

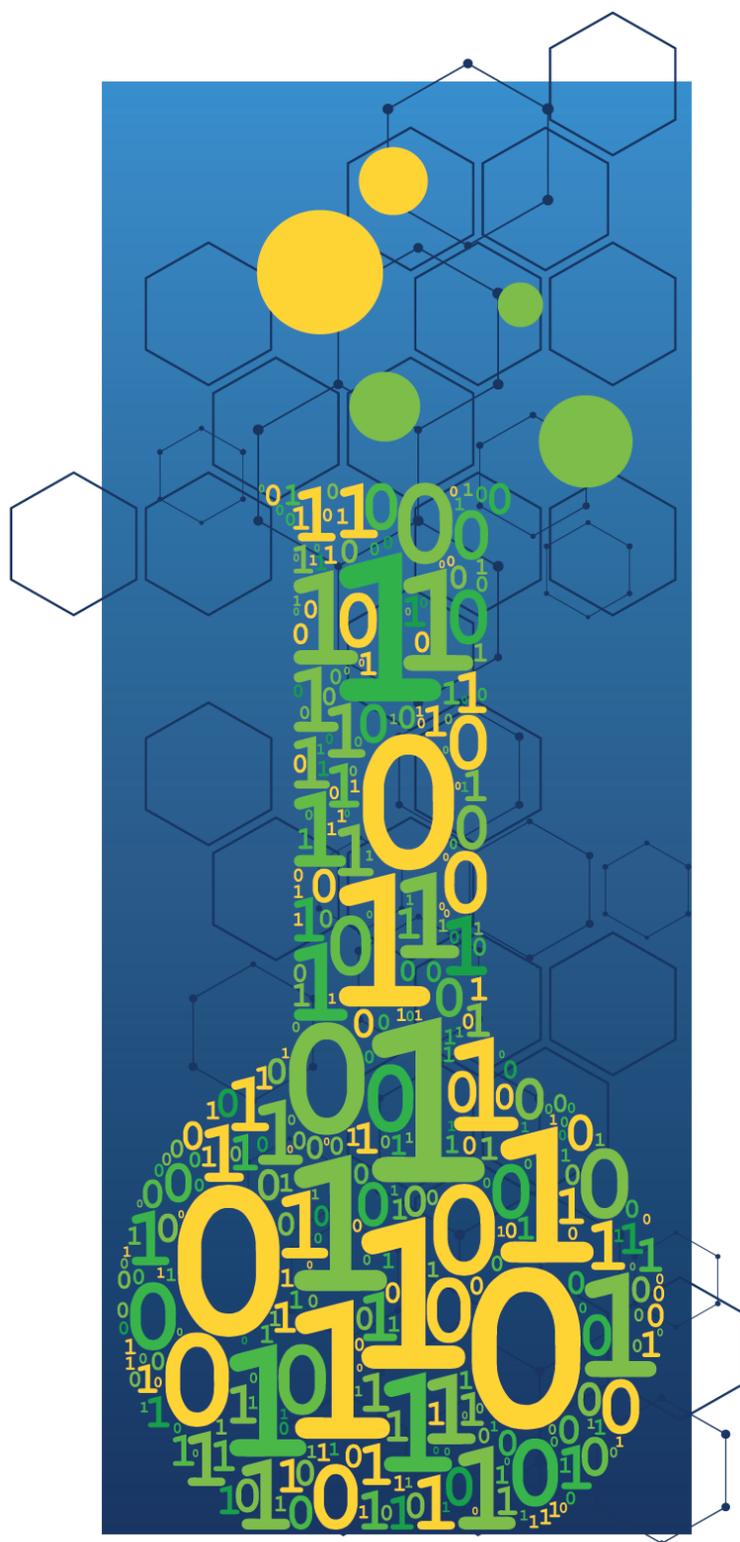
Polymerization Reactions Inhibitor Modeling

Styrene and Butyl Acrylate Incidents Case Studies

An ioMosaic Corporation White
Paper

G. A. Melhem, Ph.D., FAIChE
melhem@iomosaic.com

James Close and Ying Zhang



IO MOSAIC CORPORATION

**Polymerization Reactions Inhibitor
Modeling - Styrene and Butyl Acrylate
Incidents Case Studies**

Process Safety and Risk Management Practices

authored by

Georges A. MELHEM, Ph.D., FAIChE

and

James Close and Ying Zhang

July 28, 2020

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1 Introduction

Inhibitors are chemical substances that are used in small amounts to suppress the polymerization reaction of a monomer. An inhibitor has to be completely consumed before a polymerization reaction can proceed at normal rates. The time required to completely consume the inhibitor is often referred to as an "induction" time. Inhibitors react with polymerization initiation radicals to produce products that cannot induce further reaction. Inhibitors are different from reaction "retarders". A retarder does not suppress the reaction but merely slows it down, i.e. the reaction continues to increase at a slower rate until the retarder is consumed. Some impurities in monomers can act as retarders.

Small amounts of inhibitors can substantially prolong the shelf life of a reactive monomer. Common polymerization inhibitors, typically antioxidants, include MEHQ (monomethyl ether hydroquinone), TBC (4-t-butylcatechol), HQ (hydroquinone), PTZ (phenothiazine), etc. The effectiveness of most commonly used inhibitors depends on the presence of dissolved oxygen to convert free radicals to peroxy radicals that in turn react with the inhibitor to stabilize the monomer. Both inhibitors and oxygen deplete over time. Understanding inhibitor requirements is essential for polymerization reactions safety.

2 Inhibitor Modeling and Induction Time, L_{ip}

An inhibitor effectiveness model is usually coupled with polymerization kinetic model(s) in order to properly develop relief requirements and also for accurate hazard assessment. In general, inhibitor effectiveness models correlate the induction time with temperature and initial concentration of inhibitor [1]:

$$L_{ip} = \frac{1}{A^{\bullet} \exp\left[-\frac{E}{T}\right]} C_i^m = \frac{C_i^m}{k^{\bullet}} \quad (1)$$

where L_{ip} is the polymerization induction time, A^{\bullet} is the pre-exponential factor, E is the activation energy¹, C_i is the initial inhibitor concentration, and m is the concentration exponent.

An inhibitor depletion model is more effective when coupled with polymerization kinetic model(s) for dynamic simulation of relief requirements and hazard assessment [2]:

$$\frac{dC}{dt} = -A \exp\left[-\frac{E}{T}\right] C^n = -kC^n \quad (2)$$

where t is time and n is the reaction order². Inhibitor data is provided in the literature or measured as induction time as a function of storage temperature at a specific initial level of inhibitor concentration. If we assume the inhibitor is completely depleted when the concentration reaches a small

¹E is expressed in Kelvin and is equivalent to E/R_g where R_g is the universal gas constant.

²If $m \neq 0$ we can show that $n \simeq 1 - m$ and $A \simeq A^{\bullet}/m$ using the same activation energy E .

value, typically 1 ppm, we can develop an expression for induction time and fit the rate parameters from published or measured induction time data.

$$L_{ip} = t_f - t_i = -\frac{1}{k} \int_{C_i}^{C_f} \frac{dC}{C^n} \text{ where} \quad (3)$$

$$\int_{C_i}^{C_f} \frac{dC}{C^n} = \frac{C_f^{1-n} - C_i^{1-n}}{1-n} \text{ for } n \neq 1 \text{ and } \ln\left(\frac{C_f}{C_i}\right) \text{ for } n = 1 \quad (4)$$

For $n = 1$ and $t_i = 0$:

$$L_{ip} = t_f = -\frac{1}{k} \ln\left(\frac{C_f}{C_i}\right) = \frac{\ln(C_i/C_f)}{k} \quad (5)$$

For $n \neq 1$, $t_i = 0$, and $C_f = 0$:

$$L_{ip} = t_f = -\frac{1}{k} \left(\frac{C_f^{1-n} - C_i^{1-n}}{1-n} \right) = \frac{C_i^{1-n}}{k(1-n)} \quad (6)$$

Table 1 summarizes inhibitor depletion and effectiveness models based on data reported in references [1, 3, 4, 5, 6, 7, 2, 8, 9, 10], and this work and model development.

Table 1: Best fit inhibitor depletion and effectiveness model parameters

Inhibitor	Monomer	Depletion Model			Effectiveness Model			Figure
		A	E, K	n	A^\bullet	E, K	m	
PTZ	Acrylic Acid	3.284×10^9	11747	0.25	1.975×10^9	11680	0.73	11
TBC	Styrene	2.400×10^{12}	12615	0	3.644×10^{12}	12615	1.308	12
MEHQ	Acrylic Acid	1.527×10^{21}	19100	0	1.975×10^{21}	19100	1.19	13
MEHQ	Ethyl Acrylate	3.992×10^{11}	13419	0.45	2.116×10^{11}	13403	0.55	14
MEHQ	Butyl Acrylate	3.515×10^{13}	14912	0.55	1.479×10^{13}	14880	0.45	15
MEHQ	Methyl Methacrylate	1.085×10^{11}	12450	0.1	0.822×10^{11}	12399	0.884	16
HQ	Vinyl Acetate*	1.733×10^8	10620	0.5	9.341×10^7	10620	0.54	17
HQ	Vinyl Acetate**	3.869×10^7	10963	0.15	2.981×10^7	10963	0.777	18

A and A^\bullet are expressed in SI units (s, kmol, m³). For a 1st order reaction, A and A^\bullet will be in s⁻¹.

* Air atmosphere. ** Low Oxygen atmosphere.

3 Safety and Operational Considerations

Using the right inhibitor concentration is essential for safe operations. High levels of inhibitor can improve long term storage stability but may be detrimental to operational safety in the case

of a fire, loss of cooling, or an external heating induced runaway reaction. The use of high levels of inhibitor can cause the monomer system temperature to far exceed the onset temperature of thermal polymerization under external heating. Once the inhibitor is exhausted, the thermal runaway reaction proceeds at an elevated temperature with a substantial reaction rate and very little reactant/monomer consumption.

This can also occur in free-radical polymerization where a free-radical initiator is used. If the initiator is added and the inhibitor level is too high, the free-radical reaction will be suppressed and more initiator will be needed to counteract the inhibitor. If too much initiator is added, a runaway reaction can occur when the inhibitor is ultimately used up. A better operating practice would be to scrap the batch if the concentration of inhibitor exceeds a specified not to exceed threshold.

Inhibitors should be well mixed in the monomer or reacting mixture. If the monomer can freeze, there may be hazards associated with fractionation of the inhibitor. This can also occur in reactive distillation as it will be difficult to inhibit the overheads. Condensation of monomer in the vapor space can lead to polymerization on the vessel walls and polymer formation on instrumentation and pressure relief components. Rupture discs and pressure relief valves in such systems have to be cleaned and/or replaced regularly. Otherwise, the system may be operating without a relief device because of fouling. There are many practical means for reducing the fouling potential in polymer processing. If the monomer comes into contact with another immiscible phase such as water, the inhibitor can be depleted into the immiscible phase. TBC in styrene can be depleted by water contact for example. Note that an inhibitor is also vented during pressure relief.

Proper assessment and management of the safety of polymerization reactions require a thorough understanding of whether an inhibitor is used and how fast it is consumed during storage. A maximum level of inhibitor must be established. A minimum level of inhibitor has to also be established and both inhibitor and/or dissolved oxygen have to be replenished as necessary. In some cases it is important to maintain an air or limited oxygen atmosphere in the monomer storage vessels³ to ensure inhibitor effectiveness. Sparging of air and/or nitrogen has to be considered with care. A combination of air and nitrogen can be sparged into the tank, at flow rates such that the concentration of oxygen is sufficient for inhibitor effectiveness and the minimum oxygen concentration (MOC) for ignition is not exceeded. Reactivity testing is often necessary to establish the requirements for inhibitor levels and its effectiveness. Loss of dissolved oxygen can render the inhibitor ineffective and increase the likelihood of a runaway reaction at normal storage temperatures, especially for insulated vessels.

The presence of dissolved oxygen may decrease the effectiveness of some inhibitors. For example, dissolved oxygen significantly destabilizes vinyl acetate monomer at elevated temperatures [11] despite its importance for stabilization of acrylic and methacrylic monomer systems [12]. Calorimetry testing is required and highly recommended to confirm the effectiveness of an inhibitor under different process and storage conditions.

Calorimetry testing may also be required to establish if monomer stability is accelerated or retarded by contaminants such as rust, heat transfer fluids, etc. Some monomers are peroxide formers such as 1,3-butadiene [13]. The presence of peroxides can increase polymerization rates and the formation of popcorn polymers that can plug piping and instrumentation components.

³Without creating a flammable atmosphere and explosion hazard potential

4 Defining Chemical Reactions in SuperChems Expert™

Chemical rate expressions for simple and complex reactions can be entered in SuperChems Expert either interactively or via a reaction (.RXF) file. SI units are used by SuperChems Expert to represent chemical reactions; s for time, m³ for volume, kg for mass, kmol for moles, etc. When pressure is used in the rate expression it is first converted to bara by SuperChems Expert.

The general rate expression form used by SuperChems Expert for reaction j contains the following temperature and pressure components [14]:

$$K_j = A_j T^{a_j} P^{b_j} \exp \left[-\frac{E_j/R_g}{T} + \frac{B_j}{T^{1/3}} + \frac{C_j}{T^{2/3}} \right] F_{mult,j} R_{mult,j} \quad (7)$$

where A is the pre-exponential factor, a and b are temperature and pressure exponents, F_{mult} and R_{mult} are forward and reverse complex reaction rate multipliers, E/R_g is the activation energy in K, and B and C are additional user defined parameters.

Without temperature and pressure exponents and when only the activation energy is specified, the general rate expression reduces to the well known Arrhenius rate expression:

$$K_j = A_j \exp \left[-\frac{E_j/R_g}{T} \right] \quad (8)$$

F_{mult} and R_{mult} are used to enable the user to enter very complex reaction rate forms by just specifying additional parameters. These complex rate multipliers can be specified to be one of five forms including a differential form. It is recommended that complex reaction multipliers are specified using the interactive reaction tools because they are complex and require numerous indices and numerical constants (see Figure 1). The user can also specify the multiplier form (0 to 5) followed by the fraction type and the multiplier numerical parameters.

Form 0

No multiplier (default)

Form 1

Styrene like simple multiplier form:

$$F_{mult} = \exp \left[(a + bT) X_k + (c + dT) X_k^2 + (e + fT) X_k^3 \right] \quad (9)$$

where a , b , c , d , e , f are numerical constants and X is the fraction of species k specified as mole fraction, mass fraction, molar concentration in kmol/m³, or mass concentration in kg/m³.

Form 2

General simple multiplier form:

$$F_{mult} = (a + bX_k^c)^d \quad (10)$$

Figure 1: SuperChems Expert differential multiplier interactive input screen

THERMAL POLYMERIZATION OF BUTYL ACRYLATE WITH DECOMPOSITION RATES			
	A	B	C
1	Differential Rate Constant: $dC/dt = A (T^B) \exp(-E/T) C^N$		
2			
3	Initial concentration, C_0		50
4			
5	Pre-exponential factor A [negative for decay]	-5.511E+11	
6	Activation energy (E/R) /K	13835	
7	Temperature exponent B	0	
8	Concentration exponent N	1	
9			
10	Forward Differential Multiplier; $F_m = F_{m1} * F_{m2}$ where $F_{m1} = D + E * C^F$ for $C > G$		
11			
12	Constant D		0
13	Constant E		1
14	Constant F		-5
15			
16	Constant G		1
17			
18	Forward Differential Multiplier; $F_m = F_{m1} * F_{m2}$ where $F_{m1} = H + I * C^J$ for $C \leq G$		
19			
20	Constant H		1
21	Constant I		0
22	Constant J		0
23			
24	Forward Differential Multiplier; $F_m = F_{m1} * F_{m2}$ where $F_{m2} = \exp[(A+B*T)*X + (C+D*T)*X^2]$		
25			
26	X Compound	BUTYL ACRYLATE POLYMER	BUTYL ACRYLATE POLYM
27			
28	X Fraction Type	Mass Fraction	Mass Fraction
29			
30	Constant A		2.57
31	Constant B		-0.005
32			
33	Constant C		9.56
34	Constant D		-0.031
35			
36			

Form 3

Complex styrene like multiplier:

$$F_{mult} = \exp[(a + bT)X_k + (c + dT)X_k^2 + (e + fT)X_k^3] \times \sqrt{\frac{g \exp(-\frac{h}{T}) Y^K + l \exp(-\frac{m}{T}) W^P}{\exp(-\frac{q}{T})}} \quad (11)$$

Form 4

Ethylene oxide like multiplier:

$$F_{mult} = \left(\sum_i a_i X_i^{b_i} \right)^z \quad (12)$$

Form 5 (see Figure 1)

Differential multiplier:

$$\frac{dC}{dt} = z \exp\left(-\frac{a}{T}\right) T^b C^c \quad (13)$$

$$F_1 = d + eC^f \text{ for } C > g \text{ or } F_1 = h + iC^j \text{ for } C \leq g \quad (14)$$

$$F_2 = \exp[(A + BT)X_k + (C + DT)X_k^2] \quad (15)$$

$$F_{mult} = F_1 \times F_2; \quad (16)$$

R_{mult} can only use forms 0, 1, or 2. The following example illustrates a simple SuperChems Expert RXF file for styrene polymerization. The RXF file for styrene polymerization can be loaded using the PROCESS RXF FILE option under the DEFINE REACTIONS OPTION in the SuperChems Expert main menu.

5 Modeling Inhibitor Effectiveness with SuperChems Expert

Modeling inhibitor effectiveness requires the use of a differential multiplier. Figure 1 shows the use of multiplier type 5 to enter the decay rate of an inhibitor with an initial inhibitor concentration of 50 ppm [2].

The first part of the multiplier, F_{m1} , causes the overall reaction rate to be divided by the inhibitor concentration raised to the 5th power, C^5 . This in turn causes the overall reaction to be suppressed until C reaches a small enough concentration.

At $C = 1$, the reaction proceeds at its normal rate. Note that Figure 1 also shows the second component of the multiplier, F_{m2} to be a gel effect expression. Once $C = 1$, this component of the multiplier will influence the overall reaction rate as it is intended to when the inhibitor is depleted.

6 Case Study - Styrene Storage Runaway Incident

This incident occurred on the 7th of May 2020 in India and resulted in loss of life and numerous injuries. News and local reports about the incident indicate that the likely cause was a combination of loss of cooling and loss of inhibitor associated with a prolonged COVID-19 shutdown. In this case study we model suspected runaway reaction scenarios using SuperChems Expert and the inhibitor models developed in this paper to determine if the scenarios are plausible.

6.1 Incident Background

M/s LG Polymers Pvt Ltd is located in R. R. Venkatapuram, Vizakhapatnam district, India. The plant is surrounded by residential areas as shown in Figure 2. On the 25th of March 2020, the unit was closed, due to the nationwide lockdown to curb the spread of COVID-19 [15, 16]. The unit was proposed to resume operations on the 7th of May 2020.

Figure 2: Location of M/s LG Polymers Pvt Ltd plant and surrounding residential areas



In the early hours on the 7th of May 2020, a vapor release from a styrene monomer storage tank occurred. The tank had an inventory of 1830 tons of styrene monomer at the time of the incident. The vapor leak drifted westbound into residential areas. On the same day, 12 people died from exposure to styrene vapors and 585 were hospitalized [15, 16].

Styrene vapors were detected in the morning (2:54 am) on the 7th of May 2020 [15, 16]. The chillers at the bottom of the tank may have been turned off at 5 pm on the 6th of May as it was assumed that that at night no chilling is required [15]. At 3:02 am the tank temperature started to increase. Fire hydrants could not be reached due to the vapor cloud that had formed. The fire hydrants were opened between 4:30 and 05:15 am, and emergency chemical inhibitors (N-Dodecyl Mercaptan, Tertiary Dodecyl Mercaptan, and Eunox-76) were pumped into the tank to stop the polymerization reaction. The styrene temperature increased to 154 C at 10:45 pm. Water was continuously poured starting on the 7th of May into the tank. On the 9th of May the temperature decreased to 100 C.

Figure 3 shows styrene vapors being released from what appears to be a low pressure relief device on top of the tank. The relief device was reported to be an 8 inch relief device.

6.2 Contributing Factors

The tank was one of the oldest tanks on site and lacked sensors and gauges for the middle and top. The only sensor measuring the temperature was at the bottom where refrigeration is provided to ensure the tank contents do not reach ambient temperatures of approximately 34 C or higher [15, 16, 17, 18].

Figure 3: Styrene vapors leaking from the top of the storage tank

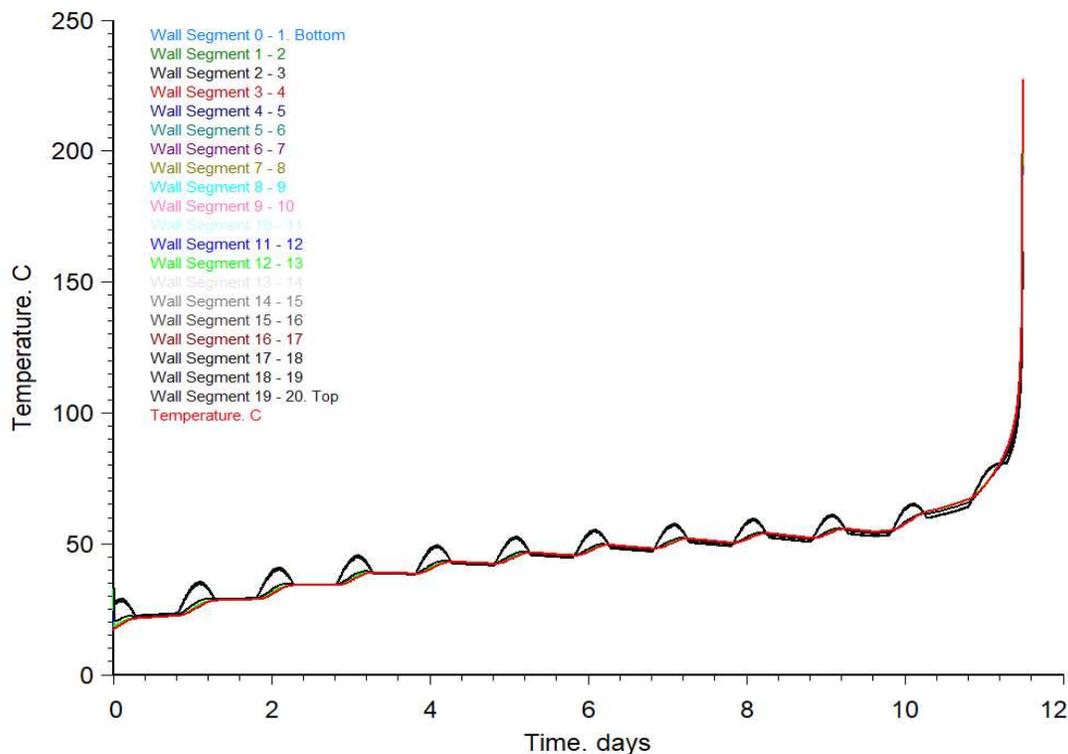


The refrigeration unit may have been shut down the day the plant was closed due to the COVID-19 lockdown. It was also reported that there may have been a malfunction of the temperature controls for the bottom of the tank and that the bottom of the tank was still at 17 C until the incident occurred [15].

There was uncertainty around the initial inhibitor TBC concentration level in the tank on March 25th, 2020. Typically, TBC is added (and replenished regularly) to styrene monomer at temperatures below 20 C to prevent polymerization during extended storage. However, it appears that TBC may have not been added or was not available on site due to the COVID-19 lockdown. The styrene was shipped from South Korea to India and would have had to be inhibited to IMO standards for sea transit. The styrene would have been unloaded to a shore tank in India (Mixed with what was in the tank or an empty tank) and then transported to the plant (Mixed into what was in the tank or an empty tank). At least 14 days (estimated) transit time with no refrigeration elapsed before the styrene arrived at the facility. This would have caused some inhibitor depletion. The inhibitor may have been further diluted if the styrene was mixed with existing styrene in the tank at the plant.

Another contributing factor may have been the lack of mechanical circulation of the styrene. Lack of mixing can create layering in the tank where polymerization could occur in hotter layers on top. In addition, natural circulation of styrene may have occurred near the top of the tank due to the vaporization and condensation of the styrene monomer onto the tank vapor walls, roof, and ancillary equipment. Condensed monomer will be uninhibited and is more likely to polymerize leading polymer build-up and clogging [19], possibly causing loss of refrigeration.

Figure 4: SuperChems Expert predicted runaway reaction duration at 15 ppm TBC, 17 C, no cooling



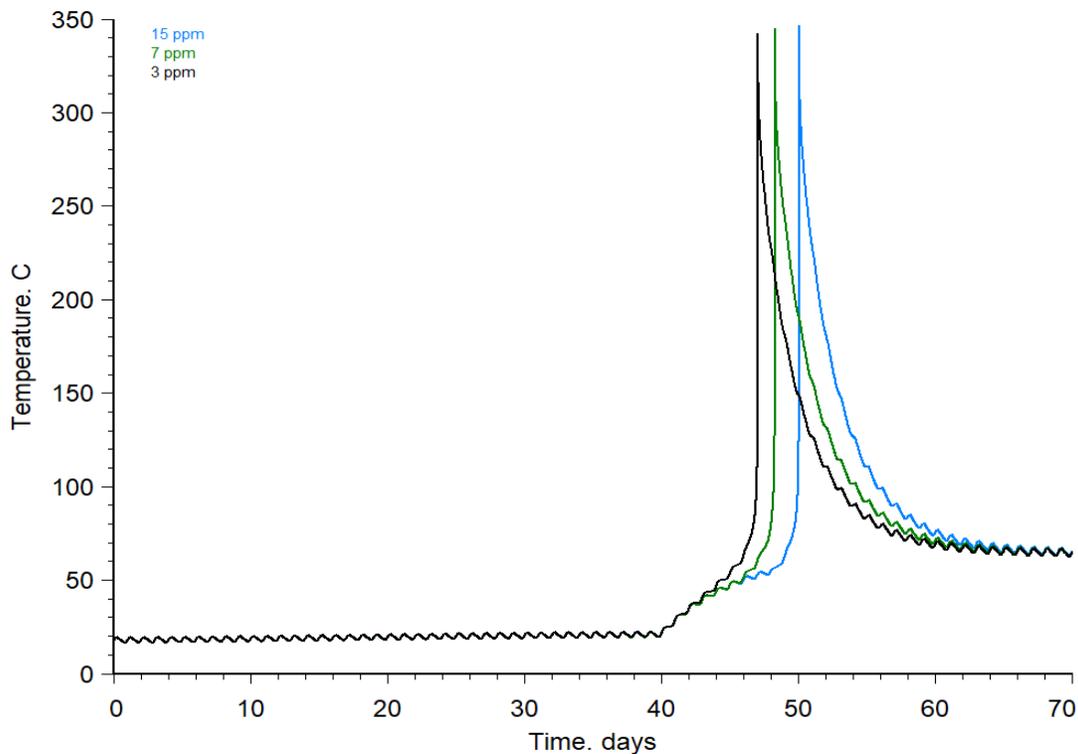
6.3 SuperChems Expert Scenario Modeling

It is very challenging to definitively identify how a multitude of contributing factors, conditions, actions, and/or a sequence of events resulted in this runaway scenario. However, using the detailed modeling capabilities of SuperChems Expert we are able to confidently rule out specific scenarios that are not consistent with what happened. SuperChems Expert can model the dynamics of runaway reactions coupled with venting, heat transfer from/to surroundings and vessel walls, and the change of solar heating over time depending on geographical location [10, 20]. SuperChems Expert requires detailed information about the storage tank dimensions and contents conditions, relief systems, atmospheric conditions, etc. Critical information is summarized in Table 2 as obtained from published data and reports about the incident.

We know that it took approximately 45 days for the runaway to occur. One of the scenarios we can rule out using the dynamics modeling capabilities of SuperChems Expert is a scenario where the tank contents start at 17 C, 15 ppm of TBC, and no cooling. In this scenario, the tank is exposed to atmospheric conditions and the cooling is not available from day 1.

Figure 4 shows the impact of heating during the day and cooling during the night on temperature in the tank. The tank walls were divided into 20 segments. We note the the top of the tank and walls near the top show significant change in temperature because they are not in contact with the liquid contents. A runaway occurs in approximately 11 days even though the initial level of TBC is 15

Figure 5: SuperChems Expert predicted runaway reaction duration at 3, 7, and 15 ppm TBC, 17 C, cooling lost at 40 days



ppm. This leads to the conclusion that the cooling system must have operated for some portion of the time it took for the polymerization reaction to runaway.

Three additional scenarios were modeled using SuperChems Expert at inhibitor levels of 3, 7, and 15 PPM and with the assumption that cooling was lost 40 days after the lockdown. The results are shown in Figure 5.

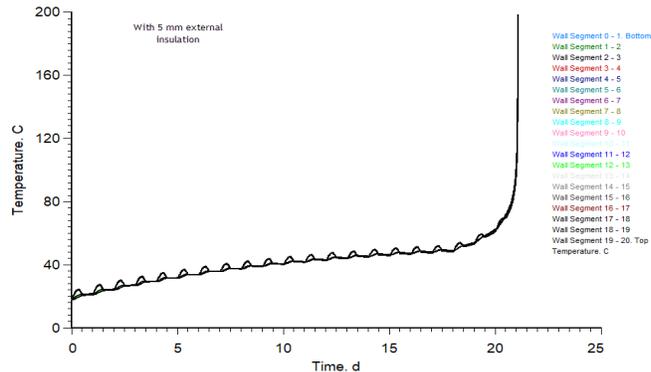
These simulations indicate that the TBC level was less or equal to 3 ppm if cooling was lost on day 40. If cooling was lost earlier than day 40, then a higher level of TBC would have existed in the tank in order to yield a runaway time in the range of 42 to 45 days.

6.4 Additional Considerations and SuperChems Expert Modeling

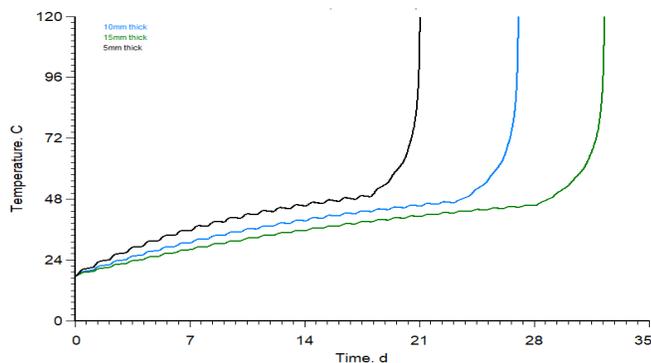
In a subsequent and what appears to be a final incident investigation report [21], additional information pertaining to tank construction, insulation, and relief systems were published.

6.4.1 Exterior Insulation

The tank was insulated. Assuming 5 mm of insulation, an initial TBC level of 15 ppm, and no cooling, the calculated runaway reaction time becomes nineteen days.



For the runaway reaction to occur at around the same time as the actual incident (i.e. 45 days after the site was locked down) the insulation will have to be greater than 15 mm thick. Calculations show that an insulation thickness of 15 mm without cooling leads to runaway conditions before day 45.



6.4.2 Circulation of styrene

There was refrigeration, however there was no effective circulation of styrene in the tank. There had been a change in the design of the suction and discharge lines of the circulation/refrigeration circuit at the beginning of the year. Originally a float valve was installed at the top of the tank, so that the cooled styrene would move down to the bottom of the tank via gravity and convection. This would reduce the risk of creating thermally stratified layers in the tank.

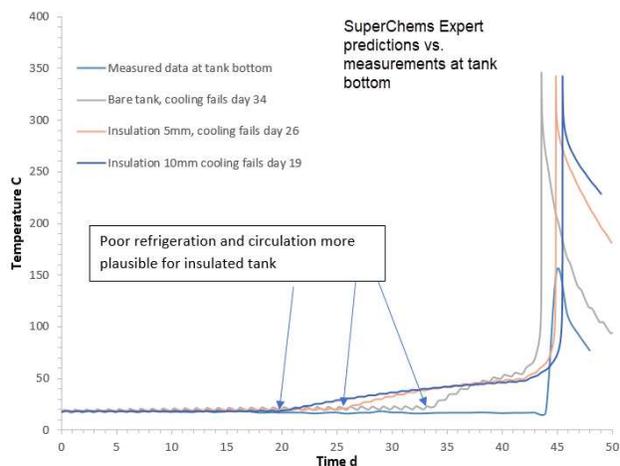
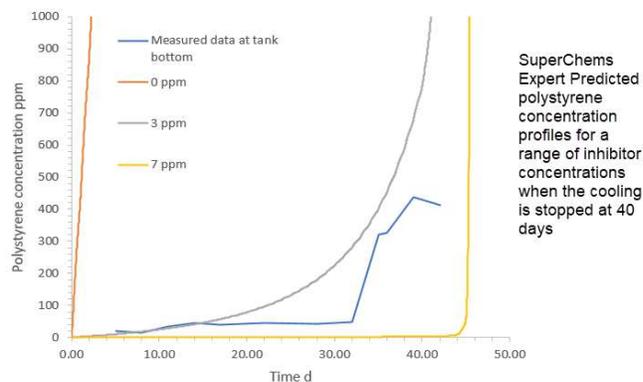
The management replaced the floating valve with a dip leg arrangement. This new arrangement provided cooling, however, did not induce circulation leading to thermal stratification within top and middle layers. Therefore, in 2019 when the float valve was installed, temperatures at the bottom of the tank read 22-30 °C. However, the reading at the dip leg was 17-18 °C, due to the temperature probe being close to refrigeration return line [21].

The cooling was therefore most likely insufficient or the suction/discharge lines had become clogged. The reaction was most likely occurring towards the top of the tank within a thermally stratified layer separate from that measured by the temperature probe, which was still measuring 17 °C. The temperature towards the top of the product fill likely reached temperatures exceeding the 150 °C recorded at the bottom.

The cooling was decreased slightly and assumed that the refrigeration unit was lost or the tank was completely thermally stratified at day 40, with only the very bottom layer remaining at 17 °C. SuperChems Expert predicts that for a TBC concentration between 3 and 7 ppm the polymer concentration was consistent with actual measurements. Even though it is stated the initial inhibitor concentration was 15 ppm this indicates that the inhibitor was most likely not well mixed into the monomer. Even with a value from the top of the tank 252 ppm on day 32, this indicates weaker concentrations of TBC in the stratified layers in the tank.

It is noted that the amount of TBC in the tank was 15 ppm on March 25. For a non-insulated tank the cooling and recirculation of styrene would have to be ineffective and the stratified layers would be fully formed at around 34 days as shown to the right. Again note the deviation from the measured data likely due to the temperature being measured at the bottom next to the refrigeration nozzle. With increasing insulation thickness the solar radiation has less of an impact on heating the stored fluid due to the restriction of heat transfer. Therefore, less cooling duty is required for the incident to occur on the 7th of May or day 45 as shown to the right. This could represent how the runaway reaction did not occur until 45 days with poor circulation due to the change from the float valve to the dip leg.

The SuperChems Expert simulations confirmed that several factors could have contributed to the incident including but not limited to: (1) Piping modification, therefore preventing adequate circulation in the tank, (2) refrigeration system was shut down prematurely before the day of the incident, (3) thermal stratification of the tank which includes stratification of the TBC inhibitor, (4) company management ignored the rise in polymer content on the 25th and 28th April, (5) likely clogging of the refrigeration lines, (6) absence of monitoring dissolve oxygen in the tank, and (7) potential presence of a catalyst as polystyrene vapor condensed and accumulated inside the roof top and wall and formed stalactites leading to localized areas where bulk polymerization is



accelerated⁴.

6.4.3 Pressure Relief Requirements

A preliminary pressure relief sizing calculation was performed with SuperChems Expert using the 8 inch vent/dip vent and the 2 inch vent with flame arrestor. The crack in the foam pourer (currently being investigated) is discounted, although it is believed to have provided an additional relief path. A total pressure relief flow area of 0.545 ft² is not adequate. A pressure relief flow area in excess of 30 ft² is required.



In general, it is not practical to provide adequate relief for large low pressure monomer storage tanks under either a process induced runaway condition or a fire induced runaway condition.

6.5 Facility Siting and Land Use Planning

Google site images for 2004, 2009, 2015, and 2019 indicate substantial dense residential developments to the west of plant [15] over the years. The plant was constructed in 1961. Such developments should have not been allowed without a detailed quantitative risk assessment (QRA) to delineate tolerable individual risk contours and societal risks. Land use individual risk criteria have been published and used by numerous countries such as Australia and England. Figure 6 illustrates such criteria for Queensland, Australia. We did not have sufficient details (PFDs, P&IDs, chemical inventories, etc.) about the plant to develop such risk contours and indicators using SuperChems Expert. SuperChems Expert includes very detailed visual consequence and QRA modeling capabilities that are used to develop societal risks and individual risk contours and to identify scenarios and process units and equipment requiring risk reductions and mitigation.

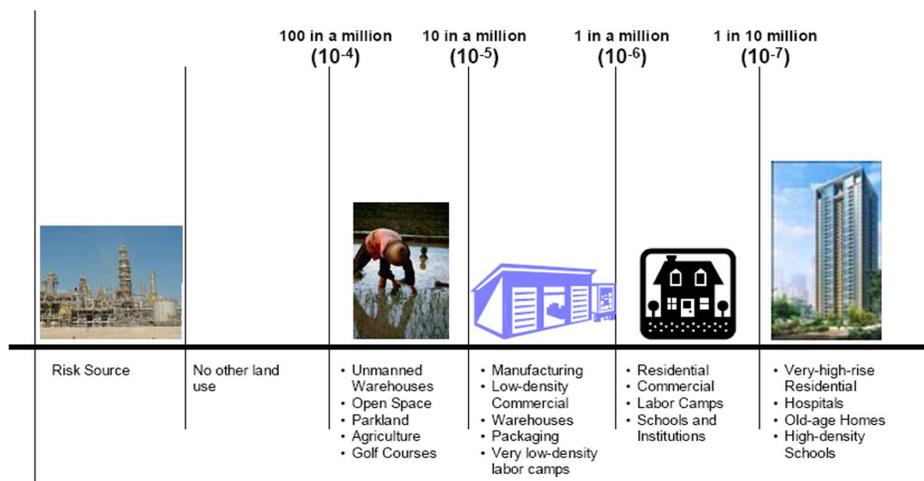
Land use planning, i.e. the control and designation of land uses, can encourage, discourage, or prohibit development in certain areas. Proper land use planning requires the balancing of often competing interests from the private sector, public sector, short and long term economic development, environmental considerations, and safety. Land use planning often relies on both qualitative and quantitative risk criteria, including individual risk criteria.

These criteria (see Figure 6) should be considered as providing target guidance rather than absolute values in all situations as the referenced land users are assumed to be exposed to involuntary risk. These criteria also assume that the individuals will be exposed to the risks 24 hours per day and continuously day after day for an entire year. In practice that is not normally the case, and these criteria are therefore conservative.

When a involuntary risk is to be imposed on an individual or a group of individuals by locating

⁴Could be the reason why there is a sharp temperature increase in measured data

Figure 6: Queensland Individual Risk Criteria [Queensland 1998]



an industrial facility such as an oil refinery or a chemical processing plant in a nearby area, the decision-making process of risk tolerability or acceptability will immediately consider if the risks are low enough relative to other commonly known and/or historically tolerated risks.

Where the number of individuals exposed to risk is low and/or where the duration of the risk exposure is low, ioMosaic recommends the use of an individual risk tolerability criteria of 1/100,000 years for land use planning. This criterion is consistent with recognized and generally accepted risk management practices⁵. Where the risk is taken with free choice and full knowledge, that risk can be described as voluntary. Where the risk exposure is voluntary, it is well established that individual risk criteria for voluntary risks are one order of magnitude higher than individual risk criteria for involuntary risk.

7 Case Study - Butyl Acrylate Runaway Incident

The butyl acrylate runaway reaction and subsequent vapor cloud explosion occurred at the Syntron, LLC facility located in Morganton, North Carolina on January 31, 2006. The runaway reaction incident resulted in one death and multiple injuries, and later led to the bankruptcy of the company. The incident was caused in part by the erroneous scale-up of the original reaction process recipe. In this case study we use SuperChems Expert to model the runaway reaction scenario and to examine the impact of inhibitor on the thermal stability of butyl acrylate. Data used to model the runaway reaction scenario(s) using SuperChems Expert can be found in Table 3.

⁵Also see Health and Safety Executive (HSE). Risk Criteria for Land-Use Planning in the Vicinity of Major Industrial Hazards. HMSO, 1989

Figure 7: Synthron runaway reaction and explosion aftermath - Photo courtesy of Morganton Department of Public Safety



7.1 Background

The normal size recipe was scaled up to produce a batch of 6,080 lbs of acrylic polymer in a 1,500 gallon reactor, which is 12 percent more than the normal amount of polymer produced in a single batch [22, 23]. On January 30, the operator(s) added solvents and a portion of the monomer to the reactor. On the morning of January 31, the operator(s) heated the reactor by applying steam to the reactor jacket. Finally, the senior operator started the reaction by pumping the additional remaining monomer into the reactor all at once.

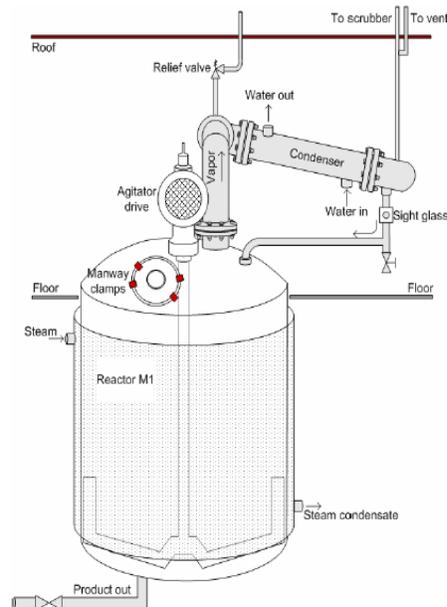
Several minutes later, a vapor release from the reactor occurred. The energy release and irritating vapor pushed the operator and other employees out of the building. An operator re-entered the building with a respirator and started emergency cooling water flow to the reactor jacket. However, the rate of energy release exceeded the cooling capacity of the reactor condenser. The building exploded less than 30 seconds after he exited. The fires following the explosion generated thick smoke. Fourteen people were injured, and one person died a few days later. The explosion destroyed the facility and damaged a few buildings in the neighborhood [22]. Figure 7 shows the extent of damage from the vapor cloud explosion which destroyed the facility.

7.2 Contributing Factors

The subsequent incident investigation indicated that Synthron did not perform proper reaction characterization or calorimetry to establish the safe operation requirements. The M1 condenser was located only slightly above the reactor, which made it prone to flooding and to loss of designed cooling capacity. Synthron scaled up the polymerization manufacturing recipe without evaluating the potential runaway reaction hazards. To avoid additional time and effort of running two half-size batches, the operators loaded additional monomer into a single reactor charge. This caused an increased rate of energy release in the reactor, exceeding the available heat removal capacity in the condenser.

In addition, the reactor manway became a weak link in the mechanical design of the reactor. The reactor manufacturer specified 18 clamps to maintain a tight seal at the reactor maximum working pressure of 75 psig. However, the operators only attached four of the 18 clamps temporarily to the reactor.

According to the CSB investigators [22], flammable solvent vapors started leaking through the manway at approximately 23 psig, well below the reactor design pressure of 75 psig. As a result, a vapor cloud formed around the reactor. The vapor cloud ignited and resulted in a catastrophic confined vapor cloud explosion. Synthron relied mostly on administrative and operating procedures for manufacturing and controls. Independent layers of protection and safeguards to control potential pressure and temperature surges due to undesired runaway reactions were missing.



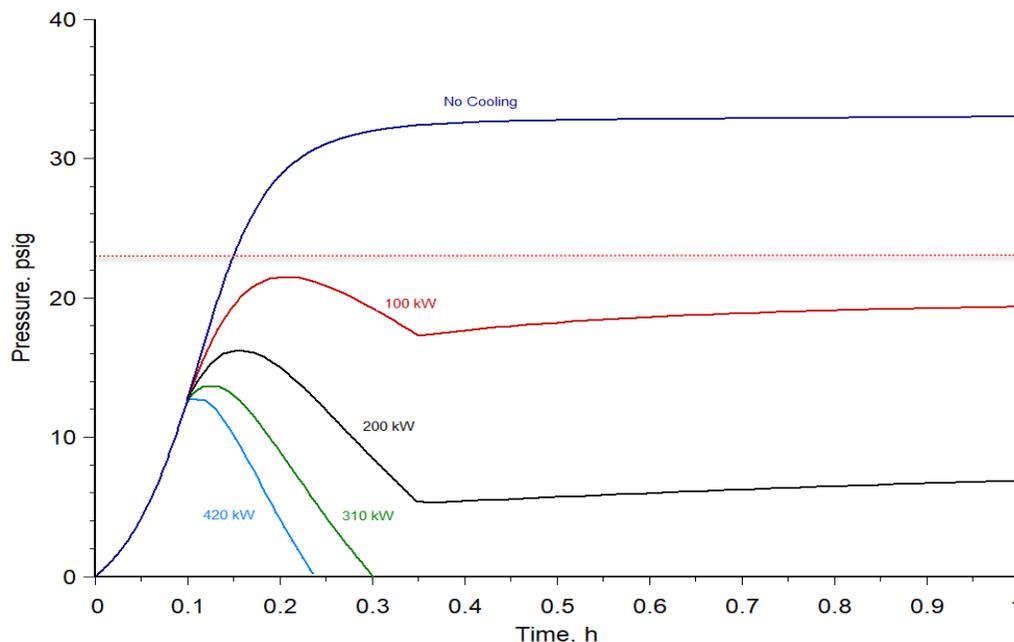
7.3 SuperChems Expert Scenario Modeling

SuperChems Expert was used to model the dynamics of the runaway reaction with the modified recipe. According to the incident report, flammable solvent vapors started leaking through the manway at approximately 23 psig. Had the standard recipe been used, the maximum system pressure would not have exceeded 20 psig.

Figures 8 and 9 illustrate the impact of cooling on the maximum pressure reached in the reactor. The CSB report [22] indicated a condenser design cooling capacity of 560 kW and a fouled cooling capacity of 310 kW. The simulation results show that there was hardly any cooling provided.

As is often the case with industrial incidents, several initiating and contributing events have to happen in the right sequence. In this case, the use of a modified recipe, partial clamping of the reactor, and the lack of cooling caused the pressure to exceed 23 psig and flammable vapors to leak through the manway. Since the reactor was inside a building, the confinement provided for a much more severe explosion outcome.

Figure 8: SuperChems Expert predicted free radical butyl acrylate runaway reaction pressure



7.4 Inhibitor Effectiveness

A reasonable question to ask is how long can the scaled up reaction mixture be held at the starting temperature (85 °C) without cooling and without initiator at different levels of MEHQ inhibitor? We note that in polymerization reactions, the inhibitor is often removed prior to the introduction of monomer into the reactor. Figure 10 shows that if all the reactant and solvent are added to the reactor and heated to 85 C, without cooling and without initiator, the butyl acrylate will runaway in approximately 10 hours without inhibitor.

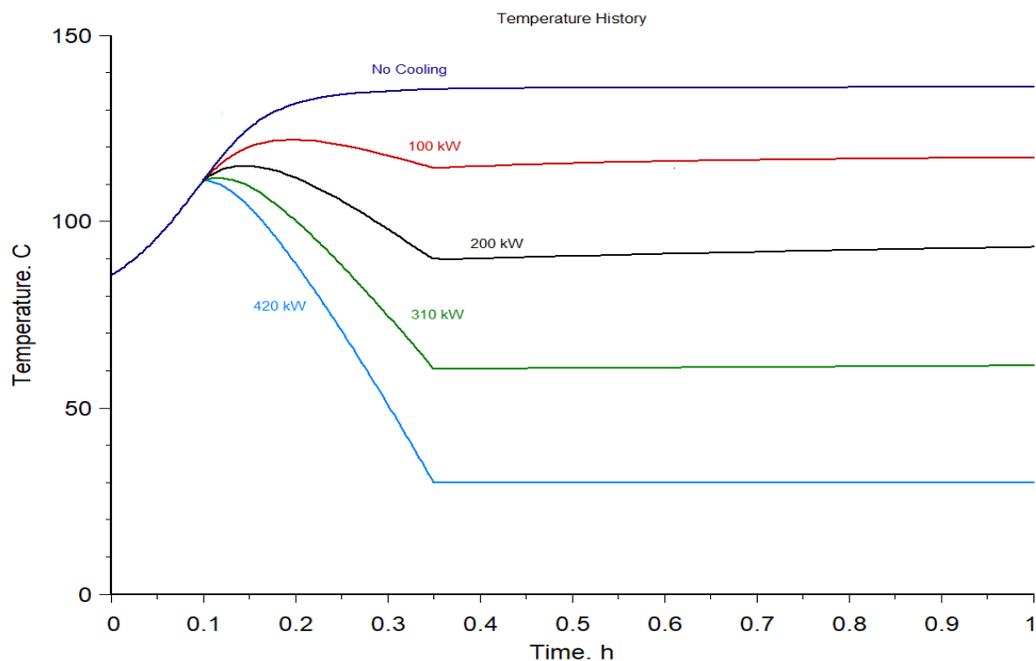
7.5 Layers of Protection

Chemical hazard identification and evaluation [24] are essential for the prevention and mitigation of runaway reaction hazards. ioMosaic⁶ has published extensively on how to characterize runaway reaction hazards by laboratory testing and advanced modeling using SuperChems Expert. In general, prevention and mitigation of runaway reaction hazards require multiple layers of protection.

A structured method, such as Layers of Protection Analysis, is recommended to review the adequacy of safeguards for systems where potential chemical reaction hazards exist [25]. Examples of independent safeguards that could prevent and/or mitigate potential runaway reaction hazards include but are not limited to: high pressure or temperature alarms, instrumentation to shut-off feed or to short stop the reaction, automatic additional emergency cooling, emergency dumping of

⁶Please visit www.iomosaic.com and www.iokinetic.com for free access to numerous publications on chemical reactivity characterization and management.

Figure 9: SuperChems Expert predicted free radical butyl acrylate runaway reaction temperature

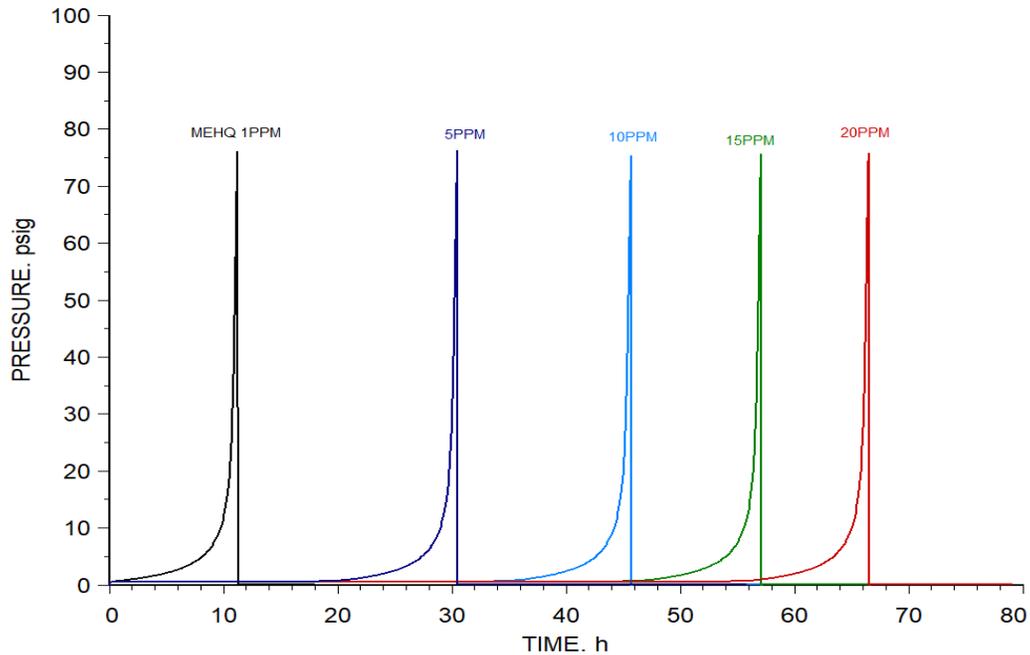


reactor contents to a safe location, etc.

8 Conclusions

Loss and excessive use of inhibitor are two scenarios that require evaluation for reactive monomer storage and pressure relief evaluation. Thermal stability information including time to maximum rate, temperature of no return, and self acceleration reaction temperature should be established. Measurements using small scale calorimetry testing coupled with practical dynamic modeling using SuperChems Expert or other suitable tools can provide a wealth of process and safety critical data and information. This information is required for PSM regulated chemical facilities in order to establish proper safe operating limits as required by the process safety information element.

Figure 10: SuperChems Expert predicted MEHQ effectiveness for modified butyl acrylate recipe with venting



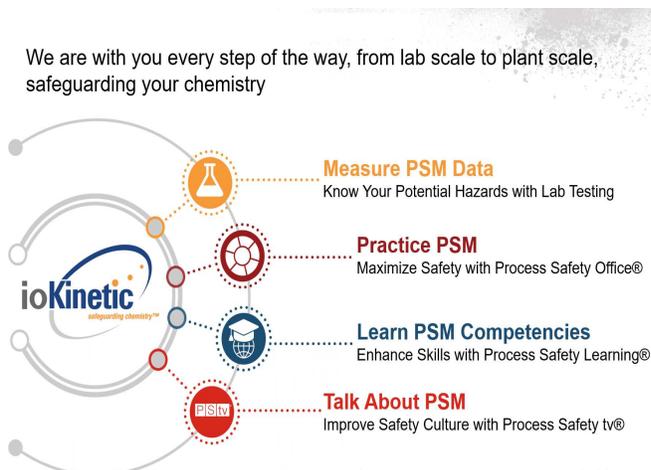
9 How can we help?

In addition to our deep experience in process safety management (PSM) and the conduct of large-scale site wide relief systems evaluations by both static and dynamic methods, we understand the many non-technical and subtle aspects of regulatory compliance and legal requirements. When you work with ioMosaic you have a trusted ISO certified partner that you can rely on for assistance and support with the lifecycle costs of relief systems to achieve optimal risk reduction and PSM compliance that you can evergreen. We invite you to connect the dots with ioMosaic.



We also offer laboratory testing services through ioKinetic for the characterization of chemical reactivity and dust/flammability hazards. ioKinetic is an ISO accredited, ultra-modern testing facility that can assist in minimizing operational risks. Our experienced professionals will help you define what you need, conduct the testing, interpret the data, and conduct detailed analysis. All with the goal of helping you identify your hazards, define and control your risk.

Please visit www.iomosaic.com and www.iokinetic.com to preview numerous publications on process safety management, chemical reactivity and dust hazards characterization, safety moments, video papers, software solutions, and online training.



A Appendix A - Common Inhibitors Induction Time Charts

The following charts were produced for common inhibitors using the models developed in Table 1 for PTZ, TBC, MEHQ, and HQ. The induction time is plotted vs. storage or processing temperature at different initial inhibitor concentration levels in ppm by weight.

A.1 PTZ Data and Chart

A.2 TBC Data and Chart

A.3 MEHQ Data and Chart

A.4 HQ Data and Chart

Figure 11: Calculated PTZ inhibitor effectiveness in acrylic acid as a function of temperature and concentration

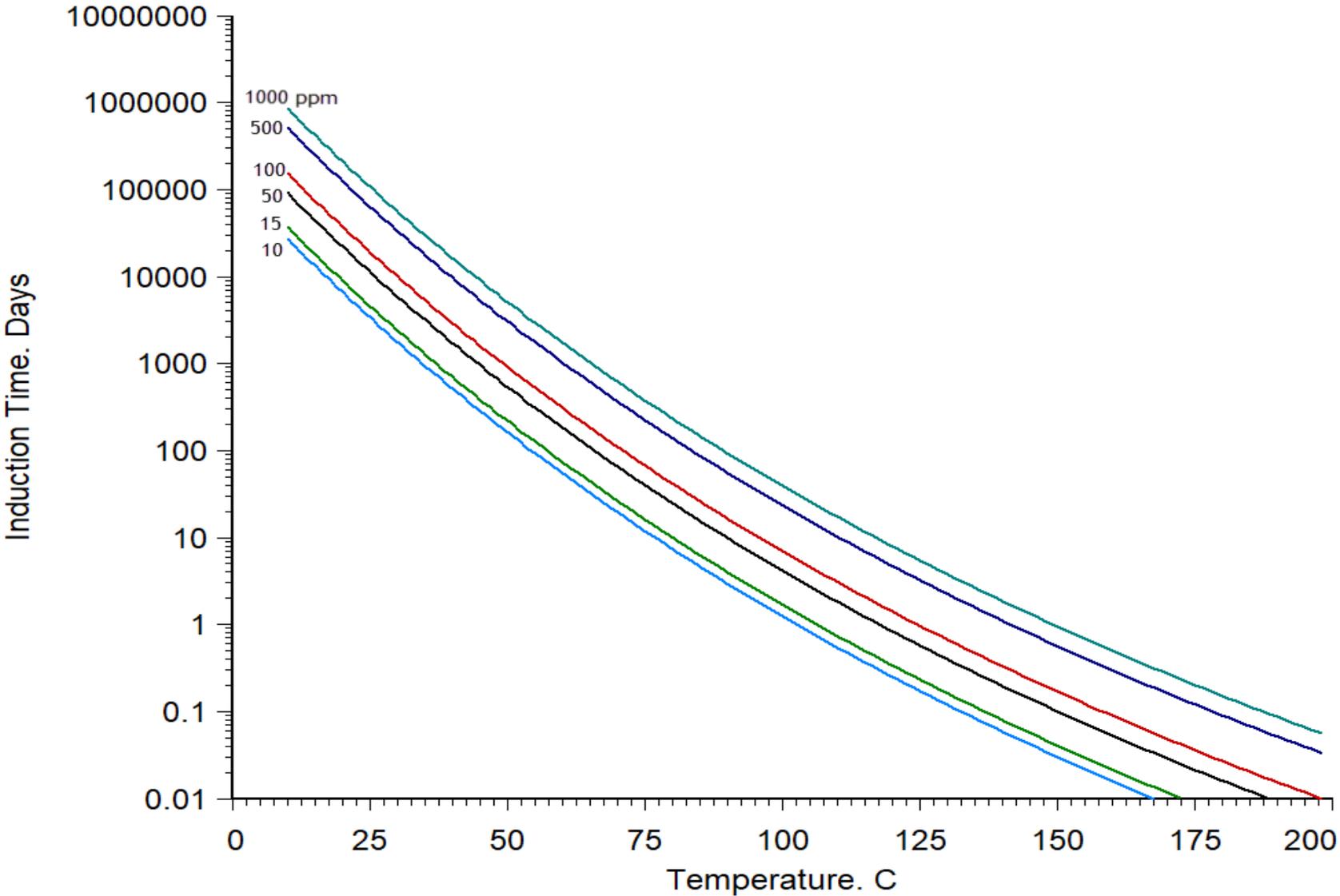


Figure 12: Calculated TBC inhibitor effectiveness in styrene as a function of temperature and concentration

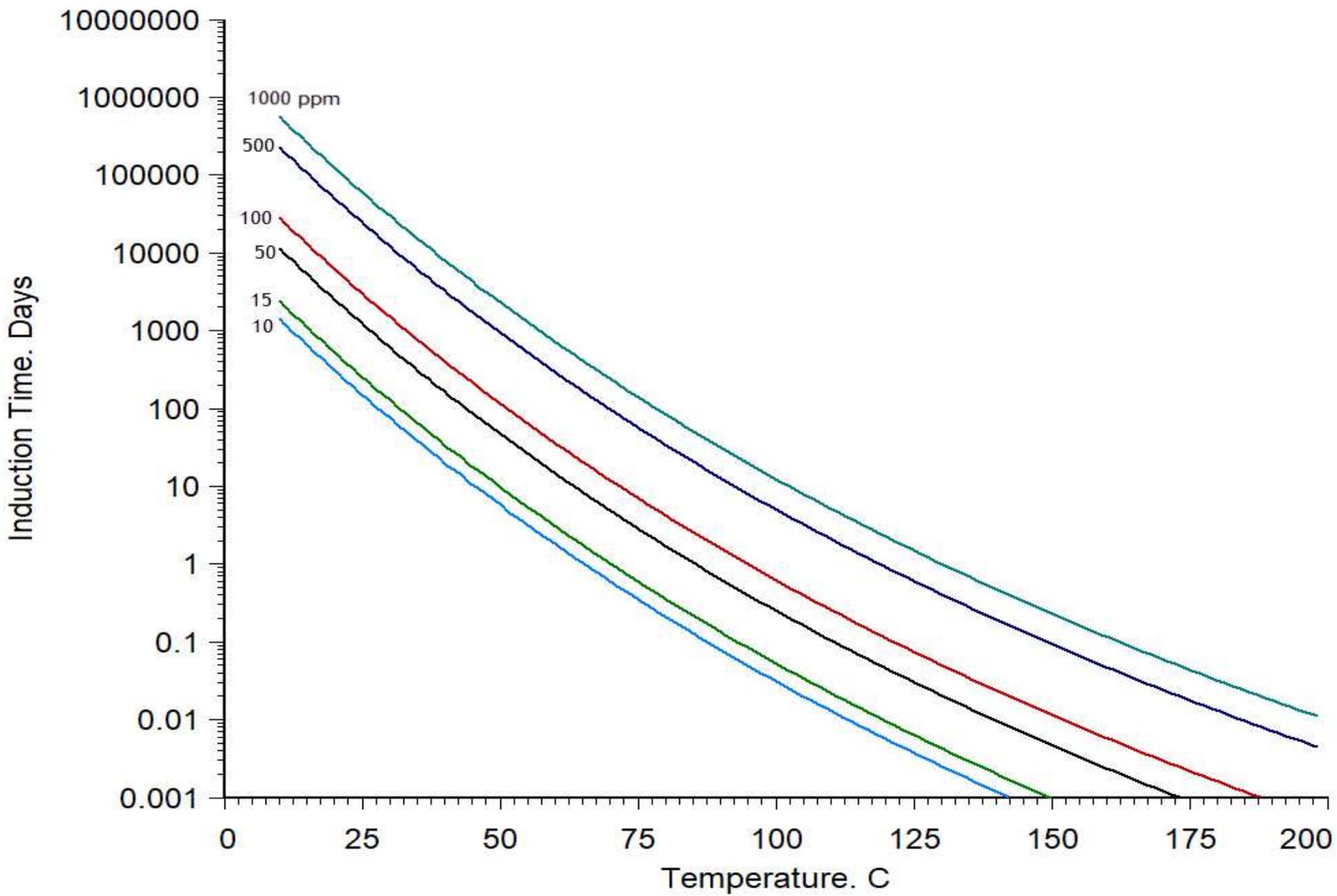


Figure 13: Calculated MEHQ inhibitor effectiveness in acrylic acid as a function of temperature and concentration

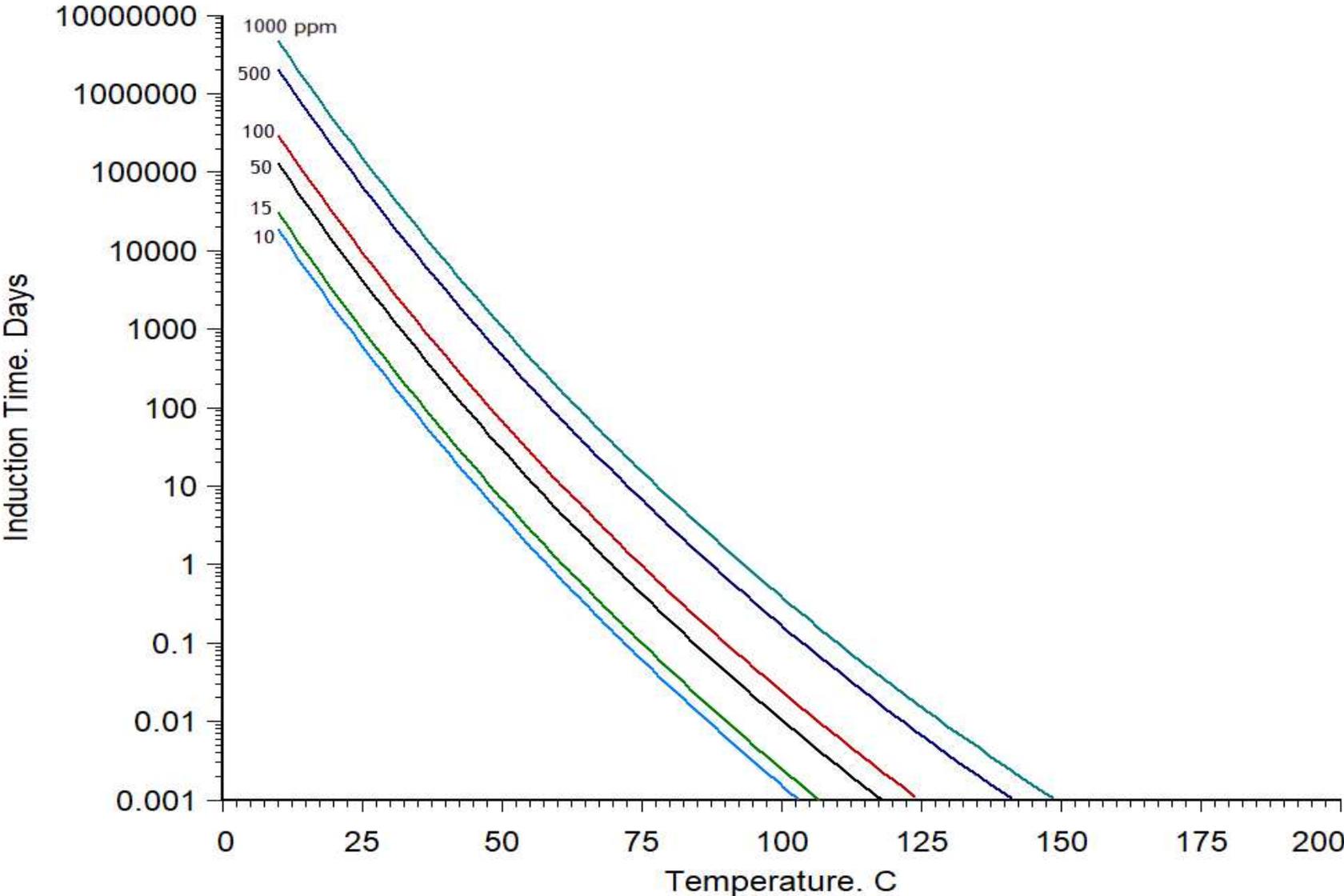


Figure 14: Calculated MEHQ inhibitor effectiveness in ethyl acrylate as a function of temperature and concentration

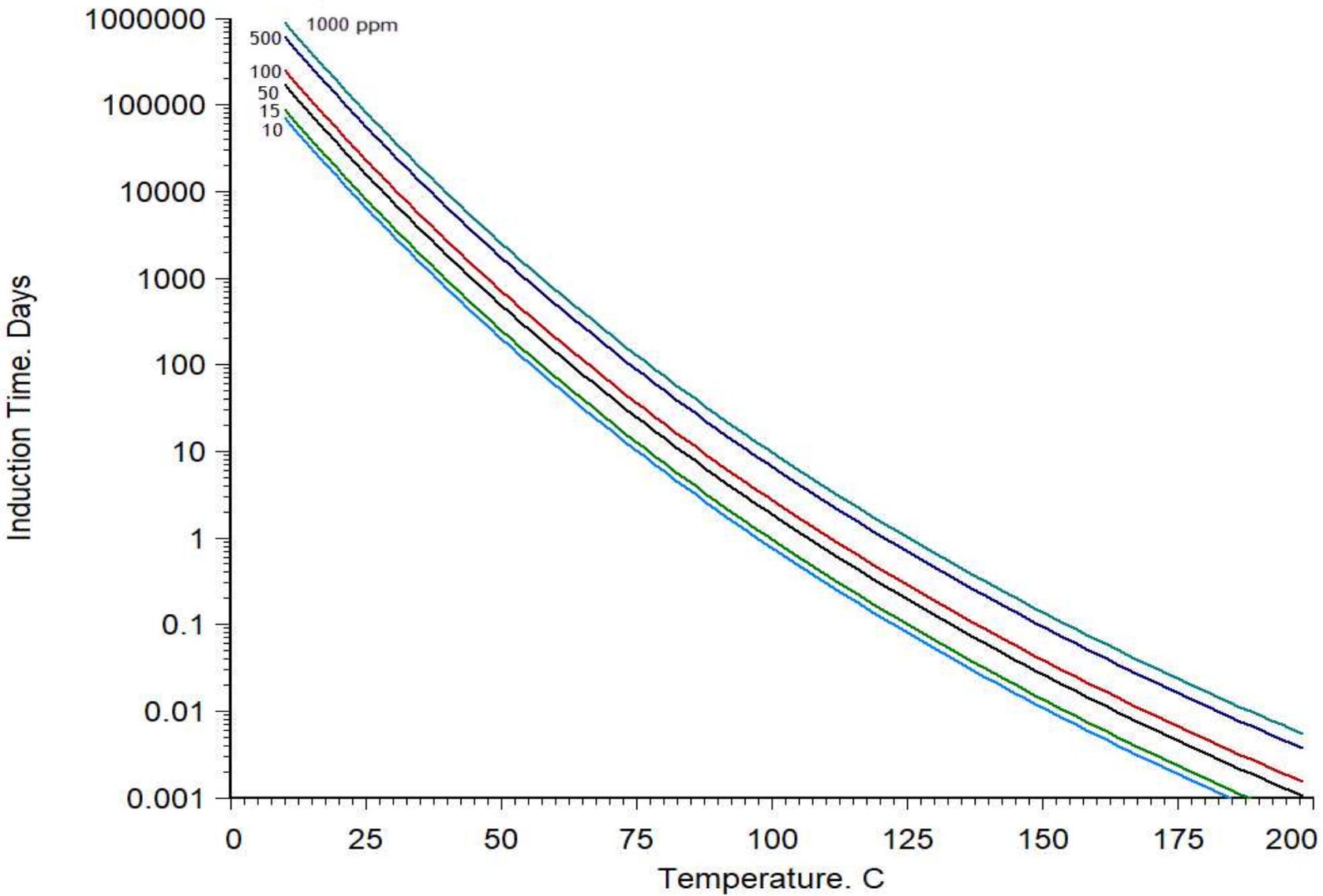


Figure 15: Calculated MEHQ inhibitor effectiveness in butyl acrylate as a function of temperature and concentration

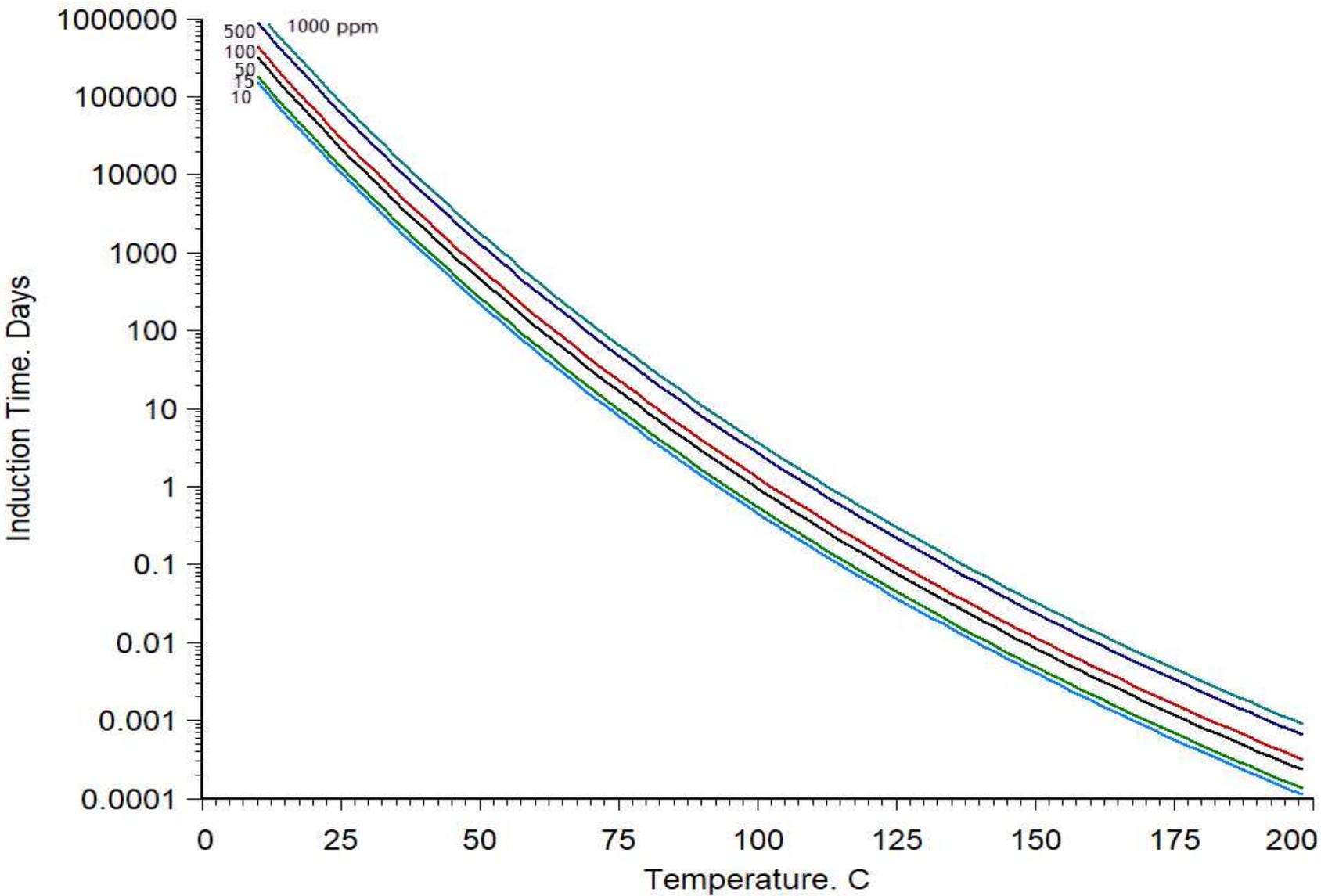


Figure 16: Calculated MEHQ inhibitor effectiveness in methyl methacrylate as a function of temperature and concentration

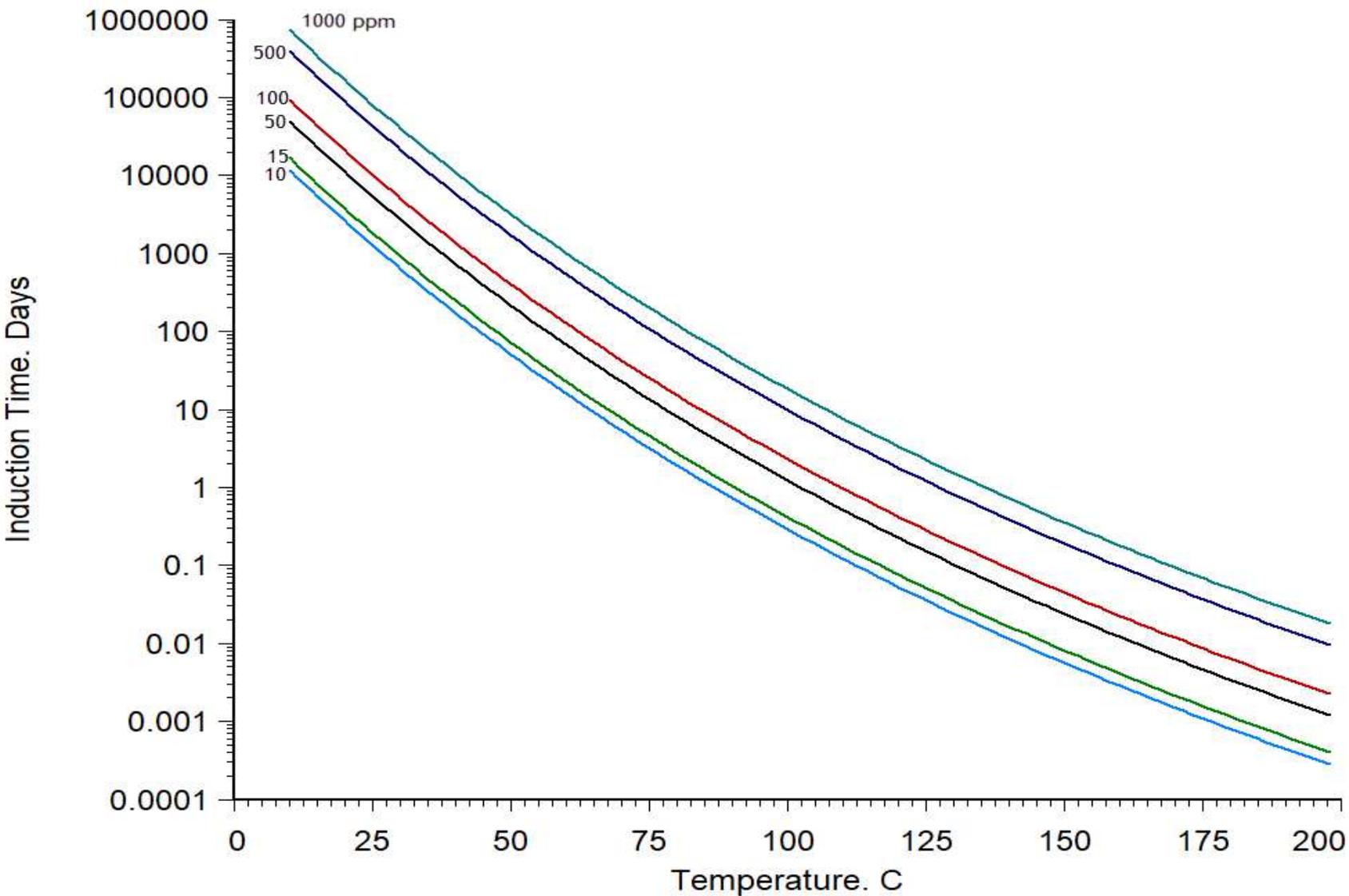


Figure 17: Calculated HQ inhibitor effectiveness in vinyl acetate as a function of temperature and concentration (air atmosphere)

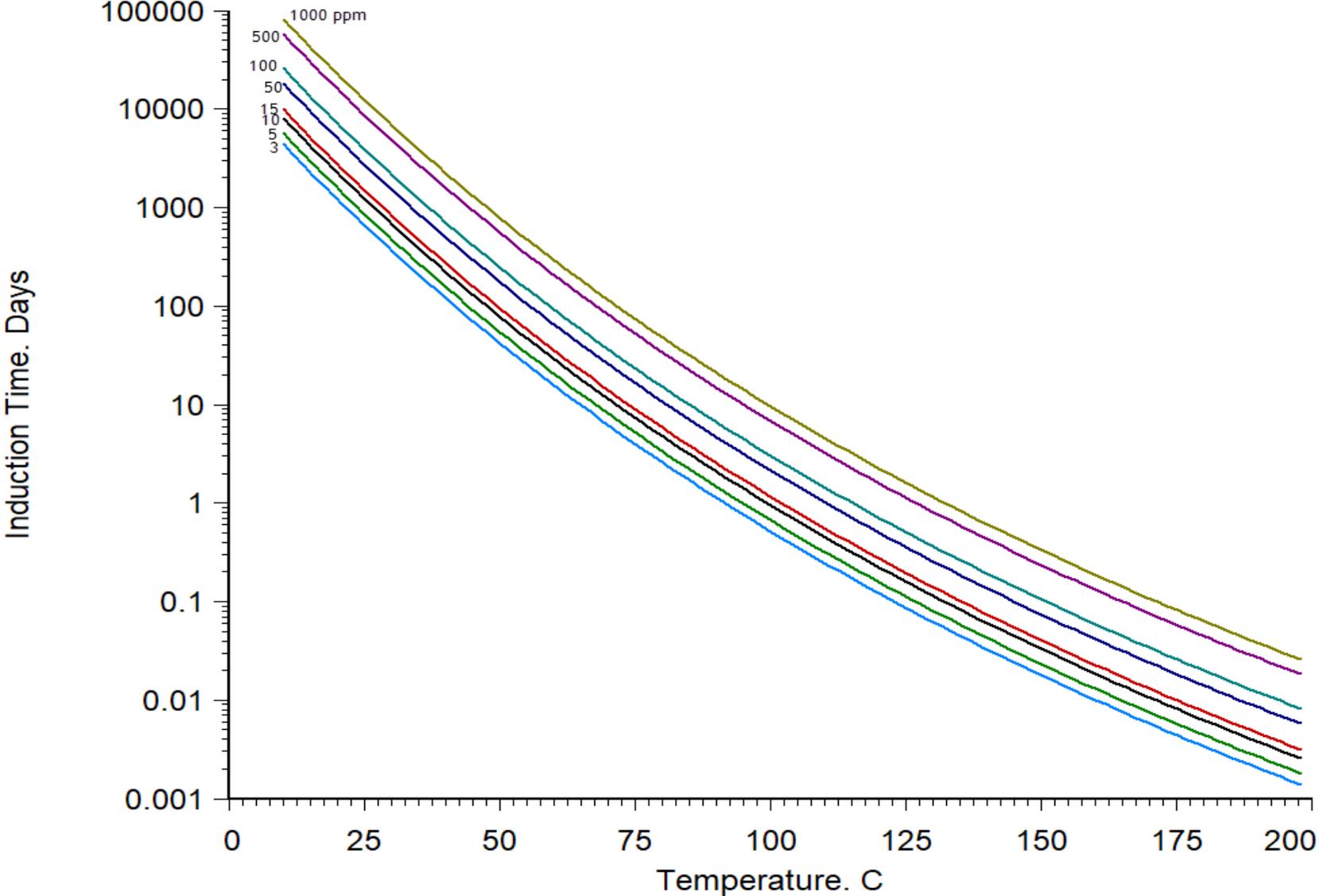
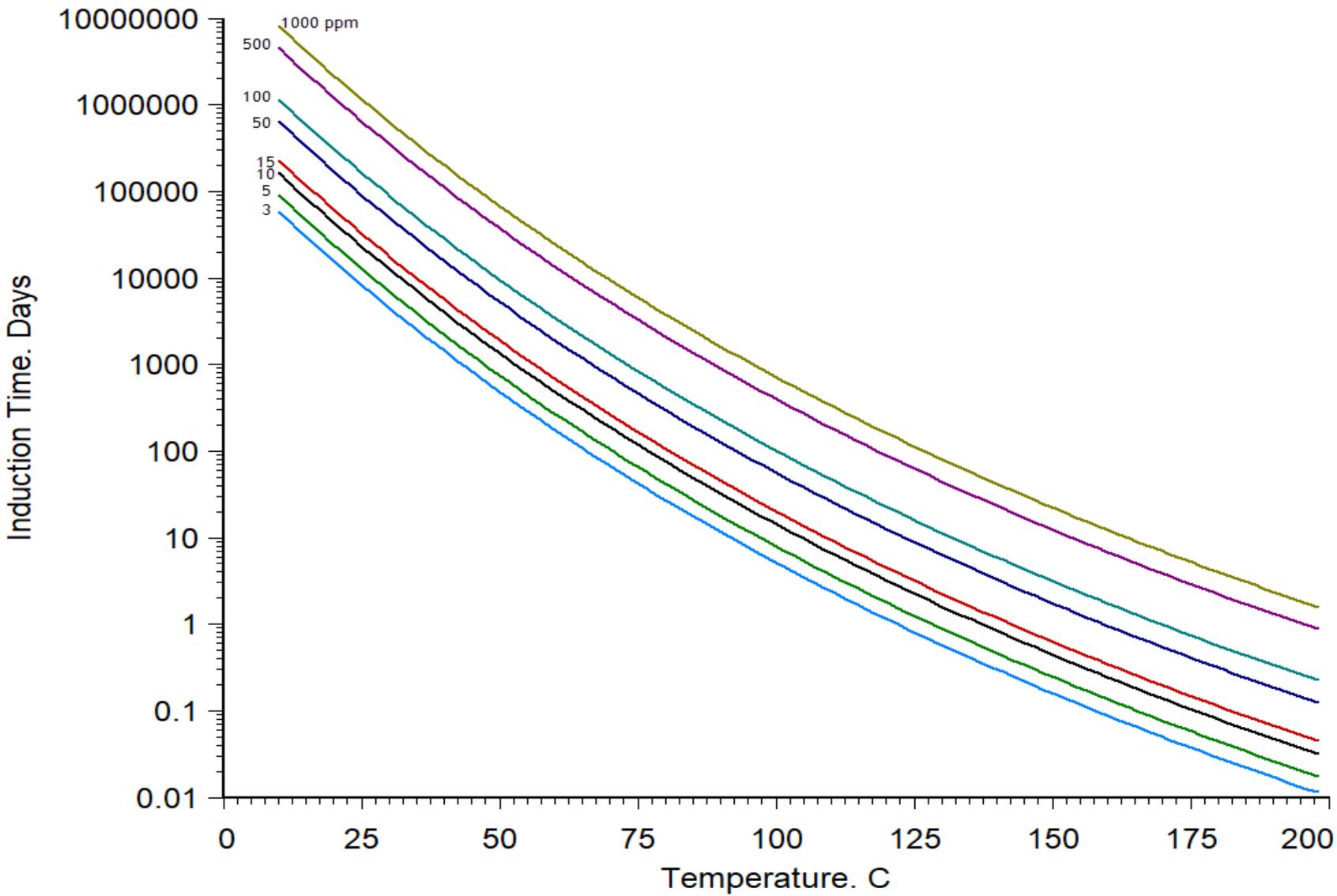


Figure 18: Calculated HQ inhibitor effectiveness in vinyl acetate as a function of temperature and concentration (low oxygen)



B Styrene Case Study SuperChems Expert Data

Table 2 provides a summary of data used to model the styrene runaway reaction dynamics using SuperChems Expert . Most of the data is obtained from reports about the incident available in the open literature and on the internet.

Table 2: Styrene case study SuperChems Expert data

Category	Description	Value
Tank Geometry	Diameter	18 m
	Length	12 m
	Wall thickness	10 mm
	Shape	Vertical cylindrical
	Conical roof 1/2 angle	85 deg
	Design pressure [26]	1.5-10 oz/in ²
Meteorological and Site Data [27, 28]	Latitude	17.755278 deg
	Longitude	83.208889 deg
	Ambient temperature	34 C
	Average wind speed	1.1 m/s
	Elevation above sea level	16 m
	Humidity	72 %
	Cloud coverage	12 %
Heat Transfer	Tank wall/vapor heat transfer coefficient	60 W/m ² /K
	Tank wall/liquid heat transfer coefficient	2500 W/m ² /K
	Outer Surface Emissivity	0.750
	Inner Surface Emissivity	1.000
	Absorptivity	0.750
Pressure Relief	Breather Vent	8 inch

C Butyl Acrylate Case Study SuperChems Expert Data

Table 3 provides a summary of data used to model the butyl acrylate runaway reaction dynamics using SuperChems Expert . Most of the data was obtained from OSHA, CSB, and open literature publications [22, 23].

Table 3: Butyl acrylate case study SuperChems Expert data

Category	Description	Value
Reactor Geometry	Diameter	15 ft
	Length	4 ft
	Wall thickness	0.375 in
	Shape	Vertical cylindrical
	Heads	2:1 Elliptical Heads
Process Conditions	Starting Temperature	85 C
	Starting Pressure	0 psig
Normal Recipe 2407 kg	n-Butyl Acrylate	33.0096 w%
	Nitrogen	0.0578 w%
	Cyclohexene	34.9403 w%
	Toluene	31.7847 w%
	Benzoyl Peroxide	0.2076 w%
Modified Recipe 2758.7 kg	n-Butyl Acrylate	41.7367 w%
	Nitrogen	0.053 w%
	Cyclohexene	28.549 w%
	Toluene	29.4186 w%
	Benzoyl Peroxide	0.2427 w%
Reaction Rates [20]	Free Radical Polymerization	$A_c = 4.74 \times 10^9$, $E_c = 9,710$
	Initiator Decomposition	$A_d = 6.47 \times 10^{13}$, $E_d = 14,946$
	Peroxide efficiency	0.5

Note recipe mass includes initial charge, triggering charge, and final dosing charge.

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About the Author



Dr. Melhem is an internationally known pressure relief and flare systems, chemical reaction systems, process safety, and risk analysis expert. In this regard he has provided consulting, design services, expert testimony, incident investigation, and incident reconstruction for a large number of clients. Since 1988, he has conducted and participated in numerous studies focused on the risks associated with process industries fixed facilities, facility siting, business interruption, and transportation.

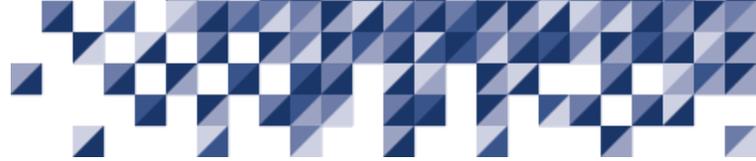
Prior to founding ioMosaic Corporation, Dr. Melhem was president of Pyxsys Corporation; a technology subsidiary of Arthur D. Little Inc. Prior to Pyxsys and during his twelve years tenure at Arthur D. Little, Dr. Melhem was a vice president of Arthur D. Little and managing director of its Global Safety and Risk Management Practice and Process Safety and Reaction Engineering Laboratories.

Dr. Melhem holds a Ph.D. and an M.S. in Chemical Engineering, as well as a B.S. in Chemical Engineering with a minor in Industrial Engineering, all from Northeastern University. In addition, he has completed executive training in the areas of Finance and Strategic Sales Management at the Harvard Business School. Dr. Melhem is a Fellow of the American Institute of Chemical Engineers (AIChE) and Vice Chair of the AIChE Design Institute for Emergency Relief Systems (DiERS).

Contact Information

Georges. A. Melhem, Ph.D., FAIChE
E-mail. melhem@iomosaic.com

ioMosaic Corporation
93 Stiles Road
Salem, New Hampshire 03079
Tel. 603.893.7009, x 1001
Fax. 603.251.8384
web. www.iomosaic.com



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Through innovation and dedication to continual improvement, ioMosaic has become a leading provider of integrated process safety and risk management solutions. ioMosaic has expertise in a wide variety of areas, including pressure relief systems design, process safety management, expert litigation support, laboratory services, training and software development.

As a certified ISO 9001:2015 Quality Management System (QMS) company, ioMosaic offers integrated process safety and risk management services to help you manage and reduce episodic risk. Because when safety, efficiency, and compliance are improved, you can sleep better at night. Our extensive expertise allows us the flexibility, resources, and capabilities to determine what you need to reduce and manage episodic risk, maintain compliance, and prevent injuries and catastrophic incidents.

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