CASE STUDIES IN THE APPLICATION OF DIERS VENTING METHODS
TO FINE CHEMICAL BATCH AND SEMI-BATCH REACTORS

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The applicability of emergency relief to batch type
reactions in the fine chemical manufacturing industry is
discussed. An outline of the key factors which
influence the selection of this form of protection is
also suggested. Reaction parameters measured using in-
house calorimetry are compared to those using DIERS
procedures, for vapour pressure and gas generating
systems. From case studies, a comparison of DIERS and
the former Factory Insurance Association (FIA) vent
sizing methods has also been made.
Keywords: Relief, Runaway, DIERS, Venting, Reactor, Batch.

1) INTRODUCTION

The chemical industry is required to provide safety systems that
control any hazard that could result from the process becoming uncontrolled
and developing into a runaway reaction.

Safety can be achieved by process control, relief venting,
containment, crash cooling/drown out or reaction inhibition (1). Process
control and relief venting are the most commonly used means of achieving
safety in manufacture.

A number of techniques (area/volume scaling, mathematical
modelling using reaction parameters and flow theory, empirical methods
(e.g. F.I.A.) (2)) have been used to size relief systems. A systematic
study of relief sizing for reactors has been carried out by the Design
Institute for Emergency Relief Systems (D.I.E.R.S.) (3) and procedures have
been produced that can be used to size relief systems directly from
laboratory tests.

Features of batch and semi-batch processing include complex
chemistry, multiproduct usage, variety of vessel sizes, interconnection
of equipment, high density siting and limited safe discharge zones
particularly in existing plants.

Selection of relief venting as the basis for safe operation
requires consideration of the following:

a) Compatibility of relief venting with the design and operation
of the plant/process.

b) The certainty with which the "worst case" situation can be
identified.

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c) The reaction type.

d) Means of measuring the reaction parameters during the runaway reaction.

e) Relief sizing procedures.

f) Design of the relief system including discharge ducting, safe discharge area.

This paper considers the above for batch and semi-batch reactors of the type used in fine chemical manufacture; applies the DIERS techniques to typical situations and compares the resultant vent sizes with those obtained using the former FIA method.

2) COMPATIBILITY OF RELIEF VENTING WITH PLANT/PROCESS

At an early stage in the relief design it is necessary to consider the ramifications of selecting this option for process safety.

The maximum pressure acceptable in a relief situation is governed by the plant item with the lowest design pressure. Weak structures with little pressure strength but interconnected to the reaction vessel (e.g. glass condensers) may give rise to significant oversizing of the vent in order to keep the pressure to a tolerable level. In this respect, the operating procedures of the process (e.g. control valve sequence, etc.) need to be examined to identify all sections of plant which can be subjected to the reactor pressure under runaway conditions.

In the fine chemicals manufacturing industry, vessel designs and configurations vary considerably, ranging in size from 1-20 m^3. Such a variation can cause problems in both the design and siting of downstream equipment such as scrubbers, knock-out pots, etc.

3) DEFINING THE WORST CASE SCENARIO

The first stage in reactor vent design involves a comprehensive study of the process chemistry and operations to define the main areas of risk. This is the most crucial step in the design of an emergency relief system. For example, maloperations can arise from one or a combination of circumstances such as:

- incorrect charging sequence

- agitator failure leading to layering

- contamination of reactants (e.g. exposed metal)

- addition of reactants too quickly

- delayed addition (occurrence of side reactions)

- temperature too low leading to accumulation

- temperature too high caused by cooling failure

- incorrect reactant concentration (recycling)

- removal of volatile diluents leading to increased rates of reaction.

Details of a typical assessment procedure have been given in a previous paper in this symposium (Ref.1).

It is on the result of this assessment that the basis of the relief design will be made.

4. REACTION TYPE

In terms of reactor venting, reactions essentially fall into three categories:

a) Vapour pressure

b) Hybrid (gas + vapour)

c) Non-condensible gas

The significance of this classification in terms of relief is that, once the vent has opened, both vapour pressure and hybrid reactions temper by losing enough heat through vaporisation, to maintain temperature and pressure at an acceptable level. In a gas generating system there is little or no control of temperature during venting so that relief sizing is based on the peak gas generation rate.

Experimental test procedures must not only be able to differentiate between the reaction types but also simulate large scale process conditions. Observations made during experimental work can also be important in the design of the relief system indicating for example, frothing or swelling, gas generation, immiscible layers, high viscosity, etc.

a) Vapour Pressure Systems

In this type of reaction, no permanent gas is generated. As such, it is the rate of temperature increase (i.e. power output) between the set pressure and the maximum pressure acceptable, which determines the vent size and not the peak rate. It should be recognised that due consideration should be given to the solvent mixtures in this type of reaction since it is the vapour pressure which governs the temperature and therefore reaction rate at disc rupture.

b) Hybrid Systems

In this type of reaction, the increase in pressure arises from the formation of non-condensable gas in addition to the vapour pressure of the solvent. However the reaction may still be moderated by removing heat through vaporisation. It is important to examine whether the solvent is acting purely as a diluent, since a single phase vapour release on plant scale may give rise to a thermal decomposition as the solvent boils off.

c) Gassy Systems

In gassy systems, the exothermic heat release is largely retained in the reaction mass since the cooling potential of volatile materials is not available. As a result, both the maximum temperature and maximum gas generation rate can be attained during venting. It is important to recognise in these situations, there is a risk of exceeding the associated design temperature of the reaction vessel.

A survey of processes within the Fine Chemical Manufacturing Organisation of ICI has been made to categorise the number of each reaction type. Data show that historically, gassy reaction systems predominate due to established processes such as nitrations, diazotisations, sulphonations, etc. More recently however, the chemistry has changed to solvent based so that now a high proportion of vapour pressure reactions exists. Very few vapour pressure systems have been identified which also generate permanent gas i.e. hybrid type.

5) DETERMINATION OF REACTION PARAMETERS

5.1. Test Methods

The experimental test procedures must be capable of simulating large scale plant conditions in terms of both thermal inertia and operating sequences (e.g. rate of addition, contaminants, etc.) Data are required that reflect the worst case process conditions at the runaway stage.

The bench-scale equipment for vent sizing developed initially for DIERS by Fauske & Associates (FAI) is currently sold as a package (VSP). Over recent months, there have been many references to this apparatus in the open literature - a detailed description is given in reference 3. Essentially the apparatus permits the measurement of a variety of relief design parameters such as gas generation rates, flow regime, heat generation rates, etc., at laboratory scale. Within ICI however, the assessment of runaway reaction hazards is based on a series of thermal stability tests ranging in size from 10 g to 1000 g.

Traditionally, low heat loss conditions in chemical reactors have been simulated by the use of dewars. However this is only valid for reactors up to 2.3 m³ and new techniques based on adiabatic dewar calorimetry have been developed within the company (ref. 4) that permit data to be obtained relevant to reactor capacities in excess of 25 m³.

A schematic diagram of the adiabatic pressure dewar apparatus is shown in figure 1. The apparatus comprises a stainless steel dewar fitted with mechanical stirrer, bursting disc, thermocouple, pressure transducer and electrical heater. Provision can also be made for remote addition of chemicals during the test sequence. In adiabatic mode heat loss to the surroundings is less than 2°C per day, i.e. equivalent to 0.04 Watts/litre.

The peak pressure in the system is limited by the mechanical seals but typical values exceed 500 psig (i.e. beyond the point of interest usually). The thermal inertia of the test vessel is similar to the DIERS cell. A low phi factor is essential to simulate low

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heat loss bulk conditions in the equilibrium process and at the early stages of runaway. At rapid rates of temperature rise, the influence of phi is reduced.

In essence, the test procedure and evaluation of data is analogous to the sealed (closed) DIERS experiment.

The pressure dewar can also be used for hybrid and gassy reactions, by means of a containment vessel (approx. vol. 3 litres). The experimental procedure is similar to the DIERS open cell test whereby the relief device operating pressure is superimposed on the dewar. In a solvent based reaction, the onset of gas generation (if any) is identified by a discontinuity in the pressure/temperature profile.

In-house equipment for measuring the rate of gas generation during exothermic decomposition is based on an accurate pressure measurement and volume displacement. A schematic diagram of the apparatus is shown in Figure 2.

The apparatus comprises a U-tube vented at the top of each leg and a gas inlet. The solenoid valve at the top of the unit is controlled by the strain-gauge pressure transducer fitted to the base of the tube in the liquid space. As gas is introduced into the equipment, the column of liquid is displaced to increase the static head pressure on the transducer. At a preset level, the solenoid valve is energised for a short period to allow the gas to vent and the liquid to equilibrate before the valve closes and the next cycle begins. The size of U-tube can be varied to accommodate different rates of gas evolution.

5.2. Comparison of Test Methods

Two vapour pressure reactions and one gassy system have been tested in the Fauske apparatus and the results obtained compared with those from 'in-house' tests.

5.2.1. Vapour Pressure Systems

The two vapour pressure systems studied, were Styrene and Methanol/Acetic Anhydride.

5.2.1.1. Styrene

The thermal polymerisation of styrene monomer inhibited with 12-15 ppm t-butyl catechol was examined in the pressure dewar test. The styrene sample was heated rapidly to 150°C and then allowed to thermally runaway, simulating the DIERS experiment described in FAI report number 83/43.

Figures 3 and 4 show the temperature/time and pressure/time characteristics of the reaction, respectively. The data show good agreement except for the 'shift' with respect to time. This is probably due to the difference in thermal inertia of the two systems.

A comparison of heats of reaction (corrected for phi) is shown below,

$$\Delta H_r \text{ (kcal/mole)}$$

I.C.I.	-17.7
FAUSKE	-15.0
STULL (ref. 5)	-17.8

The heats of reaction ΔH_r have been corrected for thermal inertia using the equation.

$$\Delta H_r = \emptyset . C_p . \Delta T_{max}$$

where $\emptyset$ is the phi factor or ratio of heat capacity of the sample plus container to the heat capacity of the sample alone.

C_p is the specific heat of the reaction mass.

ΔT_{max} the maximum temperature rise observed.

The difference in maximum temperatures and thermal inertias between the two systems is given below.

	T_{max}	$\emptyset$
I.C.I.	375	1.26
FAUSKE	379	1.05

The kinetics of the reaction in both systems have been studied and the results are plotted in figure 5. The rate constant was determined using the equation shown below.

$$K = \frac{dT}{dt} \times \frac{Tmax - To}{Tmax - T}$$

Where Tmax - To is constant, K can be expressed as

$$K = \frac{dT/dt}{Tmax - T}$$

ICI data show good agreement with both the DIERS results and that in the open literature.

5.2.1.2. Methanol/Acetic Anhydride

The thermal runaway of the stoichiometric mixture of methanol and acetic anhydride was examined in the pressure dewar, from a start temperature of 25°C. The system was also studied by Fauske & Associates Inc. with DIERS techniques, using identical chemicals (ref. 6).

Figures 6 and 7 show the temperature/time and pressure time characteristics of the reaction, respectively. The data exhibit the same characteristics as for the styrene reaction in that a 'shift' with respect to time is evident between the two tests.

The calculated heats of reaction corrected for the thermal inertia of the test cells, shown below, are in good agreement

$$\Delta H_r \text{ (kcal/mole MeOH)}$$

I.C.I.	-6.62
FAUSKE	-6.33

Also the kinetic data from the two systems show excellent reproducibility as shown in Figure 8.

5.2.2. Gassy System

A sulphonation reaction mass was used for this comparison which is an intermediate typical of many sulphonated intermediates used in dyestuffs chemistry. However this particular reaction mixture exhibits extremely high rates of gas generation and is foaming/frothing in nature during decomposition. It was because of the extreme properties of this material that a comparison of tests was made. The direct scaling method was of particular interest.

The maximum rate of gas evolution exceeds the capacity of the ICI test equipment even for relatively small quantities of material. However using simple gas displacement techniques, the maximum rate of gas generation was measured to be in excess of 4 ml/g/s.

A direct comparison of measured gas evolution rates was not possible with the DIERS method because the high rates precluded the use of the normal DIERS procedure for gassy systems. In fact because of the "natural foaming" nature of the reaction, area to volume scaling was more applicable.

The temperature-time relationship from the DIERS direct scaling test is shown in Figure 9. At a temperature of 190°C (approx.) temperature and pressure increased rapidly, peaking at 410°C and 300 psig.

One problem which can occur using direct scaling techniques in fine chemical manufacture is flow restriction or blockage in the small scale vent caused by slurries/solids in the reaction mass. By necessity the small scale vent in a 120 ml test cell is typically 1-2 mm in diameter (i.e. 20-40 cm for a 5 m^3 reactor). Therefore in certain situations this could give rise to considerable oversizing. However, in contrast, direct scaling takes account of mass loss via the vent (provided discharge is two-phase) and as such the cell (reactor) may never be subjected to the peak gas generation rate.

8) CALCULATION OF VENT SIZES

6.1. Vapour Systems

A comparison of the vent requirements was made for both the methanol/acetic anhydride reaction and the styrene polymerisation, varying overpressure in the range 0-40%. Using identical vessel parameters (fill ratio, relief temperature, reactor volume, etc.) the mean power output of the reaction at each pressure was calculated and the vent size determined from the formula for 2-phase homogeneous flashing flow (ref.7). The results are tabulated below and represented graphically in Figures 10 and 11.

a) ICI Data

Over Pressure (% g)	Pressure Rise (psi)	Max. Temp (°C)	$(d_T/d_t)m$ (°C/min)	Mean Heat Output (W/kg)	Calculated Vent. Dia. (cm.)
0	0	110	31	1007	20
5	1.5	111.6	32.6	1036	11
10	3.0	113	35	1071	9.7
20	6.0	115	37	1105	8.6
40	12	119.2	48	1288	7.6

b) FAUSKE Data

Over Pressure (% g)	Pressure Rise (psi)	Max. Temp (°C)	$(d_T/d_t)m$ (°C/min)	Mean Heat Output (W/kg)	Calculated Vent. Dia. (cm.)
0	0	108	31	1013	17.5
5	1.5	109.1	32	1029	10.7
10	3.0	110	34	1062	9.4
20	6.0	112	36	1094	8.1
40	12	115.4	41	1176	6.9

Tables 1a & 1b - Comparison of ICI and FAUSKE Vent Requirements (excluding vent pipe) for Methanol/Acetic Anhydride

a) ICI Data

Over Pressure (%g)	Pressure Rise (psi)	Max. Temp (°C)	$(d_T/d_t)m$ (°C/min)	Mean Heat Output (W/kg)	Calculated Vent. Dia. (cm.)
0	0	160	5.0	263	16.7
5	1.5	164	5.3	272	8.7
10	3.0	167	6.0	290	7.8
20	6.0	173	7.5	326	6.9
40	12	182	12.0	448	6.7

b) FAUSKE Data

Over Pressure (%g)	Pressure Rise (psi)	Max. Temp (°C)	$(d_T/d_t)m$ (°C/min)	Mean Heat Output (W/kg)	Calculated Vent. Dia. (cm.)
0	0	160	5.0	225	15.4
5	1.5	164	6.0	246	8.3
10	3.0	167	7.5	279	7.6
20	6.0	173	9.7	325	6.8
40	12	182	13.3	403	6.4

Tables 2a & 2b - Comparison of ICI and FAUSKE Vent Requirements (excluding vent pipe) for Styrene

The tables show a good correlation between data derived from both sources. Figures 10 and 11 indicate that at high overpressures, the reduction in vent size is negligible. This is because the vent capacity (G) is calculated at relief conditions whereas the power output is averaged over the range of overpressure. However a significant reduction in vent size can be achieved for a small increase in overpressure as shown.

6.2. Gassy System

A comparison of data for the gassy system shows by both methods (ICI and FAUSKE), that the thermal decomposition of this material is too rapid to consider emergency relief as a viable safety measure.

The direct scaling test (FAUSKE) on an area/volume basis scales to a vent size of 2.5 m diameter on a 13.5 m^3 reactor and the peak pressure of 300 psig still exceeds the vessel design pressure.

Substituting the relevant data from ICI tests into the DIERS formula for gassy systems gives a vent size in excess of 2.1 m which confirms that reactor relief is impracticable - on plant scale the peak gas generation rate is at least 48 m^3/s at N.T.P.

7) COMPARISON OF VENT SIZE (DIERS AND FIA)

A comparison has been made of the vent sizes obtained using kinetic data generated by the ICI tests and the DIERS calculation methods with sizes based on the empirical method prepared by the former Factory Insurance Association (2). Although this method has been withdrawn from the Engineering Procedures of the Industrial Risk Insurers (IRI), successors to FIA, it was the basis for the design of many existing vents. It should be recognised that the FIA method relief size is a function of heat of reaction and not rate of reaction, and this is no longer a recommended method.

Reaction	Reaction Category	Vessel Vol. (m^3)	Vent Diam. (cm)	FIA Method (cm)
Methanol/Acetic anhydride	C+	0.6	10	9
Polymerisation of butyl acrylate	C-	5.4	11	20
Arcton 113/113A	C-	2.3	11	9
Thiophene Intermediate	C-	6.3	16	20
Condensation/ cyclisation	B+	11.8	15	20
Dyeing Binder copolymerisation	C-	12.0	16	25
Paint resin manufacture	C-	12.5	10	28
Polymerisation reaction	B+	10.9	15	20

TABLE 3   COMPARISON OF PREDICTED VENT DIAMETERS (NO VENT PIPE) USING DIERS AD FIA METHODS

The table shows that, for short vent lines, in the majority of cases the FIA method produced a larger vent size. In the examples where a smaller vent size is estimated by the FIA method, the vent diameters are still similar.

This comparison suggests that vents sized by the former FIA method are not catastrophically unsafe. In fact in the majority of cases this method oversizes.

8) DISCHARGE SYSTEM

8.1. Design of the Vent Pipe

The nature of the discharging fluid is of prime importance in the determination of relief area. Both DIERS and ICI techniques are capable of discriminating between systems which exhibit "natural" surface-active foaming and those which do not, but there is sometimes sufficient operating experience to determine this without tests. However an important finding of the DIERS work is that very small quantities of impurities can have a marked effect on the flow regime in the reactor. Indeed, a variation in impurity level could arise by simply changing the supplier of a particular raw material. Therefore, in general terms, it is prudent to size emergency relief on homogeneous vessel behaviour i.e. 2-phase flow.

In certain situations pressure relief during a runaway can result in a three phase discharge if solids are suspended in the reaction liquors. Solids can also be entrained by turbulence caused by boiling/gassing in the bulk of the liquid. Care is needed therefore in sizing relief for this type of system particularly where there is likely to be a significant static head of fluid in the discharge pipe.

Other considerations in the design of the relief system include the possibility of blockage in the vent line. This could arise for example, from solidification of process material in cooler sections of the reactor. It is important to consider all conceivable discharge regimes when designing the discharge pipework.

8.2. Safe Discharge

Many existing vessels fitted with overpressure protection vent directly to roof level. Where such devices, often relief valves, protect only against common process misadventures and not runaway reactions, the quantity of material ejected and rate of discharge are low, frequently resulting in good dispersion.

The use of bursting discs however, can result in large quantities of material being discharged, possibly up to 95% of the reactor contents for inherently foamy systems.

The discharge of copious quantities of chemicals directly to atmosphere can give rise to secondary hazards, particularly if the materials being ejected are toxic or capable of forming flammable atmospheres (vapour or mist) in air. Therefore the provision of a knock-out device (scrubber, dump tank, etc.) which may need to be of considerable size to contain the aerated/foaming fluid, will frequently be necessary.

The ejection of particulate material at high velocity into downstream vessels can give rise to the formation of electrostatically charged mist. Furthermore, in the presence of flammable atmospheres, this can introduce a risk of ignition so that in certain cases, precautions will be necessary to protect downstream vessels from explosion damage. Where oxygen is liberated during the reaction/decomposition conventional safety measures such as explosion relief/suppression will not be suitable.

In fine chemical manufacturing, the non-availability of a safe discharge area for existing plant/processes added to the cost of secondary protection often may preclude reactor venting as a viable safety measure – the basis for safe operation is then process control using trips/interlocks of suitable integrity.

9) CONCLUSIONS

a) Existing techniques i.e. adiabatic dewar calorimetry and gas measurement, produce results that are in accord with DIERS procedures and can provide the necessary information for vent design purposes.

b) DIERS systems based on experimental data and equations provide a basis for reactor vent design. There is no reason to doubt the validity of the scaling method provided it is known that vessel flow conditions can be scaled – this may not be true if solids are present.

c) The relationship between the vent sizes obtained from DIERS and the former FIA method is not reliable. However there is nothing to date, to suggest that existing systems with short vent lines, sized by FIA are catastrophically unsafe.

d) The advantage of DIERS is that it can differentiate between reaction types and it has a more logical basis than for example the FIA method. However it is important that the process reaction is fully analysed, measurement of vent parameters should not be done in isolation but as part of a detailed assessment of the hazards of the processes.

e) In the context of fine chemical plants, the provision of a safe discharge area remains the major obstacle in adopting venting as the basis for safe operation.
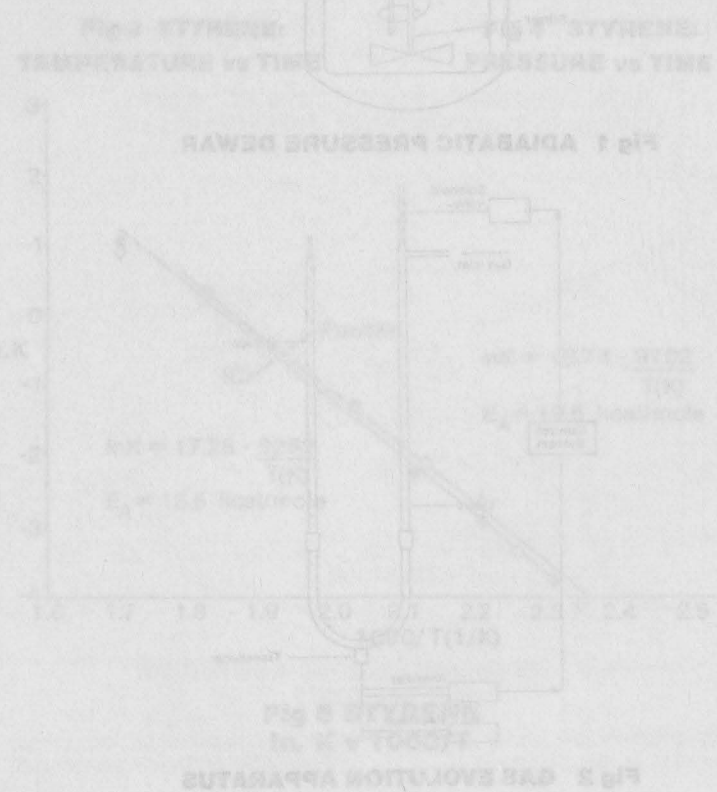
Acknowledgement

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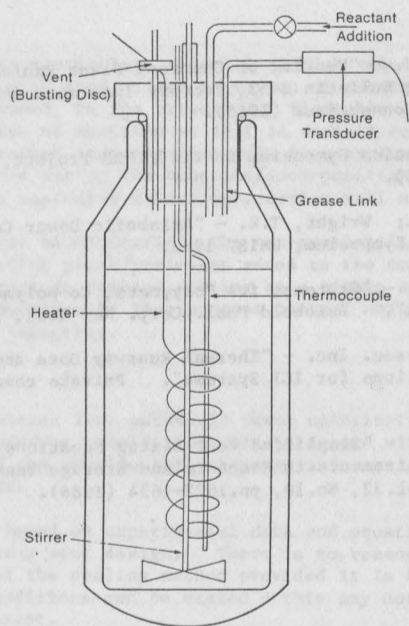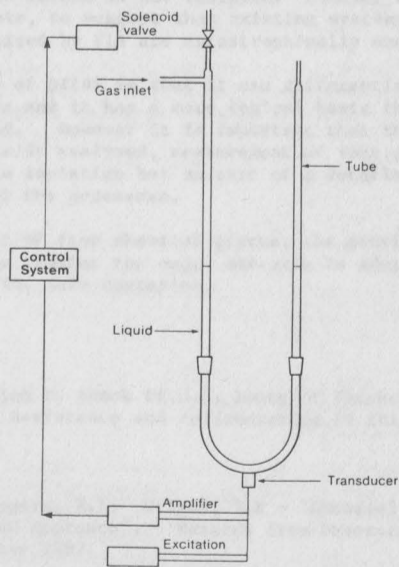
Fig 1 ADIABATIC PRESSURE DEWAR

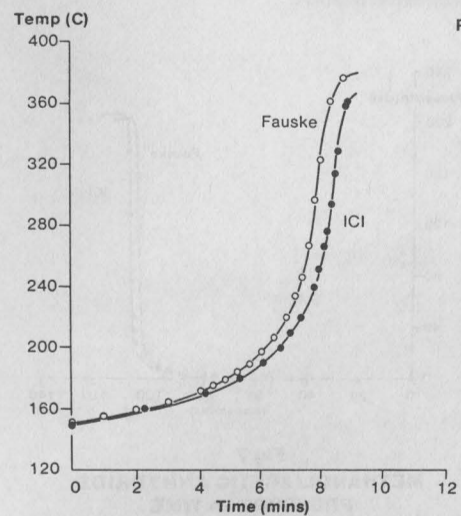Labels: Reactant Addition, Vent (Bursting Disc), Pressure Transducer, Grease Link, Thermocouple, Heater, Stirrer

Fig 2   GAS EVOLUTION APPARATUS

Labels: Solenoid valve, Gas inlet, Tube, Control System, Liquid, Transducer, Amplifier, Excitation

Fig 3 STYRENE: TEMPERATURE vs TIME

Temp (C) vs Time (mins). Curves labelled Fauske and ICI.
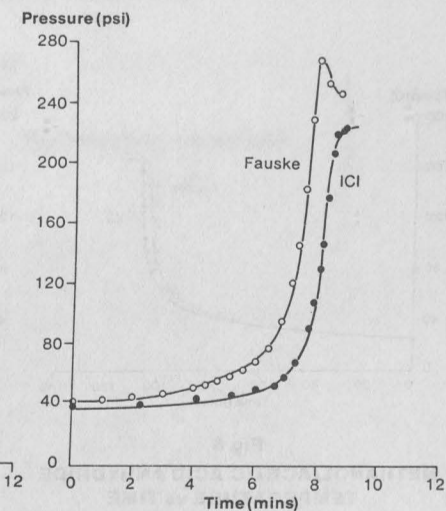
Fig 4   STYRENE: PRESSURE vs TIME

Pressure (psi) vs Time (mins). Curves labelled Fauske and ICI.

$$\ln K = 18.74 - \frac{9762}{T(K)}$$

$$E_A = 19.5 \text{ kcal/mole}$$

$$\ln K = 17.28 - \frac{9262}{T(K)}$$

$$E_A = 18.5 \text{ kcal/mole}$$

ln.K vs 1000/T (1/K). Curves labelled Fauske and ICI.
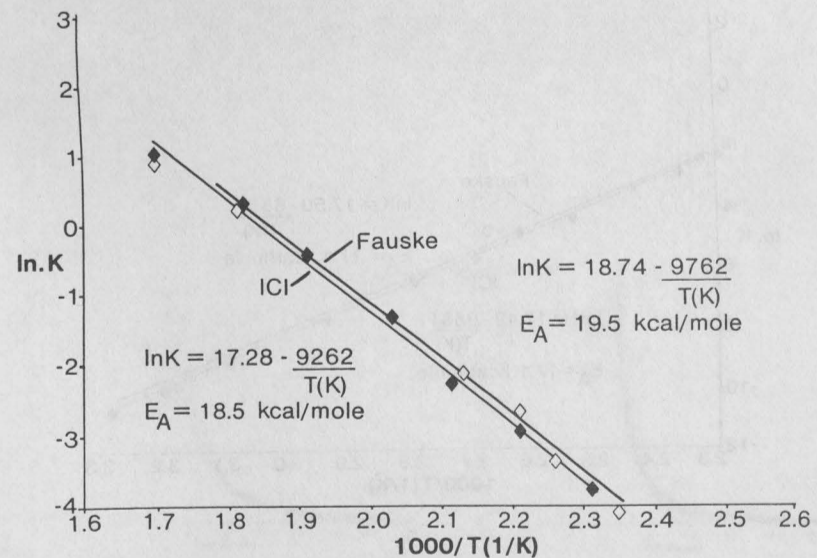
**Fig 5 STYRENE
ln. K v 1000/T**
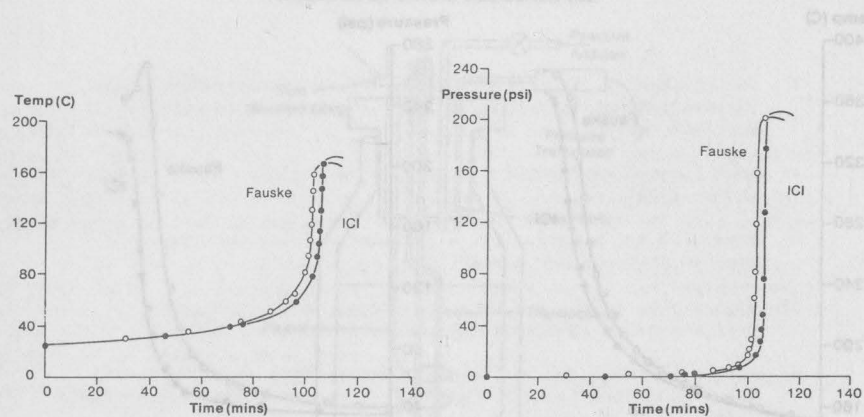
Fig 6
METHANOL/ACETIC ACID ANHYDRIDE
TEMPERATURE vs TIME
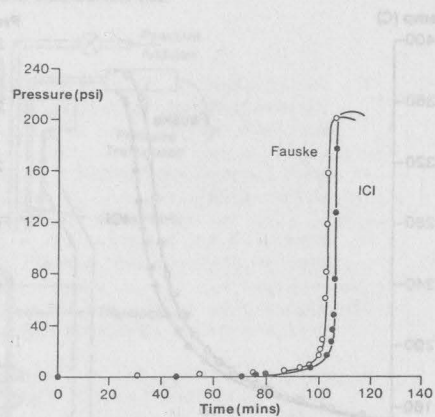
Fig 7
METHANOL/ACETIC ANHYDRIDE
PRESSURE vs TIME

$$\ln K = 17.59 - \frac{8557}{T(K)}$$
$$E_A = 17.1 \text{ kcal/mole}$$

$$\ln K = 17.49 - \frac{8581}{T(K)}$$
$$E_A = 17.1 \text{ kcal/mole}$$
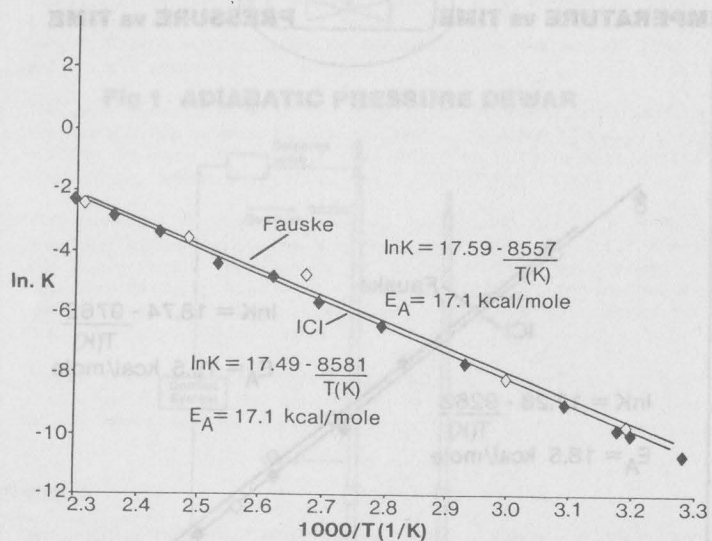
Fig 8   METHANOL/ACETIC ANHYDRIDE
In.K vs 1000/T

Self-heating observed

Heat - Wait - Search

Heat up
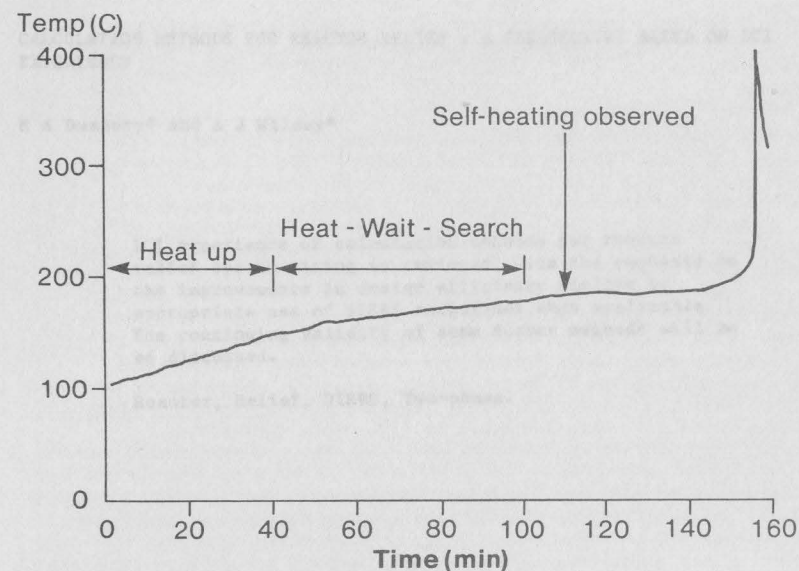
Fig 9   TEMPERATURE - TIME DATA FOR
SULPHONATION INTERMEDIATE (FAUSKE)
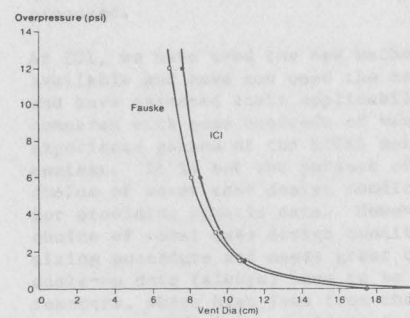
Fig 10 METHANOL/ACETIC ANHYDRIDE

Fig. 11 STYRENE POLYMERISATION

Fig 10
METHANOL/ACETIC ANHYDRIDE
OVERPRESSURE vs VENT DIA
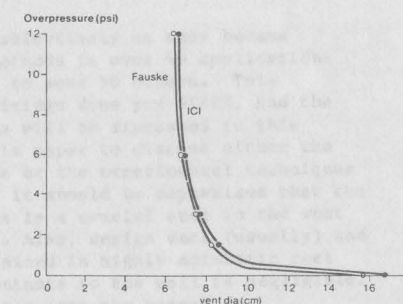
Fig 11
STYRENE POLYMERISATION
OVERPRESSURE vs VENT DIA