

## DEWAR SCALE-UP FOR REACTIVE CHEMICAL WASTE HANDLING

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The use of non-pressurised Dewar flasks has been proposed by some parts of the chemical waste treatment industry to determine the exothermic reaction incompatibility of mixtures. Temperature rises of between 6–10°C in the Dewar vessel over a period of 10 minutes have been suggested by the industry as criteria to indicate an exothermic reaction of concern. This paper reports work sponsored by the Health and Safety Executive (in discussion with the Environment Agency) to investigate the limits of this method for scale-up to vessels typically used in the waste treatment industry.

A literature review of the specific heat losses from Dewar flasks and large-scale vessels is compared to specific heat losses of Dewar flasks measured experimentally. Typical values of thermal characteristics of large-scale vessels used in the waste industries have also been assessed. The specific heat loss in the Dewar flask and large vessels are very different. Scale-up limits of four types of Dewar have been calculated for different values of overall heat transfer coefficients for large-scale vessel.

Thermal behaviour of exothermic reactions in a Dewar flask has been compared to that predicted in large vessels using reaction kinetics and heat transfer models. For fast and highly energetic reactions the reaction energy release rate can be significant compared to the heat losses and the Dewar flask can detect runaway reactions. However, for low energy reactions or reactions with long induction time, the heat losses can be significant compared to the heat release rate and the Dewar test can then miss exotherms or give non-conservative results.

It appears that the 6–10°C criterion proposed by the waste treatment industry might be observed when the heat losses do not have a significant importance compared to the reaction heat release rate. However, the reaction completion time at large scale would be shorter than at the Dewar scale. In some cases, 10 minutes might be sufficient to detect the exotherm but not the runaway reaction. The test should therefore be run to reaction completion in order to fully detect exotherms. **Reliable conclusions about the scale-up of Dewar data can be obtained when the chemical reaction kinetics are well known. Unfortunately this is not generally the case in the waste-treatment industry. So, unless the specific heat loss of the Dewar has been shown to be less than large-scale vessels, this method in isolation is likely to be unreliable for scale up to large vessels.**

KEYWORDS: Dewar flask, waste treatment, runaway reaction

### 1. INTRODUCTION

In some parts of the waste treatment industry, part of the procedures used by some companies to assess exothermic reaction incompatibility of mixtures is to use non-pressurised Dewar

flasks. The Dewar calorimeter is a flask containing a vacuum jacket that minimises the heat losses from a reacting mass to the surroundings. The results of these tests have been applied directly to quite large vessels. Temperature rises of between 6–10°C in the Dewar vessel over a period of 10 minutes have been suggested by the industry to indicate an exothermic reaction of concern, with gas bubblers being attached to such flasks to detect any gas generation.

The objective of this research was to investigate the range of applicability of the Dewar flasks in assessing thermal hazards. This was undertaken in three steps:

- a) Thermal characteristics of Dewar flasks were gathered from literature and measured experimentally.
- b) The limits of the use of Dewar flasks were calculated for different values of overall heat transfer coefficients for large-scale vessel.
- c) The thermal behaviour of two exothermic reactions in a Dewar flask were compared to that predicted in typical large-scale vessels used in the waste treatment industry using reaction kinetics and heat transfer models.

The use of Dewar flasks is recommended in the United Nations “Recommendations on the Transport of Dangerous Goods” (ST/SG/AC.10/11/ Rev.4)<sup>1</sup> to simulate transport packaging. The criterion used for the scale-up is the specific heat loss, noted as  $\dot{q}_{loss}$  (W.kg<sup>-1</sup>.K<sup>-1</sup>):

$$\dot{q}_{loss} = \frac{UA}{m} \quad (1)$$

This criterion can be understood as the cooling potential of a vessel showing a Newtonian cooling behaviour. Several authors<sup>2,3</sup> have demonstrated that this method is suitable in the case of a well-stirred tank, showing a homogeneous temperature distribution. Homogeneous systems were therefore investigated as a first approximation. The scale-up theory in the case of pure solids, high viscosity liquids or slurries, is much more complex, as the heat transfer is governed by the bulk material and not by the package or the vessel<sup>3</sup>. This makes such heterogeneous systems even more difficult to scale up.

## 2. THERMAL CHARACTERISTICS OF DEWAR FLASKS

Thermal characteristics of Dewar flasks have been gathered from the literature sources (see Table 1). These data were compared to experimental measurement of thermal characteristic of two commercial Dewar flasks.

### 2.1 DATA FROM THE LITERATURE

Table 1 presents some thermal data (including the specific heat losses values) for different types and arrangements. The general orders of magnitude of the specific heat loss are:

- 500 ml Dewar flask (unknown material): between 0.04 and 0.077 W.kg<sup>-1</sup>.K<sup>-1</sup>
- 1000 ml glass Dewar flask: 0.018 W.kg<sup>-1</sup>.K<sup>-1</sup>
- 1000 ml stainless steel Dewar flask in adiabatic oven: 0.195 W.kg<sup>-1</sup>.K<sup>-1</sup>

Table 1. Dewar flask thermal characteristics

Type of Dewar	Volume	Thermal inertia factor $\phi$	Specific heat loss $\dot{q}_{loss}$	Cooling rate	Heat transfer coefficient or conductivity	Source
Cylindrical (filled with 400g of asphalt salt mixture)	0.5 litre	1.89 ( $C_p = 840$ J/K/kg)	0.03 W//K	—	$\lambda = 1.46$ W/K/m	4
Cylindrical	0.5 litre	—	0.04 W/kg/K	—	$U = 0.6$ W/m <sup>2</sup> /K	2
Cylindrical (filled with 400 ml of water)	0.5 litre	—	Between 0.062 to 0.0768 W/kg/K	—	—	5
Glass cylindrical + cork bung	0.5 litre	—	0.03 W//K	1.6 K/hr	—	6, 7
Glass cylindrical + rubber bung	0.5 litre	$1.05 < \phi < 1.5$	—	2 K/hr	—	—
Cylindrical Sensitivity = 0.01 K/min $P_{max} = 35-50$ bar, $T_{max} = 300^\circ\text{C}$	1 litre	$1.1 < \phi < 1.2$	—	—	—	8
Glass cylindrical	1 litre	—	0.018 W/kg/K	—	—	9, 10
Stainless steel cylindrical in adiabatic oven	1 litre	—	0.195 W/kg/K	—	—	—
Spherical + PTFE bung	1 litre	1.34	—	0.8 K/day	$\lambda = 0.18$ W/K/m	11

## 2.2 EXPERIMENTAL MEASUREMENTS

As indicated in Table 1, the thermal characteristics of a Dewar flask will depend on its construction and experimental configuration. Literature data have been compared to experimental measurements of the specific heat losses for two unstirred commercial Dewar flasks (Table 2):

- “1 litre glass Dewar in a stainless steel container” which can be closed by a clipped on vacuum lid.
- “1 litre stainless steel Dewar” which can be closed by simple stainless steel lid (without vacuum). A layer of insulating polymer is stuck on the internal surface of the lid.

The flasks were placed on a laboratory table (not in a temperature controlled oven) and filled with 800g of hot water (70–80°C). Cooling of the water was recorded for both closed and open configurations. Ambient room temperature was also recorded.

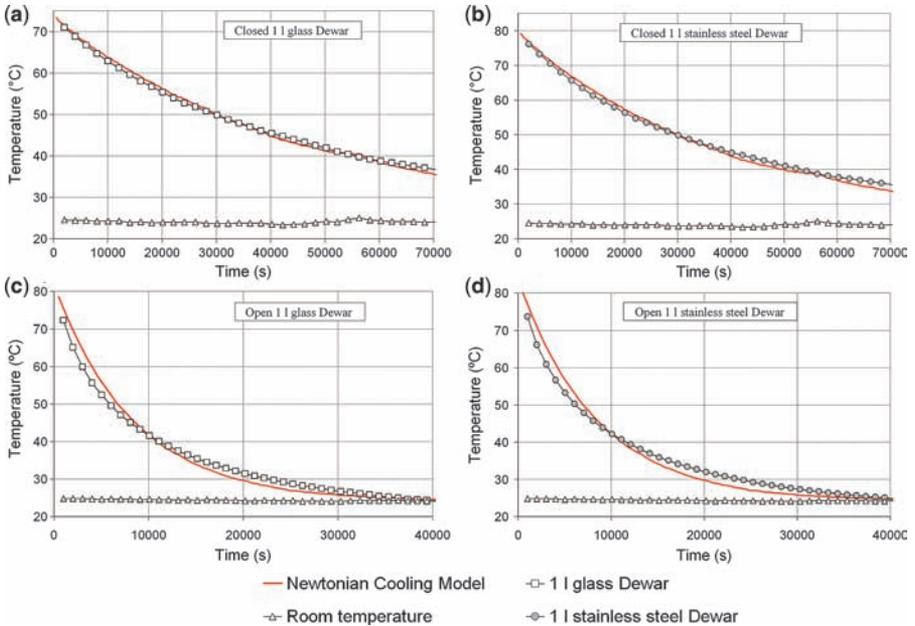
The cooling curves obtained were then used to assess the specific heat loss coefficients for the Dewar flasks, using the following Newtonian cooling model:

$$T(t) = (T_{ini} - T_{ext\,ini}) \exp\left(-t \left(\frac{\dot{q}_{loss}}{Cp_l}\right)\right) + T_{ext} \quad (2)$$

Figure 1 (a) and (b) show the results for both glass and stainless steel Dewar flasks in a closed configuration. The experimental cooling curves fit the Newtonian cooling model well, which allows the calculation of the corresponding  $\dot{q}_{loss}$ . As expected, the glass flask (0.086 W.kg<sup>-1</sup>.K<sup>-1</sup>) showed less heat losses than the stainless steel flask (0.103 W.kg<sup>-1</sup>.K<sup>-1</sup>) (Table 2). The value of  $\dot{q}_{loss}$  for the closed glass Dewar measured experimentally was approximately five times higher than the value in the literature for a typical “similar” Dewar (0.018 W.kg<sup>-1</sup>.K<sup>-1</sup>, Table 1).

**Table 2.** Thermal characteristics of two 1 litre Dewar flasks in both closed and open configuration

	Closed Dewar		Open Dewar	
	Glass	Stainless steel	Glass	Stainless steel
Internal Volume (m <sup>3</sup> )	1.04 × 10 <sup>-3</sup>	1.14 × 10 <sup>-3</sup>		
<i>m</i> water before cooling (kg)	0.8	0.8	0.8	0.8
<i>m</i> water after cooling (kg)	0.8	0.8	0.72	0.73
$\dot{q}_{loss}$ (W.kg <sup>-1</sup> .K <sup>-1</sup> )	0.086	0.103	0.5	0.5



**Figure 1.** Both glass Dewar and stainless steel Dewar cooling curves in open and closed configurations

This experiment shows that for the same volume of Dewar (1 litre), significant differences can be found between literature values and those measured for a specific system. It is therefore very important to measure the value of the specific heat loss for the particular Dewar type instead of using a value from literature without any additional investigations. The cooling curves for the open configuration are presented in Figure 1 (c) and (d). The Newtonian cooling model does not fit the experimental data properly for the two Dewar flasks. This is due to the fact that heat exchange by free convection at the water surface and by evaporative cooling occurs. This is confirmed by the decrease of liquid mass in the open flasks (approximately 10%, see Table 2). The approximated values of  $\dot{q}_{loss} = 0.5 \text{ W.kg}^{-1}.\text{K}^{-1}$  can, however, be stated for the open configuration assuming the behaviour approaches Newtonian behaviour. This value indicates that using an open Dewar instead of a closed Dewar can increase the heat losses by a factor of five.

### 3. LIMITS OF APPLICABILITY OF DEWAR FLASKS

The range of applicability of the Dewar flask method can be defined by comparing the specific heat loss of a Dewar flask and large vessels.

### 3.1 LITERATURE REVIEW

Several authors have undertaken the comparison of specific heat loss for large-scale vessels and Dewar flasks. Fierz<sup>2</sup> indicated that assuming a  $\dot{q}_{loss}$  of  $0.08 \text{ W.kg}^{-1}.\text{K}^{-1}$ , a 500 ml Dewar flask will have the same cooling behaviour as 50 l package, whereas  $0.04 \text{ W.kg}^{-1}.\text{K}^{-1}$  makes it equivalent to a 500 l package.

Rogers<sup>10</sup> ran experiments to measure  $\dot{q}_{loss}$  and half-life time (time taken for the temperature to fall to half its original value) for different size vessels, including Dewar flasks. He showed that:

- a 1 litre glass Dewar could simulate small plant reactors up to  $12.7 \text{ m}^3$ ; and
- a 1 litre stainless steel Dewar in an adiabatic oven (with  $\Delta T = -1\text{K}$ ) could simulate a  $25 \text{ m}^3$  vessel.

Wright *et al*<sup>11</sup> showed that the cooling rates of  $0.5 \text{ m}^3$  and  $2.5 \text{ m}^3$  plant vessels are equivalent to those of 250 ml and 500 ml Dewar flask, respectively. This information seems, however, to be different to Fierz's work<sup>2</sup> described previously. The variation in  $\dot{q}_{loss}$  for different Dewar flasks, as described in section 2.2, may provide some explanation for this.

The UN Recommendations on the Transport of Dangerous Goods<sup>1</sup> states that Dewar vessels, filled with 400 ml of substance, that have  $\dot{q}_{loss}$  between  $0.08$  and  $0.1 \text{ W.kg}^{-1}.\text{K}^{-1}$  shall be representative of 50 kg packaging. No literature reference could be found for scale-up over  $25 \text{ m}^3$ . The volume of the vessels used in the waste treatment industry can be well above this limit (up to several hundred cubic meters).

### 3.2 SCALE-UP LIMIT: GENERAL APPROACH

A general approach has been developed to define some scale-up limits. The specific heat loss for different vessel volumes and overall heat transfer coefficients (Figure 2) have been calculated using equation 1. The following vessel features were used:

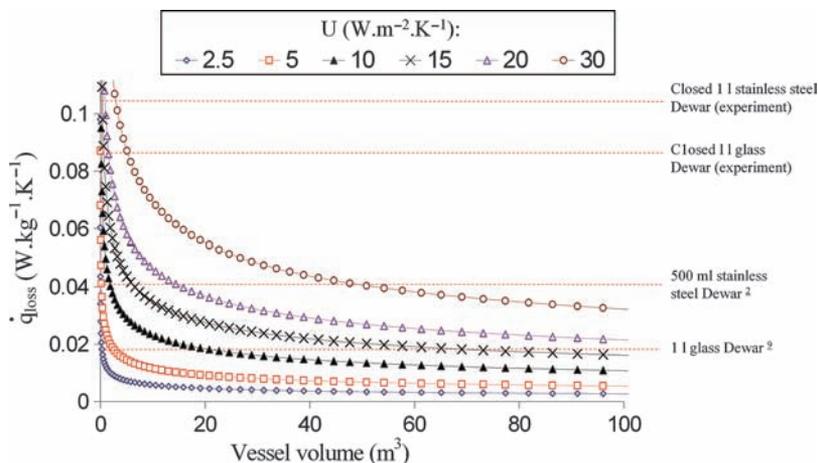
- Diameter to height ratio:  $D/H = 0.8$
- Fill level = 80%

We assume that the thermal inertia ( $\phi$ ) is 1 for all the vessel volumes.

For a given value of the overall heat transfer coefficient,  $\dot{q}_{loss}$  decreases with increasing the vessel size. This is due to the fact that the vessel heat exchange surface to mass ratio ( $A/m$ ) decreases strongly when increasing the size of a vessel.

Four values of specific heat loss for Dewar flasks (from literature and our experimental determination) are indicated in Figure 2. Provided the reaction is allowed to run to completion, then for given values of  $U$  and vessel volume:

- if  $\dot{q}_{loss \text{ Dewar}} < \dot{q}_{loss \text{ vessel}}$ : the use of Dewar vessel is conservative (heat losses are more important at the large-scale)
- if  $\dot{q}_{loss \text{ Dewar}} > \dot{q}_{loss \text{ vessel}}$ : the use of Dewar vessel is non conservative (heat losses are more important at Dewar scale)



**Figure 2.** Calculation of  $\dot{q}_{loss}$  as a function of the vessel volume and the overall heat transfer coefficient ( $U$ ). Comparison with  $\dot{q}_{loss}$  for four dewar flasks.

- if  $\dot{q}_{loss \text{ Dewar}} = \dot{q}_{loss \text{ vessel}}$ : the volume of the vessel is the maximum vessel volume for which the use of the Dewar vessel is conservative.

Following the above rule, Table 3 summarises the maximum reactor volumes for which the use of each Dewar is conservative in the case of water ( $\rho = 1000 \text{ kg/m}^3$ ). The scale-up limits proposed in Table 3 are only suitable for the specific vessel features and contents chosen for this calculation. This, however, gives an order of magnitude of the range of applicability of Dewar flask for different values of the overall heat transfer coefficient of the large-scale vessels. This type of calculation could be applied to other substances. It is also recommended that a good quality Dewar is selected and that the tests are run in a closed Dewar (minimising heat losses), providing that the suitable safety measures are followed.

#### 4. SCALE-UP OF DEWAR FLASK DATA FOR THE WASTE TREATMENT INDUSTRY

The previous part of this paper gave limits to the use of Dewar flasks by simply comparing the specific heat loss to that in large-scale vessels. We now consider the additional complication of the kinetic aspects of the scale-up and time dependence. The thermal behaviour of two exothermic reactions in a stainless steel Dewar flask are compared to that in two large-scale vessels from the waste treatment industry, using reaction kinetics and heat transfer models.

**Table 3.** Maximum vessel volume for which the use of dewar is conservative (calculation for water at 27°C,  $\rho = 997 \text{ kg/m}^3$ )

	500 ml			
	1 l Glass Dewar <sup>9</sup>	Stainless steel Dewar <sup>2</sup>	1 l Closed glass Dewar (exp)	1 l Closed stainless steel Dewar (exp)
$\dot{q}_{\text{loss}}$ Dewar ( $\text{W.kg}^{-1}.\text{K}^{-1}$ )	0.018	0.04	0.083	0.09
U of the large scale vessel ( $\text{W.m}^{-2}.\text{K}^{-1}$ )	Maximum reactor volume ( $\text{m}^3$ ) for which the use of a dewar is conservative vessel features: D/H = 0.8, fill level = 80%			
2.5	0.33	0.03	0.003	0.002
5	2.64	0.23	0.028	0.015
10	21.17	1.9	0.23	0.11
15	71	6.5	0.77	0.4
20	169	15.5	1.8	0.9
30	573	52	6.2	3.1

The suitability of the criterion suggested by parts of waste treatment industry to determine the exothermic reaction incompatibility of mixtures (temperature rise between 6–10°C in the Dewar flask over a period of 10 minutes) is also evaluated.

#### 4.1 OVERALL HEAT TRANSFER COEFFICIENT FOR A STAINLESS STEEL DEWAR FLASK

We chose to simulate the thermal behaviour of the 1 l stainless steel Dewar flask described in 2.2. The thermal balance corresponding to the Newtonian cooling of the water contained in this Dewar flask is given by:

$$\phi m C_{p_l} \frac{dT}{dt} = -UA(T - T_{ext}) \tag{3}$$

With  $\phi$ , the thermal inertia factor:

$$\phi = \frac{m C_{p_l} + m_{\text{vessel}} C_{p_{\text{vessel}}}}{m C_{p_l}} \tag{4}$$

**Table 4.** Overall heat transfer coefficient for the 1 l stainless steel Dewar flask

$A$ ( $m^2$ )	0.0434
$m$ water (kg)	0.8
$m$ flask (kg)	0.911
$C_p$ water ( $J.kg^{-1}.K^{-1}$ )	4186
$C_p$ stainless steel ( $J.kg^{-1}.K^{-1}$ )	477
$\phi$	1.13
$\dot{q}_{loss}$ ( $W.kg^{-1}.K^{-1}$ )	0.103
$U$ ( $W.m^{-2}.K^{-1}$ )	2.147

The specific heat loss criterion is then:

$$\dot{q}_{loss} = \frac{UA}{\phi m} \quad (5)$$

The overall heat transfer coefficient can then be assessed from the value of the specific heat loss criterion measured experimentally (see Table 2). For this Dewar flask the value of the overall heat transfer coefficient is  $2.147 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$  (see Table 4).

#### 4.2 ASSESSMENT OF THE OVERALL HEAT TRANSFER COEFFICIENT FOR LARGE-SCALE VESSELS USED IN WASTE TREATMENT

Some information about the design of typical storage vessels and reaction vessels within waste treatment companies was canvassed by way of a questionnaire. No experimental measurements of the thermal characteristics were available. Assessment of the overall heat transfer coefficient using heat transfer models was therefore undertaken. The results are presented for two vessels (Table 5):

- A  $112 \text{ m}^3$  stainless steel stirred reactor equipped with a flat blade turbine stirrer.
- A  $40 \text{ m}^3$  stainless steel stirred reactor equipped with a blade stirrer and 3 baffles.

For the assessment of the overall heat transfer coefficient, it was assumed that the vessels are filled with water at  $100^\circ\text{C}$  and the temperature of the air surrounding the vessels was  $27^\circ\text{C}$  (Table 6). For these two reactors the heat transfer through the vessel wall is realised by three mechanisms (Figure 3):

- i) forced convection in the liquid, the reactors being stirred;
- ii) conduction in the stainless steel wall; and
- iii) natural convection in the air outside the vessel

**Table 5.** Thermal characteristics of both 112 m<sup>3</sup> and 40 m<sup>3</sup> stainless steel stirred vessel

	Stainless steel stirred reactor	
Volume (m <sup>3</sup> )	112	40
Height (m)	6.096	4
Diameter (m)	4.8768	3.6
Wall thickness (m)	0.0127	0.006
Agitator diameter (m)	1.21	3
Agitator speed (rpm)	20	36
Baffles	No	Yes: 3 of 3 m × 0.15 m
T <sub>2</sub> -T <sub>ext</sub> (°C) (assumption)*	75°C	75°C
λ <sub>SS</sub> (W.m <sup>-1</sup> .K <sup>-1</sup> )	16.2	16.2
h <sub>liq</sub> (W.m <sup>-2</sup> .K <sup>-1</sup> )	8.5 × 10 <sup>3</sup>	5.7 × 10 <sup>4</sup>
h <sub>ext</sub> (W.m <sup>-2</sup> .K <sup>-1</sup> )	6.2	6.2
U (W.m <sup>-2</sup> .K <sup>-1</sup> )	6.2	6.2

The overall heat transfer coefficient (*U*) is then given by:

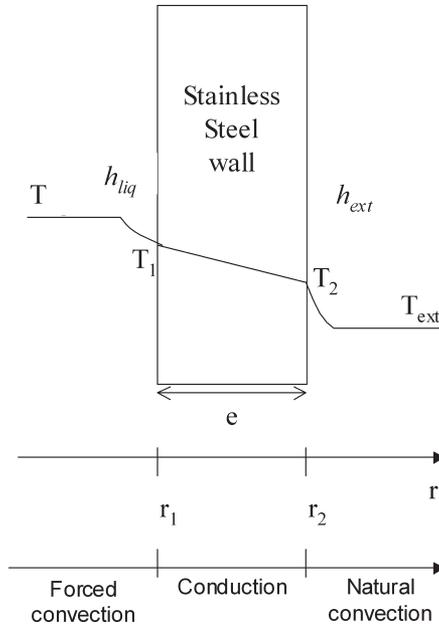
$$U = \left[ r_1 \left( \frac{1}{r_1 h_{liq}} + \frac{\ln(r_2/r_1)}{\lambda_{SS}} + \frac{1}{r_2 h_{ext}} \right) \right]^{-1} \tag{6}$$

*h<sub>int</sub>* and *h<sub>ext</sub>* are the internal and external convective heat transfer coefficients, respectively. λ<sub>SS</sub> is the thermal conductivity of stainless steel.

**Table 6.** Properties of water at 100°C and air at 27°C [Incropera *et al.*, 2001]<sup>12</sup>

	Water at 100°C	Air at 27°C
λ (W.m <sup>-1</sup> .K <sup>-1</sup> )	680 10 <sup>-3</sup>	2.63 10 <sup>-2</sup>
C <sub>p</sub> (J.kg <sup>-1</sup> .K <sup>-1</sup> )	4217	1007
ρ (kg.m <sup>-3</sup> )	957.85	1.1614
μ (Pa.s)	2.79 10 <sup>-3</sup>	1.85 10 <sup>-5</sup>
β (K <sup>-1</sup> )	7.5 10 <sup>-4</sup>	3.663 10 <sup>-3</sup>

\* For a liquid temperature of 100°C, it is realistic to assume that the vessel external surface temperature is at least 95°C because of the high efficiency of the agitation and the high conductivity of the stainless steel. Moreover, decreasing the vessel external surface temperature to 80°C does not affect significantly the value of *U*.



**Figure 3.** Heat transfer model for the two stirred stainless steel vessels (112 m<sup>3</sup> and 40 m<sup>3</sup>)

The correlations used to assess these coefficients are given in the Appendix.

For the two reactors, the stainless steel wall is a good heat conductor and agitation is highly efficient. The greatest part of the resistance to heat transfer comes from external natural convection. The assessed overall heat transfer coefficients are 6.2 W.m<sup>-2</sup>.K<sup>-1</sup> for the 112 m<sup>3</sup> and 40 m<sup>3</sup> vessels (Table 5).

Assuming that the vessels are filled at 80% with water at 27°C, then Table 7 shows that the corresponding value of specific heat loss is higher in the stainless steel Dewar flask than in the large-scale vessels by an order of magnitude. This indicates that this Dewar flask will not be able to reproduce the thermal behaviour of the large-scale vessels.

### 4.3 SIMULATION OF CHEMICAL REACTIONS

The values of overall heat transfer coefficient calculated above can then be used to simulate the thermal behaviour of two exothermic reactions. The thermal balance for a closed vessel containing a reacting mixture is given by:

$$\phi m C p_f \frac{dT}{dt} = m \dot{q}_R - UA(T - T_{ext}) \tag{7}$$

**Table 7.** Assessment of  $\dot{q}_{loss}$  for large scale vessels and Dewar flask filled at 80% with water at 27°C

	U (W.m <sup>-2</sup> .K <sup>-1</sup> )	A (m <sup>2</sup> )	m (kg)	$\phi$	$\dot{q}_{loss}$ (W.kg <sup>-1</sup> .K <sup>-1</sup> )
112 m <sup>3</sup> Reactor	6.23	92	$8.95 \times 10^4$	1.016	$6.3 \times 10^{-3}$
40 m <sup>3</sup> Reactor	6.25	46	$3.196 \times 10^4$	1.023	$8.8 \times 10^{-3}$
1 l Closed stainless steel Dewar	2.147	$4.84 \times 10^{-2}$	$9.09 \times 10^{-1}$	1.11	$1.02 \times 10^{-1}$

The reaction energy release rate ( $\dot{q}_R$ ) is linked to the reaction kinetics by the following expressions:

$$\dot{q}_R = \Delta H_r \frac{dX}{dt} \quad (8)$$

$$\frac{dX}{dt} = C \exp\left(\frac{-E}{RT}\right) f(X) \quad (9)$$

with  $\Delta H_r$  the reaction energy,  $E_a$  the activation energy and  $X$  the conversion.

The temperature rise rate in the vessel containing a chemical mixture can be obtained by numerically integrating the above differential equations.

The reactions encountered in the waste-treatment industry vary widely, depending on the chemicals being treated, their concentrations and any contaminants present. Due to their unpredictable nature there is very little information available on the reaction kinetics. Two chemical reactions on which kinetic data are available were therefore used to investigate the Dewar for scale up. These were:

- the autocatalytic hydrolysis of acetic anhydride
- the first order decomposition reaction of 20% *tert*-butyl peroxy 2-ethylhexanoate (Trigonox 21) in a solvent (Shellsol T).

#### 4.3.1 Hydrolysis of acetic anhydride

Snee *et al.*<sup>13</sup> proposed an autocatalytic kinetic equation for the hydrolysis of acetic anhydride as:

$$\frac{dX}{dt} = 24166 \exp\left(\frac{-52378}{RT}\right) (1 + 6.5X^{0.85})(1 - X)^{1.25} \quad (10)$$

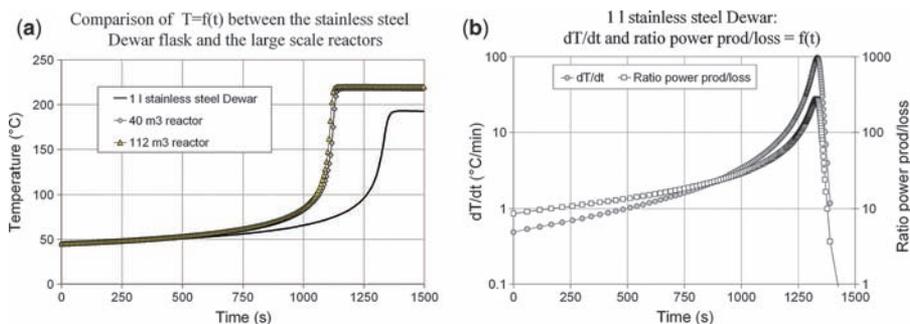
The reaction energy ( $\Delta H_r$ ) is 446.4 kJ/kg and the initial temperature is 45°C. The Cp of the chemical mixture is evaluated to be 2400 J.kg<sup>-1</sup>.K<sup>-1</sup>.

**Table 8.** Specific heat losses for the vessels containing the acetic anhydride/water mixture

Vessel	$\phi$	$\dot{q}_{loss}$ (W.kg <sup>-1</sup> .K <sup>-1</sup> )
1 l SS Dewar (exp)	1.21	$1.03 \times 10^{-1}$
112 m <sup>3</sup> Stainless steel reactor	1.03	$6.8 \times 10^{-3}$
40 m <sup>3</sup> Stainless steel reactor	1.04	$9.35 \times 10^{-3}$

Table 8 presents the calculation of the specific heat loss for the different vessels containing this chemical mixture. It appears that the heat losses will be much more important in the Dewar flask than in the large vessels. From a purely thermal point of view, i.e. only regarding the specific heat loss (as considered in sections 2 and 3 of this paper), the use of this Dewar flask would be inappropriate as a mean of simulating the chemical reaction runaway potential of these size vessels.

Figure 4 (a) shows the thermal behaviour in the Dewar flask in comparison to that modelled for the large-scale vessels when this chemical reaction occurs. A runaway reaction occurs at large scale and the 40 m<sup>3</sup> and 112 m<sup>3</sup> reactors give approximately the same results. Even with a significant larger value of specific heat loss from the Dewar, it still allows the detection of the runaway reaction. This is possible because the relative importance of the heat losses in the Dewar flask is low. Indeed, the ratio of the power produced by the reaction to the power lost to the surrounding (at least a factor of 10) for the stainless steel Dewar is important at the start of the reaction. This leads to a rate of temperature rise greater than 0.48°C/min (see “ratio power prod/loss” on Figure 4 (b)). This rate of temperature rise is close to the criterion proposed in the waste treatment industry. However, in the Dewar flask the reaction completion time is longer and the maximum temperature achieved is less than that seen in the large-scale vessels.

**Figure 4.** Modelling of the autocatalytic hydrolysis of acetic anhydride ( $T_{mi} = 45^{\circ}\text{C}$ )

**Table 9.** Specific heat losses for the vessels containing 20% Trigonox 21 in Shellsol T

Vessel	$\phi$	$\dot{q}_{loss}$ (W.kg <sup>-1</sup> .K <sup>-1</sup> )
1 l SS Dewar (exp)	1.3	$1.1 \times 10^{-1}$
112 m <sup>3</sup> stainless steel reactor	1.04	$7.8 \times 10^{-3}$
40 m <sup>3</sup> stainless steel reactor	1.06	$1.07 \times 10^{-2}$

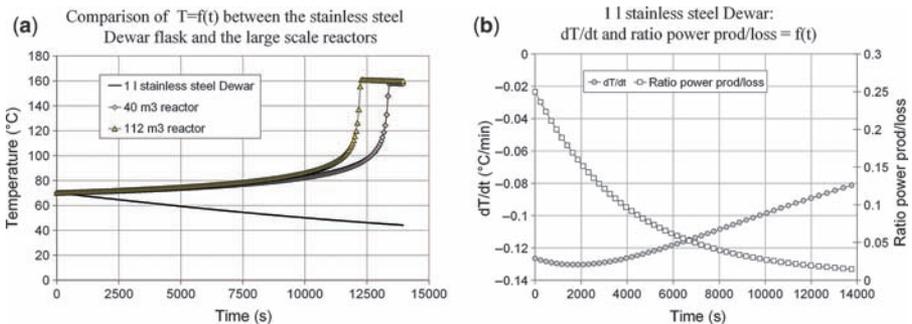
4.3.2 Decomposition of 20% Trigonox 21 in Shellsol T

Snee *et al.*<sup>14</sup> investigated the kinetics of the decomposition of 20% Trigonox 21 (*tert*-butyl peroxy 2-ethylhexanoate) in Shellsol T. They proposed the following first order kinetic equation:

$$\frac{dX}{dt} = 8.5 \times 10^{13} \exp\left(\frac{-124462}{RT}\right)(1 - X) \tag{11}$$

The reaction energy is:  $\Delta Hr = 198$  kJ/kg and the initial temperature for this experiment is 70°C. The  $C_p$  of the chemical mixture is 2000 J.kg<sup>-1</sup>.K<sup>-1</sup>. Table 9 shows that on considering only the specific heat losses then the use of this Dewar flask would be inappropriate. Figure 5 (a) shows that a runaway reaction would occur at large scale, with the 40 m<sup>3</sup> reactor exhibiting a longer completion time than the 112 m<sup>3</sup> reactor. However, the more important observation is that the reaction would not even be detected in the stainless steel Dewar flask test.

This can be explained by the fact that the induction time of this reaction is quite long. At low temperature and low conversion, the reaction heat release rate is lower than

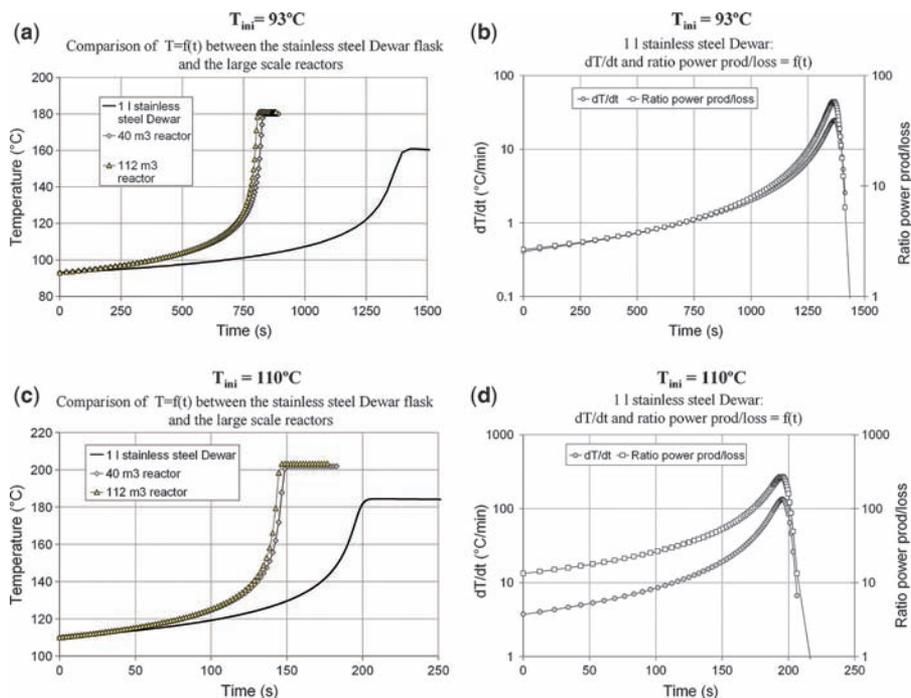


**Figure 5.** Modelling of the decomposition of 20% Trigonox 21 in Shellsol T ( $T_{ini} = 70^\circ\text{C}$ )

the heat loss rate (Figure 5 (b)). This results in temperature decreasing in the Dewar flask. In this case, the relative importance of heat loss is clearly not negligible. The use of this Dewar flask for predicting large-scale behaviour for this particular chemical reaction is therefore inappropriate.

#### 4.3.3 Sensitivity study with the first order reaction

For the decomposition reaction of 20% Trigonox 21 in Shellsol T the sensitivity to the initial temperature was investigated further. This allowed us to study the effect of different reaction rates. When increasing the starting temperature to 93°C the reaction rate is quite high from the beginning and the completion time at large scale is decreased (see Figure 6 (a)). The runaway reaction is also detected in the Dewar flask. Indeed, the reaction energy release rate is high enough to reduce the effect of the heat losses from the flask (ratio power prod/loss > 2.6 (Figure 6 (b)). The corresponding temperature rise in the Dewar flask is approximately 6°C over 10 minutes (this corresponds to the criterion under evaluation).



**Figure 6.** Modelling of the decomposition of 20% Trigonox 21 in Shellsol T: sensitivity study ( $T_{ini} = 93^{\circ}\text{C}$  and  $110^{\circ}\text{C}$ )

Even if the runaway reaction is detected, the heat losses still have a significant influence on the actual results for the Dewar flask. Indeed, the time for completion is 1.7 times greater than that in the large-scale vessels. Hence, running the chemical reaction in this Dewar flask for 10 minutes would be sufficient to detect the exotherm but not the runaway reaction.

When increasing the starting temperature to 110°C, the reaction rate is again increased, resulting in a quicker completion time at large scale (150 s, Figure 6 (c)). The Dewar flask can detect the runaway reaction. The difference in the reaction completion time between the Dewar flask and the large-scale vessel is reduced. Running the chemical reaction in this Dewar flask for 10 minutes would be sufficient to detect the runaway reaction. This result has, however, been obtained when the heat losses are at least 13 times lower than the reaction energy release rate (Figure 6 (d), leading to a rate of temperature rise in the Dewar flask greater than 3.7°C/min). This rate is approximately 3 times greater than the criterion proposed by the waste treatment industry. The maximum temperature will, however, still be smaller within the Dewar experiment.

#### 4.3.4 Reliability of the 6–10°C criterion

The simulation of the exothermic reactions showed that the 6–10°C criterion in a Dewar flask might be observed when the heat losses do not have a significant importance compared to the reaction heat release rate. In such a situation, the Dewar could detect a runaway reaction successfully. However, the reaction completion time at large scale would be shorter than at Dewar scale. In some cases, running the chemical reaction in a Dewar flask over 10 minutes could be sufficient to detect the exotherm but not the runaway reaction. The test should therefore be run until the reaction is complete to fully detect exotherms. In some cases, particularly for low energy reaction or long induction time reactions, exotherms may not be detected. **This will depend strongly on the type of Dewar flask used and on the chemical reaction parameters.**

## 5. CONCLUSIONS

A study of the specific heat loss criterion allowed the development of an approach to defining the range of applicability of Dewar flasks for different values of the overall heat transfer coefficient of large-scale vessels. The overall heat transfer coefficients, and therefore specific heat loss criteria, have been assessed for two typical vessels used in the waste treatment industry using heat transfer models. It appears that, *only* regarding the specific heat loss criterion, none of the tested Dewar flasks are suitable for direct simulation of these large-scale vessels.

The simulations of the thermal behaviour of two exothermic reactions in a 1 litre stainless steel Dewar flask and two different volume large-scale vessels show that:

- For fast and highly energetic reactions, the reaction energy release rate can be significant compared to the heat losses. The Dewar flask can therefore detect runaway reactions.

- For low energy or long induction time reactions, the heat losses may be significant compared to the heat release rate. The Dewar can, depending on the parameters, then miss exotherms and give non-conservative results.
- When an exothermic behaviour is detected in a Dewar flask, a 10 minute test, as proposed by the waste treatment industry, could be insufficient to detect a runaway reaction. The test should be run until the reaction is complete to fully detect exotherms.
- At large scale, the maximum temperature is likely to be higher and the reaction completion time shorter than at Dewar scale.

Reliable conclusions about the scale-up of Dewar data can be obtained when the chemical reaction kinetics are well known. Unfortunately this is not generally the case in the waste-treatment industry. So, unless the specific heat loss of the Dewar has been shown to be less than large-scale vessels, this method in isolation is likely to be unreliable for scale up to large vessels.

## NOMENCLATURE

$A$	Exchange surface ( $m^2$ )
$C$	Pre-exponential factor (-)
$C_{p_l}$	Liquid specific heat capacity ( $J.kg^{-1}.K^{-1}$ )
$C_{p_{vessel}}$	Vessel specific heat capacity ( $J.kg^{-1}.K^{-1}$ )
$D$	Vessel external diameter (m)
$E$	Activation energy ( $J.mole^{-1}$ )
$Gr$	Grashof number (-)
$h_{ext}$	External convective heat transfer coefficient ( $W.m^{-2}.K^{-1}$ )
$h_{int}$	Internal convective heat transfer coefficient ( $W.m^{-2}.K^{-1}$ )
$m$	Liquid mass (kg)
$m_{vessel}$	Vessel mass (kg)
$Nu$	Nusselt number (-)
$Pr$	Prandtl number (-)
$\dot{q}_{loss}$	Specific heat loss ( $W.kg^{-1}.K^{-1}$ )
$\dot{q}_r$	Reaction energy release rate ( $W.kg^{-1}$ )
$r$	Vessel radius (m)
$Re$	Reynolds number (-)
$t$	Time (s)
$T$	Liquid temperature (K)
$T_{ext}$	Room temperature (K)
$T_{ext\ ini}$	Initial room temperature (K)
$T_{ini}$	Initial liquid temperature (K)
$U$	Overall heat transfer coefficient ( $W.m^{-2}.K^{-1}$ )
$X$	Chemical reaction conversion (-)

$\Gamma$	Viscosity factor (-)
$\beta$	Volumetric thermal expansion coefficient ( $K^{-1}$ )
$\Phi$	Geometric factor (-)
$\lambda$	Thermal conductivity ( $W.m^{-1}.K^{-1}$ )
$\phi$	Thermal inertia or phi-factor (-)
$\rho$	Density ( $kg.m^{-3}$ )
$\mu$	Dynamic viscosity (Pa.s)
$\Delta H_r$	Reaction energy ( $J.kg^{-1}$ )

## APPENDIX: CORRELATION FOR CONVECTIVE HEAT TRANSFER COEFFICIENTS CALCULATION

### NATURAL CONVECTION:

$$Nu = a(GrPr)$$

For a fluid at a vertical wall, the following correlation can be used [Althaus *et al*<sup>15</sup>]:

$$\begin{aligned} Gr.Pr < 10^{-3}: & \quad Nu = 0.5 \\ 10^{-3} < Gr.Pr < 10^3: & \quad Nu = 1.18 (Gr.Pr)^{0.125} \\ 10^3 < Gr.Pr < 2.10^7: & \quad Nu = 0.54 (Gr.Pr)^{0.25} \\ Gr.Pr > 2.10^7: & \quad Nu = 0.135(Gr.Pr)^{0.33} \end{aligned}$$

### FORCED CONVECTION:

For agitated jacketed vessels, the correlation is [Rogers *et al*<sup>9</sup>]:  $Nu = \Phi Re^{0.33} Pr^{0.67} \Gamma^{0.14}$

For  $300 = Re = 7.5 \cdot 10^5$  and  $2.2 = Pr = 2500$  [Althaus *et al*<sup>15</sup>]:

- *turbine mixer*: without baffles:  $\Phi = 0.54$  / with baffles:  $\Phi = 0.76$
- *blade mixer*: without baffles  $\Phi = 0.38$  / with baffles  $\Phi = 0.78$

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