

EXPERIMENTS TO DEMONSTRATE CHEMICAL PROCESS SAFETY PRINCIPLES

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A pathy towards chemical process safety in the United States came to an abrupt end following the toxic methyl isocyanate (MIC) release from the Union Carbide India Ltd. pesticide plant in Bhopal, India, on December 2, 1984.^[1,2] The resulting MIC spread over a heavily populated area and resulted in the death of thousands. This incident led to passage and implementation of the Emergency Planning & Community Right-To-Know Act of 1987 and the chemical process safety amendments to the Clean Air Act of 1990 in the United States. In addition, the Center for Chemical Process Safety (CCPS), which is affiliated with the American Institute of Chemical Engineers, was founded in 1985 in response to the Bhopal incident. The CCPS is committed to developing engineering and management practices to prevent or mitigate the consequences of catastrophic events at chemical plants.

Recognizing the need for educating undergraduate chemical engineering students, CCPS, in a cooperative effort with engineering schools, initiated the Safety and Chemical Engineering Education (SACHE) program in 1992. SACHE provides teaching materials (*e.g.*, slide/lecture sets, video lectures, problem sets, and instructional modules) to aid educators in incorporating safety into undergraduate chemical engineering programs. The SACHE instructional materials can either be used to incorporate safety into existing chemical engineering courses, *e.g.*, using safety related problems from the SACHE problem sets, or as supplementary material for a dedicated chemical process safety course.

At the University of Iowa we have a dedicated required chemical process safety course that is taken by students during their junior year. We also incorporate problems from the SACHE problem sets into other chemical engineering courses. We believe that a dedicated chemical process safety course is highly desirable since it (i) allows coverage of material that would not fit well into existing chemical engi-

neering courses, (ii) emphasizes the importance of chemical process safety, (iii) reinforces the importance of all chemical engineering fundamentals (*e.g.*, thermodynamics, reaction kinetics, transport, and material and energy balances) to chemical process safety, (iv) provides an excellent review of the other chemical engineering courses, and (v) better prepares students for industrial employment. Major aspects of the chemical process safety course offered at the University of Iowa are summarized in Table 1. Additional approaches to incorporating chemical process safety into the chemical engineering curriculum can be found in the literature.^[3,4]

The laboratory experiments listed in Table 1 give students hands-on experience with such issues as flammability limits, flash points, electrostatics, runaway reactions, explosions, and relief design. All of these issues are important in industrial processes. It is well known that most students are more

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TABLE 1**Details of Dedicated Chemical Process Safety Course***(Additional details: <<http://icaen.uiowa.edu/~cpsafety/>>)***Major Topics Covered**

Government Regulations	Reactivity
Process Safety Management	Fires and Explosions
Toxicology	Fire and Explosion Prevention
Industrial Hygiene	Relief Design
Source Models	Hazard Identification
Dispersion Models	Risk Assessment/Reliability Engineering
Flammability	Case Studies
Electrostatics	Inherently Safer Design

Textbooks

Daniel A. Crowl and Joseph F. Louvar, *Chemical Process Safety: Fundamentals with Applications*, Prentice Hall (1990)

Safety, Health, and Loss Prevention in Chemical Processes: Problems for Undergraduate Engineering Curriculum, AIChE Center for Chemical Process Safety (CCPS) (1990)

Safety Essay

Students write an essay (1500-word maximum) regarding a topic relevant to chemical process safety consistent with the format requested for the SACHE-sponsored Student Essay Award for Undergraduate ChE Students.

Project

Group projects are performed in which students analyze safety issues relevant to the process of manufacturing the specific chemical assigned to them. A major aspect of the final report and oral presentation regards how inherently safer design concepts can be incorporated into the existing process.

Homework

There are weekly homework assignments.

Quizzes

There are weekly quizzes (generally 10-20 minutes). These seem to improve the learning process and to discourage student procrastination.

Exams

There are one or two midterm exams and a final exam.

Laboratory Experiments

• Flammability Characteristics • Electrostatics • Runaway Reactions/ Relief Design • Explosions/Relief Design

receptive to this type of hands-on learning than the traditional lecture format.^{15]} Therefore, this laboratory benefits all students by giving them a hands-on appreciation for concepts introduced in the lecture and is especially beneficial to the majority of students who are more receptive to active learning approaches. While these experiments are ideally suited to supplementing a chemical process safety course, they can also be used in other courses, *e.g.*, unit operations laboratory, to demonstrate important chemical process safety concepts.

LABORATORY EXPERIMENTS

The laboratory experiments discussed in this section are now an integral component of the chemical process safety course offered at the University of Iowa. The major equipment used, along with other key aspects of the experiments, are summarized in Table 2. In order to maximize the learning benefits, these experiments are conducted in small groups (typically 3 students) soon after discussing the corresponding topic in the lecture portion of the course. The laboratory reports consist of a title page, an abstract, an introduction, materials and methods, results and discussion, conclusions, references cited, and an appendix.

The **introduction** includes an overview of the purpose of the experiment and discusses the relevant theory. The **materials and methods** section discusses the procedures used, what data were collected and how, and diagrams of the apparatuses used. The **results and discussion** section includes a discussion of the results obtained and their relevance to industrial applications, including a comparison of theory and experimental results, and answers to all questions asked about the experiment. The **appendix** includes MSDS sheets for all chemicals used, sample calculations,

TABLE 2**Summary of Equipment**

Additional comments and equipment costs (1999 estimates) are also given. (Prices are for Advanced Reactive System Screening Tool (ARSST), successor to the RSST.)

<u>Experiment</u>	<u>Major Equipment Used</u>	<u>Comments</u>
Flammability Characteristics	<ul style="list-style-type: none"> • Miniflash FLP Flash (Model 4200, Petrolab Company, Latham, NY; ~\$12,000) • Flame Tec Flammability Limits and Data Acquisition System (Fauske and Associates, Burr Ridge, IL; ~\$24,000) 	The flammability limits experiment also uses a personal computer for data acquisition and gas cylinders with gauges to charge the apparatus with the desired amounts of propane and air. In addition, a barometer can be used to correct for deviations from atmospheric pressure.
Electrostatics	<ul style="list-style-type: none"> • Electrometer with accessories for high voltage (Model 6514, Keithley Instruments, Inc., Cleveland, OH; ~\$4,000). Accessories include a Model 6103C Voltage Divider Probe, Model 6171 2 log to 3 log Triax Adaptor, and Model 6102 Triax to UHF Adaptor. • Static Monitor (JCI-140, John Chubb Instrumentation, Cheltenham, England; ~\$1,000) • Van de Graaf Generator (Stock # CR52-587, Edmund Scientific, Barrington, NJ; ~\$500) 	These experiments are generally simple and require a few additional accessories commonly available in laboratories, as described in the main text
Runaway Reactions/ Relief Design	<ul style="list-style-type: none"> • Reactive System Screening Tool (RSST) (Fauske and Assc., Burr Ridge, IL; ~\$19,600) • Vent Sizing Software Program (Fauske and Associates; ~\$2,500) 	These experiments also require a computer for data acquisition and for running the vent sizing software. In addition, a nitrogen gas cylinder and regulator are needed to pressurize the RSST unit.
Explosions/ Relief Design	<ul style="list-style-type: none"> • Flame Tec Flammability Limits and Data Acquisition System (Fauske and Assc., Burr Ridge, IL; ~\$24,000) • Modified Hartmann Tube (Type MP-5, Adolf Kühner AG, Switzerland; ~\$12,500) 	The flammability testing apparatus requires a computer for data acquisition. The modified Hartmann tube does not require any accessories other than the test materials.

and a copy of the raw data. Experimental write-ups given to the students at the University of Iowa can be found on the Chemical Process Safety course web site (see Table 1).

Flammability Characteristics

Prior to conducting these experiments students should be introduced to the importance of flash points and flammability limits. In addition, they should understand the relationship between these two parameters, *i.e.*, the flash point of a pure substance is the temperature at which the concentration of flammable vapor in the gas phase is equal to the lower flammability limit (see Figure 1). These experiments will acquaint the students with methods used to determine flash points and flammability limits.

In our experiments we collected flash points for pure alcohols (methanol, ethanol, and 1-butanol), alcohol/water mixtures, and alcohol/alcohol mixtures. Data were collected with a Miniflash FLP Flash Point Tester (Table 2), an automated instrument that determines closed cup flash points. A manual Pensky-Marten flash point tester (Table 2) was also used to observe when a substance flashes. Data obtained from the automated instrument were used for analysis. Note that the data should be corrected for deviations from atmospheric pressure.

First, the measured flash points (FPs) for the pure alcohols were compared with accepted literature values.^[6] All of the experimental values were within 2°C of the accepted literature values, with the ethanol measurement typically within 0.5°C of the literature value (Table 3).

Second, the flash points were measured for different concentrations of alcohol/water mixtures. These values were first compared with values calculated assuming an ideal solution, *i.e.*, determining the temperature at which the vapor pressure of the flammable component (alcohol) is equal to that of the pure component vapor pressure^[7] at its flash point^[6, 8] (Table 3). The experimental values for the alcohol/water mixtures were consistently several degrees lower than the values obtained assuming ideal solutions. The largest difference between the experimental and calculated values occurred for the mixture containing 33.3 mole% 1-butanol, for which the calculated value was about 14°C higher. It should be emphasized, however, that in reality these solutions are nonideal. Therefore, the FPs were also calculated taking into account nonideal behavior. Briefly, liquid-vapor equilibrium data^[9] for the alcohol/water mixtures were used to calculate activity coefficients ($\gamma_i = P_{\text{tot}}y_i / P^{\text{sat}}x_i$) at the corresponding liquid concentration (x_i). The FP was then calculated assuming that the activity coefficient is a function of concentration only. As shown in Table 3, the corresponding calculated values are all within 2°C of the measured

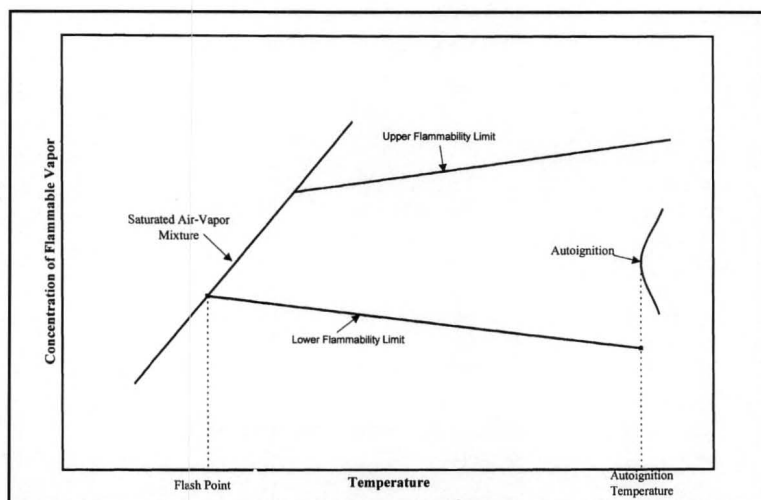


Figure 1. Diagram demonstrating the relationship between the flash point and lower flammability limit.

TABLE 3
Typical Flash Point (FP) Results

The experimental FPs for the pure alcohols were compared with literature values, while the experimental FPs for the alcohol/water mixtures were compared to calculated values assuming either ideal or nonideal solutions.

Material Tested (mole fraction)				Typical Experimental FP/(°C)	Calculated FP (°C)	
water	methanol	ethanol	1-butanol		Ideal Solution	Nonideal Solution
0.000	1.000	0.000	0.000	9.0	11*	---
0.000	0.000	1.000	0.000	13.4	13*	---
0.000	0.000	0.000	1.000	38.6	37*	---
0.667	0.333	0.000	0.000	27.5	31.3	26.4
0.500	0.500	0.000	0.000	19.4	23.3	21.2
0.333	0.667	0.000	0.000	16.8	18.0	17.3
0.667	0.000	0.333	0.000	24.1	31.6	23.0
0.500	0.000	0.500	0.000	20.1	24.4	20.9
0.333	0.000	0.667	0.000	17.4	19.5	18.3
0.667	0.000	0.000	0.333	40.9	54.7	43.9
0.500	0.000	0.000	0.500	43.2	47.7	43.6
0.333	0.000	0.000	0.667	39.6	43.1	41.4
0.000	0.333	0.000	0.667	23.5	20.5	---
0.000	0.500	0.000	0.500	18.5	16.1	---
0.000	0.667	0.000	0.333	15.2	12.5	---
0.000	0.000	0.333	0.667	25.1	22.6	---
0.000	0.000	0.500	0.500	21.4	19.0	---
0.000	0.000	0.667	0.333	18.0	15.9	---

* Literature values obtained from reference 6.

values, with the sole exception of the 1-butanol ($x = 0.333$)/water solution, for which the calculated FP was 3°C higher than the measured value.

Third, the FPs were measured for different concentrations of alcohol/alcohol mixtures, specifically, methanol/1-butanol and ethanol/1-butanol mixtures. These measured values were compared to the theoretical values obtained from the intersection of the vapor pressure and lower flammability limits

curves on a plot of flammable vapor concentration versus temperature (Figure 1). For a given liquid phase concentration the vapor phase concentration of the alcohols can be calculated by assuming an ideal solution, *i.e.*, by using Raoult's Law. The lower flammability limit (LFL) of the mixture can be estimated by

$$LFL_{\text{mix}} = \frac{1}{\sum_{i=1}^n \frac{y_i}{LFL_i}} \quad (1)$$

where LFL_{mix} is the LFL for the mixture, y_i is the mole fraction in the vapor phase of component i on a combustible basis, and LFL_i is the LFL of pure component i at 25°C.^[8] Thus, it is assumed that LFL_{mix} is not a function of temperature, *i.e.*, it is a constant in Figure 1. This is a good assumption for the experiments discussed in this paper since the temperature effect on LFL is small over the relevant temperature ranges.^[8] It should also be noted that there is some controversy regarding the equation commonly used to estimate the effect of temperature on the LFL of a pure substance.^[8,10] The "concentration of flammable vapor" given in Figure 1 is the sum of the vapor phase mole fractions of all of the alcohols. The calculated values given in Table 3 are generally 2-3°C lower than the measured values for both alcohol mixtures. It is possible that the calculated values would agree more closely with the measured values if treated as nonideal mixtures. It is suggested that the students attempt to develop other methods of estimating the FPs of alcohol mixtures. In addition, the fact that the predicted FPs agree so well with the data may lead to overconfidence in this method by students. It is known that this method works satisfactorily at room temperature and pressure, but degrades considerably at increased temperature and pressure. Thus, this approach is applicable for product or raw material shipping (done at ambient temperature and pressure), but less applicable for process conditions.^[10]

The lower and upper flammability limits of propane were determined using a Flame Tec flammability limits and data-acquisition system (Table 2) that collects pressure-time and temperature-time data. Briefly, the FlameTec apparatus is charged with a known mixture of air and propane and ignition with a spark is attempted. If the mixture ignites, *i.e.*, if an appreciable rise in pressure and temperature occurs, then it is within the flammability range. This process is repeated

with a variety of propane concentrations to determine the flammability range. Typical LFL and UFL values obtained using this procedure are compared with literature values,^[6] as shown in Table 4.

TABLE 4
Flammability Limits Results

	<i>Typical Result</i>	<i>Literature Value^[6]</i>
Propane LFL	2.0 - 2.6%	2.1%
Propane UFL	10.4 - 10.9%	9.5%

The experimental LFL value is consistent with the literature LFL, while the UFL literature values is approximately 1.0% higher than the experimental UFL range. More precise results could be obtained by using smaller incremental partial pressures of propane. In addition, it should be noted that flammability results can vary slightly based on the ignition device.^[10]

Once the LFL for a substance is known, its minimum oxygen concentration (MOC) can be estimated using

$$MOC = LFL \left(\frac{\text{Moles O}_2}{\text{Moles Fuel}} \right) \quad (2)$$

where LFL is the lower flammability limit, and the ratio is the stoichiometric ratio of oxygen to fuel for complete combustion of the substance.^[8]

Students were expected to address the following in their reports:

- ▶ *Define the following terms and discuss how they are relevant to the experiment and industry: LFL, UFL, MOC, and flash point.*
- ▶ *Calculate the LFL, UFL, and MOC of propane and compare to literature values.*
- ▶ *How do the flash points obtained in the laboratory compare to expected values?*
- ▶ *Under what conditions would the results from this experiment not represent actual process results?*

Electrostatics

A series of experiments was conducted to provide students with an improved understanding of the electrostatic charge accumulation that can occur in industrial processes. Most of these experiments were suggested by Crowl^[10] and/or Lüttgens and Glor.^[11] A high-impedance electrometer (Table 2) was used to measure electrostatic potential (V) and charge accumulation (Q). A high-impedance instrument is required for these experiments since electrostatics is a low current-high voltage phenomenon. Given V and Q, the accumulated energy (J) and capacitance (C) can be calculated by^[8]

$$J = QV/2 \quad (3)$$

and

$$C = Q/V \quad (4)$$

One set of experiments was conducted to demonstrate electrostatic charge and/or voltage accumulation during the transport of materials. First, the phenomena were measured on a metal beaker isolated from ground (using a piece of teflon or styrofoam) into which substances were added in a variety of ways. Specifically, (i) water or a powder (*e.g.*, cornstarch) was allowed to free-fall through air into the

beaker, (ii) water or a powder was poured down a plastic surface into the beaker, and (iii) water or a powder was poured down a metal surface into the beaker (see Fig. 2a). Second, the voltage and/or charge buildup resulting from recirculating diesel fuel through a metal filter (7-micron mesh size) isolated from ground was monitored (Fig. 2b). Third, experiments were conducted in which the accumulation of voltage and/or charge resulting from the agitation of a liquid in a metal vessel isolated from ground was monitored. Monitoring the dissipation of the accumulated charge following grounding of the vessel provides the means to evaluate a liquid's relative ability to dissipate charge (conductive liquids versus non- and semi-conductive liquids). This experiment was conducted with both tap water and diesel fuel, which are conductive and semi-conductive liquids, respectively.

The results of the above experiments can be analyzed qualitatively or quantitatively, or a combination of both. For example, monitoring charge and voltage accumulation for a given experiment can be used to calculate energy accumulation and capacitance, using Eqs. (3) and (4), respectively. The basic principles involved, however, can be sufficiently understood with a qualitative analysis. The dropping water/powder experiments were performed to compare different contact methods and the relative conductivities of different materials. Water poured down a metal sheet dissipates potential difference effectively due to the conductive nature of both materials. Water poured through air or down plastic demonstrates that when at least one material is a poor conductor (air or plastic), a charge separation and potential difference are observed. Since cornstarch is a nonconductive powder, charge separation is observed regardless of what additional materials or contact methods are involved. Recirculation of diesel fuel through an ungrounded metal filter demonstrates how contact between a semiconductive liquid and an improperly bonded and grounded filter can easily result in charge separation. Similar phenomena are observed in the agitation experiments, which directly contrasts the dissipative qualities of water and diesel fuel and suggests the

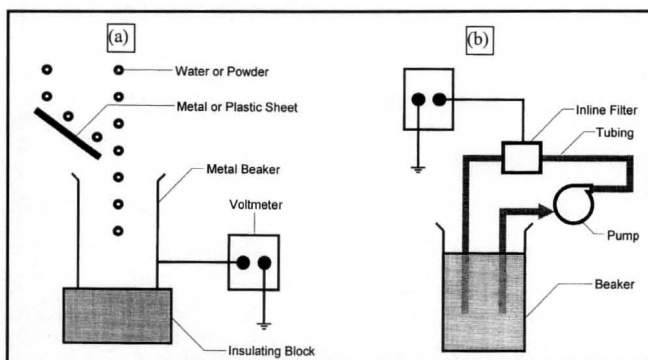


Figure 2. Experimental apparatus for demonstrating electrostatic charge accumulation in (a) pouring liquids or powders, and (b) recirculating liquids.^[10,11]

importance of understanding the conductivity of various chemicals present in a given industrial process. An additional experiment could involve the addition of an antistatic agent to the diesel fuel in the recirculation experiment in order to observe ways to alleviate charge accumulation.

A second set of experiments was conducted to demonstrate charge accumulation on humans and the potential hazards thereof. First, the potential difference caused by removing a sweater or jacket and by using a Van de Graaf generator (Table 2) was measured and used to calculate the energy and capacitance using Eqs. (3) and (4), respectively. In addition, in each of these cases it can be determined whether enough energy is generated to ignite propane (see Fig. 3). In general, any charge accumulation exceeding 350 volts and 0.1 mJ is considered dangerous in industrial operations where flammable vapors are present.^[8] It should be emphasized that these experiments work best when conducted under low

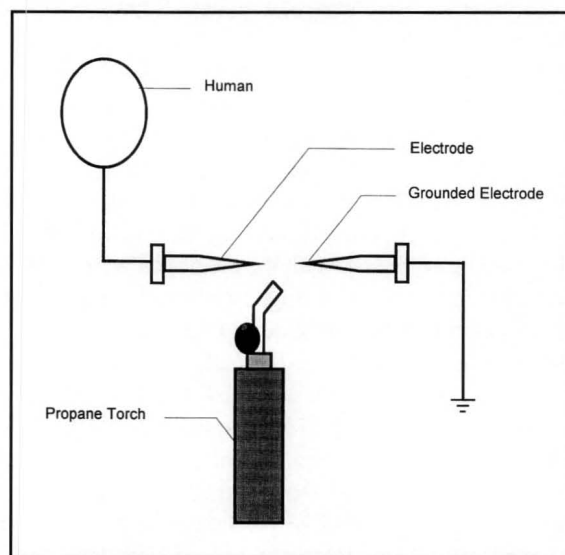


Figure 3. Experimental setup to demonstrate that electrostatic charge accumulation in humans stores sufficient energy for propane ignition.^[11]

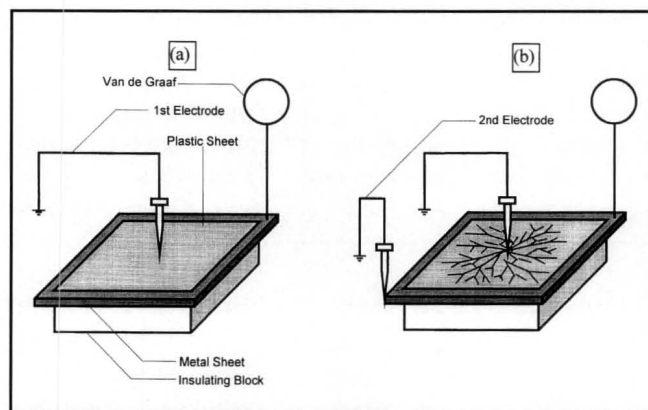


Figure 4. Experimental setup to demonstrate a propagating brush discharge.^[11]

humidity conditions, and when the insulating material is effective in isolating the lab participant from ground. This is particularly important for the Van de Graaf experiment.

Finally, a propagating brush discharge was demonstrated in a third experiment. This provides a dramatic visualization of releasing charge buildup. A propagating brush discharge is an energy-rich energy discharge in which a highly charged insulating surface (e.g., a film) is backed with a grounded conductor. The “feathery” discharge shown in Figure 4 is characteristic of this type of discharge.^[12] The demonstration uses a thin sheet of overhead projector plastic, a sheet of metal (approximately 1/4” thick), and an insulating block. Each of these listed materials was approximately 1 foot by 1 foot. The three materials were arranged as shown in Figure 4a. The metal sheet was connected via an insulated metal wire to the Van de Graaf generator (all wire connections were secured with electrical tape). In addition, two electrodes with sharp tips were grounded using insulated metal wire.

The experiment was initiated by turning on the Van de Graaf generator, which resulted in a separation of charge between the metal slab (which becomes positively charged) and the overhead plastic (which becomes negatively charged). While this charge separation is occurring, one of the grounded electrodes is held at a distance of approximately one cm from the overhead plastic. Results are best when the electrode is moved laterally across the entire area of the plastic sheet while the Van de Graaf generator is running.

While the charge separation is occurring, the experimenter should look and listen for sparks along the metal sheet, particularly at sharp corners. These sparks lead to premature charge dissipation and can diminish experimental success. An easy solution to this problem is to line the edges of the metal sheet with electrical tape prior to conducting the experiment.

Charge separation on the experimental setup is allowed to proceed for approximately one minute, at which time the Van de Graaf generator is turned off. The first grounded electrode is centered over the plastic sheet (still at a distance of approximately 1 cm), and the second grounded electrode is brought into direct contact with the edge of the metal sheet, as shown in Figure 4b. At this point, the metal sheet is grounded, leaving a large charge imbalance between the plastic sheet and the metal sheet, resulting in a propagating brush discharge through the first grounded electrode. The success of this experiment depends on developing a consistent routine; therefore, it is most effective as a demonstration instead of having each lab group attempt the experiment (though if time allows, students should attempt to recreate

the experiment after the initial demonstration is complete).

Propagating brush discharges can occur with a voltage difference of 200 kV per meter of distance between the

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surface where a charge imbalance exists and the potential dissipation route (e.g., the first electrode in the discharge experiment above). A simple experiment to investigate this maximum potential difference involves unraveling a roll of overhead projector plastic. A field meter (see Table 2) or high-voltage probe used with a high-impedance electrometer (Table 2) is placed near the expected trajectory of the unrolling plastic. This distance should be estimated for calculation purposes. The end of the rolled plastic should be pulled quickly and with some force in order to observe a significant amount of unraveling, and the maximum voltage reading should be recorded. Results for the experiment varied between lab groups, but as much as 194 kV/m potential difference was developed in some runs.

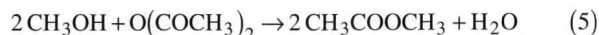
After completing the above experiments, students were expected to answer the following questions in the results and discussion section of the report based on data obtained from the laboratory experiments:

- ▶ Describe the phenomenon of charge separation between two materials in contact.
- ▶ What are the important material properties being considered in the experiment (i.e., how does one material vary from another, and how do these differences affect experimental results)?
- ▶ Relate each experiment to a typical situation in industry, and discuss the difference of magnitude between industrial and lab scale scenarios.
- ▶ What are other ways that charge accumulation can occur in an industrial environment?
- ▶ What can be done to prevent and/or counteract charge build-up?

Runaway Reaction/Relief Design

This experiment provides the students with an understanding of how to characterize a runaway reaction and how to collect and use data to size a relief vent for an industrial scale

reactor of a given volume and given charge of reactants. To demonstrate these principles, the reaction of 2 moles of methanol with 1 mole acetic anhydride, *i.e.*,



is investigated using a calorimeter (Reactive System Screening Tool [RSST], Table 2).^[13] Briefly, methanol and acetic anhydride are charged into the RSST and the temperature is increased at a constant rate of 2°C/min. Once an onset temperature is reached, the exothermic reaction self-heats and a runaway reaction occurs. Two separate tests are conducted: the first is conducted at a low pressure (representing the set pressure of a field scale vessel) and the second is conducted at a high pressure (representing the maximum allowable working pressure of a field scale vessel). The actual pressures used for these tests can be changed according to the type of vessel that is being simulated, and they also depend on the pressure of nitrogen available. Results included in this paper use pressures of 15 and 150 psig for the low- and high-pressure tests, respectively. The RSST, interfaced with a computer, collects temperature-time and pressure-time data. When the reaction “takes off,” a rapid increase in the temperature and pressure are observed, as demonstrated in Figure 5 for the methanol/acetic anhydride system at an initial pressure of 15 psig. It should be noted that, ideally, the low-pressure test should be conducted at constant pressure for the duration of the experiment (*i.e.*, pressure should be monitored and relieved under a chemical fume hood when necessary in order to maintain a vessel pressure consistent with the chosen set pressure of the relief device).

In the data presented above pressure was not regulated, which affects the observed tempering temperature. These pressure and temperature data can be used to generate heat rate and pressure rate curves for relief vent sizing by hand calculations or by the Vent Sizing Software Program (VSSP, Table 2). Whether heat-rate or pressure-rate data are used in vent-sizing calculations depends on the type of runaway reaction that occurs (vapor, gassy, or hybrid).^[13] In a “vapor” runaway reaction, the vapor is produced by components vaporizing due to the heat of reaction; in a “gassy” runaway, the gas is a product of the reaction; and in a “hybrid” reaction, both phenomena occur. For the vapor system of methanol and acetic anhydride, heat-rate curves for both the high- and low-pressure tests are sufficient. Figure 6 shows typical heat rate results for the methanol/acetic anhydride reaction system.

Two calculation methods for vent sizing were considered. The hand calculation was performed using

$$A = 1.5 \times 10^{-5} \frac{m \dot{T}_s}{FP_s} \quad (6)$$

where A (m^2) is the vent area, m (kg) is the charge of reactants to the field scale vessel, \dot{T}_s ($^\circ\text{C}/\text{min}$) is the self-

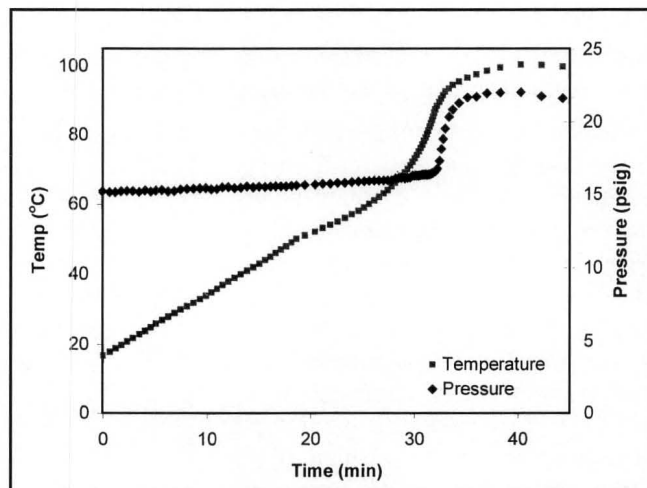


Figure 5. Typical temperature and pressure data for the methanol/acetic anhydride reaction in the RSST (15 psig).

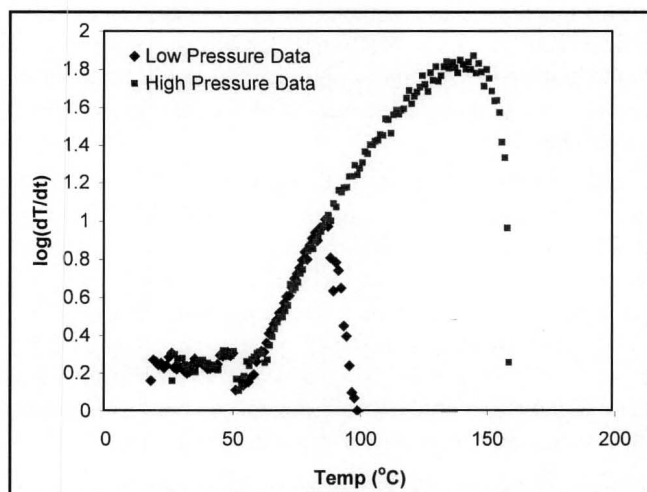


Figure 6. Typical heat rates for low (15 psig) and high (150 psig) pressure obtained for the methanol/acetic anhydride reaction in the RSST.

TABLE 5
Summary of Typical Vent-Sizing Results for the Methanol/Acetic Anhydride System

Tempering Temperature ($^\circ\text{C}$)	Self-Heat Rate (at Tempering) ($^\circ\text{C}/\text{min}$)	Set Pressure (psia)	Reactant Charge (kg)	Vent Area Hand Calc. (in^2)	Vent Area VSSP (in^2)
100.5	20.54	29.7	1500	24.1	11.4

heat rate due to exothermic reaction at the specified set pressure P_s (psia), and F is the flow reduction factor that accounts for piping connected to the relief vent (venting directly to atmosphere has a flow reduction factor equal to one).^[13] Equation (6) assumes two-phase flashing flow and assumes 20% overpressure (absolute) during venting. The

second calculation method used the VSSP. The theory behind VSSP calculations and Eq. (6) is similar and leads to similar results. Figure 7 shows typical VSSP input for the methanol/acetic anhydride system.

Inputs such as set pressure, back pressure, vessel volume and reactant charge are defined in the laboratory objectives (and can be modified for each lab group). Liquid specific heat and density are estimates based on reactant composition at set pressure. Vapor density does not play a significant role in calculations, thus it is assigned a value of $1 \text{ lb}_m/\text{ft}^3$. The Clausius-Clapeyron equation is used by the VSSP when latent heat is set equal to zero, and cross-sectional area and surface tension information are not required for homogenous vessel venting (assumed here). Pressure/temperature data are estimates based on Raoult's law, and dT - dt data points are taken from the graphs generated in Figure 6. Percent overpressure (relative in the VSSP) values are entered arbitrarily, but care should be taken to include an overpressure that corresponds to the hand calculation that assumes 20% absolute overpressure. One of the advantages of using the VSSP software is that plots can be generated, including overpressure vs. vent area and vent area vs. maximum pressure.

The VSSP calculates both a vapor vent size and an ideal vent size; only the former is used for comparison with the hand calculations. Table 5 summarizes the results obtained from the RSST data in Figures 5 and 6 for a field scale vessel with a volume of 1000 gallons and a methanol/acetic anhydride charge of 1500 kg (2:1 mole ratio).

The students compared and discussed the results they obtained from the hand calculation and the VSSP. Typical results for hand calculations for this system (1500 kg reactants, 1000 gal vessel) ranged between 17 and 24 in^2 . VSSP results for the same system ranged between 11 and 13 in^2 . Error in the above results can be attributed to a number of factors. For example, self-heat and tempering values are read visually from charts, and are susceptible to some error. Also, the fact that the low-pressure experiment was not conducted at a constant pressure introduces

VSSP Inputs		VSSP Outputs		VSSP Graph		RD Pipe Sizing		SRV Pipe Sizing	
Title	Group 5								
Set Pressure	2.04841E+05	N/m2	Relief Behavior Type	Homogeneous Vessel Venting					
Back Pressure	1.01386E+05	N/m2	Analysis Type	<input checked="" type="radio"/> Runaway Analysis <input type="radio"/> Constant Heating Q1: 0.00000 kW					
Vessel Volume	3.7854	m3	Runaway Reaction Data Input						
Vessel Charge	1500.0	kg	<input checked="" type="radio"/> Two pairs of dT-dt data points <input type="radio"/> Zeroth Order Kinetics constants						
Liquid Specific Heat	2092.0	J/kg K	dT/dt1	1.830	C/min	T1	63.00	C	
Liquid Density	800.01	kg/m3	dT/dt2	20.54	C/min	T2	100.5	C	
Vapor Density	16.020	kg/m3	Percent OverPressure						
Latent Heat	0.00000	J/kg	1	0.00	5	30.00	9	70.00	
Vessel X-Sectional Area	0.00000	m2	2	5.00	6	40.00	10	80.00	
Surface Tension	0.00000	N/m	3	10.00	7	50.00	11	90.00	
Pressure-Temperature	<input checked="" type="radio"/> Two pairs of P-T data points <input type="radio"/> Two Antoine constants								
P1	3.7244E+04	N/m2	P2	2.0691E+05	N/m2				
T1	50.00	C	T2	105.0	C				

Figure 7. Typical VSSP input data for the methanol/acetic anhydride system.

error in the tempering temperature, and subsequently the self-heat rates. The VSSP and hand calculations both use the original system pressure of 15 psig in the calculation.

The student can also complete a kinetics analysis of the RSST data (this is especially applicable to a course in chemical reaction engineering). First, the students can determine the activation energy using the straight-line data shown in Figure 6. Second, given the kinetics of the reaction, the students can calculate the temperature at which the runaway reaction should begin and compare their calculated results with the experimental data.

The students are expected to answer the following questions in the results and discussion section:

- ▶ What type of system is the methanol/acetic anhydride reaction (vapor, gassy, or hybrid)? How are the data collected used to determine this?
- ▶ What is the tempering temperature of the system?
- ▶ Which relief sizing results (hand or VSSP calculation) should be used? Why?
- ▶ What characteristics of the RSST design might prevent the results from being used for a larger reactor vessel?
- ▶ Will a larger vessel runaway faster or slower than the RSST? Why?
- ▶ Define the following terms and relate each to the RSST experiment: set pressure, back pressure, and maximum allowable working pressure.

Explosions/Relief Design

The purpose of this experiment was to demonstrate the principles of dust and gas explosions. First, a Modified Hartmann Apparatus (Table 2) was used to demonstrate dust explosions and to aid in understanding the dust classification system. Briefly, powder is loaded into a tube and a continuous spark is created from two electrodes

TABLE 6
Dust Explosion Results

Powder	Output	Visual Observation
Flour	0 or 1	Explosion
Cornstarch	1 or 2	Explosion
Baking Soda	0	No Explosion

placed approximately one-half inch apart. Compressed air at seven bar (gauge) is suddenly released, which suspends the powder inside the tube and over the spark. An explosion (*i.e.*, a sudden flash of fire) occurs under the proper conditions. Measurements are taken during the explosion and the output from the control box is 0, 1, or 2. If the output is a 1, then the dust is classified as a St-1 class dust. Anything other than a 1 means that more sophisticated equipment is needed to determine the classification. Dusts are classified into St classes based on their deflagration index, K_{St} . The K_{St} for a dust increases as the robustness of its explosion increases.^[8] Three powders were tested—flour, cornstarch, and baking soda, in the amount of 1200 mg each. Results are summarized in Table 6.

The following questions were answered in the discussion part of the report.

- ▶ *When do dust explosions occur?*
- ▶ *What characteristics must a dust have to be explosive?*
- ▶ *What are the typical lower and upper explosion limits for dusts?*
- ▶ *What were the physical differences between the three powders and how did these attribute to whether or not they created an explosion?*
- ▶ *Describe the classification system of dust explosions.*

The second part of the experiment used the Flame Tec flammability limits and data acquisition system (Table 2) to examine gas phase explosions. Pressure-time and temperature-time data were collected for a propane explosion. A propane concentration of 4.5% was used, which is equivalent to a partial pressure of 0.7 psi propane in the vessel. The pressure-time data collected can then be used to calculate the gas deflagration index K_g for propane using the "Cubic Law"

$$K_g = (dP/dt)_{\max} V^{1/3} \quad (8)$$

where V is the vessel volume and $(dP/dt)_{\max}$ is the maximum rate of pressure increase. It should be noted that K_g for a given material is dependent on several factors, including the composition of the material, mixing in the vessel, the vessel shape, and the energy of the ignition source.^[8] The pressure-time data can also be used to scale up the effects of an explosion to a field-scale vessel.

In addition to the above, the following questions were answered in the laboratory report.

- ▶ *What is the concentration of the propane in the vessel? Is it inside the flammability range for propane?*
- ▶ *Was the explosion in the vessel a detonation or a deflagration? Why?*
- ▶ *Calculate the K_g for propane.*
- ▶ *Under what conditions would the results of this experiment not represent actual process results?*

CONCLUSIONS

Chemical process safety has become a critical component of chemical engineering education, *e.g.*, it is very important to industry and is required by ABET 2000. The importance of chemical process safety in the undergraduate education of chemical engineers is certainly consistent with having a course, preferably required, dedicated to this topic. In the absence of a dedicated course, however, it is essential that safety concepts (flammability characteristics, electrostatics, runaway reactions, explosions, and relief design, be incorporated somewhere in the undergraduate curriculum. The experiments described herein provide a means for introducing these important topics into the curriculum in a hands-on manner that is known to enhance the learning process.

ACKNOWLEDGMENTS

The authors acknowledge the financial support provided by the National Science Foundation (DUE 96-50491) and matching funds provided by Praxair, 3M, Monsanto, Cargill, and the University of Iowa College of Engineering. They also thank Daniel A. Crawl, Michigan Technological University, for his thoughts on electrostatics experiments and for critical review of this manuscript.

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