Reactive monomer tank—A thermal stability analysis

T. Chakravarty[a], Harold G. Fisher[b] and Laura A. Voyt[b]

[a] *Bechtel Corporation, Houston, TX 77252 (USA)*
[b] *Union Carbide Chemicals and Plastics Company Inc., South Charleston, WV 25303 (USA)*

Abstract

Chemical production processes should always be examined to identify and, when needed, modified to prevent runaway reactions. A thermal stability analysis was therefore conducted on an existing process for producing a reactive monomer. Thermal decomposition kinetics were developed from Accelerating Rate Calorimeter (ARC) data. Due to a low Self-Accelerating Decomposition Temperature and short Time to Maximum Rate, the prevention of a runaway reaction due to a process upset was found to be more important than providing the normal fire exposure protective insulation. Runaway reaction computer simulations demonstrated that an uninsulated vessel would have a lower risk of venting toxic and flammable materials than an insulated vessel. Lessons learned from this analysis will be discussed.

1. Process description

A primary alcohol A is reacted with a reactive chemical R in a batch kettle at moderate temperature and pressure to form a reactive monomer M. The byproduct acid gas G is scrubbed and excess alcohol is refluxed to the kettle. Upon completion of the batch, the contents of the kettle are neutralized.

Excess alcohol is stripped from the kettle, condensed and collected in a lights receiver. The alcohol, however, forms an azeotrope with the product and also reacts with the product to form another bifunctional monomer T and a flammable gas H. The lights, which are a reactive mixture of the primary alcohol and the monomer, are transferred to a portable dumpster for incineration. The remaining product is transferred to intermediate storage. All process equipment is vented to prevent the build-up of non-condensible gas pressure at production conditions. Emergency relief was also to be provided for all process equipment to prevent overpressure due to a runaway reaction. Figure 1 is a schematic of the process.
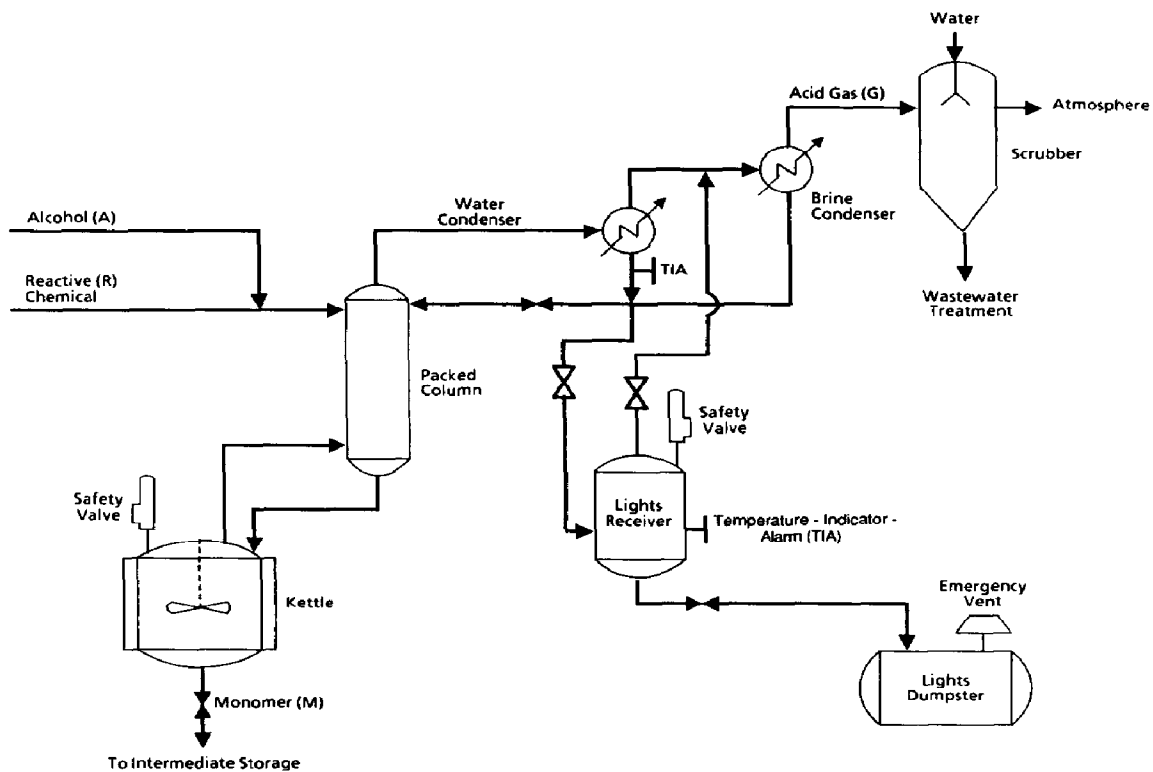
Correspondence to: Dr. T. Chakravarty, Bechtel Corporation, Houston, TX 77252 (USA).

Fig. 1. Process flow sketch.

2. Process hazards

The product M is a flammable, toxic material of moderate volatility (NBPT 85 °C). A rapid, exothermic, uncatalyzed reaction between the alcohol and the product occurs at around 55 °C. A highly flammable, non-condensible gas H and a heavy product T are produced. The operating conditions are such that a process upset is more likely than fire exposure to induce a runaway reaction in the lights receiver.

3. Objective

Emergency relief was to be designed [1] for the lights receiver based upon a model of the thermal runaway reaction of the product with the primary alcohol. Our investigation into the safety of the process led us to conclude that various reactive mixtures in the lights receiver could undergo a runaway reaction at abnormally high process or ambient temperatures. Our goal was to reduce the risk of venting toxic and flammable materials. We therefore wanted to quantify the conditions where mixtures of various composition in the lights

receiver could undergo a runaway reaction so that a preventive strategy could be developed [1].

4. Kinetic model development

A kinetic model for the runaway reaction between the monomer and the alcohol was developed. We also developed thermal stability criteria for reactive mixtures in the lights receiver. Development of the kinetic model and the thermal stability criteria for these reactive mixtures are discussed below.

To develop a kinetic model for the reaction, several Accelerating Rate Calorimeter (ARC) tests [2] were conducted with the stoichiometric amount of alcohol and monomer. The tests show that a peak heat rate of several hundred degrees C/min and pressure of a few thousand psig can be generated in an industrial vessel.

A second order kinetic model for the thermal runaway reaction was developed using the ARC data. The rate of the uncatalyzed reaction was assumed to be first order with respect to the concentrations of alcohol and monomer, respectively.

$$\text{Reaction Rate (lb mol/ft}^3 \text{ h)} = k \, C_A C_M \qquad (1)$$

where k is the specific rate constant (ft^3/lb mol h), C_A is the alcohol concentration (lb mol/ft^3), and C_M is the monomer concentration (lb mol/ft^3).

Arrhenius kinetic parameters obtained from regression [3, 4] of the raw ARC data are shown in Table 1.

These kinetic parameters, the heat of reaction value and our physical property models were then checked by simulation of the ARC data using the UCC&P Runaway Reaction Emergency Relief Sizing Program. This digital simulation computer program uses numerical integration to solve the mass and heat balance differential equations, kinetic models and physical property relationships required to model plant production processes and provide solutions to the equations required to size emergency relief systems. The DIERS SAFIRE computer program [5, 6] has similar capabilities.

Figures 2, 3 and 4 compare the predictions of the heat rate, temperature and pressure, respectively, with the raw data. Our computer simulation agrees well

TABLE 1

Summary of kinetic parameters for the reaction $A + M \rightarrow T + H$

$A \left(\dfrac{\text{ft}^3}{\text{lb mol h}} \right)$	E (cal/mol)	ΔH (Btu/lb mol)
1.89×10^{14}	23630	31770

HEAT RATE (°C/MIN)
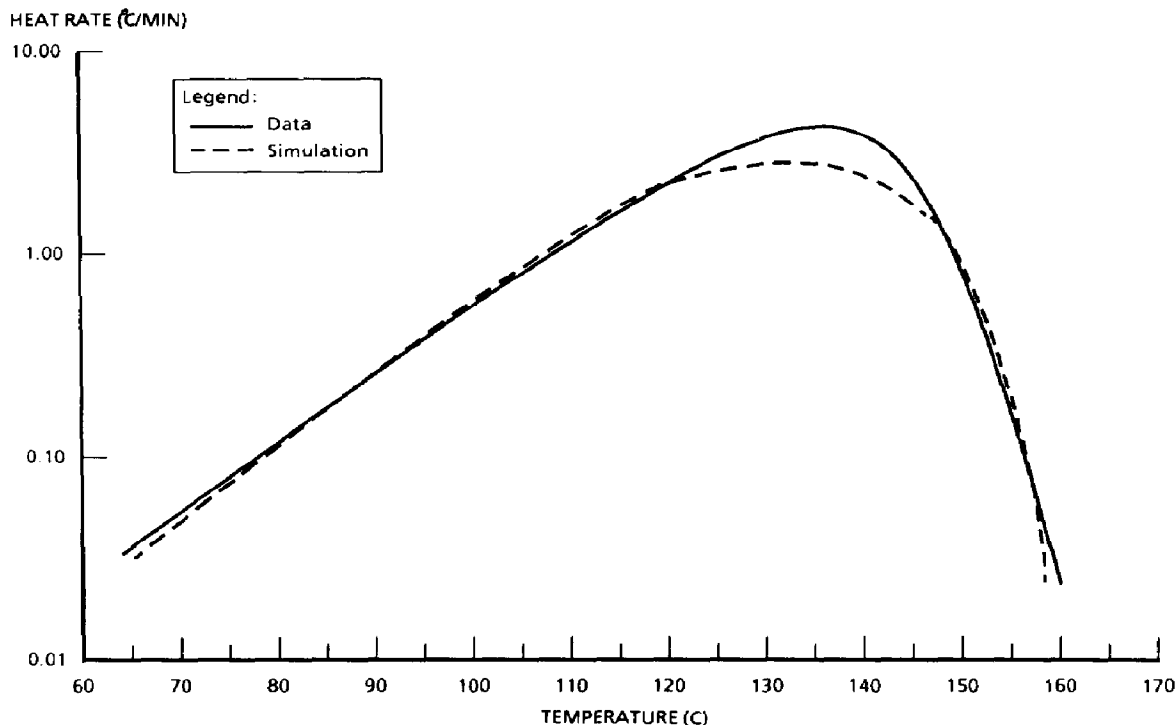

Fig. 2. Experimental data vs. simulation stoichiometric $A + M \rightarrow T + H(g)$ (PHI = 1.7).

with the experimental data and accounts for the variable thermal inertia (heat capacity effect) of the ARC bomb. Nevertheless, a few comments are worth making regarding fitting of the data.

1. The kinetic parameters were fitted based upon the assumption that the reaction rate is equal to $kC_A C_M$.
2. The kinetic model was not verified against isothermal rate data.
3. The assumption of equimolar decomposition stoichiometry and a negligible gas solubility fit the pressure data.
4. Extrapolation of model results beyond the temperature range of the data must be done with caution.

5. Effects of contamination

Possible effects of contaminants such as the acid gas and iron in ppm quantities have also been investigated. ARC tests conducted using tantalum bombs show significant effects of iron on the experimental onset temperature as well as on the peak heat rate. The experimental onset temperature of the iron catalyzed reaction is lowered by approximately 50 °C and the peak heat rate increased tenfold. The effect of iron is believed to be catalytic. The
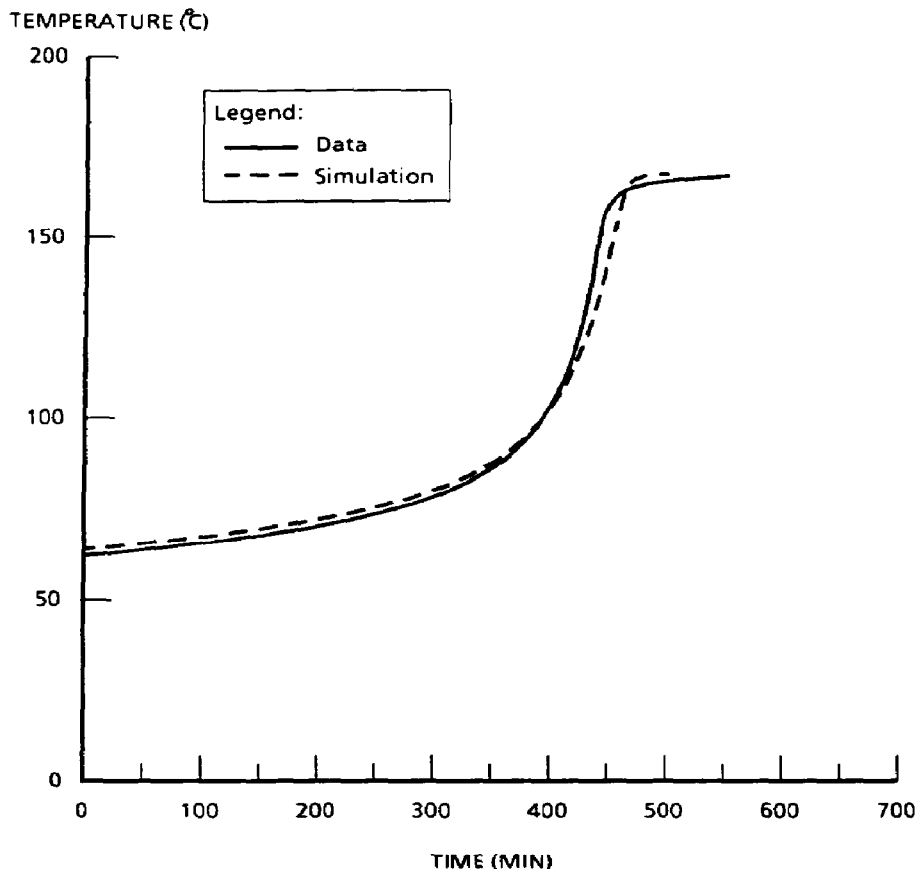
TEMPERATURE (°C)

Fig. 3. Experimental data vs. simulation stoichiometric $A + M \rightarrow T + H(g)$ (PHI = 1.7).

presence of acid gas, on the other hand, tends to raise the onset temperature, perhaps by preferentially reacting with the primary alcohol.

The best means to avoid a runaway reaction due to contamination is to avoid the presence of any contaminants. Because the penalty from contamination with iron is so great, we decided to design the system with materials such that iron contamination is not possible. Since acid gas contamination is beneficial, no action has been taken to avoid its presence.

6. Thermal stability analysis

The kinetic parameters presented above were used to determine the stability of the reactive mixture in terms of the Self-Accelerating Decomposition Temperature (SADT) and the Temperature of No Return (T_{NR}). The SADT and T_{NR} and their relation to thermal stability have been discussed by Townsend and Tou [3], Wilberforce [7] and Fisher and Goetz [8] and are based on the
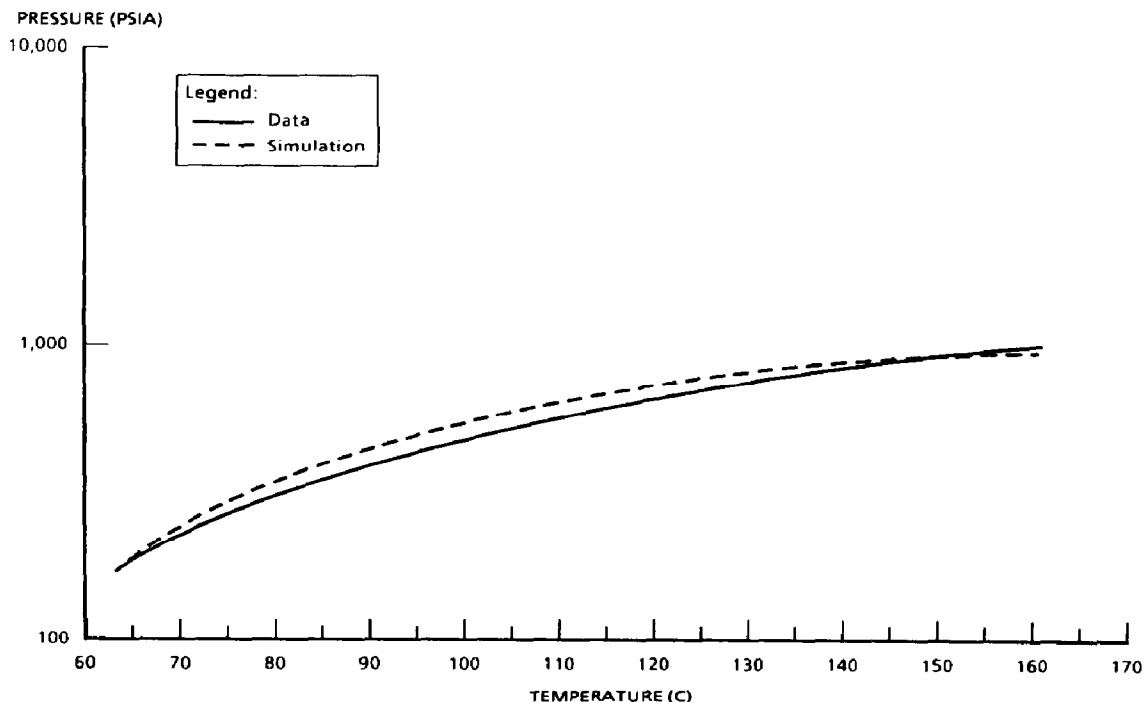
PRESSURE (PSIA)

Fig. 4. Experimental data vs. simulation stoichiometric A + M → T + H(g) (PHI = 1.7, fill ratio = 0.3).

Semenov theory of thermal explosions [9]. The relations used to calculate the SADT and T_{NR} are briefly described below.

SADT is the minimum ambient air temperature at which a reactive material of specified stability decomposes in a specified commercial package in a period of seven days or less. While the term SADT applies strictly to commercial packages, the thermal stability concepts discussed herein also apply to commercial vessels.

At the temperature of no return (T_{NR}) the heat generation from an exothermic reaction equals the heat loss from the vessel. A runaway reaction is expected whenever either the process temperature exceeds the T_{NR} or the ambient air temperature exceeds the SADT.

The following equations can be used to calculate the T_{NR} and SADT.

$$T_{NR}^2 = \frac{E(\Delta H)(V)A\exp(-E/(RT_{NR}))C_{A0}C_{M_0}}{R(U)(1.8)S} \tag{2}$$

$$SADT = T_{NR} - \frac{R(T_{NR})^2}{E} \tag{3}$$

where T_{NR} is the temperature of no return (K), E the activation energy (cal/mol), ΔH the heat of reaction (Btu/lb mol), V the initial volume of the

reactant mixture (ft^3), A the pre-exponential factor (ft^3/lb mol h), R the universal gas constant (1.987 cal/mol K), C_{AO} the initial concentration of alcohol, (lb mol/ft^3), C_{MO} the initial concentration of monomer (lb mol/ft^3), U the heat transfer coefficient (Btu/h ft^2 °F), S the heat transfer area (ft^2), and SADT the self-accelerating decomposition temperature (K).

Another quantity of interest is the Time to Maximum Rate (t_m), which is a measure of how long the reaction takes to reach the peak rate. The following equations can be used to calculate t_m.

$$k_0 = M(V)(A \exp(-E/(RT_0)))C_{A0}C_{M_0} \tag{4}$$

$$t_m = \frac{m(R)(T_0)^2 C_P}{E(\Delta H)k_0} \tag{5}$$

where k_0 denotes the initial decomposition rate (lb mol/h), t_m denotes the time to maximum rate (h), m denotes the mass of monomer (lb), T_0 denotes the initial temperature (K), and C_P denotes the specific heat (Btu/lb°C).

Parameters such as the temperature of no return, SADT and time to maximum rate can be used to select alarm levels and "never exceed points" for a process.

7. Safety investigation

At the end of a production reaction in the kettle, the azeotropic mixture of alcohol and monomer is taken overhead and condensed into the lights receiver. After all of the primary alcohol is stripped from the reaction mixture, the volatile monomer boils over to the lights receiver. Table 2 summarizes the thermal stability parameters for the lights receiver. Calculations were done for both stoichiometric and azeotropic mixtures because the material in the lights receiver can vary in composition from azeotropic (55 wt% monomer) to stoichiometric (79 wt% monomer). The T_{NR}, SADT and t_m thermal stability parameters for the lights receiver using the relationships (eqs. 2–5) discussed previously are summarized in Table 2.

The Semenov theory of thermal explosions assumes zero order kinetics (i.e. reaction rate is independent of the concentration of the reactants). The accuracy of the predictions decreases as the kinetic activation energy and/or heat of reaction decrease. The effect of reactant depletion on the thermal stability parameters for the lights receiver as determined by digital simulation is shown in Table 3.

Each of the temperatures increases about 4°C compared to the results from Semenov theory (Table 2). The critical temperature difference, $T_{NR} - R(T_{NR})^2/E$, remains constant, however, at about 8°C. The combined effects of higher temperatures and depletion of reactants decrease the time to

TABLE 2

Lights receiver thermal stability parameters from Semenov theory

Parameter	Stoichiometric mixture (79% M)		Azeotropic mixture (55% M)	
	Insulated	Uninsulated	Insulated	Uninsulated
T_{NR}, °C	28.0	45.7	24.7	42.0
SADT, °C	20.4	37.2	17.2	33.6
t_m, h, @ T_{NR}	75.2	9.4	52.6	6.6

TABLE 3

Lights receiver thermal stability parameters from digital simulation

Parameter	Stoichiometric mixture (79% M)		Azeotropic mixture (55% M)	
	Insulated	Uninsulated	Insulated	Uninsulated
T_{NR}, °C	32	50	29	46
SADT, °C	24	41	21	38
t_m, h, @ T_{NR}	68.0	8.5	65.2	9.1

maximum rate (t_m) for the stoichiometric mixture and increase the value for the azeotropic mixture.

Tables 2 and 3 serve to quantify the responses anticipated for this system. The values of T_{NR} and SADT are higher and t_m is shorter for an uninsulated compared to an insulated vessel. Also, the azeotropic mixture has a shorter t_m and lower T_{NR} and SADT in a given situation. This means that if indeed we have an azeotropic mixture, the possibility of a runaway reaction is increased. Driving the composition toward stoichiometric, however, means a greater loss of product.

The effect of the mixture composition on the t_m is shown in Fig. 5. The azeotropic mixture reaches the peak reaction rate faster than the stoichiometric mixture. The values for t_m shown in Fig. 5 are different than those from Table 3 because we selected a common initial temperature of 50°C and an adiabatic condition for the comparison.

8. Prevention approaches

Because the SADT is low compared to abnormal process or high ambient temperatures and the time to maximum rate is short, several measures were considered to prevent a runaway reaction in the lights receiver.
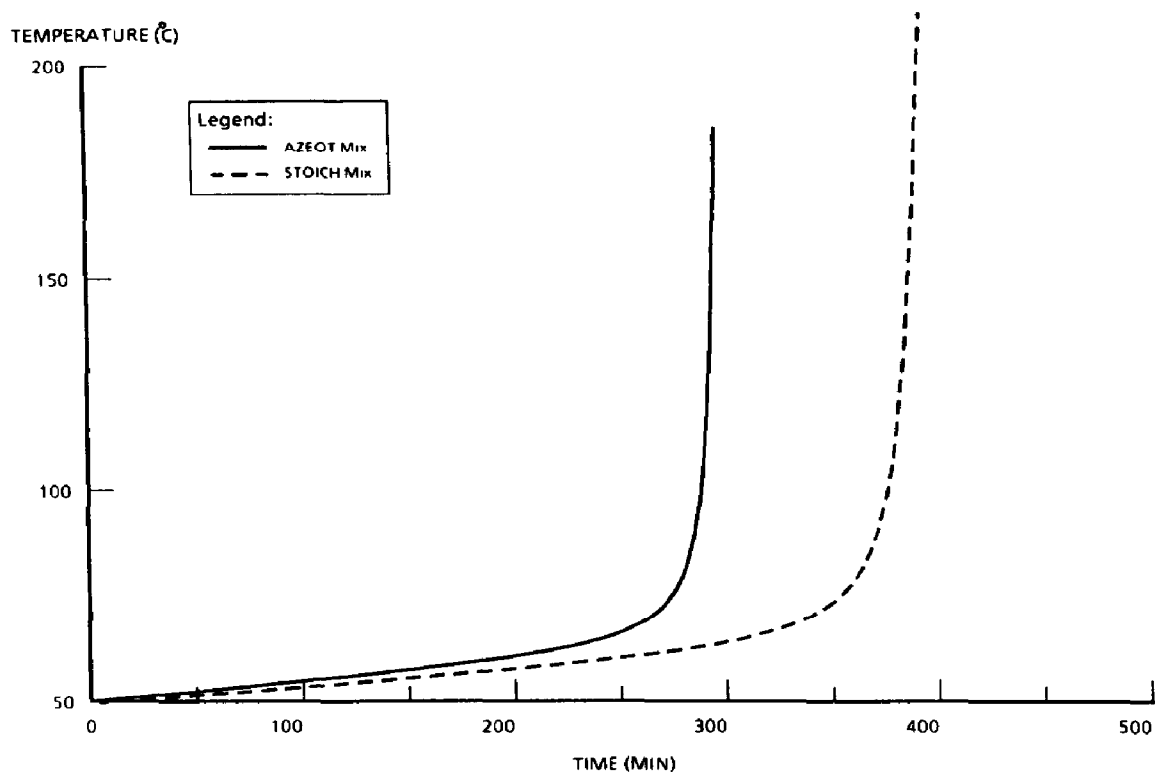
Fig. 5. Time to max rate comparison for an azeotropic vs. stoichiometric mixture of A and M (Adiabatic condition – initial temperature 50 °C).

1. Remove insulation from the lights receiver to facilitate heat loss and increase the values of T_{NR}, SADT and t_m.
2. Install temperature-indicator-alarms (TIA) in the condensate line from the water condenser and in the lights receiver to warn of high process temperatures.
3. Limit the amount of reactive mixture in the 200 gallon lights receiver to 10–20 percent of the capacity to improve the surface to volume ratio.
4. Use a cooling medium in the jacketed lights receiver to minimize the reaction rate.
5. Dilute the reactive mixture (the concept of quenching) with a nonreactive solvent or the primary alcohol.
6. Add a reaction inhibitor upon determination that a runaway reaction is occurring.
7. Convert the lights receiver into a reactor to reduce the alcohol and monomer concentration in a controlled manner.

We will discuss each of these measures separately. Of course, the most effective measure(s) will be adopted.

A fault-tree risk analysis established that the threat of a runaway reaction from an abnormal process or a high ambient temperature was more probable than one related to fire exposure. Therefore, removal of the fire protection insulation was recommended. However, it should be noted that adequate emergency relief protection was provided for the uninsulated vessel in the event of a fire.

Use of temperature-indicator-alarms will provide a warning of high process temperatures and allow time for corrective action.

The effect on thermal stability of reducing the amount of reactive material (increasing the effective surface to volume ratio) in the lights receiver was considered. Figure 6 shows the variation of T_{NR} and SADT with inventory in the vessel. The plot shows that reducing the inventory increases the values of T_{NR} and SADT thus increasing the thermal stability of the reactive mixture. However, the plots also show that removing the vessel insulation has a much greater effect on the thermal stability of the mixture than reducing the inventory.

Cooling the vessel to maintain a low temperature introduces the need for temperature control and raises the question of cooling failure. We decided to consider other measures and return to this option if necessary.
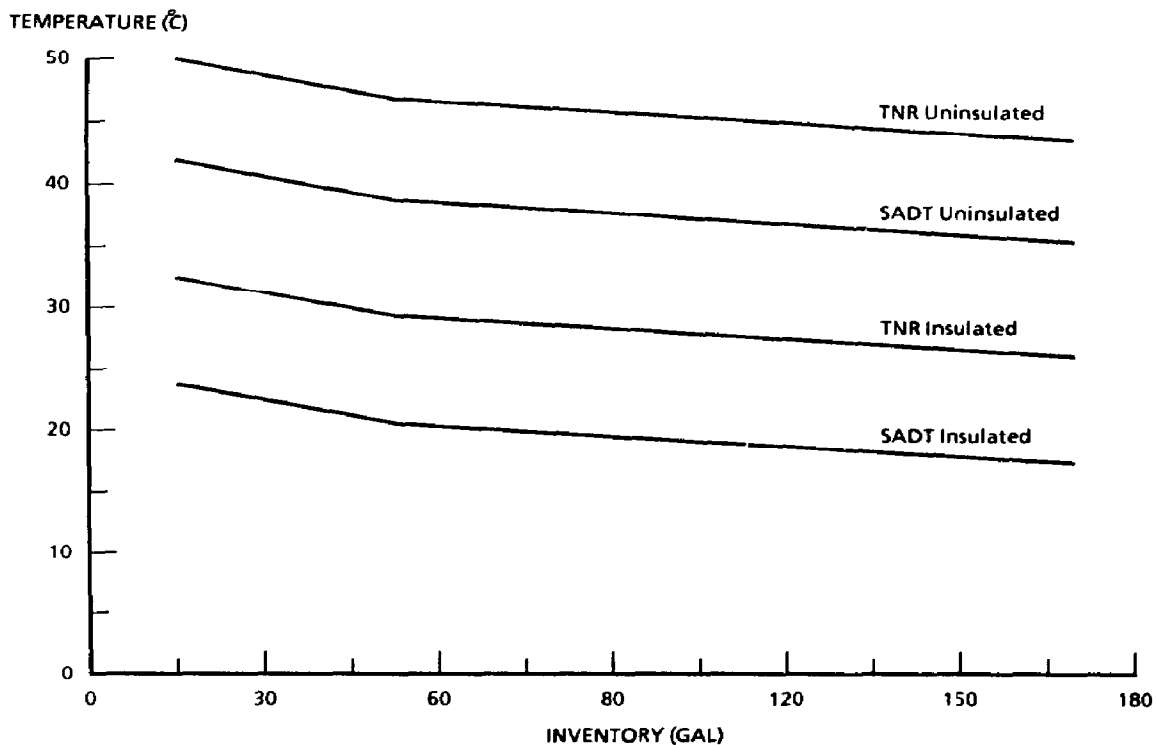
TEMPERATURE (C)

Fig. 6. Variation of T_{NR} and SADT with lights receiver inventory azeotropic mixture of A and M.

TABLE 4

Lights receiver reaction of azeotropic mixture of $A + M \rightarrow T + H$

Temperature (°C)	Residence time (h)
70	39
100	2.5
150	0.25

The concept of quenching the reaction with a non-reactive solvent or excess alcohol did not prove to be an attractive approach from both an operational and a cost viewpoint. This approach was not pursued further.

An effective inhibitor was known for this reaction. But this was not a cost-effective measure. First, the inhibitor addition system was expensive. Second, the inhibitor generates an additional hazard by creating toxic fumes when incinerated.

We used digital simulation and our kinetic model to design an isothermal recirculating batch reactor for the reaction of the alcohol with the monomer utilizing the lights receiver. Table 4 shows the residence times required to complete the reaction at various temperatures. The time required to complete the reaction is only acceptable at temperatures above 100°C.

9. Conclusions

Now that we understood how different process parameters affect the thermal stability of the system, we can select the option to reduce the runaway reaction hazard. Removing the insulation along with reducing the vessel inventory will minimize the risk of having to vent toxic and flammable materials. This recommendation is independent of whether the composition of the mixture in the lights receiver is azeotropic or stoichiometric. Furthermore, by using our kinetic model in runaway reaction simulations, we can show that either reaction mixture will be inherently stable at ambient temperature if the lights receiver is filled to no more than 20 percent of its capacity.

The principal conclusion of this study is that a detailed investigation of a process can allow straightforward selection of cost-effective solutions to improve process safety by identifying and preventing runaway reactions. Our recommendations will reduce the risk of venting toxic and flammable materials. The predicted thermal stability differences between Semenov theory and digital simulation are not significant for the cases investigated.

Acknowledgements

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