

The Essential Elements of a Successful Reactive Chemicals Program

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Dow Locations



- R&D Centers
- Service Centers
- PU Systems
- Hub Centers
- Headquarters
- Manufacturing
- Dow Facilities

**Manufacture more than 5,000 products
at 197 sites in 36 countries across the
globe**

**Employ approximately 52,000 people
worldwide**

Where I live and work



Reactive Chemicals and Process Safety at Dow

- **Process Safety** Group at Dow: responsible for:
 - PHA Reviews
 - Loss Prevention Principles and audits
 - LOPA
- **Reactive Chemicals** Group at Dow: responsible for:
 - Thermal stability, flammability, dust explosion assessments of processes
- Individuals in both areas are Business aligned globally and we interact with each other very closely

The Purpose of a Reactive Chemicals (RC) Program


To prevent uncontrolled chemical reactions that have the potential to result in **injury, property damage, or environmental harm.**




It all starts with **Recognition and Acceptance** of the fact that RC events can have negative consequences ...sometimes severe!

- **Injury**
- **Environmental release**
- **Capital costs / loss of production**
- ***Cannot forget: company reputation!***

BP Incident significant fines!



 **U.S. Department of Labor**
Occupational Safety & Health Administration
www.osha.gov Search [GO](#) [Advanced Search](#) | [A-Z](#)

OSHA News Release
2005 - 09/22/2005 - OSHA Fines BP Products North America More Than \$21 Million Following Texas City Explosion

[← OSHA News Release - Table of Contents](#)

OSHA National News Release

U.S. Department of Labor
OSHA, Office of Communications

National News Release: USDL 05-1740
Date: September 22, 2005
Contact: Pamela Groover or Al Belsky
Phone: (202) 693-4676 (202) 693-1999

OSHA Fines BP Products North America More Than \$21 Million Following Texas City Explosion
Company Agrees to Make Extensive Plant-Wide Improvements

WASHINGTON -- BP Products North America Inc. has agreed to pay more than \$21 million in penalties for safety and health violations following an investigation of a fatal explosion at its Texas City, Texas, plant March 23 that claimed the lives of 15 workers and injured more than 170 others. The penalties are part of a settlement agreement [announced](#) today by the U.S. Department of Labor's Occupational Safety and Health Administration (OSHA).

Map Ta Phut Thailand – May 5, 2012 Bangkok Synthetics Co



**Probable toluene
explosion**

12 fatalities!



Key, High Level Elements of a Reactive Chemicals Program

- **A culture of safe processes** as the only way of doing business
 - A mindset that this process is value added
- **A formal process** for identifying higher risk hazards and mitigation strategies
 - A documented work process

Key, High Level Elements, cont'd

- Internal and external **testing and calculational expertise**
- A **multi-functional review process** based on risk
 - Pre-campaign
 - Periodic for existing facilities (at Dow: 3 yrs)
 - Post incident (Root Cause Investigation)
- A process to capture “**Corporate Memory**”
 - So we don't repeat events!

Three Key **Principles** of a Successful Reactive Chemicals Program

- 1) The RC Program plays a key role in **avoiding** circumstances that put people, environment, equipment or businesses at risk.
- 2) The focus of the RC Program is the **understanding of the inherent energy** of our systems and conditions under which it can be released.

3) Owner Responsibility

The “Keystone” of a RC Program
“Owner Responsibility”

After all the testing, consultation, and reviews, ***the owner of the project, process, or facility must make the appropriate decisions concerning Reactive Chemical issues!***

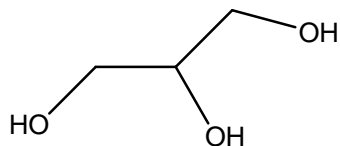
Reactive Chemical Hazards

- **Energy Release Potential**
 - Inherent energy in reactants/raw materials
 - Inherent energy of intended chemistry
 - Inherent energy from process upsets (high temperature decomposition)
- **Flammability**
- **Dust explosion**

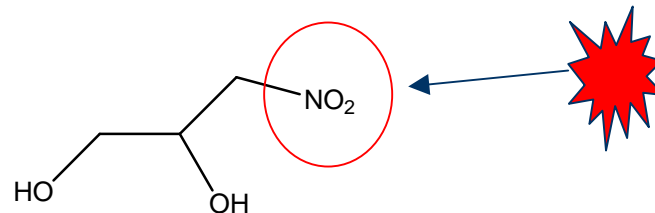
This is not necessarily “Rocket Science”!

- **Common Sense Approach**
- **Three simple questions:**
 - How much energy can be released
 - Under what circumstances
 - How fast can it happen?

Example: recognition of hazardous functional groups:



versus



Functional Group Flags

Common functional groups (partial list) that can add significant potential energy release to a molecule:

Functional Group(s)	Reactive Substance Class
-C≡C-	Acetylenic compounds
-C≡C-M	Metal acetylides
-C≡C-X	Haloacetylene derivatives
$\begin{array}{c} \text{N}=\text{N} \\ \diagdown \quad / \\ \text{C} \end{array}$	Diazirines
CN ₂	Diazo compounds
-C-N=O	Nitroso compounds
-N-N=O	
-C-NO ₂	Nitroalkanes, C-nitro
Ar-NO ₂ , Ar(NO ₂) _n	Nitroaryl and Polynitroaryl compounds
C(NO ₂) _n	Polynitroalkyl compounds
O ₂ NC-CNO ₂	
HC[OCH ₂ C(NO ₂) ₃] ₃ ,	Trinitroethyl orthoesters
C[OCH ₂ (NO ₂) ₃] ₄	
-C-O-N=O	Acyl or alkyl nitrites
-C-O-NO ₂	Acyl or alkyl nitrates
$\begin{array}{c} >\text{C}-\text{C}< \\ \quad \\ \text{O} \end{array}$	1,2-Epoxides
MC?N? O	Metal fulminates or
C=N-O-M	aci-nitro salts, oximates

A successful RC program does not need to be burdensome!

- Can base the application of the program on risk, scale, etc.
 - Can be based on a simple “Trigger Grid”
 - Lowest level of review can be a simple discussion with a knowledgeable colleague
 - Highest level of review must be with multifunctional experts (more on reviews later)
- Per US government law, this is dictated for certain materials and certain quantities (OSHA PSM)

Dow's (Published) Program

- Recognized as **Best in Class** by many
Numerous companies have visited Dow and modeled their program after Dow
Backed up by performance!
Strong and active support of external activities:
examples: CCPS, ACC Responsible Care
Strong academic support: Mich. Tech. Univ. endowed chair and Mary Kay O'Connor Process safety Center at Texas A&M, also HarsNet, REACH, etc.
- Program Documents publicly available from CCPS

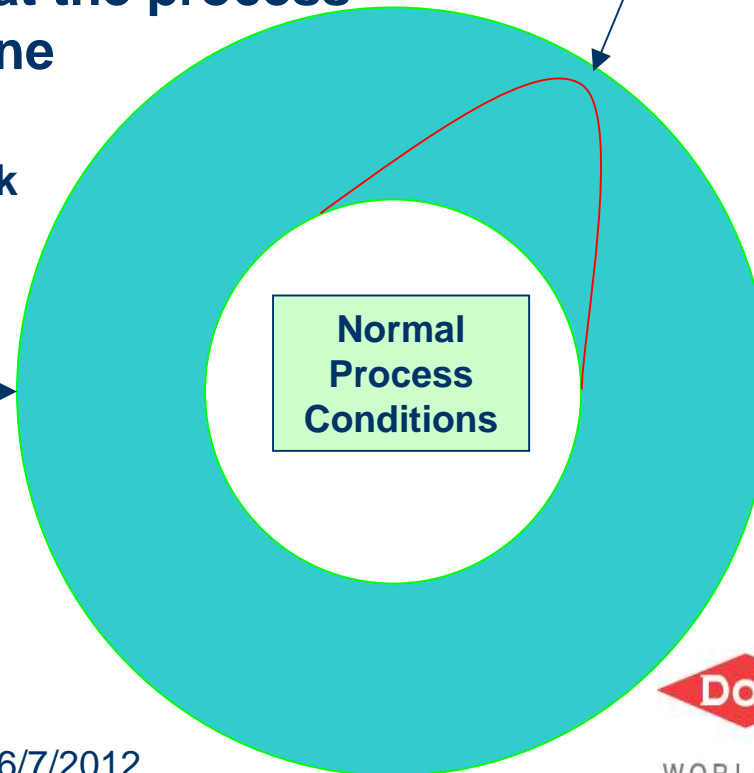
Understanding the concept of the safe operating envelope

Process Upset,
worst case

- Having sufficient knowledge about the process to assure that the process operates in a safe zone

NOT risk free!
...but acceptable risk

Safe Operating
Envelope



First Questions

- **How Much Energy**
Can It Liberate ?
(thermodynamics)
- **How Fast** Can it Go ?
(kinetics)
- A rusting pipe is very
hot chemistry...buy
very very slow!



Calculations - Used to Understand Thermodynamics

- Calculated Heats of Reaction -
 - Open Literature heats of reaction
 - Analog Reactions
 - Energetics via Quantum Mechanics

- CHETAH

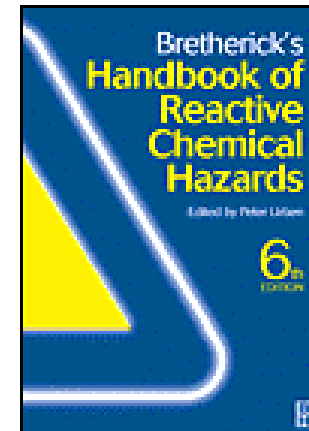
Useful for rxn heats

Also correlations with explosive properties



Bretherick's Handbook is a Must!!!

- It literally is the “Bible” of reactive chemicals!
- Hard Copy is adequate
- HazMat Navigator includes Bretherick's database



Internet Resources

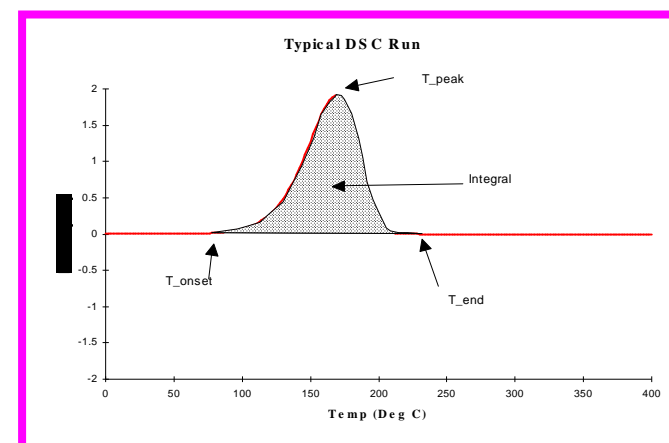
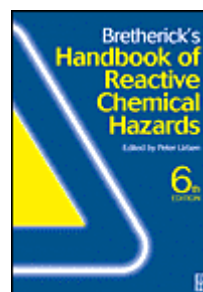
- **CSB – US Chemical Safety Board - website (great videos!)**
- **NOAA Chemical Reactivity Worksheet**
Compatibility information
- **NIST WebBook (thermo)**
- **SACHE (AIChE group...training modules)**
- **CCPS (Center for Chemical Process Safety)**
Books and free downloads

The Testing Tools

Screening Tests



- Heat of mix calorimetry
- Differential Scanning Calorimetry (DSC)
- “Desktop” methods such as Heat of Reaction Estimation, CHETAH evaluation, adiabatic temperature rise estimates, review of the literature (Bretherick, MSDS, safe handling guidelines, etc.)
- Drop weight



The Testing Tools

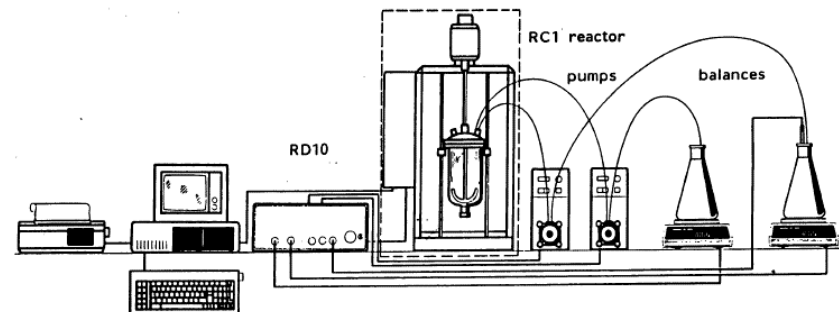
Quantitative Tests

- **ARC (Accelerating Rate Calorimetry...yields good thermokinetics with pressure data)**
- **Isothermal calorimetry (can confirm ARC kinetic extrapolation to lower T)**
- **Card gap testing (non-calorimetry, tests for detonability)**



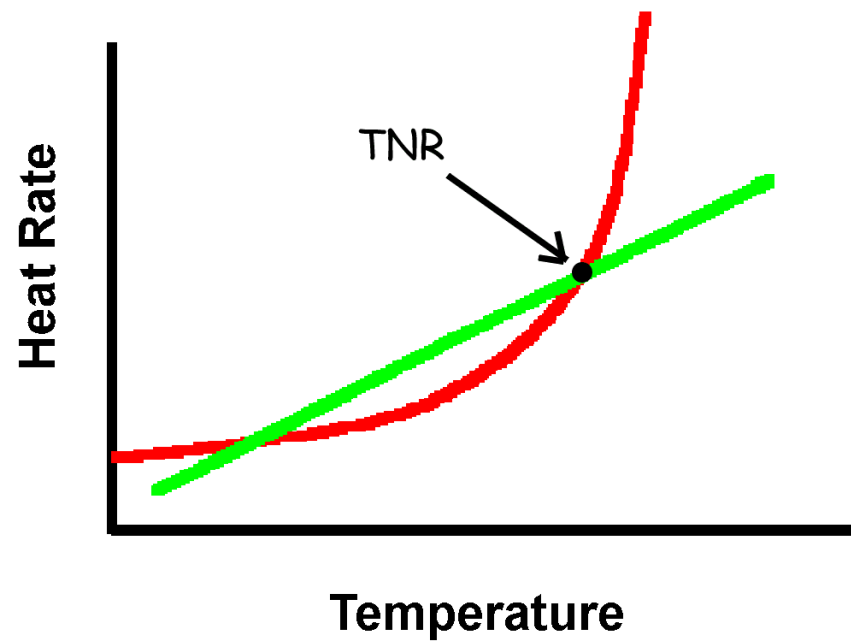
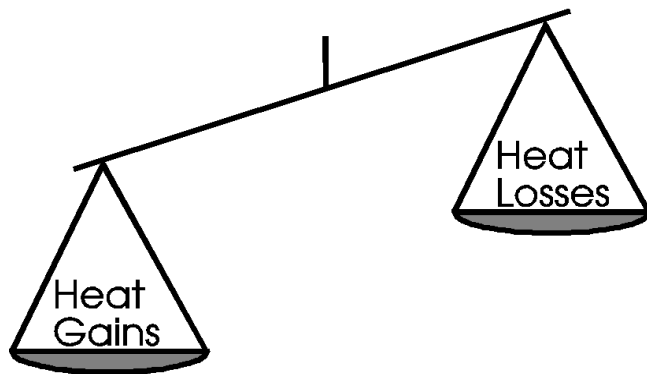
The Testing Tools Scalable Testing/Modeling

- Vent Sizing Package (VSP)
- Reaction Calorimetry
- Development of detailed kinetic models for the process/chemistry
- Heat gain, heat loss evaluation for determination of TNR (Temperature of No Return)

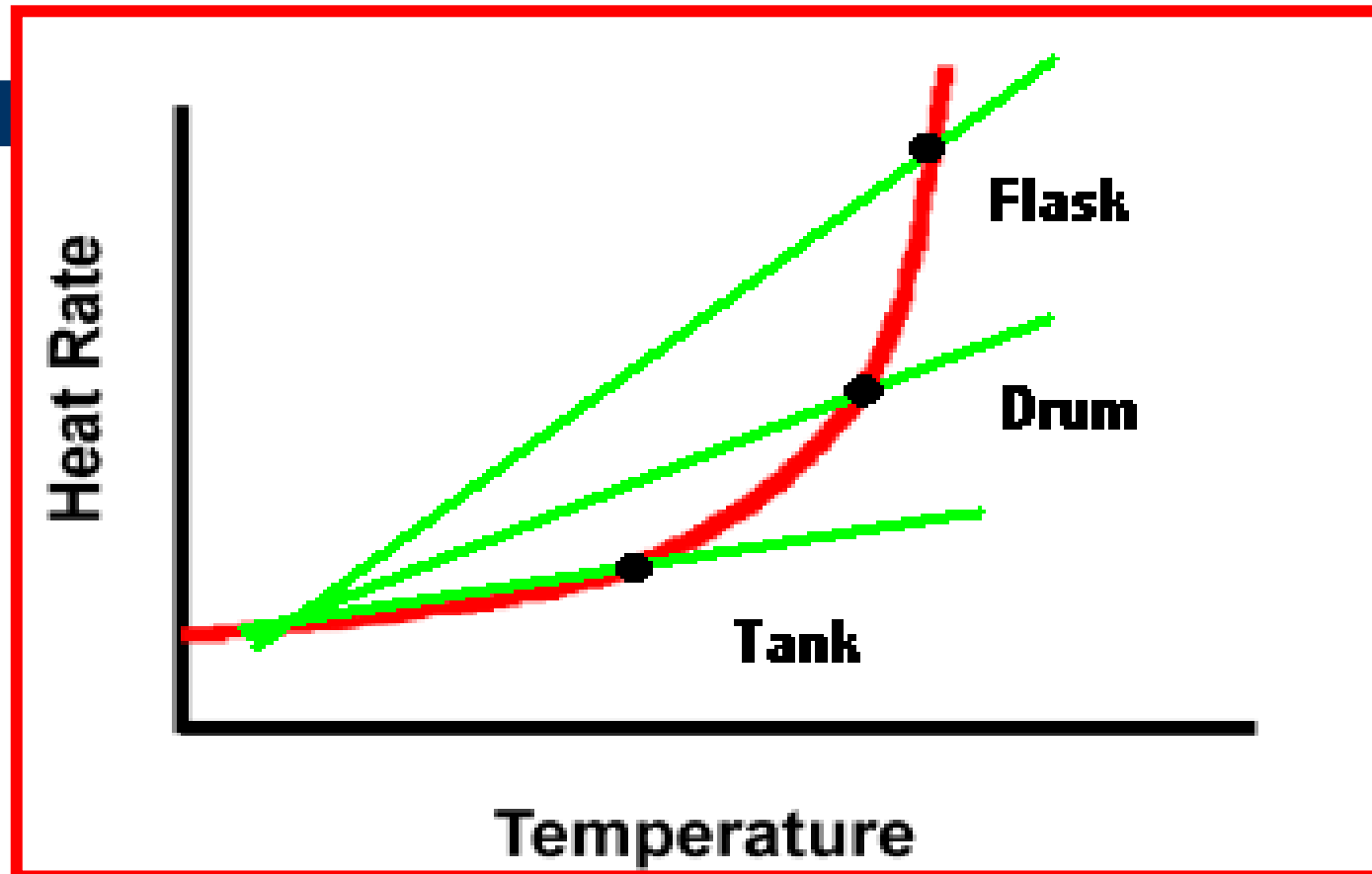


Thermal Runaway -

Whenever Heat Gain > Heat Loss



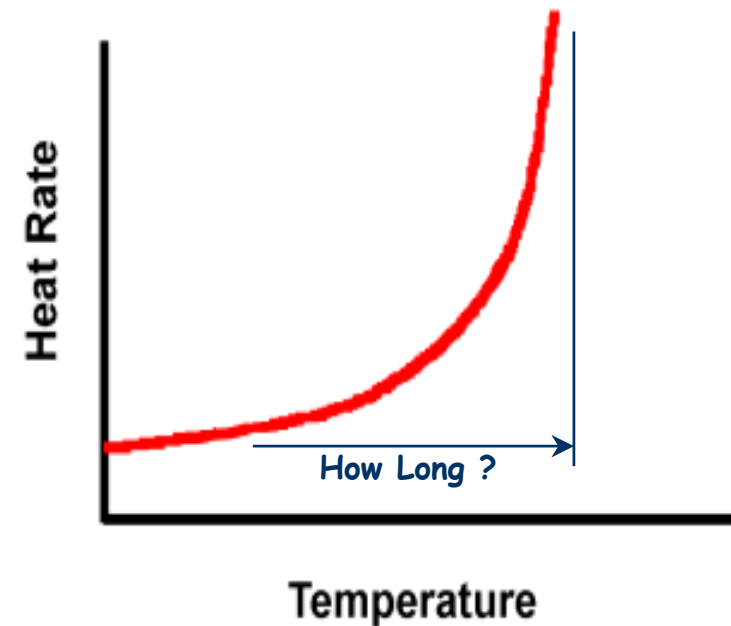
Heat is Lost From Vessels At Different Rates



Time to Maximum Rate -TMR

"Uninhibited Styrene" Adiabatic Runaway

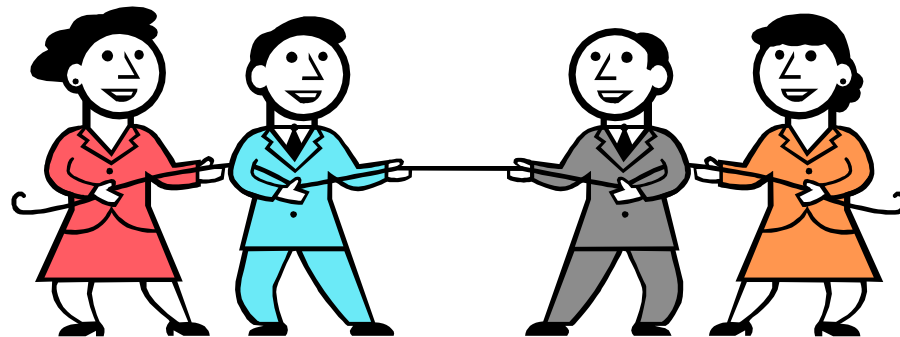
10 C	59 days
20 C	21 days
30 C	8 days
50 C	1.5 days
70 C	8 hrs



Approaches to RC hazard evaluation based on energy release potential and scale

The Two Extremes

- Test nothing
 - Can be dangerous BUT may be justified under the right conditions
- Test everything and every combination at every proportion
 - Is rarely justified



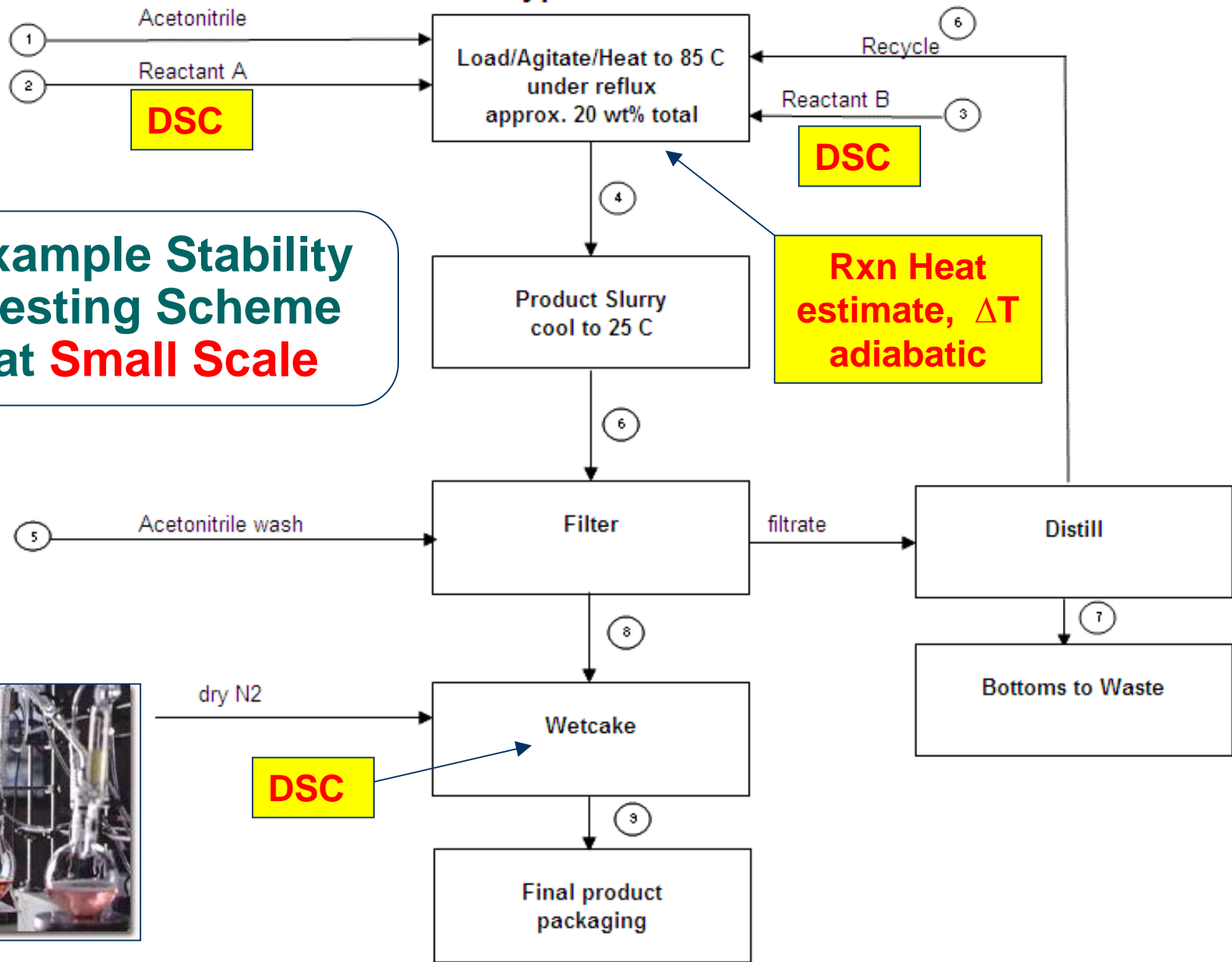
WORLDWIDE PARTNER

A Balanced Approach

- Match the **scale**,
and the **energy release potential**,
and the **testing type...**
- **...to minimize risk to an acceptable level**
 - More efficient**
 - Saves time and money**
 - Does not sacrifice accuracy**



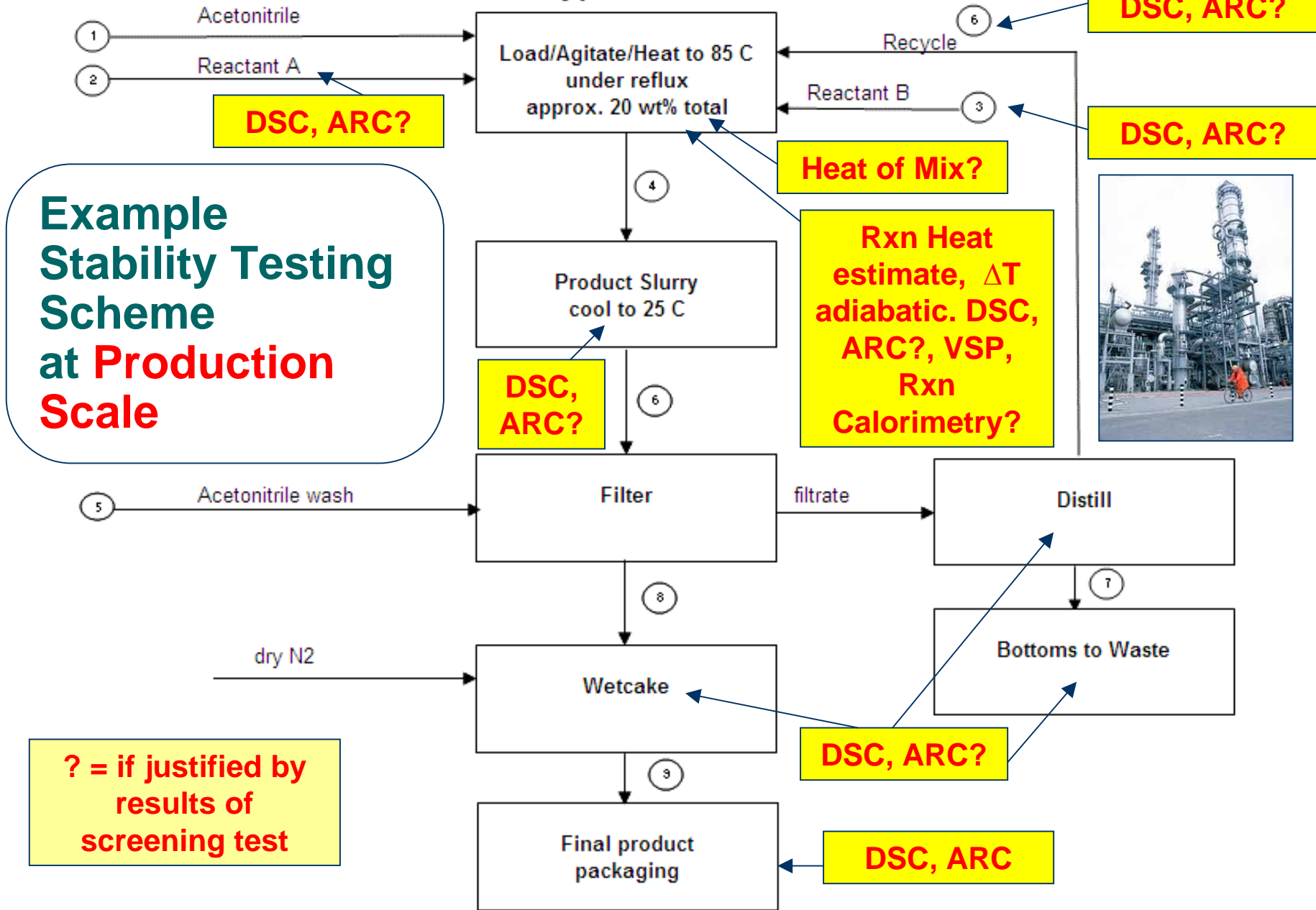
Block Flow for Hypothetical Chemical Process



Example Stability Testing Scheme at Small Scale



Block Flow for Hypothetical Chemical Process



Example Stability Testing Scheme at Production Scale

? = if justified by results of screening test

Layers of Protection Analysis (LOPA)



- An Important tool for Process Safety at Dow and other companies
- **Credible** worst case scenarios are assigned a Target Factor (Tf) based of formalized definitions

Higher Tf indicates more severe potential consequences

Example: Tf = 6 indicates a 1-2 fatalities (see below)

There MUST be at LEAST Tf number of independent protection layers to protect against this scenario

Target Factor	Impact on People On-site
4	Reportable Medical Treatment Case (RMTc) or a Day Away from Work Case [DAWC] with full rehabilitation.
5	A serious irreversible injury
6	1 to 2 fatalities
7	3 to 9 fatalities
8	10 to 49 fatalities

RC/PHA* Reviews

***Reactive Chemicals/Process Hazard Analysis**

- Reviews are a key tenet of any Reactive Chemicals Program
- These are basically formal meetings of key stakeholders with external representation
- Scope is adjusted to process scale and risk
- Formal and standardized agenda used globally



6/7/2012



WORLDWIDE PARTNER

Why Do We Have Reviews?

- Allows many external “sets of eyes” with broad and varied expertise to contribute
 - multifunctional
 - timely (**not held after the process has begun!**)
- Ensures that nothing is missed/overlooked
- All items discussed without resolution are captured and must be resolved

6/7/2012

Types of Review

- Smaller reviews or MOC
MOC = Management of Change
- New Project
- 3 Year Facility
(In the US, government requires a 5 year cycle for certain facilities)
- Unique to Dow (?): “New Leader” reviews !!
These must occur within 90 days of the leader assuming the new position

6/7/2012

Conclusions: Study, Test, Calculate, and Review!

- Reactive Chemicals management is a key part to the success of a company
- A common sense risk based approach is optimum
- Calorimetry and calculations play a key role
- Multifunctional Reviews help ensure all hazards are identified and mitigated

Questions?