

Guidelines for
*Process Safety in
Batch Reaction
Systems*

This book is one of a series of publications available from the Center for Chemical Process Safety. A complete list of titles appears at the end of this book.

Guidelines for

Process Safety in Batch Reaction Systems



AMERICAN INSTITUTE OF
CHEMICAL ENGINEERS



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of the
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This book is available at a special discount when ordered in bulk quantities. For information, contact the Center for Chemical Process Safety at the address shown above.

It is sincerely hoped that the information presented in this document will lead to an even more impressive record for the entire industry; however, the American Institute of Chemical Engineers, its consultants, CCPS Subcommittee members, their employers, their employers' officers and directors, and Arthur D. Little, Inc., disclaim making or giving any warranties or representations, express or implied, including with respect to fitness, intended purpose, use or merchantability and/or correctness or accuracy of the content of the information presented in this document. As between (1) American Institute of Chemical Engineers, its consultants, CCPS Subcommittee members, their employers, their employers' officers and directors, and Arthur D. Little, Inc., and (2) the user of this document, the user accepts any legal liability or responsibility whatsoever for the consequence of its use or misuse.

*CCPS and members of the Batch Reaction
Subcommittee dedicate this book to the
memory of Felix Freiheiter and Al Noren*



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Preface

The Center for Chemical Process Safety (CCPS) was established in 1985 by the American Institute of Chemical Engineers (AIChE) for the express purpose of assisting the Chemical and Hydrocarbon Process Industries in avoiding or mitigating catastrophic chemical accidents. To achieve this goal, CCPS has focused its work in four areas:

- Establishing and publishing the latest scientific and engineering practices (not standards) for the prevention and mitigation of incidents involving hazardous materials,
- Encouraging the use of such information by dissemination through publications, seminars, symposia and continuing education programs for engineers,
- Advancing the state-of-the-art in engineering practices and technical management through research in prevention and mitigation of catastrophic events, and
- Developing and encouraging the use of undergraduate education curricula which will improve the safety knowledge and consciousness of engineers.

The Center for Chemical Process Safety (CCPS) identified the need for a publication dealing with process safety issues unique to batch reaction systems. *Guidelines for Process Safety in Batch Reaction Systems*, is the result of a project begun in 1997 in which a group of volunteer professionals representing major chemical, pharmaceutical and hydrocarbon processing companies, worked with Arthur D. Little Inc., to produce a book that attempts to describe the safe design and operation of batch reaction systems. The objectives of the book are to

- Identify safety concerns unique to batch reaction systems;
- Provide a how-to guide for the practicing engineer to identify, define and address unique safety issues in batch reaction systems;

- Provide a range of criteria and techniques to be considered in the development, design, operation, and maintenance of batch reaction systems to reduce risk and ensure safety of people, environment, and property;
- Provide an aid to identify potential sources of unsafe conditions encountered in batch reaction systems;
- Provide guidance in applying appropriate practices to prevent accidents; and
- Identify sources for specific expertise and reference them accordingly.

The book does not focus on occupational safety and health issues, although improved process safety can benefit each area. Detailed engineering designs are outside the scope of the book. This book intends to identify issues and concerns in batch reaction systems and provides potential solutions to address these concerns. This should be of value to process design engineers, operators, maintenance personnel, as well as members of process hazards analysis teams. While the book offers potential solutions to specific issues/concerns, ultimately the user needs to make the case for the solutions that best satisfy their company's requirements for a balance between risk reduction and cost. In many instances the book provides one or more sources of additional information on the subject which could be of value to the reader.

Acknowledgments

The American Institute of Chemical Engineers (AIChE) wishes to thank the Center for Chemical Process Safety (CCPS) and those involved in its operation, including its many sponsors whose funding and technical support made this project possible. Particular thanks are due to the members of the Batch Reaction Subcommittee for their enthusiasm, tireless effort and technical contributions. Members of the subcommittee played a major role in the writing of this book by suggesting examples, by offering failure scenarios for the major equipment covered in the book and by suggesting possible solutions to the various Concerns/Issues mentioned in the tables.

AIChE and CCPS would also like to express their appreciation to Arthur D. Little, Inc. for their contribution in preparing this book for publication. It is the collective industrial experience and know-how of the subcommittee members plus the experience and expertise of Arthur D. Little, Inc. that makes this book especially valuable to the process and design engineer. Dr. Georges A. Melhem was the Director-in-Charge of this project, for Arthur D. Little, Inc.; Dr. Sanjeev Mohindra of Arthur D. Little, Inc. was the author; and Christina Hourican handled the somewhat complex word processing for this project.

The Batch Reaction Subcommittee was chaired by Walter L. Frank of EQE International. Current members of the subcommittee, listed alphabetically are: David J. Christensen, Union Carbide Corporation; Warren Greenfield, International Specialty Products; Philip P. Malkewicz, Nalco Chemical Company; Peter F. McGrath, Olin Corporation; Louisa A. Nara, Bayer Corporation; Leslie A. Scher, CCPS Staff Consultant; Robert Schisla, Eastman Chemical Company; Anthony Torres, Eastman Kodak Company; Dr. Jan C. Windhorst, Nova Chemicals; and Paul Wood, Eli Lilly & Company. Former subcommittee members who contributed much in getting this project started were Felix Freiheiter, CCPS Staff Consultant (deceased); Al Noren, Monsanto Company-Searle (deceased); John Noronha, Eastman Kodak Company (retired) and Robert Stankovich, Eli Lilly & Company.

The Batch Reaction Subcommittee would also like to acknowledge the following peer reviewers for their meaningful suggestions and contributions: Robert E. Hollenbeck, Fred Maves, Gary Paulu, Arlyn H. Poppen, and Monica R. Stiglich of 3M; Pete Lodol of Eastman Chemical Company; Michael Hofler, Lisa Morrison and Peter Monk of Nova Chemicals; Stanley S. Grossel of Process Safety & Design, Inc.; Linda Hicks of Reilly Industries, Inc.; Gary York of Rhodia, Inc.; Steve Getz of Union Carbide Corporation; and John Davenport, CCPS staff consultant.

Lastly, the members of the Batch Reaction Subcommittee would like to thank their employers for providing the time and support to participate in this project.



Acronyms and Abbreviations

ACGIH	American Conference of Government Industrial Hygienists
ACS	American Chemical Society
AGA	American Gas Association
AIChE	American Institute of Chemical Engineers
AIHA	American Industrial Hygiene Association
AIT	Autoignition Temperature
ANSI	American National Standards Institute
APFA	American Pipe Fittings Association
API	American Petroleum Institute
APTAC	Automated Pressure Tracking Adiabatic
ARC	Accelerating Rate Calorimeter
ASM	American Society for Metals
ASME	American Society of Mechanical Engineers
ASNT	American Society for Nondestructive Testing
ASSE	American Society of Safety Engineers
ASTM	American Society for Testing and Materials
AWS	American Welding Society
BLEVE	Boiling Liquid Expanding Vapor Explosion
BPCS	Basic Process Control System
CAA	Clean Air Act
CAAA	Clean Air Act Amendments
CART	Computed Adiabatic Reaction Temperature
CCPS	Center for Chemical Process Safety
CEM	Continuous Emissions Monitor
CFR	Code of Federal Regulations
CGA	Compressed Gas Association

CIA	Chemical Industries Association
CMA	Chemical Manufacturers Association
CSTR	Continuous-Flow Stirred-Tank Reactor
DCS	Distributed Control System
DIERS	Design Institute for Emergency Relief Systems
DIPPR	Design Institute for Physical Property Data
DOT	Department of Transportation
DPC	Deflagration Pressure Containment
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
EPA	Environmental Protection Agency
ERD	Emergency Relief Design
ERP	Emergency Response Planning Guideline
ERRF	External Risk Reduction Facilities
ERS	Emergency Relief System
ESD	Emergency Shutdown Device
FC	Fail Closed
F&EI	Fire and Explosion Index
FIBC	Flexible Intermediate Bulk Containers
FL	Fail Last Position
FMEA	Failure Mode and Effects Analysis
FMEC	Factory Mutual Engineering Corporation
FO	Fail Open
FRP	Fiber Reinforced Plastic
HAZOP	Hazard and Operability Study
HSE	Health and Safety Executive
HVAC	Heating, Ventilation, and Air Conditioning
ICHEME	The Institution of Chemical Engineers
IDLH	Immediately Dangerous to Life or Health
IEC	International Electrotechnical Commission
IEEE	Institute of Electrical and Electronics Engineers
IRI	Industrial Risk Insurers
ISA	Instrument Society of America
ISO	International Standards Organization
LEL	Lower Explosive Limit
LFL	Lower Flammable Limit
LNG	Liquefied Natural Gas
LOC	Limiting Oxidant Concentration
LPG	Liquefied Petroleum Gas
MAWP	Maximum Allowable Working Pressure
MEC	Minimum Explosible Concentration
MIE	Minimum Ignition Energy

MOC	Management of Change
MSDS	Material Safety Data Sheet
NACE	National Association of Corrosion Engineers
NBIC	National Board Inspection Code
NDE	Nondestructive Examination
NEC	National Electrical Code
NEMA	National Electrical Manufacturers Association
NESC	National Electrical Safety Code
NFPA	National Fire Protection Association
NIOSH	National Institute of Occupational Safety and Health
NPSH	Net Positive Suction Head
NTIAC	Nondestructive Testing Information Analysis Center
OSHA	Occupational Safety and Health Administration
P&ID	Piping and Instrumentation Diagram
PEL	Permissible Exposure Limit
PES	Programmable Electronic System
PFD	Process Flow Diagram
PFR	Plug Flow Reactor
PHA	Process Hazard Analysis
PID	Proportional Integral Derivative
PLC	Programmable Logic Controller
PPE	Personal Protection Equipment
PRV	Pressure Relief Valve
PSD	Process Safety Device
PSI	Process Safety Information
PSS	Process Safety System
PSV	Pressure Safety Valve
PVRV	Pressure-Vacuum Relief Valve
RP	Recommended Practice
RSST	Reactive Systems Screening Tool
RT	Radiographic Testing
RTD	Resistance Temperature Detector
SADT	Self Accelerating Decomposition Temperature
SAE	Society of Automotive Engineers
SCBA	Self-contained Breathing Apparatus
SCC	Stress Corrosion Cracking
SIL	Safety Integrity Level
SIS	Safety Instrumented System
SFPE	Society of Fire Protection Engineers
SRS	Safety Related Systems
TGA	Thermogravimetric Analysis
TEMA	Tubular Exchanger Manufacturer Association

THA	Thermal Hazardous Analysis
TLV	Threshold Limit Value
UBC	Uniform Building Code
UEL	Upper Explosive Limit
UFL	Upper Flammable Limit
UL	Underwriters Laboratory Inc.
UPS	Uninterruptible power supply
UT	Ultrasonic testing
VCE	Vapor Cloud Explosion
VDI	Verein Deutsche Ingenieure
VDE	Verein Deutsche Elektrotechnike
VOC	Volatile Organic Compound
VSP	Vent Sizing Package

1

Process Safety in Batch Reaction Systems

1.1. Scope

The Center for Chemical Process Safety (CCPS) has identified the need for a publication dealing with process safety issues unique to batch reaction systems. This book, *Guidelines for Process Safety in Batch Reaction Systems*, attempts to aid in the safe design, operation and maintenance of batch and semi-batch reaction systems. In this book the terms “batch” and “semi-batch” are used interchangeably for simplicity. The objectives of the book are to:

- Provide a how-to guide for the practicing engineer to identify, define, and address unique safety issues typically encountered in batch reaction systems.
- Provide a range of criteria and techniques to be considered in the development, design, operation, and maintenance of batch reaction systems to reduce risk and ensure safety of people, environment, and property.
- Provide an aid to identify potential sources of unsafe conditions encountered in batch reaction systems.
- Provide guidance in applying appropriate process safety practices to prevent accidents.
- Identify sources for specific expertise and reference them accordingly.

The book does not focus on occupational safety and health issues, although improved process safety can benefit these areas. Detailed engineering designs are outside the scope of this work. This book intends to identify issues and concerns in batch reaction systems and provide potential solutions to address these concerns. This should be of value to process design engineers, operators, maintenance personnel, as well as members of process hazards analysis teams. While this book offers potential solutions to specific issues/concerns, ultimately the user needs to make the case for the solutions that provide a balance between risk

reduction and cost. The solutions presented in the book, are possible approaches for dealing with a particular issue. The authors of this book could not anticipate all the possible issues, or all applicable solutions for a specific issue. Therefore, it is intended that the use of the suggested solutions be combined with sound engineering judgment and consideration of all relevant factors. Furthermore, all the solutions presented may not be applicable to a given situation. It should also be recognized that the solutions presented might themselves introduce potential hazards that were not originally present. Therefore, it is necessary to use the information in the context of the total design concept to ensure that all hazards have been considered, and that all applicable laws and regulations have been complied with.

1.2. Special Concerns of Batch Reaction Systems

Batch reaction systems present unique challenges for process safety (Hendershot 1987). Batch operations consist of a series of processing steps, which must be carried out in the proper order, and at the proper time. By their very nature, batch-type processes do not operate in a steady state. As the process is being carried out, the holdup of materials in the vessel varies with time as materials are charged, reacted and perhaps withdrawn, thus changing mixing characteristics and effective heat transfer area. There is a continuous variation in the physical properties, chemical compositions, and physical state of the reaction mixture with time. This makes it more difficult, both for the operators and control systems, to monitor and diagnose the process. The sequence of processing steps, and frequent start-ups and shutdowns increase the probability of human errors and equipment failures. Moreover, batch reaction systems often handle multiple processes and products in the same equipment. This can also lead to increased probability of human error.

Batch plants are often designed for general use, rather than dedicated to a specific process. The piping and layout of the equipment is often modified to meet the needs of the current process, or the process is modified to use the existing equipment. Use of the same equipment in different campaigns, complex process piping, and the use of shared auxiliary equipment, such as columns and condensers, presents greater challenges in preventing cross contamination; in selecting materials of construction; and in selecting instrumentation and control systems. Additionally, the complexity of equipment and the frequency of changes complicate the process documentation task. These frequent changes often result in complex management of change (MOC) issues.

The nature of batch operations (unsteady-state), frequently involving manual intervention, creates significant issues pertaining to the design of control systems, design of operating procedures, and the interaction between the

control system and the operators. The operator is a more integral part of the process control, supervision loop, and the safe operation of the process. The operator managing a batch process has a greater number of duties and responsibilities than his counterpart in a continuous system. Several of these duties are either specific to batch operations or are done more often in batch operations than in continuous processes. The number and variety of functions that the operator has to perform during a batch process requires effective management systems, including more rigorous training, to minimize human error. Furthermore, the batch operator is more involved and is often in closer proximity to the process. This close proximity puts the operator at increased risk to direct exposure to the hazards associated with larger inventory of raw materials and semi finished products than continuous systems with comparable throughput.

All of these issues make batch reaction systems unique, in terms of the challenges they pose for managing process safety.

Figure 1 shows a typical batch reaction system.

1.3. Approach Used in Guidelines

The book presents information pertaining to the safety issues in batch reaction systems in five chapters.

Each chapter starts with a description of the topic covered in the chapter. This is followed by a short example highlighting a reported incident involving a batch reaction system. The case study is followed by a listing of key issues and process safety practices unique to the topic. The issues and concerns presented in this book, as well as potential design solutions and sources of additional information are presented in the tables. This format concisely conveys the necessary and relevant information in a familiar and convenient format. The organization of the tables is described below.

- **Concern/Issue:** Identifies a specific safety issue or concern and its safety implications.
- **Potential Solutions and Control Mechanisms:** Lists the potential solutions and control mechanisms that may be employed to reduce the risk of a specific issue or concern.
- **Additional Resources:** Provides additional sources of information on the concerns/issues identified in the tables. Please note that the “Additional Resources” column does not attempt to include all sources of additional information.

It should be recognized that the solutions and control mechanisms presented in the table are possible approaches for dealing with a particular issue.

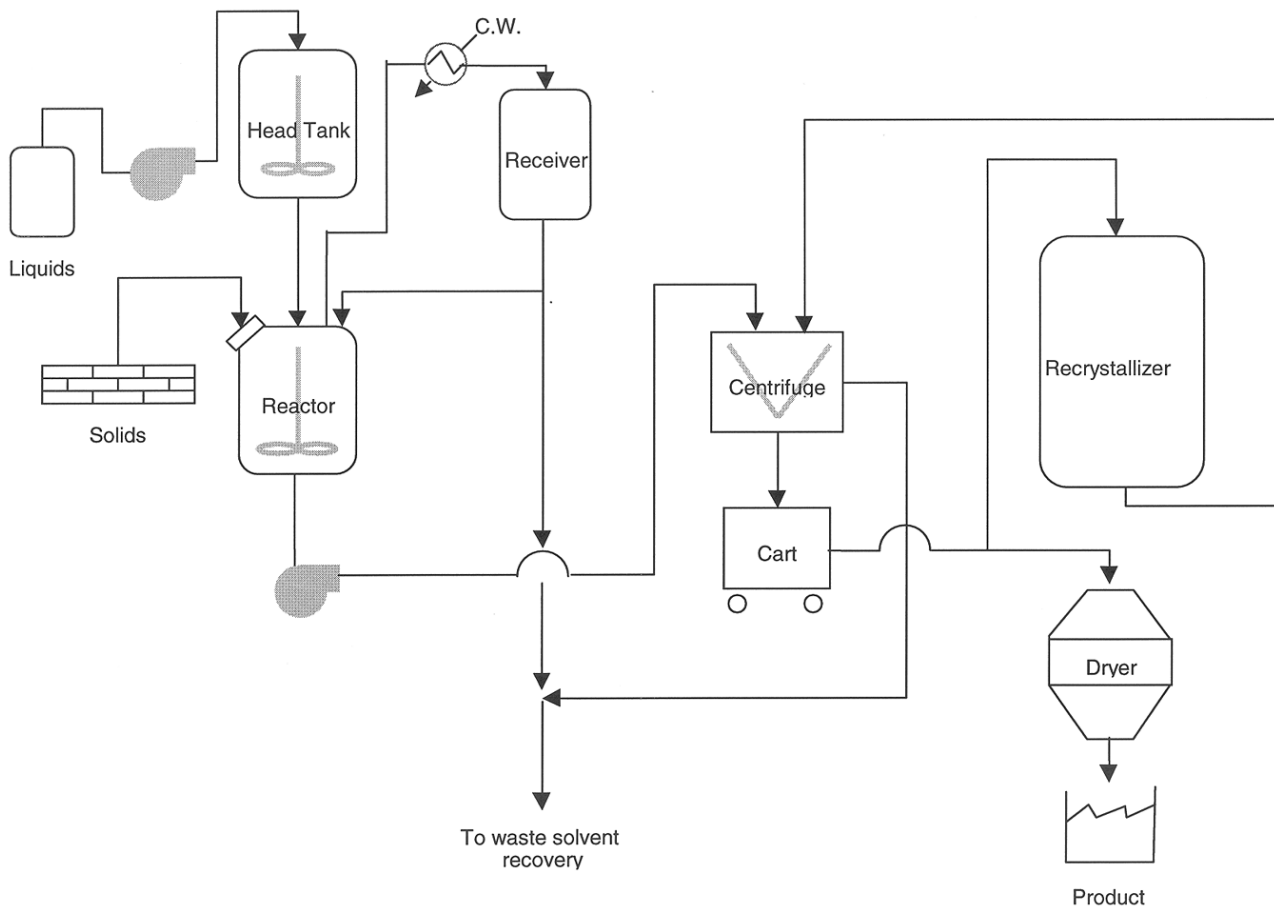


Figure 1. Typical batch reaction system.

They are solely meant to create awareness and assist designers and operators, and are *not* meant to imply that these solutions and control mechanisms are Recognized and Generally Acceptable Good Engineering Practices (RAGAGEP). The authors of this book could not anticipate all the possible issues, or all applicable solutions for a specific issue. The potential solution and controls are intended to stimulate thought and initiate discussions about the appropriateness of the potential solutions presented, and potentially stimulate the generation of other solutions not included in the table.

It is intended that the use of the tables should be combined with sound engineering judgment and consideration of all relevant factors. Furthermore, all the solutions presented may not be applicable to a given situation. It should also be recognized that the solutions presented could introduce potential hazards that were not originally present. Therefore, it is necessary to use the table in the context of the total design concept to insure that all hazards have been considered.

The information pertaining to the safety issues in batch reaction systems is presented in the following chapters:

Chapter 2. Chemistry

Understanding the behavior of all the chemicals involved in the process—raw materials, intermediates, products and by-products, is a key aspect to identifying and understanding the process safety issues relevant to a given process. The nature of the batch processes makes it more likely for the system to enter a state (pressure, temperature, and composition) where undesired reactions can take place. The opportunities for undesired chemical reactions also are far greater in batch reaction systems due to greater potential for contamination or errors in sequence of addition. This chapter presents issues, concerns, and provides potential solutions related to chemistry in batch reaction systems.

Chapter 3. Equipment Configuration and Layout

Proper equipment configuration and layout can make a significant contribution to the safety of a processing facility. In batch processes, where the material handled by the process can change frequently, providing safe separation distances presents an even greater challenge than continuous processes. Other important considerations for facility layout are the electrical classification and fire protection requirements. It also is quite common for batch processes to be located inside buildings. This leads to the need to provide adequate building ventilation to avoid buildup of hazardous vapors/gases due to leaks. This chapter presents issues/concerns, and provides potential solutions related to equipment configuration and layout in batch reaction systems.

Chapter 4. Equipment

Frequently a piece of equipment is used in different processes during its lifecycle. This could result in process conditions that exceed the safe operating limits of the equipment. Equipment inspection may provide a poor prediction of the equipment's useful life and reliability, due to the change of material handled or change in process chemistry over the life of equipment. Batch operations are also characterized by frequent start-up and shut-down of equipment. This can lead to accelerated equipment aging and may lead to equipment failure. This chapter presents issues and concerns related to the safe design, operation, and maintenance of various pieces of equipment in batch reaction systems, and provides potential solutions.

Chapter 5. Instrumentation/Control Systems

The fact that batch processes are not carried out at steady state conditions imposes broad demands on the control system. The instrumentation and control system have to be selected to provide adequate control for a wide variety of operating conditions and a wide variety of processes. In addition, basic process control and shutdown systems have to deal with sequencing issues. This chapter presents issues and concerns related to safety of instrumentation and control in batch reaction systems, and provides potential solutions.

Chapter 6. Operations and Procedures

The operator is an integral part of the process in a batch reaction process. Some of the functions a typical operator working in a batch processing facility may have to perform are scheduling, equipment setup, cleaning, charging, executing and controlling procedure, monitoring, fault diagnosis and corrective action, sampling, handling of finished and off-spec/partially finished products, maintenance, emergency response, process logging and communication. Several of these are either specific to batch operations, or are done more often in batch operations than in continuous processes. The greater number and variety of functions that the operator has to perform during a batch process presents more opportunities for errors than for continuous operations. This chapter presents issues related to operations and procedures in batch reaction systems, and provides potential solutions.

2

Chemistry

2.1. Introduction

Understanding the behavior of all the chemicals involved in the process—raw materials, intermediates, products and by-products is a key aspect of understanding the process safety issues relevant to a given process. A knowledge of how these chemicals behave individually and how they interact with other chemicals, utilities, materials of construction, potential contaminants or other materials that they can come in contact with during shipment, storage, and processing is essential for understanding and managing process safety.

Understanding the chemistry of the process also provides the greatest opportunity in applying the principles of inherent safety at the chemical synthesis stage. Process chemistry greatly determines the potential impact of the processing facility on people and the environment. It also determines such important safety variables as inventory, ancillary unit operations, by-product disposal, etc. Creative design and selection of process chemistry can result in the use of inherently safer chemicals, a reduction in the inventories of hazardous chemicals and/or a minimization of waste treatment requirements.

Reactors often represent a large portion of the risk posed by a batch chemical operation. A better understanding of the reaction behavior and kinetics allows for an optimization of reactor control and safety systems. Knowledge of the reaction behavior includes desired reactions as well as undesired side-reactions that can take place in the reactor itself and other parts of the process. Knowledge of the physical properties of the materials involved in the process and the effects of physical phenomena such as mass transfer, heat transfer, mixing, phase of reaction on the overall reaction rate may be used to identify designs that maximize the economical benefits while reducing risk. As outlined in Chapter 1, batch chemical reactors present unique challenges to the designers in terms of process safety. The transient nature of the batch processes makes it more likely for the system to reach a condition (pressure, temperature, and composition) where undesired reactions could take place. The opportunities for

undesired chemical reactions also are far greater in batch reaction systems due to greater potential for contamination.

The importance of understanding the chemistry of the process is not limited to the research and development phase of the process lifecycle. It manifests itself again and again in all the lifecycle stages ranging from research and development to plant decommissioning. Process development in the conceptual design stage and the pilot plant stage can identify opportunities for inherent process safety in selecting the process chemistry and simplifying, i.e., improving control and operation schemes to keep the chemical reactants within safe operating limits. Knowledge of chemistry also can be used to design mitigation measures for releases of hazardous chemicals to the environment (CCPS-G12). In the detailed engineering stage, engineers and chemists can identify safety issues and provide design solutions to reduce the risk posed by the process. During the construction and start-up phase, knowledge of process chemistry can be used to identify operations that need to be strictly followed to reduce potential hazards. Special attention needs to be focused on cleaning to prevent cross contamination. It also can be used to provide safer equipment layout and ergonomics. The operator of the process needs to have an understanding of the process chemistry and the hazards associated with the various chemicals in order to perform routine operations and to identify, diagnose and respond to incipient hazardous situations. Plant modifications, plant expansions, proposed catalysts modifications and changes to the feedstock composition, or other raw materials need to undergo a management of change review. It is also important to analyze the effect of such modifications on the by-product and waste streams. During shut-down and decommissioning, attention needs to be focused on hazards associated with the residues left in the unit after shutdown.

There are several issues that are unique to batch reaction system design. The process development time is often shorter due to the need to respond quickly to market demands. The small-scale batch process development may not receive the same effort and rigor as larger batch or continuous processes. Moreover, batch processes are often made to fit the existing facilities. This could lead to operating key equipment and emergency relief systems at the edge of their original design limits.

2.2. Case Study

A weigh tank containing chlorosulfonic acid needed to be cleaned to remove salt deposits. The salt deposits precipitated from the material and occasionally plugged the downstream control valve. Since the material was water reactive, heptane was chosen to clean the vessel. Chemists had not anticipated the material would be reactive with heptane. While cleaning the vessel the pressure

started to rise from the reaction, causing the vessel bottom head to fail at the weld seam. The force from the escaping gases propelled the tank into the ceiling and overhead structural steel. A small fire erupted which was quickly brought under control by the automatic sprinkler system. Even though the chemists had reviewed the chemistry and did not anticipate any problems, use testing could have identified this problem in the laboratory rather than the plant.

2.3. Key Issues

Process chemistry issues and their effects on batch reaction systems safety are presented in Table 2, beginning on page 11. This table is meant to be illustrative but not comprehensive.

Some key issues are listed below.

- The hazardous materials used in the process may be raw materials, intermediates, products, by-products, cleaning materials, decomposition, or unintended products.
- Inadvertent contact between two or more chemicals may lead to a hazardous condition.
- Process materials may be pyrophoric, water reactive, strong oxidizers or strong reducers.
- Process chemistry should be selected to fit existing batch equipment.
- Disposal issues pertaining to unreacted batches, incomplete batches or off-spec products.

2.4. Process Safety Practices

Listed below are safety practices aimed at minimizing the incidents caused by process chemistry issues.

- Select a process chemistry or synthesis route that is inherently safer.
- Perform chemical reactivity testing, including the analytical verification of reactants, catalyst, quenchers, initiators, and inhibitors. More details are provided in Appendix 2A of this chapter.
- Use reactor calorimetry testing to determine thermodynamics and kinetics of process. See Appendix 2A (Chemical reactivity hazards screening).
- Pilot process before putting into operation.
- Provide system to maintain process safety information (PSI)
 - Systems for the identification, compilation, and update of information
 - Assign responsibility for developing new PSI, updating existing PSI and approval of changes to PSI.

- Controls to verify and/or cross check completion and accuracy of development and update of PSI.
- Maintain Process Safety Information (PSI) related to chemistry such as:
 - Information pertaining to the hazards of the chemicals used in the process. This should contain at least the following information: toxicity, flammability, permissible exposure limits, physical data, reactivity data, corrosivity data, thermal and chemical stability data, and hazardous effects of inadvertent mixing of different materials that could occur.
 - Document safety issues pertaining to process chemistry
 - Share knowledge between chemists, engineers and operators.
- Use chemical interaction matrices to identify potential incompatibilities between combinations of materials (not just binary reactions) and interactions with cleaning solvents, heat transfer fluids and other utilities, equipment lubricants, scrubbing media, materials of construction, etc.
- Implement management of change procedures for changes in design, operation, equipment and chemistry.
- Provide emergency relief where needed.
- Provide for addition of diluent, poison, or inhibitor directly to reactor.
- Provide for automatic or manual actuation of bottom discharge valve to drop batch into a dump tank with diluent, poison or inhibitor, or to an emergency containment area.
- Design equipment to accommodate maximum operating envelope.
- Appropriate use of Safety-Related Systems (SRS) such as Safety-Instrumented Systems (SIS).
- Inert equipment where appropriate.
- Specialized training or technical literature by raw material suppliers to address special use or handling requirements.
- Careful analysis of cleaning practices, especially nonperiodic or special purpose cleaning.

Table 2: Chemistry

No.	Concern/Issue	Potential Solutions and Control Mechanisms	Additional Resources
Selection of Chemistry/Process Chemistry			
1.	Raw materials, intermediates, products, by-products, decomposition or unintended products are hazardous. Use of the hazardous materials poses a potential risk to the people and the environment.	• Select a process chemistry or synthesis route that is inherently safer (e.g., nontoxic, non-flammable materials, less severe operating condition) • Use Process Safety Management techniques to minimize the risk to people, and the environment • Select equipment design for high integrity containment	CCPS G-1 CCPS G-6 CCPS G-10 CCPS G-21 CCPS G-24 CCPS G-25 CCPS G-31 CCPS G-41
2.	Use of materials sensitive to shock, high temperature or high pressure. If the material is inadvertently exposed to an unsuitable condition, or if the process moves out of the safe operating limits, it could result in a loss of containment.	• Select a process chemistry that is inherently safer (e.g., replace shock sensitive, high temperature sensitive and high pressure sensitive materials with more benign materials, less severe operating conditions) • Prevent exposure to shock, high temperature or pressure • Design for pressure containment • Provide adequately designed relief device • Use less severe operating conditions	ASME VIII Div I and II CCPS G-11 CCPS G-13 CCPS G-23 CCPS G-30 CCPS G-41 DIERS NFPA 68 NFPA 69
3.	Chemical/materials that may potentially come in contact are incompatible. Inadvertent contact between two or more chemicals may lead to a hazardous condition.	• Use inherently safer chemistry (e.g., when phosgene is cooled in a heat exchanger, consider use of an inert oil as the coolant rather than water as heat exchanger tubes may fail) • Use chemical interaction matrices to identify potential incompatibilities between chemicals including utilities, solvents and materials of construction • Use chemical reactivity testing to identify and evaluate the hazards • Use written operating procedures and provide training • Use consistent labeling system • Select equipment to minimize inadvertent contact as a result of equipment failure • Isolate process from sources of incompatible material	API RP750 CCPS G-1 CCPS G-13 CCPS G-22 CCPS G-3 CCPS G-30 CCPS G-32 CCPS G-41 Hendershot 1987 Kletz 1991 Lees 1996

No.	Concern/Issue	Potential Solutions and Control Mechanisms	Additional Resources
Selection of Chemistry/Process Chemistry			
4.	Ingress of air into reactor containing pyrophoric material. Possibility of fire / deflagration.	• Use management systems (tagging) or interlocks to prevent opening of reactor during reaction progress • Provide emergency purge and/or isolation activated on detection of oxygen • Provide isolation valves to isolate equipment • Design system to accommodate deflagration pressure • Provide fire and/or deflagration suppression system • Provide closed feed system • Provide explosion venting	AGA-XK0775 CCPS G-29 NFPA 2001 NFPA 68 NFPA 69
5.	Water reactivity of chemicals involved in reaction. Possibility of runaway.	• Avoid use of water as cooling/heating medium • Avoid use of water/steam for cleaning of reactor • Avoid direct water connection to reactor • Prevent backflow from scrubber into reactor • Eliminate water as a mechanical seal barrier fluid • Clean and chemically dry vessel prior to charging water reactive material • Provide dry compressed gas feeds • Ensure that alternate sources of inert gas feeds are dry • Confirm that raw materials feeds are dry • Preplan fire protection requirements and procedures • Use inherently safer equipment (e.g., jacketed vessels instead of tube heat exchangers) • When water or steam is used as a utility, insure appropriate mechanical integrity program for equipment	CCPS G-13 CCPS G-41

Table 2: Chemistry

No.	Concern/Issue	Potential Solutions and Control Mechanisms	Additional Resources
Selection of Chemistry/Process Chemistry			
6.	Raw materials, intermediates, products, by-products and/or undesired byproducts are subject to runaway reactions that produce extreme heat and/or extreme amounts of gaseous/vapor products.	• Test suspect materials for undesired properties, (e.g., endothermic compounds, compounds containing oxidizing and reducing group such as ammonium nitrate) • Substitute or attenuate hazardous materials (inherently safer alternative) • Construct equipment to handle extreme temperatures and or pressures • Provide emergency relief systems • Provide process monitoring and control systems • Provide External Risk Reduction Facility (ERRF)	CCPS G-11 DIERS IEC 61508
7.	Unknown intermediate / side reaction. Unknown thermal hazards. Possibility for runaway reaction.	• Test suspect materials to characterize undesired properties • Conduct thermal hazards analysis • Evaluate methods for controlling runaway reactions (e.g., short stop, inhibitors) • Determine consequences of runaway reactions and ensure mitigation techniques are in place	CCPS G-13 DIERS
8.	Chemicals for use in the process are selected because they are convenient and not necessarily because they are the most suited. Nonoptimal system design in terms of safety and economics.	• Carefully and deliberately select process chemicals and synthesis route • Emphasize consequences of chemical choices to Research and Design Engineering	CCPS G-23 CCPS G-41

No.	Concern/Issue	Potential Solutions and Control Mechanisms	Additional Resources
Selection of Chemistry/Process Chemistry			
9.	Process chemistry selected to fit in existing batch equipment. Nonoptimal process design in terms of safety and economics. Possibility of operating close to, or outside of, the safe operating envelope of the equipment and the relief capability.	• Use inherently safer chemistry • Consider the consequences of using existing equipment for new processes (e.g., batch size, corrosion, cost) • Anticipate future product needs before purchase of equipment • Match batch sizes to equipment capabilities • Provide equipment with comparable pressure rating for the entire system • Implement management of change procedures	CCPS G-1 CCPS G-8 CCPS G-23 CCPS G-41
10.	Short development time may result in a less than complete knowledge of the hazards.	• Allocate enough time for development • Use more time-efficient PHA techniques • Use administrative controls to decide when to go to full scale production • Establish minimum requirements “transfer package” for process knowledge • Require development chemist to be present during initial product runs	API RP 750 CCPS G-1 CCPS G-10 CCPS G-25
Chemical Identification			
11.	Trade name of process chemical changes or trade name prevents immediate recognition of harmful effects/ interaction of chemical. Sometimes different vendors use different names for chemicals. Use of incorrect chemicals leads to hazardous conditions.	• Establish procedures for testing and verification of raw materials, including use testing • Implement management of change procedures • Implement operating procedures and training • Use consistent internal labeling system	CCPS G-13 CCPS G-22 NFPA 325M NFPA 401 NFPA 704

Table 2: Chemistry

No.	Concern/Issue	Potential Solutions and Control Mechanisms	Additional Resources
Composition			
12.	Addition of incorrect reactant or unanticipated material to the reactor. Possibility for runaway reaction.	• Use dedicated feed tank and reactor • Implement procedure for double checking reactant identification and quality • Implement procedure for double checking addition of correct reactant in correct order • Develop operating instructions on the correct or permitted connections between tanks and vessels • Color code and label lines • Provide dedicated storage areas/unloading facilities for reactants • Use dedicated connections and/or unique couplings • Physically separate points of connection of incompatible materials • Use interlocks which prevent addition of certain combination of chemicals • Use batch sequencing in control systems when possible • Require certificate of analysis for raw material	API RP 750 CCPS G-13 CCPS G-22 CCPS G-29 CCPS G-30
13.	Change in feed composition. This may happen due to change in suppliers or due to introduction of reworked material. Unwanted effect on reaction products, by-products. Varying inhibitor concentrations in monomers from different vendors. Potential for runaway reaction.	• Design for feed variations • Obtain certificate of analysis • Establish purity limits for each feed • Bench scale use testing • Sample and analyze feed stocks before addition • Design system to accommodate maximum expected pressure • Provide adequately designed emergency relief device • Implement procedure for double checking reactant identification and quality • Implement management of change	CCPS G-1 CCPS G-11 CCPS G-13 CCPS G-23 CCPS Y-28 DIERS

No.	Concern/Issue	Potential Solutions and Control Mechanisms	Additional Resources
Runaway Reaction			
14.	Runaway reaction (caused by, e.g., generation of excessive heat during "fast" charging).	• Provide automatic or manual addition of diluent, poison, or inhibitor directly to reactor • Provide automatic or manual actuation of bottom discharge valve to drop batch into a dump tank with diluent, poison or inhibitor, or to an emergency containment area • Provide automatic/manual isolation based on detection of undesired reaction rate • System design accommodating maximum expected pressure and temperature • Provide adequately designed relief device • Provide emergency cooling • Design equipment to limit excessively fast feedrate	CCPS G-11 CCPS G-13 CCPS G-23 DIERS Kletz 1991
15.	Overcharge/overfeed of reactants Possibility of overfilling vessel, or initiating runaway reaction.	• Use of dedicated reactant charge tank sized only to hold amount of reactant needed • Interlock reactant feed charge ed via feed totalizer or weight comparison in charge tank • Provide automatic/manual response to level or other indication of abnormal quantity of vessel contents • Monitor reaction initiation and progress during charging • Provide batch sequencing interlocks that demand operator action • Provide adequately designed relief device	CCPS G-13 CCPS G-23
16.	Undercharge/ underfeed of reactants. Possibility of unreacted mixed reactants left at end of batch, leading to a subsequent runaway reaction.	• Use dedicated reactant charge tank sized to hold correct amount of reactant needed • Interlock reactant feed charge via feed totalizer or weight comparison in charge tank • Provide automatic/manual response to level or other indication of abnormal quantity of vessel contents • Provide means for detecting reaction completion before proceeding • Design reactor and/or downstream system to accommodate maximum expected pressure • Install adequately designed emergency relief device • Establish procedure for disposal of materials	CCPS G-11 CCPS G-13 CCPS G-23 DIERS Kletz 1991

Table 2: Chemistry

No.	Concern/Issue	Potential Solutions and Control Mechanisms	Additional Resources
Runaway Reaction			
17.	Overcharge of catalyst or initiator, too much or too fast. Possibility of runaway reaction.	• Use dedicated catalyst or initiator charge tank sized to hold only the amount of catalyst needed • Limit quantity of catalyst or initiator added by flow totalizer • Implement procedural controls on the amount or concentration of catalyst or initiator to be added • Use staging area for preweighed single catalyst charges • Design equipment to prevent excessively fast feed. Do not oversize pumps or control valves • Install flow restriction orifice • Provide means of detecting reaction progress and completion before proceeding further • Design reactor and downstream system to accommodate maximum expected pressure	CCPS G-15 CCPS G-23 CCPS G-29
18.	Undercharge of catalyst. Potential for accumulation of reactants and subsequent runaway reaction. Possibility of no reaction resulting in a waste disposal issue.	• Use dedicated catalyst charge tank sized to hold only the amount of catalyst needed • Implement administrative (procedural) controls for catalyst on the amount or concentration to be added • Use staging area for preweighed single catalyst charges • Provide means of detecting reaction progress and completion before proceeding further • Design reactor and downstream system to accommodate maximum expected pressure • Provide adequately designed relief device • Establish procedure for disposal of unreacted materials	CCPS G-11 CCPS G-13 CCPS G-23

No.	Concern/Issue	Potential Solutions and Control Mechanisms	Additional Resources
Runaway Reaction			
19.	Overactive and/or wrong catalyst. Possibility for runaway reaction.	• Use dedicated catalyst charge tank sized to hold only the amount of catalyst needed • Passivate fresh catalyst prior to use or use prediluted catalyst • Establish procedures for testing and verification of catalyst activity and identification including use testing. Include procedure to monitor shelf life of catalyst to maintain activity • Develop and install emergency system and procedures to shortstop runaway reaction. • Establish administrative (procedural) controls on the amount or concentration of catalyst to be added • Use staging area for preweighed single catalyst charges • Provide means of detecting reaction progress and completion before proceeding • Design reactor and downstream system to accommodate maximum expected pressure • Provide adequately designed relief device • Establish procedure for disposal of unreacted materials • Require certificate of analysis for catalyst	CCPS G-3 CCPS G-11 CCPS G-13 CCPS G-22 CCPS G-29 CCPS G-32 DIERS
20.	Inactive and/or wrong catalyst. Possibility for accumulation of reactant and subsequent runaway reaction in reactor or downstream vessel. Possibility of no reaction resulting in a waste disposal issue.	• Establish procedures for testing and verification of catalyst activity and identification including use testing • Provide means of detecting reaction completion before proceeding • Design reactor and/or downstream system to accommodate maximum expected pressure • Provide adequately designed relief device • Establish procedure for disposal of unreacted reactant mixture	CCPS G-11 CCPS G-13 CCPS G-23 DIERS Kletz 1991

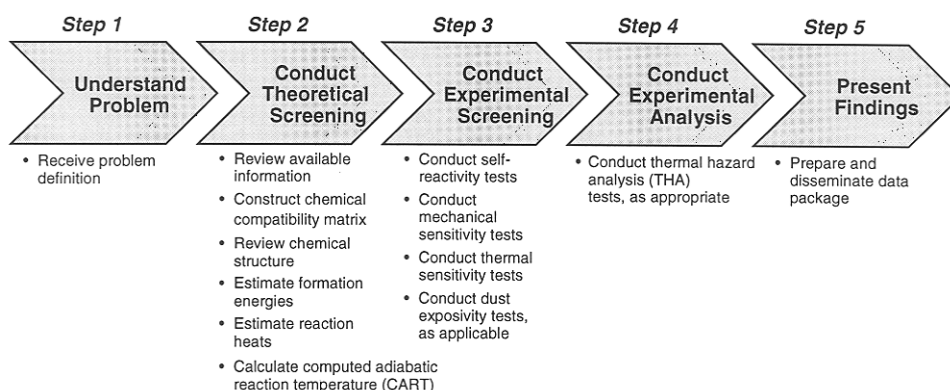
Table 2: Chemistry

No.	Concern/Issue	Potential Solutions and Control Mechanisms	Additional Resources
Runaway Reaction			
21.	Incorrect inhibitor / initiator composition or concentration or amount. Reaction proceeds too rapidly.	• Provide automatic control of inhibitor/initiator addition • Provide analytical verification of inhibitor / initiator effectiveness including use testing (including shelf life issues) • Avoid conditions for precipitating, or otherwise separating inhibitor from reacting species • Design system to accommodate maximum expected pressure and temperature • Provide emergency cooling • Provide adequately designed relief device	CCPS G-11 CCPS G-13 CCPS G-23 DIERS Kletz 1991
22.	Insufficient diluent due to under feed or excessive evaporation resulting in insufficient heat sink. Possibility of runaway reaction due to high temperature excursion or high concentration of reacting species	• Provide automatic control of diluent addition • Select diluent less susceptible to evaporation • Install automatic/manual isolation based on detection of unexpected reaction rate • Provide emergency cooling • Provide adequately designed relief device • Monitor liquid level	CCPS G-11 CCPS G-23
23.	Incomplete reaction due to insufficient residence time, low temperature, overactive inhibitor etc. Possibility of no reaction. Possibility of unexpected reaction in subsequent processing steps. Problem of disposing of unreacted mixture.	• Auto/Manual response to low reaction progress • Decision not to proceed to next step based on detection of low reactor temperature and/or reactor composition sampling • Design reactor or downstream vessel to accommodate maximum expected pressure • Provide adequately designed relief device • Implement procedure for disposing of unreacted mixture	CCPS G-11 CCPS G-13 CCPS G-15 CCPS G-22 CCPS G-23 CCPS G-31 DIERS
Contamination			
24.	Chemical reaction due to equipment not being properly cleaned/ drained from previous run. Possibility of unwanted reaction or insufficient desired reaction.	• Develop written procedures to clean and verify reactor readiness • Implement checklist verification • Analyze used cleaning solvent	CCPS G-15 CCPS G-22 CCPS G-29

No.	Concern/Issue	Potential Solutions and Control Mechanisms	Additional Resources
Contamination			
25.	Contamination from leakage of heating/cooling media or introduction of other foreign substances (e.g., corrosion) or possibility of unwanted reaction between the heating/cooling medium and the reactor contents, leading to runaway reaction. Possibility of no reaction or inhibited reaction resulting in accumulation of reactants and delayed runaway.	• Use heating/cooling medium which does not react with or inhibit reactor contents • Use external heater/cooler (panel coil) • Use electrical heating with proper consideration of maximum possible heating element temperature • Use lower pressure heating or cooling medium to avoid flow into reactor in the event of a leak • Consider impact of reactor contents leaking into utility • Implement procedures for leak/pressure testing of jacket, coil or heat exchanger prior to operation • Provide emergency cooling • Transfer reactor contents to dump tank with diluent quench.	CCPS G-23
Off-spec product/intermediate raw material			
26.	The raw materials are off-spec resulting in generation of excessive waste products.	• Implement effective quality control program • Employ good operating procedures • Provide procedures to safely handle the unplanned waste generation and/or neutralize off-spec materials.	CCPS G-29
Waste Minimization			
27.	Variation in waste by batch. Feed variability to downstream waste processing equipment. Possibility of reaction in waste streams, flammable/ toxic hazard.	• Implement strict quality control program • Employ good operating procedures • Develop effluent handling procedures	CCPS G-29 CCPS G-32

Appendix 2A. Chemical Reactivity Hazards Screening

Characterizing chemical reactivity hazards involves a review of the inherent thermal hazards of the pure process materials as well as the thermal hazards of the materials under processing conditions. Gaining this understanding and characterizing thermally hazardous systems is a multistep process.



A.1. Understand the Problem

The first step is to understand the context in which the thermal hazard information is needed. This might include information on materials, reactions, processing conditions, previous incidents, if any, and any other available information that can help with the characterization.

A.2. Conduct Theoretical Screening

After understanding the problem, the second step is to conduct a theoretical screening to determine the expected thermal hazards of a system. Table A.1 identifies properties of materials to be considered, and some potential sources of information, in formulating an opinion about the thermal hazards of particular materials and reactions.

The first place to look for information describing the physical properties and known reaction hazards of an individual chemical or process is the literature. Once literature sources have been exhausted, theoretical information should be developed. This determination of theoretical values involves the development of worst-case theoretical estimates based on chemical compatibility information and thermophysical properties such as formation energies, heats

Table A.1: Potential Sources of Theoretical Screening Data

Material Properties	Potential Sources
1. Basic chemical data	MSDSs, manufacturer's data, The Merck Index
2. Reactivity data	Bretherick's Handbook, NFPA 49, 325 and 432 hazard ratings, Sax, <i>Handbook of Hazardous Chemical Properties</i> , Kirk-Othmer <i>Encyclopedia of Chemical Technology</i> or as determined
3. Incident data	Open literature
4. Chemical compatibility matrix	Literature or as determined
5. Chemical structure	Supplied by research scientist, <i>CRC Handbook of Chemistry and Physics</i>
6. Formation energies	Literature (e.g., Pedley's Handbook) or as determined, Perry's <i>Chemical Engineers' Handbook</i> , DIPPR, <i>CRC Handbook of Chemistry and Physics</i>
7. Heats of reaction, decomposition, solution	Literature or as determined <i>CRC Handbook of Chemistry and Physics</i>
8. Chetah hazard criteria	ASTM Chetah Software (see discussion)
9. Computed Adiabatic Reaction Temperature (CART) at constant pressure and/or volume	As calculated

of reaction, decomposition and solution, hazard criteria, and computed adiabatic reaction temperature (CART).

Chemical Compatibility

Chemical incompatibility charts can help in organizing available data on the incompatibilities existing between expected mixtures. Frurip (Frurip et al., 1997) gives one procedure for developing a chemical compatibility chart while describing some of the tools available. CCPS G-13 also provides a table of known incompatibility hazards.

Data can also be gathered experimentally on the compatibility of materials. Incompatibility charts have been published by the U.S. Coast Guard (1994), ASTM (1980) as well as others. See Frurip (Frurip et al., 1997) for a description of experimental tests and published compatibility charts.

Thermophysical Properties

Much information can be understood by a review of certain thermophysical properties of materials and mixtures. In comparing the values of heats of reaction, heats of decomposition and CART to values for known hazardous compounds, an estimation of thermal hazard potential can be made. Table A.2 outlines thermal hazard ranking values that could be used in classifying materials and processes based on heats of reaction and CART determinations (Melhem and Shanley 1997).

Two standard estimation methods for heat of reaction and CART are Chetah 7.2 and NASA CET 89. Chetah™ Version 7.2 is a computer program capable of predicting both thermochemical properties and certain reactive chemical hazards of pure chemicals, mixtures or reactions. Available from ASTM, Chetah 7.2 uses Benson's method of group additivity to estimate ideal gas heat of formation and heat of decomposition. NASA CET 89 is a computer program that calculates the adiabatic decomposition temperature (maximum attainable temperature in a chemical system) and the equilibrium decomposition products formed at that temperature. It is capable of calculating CART values for any combination of materials, including reactants, products, solvents, etc. Melhem and Shanley (1997) describe the use of CART values in thermal hazard analysis.

A.3. Conduct Experimental Screening

Experimental screening involves conducting experimental tests to gauge the thermal hazard of materials and processes. The goal of these tests is to provide information by which the materials and processes may be characterized. Experimental screening can be performed for the following:

- Self-reactivity
- Mechanical sensitivity
- Thermal sensitivity
- Deflagration and explosion, including dust explosibility and ignitability

Table A.2: Theoretical Hazard Rankings

Hazard Ranking	Heat of Reaction (ΔH_r) Estimate	CART Estimate
Negligible to Low	Less exothermic than -1.2 kJ/g (-0.28 kcal/g)	< 700 K
Intermediate	-1.2 kJ/g < ΔH_r < -3.0 kJ/g (-0.28 kcal/g < ΔH_r < -0.7 kcal/g)	< 1600 K
High	More exothermic than -3 kJ/g (-0.7 kcal/g)	> 1600 K

Self-Reactivity Hazards

Self-reactivity can be defined as the potential for a material to decompose or undergo energetic changes. Some of the methods for characterizing self-reactivity hazards are listed in Table A.3.

Mechanical Sensitivity

Mechanical sensitivity can be divided into two categories—mechanical friction and mechanical shock. Mechanical friction can be defined as mechanical energy imposed by materials being wedged between surfaces and mechanical shock can be defined as mechanical energy imposed by materials undergoing an impact. Several tests for measuring the sensitivity to friction and the impact of materials are detailed in CCPS G-13.

Thermal Sensitivity

Thermal sensitivity is the potential for a material to explode under a thermal stimulus. Test methods are outlined in CCPS G-13.

Explosion Testing, Including Dust Explosibility and Ignitability

Explosion testing should be performed to establish safe operating limits. Dust explosibility and ignitability are measurements of the potential for a combustible material, in dust form, to explode or ignite. Any combustible material has the potential to cause a dust explosion if dispersed in air as a dust and ignited. Further details on explosibility testing can be found in Palmer (1973), Bartknecht (1989) and Eckhoff (1997).

Table A.3: Methods for Conducting Self-Reactivity Experimental Screening

Method	Information Gained
Differential scanning calorimetry (DSC)	Onset temperature of exotherms, heat of reaction
Thermogravimetric analysis (TGA)	Onset temperature of weight loss
Differential thermal analysis (DTA)	Onset temperature of exotherms, heat of reaction, C_p , approximate kinetics
Reactive Systems Screening Tool (RSST™)	Temperature history of runaway reaction, rates of temperature and pressure rise (for gas producing reactions)
ARC™	Temperature history of runaway reaction, rates of temperature and pressure rise (for gas producing reactions)

A.4. Conduct Experimental Analysis

Experimental analysis involves the use of thermal hazard analysis tests to verify the results of screening as well as to identify reaction rates and kinetics. The goal of this level of testing is to provide additional information by which the materials and processes may be characterized. The decision on the type of experimental analysis that should be undertaken is dependent on a number of factors, including perceived hazard, planned pilot plant scale, sample availability, regulations, equipment availability, etc.

Table A.4, taken from the CCPS *Guidelines for Chemical Reactivity Evaluation and Application to Process Design*, shows the questions which need to be asked regarding the safety of the proposed reaction, the data required to answer those questions and some selected methods of investigation. The experimental analysis is extremely specialized, and companies should consider outsourcing the tests if they do not have specialists in this area.

Table A.4: Essential Questions on Safety Aspects of Reactions

Question	Data Required	Selected Methods of Investigation
1. What is the potential temperature rise by the desired reaction? What is the rate of the temperature rise? What are the consequences? What is the maximum pressure?	• Enthalpy of desired reaction • Specific heat • Vapor pressure of solvent as a function of temperature • Gas evolution	• Table of data • Thermodynamic data • Calculations; estimations • Differential Thermal Analysis (DTA) / Differential Scanning Calorimetry (DSC) • Dewar flask experiments • Reaction calorimetry with pressure vessel • Thermometry/manometry • APTAC™ /ARC™ /RSST/VSP
2. What is the potential temperature rise by undesired reactions or thermal decomposition, such as from contaminants, impurities, etc.? What are the consequences? What is the maximum pressure?	• Enthalpy of undesired reaction • Specific heat • Rate of undesired reaction as a function of temperature	• DTA/DSC • Dewar flask experiments • APTAC™ /ARC™ /RSST/VSP
3. Is reactant accumulation possible? What are the consequences?	• Steady state concentrations • Kinetic data • Data from 1 and 2	• Reaction calorimetry combined with analysis • Potential energy by DSC/DTA • VSP / APTAC™
4. What is the safe storage temperature for shelf life?	• Kinetic data • Data from 1 and 2	• Isothermal Storage Test



3

Equipment Configuration and Layout

3.1. Introduction

Proper equipment configuration and layout can make a significant contribution to the safety of a processing facility. Safe separation distances are usually based on hazard considerations, but often the demands for safe access during construction, operation, and maintenance are governing factors. In batch processes, where the material utilized in the process can change frequently, providing safe separation distances presents an even greater challenge. In general, larger spacing between equipment leads to a safer layout. However, this may lead to an increase in pipe work, which in itself may increase the probability of accidental releases. The larger spacing between equipment may also increase operator effort and workload in operating the process.

Often batch process equipment needs to be located inside buildings. This is usually the case when the process needs to be shielded from extreme heat/cold conditions, the elements, and/or needs to be kept sterile. This leads to the need to provide adequate building ventilation to avoid buildup of hazardous material due to leaks and other process emissions. When the operation of a process involves opening, cleaning, charging etc., point source ventilation may also need to be provided.

Layout also has a significant role in minimizing the probability of ignition of a flammable release. Area electrical classification provides the basis for the control of electrical ignition sources. This classification is also used to determine the areas that require protection from vehicular access, etc. Frequently, highly hazardous processes that can result in overpressure (e.g., hydrogenation) are placed behind blast resistant structures/walls.

Another important issue in layout is the provision of safe access to equipment for emergency response needs such as fire-fighting etc. The layout also needs to provide for safe escape and rescue routes. As far as off-site population is concerned, the most important siting factor is the distance between the process

and the off-site receptors. Physical effects of accidental releases, fires and explosions decay rapidly with distance. Low population density in the immediate vicinity of the plant reduces the number of people potentially affected by the accidental releases.

3.2. Case Studies

Pump Leak Incidents

A high-pressure reciprocating pump, originally used for pumping heavy hydrocarbons, was put into service to pump propylene in an unventilated building. A leak occurred from the gland due to failure by fatigue of the studs holding the gland in position. The escaping liquid vaporized and was ignited by a furnace 76 meters away. Four men were badly burned and the glass windows on the buildings were broken. The failure was attributed to the fact that plant management had not implemented effective management of change procedures. As a result of the deflagration, gas detectors and remote isolation capability were provided. Also, the pump was moved to an open building where small leaks would be dispersed by natural ventilation (CCPS G-39).

Tank Farm Fire

In November 1990 a fire occurred at a flammable liquid tank farm supporting Denver's Stapleton international airport. Eight of the farm's twelve storage tanks contained jet fuel, totaling almost 4.2 million gallons. The fire burned for 55 hours, destroying seven tanks.

Investigators concluded that a damaged pump in a valve pit near the storage tanks may have caused the initial leak and also may have ignited the fuel. In addition, the investigators concluded that a pipe simultaneously cracked, thus releasing fuel into the fire area. The subsequent fire fed on the fuel collecting in the pit and spewing from the two leaks, and impinged on piping and related equipment in the valve pit. As this fire continued to burn, flange gaskets deteriorated, causing more leaks and allowing more fuel to flow out of the storage tanks. The growing fire encroached on two storage tanks adjacent to the valve pit. Approximately 12 hours into the incident, a friction coupling parted, allowing fuel from one storage tank to suddenly increase the fire size. The fire spread to an impounding area and involved two more fuel tanks.

The following changes to the tank farm site would have mitigated the outcome of this incident:

- Increased distance between the tanks and the pumping/valve area
- Increased tank-to-tank separation

- Installation of internal excess flow or fail-safe remotely operated valves for tanks at locations where piping connects
- Provisions for the removal of fuel in the event the storage tanks' primary discharge means becomes inoperable
- Simple and recognizable means for fire fighters to shut off fuel flow into the facility
- Increased structural support for piping (CCPS G-39)

3.3. Key Issues

Safety issues in batch reaction systems relating to equipment configuration and layout are presented in Table 3. This table is meant to be illustrative but not comprehensive. A few key issues are presented below.

- Shared vent systems, utility systems, or equipment may result in incompatible materials coming together.
- Potential for fire traveling through the shared vent system.
- Possibility of combining incompatible materials in drainage and dikes.
- There is a greater need to provide ready access to equipment in batch plants because these require more manual operations. If the access is difficult, it may lead to operator injury and/or inability of operator to carry out responsibilities.
- Close proximity of hazardous processes may result in releases or other hazardous conditions in one process affecting the neighboring process areas, thereby resulting in escalation of the hazard.

3.4. Process Safety Practices

Listed below are safety practices aimed at minimizing hazards due to equipment configuration and layout.

- Provide safe separation distances for normal operation, maintenance, emergency egress, ergonomics
- Design systems to prevent incompatible materials coming together
- Provide appropriate area electrical classification
- Provide appropriate building, and point source ventilation
- Provide ignition source control
- Monitor utility systems for contamination
- Proper control room design
- Use damage limiting construction
- Provide spill control
- Install adequate sprinkler protection

Table 3: Equipment Configuration and Layout

No.	Concern/Issue	Potential Solutions and Control Mechanisms	Additional Resources
Shared Systems			
1.	Shared vent systems. Possibility of incompatible materials coming together.	• Design to avoid incompatible materials present in the same vent system • Install deflagration suppression systems • Design vent to prevent backflow/accumulation • Prescrub vent discharge before transfer to vent header • Monitor circulating utility systems for contamination	ACGIH 1986 CCPS G-11 NFPA-69 NFPA-91
2.	Shared utility supply systems. Possibility of incompatible materials coming together via contamination of the shared utility system	• Design to avoid common utility supply headers and/or systems to processes with incompatible materials • Install backflow protection on supply lines • Implement mechanical integrity program to prevent contamination of utility systems • Monitor circulating utility systems for contamination	API RP 750 CCPS G-7 CCPS G-22 CCPS G-29 CCPS G-57 NFPA-91
3.	Shared equipment (e.g. auxiliary processing "scrubbers"). Possibility of incompatible materials coming together.	• Design to avoid or minimize use of common equipment for incompatible materials • Implement proper cleaning procedure between incompatible uses to prevent cross contamination • Prescrub or treat process streams before transfer to common equipment	API RP 750 CCPS G-11 CCPS G-22 Kletz 1991 Lees 1996 NFPA-91
4.	Shared transfer systems.	• Avoid the use of incompatible materials in shared transfer systems • Ensure cleaning procedures are followed • Avoid pockets in lines • Install dedicated transfer system	API RP 750 Kletz 1991 Lees 1996 NFPA-91

Table 3: Equipment Configuration and Layout

No.	Concern/Issue	Potential Solutions and Control Mechanisms	Additional Resources
Ignition Sources			
5.	Ignition of flammable release resulting in fire or explosion.	• Provide safe separation distances • Develop appropriate area electrical classification • Provide ignition source control • Place ignition sources in positive pressure enclosure and buildings • Provide adequate ventilation	API RP 500 BS 5345 BS 5958 NFPA-70 NFPA-77
Fire/Explosion			
6.	Shared vent systems. Potential for fire traveling through the shared vent system.	• Design vent system to prevent backflow/accumulation • Prescrub or treat vent discharge before transfer to the vent header • Install detonation and / or deflagration arresters • Install deflagration suppression system • Provide explosion venting and isolation mechanism • Provide vent system inerting or purging • Install dedicated vent systems	33 CFR 154 NFPA-69 NFPA-91
7.	Liquid spills. Possibility of accumulation of flammable liquids resulting in fire or explosion hazard.	• Provide spill control through adequate drainage and curbs or dikes • Provide adequate ventilation • Wash down systems • Minimize possibility of ignition • Minimize possibility of spills	API RP 750 CCPS G-22 CCPS G-24 CCPS G-30 Lees 1996 NFPA 69 NFPA-15
8.	Liquid spills. Possibility of combining incompatible materials in drainage and dikes.	• Provide segregation storage of incompatible materials • Don't put incompatible materials in the same dike • Use segregated drainage & sewer systems • Wash down systems • Minimize possibility of ignition • Minimize possibility of spills	API RP 750 CCPS G-22 CCPS G-22 CCPS G-24 CCPS G-30 NFPA-328 NFPA-329

No.	Concern/Issue	Potential Solutions and Control Mechanisms	Additional Resources
Fire/Explosion			
9.	Control room sited closer to the batch process due to need for more operator interaction with batch processes. Infiltration of flammable/toxic release from outside. Possible overpressure from external explosion.	• Proper location of air intake • Provide adequate control room ventilation system • Provide positive control room pressure to prevent inflow of hazardous material • Provide flammable/toxic detection systems in buildings • Provide control room or facility alarm to warn occupants • Provide personal protective equipment • Provide sufficient bottled air / SCBA • Provide doors on the side of the control room opposite to expected hazard sources • Provide wind direction indication visible from inside the building / control room • Employ damage limiting construction • Develop emergency response procedures • Develop evacuation plans • Provide exterior (and interior) fire extinguishing equipment • Design control room to withstand blast overpressure	API RP 752. CCPS G-26 NFPA-101
10.	Batch equipment located indoors. A release of flammable/toxic material tends to disperse slower than if the release is outdoors. May lead to large concentration buildup and result in operator exposure. Confined flammable releases are also more likely to result in explosion with larger overpressures.	• Provide adequate building ventilation • Install flammable/toxic detection systems in buildings with alarms to warn building occupants of hazardous accumulations • Provide personal protective equipment • Provide sufficient bottled air/SCBA • Develop emergency response procedures • Develop evacuation plans • Install explosion venting for room and/or building • Damage limiting construction of processing building	ACGIH 1986 CCPS G-3 CCPS G-13 CCPS G-26 NFPA-68