

Risk Analysis Screening Tools (RAST) Overview / Demonstration

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Center for Chemical Process Safety

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



**Runaway Reaction and Explosion
Jacksonville, Florida
December 19, 2007**

March 24, 2022

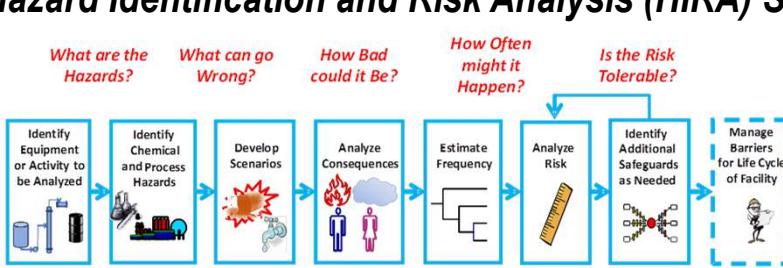
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Hazard Identification and Risk Analysis (HIRA) Study



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.

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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:



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This is an illustrative example and does not reflect a thorough or complete study.



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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.

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Process Description

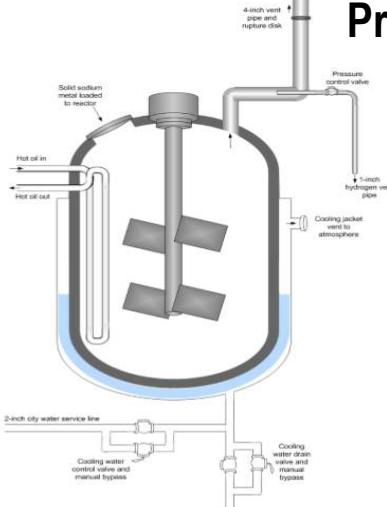
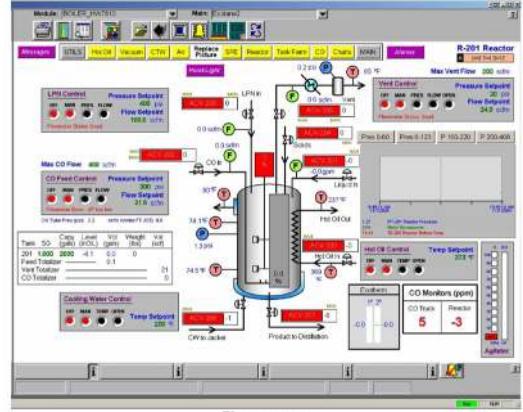


Diagram of MCMT Reactor



Process Control Screen for MCMT Reactor

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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).

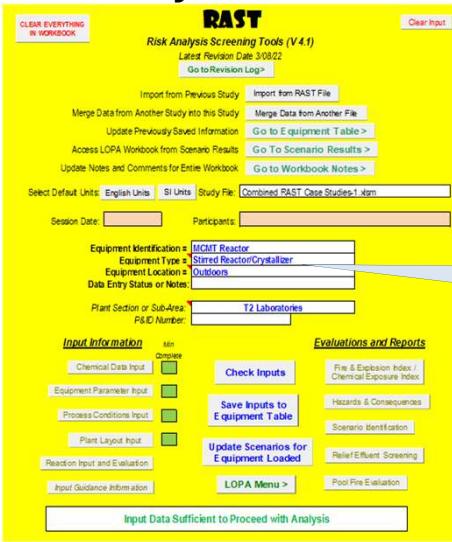
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Begin by entering information on the Main Menu worksheet. Start with the MCMT Reactor



Enter Equipment Identification, Equipment Type and Location

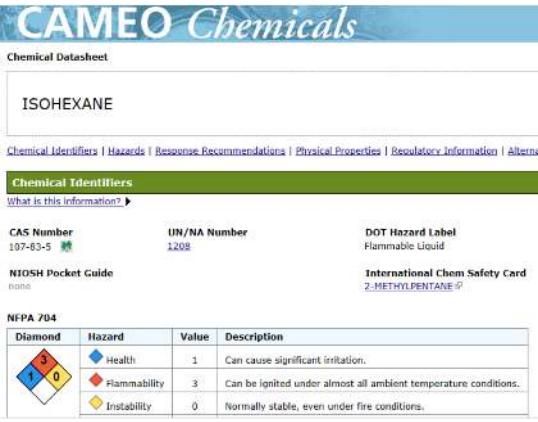
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Diglyme solvent and Methylcyclopentadiene Dimer (MCPD) are major components of the feed but not listed in the RAST chemical data table, so we will enter this as a new chemical. Many companies have access to large chemical property databases that contain 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.



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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.

Started with chemical information for 2-butoxyethanol

Information Sources may be noted

The normal boiling point and vapor pressure at 25 C from Molbase SDS

Liquid density, liquid heat capacity and heat of vaporization for 2-butoxyethanol were used

Flash Point, Flammable Limits, NFPA Ratings and ERPG (in this case PAC) concentrations are from Cameo Chemicals

Estimated Boiling Point, C = 162.0

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

Started with chemical information for triethyl benzene

Information Sources may be noted

The normal boiling point and vapor pressure at 25 C from Molbase SDS

Liquid density, liquid heat capacity and heat of vaporization for triethyl benzene were used

Flash Point, Flammable Limits, NFPA Ratings and ERPG (in this case PAC) concentrations are from Cameo Chemicals

Estimated Boiling Point, C = 200.0

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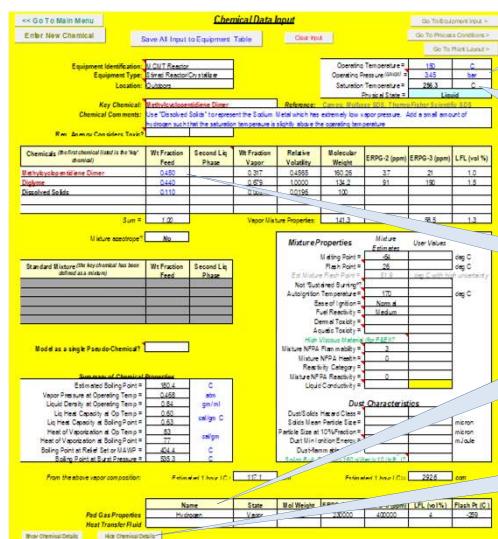
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Chemical Data

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

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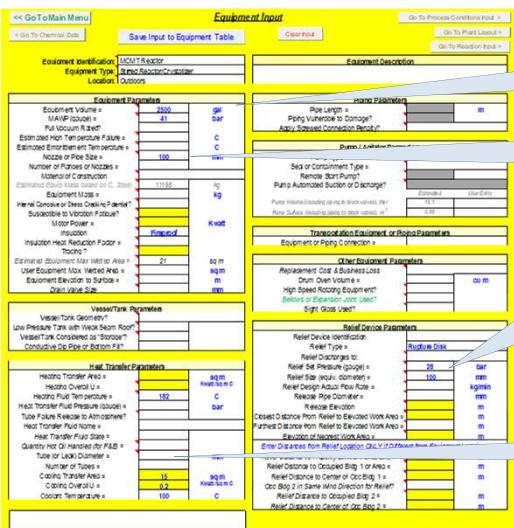
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Equipment Input

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 ft² (15 m²) and cooled with evaporating water at 100 C. Assume a heat transfer coefficient for the jacket of 0.2 kwatt/m² 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

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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.)

Note that with an entry of zero federate, no overfill scenario will be suggested.

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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.

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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.

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Reaction Data Input and Evaluation

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.

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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.

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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.

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File Home Insert Page Layout Formulas Data Review View Developer Help

A4 MCMT Reactor

Load Selected

Equipment Identification

Equipment Tag: MCMT Reactor

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

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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).

Risk Matrix: Risk = Consequence Severity times Frequency

Description	Human Harm	Consequence Severity Description					Frequency				
		Environment					Business Loss				
Severity Level 1	Minor Injury - Oracle < 0.1 Person Severely Impacted On-site Potential for Adverse Local Publicity	> Reputable Incident to Environmental Agency, OR < 10 kg Very Toxic to Waterway, OR > 100 kg NPFPA-H4 to Soil < 100 kg Toxic to Waterway, OR > 1000 kg NPFPA-H3 to Soil					Property Damage and Business Loss < \$5M				
Severity Level 2	Major Injury - Oracle (or 0.01 to 1 Person Severely Impacted On-site) Potential for Adverse Local Publicity (or Minor Injury Off-site)	> Environmental Contamination Confined to Site, OR < 100 kg Very Toxic to Waterway, OR > 1000 kg NPFPA-H4 to Soil < 100 kg Toxic to Waterway, OR > 10000 kg NPFPA-H3 to Soil < 1000 kg Harmful to Waterway, OR > 100000 kg NPFPA-H2 to Soil					Property Damage and Business Loss \$5 M to \$50 M				
Severity Level 3	Potential Facility Oracle (or 0.1 to 1 Person Severely Impacted On-site) or Potential Major Injury Off-site	> Environmental Contamination of Local Groundwater, OR < 1000 kg Very Toxic to Waterway, OR > 10000 kg NPFPA-H4 to Soil < 1000 kg Toxic to Waterway, OR > 100000 kg NPFPA-H3 to Soil < 10000 kg Harmful to Waterway, OR > 100000 kg NPFPA-H2 to Soil					Property Damage and Business Loss \$5 MM to \$50 MM				
Severity Level 4	1 to 10 People Severely Impacted Oracle (or 1 Person Severely Impacted Off-site)	> Incident Requiring Significant Off-Site Remediation, OR < 10000 kg Very Toxic to Waterway, OR > 100000 kg NPFPA-H4 to Soil < 10000 kg Toxic to Waterway, OR > 100000 kg NPFPA-H3 to Soil < 100000 kg Harmful to Waterway, OR > 100000 kg NPFPA-H2 to Soil					Property Damage and Business Loss \$50 MM to \$500 MM				
Severity Level 5	> 10 People Severely Impacted Oracle > 1 Person Severely Impacted Off-site	> Incident with Significant National Media Attention, OR < 100000 kg Very Toxic to Waterway, OR > 1000000 kg NPFPA-H4 to Soil < 100000 kg Toxic to Waterway, OR > 1000000 kg NPFPA-H3 to Soil < 1000000 kg Harmful to Waterway, OR > 1000000 kg NPFPA-H2 to Soil					Property Damage and Business Loss > \$50 MM				

Legend: Acceptable (Green), Tolerable (Yellow), Unacceptable (Red)

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Suggested Scenarios for the MCMT Reactor

Additional Scenarios are Added using "Create User Scenario"

The high consequence severity for the uncontrolled reaction scenarios also suggest that additional reactive chemicals testing and/or evaluation is warranted.

Evaluation Date(s) and Participant Names are entered on the Main Menu

A very serious scenario is overpressure and rupture of the MCMT Reactor from an uncontrolled reaction. Even if the vent system can prevent the rupture, venting flammable and toxic gases may also be an issue.

RAST is also suggesting the Vapor Cloud explosion may be a concern from the sudden release of flammable material if the vessel ruptures. However, the vapor may immediately ignite if the release is above the Autolignition temperature or from sparks emitted during rupture leading to fire rather than explosion.

Once Inputs are Entered use "Update Input this Worksheet" to Save

Analysis Team captures which Scenarios warrant more Detailed Evaluation (Layers of Protection Analysis)

Analysis Team captures Existing Safeguards and Recommendations for Scenarios Identified

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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?**

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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).

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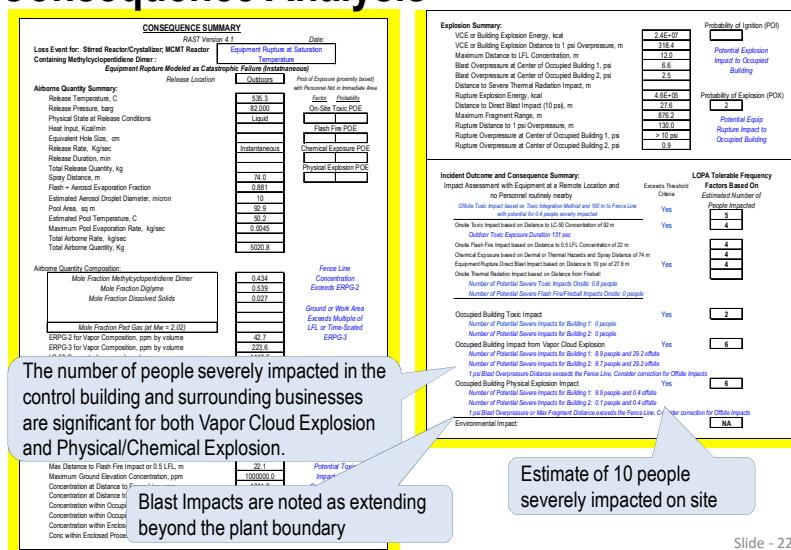
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Case Study – T2 Industries Consequence Analysis

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.



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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.

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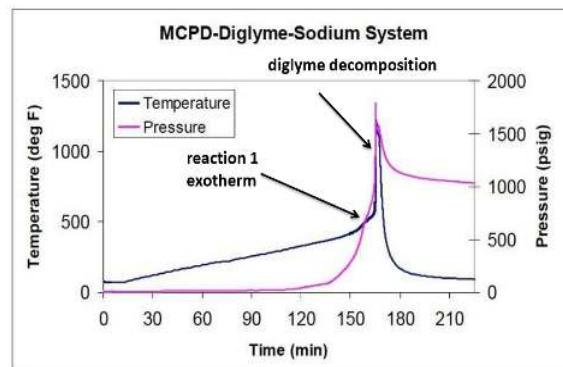


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Consequence Analysis

Adiabatic Reaction Calorimetry used for kinetic constants estimates

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.



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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.

The figure shows the RAST software interface. The top navigation bar includes 'Go To Main Menu', 'Save Input in Raster's Table', 'Save Reaction Data in Table', 'Go To Previous Location', and 'Go To Next Location'. The main window is divided into two main sections: 'Reaction Data Input and Evaluation' on the left and 'Reaction Heat Gain or Cooling Loss versus Temperature (Exothermic Reaction Assuming First Order Kinetic)' on the right.

Reaction Data Input and Evaluation:

- Reaction Type:** Exothermic
- Reaction Order:** 1.0
- Reaction Kinetics:** $Ae^{-Ea/RT}$
- Reaction Parameters:**
 - $A = 1.0$
 - $Ea = 100$
 - $T_{ref} = 298$
 - $T_{max} = 400$
 - $T_{min} = 200$
 - $T_{cool} = 180$
 - $T_{heat} = 200$
 - $T_{rupture} = 200$
 - $T_{jacket} = 180$
 - $T_{pump} = 180$
 - $T_{vessel} = 180$
 - $T_{piping} = 180$
 - $T_{valve} = 180$
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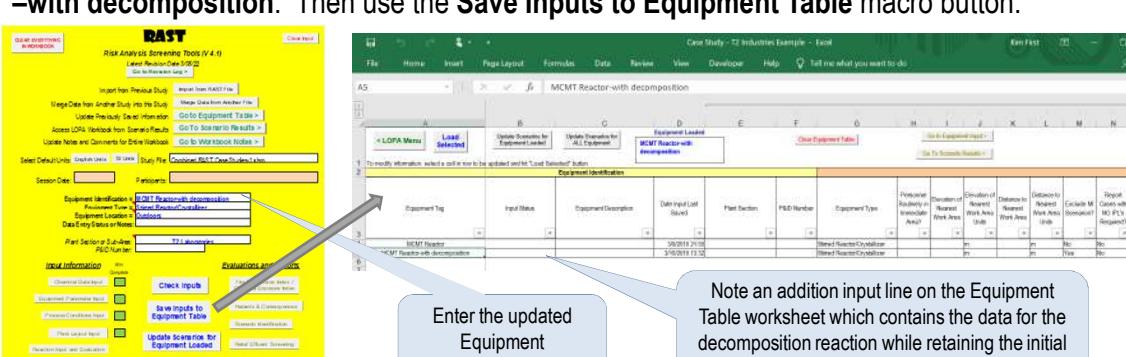
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Risk Analysis Screening Tools (RAST) Overview / Demonstration

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.



The screenshot shows the RAST software interface. On the left, the Main Menu is open with the 'Save Inputs to Equipment Table' macro button highlighted. On the right, the 'Equipment Table' worksheet is displayed. The worksheet has columns for Equipment Identification, Equipment Tag, Input Status, Equipment Description, Date Input Last Saved, Plant Section, HLD/Number, Equipment Type, Previous Reactivity in Current Work Area, Current Reactivity in Previous Work Area, Estimated No. Reacted in Current Work Area, Estimated No. Reacted in Previous Work Area, Duration No. Reacted in Current Work Area, Duration No. Reacted in Previous Work Area, and Report Details with RAST Response. A callout box points to the 'Equipment Identification' column with the text 'Enter the updated Equipment Identification'. Another callout box points to the 'Equipment Table' with the text '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.'

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Risk Analysis Screening Tools (RAST) Overview / Demonstration

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 $\frac{1}{2}$ 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.

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Risk Analysis / Layers of Protection Analysis (LOPA)

File Home Insert Page Layout Formulas Data Review View Developer Help Tell me what you want to do

Instrumented Protection Credits Taken

Protection Gap Scenario / Cross Ref Description of Undesired Consequence > Possible IPAs

LOPA Tolerable Frequency Factor (chemicals, quantity involved, and basis for calculations) > Human Error...

Initiating Event > Human Error...

Probability of Ignition

Probability of Exposure (Presence Factor) & Time at Risk or Other Enabling Factor

Loss of Cooling results in Uncontrolled Exothermic Reaction

Probability of Personnel to be in Close Proximity Chemical Release based on Physical Expn'

PL Status?>

Tolerable Frequency Factor 6

BPCS Instrument Loop Failure

POE Probab

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

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Risk Analysis Screening Tools (RAST) Overview / Demonstration

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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, MCM 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 Overpressure 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	POE Probability Factor 0	0	
		Safety Analysis						Tolerable Frequency Factor 6
5		6	1					

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

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Risk Analysis Screening Tools (RAST) Overview / Demonstration

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Risk Analysis / Layers of Protection Analysis (LOPA)

		Not Allowed							Notes / Comments	Issues to Resolve
BP/CS Control or Human Response to Alarm	BP/CS Control or Human Response to Alarm	SIS Function A	SIS Function B	Pressure Relief Device	SRPS 1	SRPS 2	SRPS 3			
		High temperature activates emergency cooling water addition		Two separate and independent pressure relief devices set at a relative overpressure 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.

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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 in 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).

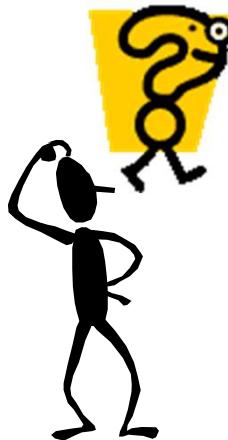
THE USER MUST KNOW THE CHEMISTRY THEY ARE DEALING WITH.

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Questions?



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