A Systematic Procedure for the Assessment of the Thermal Safety and for the Design of Chemical Processes at the Boiling Point

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Abstract. A systematic procedure is presented for application in designing safe processes or in assessing safety of existing processes that are performed at or could reach the boiling point. The evaporative cooling is very efficient, but the maximal rate of heat dissipation is limited by two factors.
One is the flooding of the vapor tube; the second is the swelling of the reaction mass due to ebullition. No reliable method is available for predicting the behaviour of a reactor at boiling point. For both cases, correlations are proposed for calculating the maximum admissible rate of heat release. They are based on the physico-chemical properties of the boiling solvent and on the geometric data of the reactor.
These tools are linked together in a general procedure for the design of safe reaction processes where the boiling point plays an important role. They can also be used to assess the safety of existing processes.

1. Introduction

Risk is traditionally defined as the product of the severity of a potential incident and its probability of occurrence. In order to assess the risk of losing control of an exothermic chemical reaction or of triggering a runaway reaction, it is necessary to analyse how a reaction can 'switch' from its normal course to a runaway reaction.

Such a risk analysis can only be carried out by following a systematic procedure: a very powerful tool for that task is to assume a runaway scenario. The scenario recently developed in our company [1] includes the right questions related to the

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severity and probability of a runaway reaction and helps to collect the data required for the risk assessment.

If the b.p. is reached during a runaway, then an explosive vapor cloud of solvent may form by evaporation. The amount of solvent evaporated can be easily calculated using the energies of the reaction and of the decomposition, but there is no method available for assessing the effect of boiling in relation to the technical performance of the equipment: either the temperature will be stabilised when the b.p. is reached and evaporative cooling helps to control the runaway or the boiling rate is too high thus increasing the pressure with the consequences described above. Reaching the b.p. may be a safeguard or a hazard.

The present work proposes a new approach that allows a quantitative prediction of the behaviour of a reactor at the b.p.

The safety assessment of a process performed at b.p. or that could reach it in case of a cooling failure must include the following estimations:

1) Estimate the heat release rate of the reaction mass at b.p. Different methods may be used for that purpose: It can be measured directly by calorimetry at reflux conditions [2] or by applying higher pressure to suppress boiling.

Another method is to extrapolate data from measurements performed at different temperatures: below the b.p. for the synthesis reaction using a reaction calorimeter, or above the b.p. from DSC experiments performed in sealed crucibles. The latter method is used essentially to measure the heat release rate of decomposition reactions. This point will not be developed further in this paper.

2) Calculate the cooling capacity of the condenser. This is a classical process engineering problem and does not enter in the scope of this paper.

3) Determine when flooding of the vapor tube will occur when condensate flows down in counter-current with the vapor. In this paper a new correlation will be presented for this purpose. It bases on physico-chemical properties of the solvent and the geometric dimensions of the vapor tube and gives the maximal admissible rate of heat release before flooding sets in.

4) Estimate the apparent increase in volume of the reaction mass due to the presence of vapor bubbles. A correlation developed for water/air allows to calculate the apparent increase in volume using physical-chemical properties and technical parameters of the equipment. This correlation was validated for various solvents in equilibrium with their vapor, and since the flow rate of the vapor across the liquid surface is linked to the heat release rate it can be used for our purpose.

The purpose of this paper is to focus on the two latter points and to combine them into a global method for assessing the safety of processes at the b.p.

2. Determination of the Flooding Limit in the Vapor Tube

If the cross-section of the vapor tube is insufficient for a given vapor release rate, the high vapor generation rate results in a pressure increase in the reactor leading to a temperature increase and a further acceleration of the reaction. Ultimately, the consequence will be a so-called thermal explosion until the rupture of weak parts of the equipment allows pressure relief. In order to prevent this happening, it is important to know the maximum vapor velocity admissible in a given tube.

In principle, two designs can be distinguished: one, where the condensate flows back counter-currently to the reactor in the vapor tube and a second, where a separate tube is used to return the condensate to the reactor. In the latter case, the maximal vapor velocity will be given by the pres-

sure drop across the tube and is limited by the sound velocity in the vapor. In the first case, when the condensate flows down as a film along the wall of a vertical pipe in which the vapor is flowing upward, a critical gas velocity is reached when waves are formed that can grow so large as to bridge the tube [3].

Brauer has described the different stages of this flooding phenomenon (see *Fig. 1*) [4].

The mechanism of flooding has been the subject of a number of previous experimental works. The objective was to develop a correlation to estimate the critical vapor velocity as a function of engineer-

ing parameters [5–11]. Two of the most significant flooding correlations are those presented by *Feind* [7][8] and by *Wallis* and *Makkenchery* [9][10]. These authors studied the counter-current flow of liquids (H₂O, aqueous glycerol solutions, ethylene glycol) with air. Therefore, the experimental conditions were not identical with ours. For this reason we performed an experimental study based on the direct measurement of the boiling rate by a heat balance.

This study was carried out in the laboratory, in the pilot plant and on the industrial scale with various organic solvents and H_2O for pipes with an inside diameter between 6 and 141 mm.

Fig. 1. *Vapor and liquid counter-current flow in an upright tube*

Vapor-film flow   Entrainment of the liquid film

Vapor upstream
Liquid downstream
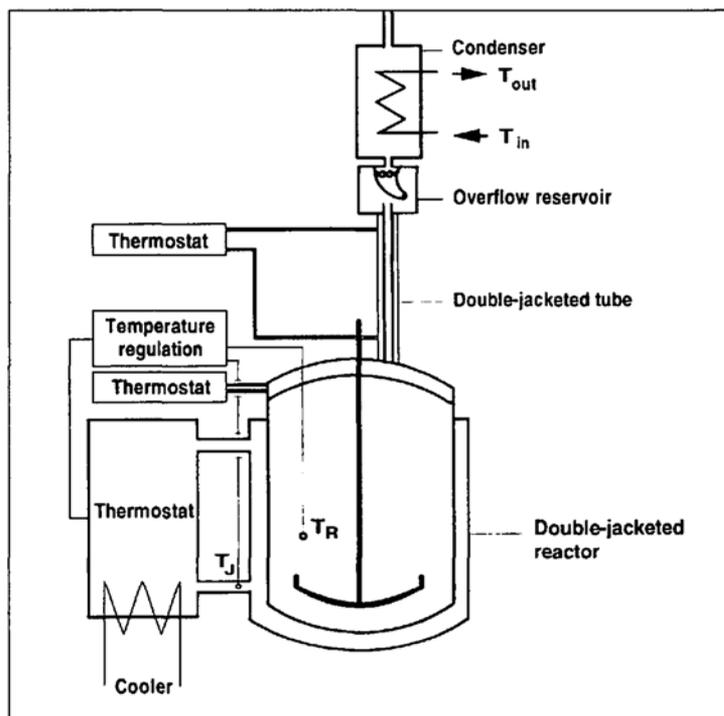
Fig. 2. *Experimental device for the determination of the flooding limit in a vapor tube*

Condenser
T_{out}
T_{in}
Overflow reservoir
Thermostat
Double-jacketed tube
Temperature regulation
Thermostat
Thermostat
T_R
T_J
Double-jacketed reactor
Cooler

Experimental Equipment

The experimental device used in the laboratory for risers with a diameter up to 20 mm is shown in *Fig. 2*. A heat flux reaction calorimeter *Mettler RC1* with a heated reactor lid (temperature near to the b.p. of the solvent) was equipped with a thermostated jacketed tube topped by a condenser. Between these two parts of equipment an overflow reservoir allowed a regular distribution of the falling liquid film. This overflow reservoir was thermally insulated with glasswool and aluminum foils to avoid heat losses. The reactor was either the standard reactor with a capacity of 2 l or a 10 l reactor, which was adapted to the calorimeter.

The experiments with tube diameters between 50 and 70 mm were performed in a pilot plant, using a 400 l reactor. An industrial scale 15 m³ reactor was used for the experiment with the 141 mm diameter pipe.

Mode of Operation

The solvent was charged into the reactor and the jacket temperature of the reactor, T_J, was continuously increased until flooding occurred in the vapor tube. At this state the vapor velocity was determined by using the heat release rate in the condenser, q_{reflux}. This is calculated from the temperature difference ΔT_{Cond} between
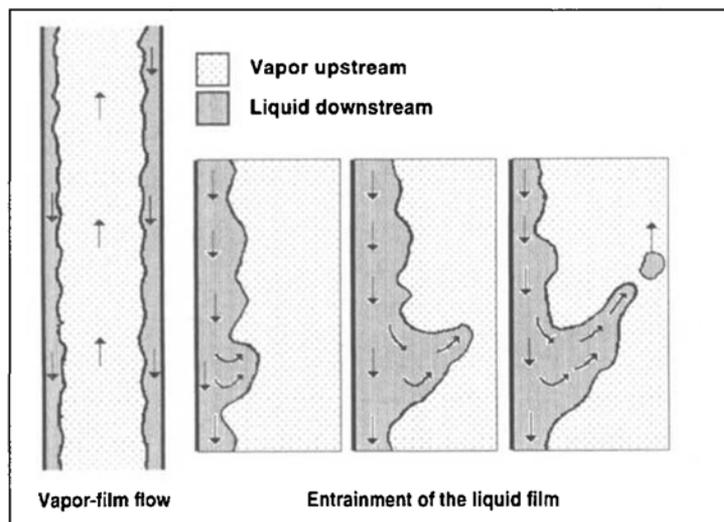

Fig. 3. *Measurement of the pressure gradient across the vapor tube at flooding*

q
Tj-Tr
■ : q [W]
▲ : Tj-Tr [°C/10]
◆ : P [bar/100]
Flooding
P
Experiment time [s]

Table 1. *Physical Properties of the Solvents*

Solvent	B.p. [°C]	ΔH_V [kJ/g]
Dichloromethane	40.0	0.329
Hexane	68.9	0.335
Toluene	110.6	0.356
Acetone	56.2	0.502
Isopropanol	82.4	0.665
Ethanol	78.5	0.852
Methanol	65.0	1.099
Water	100.0	2.250

the cooling water outlet (T_{out}) and inlet (T_{in}) in the condenser, while the mass flow m* of the cooling water (specific heat capacity C_p) was kept constant and measured by a flow-controller.

$$q_{reflux} = (T_{out} - T_{in}) \cdot C_p \cdot m^* = \Delta T_{Cond} \cdot C_p \cdot m^* \qquad (1)$$

Criteria for Flooding

Flooding was determined simultaneously by two methods:
- visual observation;
- measuring the pressure gradient across the vapor tube.

The pressure was monitored with a piezoresistive pressure gauge. As the vapor rate is increased, the pressure drop also increased slowly until the liquid begins to load up in the tube. At this point, the pressure drop will increase sharply with a small increase in vapor rate. This portion of the curve represents the transition between loading and flooding. The variation of the pressure as a function the heat flow is shown in *Fig. 3*. The heat flow, q_{max}, corresponding to the maximum admissible vapor velocity is measured at this transition point.

Results

During the experiments, eight solvents and eleven tubes with internal diameters between 5.9 and 141.0 mm, were used for the determination of the maximal allowable heat flux, q_{max}. The physical properties of the solvents (b.p. and latent heat of vaporization ΔH_v) are summarized in *Table 1*. The measured maximal heat fluxes at the flooding limit are shown in *Table 2*. As expected, the maximal heat flow q_{max} is a linear function of the enthalpy of vaporization of the solvent in the studied range (see *Fig. 4*).

For cross-sections with an area larger than 50 mm² ($d \geq 8$ mm), q_{max} is also a linear function of the tube cross-section (see *Figs. 5* and *6*).

The results are independent of the stirrer speed and of the filling volume of the reactor.
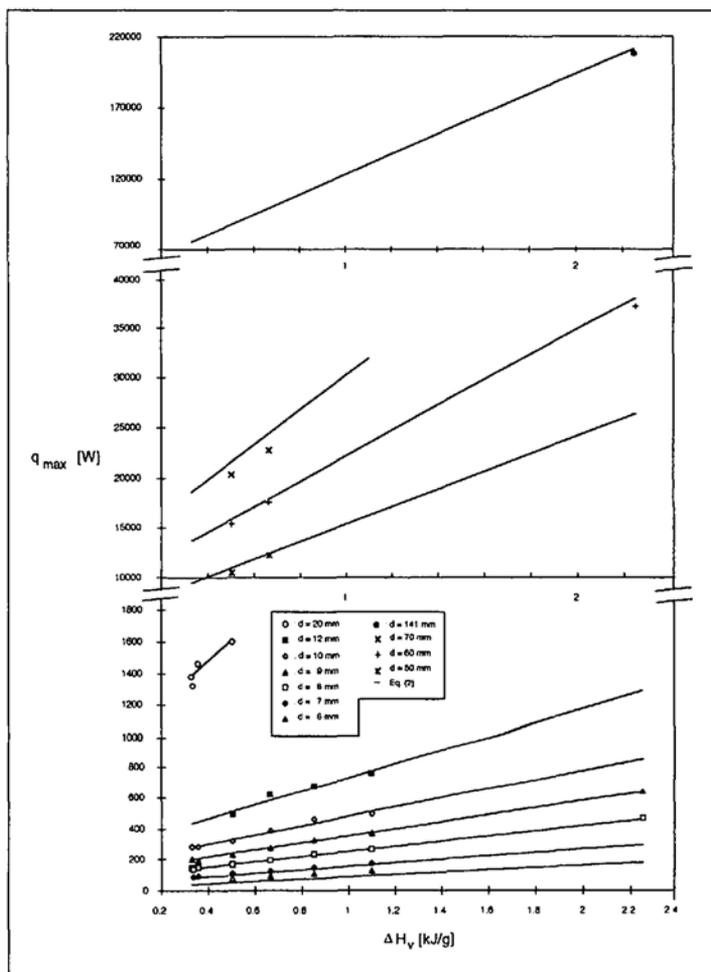

Fig. 4. *Maximal allowable heat release rate as a function of the enthalpy of vaporization of the solvent*

The maximal admissible heat release rate q_{max} for a tube of cross-section s is given by the following correlation, valid for cross-sections larger than 50 mm²:

$$q_{max} = (4.52 \; \Delta H_v + 3.37 \cdot 10^6) \cdot s - (49.51 \cdot 10^{-6} \Delta H_v + 77.15) \qquad (2)$$

with

q_{max}: maximal allowable heat release rate, W

s: tube cross-section, m²

ΔH_v: enthalpy of vaporization of the solvent, J/kg

This *Eqn.* describes a surface in the tridimensional space q_{max}, ΔH_v, and s (see *Fig. 7*).

When the tube cross-section is greater than or equal to 50 mm² ($d \geq 8$ mm), the mean relative deviation between the calculated and the experimental maximal allowable heat release is ± 2.7% and the maximal deviation amounts to ± 8.1%. This accuracy is sufficient in risk assessment, because an additional safety margin is usually applied between real operating conditions and the limit for safe operation.

Obviously, this *Eqn.* can also be used for the determination of the maximum possible heat flux when a reaction is performed under flooding conditions.

The second term of this *Eqn.* is a mathematically correction expression. It is negligible with regard to the magnitude of the first one. Thus, the *Eqn. 2* becomes:

Table 2. *Maximal Heat Flux [W] Measured at the Flooding Point as a Function of the Vapor Tube Diameter*

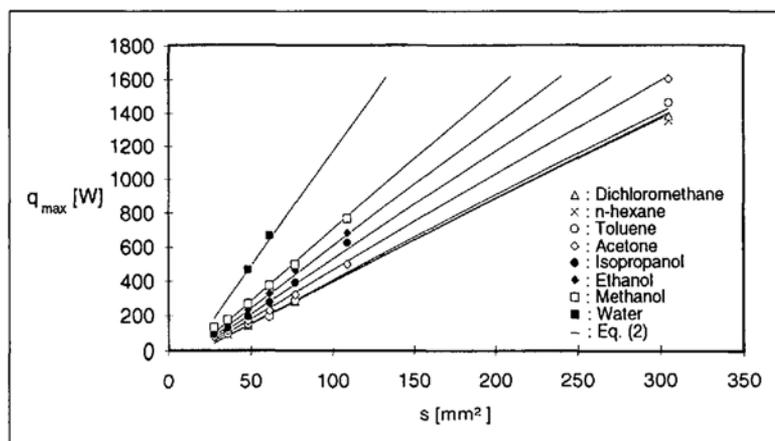| Solvent	Diameter [mm]										
	5.90	6.76	7.82	8.82	9.90	11.78	19.70	50.00	60.00	70.00	141.00
Dichloromethane			145	202	284		1380				
Hexane		90	136				1320				
Toluene		95	149	192	286		1460				
Acetone	78	111	168	229	321	496	1600	10480	15375	20360	
Isopropanol	92	128	194	275	392	621		12245	17605	22765	
Ethanol	108	151	233	326	463	680					
Methanol	129	176	267	374	497	762					
Water			470	665					37265		207700

Fig. 5. *Maximal allowable heat release rate as a function of the cross-section of the vapor tube* (< 300 mm²)
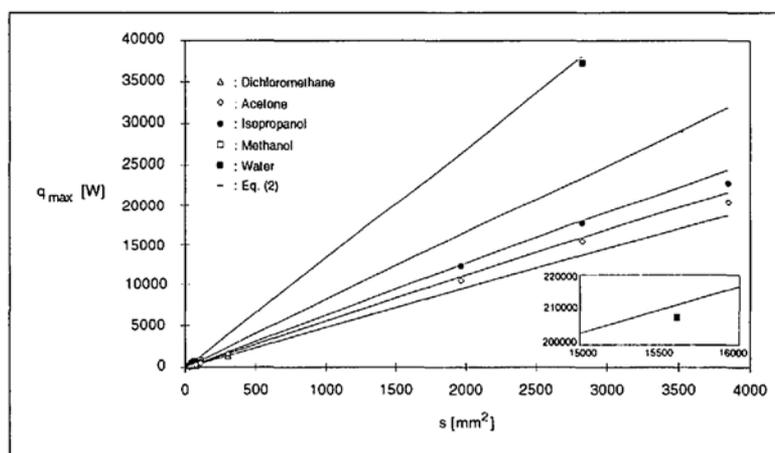
Fig. 6. *Maximal allowable heat release rate as a function of the cross-section of the vapor tube* (< 15 600 mm²)
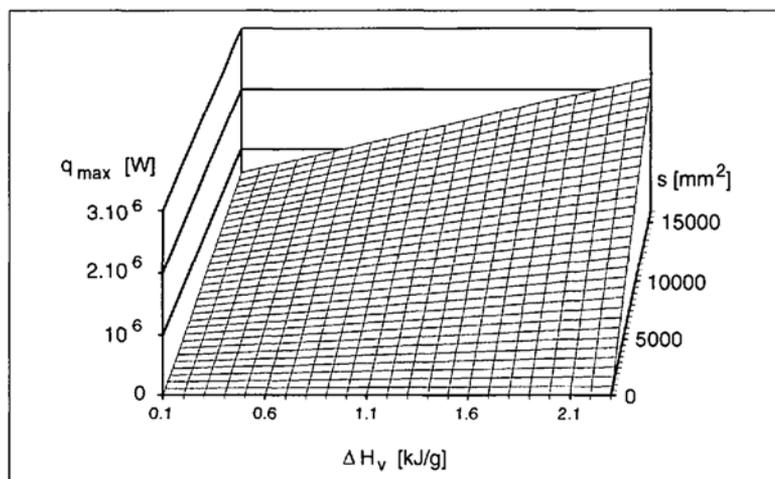

Fig. 7. *Maximal allowable heat release rate as a function of the heat of vaporization of the solvent and of the cross-section of the vapor tube*

$$q_{max} = (4.52 \; \Delta H_v + 3.37 \cdot 10^6) \cdot s \quad (3)$$

The vapor limit superficial velocity, j_{Gmax}, can be calculated from the maximal allowable heat release rate:

$$j_{Gmax} = q_{max}/(\Delta H_v \cdot \rho_G \cdot s) \quad (4)$$

or

$$j_{Gmax} = (4.52 \; \Delta H_v + 3.37 \cdot 10^6)/(\Delta H_v \cdot \rho_G) \quad (5)$$

with

j_{Gmax}: vapor limit superficial velocity, m · s⁻¹

ρ_G: vapor specific mass, kg · m⁻³

This vapor limit velocity in the vapor tube is a function of its specific mass and of the latent heat of vaporization of the liquid phase. Thus, this maximal superficial velocity is constant for a given solvent at a given pressure.

Discussion of Results

Our experimental results were compared to the flooding correlations presented by *Feind* [7][8], and by *Wallis* and *Makkenchery* [9][10]. For $d \geq 8$ mm, the mean relative deviation between the correlation of *Feind* and our experimental values is ± 14% and the maximal deviation is ± 32%.

However, our experimental data for water, CH_2Cl_2 and the alcohols compare more favourable with the predictions of the correlation of *Wallis* and *Makkenchery*. The value of the constant used in their equation is between $C = 0.70 \pm 0.02$ (for the 50-mm diameter tube) and $C = 0.94 \pm 0.04$ (tube of 8 mm).

But, it is important to remember that both correlations were not established under refluxing conditions.

For plants, where the condensate returns to the reactor using a separate tube that meets perpendicularly the base of the vapor tube, experiments show that the values calculated with our correlation must be reduced by *ca.* 40%.

3. Variation in the Apparent Volume of the Reaction Mass

The determination of the volume increase in a chemical reactor during boiling of a solvent is absolutely necessary. Indeed, it was observed that during a gas or vapor release with a velocity higher than 5–10 cm · s⁻¹ at the free interface of the reaction mass, the liquid level swells up to the vapor tube in the form of a two-phase mixture [12]. This phenomenon, due to the presence and the motion of the vapor bubbles, represents an important risk of flooding and pressure increase with possibly serious consequences. The maximum degree of filling of the reactor to avoid this event must also be determined.

It is necessary to calculate the fraction of vapor in the liquid phase, α, as a function of the dissipated thermal power. This vapor fraction must always remain below the reactor void volume fraction, V_{free}.

The mean vapor fraction in the liquid phase is defined as following [13]:

$$\alpha = (H_B - H_0)/H_B \quad (6)$$

where

H_B: liquid level in the reactor at the boiling temperature;
H_0: liquid level below the b.p. (reference state).

The first experimental study seems to have been performed by *Behringer* with H_2O and vapor [14]. The diameter of his reactors was below 82 mm and the wall influence can not be regarded as negligible.

The newer studies on the level swell in a vessel were principally performed within the framework of the nuclear industry in case of a nuclear reactor runaway.

Several authors have proposed empirical correlations allowing the determination of the vapor fraction in a liquid [15][16].

These correlations are only valid for non-foaming two-phase systems. It will be assumed in the following that the reactor does not contain foaming chemicals. This is a reasonable assumption for refluxing processes. If it is not the case, antifoaming agents must be employed.

Margulova [17] has proposed an empirical correlation for a steam/H_2O system, where the mean vapor fraction only depends on the pressure and the vapor velocity.

The correlation of *Sterman* [18] reads as follows:

$$\alpha = 1.07 j_G^{*0.63} D_H^{*0.25} (\rho_G/\Delta\rho)^{0.17} \quad (7)$$

where D_H^* is the dimensionless hydraulic diameter of the vessel defined by:

$$D_H^* = D_H/\sqrt{(\sigma/g(\rho_L-\rho_G))} \quad (8)$$

and j_G^* is the dimensionless vapor velocity:

$$j_G^* = j_G / [g \sqrt{(\sigma/g(\rho_L-\rho_G))}]^{1/2} \quad (9)$$

Wilson et al. [19][20] have proposed a dimensionless correlation similar to that of *Sterman*:

$$\alpha = K (\rho_G/\Delta\rho)0.17 D_H^{*-0.1} j_G^{*a} \quad (10)$$

with the following parameters:

if $j_G^* < 2$ then $K = 0.68$ and $\alpha = 0.62$
if $j_G^* \geq 2$ then $K = 0.88$ and $\alpha = 0.40$

Finally, *Viecenz* [21][22] has established the following relation:

$$\alpha = C (j_G^{*2})^n D_H^{*-0.174} (\rho_L/\Delta\rho)^{-0.585} (v_L/v_G)^{0.256} \quad (11)$$

with the following values for the parameters C and n:

if $j_G^{*2} < 3$ then $C = 0.73$ and $n = 0.376$
if $j_G^{*2} \geq 3$ then $C = 0.86$ and $n = 0.293$
and where v_G, v_L, respectively, are the cinematic viscosities of vapor and liquid.

In total, these correlations show that the vapor fraction in the liquid depends on the vapor superficial velocity, the hydraulic diameter of the vessel and the ratio of specific masses.

The easiest method to determine the vapor fraction is to measure the reactor content volume variation during the vapor generation [23]. It allows the knowledge of the total vapor fraction [24–27]. The most of the other methods consist to meas-
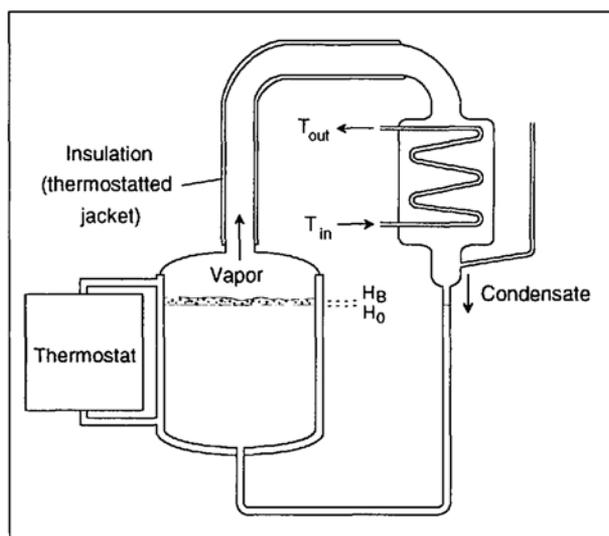

Fig. 8. *Experimental device for the determination of the void fraction in the liquid phase*

ure the γ-rays absorption of the studied liquid and vapor [28].

Gardner shows in a comparison of some correlations that the equations of *Wilson* and of *Viecenz* approximate the best the experimental values cited in [29].

Our experiments were performed in the laboratory with two solvents (H_2O and CH_2Cl_2) to verify the validity of these relations for H_2O and other liquids. The experimental equipment is shown in *Fig. 8*.

The studied solvent was charged in a 10 l jacketed reactor with an inner diameter of 190 mm. The initial level H_0 was measured before boiling (static situation) with a cathetometer. The jacket temperature was gradually increased stepwise. Then, the new level H_B at the b.p. and the heat release rate measured in the condenser, q_{reflux}, were determined. This heat release rate q_{reflux} was calculated by the heat balance of the condenser as described in *Sect. 2*.

The experiments have shown that the results were independent of the degree of agitation. The volume increase due to the thermal expansion of the liquid was counterbalanced by the evaporation of the solvent when the boiling temperature was reached.

Our experimental results values can be reproduced by the calculational values according to the *Wilson*'s correlation and this relation will, therefore, be used here for further calculations (see *Figs. 9* and *10*). The variation of α as a function of j_G according to the relation of *Viecenz* was something less than that predicted by *Wilson*.

Maximal Allowable Thermal Power

The maximal superficial vapor velocity j_{Gmax} can be determined when the possible volume increase V_{free} (corresponding to α) is known. Indeed, according to *Eqns. 9 and 10*:

$$j_{Gmax} = [g \sqrt{(\sigma/g(\rho_L-\rho_G))}]^{1/2} \cdot [V_{free}/[K (\rho_G/\Delta\rho)^{0.17} D_H^{*-0.1}]]^{1/a} \quad (12)$$

The maximal admissible heat release rate to avoid the overflow of the reactor content is given by:

$$q_{Swell} = (\pi \cdot \rho_G \cdot \Delta H_v \cdot D_H^2 \cdot j_{Gmax}/(4 \cdot M_R) \quad (13)$$

The maximal thermal power dissipated by the chemical reaction, q_{Rmax}, must be less than the value q_{Swell} calculated by *Eqn. 13* to avoid the blocking of the reactor nozzle with a two phase mixture.

The relative importance of both limiting factors (flooding of the vapor tube and swelling of the reaction mass) are summarized in *Table 3* which was established for stirred tank reactors after DIN-Norm 28136 filled to their nominal volume.

4. Method for the Investigation of a Chemical Process under Refluxing Conditions

To estimate the thermal risks and to design a safe industrial plant for a process under refluxing conditions, it is necessary to take the various limiting factors into account. A method allowing this is summarized in a decision tree (see *Fig. 11*). This latter is drawn in such a way that it can be used for the different standard technical configurations of the chemical industry. It takes account of the thermokinetical parameters of the reaction, as well as the technical data of the experimental equipment.

The Chemical Reaction

Obviously, it is necessary to have a good knowledge of the studied reaction. To perform a safety study, the heat of reaction and the dissipated heat release

rate must be known. The calorimetric methods lend themselves well to this determination.

When experimental measurements under refluxing conditions are not possible in the laboratory, simulation software allows, from the knowledge of the kinetics, to calculate the variation of the heat release rate as a function of the time at the boiling temperature [30]. This reaction kinetics can be determined with isothermal measurements with the reaction calorimeter or with a differential thermal analysis device (D.T.A.).

The heat release rate that would be dissipated if a reaction, which runs normally at the temperature T_o, would reach the boiling temperature T_{reflux} in case of a cooling failure must be estimated. During thermal runaway, the reaction would be accelerated by the temperature increase, but the depletion of reactants will slow it down. The effective heat release rate would be balanced by these opposite effects. A convenient way for this estimation is to use an acceleration factor φ, defined as the ratio of the heat release rate at b.p., q_{reflux}, to the heat release rate at process temperature T_o, q_o [30]:

$$\varphi = q_{reflux}/q_o \qquad (14)$$

When the maximum heat release rate dissipated by a reaction under refluxing conditions is determined, it is necessary to study the technical equipment in which the reaction will be performed.

The Vapor Tube

The necessary data to use the correlation presented in this work for determination of the maximum possible heat release rate of a reaction to avoid the flooding phenomenon are the tube inside diameter and the enthalpy of vaporization of the solvent (see *Eqn.* 2). This latter, when it is not given in the literature, can be determined experimentally from vapor pressure/temperature relations or calorimetric measurements with a vaporizer [31][32].

The Condenser

The necessary parameters to determine the maximal heat release rate that can be removed through a condenser are the heat exchange area A, the heat exchange coefficient U and the possible temperature difference ΔT between the condensing vapor and the cooling water.

The Filling Level of the Reactor

The formation and the motion of vapor bubbles in the reaction mass cause an apparent rise in level. If the content of the vessel swells up to the vapor tube, this latter is immediately flooded and the pressure increases dangerously in the reactor.

The maximal allowable heat release rate to avoid the overflow of the reactor, q_{Swell}, is determined by using the relation of *Wilson*.

The necessary informations are the reactor geometry (diameter, maximum level), its filling degree, the specific masses of liquid and vapor, and the surface tension of the reaction mass. If this surface tension is not cited in the literature, it can be determined experimentally with the method of the capillary ascension or with the *Wilhelmy*'s method [33].

A regular boiling must be performed to avoid any boiling delay, *e.g.* by a small bubble flow of nitrogen to assure the nucleation.
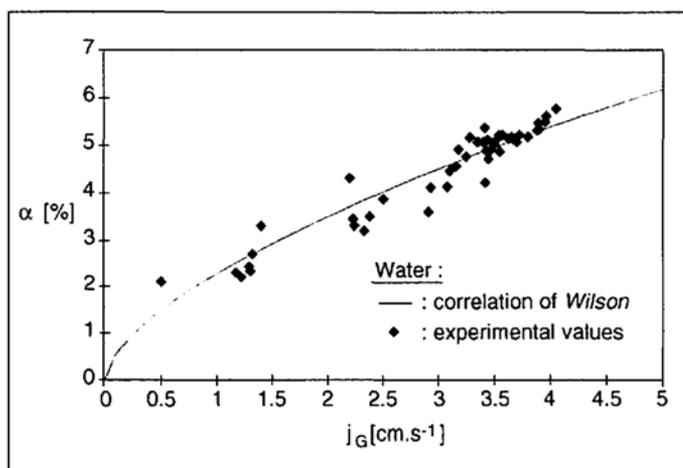

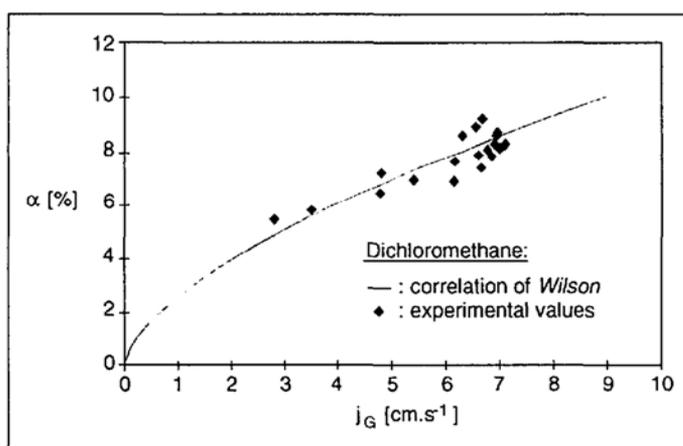Fig. 9. *Determination of the void Fraciton in the liquid phase – experiment with water*

Fig. 10. *Determination of the void fraction in the liquid phase – experiment with dichloromethane*

Table 3. *Relative Importance of Both Limiting Factors for Stirred Tank Reactors* (of volume V equipped with standard vapor tubes of diameter D) *Filled to Their Nominal Volume*[a])

V [m³]	0.063	0.1		0.16	0.25		0.04	0.63		1		1.6		2.5		4		6.3		10		16	25
D [mm]	50	100	80	125	100	150	100	150	150	200	100	200	100	200	100	250	150	250	150	300	200	300	200	300	300	300
CH₂Cl₂	113	404	96	96	180	221	115	259	162	176	45	144	28	115	18	84	26	72	16	65	18	41	11	26	16	10
Acetone	221	464	107	107	253	253	223	336	204	204	88	167	56	224	35	94	50	102	31	117	35	68	22	50	31	18
MeOH	325	644	147	147	353	353	329	455	281	281	130	229	82	330	51	130	74	141	46	162	52	94	33	74	46	25
Water	419	804	185	185	438	438	425	572	348	348	168	284	106	425	66	162	95	176	59	198	67	116	42	95	59	31

[a]) *XX*: The flooding of the vapor tube is the limiting factor.
　XX: The swelling of the reaction mass is the limiting factor.

5. Conclusion

No reliable procedure is available to predict the effect of two limiting factors in performing chemical processes under reflux conditions: the flooding of the vapor tube and the swelling of the reaction mass. This paper proposes two methods to provide this information. Correlations which calculate the maximum admissible heat release rate are proposed based on readily available physico-chemical properties of the boiling solvent and on geometric data of the reactor.

These methods are linked together in a whole set of measurement and calculation technics, which form a complete tool at the disposal of production and development chemists and engineers for the design of safe processes or for the assessment of the safety of existing processes.

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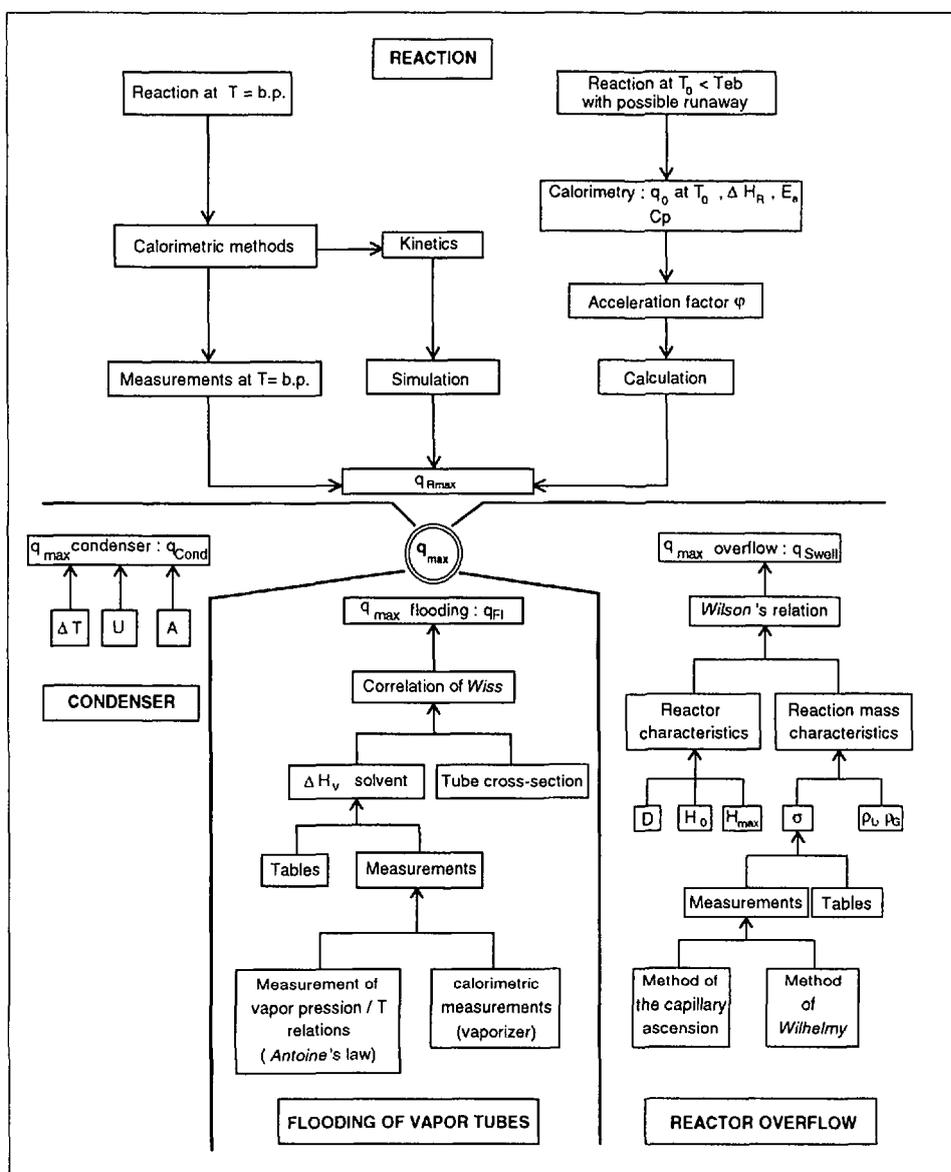
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Fig. 11. Systematic procedure for the assessment of the thermal safety of chemical processes under refluxing conditions