1$ for flashing flows, and $\omega < 1$ for nonflashing flows.**

solution and water were charged to a closed Hastelloy C VSP test cell. The reaction mixture temperature was raised to 50 °C by a temperature scan, and the catalyst, caustic soda 50% aqueous solution, was injected into the test cell. After the catalyst injection, the reaction was initiated.

The thermal inertia or ϕ factor of this VSP experiment was $\phi = 1.088$. This ϕ factor value was obtained considering a reaction mixture specific heat of $C_P = 0.7$ cal·g^{-1}·°C^{-1} = 2926 J·kg^{-1}·°C^{-1}.

The curve "Pressure corrected from the nitrogen pad in log scale as a function of the temperature in reciprocal scale" for this VSP experiment is shown in Figure 9. In this representation, the sample vapor pressure during the runaway reaction is represented by a straight line.

The curve "Experimental self-heat rate in log scale as a function of the temperature in reciprocal scale" for this VSP experiment is shown in Figure 10. This figure is the Arrhenius representation of the self-heat rate.

The reaction is carried out at industrial scale, on a charge of 10 833.6 kg in a 14 m^3 total volume reactor with a maximum allowable working pressure of 2 bar G, i.e., an absolute pressure of 3 bar abs. The reactor filling ratio was of $\tau = 85.72\%$. The reactor emergency relief vent is equipped with a rupture disk. The downstream vent line equivalent L/D ratio is $L/D = 90.3$. The back-pressure applied to the vent line exit is atmospheric. The change of elevation between the rupture disk and the vent line exit is $H = 1.4$ m.

The runaway reaction onset temperature was $T_0 = 50$ °C.

The experimental temperature rise of the runaway reaction was $\Delta T_{\text{EXP}} = 220$ °C.

The adiabatic temperature rise was $\Delta T_{\text{AD}} = \phi * \Delta T_{\text{EXP}} = 1.088 * 220\ °\text{C} = 239.36$ °C.

The experimental heat of reaction deduced from the adiabatic temperature rise was $\Delta H_R = -81.5$ kJ/mol of HCHO.

The expected heat of reaction was $\Delta H_R = -90$ kJ/mol of HCHO.

The lower heat of reaction obtained may be due to a lower conversion ratio of the cross-linking reaction. Another possible explanation would be a change of the final reaction mixture specific heat compared to the current accepted data. It is difficult to reach a conclusion on this issue.

For the reaction initiated at 50 °C, the adiabatic gelation temperature would be

$$T_{\text{Gel,ad}} = 50\ °\text{C} + 0.4 * 239.36\ °\text{C} = 145.7\ °\text{C}$$

However, the experimental gelation temperature for our VSP experiment would be

$$T_{\text{Gel, exp}} = 50\ °\text{C} + \frac{145.7\ °\text{C} - 50\ °C}{1.088} = 138\ °\text{C}$$

The reactor emergency relief vent is fitted with a rupture disk with an actuation pressure of $P_S = 0.2$ bar G = 1.2 bar abs. The reaction mixture boiling point T_S under the vent actuation pressure P_S is obtained from Figure 9: $T_S = 124.7$ °C.

The experimental self-heat rate measured at T_S is obtained on the heat−rate curve in Figure 10:

$$\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_S = 50\ °\text{C/min}\ .$$

The maximum temperature allowed during venting is chosen to be equal to the experimental gelation temperature: $T_{\text{Max}} = T_{\text{gel,exp}} = 138$ °C. This decision is made to prevent the reaction mixture gelation during venting.

The reaction mixture vapor pressure at T_{Max} is obtained from Figure 9: $P_{\text{Max}} = 2.2$ bar abs = 1.2 bar G. The experimental self-heat rate measured at T_{Max} is obtained from Figure 10:

$$\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\text{Max}} = 80\ °\text{C/min}$$

The slope of the vapor pressure curve is estimated between T_S and $T_{\text{Gel,ad}} = 145.7$ °C.

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta P}{\Delta T} = \frac{(2.2 - 1.2) \times 10^5\ \text{Pa}}{145.7\ °\text{C} - 124.7\ °\text{C}} = \frac{10^5}{21} = 4.76 \times 10^3\ \text{Pa/°C}$$

The required mass flow rate is estimated using Leung's formula for high vapor systems:

$$W = \frac{\frac{1}{2} * 10863.6 * 2926 * 1.088 * (50 + 80)\frac{1}{60}}{\left[\left(\frac{14}{10863.6} * 397.7 * (4.76 \times 10^3)\right)^{1/2} + (2926 * 21)^{1/2}\right]^2} = 423.9\ \text{kg/s}$$

The required ideal vent area is given by the relation: $A_0 = W/G_{0C}$.

Determination of G_{0C} Using Leung's Omega Method. The ω parameter for the two-phase flow is estimated under the stagnation conditions in the vessel.

The vessel average void fraction is

$$\alpha_0 = 1 - \tau = 0.1428$$

The vessel average specific mass is

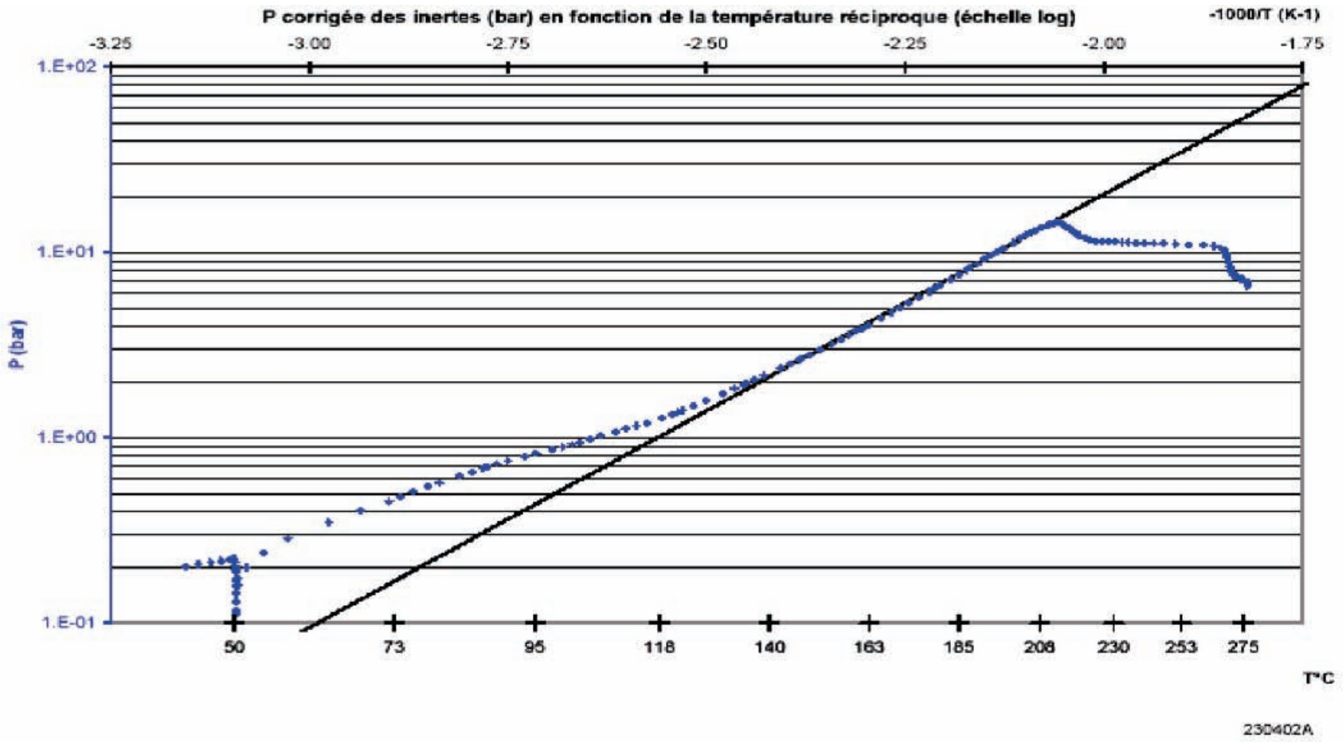

Figure 9. **Results of a VSP experiment representing the "loss of cooling" scenario. Vapor pressure corrected from the nitrogen pad in log scale as a function of the temperature in reciprocal scale. The straight line represents the vapor pressure law fitting the experimental data.**

$$\rho_0 = \frac{m_0}{V} = \frac{10863.6\ \text{kg}}{14\ \text{m}^3} = 775.97\ \text{kg/m}^3$$

The ω parameter is

$$\omega = \alpha_0 + \rho_0 C_P T_0 P_0 \left(\frac{1}{T\frac{\mathrm{d}P}{\mathrm{d}T}}\right)^2$$

$$\omega = 0.1428 + 775.97 * 2926 * 397.7 * (1.2 \times 10^5)\left[\frac{1}{397.7 * (4.76 \times 10^3)}\right]^2 = 30.379$$

The nozzle critical pressure ratio and the nondimensional critical mass flux are obtained from the generalized HEM correlation for flashing flows in perfect nozzles presented on Figure 4:

$$\eta_C = \frac{P_C}{P_0} = 0.92$$

Thus the nozzle absolute choke pressure is

$$P_C = 0.92 * 1.2\ \text{bar abs} = 1.104\ \text{bar abs}$$

The flow is choked as long as the superimposed back-pressure is lower than $P_C = 1.104$ bar abs $= 0.104$ bar G

$$G_C{}^* = \frac{G_C}{\sqrt{P_0 \rho_0}} = 0.16$$

The nozzle critical mass flux is

$$G_{0C} = 0.16 * \sqrt{P_0 \rho_0} = 0.16[(1.2 \times 10^5) * 775.97]^{1/2} = 1543.9\ \text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$$

The required ideal vent area is

$$A_0 = \frac{W}{G_{0C}} = \frac{423.9\ \text{kg/s}}{1543.9\ \text{kg/m}^2\text{/s}} = 0.274\ \text{m}^2$$

The ideal vent diameter is

$$D_0 = \sqrt{\frac{4 * A_0}{\pi}} = 0.59\ \text{m}$$

This ideal vent area does not take into account the detrimental effect of the downstream vent line necessary to collect the two-phase release to a quench tank.

Influence of the Downstream Vent Line on the Required Vent Area. The equivalent length-to-diameter ratio of the downstream vent line was found to be $L/D = 90.3$.

The two-phase pipe resistance is $4f\,(L/D) = 4 * 0.005 * 90.3 = 1.806$.

Taking into account a positive change of elevation of 1.4 m between the vent line inlet and exit, the vent line flow inclination factor is

$$Fi = \frac{\rho_0 g H}{\left(4f\frac{L}{D}\right)P_0} = \frac{775.97 * 9.81 * 1.4}{1.806 * (1.2 \times 10^5)} = 0.0492$$

Vent line flow inclination factor falls between $Fi = 0$ (horizontal line) and $Fi = 0.1$ (inclined line). An interpolation is necessary between the relevant curves of Figures 6 and 7.

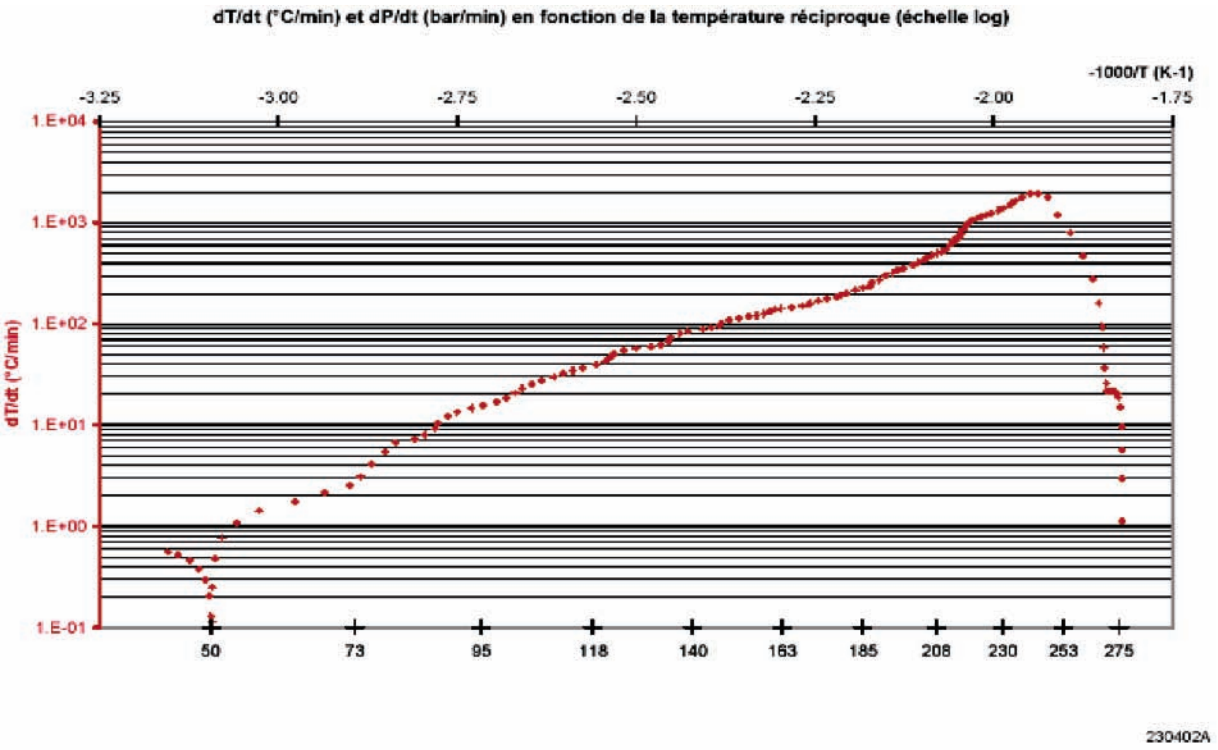

Figure 10. **Results of a VSP experiment representing the "loss of cooling" scenario. Experimental heat−rate curve in log scale as a function of the temperature in reciprocal scale.**

- For $Fi = 0$, $4f(L/D) = 1.806$, and $\omega = 30.3$, the flow reduction factor is $G_C/G_{0C} = 0.8$.

- For $Fi = 0.1$, $4f(L/D) = 1.806$, and $\omega = 30.3$, the flow reduction factor is: $G_C/G_{0C} = 0.7$.

- For $Fi = 0.0492$, $G_C/G_{0C} = 0.751$.

Thus, the required vent area taking into account the downstream vent line is

$$A = \frac{A_0}{0.751} = \frac{0.274\ \mathrm{m}^2}{0.751} = 0.365\ \mathrm{m}^2$$

The required vent diameter is

$$D = \sqrt{\frac{4 * A}{\pi}} = 0.68\ \mathrm{m}$$

The vent line exit critical pressure ratio is

$$\frac{P_{2C}}{P_0} = \frac{P_C}{P_0}\left(\frac{G_C}{G_{0C}}\right) = 0.92 * 0.751 = 0.691$$

The vent line exit critical pressure is

$$P_{2C} = P_0 * 0.691 = 0.691 * 1.2\ \text{bar abs} = 0.829\ \text{bar abs}$$

The vent line exit critical pressure is lower than the atmospheric pressure; therefore the vent flow is unchoked or subcritical as long as the vent line exit pressure P_{2C} does not exceed 1 bar abs. This would be obtained for a vessel stagnation pressure of $P_0 = 1.447$ bar abs.

The line exit unchoked two-phase mass flux is a function of the stagnation pressure and of the superimposed back-pressure. A flow reduction factor G/G_C is obtained from Figure 8 as a function of ω and of the pressure ratio

$$\frac{\left(1 - \frac{P_b}{P_0}\right)}{\left(1 - \frac{p_C}{P_0}\right)} = \frac{1 - \frac{1}{1.2}}{1 - \frac{0.829}{1.2}} = \frac{0.1666}{0.3092} = 0.5388$$

For this pressure ratio and $\omega = 30.3$ the flow reduction factor to account for unchoked conditions is

$$\frac{G}{G_C} = 0.96$$

The exit mass flux is only slightly influenced by the atmospheric back-pressure in this example.

Finally, the requested vent area should be modified as follows:

$$A_{\text{unchoked}} = \frac{A}{0.96} = \frac{0.365}{0.96} = 0.380\ \mathrm{m}^2$$

The required vent diameter would be

$$D = \sqrt{\frac{4 * A_{\text{unchoked}}}{\pi}} = 0.696\ \mathrm{m}$$

Comments. The required vent size for this phenol−formaldehyde Resole reaction and the "loss of cooling" scenario is large as usual. This result is typical of the phenol + formaldehyde reaction. The required vent area is determined using the following data:

- The reaction mixture vapor pressure curve.

- The experimental self-heat rate curve.

- The temperature at which the reaction mixture gelation will occur during runaway.

As the reaction mixture vapor pressure is essentially the vapor pressure of water, this data should not induce any significant difference between the various recipes. The experimental self-heat rate for a given experiment phi-factor is influenced by the catalyst concentration and by the concentration of the reactants. A high initial concentration of water in the recipe would lower the heat rate observed at a given temperature. The gelation temperature is an important factor determining the vent size. The higher the formaldehyde-to-phenol mole ratio, the lower the conversion ratio at which gelation will occur and the lower the gelation temperature and maximum pressure P_{MAX} allowed. The vent actuation pressure P_{S} is chosen as low as possible to reduce the heat rate during venting. The pressure and temperature range in which the reactor must be emptied may be limited, leading to a large vent size.

Quench Tank Design Considerations. As pointed out earlier, the two-phase release must be collected and not sprayed out over the neighborhood since the vented material may be toxic due to the presence of unreacted formaldehyde or phenol. The release may also be flammable because the temperature is higher than the flash point of formaldehyde and phenol. Autoignition of the release is possible if the autoignition temperature of formaldehyde is reached. This is possible for some recipes. The best choice for a collection system is a quench tank. A scrubber would not accommodate the release mass flow rate. A simple catch-pot would not stop the runaway reaction which could restart in this vessel. A cyclone would be very large to obtain a good separation of the condensed phase.

Considering a quench tank, the best quench liquid for this reaction is cold water. Cold water allows the cooling of the vented reaction mixture and the dilution of unreacted reactants or intermediates, i.e., formaldehyde, phenol, and methylolated phenol. The quenching effect of water is both a thermal and a chemical effect.

The best choice for the quench-tank design is probably a horizontal cylinder placed on the ground, so that the reactor bottom valve allows the reactor inventory to be emptied to the quench tank also, by gravity. The quench-tank volume should be at least four times the reaction mixture volume. The volume of cold water charged to the quench tank should be equal to the reaction mixture volume, so that a filling ratio of 50% is reached when the reaction mixture has been transferred to the quench tank by top venting. This would provide the larger vapor/liquid interface and the best conditions for gas liquid disengagement. However, complete vapor dissolution is expected. The vent inlet to the quench tank should be through a dip pipe, taking care to limit the liquid head over the dip pipe end, to limit the superimposed back-pressure. The quench-tank gas exit may be directed to the atmosphere or to a scrubber, depending on the process recipe and on the local regulations. If necessary, the initial quench tank gas phase may be kept under a nitrogen blanket to prevent the formation of a flammable atmosphere.

Conclusion

The manufacture of phenol−formaldehyde resins is subject to frequent runaway reaction accidents. This paper gives an overview of the different recipes and process conditions for the manufacture of phenolic resins. It is generally considered that the synthesis reactor where this type of reaction is carried out should be protected by an emergency relief vent. This emergency relief vent is sized on the basis of a selected process deviation scenario. The process deviations leading to a runaway reaction are presented. The “loss of cooling” scenario is generally considered as a design basis for an emergency relief vent. The design methods applied for emergency relief vent sizing are the DIERS methods, taking into account the occurrence of a two-phase release. The phenol + formaldehyde reaction is a high vapor system. The vent sizing method applied in this paper involves the use of J. C. Leung’s equation to determine the requested vent mass flowrate and J. C. Leung’s omega method to determine the requested vent area, taking into account the necessary downstream vent line. The method applied is well described in J.C. Leung’s “Chemical Process Relief System Design Seminar”/course.[8] The calculation method followed is explained and exemplified by its numerical application to a Resole recipe. The necessary experimental data consisted of a VSP experiment representing the selected process deviation scenario “ loss of cooling” once the reaction was initiated. The author hopes that this paper is practical and comprehensive and will be of help to phenolic resin manufacturers.

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