Screening Tool for Runaway Reaction Characterization

Minimizing Time. Optimizing ERS Design

An ioMosaic White Paper

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Introduction

Proper characterization of reactive systems is required to ensure the mechanical integrity of processing equipment and to avoid potential hazards such as fires, explosions, and toxic cloud dispersions. As the temperature of the vessel contents deviates from safe operating limits and becomes too high, the rate of heat production by the chemical reaction (i.e., exponential function of temperature) can exceed the processing equipment rate of heat loss and/or cooling capacity (i.e., linear function of temperature) leading to a runaway reaction. However, not all reactive systems present the same thermal risk level, and accordingly, not all of them require the same level of detail for Emergency Relief System design.

The present paper illustrates and easy-to-use screening tool for characterizing any reactive system based on information extracted from basic calorimetric tests. Two parameters have to be estimated for both desired and potential secondary reaction in case of a runaway:

- Adiabatic Temperature Rise, ΔT_{ad};

- Time to Maximum Rate under adiabatic conditions, TMR_{ad}.

The screening tool is based on the following criteria intended to estimate four (4) key temperature levels which contain the thermodynamic and kinetics information of the runaway reaction:

- Calorimetric Testing; Accelerating Rate Calorimeter

  - ✓ Acquiring ΔT_{ad} and TMR_{ad} and defining the runaway reaction risk level based on Stoessel criteria [1].

- Consideration of the so-called "cooling failure scenario" approach developed by Gygax [2], [3].

  - ✓ An inherent conservative assumption is taken from Grewer [4] when considering zero reaction orders for estimating basic kinetic parameters of the runaway reaction.

- Consideration of the "Criticality Classes" approach developed by Stoessel [1]. Based on the critical classes, the proposed screening tool recommends how to proceed for ensuring a reliable and effective ERS design while optimizing the required time to achieve the final results.

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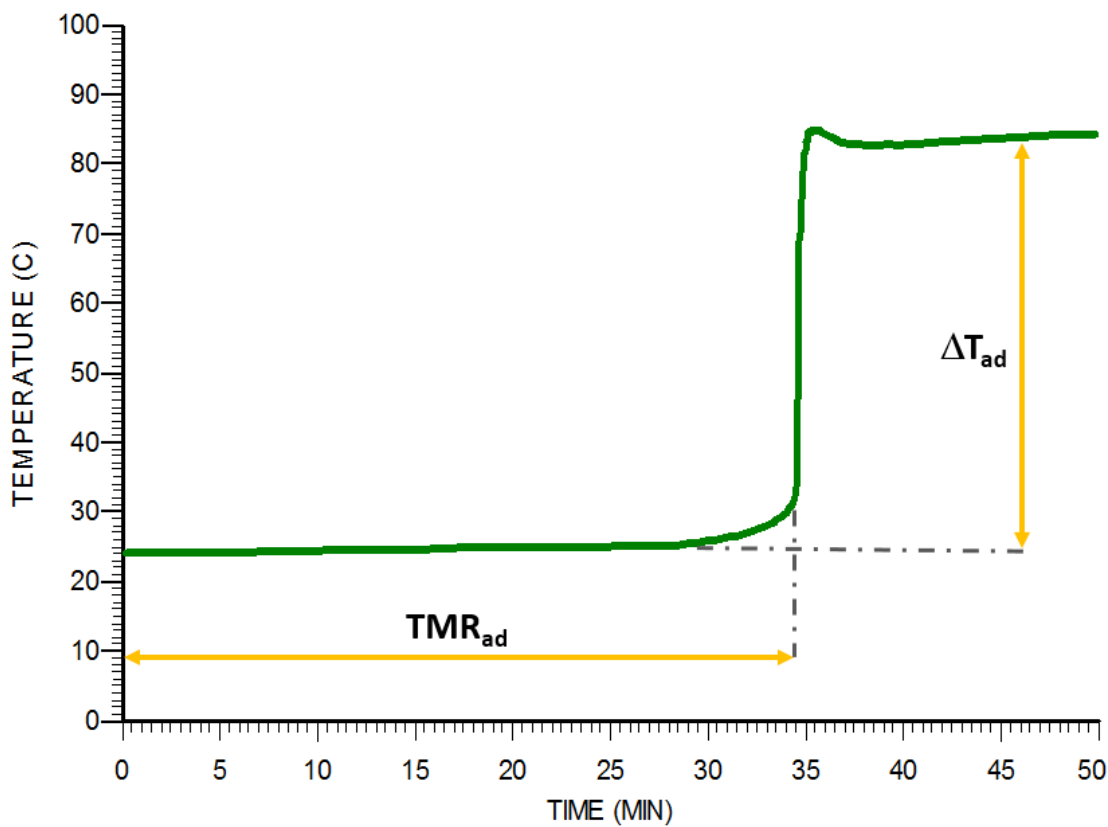
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Calorimetric Testing: Accelerating Rate Calorimeter (ARC)

Townsend and Tou [5] developed the Accelerating Rate Calorimeter (ARC) with the intention to assess the safety of reactive chemicals and mixtures. When performing a test, the sample is stored in a heated environment and the temperature, T_{oven}, is raised in steps until a given heat production is measured. The temperature controller switches to an adiabatic mode (i.e. T_{oven} is kept equal to the T_{sample}). As the temperature difference between sample and oven is very low, the heat flow is nearly zero, and the resulting temperature curve represents approximately the thermal runaway scenario. The ARC test is able to directly provide the values of ΔT_{ad}, and TMR_{ad} via the temperature history graph (see Figure 3) after correcting the thermal inertia of the sample bomb (i.e., the so-called phi-factor).

The ARC test is not only valuable for recording the temperature history, but also the pressure history. Thus, all data required for kinetic modeling purposes is available in case that the proposed screening tool confirms it is required: (1) temperature history; (2) pressure history; (3) $dT \cdot dt^{-1}$ versus temperature; and (4) pressure versus temperature.

Figure 1: ARC Approach – Temperature History Illustration

A risk ranking criteria is based on ΔT_{ad} and TMR_{ad} and proposed in [1] as follows.

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Runaway Reaction Severity

The consequences of loss of control of a reaction are linked to the energy released. The ΔT_{ad}, which is proportional to the reaction energy, represents an easy-to-use criterion for the evaluation of the severity (potential of destruction of an uncontrolled energy release as a runaway reaction). Table 1 illustrates three severity levels of a runaway reaction.

Table 1: Severity Levels of a Runaway Reaction

Level	ΔT_{ad} [K]	Comments
High	> 200	The temperature increase under adiabatic conditions as a function of time becomes very sharp. This results in a violent reaction with severe impacts.
Medium	50 - 200	-
Low	< 50	The temperature curve is smooth and corresponds to self-heating rather than to an explosion. If there is no risk of pressurization, the severity is expected to be low.

Runaway Reaction Probability

There is no direct quantitative measure of the probability of occurrence of a runaway reaction. However, the probability of thermal risk may be described by the time to maximum rate under adiabatic conditions (**TMR_{ad}**). This criterion also was highlighted by Keller et al. **[6]**. The estimation method using dynamic DSCs and criteria was demonstrated to be a good tool for preliminary screening. Table 2 illustrates probability levels based on **TMR_{ad}**.

Table 2: Assessment Criteria for the Probability of a Runaway Reaction

Level	TMR_{ad} [hr]	Comments
High	< 8	High if the TMR_{ad} becomes less than 8 hours (1 shift)
Medium	8 - 24	-
Low	> 24	Probability is low if TMR_{ad} is longer than 1 day

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Runaway Reaction Risk Level

The risk level of a runaway reaction is defined as illustrated in Table 3.

Table 3: Runaway Reaction Risk Level

Level	$TMR_{ad} < 8$ hr	$8h < TMR_{ad} > 24$ hr	$TMR_{ad} > 24$ hr
$\Delta T_{ad} > 200°C$	High	Medium	Low
$50°C < \Delta T_{ad} < 200°C$	Medium	Medium	Low
$\Delta T_{ad} < 50°C$	Low	Low	Low

- Low Level: process inherently safe. No additional safeguards required

- Medium Level: implementation of safeguards required; i.e., control, prevention, mitigation. For example: detailed ERS design, and kinetic model development

- High Level: it is recommended to define process alternatives; e.g., change of the synthetic route

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The "Cooling Failure Scenario"

The so-called "cooling failure scenario" assumes a cooling failure when the reactor is at the intended reaction temperature; i.e., process temperature, T_P (refer to Figure 2, which has been extracted from [1]).

If unreacted material is still present in the reactor when the cooling failure occurs, the temperature increases due to the completion of the reaction based on the amount of unreacted material. The worst case scenario occurs when 100% of the unreacted material is inside the reactor and the runaway reaction occurs under adiabatic conditions; i.e., no heat transfer from the reactor to the surroundings.

The thermal assessment is based on the definition of specific temperature levels arising from this scenario, and critical classes are defined for risk ranking. This approach requires answering seven (7) questions intended to describe the temperature evolution after the cooling failure (see Table 4)

As illustrated in the previous section, calorimetric testing provides the required information; i.e., ΔT_{ad}, and TMR_{ad} for answering the seven (7) mentioned questions.

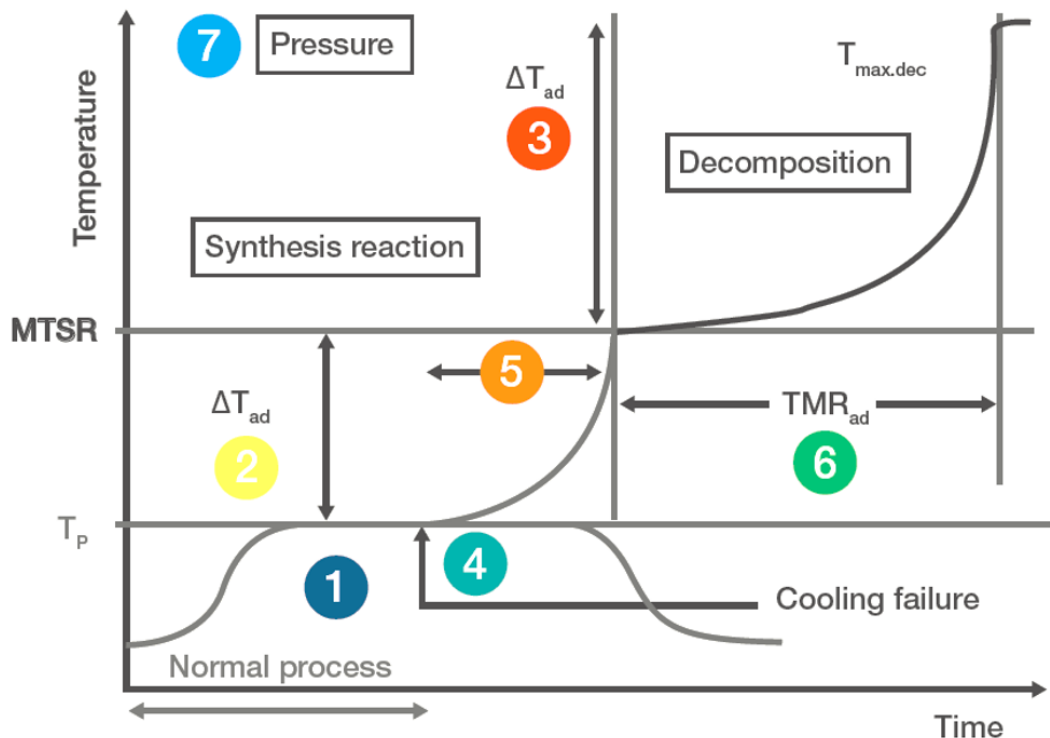**Figure 2: Graphical Representation of the Cooling Failure Scenario**

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Table 4: Definition and Characterization of the Cooling Failure Scenario

| ID	Question	Key Parameter	Process-Induced Runaway
1	Can the process temperature be controlled by the cooling system?	T_p Process Temperature	Temperature at which the cooling failure is expected to occur
2	What temperature can be attained after the runaway of the desired reaction?	MTSR Maximum Temperature of the Synthesis Reaction	$\Delta T_{ad,rx} = \dfrac{Q_{ad,rx}}{C_p}$ $\qquad MTSR = T_p + X_{acc} \cdot \Delta T_{ad,rx}$
3	What temperature can be attained after runaway by secondary reactions?	T_{end} Final temperature starting from MTSR	$\Delta T_{ad,s} = \dfrac{Q_{ad,s}}{C_p}$ $\qquad T_{end} = MTSR + \Delta T_{ad,s}$
4	At which moment does the cooling failure have the worst case consequences?	t_{worst} Time for worst case consequences	Time considered when maximum accumulation in the vessel
5	How fast is the runaway of the synthesis reaction?	$TMR_{ad,\,rx}$ Time to Maximum Rate for synthesis reaction	$TMR_{ad,rx} = \dfrac{C_p \cdot R \cdot T_p^2}{Q_{(Tp)} \cdot E_{a,rx}}$
6	How fast is the runaway of the decomposition starting at MTSR?	$TMR_{ad,s}$ Time to Maximum Rate for secondary reaction	$TMR_{ad,d} = \dfrac{C_p \cdot R \cdot T_{MTSR}^2}{Q_{(MTDR)} \cdot E_{a,s}}$
7	What will be the pressure resulting from the increase in temperature?	P_{end} Final pressure after runaway reaction	Final pressure build-up due to the vapor pressure of over-heated solvents, gases produced in the synthesis reaction, and decomposition reactions of the reaction mass

X_{acc} refer to *reactant accumulation*: this can arise in semi-batch processes where the reaction is controlled by slow introduction of a specified reactant. At low reaction temperatures, the rate of consumption of reactant is less than the addition rate. As a result, the reactant accumulates in the reactor vessel. Afterwards, a small increase in temperature and/or the higher concentration of reactant initiates a runaway reaction.

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Fire-induced runaway reactions are not covered in the "cooling failure scenario". DIERS methodology addresses emergency relief requirements for reactive systems. See references **[5]**, **[7]**, **[8]**, **[9]**, **[10]**, **[11], [12],** and **[13]** for detailed information.

Advanced dynamic simulations are required with the aim to analyze a system under fire exposure in a case-by-case basis. Figure 2 illustrates the impact of fire on pressure history for a vessel containing hydrogen peroxide.

Figure 3: Fire versus Process Induced Runaway Reactions
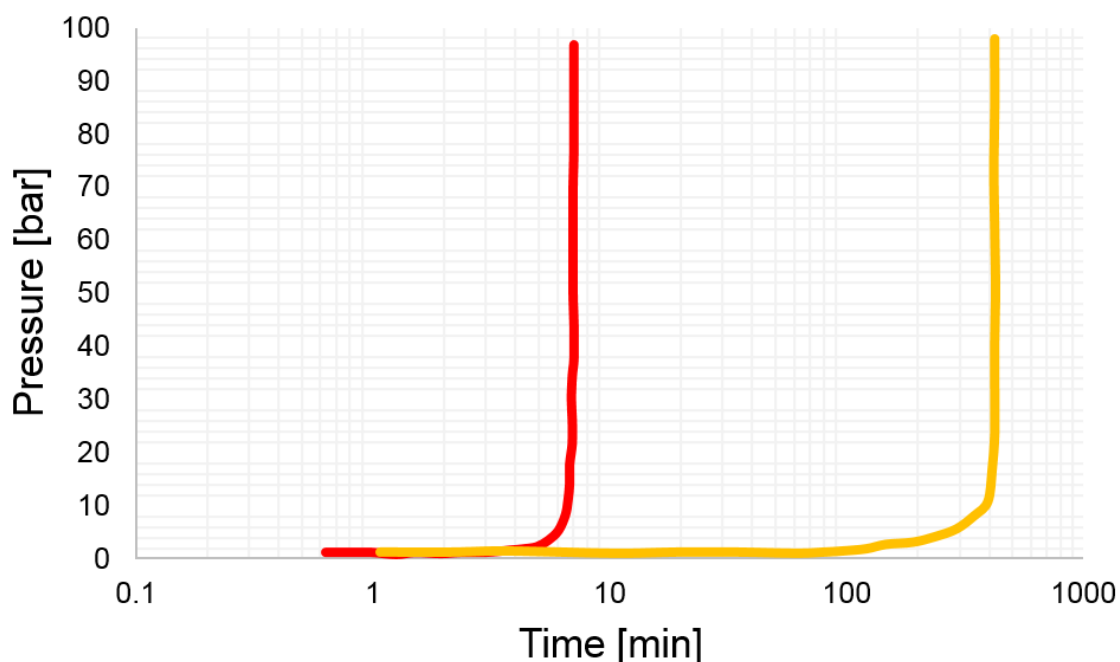
Runaway Reaction Criticality Index

The assessment of the criticality is based on four (4) temperature levels, and depending on the order in which the different temperature levels follow each other, different types of scenarios arise. These differ by their respective criticality, allowing classification by a criticality index.

This index is a useful tool, not only for the risk assessment, but also for the choice and the definition of adequate risk reducing measures.

Table 5 defines the criticality classes **[1]**

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Table 5: Criticality Classes Definition

Class	Definition	Criteria	Comments
1	MTT cannot be reached (MTSR < MTT) and the decomposition reaction cannot be triggered (MTSR < T_{D24})	T_P < MTSR < MTT < T_{D24}	Only if the reaction mass is maintained for a long time under heat accumulation conditions, can the MTT be reached. Then the evaporative cooling may serve as an additional safety barrier. The process presents a low thermal risk.
2	MTT cannot be reached (MTSR < MTT) and the decomposition reaction cannot be triggered, (MTSR < T_{D24})	T_P < MTSR < T_{D24} < MTT	If the reaction mass is maintained for a longer time under heat accumulation conditions, the decomposition reaction could be triggered and reach the MTT. In this case, reaching the boiling point could be a hazard if the heat release rate at MTT is too high. The process presents a low thermal risk (as long as the reaction mass is not kept for a longer time under heat accumulation conditions).
3	The technical limit (MTSR > MTT) will be reached, but the decomposition reaction cannot be triggered (MTSR > T_{D24})	T_P < MTT < MTSR < T_{D24}	The safety of the process depends on the heat release rate of the synthesis reaction at the MTT. First measure: use the evaporative cooling or controlled depressurization to keep the reaction mass under control. Additional measures: a backup cooling system, dumping of the reaction mass, or quenching could also be used. A pressure relief system must be designed for two-phase flow.
4	The technical limit will be reached (MTSR > MTT) and the decomposition reaction could theoretically be triggered (MTSR > T_{D24}).	T_P < MTT < T_{D24} < MTSR	The safety of the process depends on the heat release rate of the both the synthesis reaction an decomposition reaction at the MTT. This scenario is similar to class 3, with one important difference; if the technical measures fail, the secondary reaction will be triggered (i.e., the additional heat release rate due to the secondary reaction has to be taken into account). A pressure relief system must be designed for two-phase flow.
5	Specific criteria for fire-induced reactions	External Fire Loading	For vessels containing reactive chemicals the rate of energy/pressure accumulation is significantly increased because the reaction temperature reaches onset with less reactant consumption. The effect of fire on reaction rates is highly non-linear. A pressure relief system must be designed for two-phase flow.

1. **T_p - Process temperature:** temperature when the cooling failure occurs.

2. **MTSR - Maximum Temperature of Synthesis Reaction**: temperature that depends on the degree of accumulation of unconverted reactants (see Table 1)

3. **T_{D24} - Temperature at which TMR_{ad} is 24 hours:** highest temperature at which the thermal stability of the reaction mass is unproblematic.

4. **MTT - Maximum Temperature for Technical reasons:** boiling point in an open system. For a closed system, it is the temperature at the maximum permissible pressure; i.e., relief pressure.

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Screening-Tool ERS Design Strategy

The proposed screening tool is intended to technically justify the required effort and detail level for designing a reliable ERS

Table 6: Screening Tool ERS Design Strategy

Class	Thermal Risk	ERS Design Strategy
1 or 2 (process-induced runaway)	**LOW**	Short-cut steady-state calculation based on criteria from the Vapor Relief under Fire or external heating using the vent for vessels containing a volatile liquid and exposed to external fire (i.e., calculated based on the liquid evaporation rate and all vapor flow at the maximum allowable internal pressure). * Short-cut steady state vent sizing: $$A_h = \frac{\dot{M}_v}{G_v} = \delta \frac{qA_{wetted}}{G_v} \cdot \frac{M_w}{\lambda} \left(1 - \frac{\rho_v}{\rho_l}\right)$$
3 or 4 (process-induced runaway)	**MEDIUM & HIGH**	1. Detailed kinetic model development using ARC test results 2. Two-phase dynamic simulation based on kinetic model and DIERS criteria * Note that it is recommended to consider an alternative design of the process
5 (fire-induced runaway)	**HIGH**	Criteria for fire-induced runaway reaction scenarios: 1. Detailed kinetic model development via ARC test results 2. Two-phase dynamic simulation based on kinetic model and DIERS criteria

Classes 3 or 4, and 5 based on DIERS criteria **[13]**

Short-cut steady state vent sizing based on API 520 **[14]** and focused on liquid reactive systems.

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Conclusions

The present paper illustrates and easy-to-use screening tool for characterizing any reactive system based on information extracted from basic calorimetric tests. Two parameters have to be estimated for both desired and potential secondary reactions in case of a runaway:

- Adiabatic Temperature Rise, $\Delta \mathbf{T_{ad}}$;

- Time to Maximum Rate under adiabatic conditions, $\mathbf{TMR_{ad}}$.

These two parameters provide thermodynamic and kinetic information of the runaway reaction, and both parameters are the basis for defining the expected risk level of the runaway reaction.

The screening tool is based on criteria established in the so-called "loss of cooling scenario" developed by Gygax and also takes into account the criteria established by Stoessel for defining the "critically classes".

Accelerating Rate Calorimeter testing and the illustrated procedure are added value tools for the decision-making process able to minimize time and money when questioning if complex, time-consuming and laborious two-phase dynamics simulations and kinetic model developments are required or not. The proposed screening tool is intended to provide sufficient information in order to ensure the right level of effort for relief systems design.

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Nomenclature

m_{rx}: reaction mass [kg]

$Q_{ad,rx}$: Heat of desired reaction [kJ·K^{-1}]

$C_{p,rx}$: Specific heat capacity of the reaction mass [kJ·kg^{-1}·K^{-1}]

$\Delta T_{ad,rx}$: Adiabatic temperature rise of the desired reaction [K]

X_{acc}: Percentage accumulation [%]

T_p: Process Temperature [K]

MTDR: Maximum Temperature Desired Reaction

T_{end} Final temperature starting from MTDR

$Q_{ad,s}$: Heat of secondary reaction [kJ·K^{-1}]

$\Delta T_{ad,s}$: Adiabatic temperature rise of the secondary reaction [K]

R: Universal gas constant [J·mol^{-1}·K^{-1}]

$Q_{(Tp)}$: Specific heat release rate @ process temperature [W·kg^{-1}]

$Q_{(MTDR)}$: Specific heat release rate @ process temperature [W·kg^{-1}]

$E_{a,rx}$: Activation energy desired reaction [J·mol^{-1}]

$E_{a,s}$: Activation energy secondary reaction [J·mol^{-1}]

t_{worst}: Time for worst case consequences [s]

$TMR_{ad,rx}$: Time to Maximum Rate for the desired reaction

$TMR_{ad,s}$: Time to Maximum Rate for the secondary reaction

P_{end}: Final pressure after runaway reaction

k: rate of the reaction based on Arrhenius Equation [function of reaction order]

k_0: Pre-exponential factor, or frequency factor [function of reaction order]

A_h: Required vent area [m^2]

G_v: Vapor mass flux [kg·s^{-1}·m^{-2}]

δ: Environmental factor which accounts for effects of insulation, etc. [-]

q: Fire Flux based on API-520 or heat load [W·m^{-2}]

M_w: Molecular weight of the flowing vapor

λ: Latent heat of vaporization of the liquid [J·kg^{-1}]

ρ_v: Vapor mass density [kg·m^{-3}]

ρ_l: Liquid mass density [kg·m^{-3}]

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