An AIChE Technology Alliance
CCPS Center for Chemical Process Safety

Risk Analysis Screening Tools (RAST)

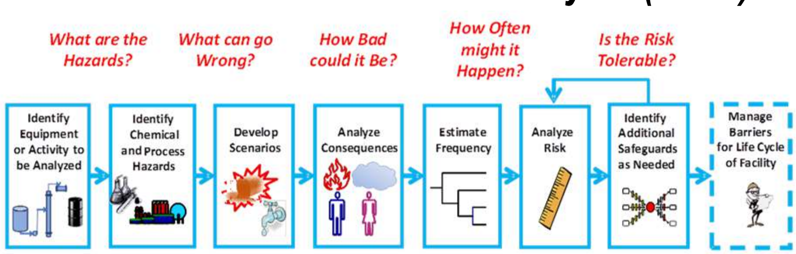
Case Study – T2 Industries

Runaway Reaction and Explosion
Jacksonville, Florida
December 19, 2007

An AIChE Technology Alliance
CCPS Center for Chemical Process Safety

Case Study – T2 Industries

Hazard Identification and Risk Analysis (HIRA) Study



We begin the study by **Identifying the Equipment or Activity** for which we intend to perform an analysis. RAST uses the operation of a specific equipment item containing a specific chemical or chemical mixture to define the activity. For example, the operation of a storage tank, a reactor, a piping network, etc. Inputs are chemical data, equipment design information, operating conditions, and plant layout.

An AIChE Technology Alliance
CCPS
Center for Chemical Process Safety

Risk Analysis Screening Tools (RAST) Overview / Demonstration

Case Study – T2 Industries
Process Description

We have been asked to perform a HIRA study of the MCMT Process. Methylcyclopentadienyl manganese tricarbonyl (MCMT) is an organo-manganese compound used as an octane-increasing gasoline additive. The Ethyl Corporation originally developed MCMT in the late 1950s. T2 manufactured and sold MCMT under the trade name Ecotane.

MCMT is produced in three steps that occur sequentially within a single process reactor. In the first reaction step (called metalation), the process operator feeds a mixture of methylcyclopentadiene (MCPD) dimer and diethylene glycol dimethyl ether (diglyme) solvent into the reactor. An outside operator then hand-loads blocks of sodium metal through a 6-inch gate valve on top of the reactor, closing the valve when complete. The process operator then heats the mixture with the hot oil piping system, setting reactor pressure control at 3.45 bar and hot oil temperature control at 182°C.

Intended Chemistry:

March 24, 2022 ***This is an illustrative example and does not reflect a thorough or complete study.*** Slide - 3

An AIChE Technology Alliance
CCPS
Center for Chemical Process Safety

Risk Analysis Screening Tools (RAST) Overview / Demonstration

Case Study – T2 Industries
Process Description

The initial reaction mixture contains approximately 0.11 weight fraction sodium, 0.45 weight fraction MCPD dimer and 0.44 weight fraction diglyme solvent. Heating this mixture begins the metalation reaction by melting the sodium and splitting each MCPD dimer molecule into two MCPD molecules. The melted sodium then reacts with the MCPD to form sodium methylcyclopentadiene, hydrogen gas, and heat. The hydrogen gas vented to the atmosphere through the pressure control valve and 1-inch vent line.

Once the mixture temperature reaches 99°C, the process operator starts the agitator. The mixing and higher temperature acts to increase the metalation reaction rate. At a reaction temperature of about 149°C, the process operator turns off the hot oil system and heat generated by the metalation reaction continues to raise the mixture temperature. At a temperature of about 182°C, the process operator initiates the control system cooling program, which intermittently injects water into the jacket based on the rate of reaction temperature increase. The heat of reaction for this step is approximately -45.4 kJ/mol sodium, -1975 J/g sodium, or -217 J/g reaction mixture.

March 24, 2022 Slide - 4

AnAIChE Technology Alliance
CCPS
Center for Chemical Process Safety

Case Study – T2 Industries
Process Description

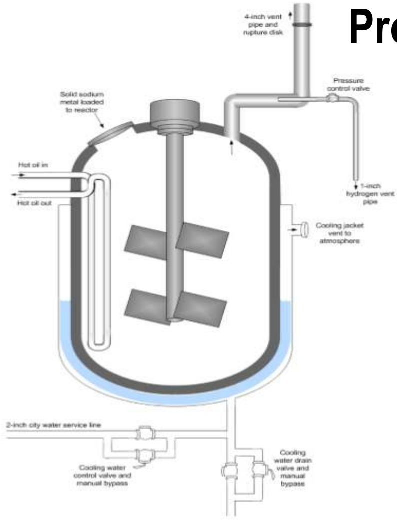
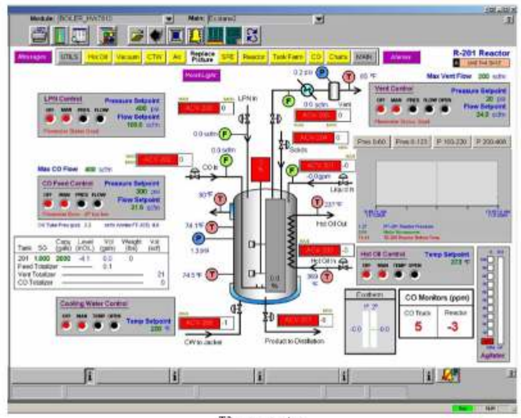


Diagram of MCMT Reactor


T2 screen capture

Process Control Screen for MCMT Reactor

AnAIChE Technology Alliance
CCPS
Center for Chemical Process Safety

Risk Analysis Screening Tools (RAST)
Case Study – T2 Industries

We will start by entering information for the MCMT Reactor. At some point, we may decide to include other equipment in the study.

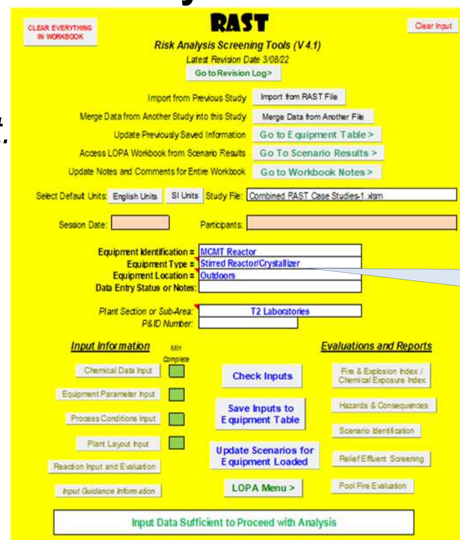
One the Main Menu, enter the equipment identification as the **MCMT Reactor**, equipment type as **Stirred Reactor/Crystallizer** and location as **Outdoors**.

Chemical Data – RAST requires a chemical or chemical mixture that is representative of the hazards. RAST does not perform time-dependent or location-dependent composition changes (such as within a reactor or distillation column). Where hazards may be significantly different between reactor feed and products, or distillation overheads versus bottoms; evaluation of the equipment may be repeated using different composition (such as Reactor A with feed composition and Reactor B with products composition).

Risk Analysis Screening Tools (RAST) Overview / Demonstration

Risk Analysis Screening Tools (RAST)
Case Study – T2 Industries

Begin by entering information on the Main Menu worksheet. Start with the MCMT Reactor

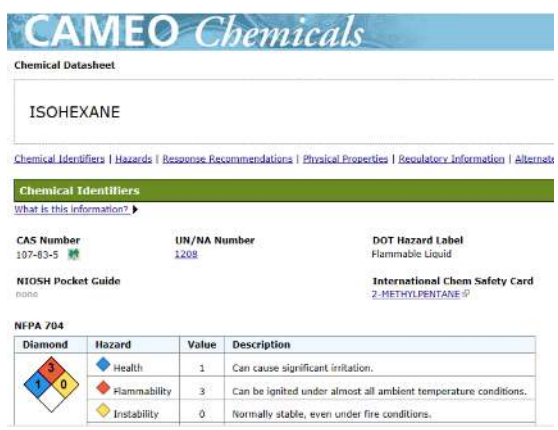


Enter Equipment Identification, Equipment Type and Location

Risk Analysis Screening Tools (RAST) Overview / Demonstration

Risk Analysis Screening Tools (RAST)
Case Study – T2 Industries

Diglyme solvent and Methylcyclopentadiene Dimer (MCPD) are major components of the feed but not listed in the RAST chemical data table, so we will enter this as a new chemical. Many companies have access to large chemical property databases that contain the information we will need. In other cases, vendor Safety Data Sheets, Cameo Chemicals (US National Oceanic and Atmospheric Administration), or literature references may be used. It is good to look for agreement among multiple sources.



Risk Analysis Screening Tools (RAST) Overview / Demonstration

An AIChE Technology Alliance CCPS Center for Chemical Process Safety

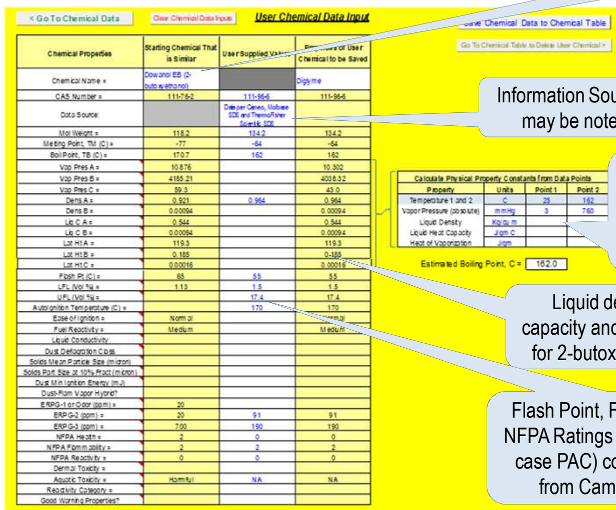
Case Study – T2 Industries

Chemical Data

Select “Add New Chemical” from the Chemical Data worksheet to access the “New Chemical” worksheet. Start with “Diglyme”

Since the information available from common sources is very limited, we will start with data from a chemical with nearly the same molecular weight and boiling point (2-butoxyethanol), then update with what little we know.

Save as “diglyme”. RAST uses relatively simple correlations for chemical properties that require only one or two data points.



Risk Analysis Screening Tools (RAST) Overview / Demonstration

An AIChE Technology Alliance CCPS Center for Chemical Process Safety

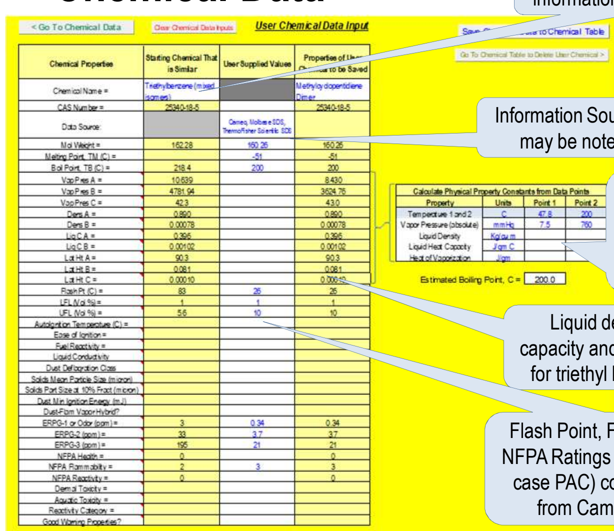
Case Study – T2 Industries

Chemical Data

Select “Add New Chemical” from the Chemical Data worksheet to access the “New Chemical” worksheet.

Since the information available from common sources is very limited, we will start with data from a chemical with nearly the same molecular weight and boiling point (triethyl benzene), then update with what little we know.

Save as “Methylcyclopentidiene Dimer”. RAST uses relatively simple correlations for chemical properties that require only one or two data points.



An AIChE Technology Alliance
CCPS Center for Chemical Process Safety

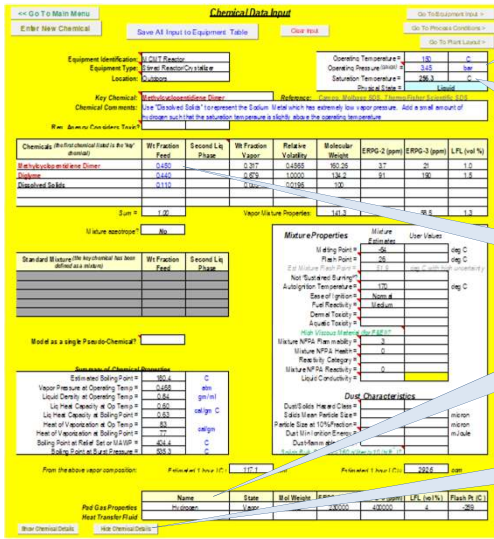
Risk Analysis Screening Tools (RAST) Overview / Demonstration

Case Study – T2 Industries
Chemical Data

A composition (weight fraction):
- 0.45 Methylcyclopentadiene Dimer
- 0.44 Diglyme
- 0.11 Dissolved Solids *(representing Sodium metal)*

was used as representative of the initial charge to the reactor.

The operating pressure was entered as 3.45 barg and the operating temperature was entered as 150 C.



The operating pressure entered as the initial pressure set pressure.

Saturation temperature is estimated and physical state as “liquid”

RAST allows up to 5 components.

Hydrogen as the Pad Gas is entered on the Process Conditions worksheet

Chemical details may be shown or hidden

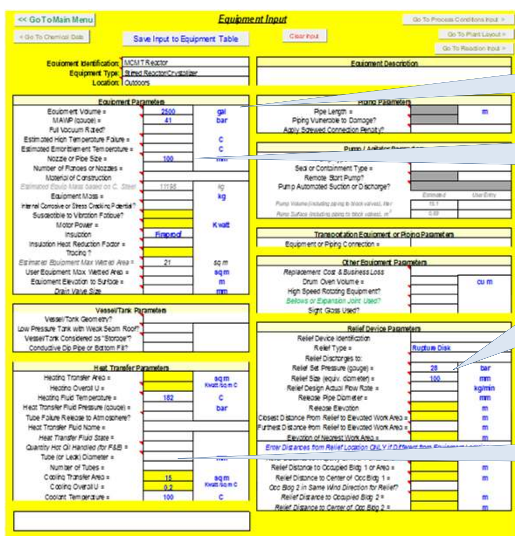
An AIChE Technology Alliance
CCPS Center for Chemical Process Safety

Risk Analysis Screening Tools (RAST) Overview / Demonstration

Case Study – T2 Industries
Equipment Input

The reaction equipment is a 2450 gallon vessel with a Maximum Allowable Work Pressure (MAWP) of 600 psig (41 bar). The cooling surface area is approximately 160 ft^2 (15 m^2) and cooled with evaporating water at 100 C. Assume a heat transfer coefficient for the jacked of 0.2 kwatt/m^2 C. The hot oil heating media temperature is 182 C and the vessel is insulated.

Only minimal data will be entered at this time.



The equipment volume and maximum allowable working pressure

A 4 inch (100 mm) nozzle is assumed the largest liquid connection to the vessel.

The reactor was equipped with a 4 inch (100 mm) rupture disk set at 28 barg (400 psig)

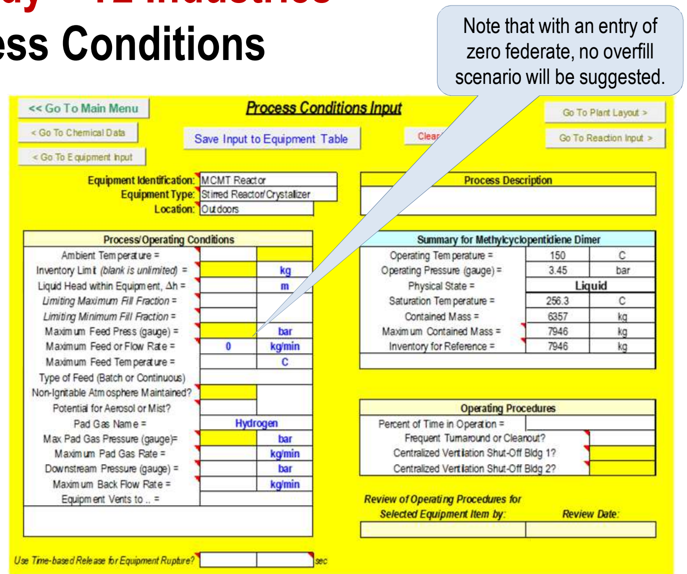
Information related to heat transfer of the equipment

Case Study – T2 Industries

Process Conditions

The maximum flowrate during the methylation reaction step is zero (all is added batchwise at the start of reaction). We can evaluate the loading step by entering the equipment information with a separate identification (such as MCMT Reactor-loading). The temperature and pressure conditions during this step would be different from the reaction step.

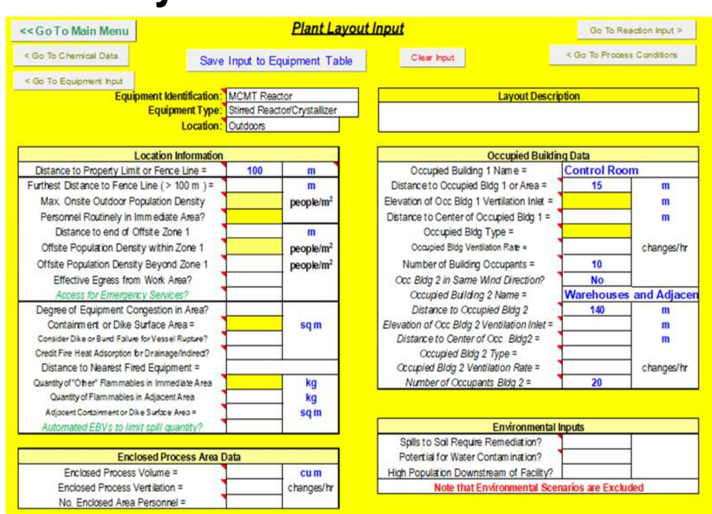
Hydrogen has been entered as the pad gas since it is a reaction product not present initially. (Also, the flash routines in RAST do not handle trace amounts of highly volatile component in the liquid phase.)



Case Study – T2 Industries

Site Layout

The manufacturing facility is located on a 5 acre site north of a Jacksonville, Florida industrial area. A small control building is located roughly 50 ft (15 m) from the reactor with up to 10 occupants. There is a trucking company and other businesses adjacent to the T2 site, roughly 140 m away with possibly 20 occupants.



An AIChE Technology Alliance
CCPS
Center for Chemical Process Safety

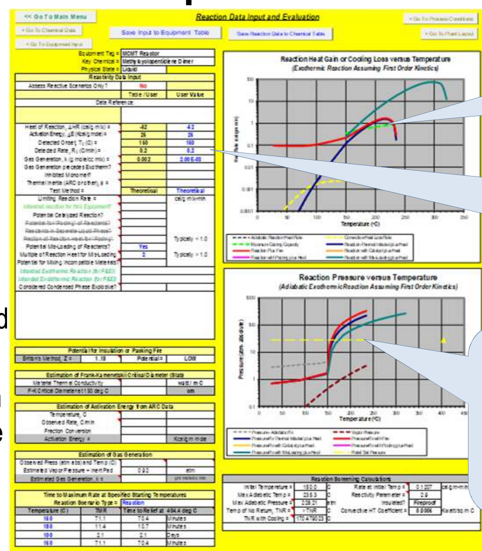
Case Study – T2 Industries

Reaction Input

Each ml of reaction mixture contains 0.84 g and roughly 0.09 g sodium or 0.004 gmole. From the reaction stoichiometry, 0.5 mole hydrogen is evolved per mole of sodium or 0.002 gmole hydrogen per ml of reaction mixture.

The known heat of reaction for the methylation step is -217 J/g or -52 cal/g reaction mixture. The activation is assumed a typical value of 25 to 30 kcal/gmole.

Finally at temperature rise rate of 0.2 C/min is assumed at 150 C such that it would take approximately 60 minutes for the reaction mass to heat from 150 to 180 C.



Dashed green line is the cooling capability of the reactor jacket

Reaction parameters are entered. Ideally, experimental values or a kinetic model would be available.

The maximum reaction pressure far exceeds the MAWP of the reactor. However, the rate of pressure rise would be such that the vent system would normally be capable of handling it.

An AIChE Technology Alliance
CCPS
Center for Chemical Process Safety

Case Study – T2 Industries

Reaction Evaluation

In addition to the chemical hazards of flammability and toxicity, there are significant hazards associated with the methylation reaction. It is exothermic such that loss of temperature control will allow the reaction to proceed more quickly than the equipment may be designed for. Secondly, the reaction includes a gaseous product (hydrogen) such that extremely high pressure could be attained (far greater than the design limits of the equipment) if the system is not properly vented.

Another process upset to consider would be misloading of the initial materials, particularly the diglyme solvent. If there is less solvent to adsorb the reaction heat, the maximum reaction temperature would be higher with a corresponding higher reaction rate. (Note the “yes” to misloading with a multiple of 2 on the heat as solvent is nearly 50% of the initial charge.)

There is very little reaction information available to better understand what might happen under upset conditions suggesting that additional reactive chemicals testing should be done.

Center for Chemical Process Safety — An AIChE Technology Alliance

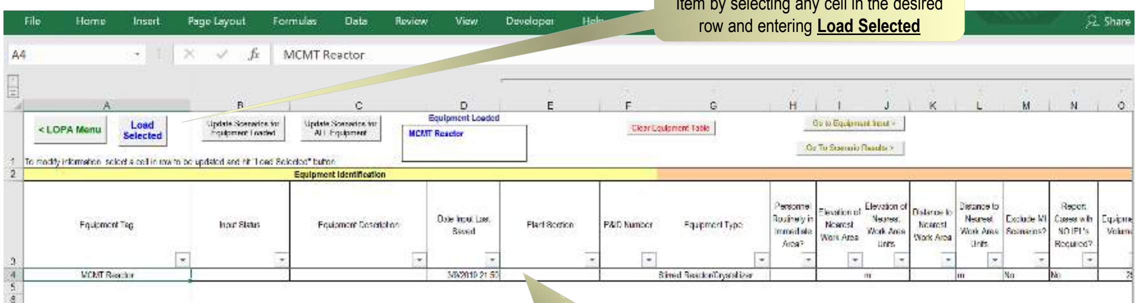
Risk Analysis Screening Tools (RAST) Overview / Demonstration

Risk Analysis Screening Tools (RAST)

Case Study – T2 Industries

Select Save Inputs to Equipment Table (blue macro button). All Input Information will be stored in the Equipment Table in a single row identified by a unique Equipment Identification or Tag.

Retrieve Information for an Equipment Item by selecting any cell in the desired row and entering **Load Selected**



Input Data for an Equipment Item stored in one row by Equipment Tag

March 24, 2022 Slide - 17

Center for Chemical Process Safety — An AIChE Technology Alliance

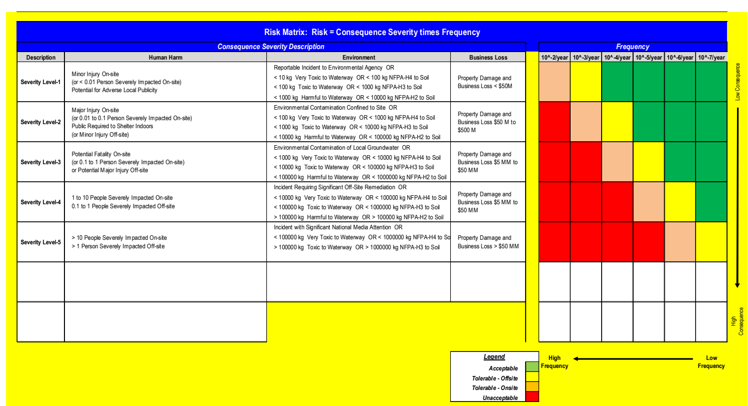
Risk Analysis Screening Tools (RAST) Overview / Demonstration

Risk Analysis Screening Tools (RAST)

Risk Matrix

To understand the Consequence Severity and Tolerable Frequency, the values for key Study Parameters and a Risk Matrix may be viewed on the Workbook Notes worksheet. These values may be updated on hidden worksheets and should reflect the company's specific risk criteria.

For this case study, the Risk Matrix (right) has been used. The Human Harm criteria is based on an estimated number of people severely impacted (severe injury including fatality).

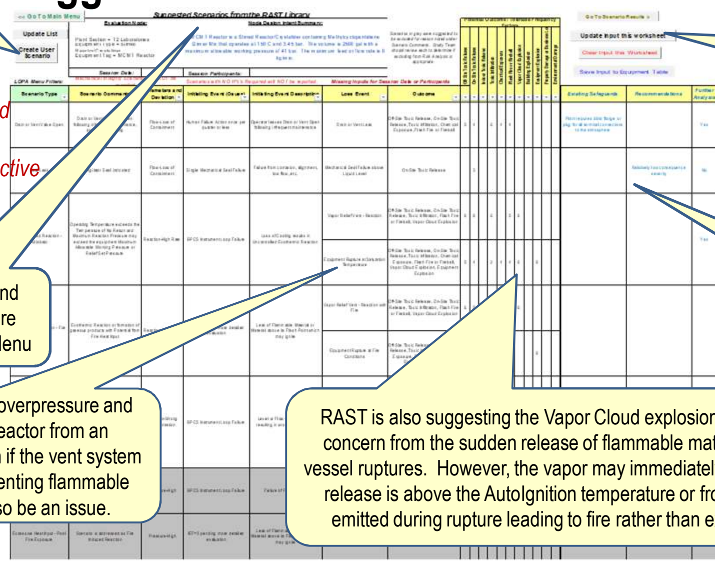


March 24, 2022 Slide - 18

An AIChE Technology Alliance
CCPS
Center for Chemical Process Safety

Case Study – T2 Industries

Suggested Scenarios for the MCMT Reactor



An AIChE Technology Alliance
CCPS
Center for Chemical Process Safety

Case Study – T2 Industries

Suggested Scenarios for MCMT Reactor

WORKING WITH YOUR EVALUATION TEAM:

- ❑ **Review the suggested list of scenarios. Do these represent what you would expect for a batch reactor?**
- ❑ **Are there scenarios that have been "screened out" (shown in gray) that should be considered?**
- ❑ **Are there scenarios missing? (Possibly similar scenarios with different Initiating Events)**
- ❑ **Do you agree with the "worst" Consequence (Tolerable Frequency Factor) for the scenario listed?**

AnAIChE Technology Alliance
CCPS
Center for Chemical Process Safety

Risk Analysis Screening Tools (RAST) Overview / Demonstration

Case Study – T2 Industries
Suggested Scenarios for MCMT Reactor

WORKING WITH YOUR EVALUATION TEAM:

- ❑ **Utilize an Appropriate Hazard Evaluation Technique (HAZOP, What If, etc.) to capture additional scenarios.**
- ❑ **Capture existing Safeguards and Recommendations for each Scenario. Note the Dates and Names of participants in the Study.**
- ❑ **Select which Scenarios warrant more detailed Risk Evaluation (such as Layers of Protection Analysis).**

March 24, 2022 Slide - 21

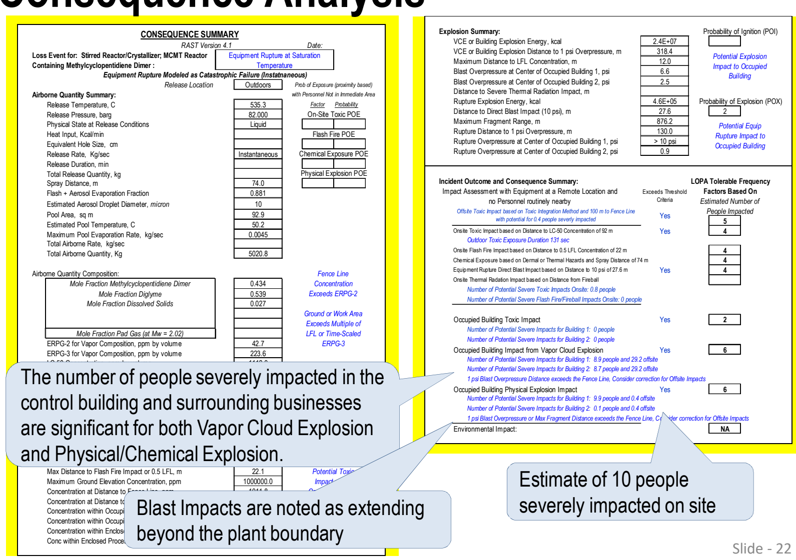
AnAIChE Technology Alliance
CCPS
Center for Chemical Process Safety

Risk Analysis Screening Tools (RAST) Overview / Demonstration

Case Study – T2 Industries
Consequence Analysis

For the MCMT Reactor, select **Rupture at Saturation** as the Loss Event. This represented a "worst" Consequence for rupture. *(The maximum reaction temperature is lower than the estimated 522 C but greater than the operating temperature.)*

The distance to 1 psi overpressure is estimated at 130 m and overpressure at the distance to the control building is estimated at >10 psi.



March 24, 2022 Slide - 22

Case Study – T2 Industries
Consequence Analysis

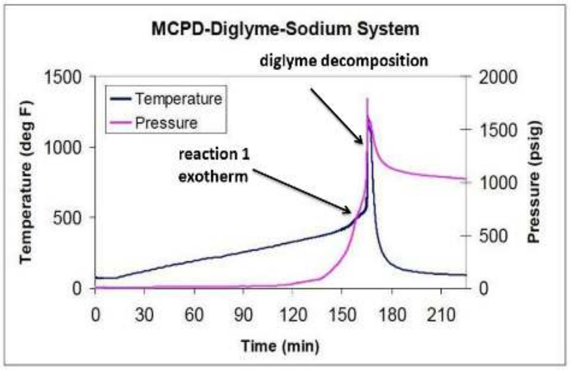
What was unknown to the T2 owners is that the diglyme solvent decomposes exothermally at elevated temperature in the presence of sodium or possibly sodium methylcyclopentadiene. The heat of reaction and reaction rate at elevated temperature is such that the normal hydrogen vent, cooling capability and the relief device are not effective. The uncontrolled reaction scenario considering decomposition is a much higher risk as the heat generated in the methylation reaction will cause the system temperature to reach that where the decomposition proceeds at a very significant rate – only a loss of cooling is needed.

Heat of diglyme decomposition ~ -320 kJ/mol diglyme or -1050 J/g reaction mixture. This may have sufficient energy for deflagration or detonation depending on peak reaction rate. The activation energy from modeling is roughly 19 kcal/mol.

Case Study – T2 Industries
Consequence Analysis

Following the incident at T2 Industries, a VSP test was run for the typical recipe with results used to create a kinetic model. Test results indicated a maximum temperature rate of 1300°C/min and maximum pressure rate of 2200 bar/min with maximum temperature of 650°C. These conditions are well above the design limits of the equipment. In addition, the higher reaction rate evolves hydrogen at a rate which likely far exceeds the design of the vent system.

Adiabatic Reaction Calorimetry used for kinetic constants estimates

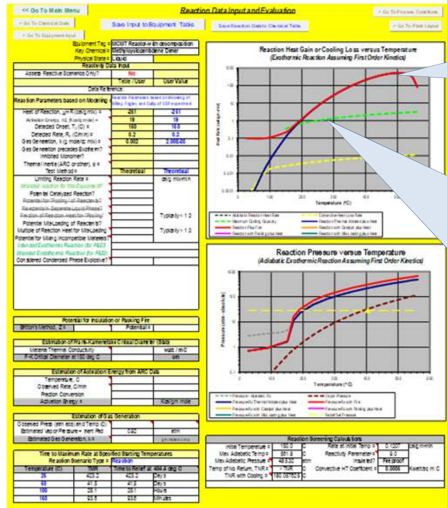


An AIChE Technology Alliance
CCPS
Center for Chemical Process Safety

Case Study – T2 Industries
Updated Reaction Input

The VSP experimental data was fit to a kinetic model to better understand the behavior of the reaction during process upsets. Reference Willey, Fogler and Cutlip; "The Integration of Process Safety into a Chemical Reaction Engineering Course: Kinetic Modeling of the T2 Incident", Process Safety Progress 30 (2010).

A key finding is that if the rupture disk had been set to a much lower pressure (maybe 100 psig), it may have had sufficient capacity to prevent the rupture.



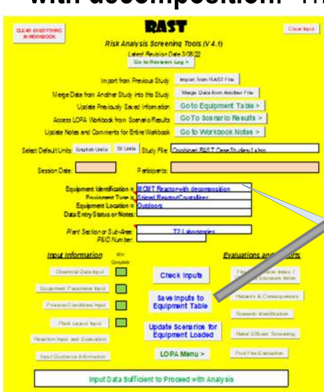
Note the much higher reaction rate and final temperature than form the intended reaction only.

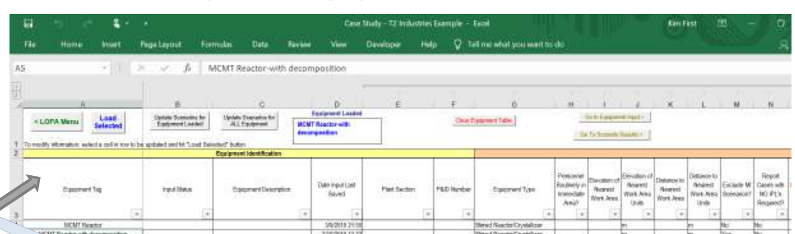
Note the estimated point where the reaction rate exceeds the cooling capability is 180 C. The plant routinely operated without cooling to 190 C, so the kinetic parameters or jacket heat transfer coefficient may be low. However, this indicates that normal operation was very close to the estimated "temperature o no return".

An AIChE Technology Alliance
CCPS
Center for Chemical Process Safety

Case Study – T2 Industries
Updated Reaction Input

The MCMT reaction including the decomposition reaction information may be easily saved as an additional equipment item. On the Main Menu, change the equipment ID to **MCMT Reactor –with decomposition**. Then use the **Save Inputs to Equipment Table** macro button.





Enter the updated Equipment Identification

Note an addition input line on the Equipment Table worksheet which contains the data for the decomposition reaction while retaining the initial equipment item with the intended reaction data.

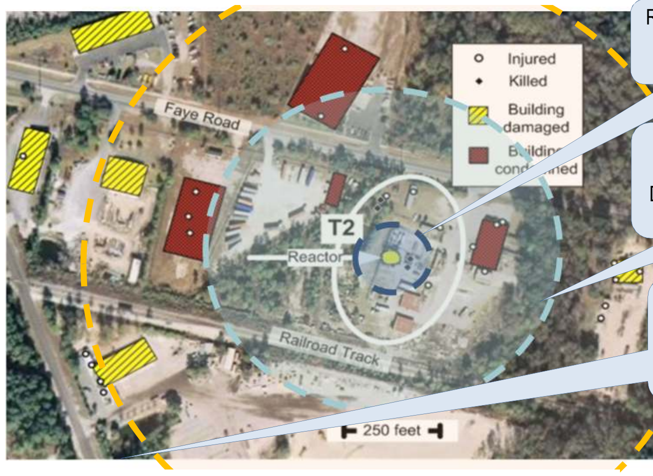
An AIChE Technology Alliance CCPS Center for Chemical Process Safety

Case Study – T2 Industries

Consequence Analysis – Physical Explosion

RAST estimated a maximum fragment range of 876 m (2870 ft). The reactor head was found 400 ft away, the agitator 350 ft away, and support columns 1000 ft from the original location.

RAST estimated a blast energy equivalent to 900 lb TNT *(and assumes ½ this energy is consumed in rupturing the vessel)* versus CSB estimate of 1400 lb TNT equivalent.



RAST estimate of Direct Blast Impacts (10 psi overpressure)

RAST estimate of 1 psi Blast Overpressure Damage to Conventional Constructed Buildings

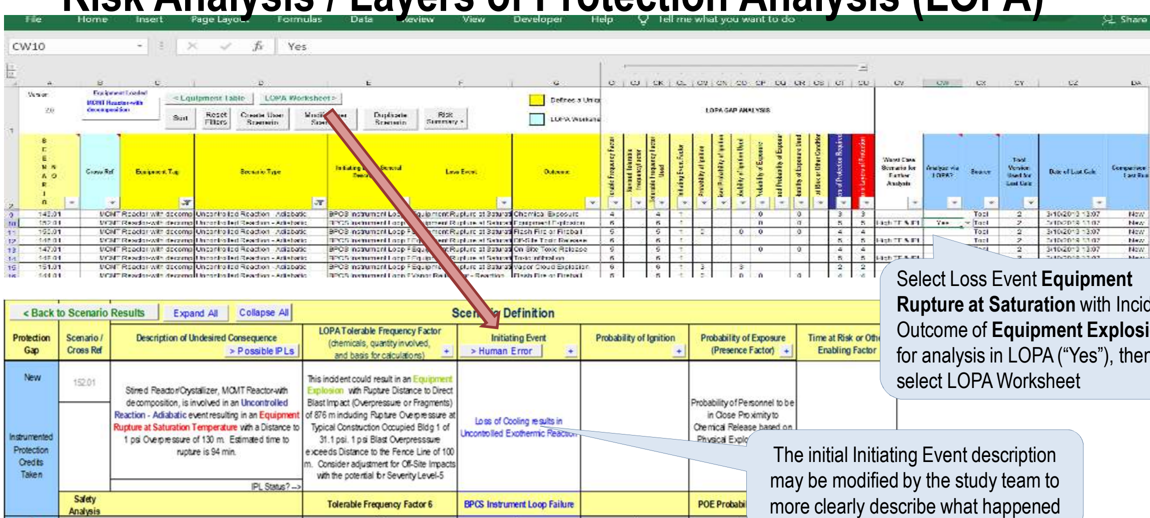
RAST estimate of 0.5 psi Blast Overpressure Damage to Low Strength Buildings

REPORT NO. 2008-3-I-FL , US Chemical Safety Board, Figure 4. Injury and business locations.

An AIChE Technology Alliance CCPS Center for Chemical Process Safety

Case Study – T2 Industries

Risk Analysis / Layers of Protection Analysis (LOPA)



Select Loss Event **Equipment Rupture at Saturation** with Incident Outcome of **Equipment Explosion** for analysis in LOPA ("Yes"), then select LOPA Worksheet

The initial Initiating Event description may be modified by the study team to more clearly describe what happened

An AIChE Technology Alliance
CCPS
Center for Chemical Process Safety

Risk Analysis Screening Tools (RAST) Overview / Demonstration

Case Study – T2 Industries

Risk Analysis / Layers of Protection Analysis (LOPA)

< Back to Scenario Results	Expand All	Collapse All	Scenario Definition				
Protection Gap	**Scenario / Cross Ref**	**Description of Undesired Consequence** > Possible IPLs	**LOPA Tolerable Frequency Factor** (chemicals, quantity involved, and basis for calculations) +	**Initiating Event** > Human Error +	**Probability of Ignition** +	**Probability of Exposure (Presence Factor)** +	**Time at Risk or Other Enabling Factor**
New Instrumented Protection Credits Taken	152.01	Stirred Reactor/Crystallizer, MCMT Reactor-with decomposition, is involved in an Uncontrolled Reaction - Adiabatic event resulting in an Equipment Rupture at Saturation Temperature with a Distance to 1 psi Overpressure of 130 m. Estimated time to rupture is 94 min. IPL Status? -->	This incident could result in an Equipment Explosion with Rupture Distance to Direct Blast Impact (Overpressure or Fragments) of 876 m including Rupture Overpressure at Typical Construction Occupied Bldg 1 of 31.1 psi. 1 psi Blast Overpresssure exceeds Distance to the Fence Line of 100 m. Consider adjustment for Off-Site Impacts with the potential for Severity Level-5	Loss of Cooling results in Uncontrolled Exothermic Reaction		Probability of Personnel to be in Close Proximity to Chemical Release based on Physical Explosion Impact Area to 876 m	
	Safety Analysis		**Tolerable Frequency Factor 6**	**BPCS Instrument Loop Failure**		**POE Probability Factor 0**	
5			6	1		0	

RAST is suggesting that the damage distance is very significant such that a Probability of Exposure enabling condition would not be appropriate.

An AIChE Technology Alliance
CCPS
Center for Chemical Process Safety

Risk Analysis Screening Tools (RAST) Overview / Demonstration

Case Study – T2 Industries

Risk Analysis / Layers of Protection Analysis (LOPA)

	Not Allowed								
BPCS Control or Human Response to Alarm +	**BPCS Control or Human Response to Alarm** +	**SIS Function A** +	**SIS Function B** +	**Pressure Relief Device**	**SRPS 1**	**SRPS 2**	**SRPS 3**	**Notes / Comments**	**Issues to Resolve**
		High temperature activates emergency cooling water addition		Two separate and independent pressure relief devices set at a releatively low pressure confirmed by kinetic modeling					
		SIS - SIL 1		Two Independent PRDs on Separate Nozzles with Independence Audit					
		1		4					

In addition to a high temperature interlock with an emergency cooling water supply, one of the most cost effective Protective Layers would likely be a second Pressure Relief Device. However, a Relief Device may not be effective for the Diglyme decomposition which would not be predicted in RAST and need to be confirmed by kinetic modeling.

An AIChE Technology Alliance CCPS Center for Chemical Process Safety

Risk Analysis Screening Tools (RAST)
Case Study – T2 Industries

Risk Analysis and Incident Investigation often use similar methods to better understand the scenario. Risk Analysis “anticipates” what could go wrong and what the potential consequences may be. For Incident Investigation, the Incident Outcome and Consequences are known in addition to the actual weather conditions and wind direction.

For the MCMT Reactor, RAST did suggest Uncontrolled Reaction as one of many scenarios to consider. RAST also recognized that a Physical Explosion could be a feasible Incident Outcome for the scenario. RAST was is good agreement with the CSB estimate of damage. RAST estimated 10 people severely impacted versus 4 fatalities and 32 injured in the actual incident.

RAST can not predict reaction hazards if the data is not entered (decomposition).

THE USER MUST KNOW THE CHEMISTRY THEY ARE DEALING WITH.

An AIChE Technology Alliance CCPS Center for Chemical Process Safety

Questions?