

The CCPS Chemical Reactivity Evaluation Tool

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1 Abstract

Incidents involving uncontrolled chemical reactions continue to result in injuries, fatalities and economic loss and harm in industry. These incidents are often the result of not identifying or understanding the chemical reactivity hazards involved in storage, mixing or processing operations. The chemical reactivity evaluation Tool (RMT) and the Help Guide that accompanies it can be used as an aid in identifying and evaluating chemical reactivity hazards so that they may be effectively avoided or controlled. This paper will describe the RMT and demonstrate its use in identifying reactivity hazards in chemical storage, handling and processing operations. The RMT and Help Guide are available as a free download from AIChE (www.aiche.org) and search "RMR".

2 Background

AIChE created the Center for Chemical Process Safety (CCPS) in 1985 after the chemical disasters in Mexico City, Mexico, and Bhopal, India. The CCPS was chartered to develop and disseminate technical information for use in the prevention of major chemical accidents. The center is supported by more than 140 chemical process industry (CPI) sponsors who provide the necessary funding and professional guidance to its technical committees. The major products of CCPS activities has been a series of guideline books to assist those implementing various elements of a process safety and risk management system. The RMT program and help guide are part of that series.

The Reactivity Management Roundtable (RMR) was founded in 2003 by a small group of process safety professionals that meet independently of both AIChE and CCPS with the goal of reviewing the newly published Chemical Safety Board Reactive Hazard Investigation report that analyzed 167 serious chemical reactivity incidents over a twenty year period in order to recommend best practices that could reduce or eliminate reactivity incidents in the future¹. The group quickly swelled to over 100 members.

The work of the RMR has been directed toward part time process safety specialists who own or are employed by small to mid-size firms where chemicals are stored, handled or used. It was anticipated that these specialists would be employees actively engaged in primary functions other than process safety, and thus would not have the skills to assess reactivity hazard risk themselves nor the funds to employ a process safety professional or consultant to assess the risk for them. It is sincerely hoped that this product will help identify chemical reactivity risks within the workplace and direct the user, owners and managers of those at risk workplaces to resources to aid in quantifying and remediating that risk. This computer program is not designed to fulfill any legal requirement for a chemical reactivity management system but it is hoped that it will form the basis for developing a strong chemical reactivity management system.

3 Introduction

The AIChE defines a chemical reactivity hazard (also known as a reactive chemical hazard) as a situation with the potential for an uncontrolled chemical reaction that can result directly or indirectly in serious harm to people, property or the environment.

Reactivity management is the application of management system principals to control chemical reactivity hazards. A strong reactivity management system is based on four simple principles: Inform, Implement, Communicate, and Verify. The CCPS publication *Essential Practices for Managing Chemical Reactivity Hazards*² contains a detailed discussion on reactivity management and how it can be implemented.

Chemical reactivity management is important because reactivity hazards have been involved in some of the most severe industry incidents in history including:

- The 1975 runaway reaction in Seveso, Italy that resulted in the contamination of several square miles of land with dioxin, a toxic chemical. This incident resulted in regulations requiring extensive safety analysis before constructing new chemical facilities in Europe.

- The 1984 methyl isocyanate release in Bhopal, India that resulted in over 2000 fatalities because of the exposure to this toxic chemical. This incident significantly damaged the financial condition and reputation of Union Carbide, the joint owner of the facility, leading to its eventual acquisition by the Dow Chemical Company.

- The 2001 massive ammonium nitrate explosion in Toulouse, France that resulted in 30 fatalities, 2500 injuries, damage to nearly a third of the city of Toulouse, and permanent closing of the facility involved in the incident.

- In 2009 a runaway reaction and explosion during the routine production of a gasoline additive at T2 Laboratories in Jacksonville FL killed 4 and hospitalized 13 others. The entire site was leveled and several nearby buildings severely damaged. The company never resumed operations. This incident highlighted the need for the inclusion of process safety and reactive chemicals in the undergraduate chemical engineering curriculum.

Numerous other recent incidents could also be cited. The U.S. Chemical Safety and Hazard Investigation Board report entitled —Improving Reactive Hazard Management analyzed over 167 serious reactive chemical incidents that occurred over a twenty year period from January 1980 to June 2001. The primary objective of the reactivity evaluation software tool discussed in this Help Guide is to allow users, especially small to medium size companies, to identify most chemical reactivity hazards in their chemical processing and support operations so that serious reactive chemical incidents like those discussed can be prevented.

3.1 Program Objectives

The chemical reactivity evaluation tool and help guide have the following objectives:

1. Allow users, especially small to medium size companies, to identify most chemical reactivity hazards associated with their chemical processing and support operations.
2. Emphasize ease of use for non-experts.
3. Direct users to CCPS documentation and other references of the best chemical engineering practices for the identification of reactivity hazards.
4. Briefly summarize the targeted CCPS documentation in the directions for inputting data.
5. Provide sufficient Help Screens and examples so that users gain an understanding of how to use the reactivity evaluation software tool.

3.2 *Programming Approach*

The program utilizes and builds on two published approaches for identifying chemical reactivity. Binary chemical interactions are predicted by the method of Farr and Johnson⁴ in the NOAA CRW2 program. This method reduces molecular structure to a standardized list of reactive functional groups. Reactivity is predicted by comparing between all reactive group pairings between the two chemicals. Chemical segregation predictions are derived from comparing DOT codes utilizing the work of Chastain et al⁵ in a slightly modified form. The scenario generation section is based on the CCPS guide book *Essential Practices for Managing Chemical Reactivity Hazards (2003)*². Guidelines for the evaluation results were developed by the RMR committee³.

3.3 *Help Guide Approach*

The Help Guide was written and formatted to walk the user through the reactivity evaluation protocol describing how the program works, providing a detailed discussion on how to use the software tool including installation and help screens, and to providing worked examples of the use of the reactivity evaluation software tool. The intent of the Help Guide is to quickly assist the user in becoming proficient in the use of the reactivity evaluation software tool.

The guide is formatted and cross referenced such that the user can quickly find help with specific sections of the program without having to laboriously wade through information that does not pertain to the immediate need. Helpful tips and common pit falls are flagged in the margin of the text with a small graphic. The one page main table of contents is set up to show only high level headings describing general subjects, allowing the user to quickly select a topic without being overwhelmed with endless sub-headings. Sectional table of contents hyperlinked from the main TOC provide detailed listings of all sub-heading topics covered within that section. The entire document is indexed for key words and phrases. There is a detailed FAQ section with concise answers to common user questions and hyper links to pertinent sections for more detail.

4 **Program Flow**

The primary page of the RMT Flowchart shows the overall workflow for the chemical reactivity evaluation tool. The individual steps involved are explained in detail by the identifiers next to each block (1A, 1B, etc.).

4.1 *Chemical Reactivity Evaluation Protocol: Page 1 of the program flow diagram (Figure 1)*

1A. Limit the scope to something less than an entire production site
The reactivity hazard evaluation protocol will best be applied to one chemical process or unit at a time. Attempting to apply it to an entire production site will generally be too cumbersome.

For example, say a company named Charbroiled Chemicals owns a production facility that includes a warehouse and process units making ethylene, chlorine, and vinyl chloride. In this case, the protocol would best be applied four times, once for each of the three process units and once for the warehouse.

1B Enter name of process and facility and the date of evaluation

1C Enter names of evaluation team members

The evaluation should be completed by a team that collectively has knowledge of the process chemistry, chemical reactivity hazards, process equipment and controls, process technology and processing operations.

1D Laboratory-scale facility? The RMT protocol is not designed for laboratory-scale reactions and processes.

1G List all chemicals used or stored

The user is asked to compile a list of all chemicals that are expected to be used or stored in the process area, plus those that may potentially be involved under abnormal or unusual situations.

1H Enter all chemicals into the software

All compiled chemicals are entered one at a time into the software tool. This list of chemicals forms a database that will be used throughout the remaining steps of the evaluation. The user should obtain the MSDS for the chemicals to be entered. The evaluation tool contains the same database of over 5,000 chemicals that is used by the U.S. National Oceanic and Atmospheric Administration's Chemical Reactivity Worksheet⁴, or CRW2. The user can search for a chemical by name, synonym, Chemical Abstracts Service (CAS) number, UN/NA or DOT number. If the correct chemical cannot be found by using the search features, such as for unusual or proprietary chemicals, then it will need to be entered as a "custom chemical" along with its associated reactive group(s). The program checks all chemicals for complete data and presents the user with a screen requesting any missing data. The program will not allow the user to continue until all required data is entered.

1M Warehousing only? Warehousing here means storing or transporting materials where the containers are never opened. The approach for warehousing is significantly different than that taken for physical or chemical processing. Warehousing poses fewer opportunities for an uncontrolled reaction to take place than for physical processing or intentional chemistry, so fewer measures are needed to contain and control the chemical reactivity hazards.

1O Warehouse report⁵: (see section 4.6.1) If the process involves chemical warehousing only, then the reactivity evaluation report generated at this step will include process identifying information, evaluation team members, a chemical listing and a warehouse segregation report and a binary chemical interaction matrix.

1P Chemical reactivity evaluation protocol, sends the program into the sub-routine detailed on page 2 (see section 4.2).

1Q Chemical reactivity evaluation protocol, page 3: Evaluate chemical interaction hazards sends the program into the sub-routine detailed on page 2 (see section 4.3).

1R Chemical reactivity evaluation protocol, page 4: Develop chemical reactivity scenarios sends the program into the sub-routine detailed on page 2 (see section 4.4).

1S Reactivity evaluation protocol, page 5: Evaluate heat release and gas generation hazards. Sends the program into the sub-routine detailed on page 2 (see section 4.5.4.4). User is lead step by step through a protocol that helps evaluate each scenario for heat release and pressure generation hazards.

IT Reports are generated for the reactivity evaluation, warehousing segregation, and binary chemical reactivity matrix (see section 4.6)

4.2 Chemical Reactivity Evaluation Protocol, Figure 2: Page 2 Subroutine to Evaluate Pure Component Reactivity Hazards

For each chemical entered the following pure-component chemical reactivity properties are automatically identified by the software tool using the NOAA Chemical Reactivity Worksheet database:

- *Highly Flammable*
- *Explosive*
- *Polymerizable*
- *Strong Oxidizing Agent*
- *Strong Reducing Agent*
- *Water-Reactive*
- *Air-Reactive*
- *Pyrophoric*
- *Peroxidizable Compound*
- *Radioactive Material*

4.3 Chemical Reactivity Evaluation Protocol, Figure 3: Page 3 Subroutine to Evaluate Chemical Interaction Hazards

Binary chemical interaction hazards are identified based on the NOAA CRW2 worksheet.⁴

4.4 Chemical Reactivity Evaluation Protocol, Figure 4: Page 4 Subroutine to Develop Chemical Reactivity Scenarios

User is lead step by step through a protocol that helps develop a list of possible chemical reactivity incident scenarios. The user is presented with 7 different categories of failure. Each has an accompanying list of examples in the help guide.

1. Loss of utilities
2. Process variation or upset
3. Energy input variation
4. Mechanical failure
5. Inadvertent mixing or material of construction
6. Human error
7. Other including desired chemistry and side reactions / decompositions

4.5 Chemical Reactivity Evaluation Protocol, Figure 5: Page 5 Subroutine to Evaluate Heat Release and Pressure Generation Hazards

User is lead step by step through a protocol that helps evaluate each scenario for heat release and pressure generation hazards. Users are requested to supply the following information.

1. Heat of reaction (KJ/Kg)
2. Adiabatic heat rise or heat capacity of system so program can calculate it.
3. Starting temperature of the system so that maximum scenario temperature can be calculated by the program.
4. Temperature of concern that must not be exceeded
5. Maximum possible scenario pressure
6. Pressure of concern that must not be exceeded

Reactions with a heat of reaction less than 450KJ/Kg are screened out as unlikely to cause major a thermal reactivity event. These proceed directly into the pressure analysis protocol. Reactions that have a heat of reaction of more than 450KJ/Kg are screened for maximum system temperature greater than temperature of concern and maximum pressure greater than pressure of concern.

Once reactivity hazards have been identified, appropriate safeguards must be implemented to contain and control the chemical reactivity hazards. Reactivity management systems must also be developed and implemented to ensure procedures are in place to identify and control the hazards.

4.6 Reporting

The information generated in the reactivity evaluation protocol, including the hazards identified as requiring additional evaluation are presented to the user in a report that can be used as the starting point for developing and implementing a Chemical Reactivity Management System to contain and control the identified chemical reactivity hazards and to provide preventive and mitigative safeguards for managing the risks associated with the identified scenarios of concern.

4.6.1 Warehouse Segregation Report

Warehouse segregations based are on the DOT codes entered for each chemical. The recommended segregations must be checked against the Chemical Reactivity Binary interaction matrix as well as special hazards codes to make sure incompatible materials are properly segregated. Hidden hazards like storage of large quantities of water reactive materials in a warehouse that is fire protected by a water spray or water deluge system must also be thoughtfully considered.

4.6.2 Binary Chemical Interaction Matrix

This report presents a graphical representation of the chemical reactivity for every pairing the of compounds entered. It is based on the predictive algorithm utilized by the NOAA CRW2⁴. The generalities of this system can cause both false positives and negatives. Generally the most highly reactive compounds of the classes being compared are utilized to present the user with a “worst case” reactivity prediction. Much time and capital can be wasted mitigating non-existent problems unless the report is carefully scrutinized by an expert in chemistry or chemical reactivity. Samples are presented in Figure 6 Binary interaction matrix generated by the program Figure 6 and Table 6.

4.6.3 Pure Component Hazard Report

Reports the hazardous properties of each chemical either as listed in the NOAA database or as entered under the custom chemical section. A sample report is presented in Table 5.

4.6.4 Chemical Reactivity Hazards Scenario Evaluation Report

This report lists all the user entered scenario information along with the program generated conclusions as to thermal and pressure incident risk. A sample is presented in Table 7.

Figure 1: Primary Flow Chart (Page 1)

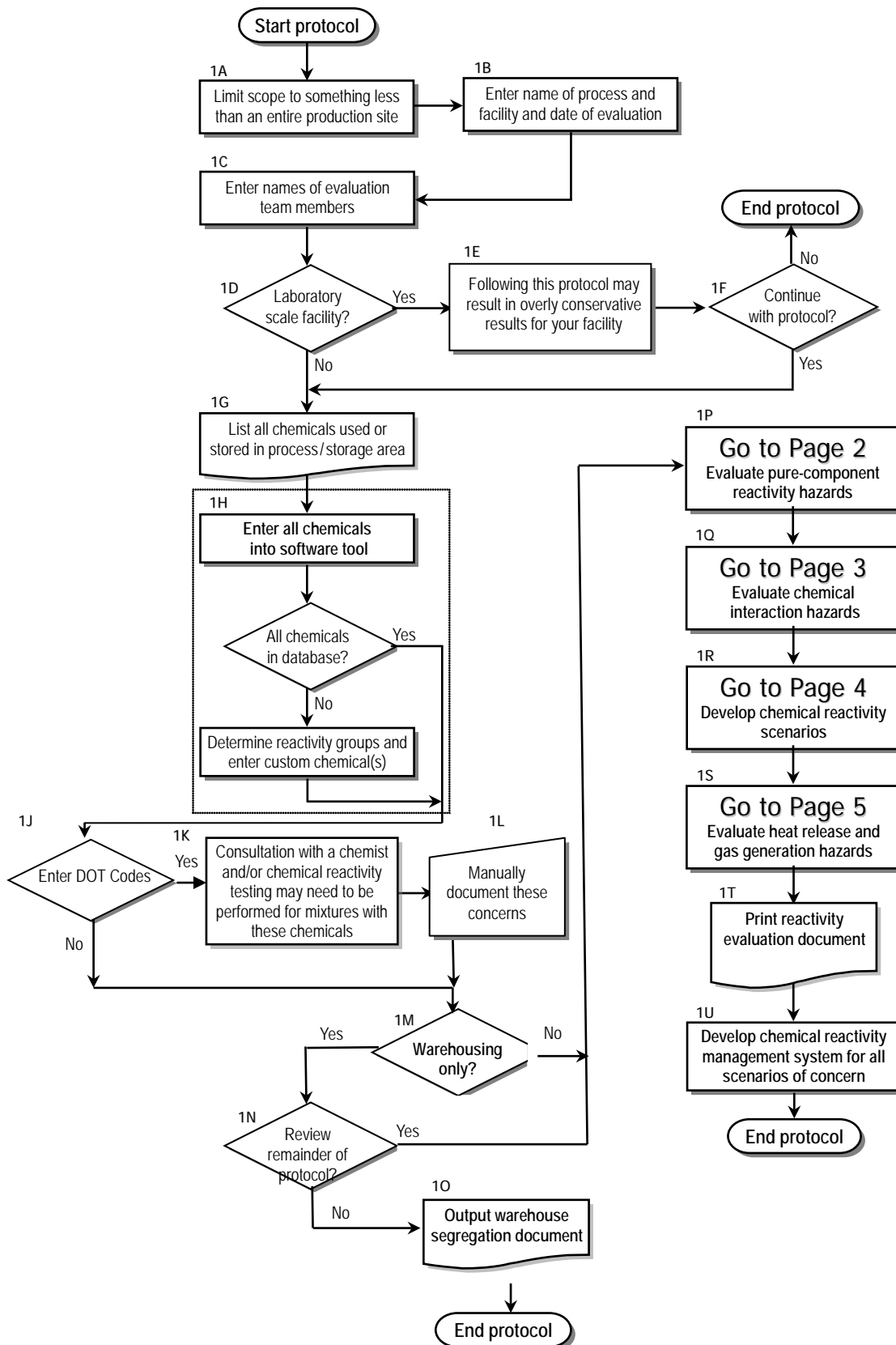


Figure 2: Page 2 Subroutine to Evaluate Pure Component Reactivity Hazards

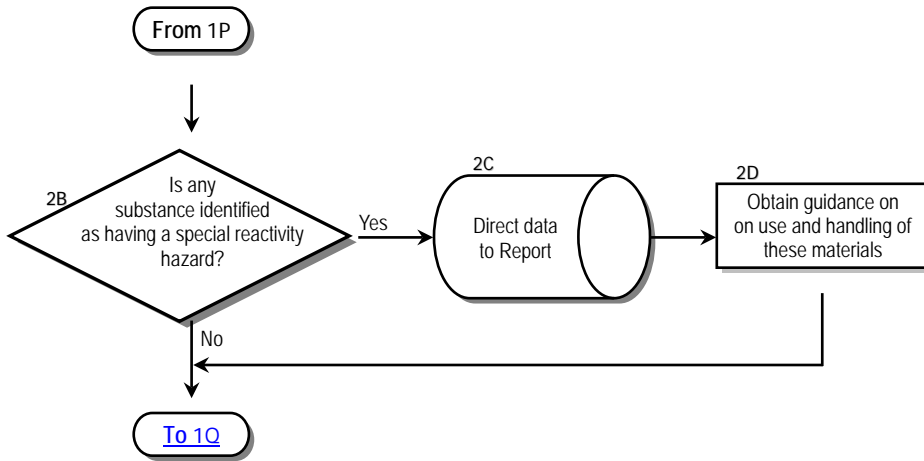


Figure 3: Page 3 Subroutine to Evaluate Chemical Interaction Hazards

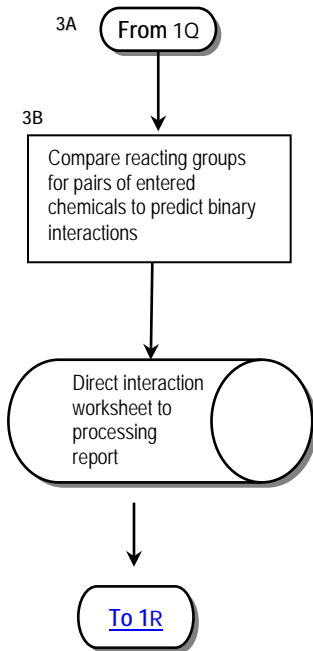


Figure 4: Page 4 Subroutine to Develop Chemical Reactivity Scenarios

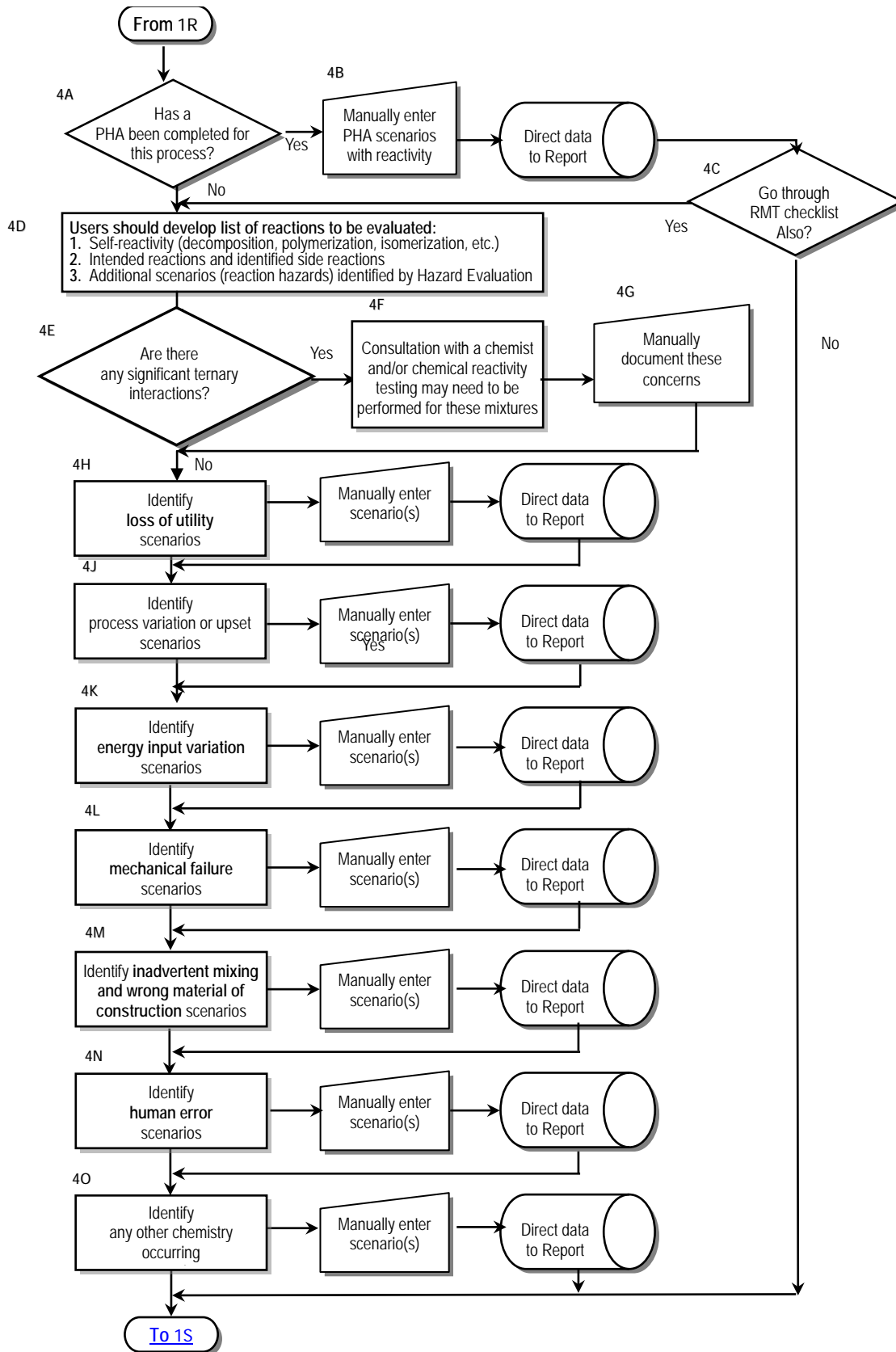
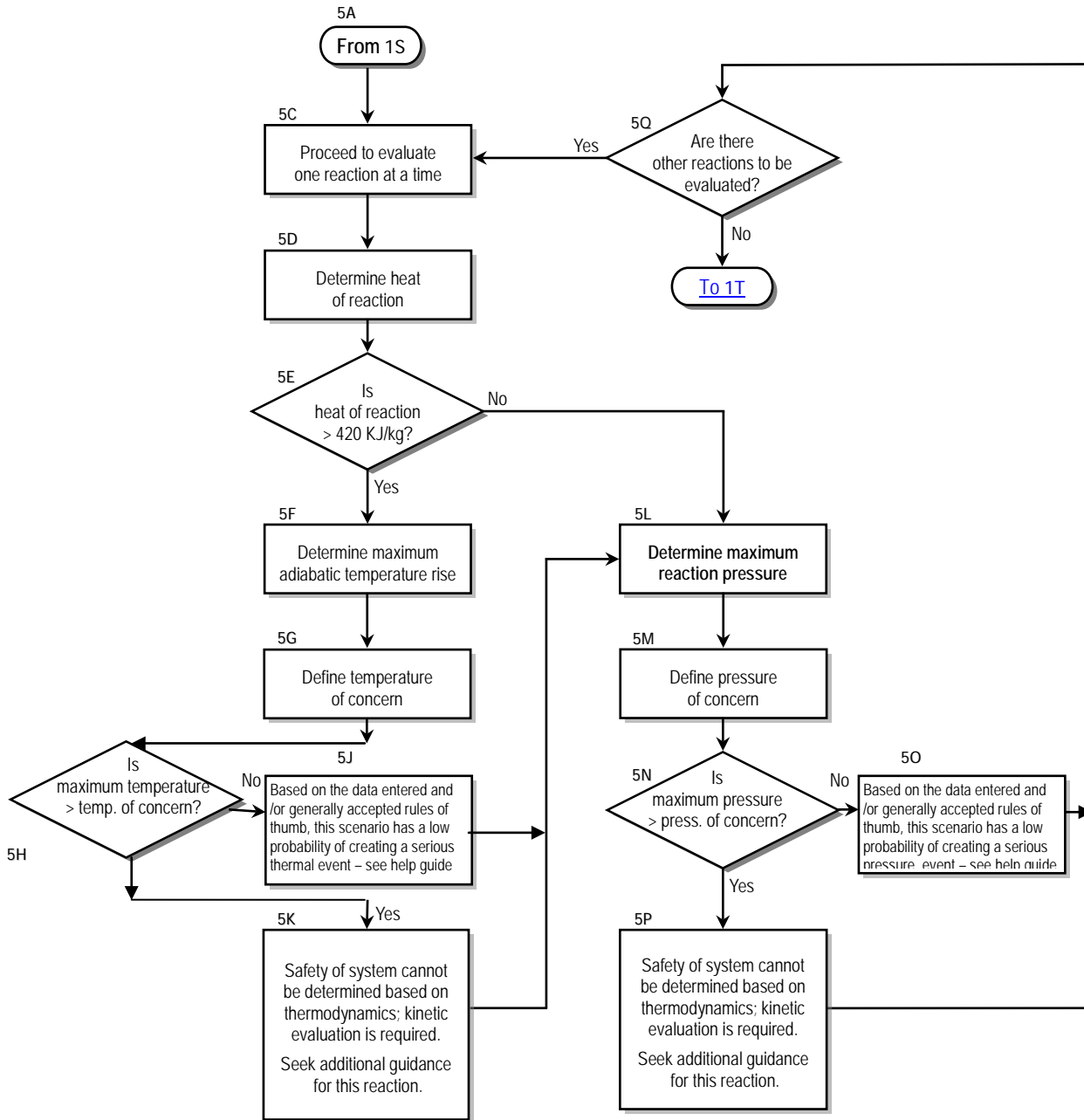


Figure 5: Page 5 Subroutine to Evaluate Heat Release and Pressure Generation Hazards



5 Worked Example

“On April 21, 1995, at approximately 7:45 a.m., a violent explosion and fire occurred at the Napp Technologies, Inc. specialty chemical plant in Lodi, New Jersey. Five employees of Napp ultimately died. A majority of the facility was destroyed as a result of the fire, and other businesses near the facility were destroyed or significantly damaged. Approximately 300 residents in the area were evacuated from their homes and a school. Additionally, firefighting efforts generated chemically contaminated water that ran off into the streets and nearby Saddle River. At the time of the explosion and fire, Napp was conducting a blending operation...to produce a formulation called ACR 9031 GPA⁶, a gold precipitating agent.”⁷

The following example is based on the information provided in the referenced report and other publically available data.

5.1 Identify the Scope and Process

Process Materials:

- Sodium hydrosulfite
- Aluminum powder
- Potassium carbonate
- Benzaldehyde

Other Materials Present in the processing area

- Water
- Isopropyl Alcohol

Intended Procedure:

- To a clean and dry 6 m³ tumble dryer / mixer PK-125 add:
- 1,800 lb Aluminum powder
- 900 lb Potassium Carbonate
- 5,400 lb Sodium hydrosulfite
- Blend for 1 hour – Rotating 10 min with intensifier bar off and 5 min with intensifier on
- Spray in 8 L of benzaldehyde
- Blend
- Dispense into 18 to 22 - 55 gal plastic lined drums

5.2 Entering the Process Chemicals

The following chemicals can be found in the pre-loaded NOAA database

- Sodium hydrosulfite (Sodium hydrogen sulfite)
- Aluminum powder uncoated
- Benzaldehyde

The following chemicals must be entered into the user’s database using information from Table 1.

- Potassium Carbonate
- ACR 9031 GPA

Table 1 Information required for entering chemicals

Name	Primary DOT code	Secondary DOT	Reactivity groups	Reactivity hazard
Sodium hydrogen sulfite	4.2 Spontaneously combustible	none	Already in database	Already in database
Aluminum powder uncoated	4.3 Dangerous when wet	None	Already in database	Already in database
Benzaldehyde	3.X Flammable liquid	None	Already in database	Already in database
Potassium Carbonate	Non-hazardous	None	39	none
ACR 9031 GPA	4.3 Dangerous when wet	4.2 Spontaneously combustible	5,22,39,45	Highly Flammable Strong reducing agent, Water- Reactive Pyrophoric
Isopropanol	3.X Flammable liquid	none	Already in database	Already in database

5.3 Entering Missing Chemical Information

Utilizing various sources Table 1 was compiled and utilized to complete data entry for our compound list.

5.4 Pure compound hazards identified by program

Table 2 Display of the pure component hazards for ACR 9031 GPA process

Chemical Name	Special Hazard
ALUMINUM POWDER, UNCOATED, ISOPROPANOL, ACR 9031 GPA	Highly Flammable
ALUMINUM POWDER, UNCOATED, SODIUM, HYDROSULFITE, ACR 9031 GPA	Water-Reactive
SODIUM HYDROSULFITE	Air-Reactive
ALUMINUM POWDER, UNCOATED, ACR 9031 GPA	Pyrophoric
ISOPROPANOL	Peroxidizable Compound

5.5 Binary chemical interactions are identified by the program

Chemical reactivity is assessed by the program using the functional group approach developed by Farr and Johnson⁴.

Figure 6 Binary interaction matrix generated by the program

Chemical Reactivity Matrix: ACR 9031 Napp Technologies

Process:

Matrix	ALUMINUM POWDER, UNCOATED	BENZALDEHYDE	ISOPROPANOL	SODIUM HYDROSULFITE	WATER	Potassium carbonate
ALUMINUM PO...						
BENZALDEHYDE	B5, D1					
ISOPROPANOL	B5, C	C, G				
SODIUM HYDR...	A2, C, G	B5, C	A6, B1, B5, C			
WATER	B6			B6, D3, D6, D7		
Potassium carbo...	A3, A6, B1, B5, C	A6, C, D4		C, D3	B5, D7, E	
ACR 9031	B5, D1, A3, A6, ...	B5, D1, A6, C, D4	C, G, B5, A6, B1	B5, C, A2, G, D3, F	B6, B5, D7, E, D...	A6, C, D4, A3, B...

5.6 *Developing and Entering Scenarios*

A quick read of the referenced report identifies the following **abbreviated** list of example failure scenarios. There are many more scenarios evident from reading the text. In developing a list for an actual process you would be expected to develop a list at least several pages long. Many of the listed scenarios could be simply assessed without a formal evaluation because their consequences are obvious. For instance, a static ignition of benzaldehyde need not be evaluated through this program because the obvious result is a fire however the consequences of the fire must be thought through, Fire suppression activated, initiation of the combustion of a large amount of aluminum powder, etc.. One does not need a computer program to determine that inerting and scrupulous exclusion of water are very important to the safety of this operation.

- Bearing failure
 - Coolant leak into blender
 - Overheat could lead to decomposition
- Jacket temperature control lost
 - Overheat could lead to decomposition
- Miss-charge / over charge
 - Wrong ratio of materials
 - Over fill of blender
 - Under fill of blender
- Loss of inertion gas
 - Introduction of humidity
 - Static ignition of benzaldehyde
- Inadvertent mixing
 - Water + sodium hydrosulfite
 - Water + GPA
 - Sweating – pipes or perspiration – drum filling
 - Fire suppression system
 - Cleaning operations near-by
 - Humidity during charging or dispensing
 - Blender water wet from cleaning
 - Header pipes have trapped water
 - Residual GPA in blender during cleaning
 - Potassium carbonate wet from improper storage
 - Water in inerting gas line
 - Water + Al
 - →Combustion of aluminum
 - Hydrogen build-up in mixer with static ignition

For illustration purposes we will only enter a few of the scenarios from the list above. In practice you would enter all scenarios generated.

5.6.1 Loss of Utilities Example

Inertion gas flow interrupted causing blender inertion to be lost.
This scenario would be entered under the Loss of Utilities Tab

Figure 7 Screen shot of loss of utility scenario entry form

- Enter the information as shown in Figure 7.
- Use the “Save” button to save the entry then the “Next Button to continue with adding the next scenario.

5.6.2 Process variation or upset example

Over fill of blender causes stress on intensifier bar seals causing leakage of coolant into blender.

- Enter the information as shown in Figure 8.

Figure 8 Screen shot of process variation or upset scenario entry form

- Use the “Save” button to save the entry then the “Next Button to continue with adding the next scenario.

5.6.3 Energy Input variation example

Jacket steam valve leak causes jacket to exceed setpoint. Worst case jacket reaches boiling at 120°C.

- Enter the information shown in Figure 9.

Figure 9 Screen shot of energy input variation scenario entry form

Process Name - Intentional Chemistry Example; Facility Name-NAPP Technologies

Reactivity Evaluation Protocol | Chemical Reactivity Hazards | Evaluate Heat Release and Pressure Generation Hazards

Identify Process Variation or Upset Scenarios | Process Variation and Upset Scenario | Identify Energy Input Variation | Energy input Variation Scenario | Identify Mechan

Create Energy Input Variation Scenario

Scenario Name: ENG-01

Full Description: Jacket steam valve leak causes jacket to exceed setpoint

Comments: assume complete failure to approximate jacket max of 120C

Heat of Reaction: Kj/Kg of Total mixture

Prev Reset Save List all Scenarios Help Next

- Use the “Save” button to save the entry then the “Next Button to continue with adding the next scenario.

5.6.4 Mechanical failure example

Bearing failure leads to overheating of material contacting the near-by surfaces with resulting self sustaining decomposition spreading to entire batch.

- Enter the information shown in Figure 10.

Figure 10 Screen shot of mechanical failure scenario entry form

Process Name - Intentional Chemistry Example; Facility Name-NAPP Technologies

Reactivity Evaluation Protocol | Chemical Reactivity Hazards | Evaluate Heat Release and Pressure Generation Hazards

Process Variation and Upset Scenario | Identify Energy Input Variation | Energy input Variation Scenario | Identify Mechanical Failure | Mechanical Failure Scenario | Ide < >

Create Mechanical Failure Scenario

Scenario Name: MEC-01

Full Description: Bearing failure leads to overheating of material contacting the near-by surfaces with resulting self sustaining decomposition spreading to entire batch.

Comments:

Heat of Reaction: KJ/Kg of Total mixture

Prev Reset Save List all Scenarios Help Next

- Use the “Save” button to save the entry then the “Next Button to continue with adding the next scenario.

5.6.5 Inadvertent mixing example

Fire suppression system activated by event not connected with process during charging. (note that same event during packaging has different consequences and must be entered separately.)

- Enter the information shown in Figure 11.

Figure 11 Screen shot of inadvertent mixing scenario entry form

Process Name - ACR 9031 Napp Technologies; Facility Name-Lodi NJ

Reactivity Evaluation Protocol | Chemical Reactivity Hazards | Evaluate Heat Release and Pressure Generation Hazards

Energy input Variation Scenario | Identify Mechanical Failure | Mechanical Failure Scenario | Identify Inadvertent Mixing | Inadvertent Mixing Scenario | Identify Human E < >

Create Inadvertent Mixing and Wrong Material of Construction Scenario

Inadvertent Mixing and Wrong Material of Construction scenario description will be displayed here..

Scenario Name: MIX-01

Full Description: Fire suppression system activated by event not connected with process during a charging operation

Comments: Must determine best course of action. Close manway or something else. What are the consequences of disabling fire protection during charging?

Heat of Reaction: KJ/Kg of Total mixture

Prev Reset Save List all Scenarios Help Next

- Use the “Save” button to save the entry then the “Next Button to continue with adding the next scenario.

We have completed entering the demonstration scenarios for this example.

5.6.6 Evaluating the Scenarios

Each scenario will be evaluated individually for thermal and pressure risk

- The “scenario” tab allows the user to view all entered scenario information and quickly see the evaluation status of each one.
- Double clicking on a scenario will display the scenario information in the lower part of the window and activate the “Evaluate Scenario” button
- The window shown in Figure 12 will open. You must enter a heat of reaction in KJ/Kg of reaction mixture at this time
- Since this is a fire scenario enter any large number or calculate the heat of combustion.
- Press Update and Evaluate scenario to open the first evaluation screen shown in Figure 13.

Figure 12 Screen shot of the Scenarios Tab

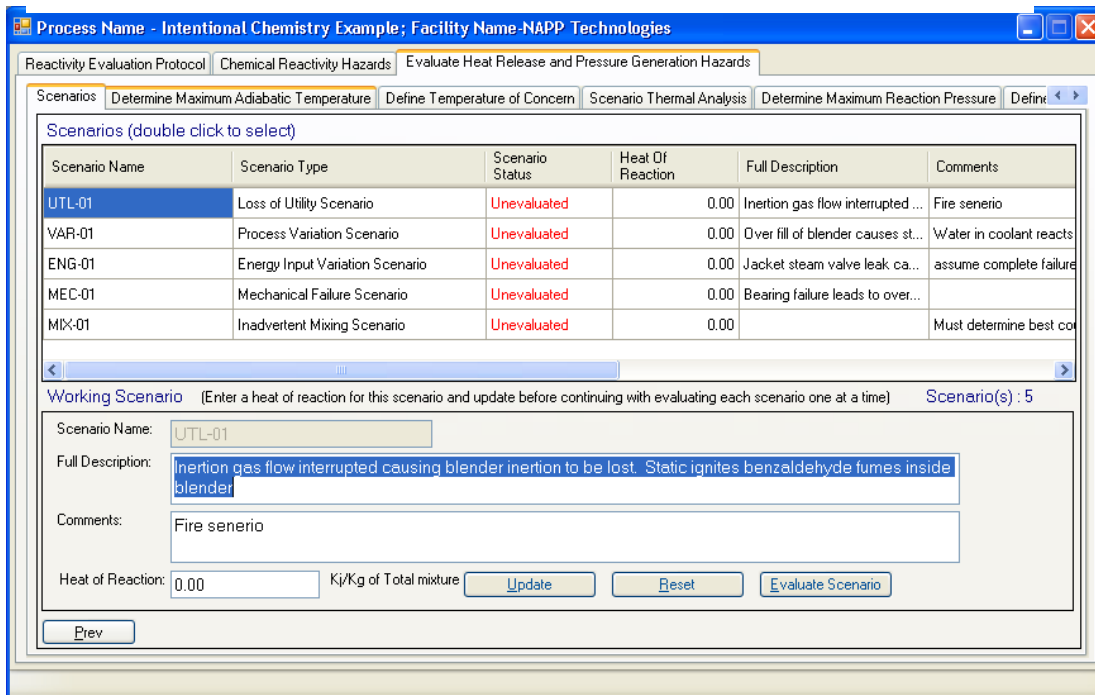


Figure 13 Screen shot of the determine scenario adiabatic temperature rise form

Process Name - ACR 9031 Napp Technologies; Facility Name-Lodi NJ

Reactivity Evaluation Protocol | Chemical Reactivity Hazards | Evaluate Heat Release and Pressure Generation Hazards

Scenarios | Determine Maximum Adiabatic Temperature | Define Temperature of Concern | Scenario Thermal Analysis | Determine Maximum Reaction Pressure | Define

Determine Max Adiabatic Temperature Rise

You are being asked to either enter the adiabatic temperature rise of the reaction or the program can help you calculate it.

Scenario Name: UTL-01

Full Description: Inertion gas interrupted causing loss of inertion in Blender. Static ignites Benzaldehyde vapors

Comments: Fire Senerio, fire senerio 1500Kj/Kg used to represent complete combustion, assumed cp=2, used 10X rule of thumb to determine Pmax. MWAPx2.5 for pressure of concern

Heat of reaction: 1500.00 Kj/Kg of total mixture

Adiabatic Temperature Rise: 750 degrees C Initial Temperature: 20 degrees C

Heat of Capacity: J/g*degreeC

Save Reset Help

Prev Next

- Press ‘save’ then ‘Next’ to open the next evaluation screen shown in Figure 14.
- Enter the max working temperature of the vessel because we are concerned with combustion not decomposition in this scenario. This temperature could also be the decomposition onset or any other temperature at which something undesirable might occur.
- Press ‘save’ then ‘Next’ to open the next evaluation results screen where the program displays the message: **“The safety of this scenario cannot be determined based on thermodynamics, a kinetic evaluation or other evaluation methodology is required. Seek additional guidance for this reaction.”**
- Press ‘next’ to evaluate the pressure portion of the scenario as shown in Figure 15.
- Enter the Maximum pressure. For this example we are assuming a sealed vessel so the rule of thumb is 10 times the starting pressure under ambient oxygen concentration.

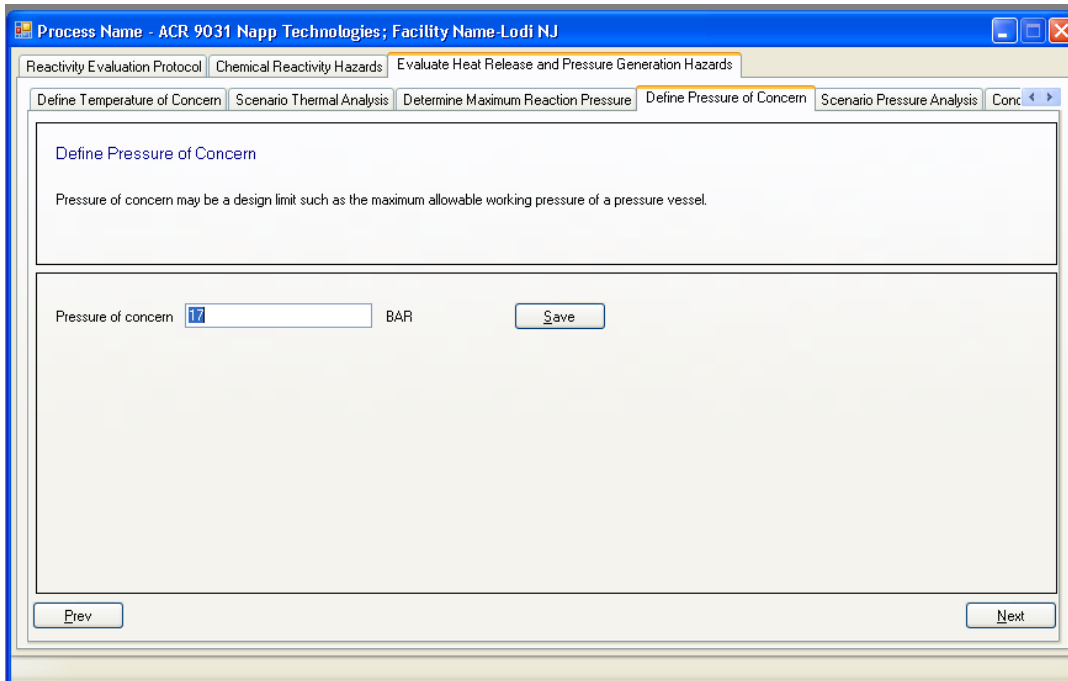
IMPORTANT: *In all likelihood this fire would cause a runaway decomposition of the remaining ingredients creating large amounts of gas. We have ignored this possibility for the sake simplicity in this example only because this scenario has already been flagged as posing a credible reactivity hazard..*

Figure 14 Screen shot of the enter a temperature of concern form

Figure 15 Screen shot of the enter maximum reaction pressure form

- Press ‘save’ then “Next” to open the next evaluation screen shown in Figure 16.

Figure 16 Screen shot for entering a pressure of concern form



- Enter a pressure of concern. In this case you could either enter the rupture disk setting, the MAWP of the tank or tank the failure pressure (2.5 times MAWP for an ASME rating)
- We will imagine the vessel was rated at 100psi. 2.5 times 100psi = 250psi
- Note PSI cannot be entered here because Bar was selected as the pressure units on the previous page. 250psi=17.2bar
- Press ‘save’ then “Next” to open the evaluation results screen.
- The program displays the message: “The information entered for the pressure analysis indicates that this scenario has a low probability of causing a major chemical reactivity incident. See “Help Guide”. The pressure generated by this scenario should be contained by the vessel and not pose a danger to plant or equipment. A word of caution before you except this conclusion blindly. This pre-supposes that no decomposition of the material inside the vessel occurred. The binary interaction matrix suggests that thermal decomposition of several of the components causes gas formation. Given this information it would be prudent to re-think this scenario. Consulting an expert would be a prudent choice as the consequences and preventive measures associated with this scenario are considered.
- Pressing “Next” takes the user to a form where the status of the scenario can be reset from “unevaluated” to “completed” or “needs updating”
- Press ‘save’ then select “evaluate another scenario” and “Next” to return the scenarios tab as shown in Figure 12.
- Repeat the above process until all scenarios have been evaluated.

Table 3 Scenario evaluation data

Scenario	Heat KJ/Kg	Adiabatic temp rise °C	Heat capacity KJ/Kg°C	Temp of concern °C	Starting temp °C	Max pressure	Pressure of concern
UTL-01	5000 ¹		2	200	20	10bar	17.2bar
VAR-01	972	486		200	20	175bar	17.2bar
ERG-01	972	486		200	20	175bar	17.2 bar
MEC-01	972	486		200	20	175bar	17.2bar
MIX-01	5000 ¹		2	200	20	unknown ²	17.2bar

5.6.7 Calculating P_{max} for scenario VAR-01, ERG-01 and MEC-01

We know from the CSB report that the adiabatic heat rise of the ACR 9031 is 486°C. Thus even a little water would initiate a self sustaining decomposition throughout the batch.

The reactor charge of compounds evolving gas was:

- 5400 lb = 2,115.5 kg Na₂S₂O₃ molecular weight 158g/mole
2,115,500g / 158 g/mole = 13,389 moles Na₂S₂O₃

Each mole of decomposing Na₂S₂O₃ gives off 1 mole of SO₂ thus 13,389 moles of SO₂ are released on complete decomposition.

- 900 lb = 335.9 Kg K₂CO₃ molecular weight 138 g/mole
335900g / 138 g/mole = 2,434 moles

Each mole of decomposing K₂CO₃ gives off 1 mole of CO₂ thus 2434 moles of CO₂ are released on complete decomposition.

$$R = 0.083 \text{ bar} \cdot \text{L} / \text{mole} \cdot \text{K}$$

$$T = 779\text{K} : 7293\text{K} (20^\circ\text{C starting temp}) + 486 \text{ (adiabatic heat rise)}$$

$$V = 6 \text{ m}^3 = 6,000\text{L} \quad \text{see } ^3$$

$$n = 15823 = 13389 \text{ moles SO}_2 + 2434 \text{ moles CO}_2$$

¹ Large number as a place holder to represent combustion

² Requires a venting calculation based on an open manway. But does it really matter since you have flames shooting out of the manway?

³ Assumed from drawing in CSB report that head volume is roughly equal to the fill volume of 6 m³

5.7 Report Generation and Proof Reading

Reports should be examined carefully for incorrect or misleading information. This program must by necessity simplify chemical reactivity evaluation, binary chemical reactivities and warehousing segregation into general rules of thumb and generalized assumptions of chemical behavior. This can lead to either under estimation and overestimation of the potential for an incident.

These Reports are intended to be a starting point toward an in depth discussion of the results in the context of an overall process safety management system and not the fulfillment of either a legal or moral obligation to handle and use chemicals safely.

5.7.1 Selected screen shots of reports:

Table 4 Chemicals report exported to Excel

DBIdentification	Chemical Name	CAS Number	DOT Labels	Chemical Formula	Chemical_Id	Reactivity Ids
NOAA	ALUMINUM POWDER, UNCOATED	7429-90-5	4.2 Spontaneously Combustible 4.3 Dangerous when wet	Al	14008	22
NOAA	SODIUM HYDROSULFITE	7775-14-6	4.3 Dangerous when wet	Na2S2O4	4500	45
NOAA	BENZALDEHYDE	100-52-7	9.0 Other Hazard	C7H6O	216	5
NOAA	ISOPROPANOL	67-63-0	3.X Flammable liquid	C3H8O	946	4
SQL	WATER	7732-18-5	Non-hazardous material	H2O	1	100
SQL	Potassium carbonate	584-08-7	Non-hazardous material	K2CO3	2	39
SQL	ACR 9031		4.3 Dangerous when wet		3	5, 22, 39, 45

Table 5 Pure component hazards report

Chemical Name	Reactive Group Name
ALUMINUM POWDER, UNCOATED, ISOPROPANOL	Highly Flammable
ALUMINUM POWDER, UNCOATED, SODIUM HYDROSULFITE	Water-Reactive
SODIUM HYDROSULFITE	Air-Reactive
ALUMINUM POWDER, UNCOATED	Pyrophoric
ISOPROPANOL	Peroxidizable Compound

Table 6 Binary interaction matrix reformatted in Excel for readability

Matrix	ALUMINUM POWDER, UNCOATED	BENZALDEHYDE	ISOPROPANOL	SODIUM HYDROSULFITE	WATER	Potassium carbonate
BENZALDEHYDE	B5, D1					
ISOPROPANOL	B5, C	C, G				
SODIUM HYDROSULFITE	A2, C, G	B5, C	A6, B1, B5, C			
WATER	B6			B6, D3, D6, D7		
Potassium carbonate	A3, A6, B1, B5, C	A6, C, D4		C, D3	B5, D7, E	
ACR 9031	B5, D1, A3, A6, B1, C, A2, G	B5, D1, A6, C, D4	C, G, B5, A6, B1	B5, C, A2, G, D3, F	B6, B5, D7, E, D3, D6	A6, C, D4, A3, B1, B5, D3

A1: Explosive when dry.

A2: Risk of explosion by shock, friction, fire or other sources of ignition.

A3: Forms very unstable explosive metallic compounds.

A4: External heating may cause an explosion.

A5: May form explosive peroxides.

A6: Reaction proceeds with explosive violence and/or forms explosive products.

A8: Explosive when mixed with combustible material.

A9: Heat generated from chemical reaction may initiate explosion.

A10: Increased sensitivity to detonation.

B1: May become highly flammable or may initiate a fire, especially if other combustible materials are present.

B3: Spontaneously flammable in air.

B4: Spontaneous ignition of reactants or products due to reaction heat.

B5: Combination liberates gaseous products, at least one of which is flammable. May cause pressurization.

B6: Combination liberates gaseous products, including both flammable and toxic gases. May cause pressurization.

C: Exothermic reaction. May generate heat and/or cause pressurization.

D1: Exothermic, potentially violent polymerization. May cause pressurization.

D3: Combination liberates gaseous products, at least one of which is toxic. May cause pressurization.

D4: Combination liberates nonflammable, nontoxic gas. May cause pressurization.

D5: Combination liberates combustion-enhancing gas (e.g., oxygen). May cause pressurization.

D6: Exothermic, generation of toxic and corrosive fumes.

D7: Generation of corrosive liquid.

E: Generates water soluble toxic products.

F: May be hazardous but unknown.

G: Reaction may be intense or violent.

H: Possible exposure to radiation.

I: Members of this group are highly reactive. They may be incompatible with members of the same group.

Table 7 Reactivity Hazards Scenario Evaluation Report

Scenario Name	Scenario Type	Scenario Status	Heat Of Reaction	Full Description	Comments	Adiabatic Temp Rise	Initial Temperature	Max Reaction Pressure	Temperature Of Concern	Pressure Of Concern	MITSR	Temperature recommendation	Pressure recommendation
UTL-01	Loss of Utility Scenario	Completed	1500	Inertion gas interrupted causing loss of inertion in Blender. Static ignites Benzaldehyde vapors.	Fire Scenario 1500KJ/Kg used to represent complete combustion, assumed Cp=2, used 10X rule of thumb to determine Flmax. MITM/PX2.5 pressure of concern. Pressure analysis assumes no decomp - improbable	750	20	10	200	17	770	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.	The information entered for the pressure analysis of this scenario indicates that this scenario has a low probability of causing a major chemical reactivity incident. See help guide.
VAR-01	Process Variation Scenario	Completed	972	Overfill causes stress in intensifier bar bearings causing a coolant leak.	Water reacts with vessel contents. Gas and heat evolved. Heat of reaction very high - expect spontaneous ignition of Al and or Na2O4S2. 5000KJ/Kg chosen to represent large heat of reaction	486	20	175	200	17	506	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.
ERG-01	Energy Input Variation Scenario	Completed	972	Jacket stem valve leak causes jacket to exceed setpoint	assume complete failure to ~130C	486	20	175	200	17	506	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.
MEC-01	Mechanical Failure Scenario	Completed	972	Bearing failure leads to localized overheating. Self-sustaining decomposition initiated that spreads to entire batch		486	20	175	200	17	506	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.
MIX-01	Inadvertent Mixing Scenario	Completed	5000	Fire suppression system activated by event not connected with process during a charging operation	Close manway or something else. What are the consequences of disabling fire protection during charging? Ignore Pressure because requires venting calc not done	2500	20	0	200	17	2520	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.	The safety of this scenario can not be determined based on thermodynamics, a kinetic evaluation or other evaluation is required. Seek additional guidance for this reaction.

6 Discussion and Conclusions

It is clear that the outputs of this program, had they been utilized properly, would have prevented the devastating events of April 21st, 1995 at the Napp Technologies facility. Given Napp's attention to details like covering floor drains to avoid the GPA from contacting water in the sewer, it is clear that some thought was put into fault scenarios. The fact that they missed the potential of a leaky seal, an un-clean header pipe, energy input from the intensifier bar, miss charging of raw materials, charging to a wet blender and many more shows the importance of exploring the consequences all possible failures. A good rule of thumb when assessing failures is: If it absolutely could not happen it will. The use of this program alone will not provide adequate protection from chemical reactivity incidents. The program was designed to be just one of many inputs into a complete chemical reactivity management system. CCPS has developed a series of guide books to help chemical users and handlers develop comprehensive reactivity management systems that protect businesses, workers and the community from losses due to these often devastating events.

6.1 Limitations of the Program and its Predictions

The chemical reactivity evaluation tool can only assist the user in identifying reactivity hazards. The software tool is designed to complement the user's understanding of known reactivity hazards. There is no guarantee that all reactivity hazards will be identified. Also, the results obtained from using the software tool can be no better than the accuracy and completeness of the information entered into the program.

Chemical reactivity is assessed by the program using a functional group approach. This can lead to errors. All predictions should be checked by either experiment or a competent chemist trained in chemical synthesis and chemical reactions.

The suggested warehousing segregations are just that - suggested. All predictions should be checked by a competent person trained in chemical segregation. Expert advice should be sought when storing those compounds designated as extremely toxic, infective, radioactive or explosive.

The scenarios generated by the user are only assessed on thermal and pressure hazards. Serious risk can exist in many other forms such as toxicity or damage to the environment that are not addressed in this program. Generalized rules of thumb are utilized to screen out those scenarios that are unlikely to pose serious risks. It should be understood by the user that these rules of thumb may screen out as unlikely a scenario consequences that the user or the user's affiliated company may find unacceptable. The protocol in the computer program is targeted to identify only 80% of the 167 serious incidents listed by the CSB. The CSB did not consider an incident serious unless there were fatalities or injuries and severe property damage, or a significant impact to the public outside the perimeter fence of the facility. You and/or your company may have a much more conservative idea of what a serious incident looks like. One major international chemical company with a strong reactive chemical program often reports over 90 reactive chemical incidents per year because employees are encourage to report near misses and minor incidents so they may be investigated. Lessons learned from the investigation of near

misses and minor incidents can prevent major incidents. It should be noted that the CSB's version of serious incident usually results in severe restrictions on the company's freedom to operate within the local community often resulting in facility closure and more than occasionally the insolvency of the facility owner.

The software tool does not address oxidation reactions (burning) of flammable and combustible materials, including combustible dusts. It does not assess the toxicity risks or radiation risks of a scenario or release nor does it consider environmental impact. In addition, the software tool is not intended to be used to determine what materials of construction are appropriate to use to contain or convey reactive materials.

7 Afterword: Future Direction

As currently implemented, the chemical reactivity evaluation tool gives the basic framework for identifying and evaluating chemical reactivity hazards.

Future revisions of the NOAA CAMEO database will contain DOT labels for many entries. Future releases will likely extract this data from the updated CAMEO database.

This tool currently utilizes manually inputted data to help evaluate reactivity scenarios. Often heat of reaction information is not readily available in the literature. Empirical methods to determine this information are available but require comprehensive and time consuming analytical work. Future enhancements for this software tool could include use of computational programs such as CHETAH™ for predicting thermochemical properties, such as ΔH and certain "reactive chemicals" hazards associated with a pure chemical, a mixture of chemicals, or a chemical reaction.

It has also been suggested that the hard coded warehouse separation distances be editable by the user allowing greater flexibility.

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⁶ *ACR 9031 GPA* is a trademark of Technic Inc, Cranston RI

⁷ EPA/OSHA Joint Chemical Accident Investigation Report, Napp Technologies, inc. Lodi, NJ EPA 550-R-97-002, October 1997