

Runaway Simulation and Vent Sizing for Batch Stirred Tank

BST software
Tutorial

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Introduction

This part is to help you to become familiar with the methodology of selecting parameters of vent systems, which prevent dangerous excess of the pressure in a batch-stirred tank under the heat explosion of reacting mixture. We consider a rupture disk and a valve as the basic pressure relief devices¹.

The valve is a stop valve in a piping, which opens as a predicted pressure (it is called the actuation pressure) is attained.

If discharge through the open valve restores the pressure in the tank to a value less than the actuation pressure, the valve closes again. A standard spring-based stop valve usually opens incompletely at some pressure interval², so the effective area of its throttle is less than the maximal one in this case.

Unlike the valve, the rupture disk cannot be restored, since the actuation pressure destroys it (partially or completely). Thus, the vent system activated once shall never close and should act until complete pressure relief.

BST considers only the batch reactors, which can be represented with the well-stirring model.

To prevent the inadmissible pressure growth during a heating accident in reactor, the vent system should provide necessary flux, so it must be sized properly. In this view one should consider the physical properties of the flow as well as geometry of the vent system.

It should be noted that depending on the circumstances a tank can emit either pure gas or pure liquid or two-phase flow.

Sufficiently large pressure differential between reactor and the vent system outlet forces the critical mode of the flow, when the flow velocity attains the local speed of sound at some point. Such point is called the critical section. In this mode, discharge is independent of the pressure at any point downstream the critical one, since the supersonic flow takes place and flow disturbance is transmitted only down by the vent system there. The critical section usually appears either at the outlet of the vent system or at a local contraction of it. Frequently the critical section coincides with the least effective section of a valve or rupture disk³.

Consider the case of top venting. Here, a gas from the gas region flows away while a heat explosion occurs, but the liquid can displace the gas region completely when its level attains the vent system inlet due to boiling. At that, two-phase flow flashes through the vent system. Here the volumetric discharge rate can decrease dramatically since the speed of sound in a two-phase mixture is substantially less than that in a pure gas all the more as in pure liquid.

When discharging a pure subcooled liquid, two-phase flow may also occur. Here the liquid can boil in the vent system if the pressure decreases to the equilibrium pressure of the characteristic vapor of the mixture.

To solve this problem⁴, one should simulate one- or two-phase flow through the vent system of variable section simultaneously with physicochemical processes in a well-stirred batch reactor.

This chapter is intended to studying the backgrounds of the above processes and mastering the software suit BST, developed by Cheminform St-Petersburg.

The following list summarizes the contents of the chapter:

- The first part is introductory. It outlines the subject of BST and the models being used.
- Part 2, "Backgrounds of BST" describes intention of the software, types of experimental data can be processed, and mathematical aspects of simulation. First four chapters contain the basic information on BST, so they should be read by all means. Other chapters deal with mathematical backgrounds, so they are optional.

¹ The pressure is relieved by discharging a part of the reacting mixture into the environment or special vessel.

² From the actuation pressure to the pressure the valve is completely opened at.

³ If the vent system includes sufficiently long tubes, the critical section can be located at the outlet despite of a local contraction.

⁴ It is called the vent sizing.

- Part 3, “Samples”, considers several examples of simulation.

Details of using Vent and Mixture software can be found in the other chapters of this document.

All the examples described in this chapter are based on the data included into the Demo Database of BST. This feature is to help you to solve any problem and to illustrate handling data while you are reading

Heat explosion in a well-stirred batch reactor. Problem statement

Reactor shape

To simplify the problem, two shapes are under consideration, namely they are a spherical vessel for storing/transporting a liquid and cylindrical reactor. The cylindrical reactor can be mounted either in horizontal or in vertical position⁵.

A reactor can be supplied with a jacket to force its cooling or heating.

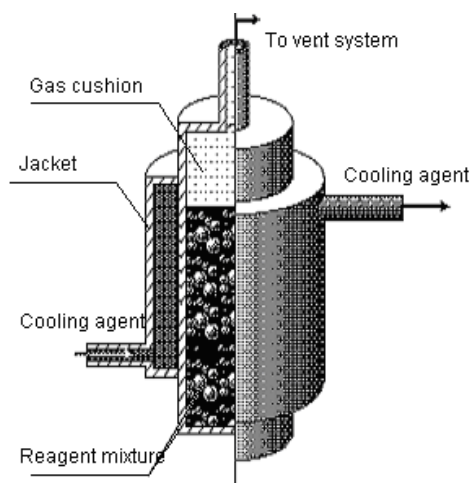


Fig. 1 Cylindrical reactor

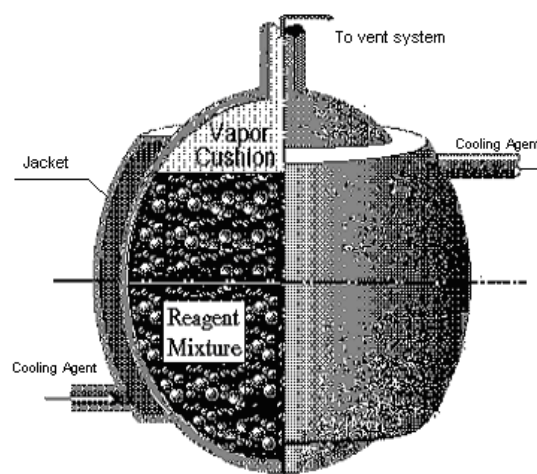


Fig. 2 A spherical reactor

Moreover, you can define an external heat flux explicitly dependent on the pressure as well as a radial heat exchange with the environment.

The basic physicochemical processes in a well-stirred batch reactor

The processes in a well-stirred batch reactor are complex and diverse. To solve the simulation problem, we should choose the most substantial ones and advance some assumptions with a view to simplify it.

Let us assume that there are three zones in a reactor, which can be subject for simulation:

- The liquid reacting homogeneous mixture of some components;
- The bubble zone in liquid. It contains a mixture of vapors and insoluble gases that may be produced during the reaction.
- The gas region⁶ over the free surface of the liquid. It is a homogeneous mixture of various gaseous components (both insoluble gases and vapors of the liquid mixture). The gas region must be at the start of a process; however it can vanish because of the vent system activities.

The model is based on the assumption that the gradients of temperatures, concentrations and pressures⁷

⁵ Here we mean the position of the axis of symmetry.

⁶ I.e. gas or vapor space above the liquid.

⁷ Excluding additional hydrostatic pressure at the inlet of a bottom-mounted relief system.

are negligibly small. According to this assumption any one of the objects above is completely defined by a temperature value and mass fractions of the mixture species that are functions of time only. Here the bubbles and the liquid are assumed to be of the same temperature since the surface of heat exchange is well-developed (bubbles are of small diameters as their number in a volume unit of the gas-liquid mixture is great) and heat capacity of the bubbles is negligible comparing to that of the liquid. Pressures at all the zones are also assumed to be equal to each other⁸. The zones fill all the reactor volume, which is considered as a constant⁹.

Now let us describe the processes and factors to be considered when simulating a heat explosion in reactor.

A chemical reaction

A chemical reaction in liquid can be accompanied with heat emission or heat absorption, producing an insoluble gas or changing the mixture composition (which implies the liquid properties to vary). Kinetics of a chemical mixture must be defined by user. Two types of kinetic data are available.

Formal Kinetics

In this case the reaction rate is a function of temperature and formal kinetic variables called conversions (the detailed description can be found in the FORK tutorial). Therefore, some additional assumptions are needed in order to simulate varying liquid mixture composition under chemical reaction. This approach suits to a case of quasi-one-component mixture, where the mixture properties are assumed to be independent of the composition (may be since some data are absent).

Descriptive Kinetics

Here the reaction rate is a function of the temperature and composition of the liquid. In this case kinetics defines the rate of varying the liquid composition explicitly. The Law of Acting Masses is a particular case of descriptive kinetics.

Boiling of the liquid mixture

The liquid in reactor can be heated by a chemical reaction or an external heat flux. As the liquid attains its equilibrium boiling point, the bubble boiling may begin in reactor, i.e. some liquid may turn into the vapor bubbles, which can grow then pivot under the buoyancy force. Here the liquid evaporates from the bubble surface and the significant amount of heat is absorbed due to the implicit heat of vaporization. The number of bubbles caused by boiling is used to be substantially large (10^{10} — 10^{14} per m^3), so as the specific area of heat and mass exchange. In these terms, the assumption that the equilibrium boiling point approximates the temperature of vapor—liquid mixture after boiling starts. In turn, the equilibrium boiling point is the known function of the pressure and composition of liquid.

Whence it follows that the temperature of a boiling liquid does not depend on heat produced by chemical reaction but is bounded above with an equilibrium boiling point. The vapor discharge explicitly depends on the heat production rate. A system where the self-accelerating heat-producing reaction takes place under boiling is called a tempered one, since here the temperature excess can be suspended by taking away the vapor surplus and preventing the pressure growth¹⁰. In this case the vapor discharge can be evaluated by solving heat balance equations together with the state equations for the three zones accounting that the

tank volume is constant and the following identity is valid: $\frac{dT_m}{d\tau} \equiv \frac{dT_s}{d\tau}$, where T_m is the temperature of the vapor—liquid mixture, T_s is the equilibrium boiling point and τ stands for time.

⁸ i.e. the influence of the surface tension forces on the pressure in bubbles is also neglected.

⁹ i.e. changing reactor volume caused by alteration of pressure and temperature is neglected too.

¹⁰ Usually the boiling point strongly depends on pressure and weakly on temperature, however there are some exceptions.

Insoluble gases produced by reaction

Some reactions generate insoluble gases. Here a gas is also emitted as bubbles but no significant heat emission/absorption takes place. Obviously, producing insoluble gas is always accompanied with liquid evaporation (in accordance with the partial pressure of the vapor at certain liquid temperature), however if the partial pressure is small the temperature growth cannot be significantly restrained with heat absorption caused by evaporation to bubbles. In this case, discharge through the vent system may influence on the temperature growth induced by the chemical reaction only slightly.

A system where gas-generating reaction takes place while the partial pressure of the vapor can be neglected comparing with the whole pressure is called gassy. If heat absorption caused by evaporation is significant, it is called hybrid.

The vapor discharge under insoluble gas generation can be defined if assume that the vapor composition and its partial pressure are equilibrium on the border of bubbles with liquid in the vapor-gas stream:

$$G_S = G_{gR} \cdot \frac{m_s}{m_{gR}} \cdot \frac{P_S}{P - P_S}$$

Here G_S is vapor generation rate, G_{gR} is discharge of the insoluble gases due to chemical reaction, P is the total pressure, P_S is the saturation pressure, m_s is the average molecular mass of vapors, m_{gR} is that of the insoluble gases.

Various models of vapor—gas bubbles disengagement in a reactor

Consider the gas—liquid mixture in a top-vented tank.

Discharge through the vent system in purely gaseous or two-phase mode is defined by the volume of the bubbles in liquid. In turn, the volume of the bubbles is defined by the disengagement rate. The more is the disengagement rate the less is the volume of bubbles. In these terms, the rise of the liquid level is negligible. As the gas generation rate decrease the gas—liquid mixture level grows faster and the gas region diminishes. When the free surface attains the vent system inlet the discharge continues in two-phase mode.

The conventional DIERS system considers three basic modes of gas generation:

- FOAMY;
- BUBBLY;
- CHURN TURBULENT.

The foamy model suits to highly viscous liquids as well as to liquids with surfactant added. In this case, the gas and the liquid are not separated from one another. Consider pressure relief in a vessel with such a liquid under heat emission. Here almost all the liquid runs away through the vent system. There is no return to one-phase gas discharge despite of dramatically drop of vapor/gas generation caused by temperature and liquid mass decrease.

The bubbly model suits to moderately viscous liquids with numerous alien inclusions that generate gas/vapor. There is plenty of bubbles here and they are relatively small (0.1-1 mm)¹¹.

The churn turbulent model suits to low viscous liquids (e.g. water) with few alien inclusions that generate gas/vapor. There are not many bubbles here and they are of relatively large size (up to 10—50 mm) and irregular shape. They can split or flow together while disengaging. Their flow is turbulent. This model is characterized by the most rate of gas emission through the free surface.

Two last models admit returning to one-phase (gassy) flow and forming a steady gas region while relieving pressure from a vessel a heat-emitting reaction proceeds in. Usually such an event occurs at the end of a process when gas generation falls dramatically due to decrease of the liquid mass and temperature.

Choosing a disengagement model depends on the liquid type. Indeed, an experiment is the best way to determine it. If the experimental data are of lack and you are in doubt we recommend to use the foam

¹¹ They are not small enough for pressure of the surface tension forces and viscosity forces to be neglected, so these forces should be considered together with inertial ones when evaluating disengagement rate of a single bubble.

model rather than the bubbly one and the bubbly one rather than churn turbulent.

In general case, the local volumetric velocity of the gas regarding to liquid is defined by the following formula:

$$j'_g = U_\infty \cdot f(\alpha)$$

where $f(\alpha) = \frac{\alpha \cdot (1-\alpha)^n}{1 - C_0 \cdot \alpha}$,

- $n=2$, $C_0 \geq 1.0$ for a bubble model;
- $n=0$, $C_0 \geq 1.0$ for a churn-turbulent model;

The typical disengagement rate is:

$$U_\infty = \frac{1.18 \cdot (\sigma \cdot g_0 \cdot (\rho_f - \rho_g))^{1/4}}{\rho_f^{1/2}} \text{ for a bubble model;}$$

$$U_\infty = \frac{1.53 \cdot (\sigma \cdot g_0 \cdot (\rho_f - \rho_g))^{1/4}}{\rho_f^{1/2}} \text{ for a churn-turbulent model.}$$

Here α is the volume fraction of the gas phase;

σ is the surface tension of the liquid

g_0 is the gravity force acceleration

ρ_f is the density of liquid; ρ_g is that of the gas.

C_0 is the adjusting coefficient. Its recommended values are 1.5 for a churn-turbulent model and about 1 for a bubble one.

External Heat Exchange

External heat exchange simulates both cooling with a jacket and a heat flux by fire.

To simulate the cooling mode, you should define cooling agent temperature and heat emission as functions of time (in tabular form).

The heat flux of fire considers an external heat flux (to be defined as a function of time), convection heat exchange with time-dependent heat emission coefficient and a radial heat exchange with environment.

In its most general form, the heat exchange is defined by the following formula:

$$q = q_0(\tau) + \alpha(\tau) \cdot [T_e(\tau) - T_w] + \varepsilon \cdot \sigma_0 \cdot [T_e^4(\tau) - T_w^4],$$

where ε is the effective blackness for the radial heat exchange with environment,

σ_0 is the Stephen—Boltzman constant,

T_w is the temperature of the wall being in contact with the liquid or gas.

In these terms, the heat exchange between the wall and the liquid is assumed to be large enough for difference of their temperatures to be neglected, i.e. $T_w|_{liq} \cong T_{liq}$.

As for the wall—gas contact, the gas temperature is defined by the energy equation for the wall. In this view the thin wall assumption is applied, i.e. the heat capacity and lengthwise heat conductivity of the wall are neglected. Here the wall temperature can be evaluated basing on the balance of heat fluxes into and out of the vessel.

Mass losses through the vent system

The vent system can be actuated when some prescribed conditions on reactor are attained (they may be

either pressure or temperature or mass fraction of some species). The vessel can be top- or bottom-vented. In a top-vented vessel, one can observe a purely gaseous flow (as a gas region exists) as well as a two-phase one. Under the bottom-venting, the gas region always exists. Here the flow can be either two-phase or purely liquid. If there is no stirring in the tank and non-foam model is chosen, the volume fraction of bubbles at the bottom of the tank is small, so we can assume that the flow at the vent system inlet is a pure liquid. However, if pressure declines below the vapor pressure while flowing through the vent system, the flow turns into the two-phase mode again. Then, for calculation of mass flow rate through the vent line, BST uses the VENT software (see the next chapter) as a COM-server.

Initial data for solving a reactor

The initial data includes:

- Initial loading of the tank, which can be defined as its initial filling as well as the initial mass of the liquid;
- Initial composition of the liquid reacting mixture
- Initial temperature of the reacting mixture;
- Initial pressure in the tank¹².

If the set initial pressure exceeds the pressure of liquid's proper vapor, the initial composition of insoluble gases in the gas region should be defined.

Main tasks

The BATCH STIRRED TANK (BST) software is designed for computer simulation of physical and chemical processes in a well-stirred batch tank with a pressure relief system also called the vent system.

BST provides:

- Simulation of emergencies in batch well-stirred reactors with runaway reactions (RUNAWAY);
- Simulation of pressure release in the tank without chemical reactions (BLOWDOWN);
- Simulation of heating up or cooling the tank with an external heat flux (HEATING)
- Matching of the critical value of the cross-sectional area of a vent system (VENT SIZING).

Basic Features

- BST possesses the following features:
- Using fundamental physical laws of conservation and state equations for liquid and gas phases for modeling.
- Using DIERS methodology
- Supporting two types of kinetic data: formal kinetics (FORK) and descriptive kinetics (DESK).
- Calculation of physical properties of liquid and gas mixtures over a wide range of state parameters by means of the MIXTURE software (see *Appendix B*).
- Using "conservative" approach.
- User-friendly interface.

Other initial data include:

- correspondence between kinetic model and mixture composition;
- the tank geometrical and physical parameters (e.g. maximum allowed pressure);
- loading conditions in the tank;
- heat exchange data according to the worst credible scenario of an accident;
- the model options.

All the data used by BST for a particular process investigation together with calculation results form a

¹² Either the tank pressure or initial liquid temperature can be omitted. In this case the missing component is evaluated for equilibrium between the liquid and gas cushion.

project. BST can save the current data in a project and load it later for further work. BST projects can only be read by BST.

Software Structure

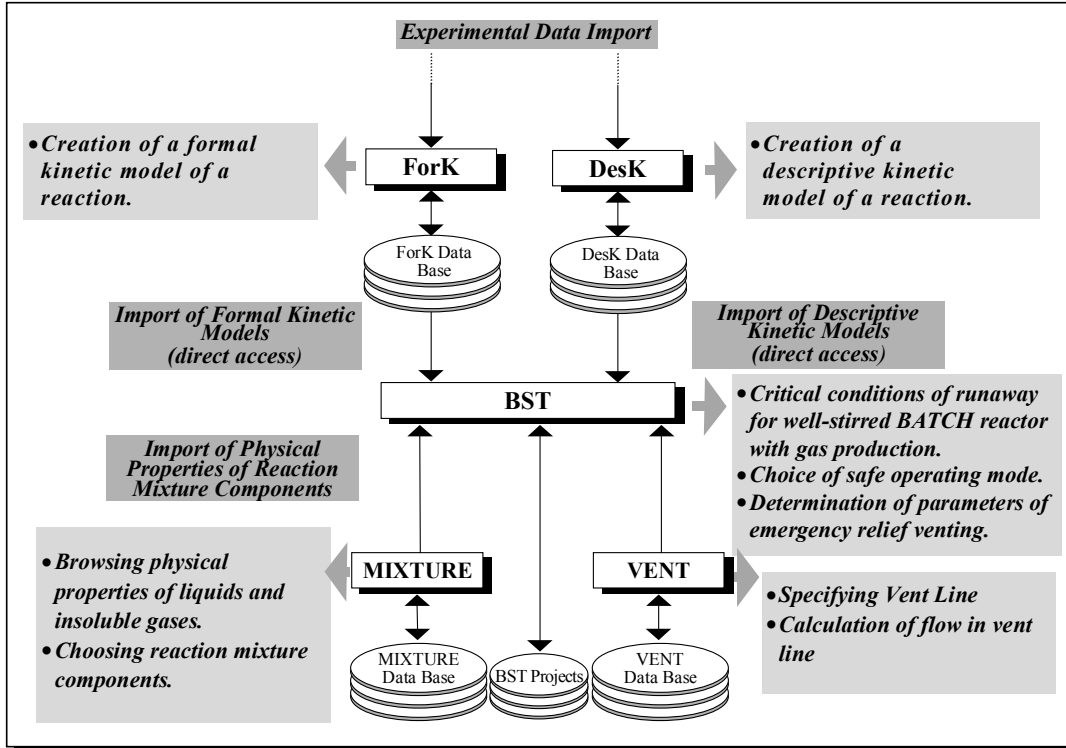


Fig. 3. A part of a thermal hazard assessment system.

BST Logical Structure

BST logical structure is shown in Fig. 4The figure illustrates data exchange paths between BST modules.

BST includes the following relatively independent Subsystems (S/S):

1. DATA INPUT;
2. SIMULATION;
3. RESULT VIEW.

The user works with these subsystems in the order specified above.

The DATA INPUT subsystem provides input of initial data. It is the interface for preparing the data file for initialization of the SIMULATION subsystem. You cannot enter correspondence data between kinetic model and mixture composition unless kinetics and composition data are entered; and you cannot enter tank data unless correspondence data are entered.

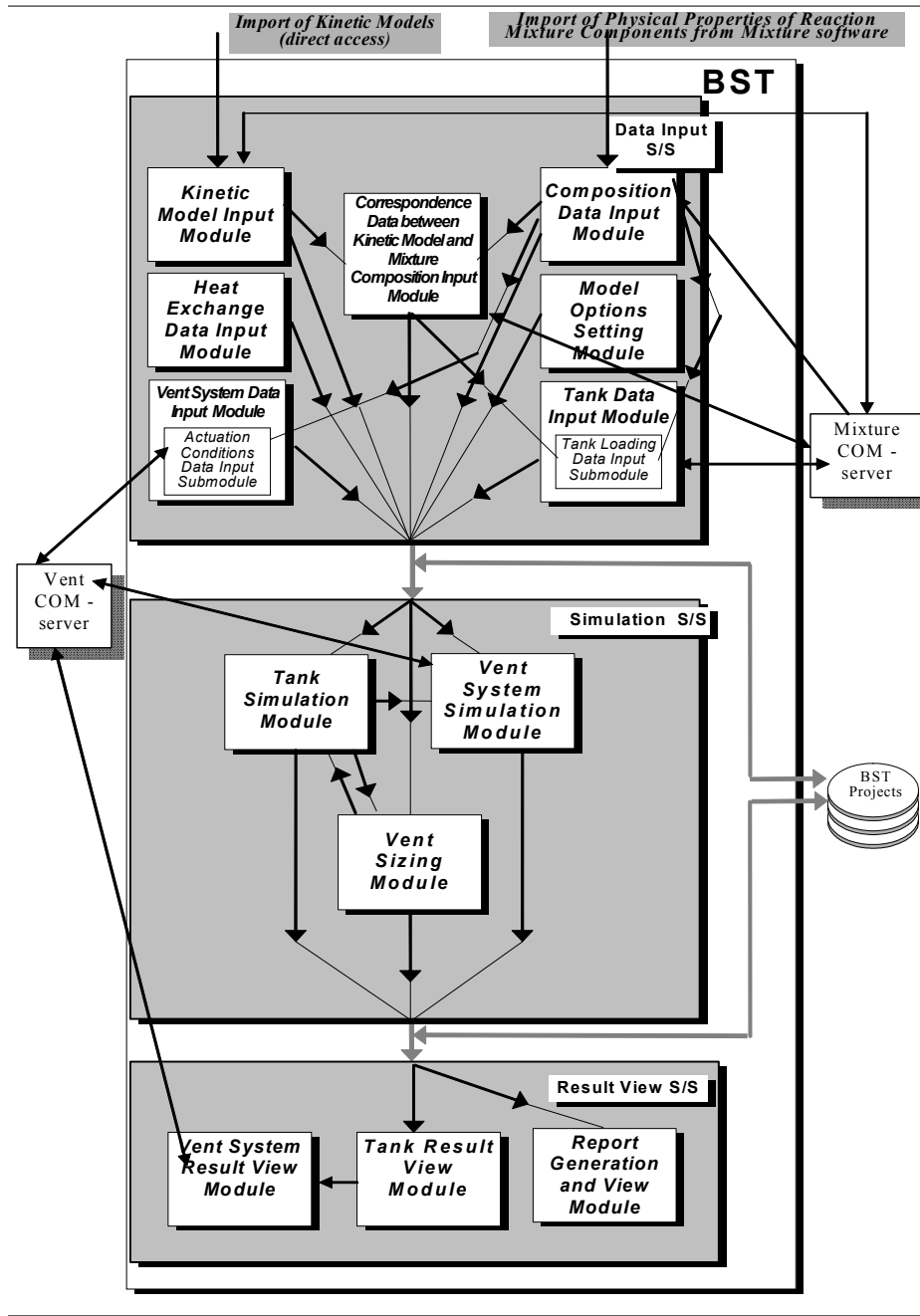


Fig. 4 BST logical structure

The SIMULATION subsystem provides simulation of a runaway reaction that may occur in well-stirred batch tanks because of insufficiency of external cooling; simulation of pressure release in the tank without chemical reactions; simulation of heat exchange between the tank and the environment; and sizing pressure relief systems. This subsystem is a computational module. It is not available unless initial data are entered properly. After reading initial data and performing simulation, this subsystem passes the results of simulation to the RESULT VIEW subsystem.

The RESULT VIEW subsystem transforms the result data for graphic and table presentations on the screen or another device. It also allows generating and viewing a report, which contains detailed information on the task accomplished. This subsystem is not available unless simulation has been performed.

Basic Problems Solved with BST

According to your choice, BST can solve the following problems (see Fig. 4):

1. Simulation of a thermal explosion of a liquid reaction mixture in a well-stirred batch tank (RUNAWAY SIMULATION task). This task can include preliminary heating of a reaction mixture by a heat transfer agent. Integration of math model equations is completed if one of the following conditions is satisfied:
 - full conversion of all given substances (98%);
 - drain or evaporation of 95% of liquid;
 - excess of the tank pressure over MAWP preset by user;
 - tank pressure drops nearly down to the BACK PRESSURE (P_b) in the vent system (down to 105% of P_b).
2. Simulation of pressure release in the tank without chemical reactions (BLOWDOWN SIMULATION task). In this case, integration of the equations stops either at the pressure of 105% of P_b or at evaporation (or drain) of 95% of the liquid initial mass.
3. Simulation of heating up the tank with an external heat flux or cooling it with a convective heat flux (HEATING SIMULATION task). In this case, integration of the equations stops either when reaching the final time (set when entering boundary conditions of heat exchange as piecewise-linear functions versus time) or at evaporation (or drain) of 95% of the liquid initial mass or after exceeding MAWP.
4. The problem of matching of the critical value of the cross-sectional flow area of a vent system (VENT SIZING) is actual if the determining element of the vent system is the nozzle whose resistance far exceeds the resistance of the tail and inlet pipes. With BST, you can solve this problem (find the minimum area of the main element¹³ A_{im} at which the tank pressure does not exceed MAWP) by successive solution of tasks 1 or 3 for various values of the nozzle throat area. BST can automatically perform calculations on the tasks 1 or 3 at various values of the cross area of main element of vent system A_{im} for determination of the A_{im} minimum value when the tank pressure does not exceed maximum allowed pressure in tank. For a complex vent line, the cross-section area of every element is proportional to A_{im} .

Fundamental physical and chemical processes in a well-stirred batch tank

- The Tank Solver simulates:
 - Heat and gas generation caused by a chemical reaction;
 - Boiling of a liquid mixture;
 - "Swelling" of gas-liquid mixture and compression of the tank gas volume. "BUBBLE", "FOAM" and "CHURN-TURBULENT" models are available;
 - Various dependencies of external heat exchange;
 - Various initial conditions in the tank before a runaway starts;
 - Mass losses through the vent system
 - Heat and mass transfer between the gas space of tank and liquid
 - Wide range of physical properties of liquid and gas mixtures

Dependencies of external heat exchange

The external heat transfer takes place only inside the jacket region, which have two parameters: downside and upper boundaries measured from the tank bottom.

The temperature of a heat-transfer agent and effective coefficient of heat exchange are approximated with a linear-piecewise function of time. Besides, heat flux toward the tank can also be considered as a linear-piecewise function of time. This representation can be useful when simulating an accident of external heating (e.g. fire).

¹³ The main element is selected by the user. It is usually the element with the minimum cross-section area.

In a general case, the external heat flux is

$$q = q_0(\tau) + \alpha(\tau) \cdot [T_e(\tau) - T_w] + \varepsilon \cdot \sigma_0 \cdot [T_e^4(\tau) - T_w^4],$$

where ε is effective blackness of the radiate heat exchange with environment;

σ_0 is the Stephen-Boltzman constant

T_w is the temperature of the wall adjacent either to the liquid or to the gas. Here, it is assumed that the coefficient of heat exchange between the liquid and the wall is large enough for difference between their temperatures to be neglected, i.e. $T_w|_{liq} \cong T_{liq}$. When contacting with gas, the wall temperature should be calculated by the energy equation for the wall.

Here the time-dependent parameters are to be tabulated.

Basic assumptions

Real processes in the tank are very complex, so they are to be simplified in a way. We adopt the following conventional assumptions:

- gradients of temperature, pressure¹⁴, and composition of reaction and gas region mixtures are negligible;
- Temperature of a boiling liquid mixture is identically equal to T_s ($P \cong P_s$);
- the liquid and its bubbles are of the same pressure and temperature;
- Tank volume is constant.
- Distribution of the void fraction in liquid is quasi state (according to "BUBBLE", "FOAM", "CHURN-TURBULENT" DIERS correlation);
- Tank walls are thin.
- Initial equilibrium in the tank has set in;
- Local thermodynamic equilibrium boundary conditions on gas-liquid inter-phase surface (for vapor flux determination for "gassy" reaction and for liquid—tank vapor space interaction) are assumed
- The gas and liquid mixture with insoluble gases present are ideal.

We use the basic laws of conservation as well as thermodynamic relationships in the most complete form, namely:

- Mass balance of liquid components
- Mass balance of gas components in gas volume
- Mass balance of insoluble gas components in bubbles
- Energy balance for liquid and bubbles
- Energy balance for gas(vapor) volume
- Volume balance for tank
- Equations of state for liquid, bubbles and gas volume

We use two ways to determine the vapor flux at boiling:

- For pure vapor system (no insoluble gas generation) the vapor generation rate can be determined basing on the assumption that the temperature of vapor—liquid mixture is close to equilibrium $T \approx T_s(P, c_i)$, where c_i are the mass fractions of components of liquid mixture.
- For "GASSY"¹⁵ reaction vapor flux can be determined on the base of the assumption of local equilibrium in flux of vapor-gas mixture on liquid - bubble boundary.

¹⁴ Exceptions: hydraulic head and a bottom-mounted vent system

¹⁵ By "GASSY" reaction we mean the one that generates insoluble gas. Gas generation is always combined with vapor generation, i.e. in practice only a hybrid reaction can take place in a liquid mixture.

No gas generation	"Gassy" reaction
Temperature of vapor-liquid mixture is close to equilibrium $T \equiv T_s(P, c_i) \Rightarrow \dot{T} \equiv \dot{T}_s$	Local equilibrium in flux on liquid-bubble boundary $W_s = W_{gR} \cdot \frac{m_s}{m_{gR}} \cdot \frac{P_s}{P - P_s}$

Tank solver algorithm

Mass balances of the components in a liquid mixture

$$\frac{dM_{l_i}}{d\tau} = W_{lR_i} + W_{l_i} \quad (1)$$

where M_{l_i} is the mass of i-th component of the liquid mixture, W_{l_i} is the mass fraction of flow of i-th component of the liquid mixture through the vent system, W_{lR_i} is the rate of changing mass of i-th liquid component caused by the chemical reaction.

For **DESK** kinetics, W_{lR_i} are calculated exactly by means of the specific DLL of **DESK** software. As for the **FORK** one, they can be estimated only in rough-and-ready manner by using linear relations of changing formal conversions:

$$W_{lR_i} \cong M_{l_i} \cdot \bar{M}_{lR} \cdot \sum_{j=1}^{N_r} A_{K_{ij}} \cdot \frac{da_j}{d\tau} \quad ,$$

where $M_{l_i} \equiv \sum_{i=1}^{N_l} M_{l_i}$; $\bar{M}_{lR} \equiv \frac{c_{lr}}{c_{lr}|_{\tau=0}}$; $c_{lr} = \sum_{i=1}^{N_l} I_{K_i} \cdot c_{l_i}$ is the mass fraction of a reactant in the liquid

mixture; c_{l_i} is the mass fraction of i-th component of the liquid mixture;

$$I_{K_i} = \begin{cases} 0, & \text{if } A_{K_{ij}} = 0 \quad \text{for } j=1, \dots, N_r \\ 1, & \text{otherwise} \end{cases}$$

$A_{K_{ij}}$ is an element of a relation matrix (let us call it the connection matrix), indicating the connection between alteration of the mass fraction of i-th component of the reaction mixture and conversion degree for j-th reaction (stage); a_j is the degree of conversion for j-th reaction (stage).

For a bottom-vented tank, two cases are available:

no stirring in the tank: $W_{l_i} = -W_{v_{mix}} \cdot c_{l_i} - W_s \cdot c_{s_i}$,

where c_{s_i} is the mass fraction of i-th component of the gas mixture in bubbles, G_s is the mass rate of vapor flow from liquid to bubbles.

stirring in the tank: $W_{l_i} = -W_{v_{mix}} \cdot c_{l_i} \cdot (1 - X_b) - W_s \cdot c_{s_i}$,

where $W_{v_{mix}}$ is the mass rate of gas-liquid mixture flow through the vent system,

$$X_b \equiv \left(1 - \sum_{j=1}^{N_g} X_{0_j} \right),$$

where X_{0_j} is the mass fraction of j-th component of the gas mixture in the mass flow at the vent system inlet.

Mass balances of the components in gas phase inside bubbles

$$\frac{dM_{b_i}}{dt} = \begin{cases} W_s \cdot c_{s_i} - j_{g\infty} \cdot \rho_b \cdot c_{b_i} \cdot A_{fs} - W_{vb}, & \text{for } i=1, \dots, N_1 \\ W_{gR_i} - j_{g\infty} \cdot \rho_b \cdot c_{b_i} \cdot A_{fs} - W_{vb}, & \text{for } i=N_1+1, \dots, N_g \end{cases}, \quad (2)$$

where M_{b_i} is the mass of i -th component of the mixture in bubbles (vapor if $1 \leq i \leq N_k$; insoluble gas if $N_1 + 1 \leq i \leq N_g$).

For DESK kinetics G_{gR_i} are calculated exactly by means of the specific DLL of DESK software. As for the FORK one, they can be estimated only in rough-and-ready manner by using linear relations of changing formal conversions:

$$W_{gR_i} \equiv M_1 \cdot \bar{M}_{1R} \cdot \sum_{j=1}^{N_f} A_{K_{ij}} \frac{da_j}{dt}, \quad \text{for } i = N_1 + 1, \dots, N_g,$$

where c_{b_i} is the mass fraction of i -th component of the mixture in bubbles (vapor if $1 \leq i \leq N_1$; insoluble gas if $N_k + 1 \leq i \leq N_g$), $j_{g\infty}$ is the vapor superficial velocity at the liquid surface, S_{fs} is the area of the free surface of liquid.

Mass rate of the gas phase flow through the vent system W_{vb} is calculated as follows:

- In case of top venting and zero gas region:

$$G_{vb} = 0.$$

- In case of top venting and non-zero gas region we use DIERS coupled equation for determining the W_{vb} (see formula I-A1 from [1])¹⁶:

$$W_{vb} = \frac{\alpha_m \cdot \rho_b}{\alpha_m \cdot \rho_b + (1 - \alpha_m) \cdot \rho_l} \cdot (W_{v_{mix}} - j_{g\infty} \cdot \rho_b \cdot A_t). \quad (3)$$

Here α_m is the void fraction on the free surface of liquid, ρ_b is the density of gas mixture in bubbles, ρ_l is the density of liquid mixture,

$$S_t \text{ is the effective cross-section area of the tank, } A_t = \begin{cases} \pi \cdot R_{cyl}^2, & \text{for a vertical cylindrical tank} \\ \frac{\pi \cdot R_{cyl} \cdot L_{cyl}}{2}, & \text{for a horizontal cylindrical tank,} \\ \frac{2 \cdot \pi \cdot R_{sphere}^2}{3}, & \text{for a spherical tank} \end{cases}$$

where R_{cyl} is the radius of cylindrical tank, L_{cyl} is the length of cylindrical tank, R_{sphere} is the radius of spherical tank.

Values α_m and $j_{g\infty}$ are computed by the relations from [1], Appendix I-A (section I-A2). See also [3].

- In case of bottom venting and no stirring in the tank:

$$W_{vb} = 0$$

- In case of bottom venting and stirring in the tank:

$$W_{vb} = \frac{\bar{\alpha} \cdot \rho_b}{\bar{\alpha} \cdot \rho_b + (1 - \bar{\alpha}) \cdot \rho_l} \cdot W_{v_{mix}},$$

where $\bar{\alpha}$ is the average void fraction in liquid.

¹⁶ In this case, mass fraction of the gas phase flowing into the vent line depends on the total flow rate through the vent line, and additional iterations are required.

Calculating vapor superficial velocity at the liquid surface

For a vertical cylinder, variables α_m and $j'_{g\infty}$ are evaluated by the work formulas from [1].

$$j'_{g\infty} = U_{\infty} \cdot \frac{\bar{\alpha} \cdot (1 - \bar{\alpha})^2}{(1 - \bar{\alpha}^3) \cdot (1 - C_0 \cdot \bar{\alpha})} \quad \text{for a Bubble model,}$$

$$j'_{g\infty} = U_{\infty} \cdot \frac{2 \cdot \bar{\alpha}}{(1 - C_0 \cdot \bar{\alpha})} \quad \text{for a Churn-Turbulent model.}$$

In the most general case, $f(\alpha) = \frac{\alpha \cdot (1 - \alpha)^n}{(1 - p \cdot \alpha^m) \cdot (1 - C_0 \cdot \alpha)}$,

where:

- $m=0, n=2, p=0, C_0 \geq 1.0$ for a Bubble model;
- $m=0, n=0, p=0, C_0 \geq 1.0$ for a Churn-Turbulent model.

The typical disengagement rate of the bubbles is

$$U_{\infty} = \frac{1.18 \cdot (\sigma \cdot g_0 \cdot (\rho_f - \rho_g))^{1/4}}{\rho_f^{1/2}} \quad \text{for a Bubble model;}$$

$$U_{\infty} = \frac{1.53 \cdot (\sigma \cdot g_0 \cdot (\rho_f - \rho_g))^{1/4}}{\rho_f^{1/2}} \quad \text{for a Churn-Turbulent model.}$$

Mass balances of a component of the gas region

$$\frac{dM_{g_i}}{d\tau} = j'_{g\infty} \cdot \rho_b \cdot c_{b_i} \cdot A_{fs} - W_{v_g} - W_{cond}, \text{ for } i=1, \dots, N_g, \quad (4)$$

where M_{g_i} is the mass of an insoluble individual component of the gas region,

c_{g_i} is the mass fraction of i-th component of the gas region.

In the case of bottom venting:

$$G_{vg} = 0,$$

otherwise:

$$G_{vg} = G_v \cdot c_{g_i}.$$

For the zero gas region:

$$\frac{dM_{g_i}}{d\tau} = 0.$$

Energy balance for a gas-liquid mixture in a tank

Let the reaction mixture and elements of the tank construction being in contact with the liquid have equal temperature. In this case:

$$\dot{T}_{mix} = \frac{Q_{mix0}}{\hat{C}_{P_{total}}} + \frac{\dot{P}}{C_{PV_{mix}}} - \frac{L_s}{\hat{C}_{P_{total}}} \cdot W_s + \frac{\tilde{L}_s}{\hat{C}_{P_{total}}} \cdot W_{cond} \quad (5)$$

where $Q_{mix0} = Q_{ext} + Q_{react} + Q_{gFs}$, Q_{gFs} is the heat flux from the gas region to the free surface of liquid,

Q_{ext} is external heat transfer to reaction mixture, Q_{react} is the rate of heat generation caused by chemical

$$\text{reaction, } \dot{T}_m = \frac{Q_{m_0}}{\hat{C}_{P_{\text{total}}}} + \frac{\dot{P}}{C_{PV_m}} - \frac{L_s}{\hat{C}_{P_{\text{total}}}} \cdot G_s + \frac{\tilde{L}_s}{\hat{C}_{P_{\text{total}}}} \cdot G_{\text{cond}}$$

$$C_{PV_{\text{mix}}} \equiv \frac{m c_{p_{\text{mix}}}}{V_{\text{mix}} - M_{\text{mix}} \cdot \left. \frac{\partial H_{\text{mix}}}{\partial P} \right|_{T, c_i}}$$

Here, for the ideal liquid mixture:

$$\tilde{L}_S = L_S = \sum_{j=1}^{N_k} c_{s_j} \cdot (H_{1j} - H_{s_j}),$$

otherwise:

$$L_S \equiv H_b - H_l + \sum_{i=1}^{N_l-1} \frac{\partial H_b}{\partial c_i} \cdot (c_{s_i} - c_{b_i}) - \sum_{i=1}^{N_l-1} \frac{\partial H_l}{\partial c_i} \cdot (c_{s_i} - c_{l_i}), \quad \tilde{L}_S \equiv H_s - H_l - \sum_{i=1}^{N_l-1} \frac{\partial H_l}{\partial c_i} \cdot (c_{s_i} - c_{l_i}),$$

where H_l is the enthalpy of liquid mixture, H_b is the enthalpy of vapor mixture in bubbles,

$$\hat{C}_{P_{\text{total}}} \equiv M_{\text{mix}} \cdot C_{P_{\text{mix}}} + M_{\text{tank}} \cdot C_{P_{\text{tank}}}.$$

External heat flow Q_{ext} is presented as follows:

$$Q_{\text{ext}} = \{q_0(\tau) + A_0(\tau) \cdot [T - T_{\text{ext}0}(\tau)]\} \cdot S_{t_{\text{mix}}},$$

where $S_{t_{\text{mix}}}$ is the area of contact between the mixture and the side surface of the tank,

$Q_0(\tau), A_0(\tau), T_{\text{ext}0}(\tau)$ are the parameters of external heat transfer. They should be preset as an array of values versus time suitable for the linear approximation.

Energy balance for a gas mixture in the gas region

$$\dot{T}_g \equiv \frac{Q_{g_0} + W_{\text{cond}} \cdot \Delta H_{gs}}{M_g \cdot C_{P_g}} + \frac{\dot{P}}{M_g \cdot C_{PV_g}}, \quad (6)$$

where

$$Q_{g_0} = Q_{\text{gext}} - Q_{\text{gFs}} - W_{\text{fs}} \cdot \Delta H_{gb}; \quad C_{PV_g} \equiv \frac{C_{p_g}}{\left. \frac{1}{\rho_g} - \frac{\partial H_g}{\partial P} \right|_{T, c_i}}; \quad W_{\text{fs}} \equiv j'_{\text{g}\infty} \cdot \rho_b \cdot A_{\text{fs}};$$

$$\Delta H_{bg} \equiv H_g - H_b + \sum_{i=1}^{N_g-1} \frac{\partial H_g}{\partial c_i} \cdot (c_{b_i} - c_{g_i}), \quad \Delta H_{gs} \equiv H_g - H_s + \sum_{i=1}^{N_g-1} \frac{\partial H_g}{\partial c_i} \cdot (c_{s_i} - c_{g_i}).$$

For ideal gas mixture:

$$\Delta H_{gs} = \sum_{i=1}^{N_l-1} (H_{g_i}(T_g) - H_{g_i}(T_s)) \cdot c_{s_i}, \quad \Delta H_{gb} = \sum_{i=1}^{N_g-1} (H_{g_i}(T_g) - H_{g_i}(T_l)) \cdot c_{b_i}.$$

Condition of constant tank volume

$$\sum_{j=1,b,g} \frac{M_j}{\rho_j} = V_{\text{tank}}, \quad (7)$$

where

$$\begin{aligned} \rho_l &= \rho_l(P, T_{\text{mixt}}, c_{l_i}), \quad i=1, \dots, N_l - 1; \\ \rho_b &= \rho_b(P, T_{\text{mixt}}, c_{b_i}), \quad i=1, \dots, N_g - 1; \\ \rho_g &= \rho_g(P, T_g, c_{g_i}), \quad i=1, \dots, N_g - 1 \end{aligned}$$

Hence, if $\dot{V}_{\text{tank}} = 0$, then:

$$\dot{V}_{00} - \tilde{\beta}_P \cdot \dot{P} = 0 \quad (8)$$

$$\dot{V}_{00} = \dot{V}_{\Sigma 2} + W_s \cdot (\Delta \tilde{v}_{bl} - \hat{v}_s) - W_{\text{cond}} \cdot (\Delta \tilde{v}_{gl} - \hat{v}_{sg}) + \bar{\beta}_{T_m} \cdot \dot{T}_{m_0}$$

$$\text{Where } \dot{T}_{g_0} \equiv \frac{Q_{g_0}}{m_g \cdot C_{p_g}}; \quad \dot{T}_{\text{mix}_0} \equiv \frac{Q_{\text{mix}_0}}{\hat{C}_{P_{\text{total}}}}$$

$$\bar{\beta}_{T_{\text{mix}}} \equiv \sum_{j=1,b} \frac{M_j}{\rho_j} \cdot \beta_{T_j}; \quad \bar{\beta}_{T_g} \equiv \frac{M_g}{\rho_g} \cdot \beta_{T_g}; \quad \bar{\beta}_P \equiv \sum_{j=1,b,g} \frac{M_j}{\rho_j} \cdot \beta_{p_j}; \quad \tilde{\beta}_P \equiv \sum_{j=1,b,g} \frac{M_j}{\rho_j} \cdot \beta_{p_j} - \frac{\bar{\beta}_{T_{\text{mix}}}}{C_{PV_{\text{mix}}}} - \frac{\bar{\beta}_{T_g}}{C_{PV_g}};$$

$$\Delta v_{bl} \equiv v_b - v_l; \quad \Delta \tilde{v}_{bl} = \Delta v_{bl} + \sum_{j=1}^{N_g-1} \frac{\partial v_b}{\partial c_j} \cdot (c_{s_j} - c_{b_j}) - \sum_{j=1}^{N_l-1} \frac{\partial v_l}{\partial c_j} \cdot (c_{s_j} - c_{l_j})$$

$$\Delta v_{gl} \equiv \frac{1}{\rho_g} - \frac{1}{\rho_l}; \quad \Delta \tilde{v}_{gl} = \Delta v_{gl} + \sum_{j=1}^{N_g-1} \frac{dv_g}{dc_j} \cdot (c_{s_j} - c_{g_j}) - \sum_{j=1}^{N_l-1} \frac{dv_l}{dc_j} \cdot (c_{s_j} - c_{l_j})$$

$$\Delta v_{bR} \equiv \sum_{j=1}^{N_g-1} \frac{dv_b}{dc_j} \cdot (c_{r_j} - c_{b_j});$$

$$\Delta v_{lR} \equiv \sum_{j=1}^{N_l-1} \frac{dv_g}{dc_j} \cdot (c_{s_j} - c_{g_j}) - \sum_{j=1}^{N_l-1} \frac{dv_l}{dc_j} \cdot (c_{s_j} - c_{l_j})$$

$$\dot{V}_{\Sigma 0} = -W_{v_{\text{mix}}} \cdot \left(\frac{1 - X_b}{\rho_l} + \frac{X_b}{\rho_b} \right) + W_{fs} \left(\frac{1}{\rho_b} - \frac{1}{\rho_g} \right) - \frac{W_{v_g}}{\rho_g};$$

$$\hat{v}_s \equiv \frac{L_s \cdot \bar{\beta}_{T_{\text{mix}}}}{\hat{C}_{P_{\text{total}}}}; \quad \hat{v}_{sg} \equiv \frac{\tilde{L}_s \cdot \bar{\beta}_{T_{\text{mix}}}}{\hat{C}_{P_{\text{total}}}} - \frac{\beta_{tg} \cdot \Delta H_{sg}}{\rho_g \cdot C_{p_g}};$$

$$\dot{V}_{\Sigma 2} = \dot{V}_{\Sigma 0} + W_{gR} \cdot (\Delta v_{bR} + \Delta v_{lR}).$$

Using equation (8) we obtain the equation for the pressure rate:

$$\dot{P} = \frac{\dot{V}_{\Sigma 2} + W_s \cdot (\Delta \tilde{v}_{bl} - \hat{v}_s) - W_{\text{cond}} \cdot (\Delta \tilde{v}_{gl} - \hat{v}_{sg}) + \bar{\beta}_{T_{\text{mix}}} \cdot \dot{T}_{\text{mix}_0} + \bar{\beta}_{T_g} \cdot \dot{T}_{g_0}}{\tilde{\beta}_P} \quad (9)$$

$$\bar{\beta}_{T_{\text{mix}}} \equiv \sum_{j=l,b} \frac{M_j}{\rho_j} \cdot \beta_{T_j}; \quad \bar{\beta}_{T_g} \equiv \frac{M_g}{\rho_g} \cdot \beta_{T_g}; \quad \bar{\beta}_P \equiv \sum_{j=l,b,g} \frac{M_j}{\rho_j} \cdot \beta_{P_j}; \quad \tilde{\beta}_P \equiv \bar{\beta}_P - \frac{\bar{\beta}_{T_{\text{mix}}}}{C_{PV_{\text{mix}}}} - \frac{\bar{\beta}_{T_g}}{C_{PV_g}}$$

Vapor mass flow rate from the liquid to bubble region

Approximation on bubble-liquid equilibrium for non-ideal liquid and vapor mixtures.

In this case, the vapor-liquid equilibrium relations can be represented as follows:

$$\begin{cases} T_s = T_s(P, c_i) \\ K_j = K_j(P, c_i) \end{cases} \quad i=1, \dots, N_l-1; j=1, \dots, N_l.$$

where $K_i = Y_{gi} / Y_{li}$ are the equilibrium interphase distribution coefficients.

According to the law of conservation of energy for the reaction mixture and since $T_{\text{mix}} \equiv T_s$

$$\dot{T}_{\text{mix}} = \dot{T}_{\text{mix}_0} + \frac{\dot{P}}{C_{PV_{\text{mix}}}} - \frac{L_s}{\hat{C}_{P_{\text{total}}}} \cdot W_s = \frac{\partial T_s}{\partial P} \cdot \dot{P} - \frac{W_s}{M_l} \cdot \sum_{i=1}^{N_l-1} \frac{\partial T_s}{\partial c_i} \cdot (c_{s_i} - c_{l_i}).$$

Hence:

$$\dot{P} = - \frac{\frac{L_s}{\hat{C}_{P_{\text{total}}}} - \frac{1}{M_l} \cdot \sum_{i=1}^{N_l-1} \frac{\partial T_s}{\partial c_i} \cdot (c_{s_i} - c_{l_i})}{B_v} \cdot W_s + \frac{\dot{T}_{\text{mix}_0}}{B_v}, \quad (10)$$

$$\text{where } B_v \equiv \frac{dT_s}{dP} - \frac{1}{C_{PV_{\text{mix}}}}.$$

By substituting (10) into (8) obtain the following equation for computing a vapor generation rate:

$$W_s = \frac{(\tilde{\beta}_{PT} - 1) \cdot \bar{\beta}_{T_{\text{mix}}} \cdot \dot{T}_{\text{mix}_0} - \bar{\beta}_{T_g} \cdot \dot{T}_{g_0} - \dot{V}_{\Sigma 2}}{\Delta \tilde{v}_{bl} - \hat{v}_s \cdot \left(1 - \tilde{\beta}_{PT} \frac{\hat{L}_s}{L_s} \right)}, \quad (11)$$

$$\text{where } \dot{V}_{\Sigma 2} = \dot{V}_{\Sigma 1} + W_{gR} \cdot \Delta v_{bR} + \Delta v_{lR}, \quad \tilde{\beta}_{PT} \equiv \frac{\tilde{\beta}_P}{B_v \bar{\beta}_{T_{\text{mix}}}}; \quad \hat{L}_s \equiv L_s - \frac{\hat{C}_{P_{\text{total}}}}{M_l} \cdot \sum_{i=1}^{N_l-1} \frac{\partial T_s}{\partial c_i} \cdot (c_{s_i} - c_{l_i}).$$

Approximating bubble-liquid equilibrium for ideal gas and liquid mixtures when an insoluble gas presents.

This case is available only if the liquid mixture is ideal as well as the gas in bubbles and gas region. Local equilibrium in flux on liquid-bubble boundary can be represented as:

$$W_s = W_{gR} \cdot \frac{m_s}{m_{gR}} \cdot \frac{P_s}{P - P_s}, \quad (12)$$

where $\tilde{\beta}_{pT} \equiv \frac{\tilde{\beta}_p}{B_v \cdot \tilde{\beta}_{Tmix}}$.

Heat and mass transfer through liquid surface

While pressure in a tank raises and there are no bubbles in a liquid, some vapors of a gas region may condense on the liquid surface. If the gas region includes insoluble gases the condensation of vapors is supervised by diffusion and hence is usually small. At presence of a pure vapor cushion it is necessary to account a flow of vapors from the core of a gas region to the free surface of a liquid. Thus, an influence of the Stephen's flow to the heat exchange on a free surface of a liquid must be considered.

Heat transfer between gas region and for pure vapor condensation.

Let us consider the heat transfer equation with regard to the flux through laminar sublayer above the liquid surface

$$\frac{C_p \cdot g_{cond}}{h} \cdot \frac{dT}{d\bar{y}} = -\frac{\lambda}{h^2} \cdot \frac{d^2T}{d\bar{y}^2},$$

where h is the sublayer height; $\bar{y} = \frac{y}{h}$; y is a transversal coordinate; g_{cond} is the specific mass flux caused by condensation of pure vapors; λ is thermoconductivity of the vapor; $T|_{\bar{y}=0} = T_s$; $T|_{\bar{y}=1} = T_g$ is the boundary condition.

Using the approach of constant physical properties we can integrate the last equation:

$$T = T_s + \frac{T_g - T_s}{1 - e^{-k}} \cdot (1 - e^{-k \cdot \bar{y}}),$$

where $k = \frac{h \cdot \bar{C}_p \cdot g_{cond}}{\lambda}$;

$$\left. \frac{dT}{d\bar{y}} \right|_{\bar{y}=0} = k \cdot \frac{T_g - T_s}{1 - e^{-k}}$$

$$q_{Fs} = \lambda_{Fs} \left. \frac{dT}{dy} \right|_{y=0} = \frac{\lambda_{Fs}}{\lambda} \cdot \bar{C}_p \cdot g_{cond} \cdot \frac{T_g - T_s}{1 - e^{-k}}$$

$\bar{\lambda}$, \bar{C}_p are the mean values of thermoconductivity and specific heat capacity of the vapors across the laminar sub-layer in the free surface boundary layer, respectively.

Assuming that a free surface boundary layer is induced by thermal convection in the gas region along the walls of the tank, we can suggest that the thickness of laminar sub-layer at free surface have the same magnitude at the side walls as the optimal one:

$$h \approx \frac{\bar{\lambda}_{gw0}}{\alpha_{gw0}},$$

where α_{gw0} is the heat transfer between the gas region and side walls, d_{eff} is the

characteristic length of side wall boundary layer.

Finally, we can get the following equation for specific heat flux from gas region to liquid:

$$Q_{Fs} = \frac{\lambda_{Fs}}{\bar{\lambda}} \cdot \bar{C}_p \cdot W_{cond} \cdot \frac{T_g - T_s}{e^k - 1}$$

$$k = \frac{\bar{\lambda}_{gw0}}{\bar{\lambda}} \cdot \frac{\bar{C}_p \cdot g_{cond}}{\alpha_{gw0}} \equiv \frac{\bar{\lambda}_{gw0}}{\bar{\lambda}} \cdot \frac{\bar{C}_p \cdot W_{cond}}{A_{Fs} \cdot \alpha_{gw0}}$$

Without too big loss of accuracy we can neglect the difference in physical properties at side walls, center

of gas region and free surface.

Therefore, we have for a heat flux from gas region to free surface of liquid

$$Q_{Fs} \approx C_{p_g} \cdot A_{cond} \cdot \frac{T_g - T_s}{1 - e^{-k}}, \text{ where } k \approx \frac{C_{p_g} \cdot W_{cond}}{A_{Fs} \cdot \alpha_{gw0}},$$

and

$$\dot{T}_g \cong \frac{Q_{gext}}{M_g \cdot C_{p_g}} - \frac{C_{p_g} \cdot W_{cond} \cdot \frac{T_g - T_s}{1 - e^{-k}} \cdot e^{-k}}{M_g \cdot C_{p_g}} + \frac{\dot{P}}{M_g \cdot C_{p_{Vg}}}$$

for a heat flux from gas region to free surface of liquid.

Heat transfer between gas region and liquid surface in case of the gas-vapor flow from a liquid to the gas region through a free surface.

In this case we can get the similar equation by replacing the value of W_{cond} with $-W_{fs}$:

$$Q_{Fs} \approx C_{p_b} \cdot W_{cond} \cdot \frac{T_g - T_s}{1 - e^k}, \text{ where } k \approx \frac{C_{p_b} \cdot W_{fs}}{A_{Fs} \cdot \alpha_{gw0}}.$$

Condensation vapor mass flow rate from the pure vapor region to the liquid.

Mass flow rate of condensation from pure vapor cushion through the free surface is calculated under assumption that the liquid temperature is in equilibrium with total pressure in gas region during condensation. When the condensation is possible, the vapor flux caused by bubble boiling (G_s) vanishes.

According to the law of energy conservation for a reaction mixture and $T_{mix} \equiv T_s$:

$$\dot{T}_{mix} = \dot{T}_{mix0} + \frac{\dot{P}}{\hat{C}_{P_{total}}} + \frac{\tilde{L}_s}{\hat{C}_{P_{total}}} \cdot W_{cond} = \frac{\partial T_s}{\partial P} \cdot \dot{P} + \frac{W_{cond}}{M_l} \cdot \sum_{i=1}^{N_l-1} \frac{\partial T_s}{\partial c_i} \cdot (c_{s_i} - c_{l_i})$$

$$\text{Hence, } \dot{P} = \frac{\frac{\tilde{L}_s}{\hat{C}_{P_{total}}} - \frac{1}{M_l} \cdot \sum_{i=1}^{N_l-1} \frac{\partial T_s}{\partial c_i} \cdot (c_{s_i} - c_{f_i})}{B_v} \cdot W_{cond} + \frac{\dot{T}_{mix0}}{B_v}.$$

$$\dot{V}_{\Sigma 2} - W_{cond} \cdot \left(\Delta \tilde{v}_{gl} - \tilde{v}_s + \bar{\beta}_{T_g} \cdot \frac{T_g - T_s}{M_g} \cdot \frac{1 - e^{-k}}{1 - e^{-k}} \cdot e^{-k} \right) + \bar{\beta}_{T_{mix}} \cdot \dot{T}_{mix0} + \frac{Q_{gext}}{M_g \cdot C_{p_g}}$$

$$\text{On the other hand, } \dot{P} = \frac{\dot{V}_{\Sigma 2} - W_{cond} \cdot \left(\Delta \tilde{v}_{gl} - \tilde{v}_s + \bar{\beta}_{T_g} \cdot \frac{T_g - T_s}{M_g} \cdot \frac{1 - e^{-k}}{1 - e^{-k}} \cdot e^{-k} \right) + \bar{\beta}_{T_{mix}} \cdot \dot{T}_{mix0} + \frac{Q_{gext}}{M_g \cdot C_{p_g}}}{\tilde{\beta}_p}$$

$$W_{cond} = \frac{\dot{V}_{\Sigma 2} + \bar{\beta}_{T_{mix}} \cdot (1 - \tilde{\beta}_{PT}) \dot{T}_{mix0} + \bar{\beta}_{T_g} \cdot \frac{Q_{gext}}{M_g \cdot C_{p_g}}}{\Delta \tilde{v}_{gl} - \hat{v}_s \cdot \left(\frac{\tilde{v}_s^*}{\hat{v}_s} - \tilde{\beta}_{PT} \cdot \frac{\tilde{L}_s}{L_s} \right)}, \quad (13)$$

$$\text{where } \tilde{L}_s \equiv \tilde{L}_s - \frac{\hat{C}_{P_{total}}}{M_l} \cdot \sum_{i=1}^{N_l-1} \frac{\partial T_s}{\partial c_i} \cdot (c_{s_i} - c_{l_i}); \quad \tilde{v}_s^* = \tilde{v}_s - \frac{\beta_{T_g}}{\rho_g} \cdot \frac{T_g - T_s}{e^k - 1}.$$

It is easy to see that the last equation is a non-linear transcendental algebraic equation can be solved by an

iterative method.

The general system of equations and calculation procedures

The model includes both ordinary differential equations (ODE) and transcendent algebraic ones.

The general system of equations consists of:

1. Ordinary differential equations of conservation and balance laws:
 - Mass balance of the liquid mixture components;
 - Mass balance of the components of the gas region;
 - Mass balance of the insoluble gas mixture in bubbles;
 - Energy equation for the liquid—bubbles mixture;
 - Energy equation for the gas region;
 - Condition of the constant vessel volume (in differential form);
 - State equations for the liquid, gas region and the bubbles in the tank (in differential form);
2. Kinetics Ordinary differential equations (see FORK tutorial e.g.);
3. Equations for the mass flux through the vent system (see the following section).

BST uses methods of the Runge-Kutta family and the Gear method in order to solve system of ODE.

Nonlinear algebraic equations are solved by the golden section method.

Initial data.

Initial data includes:

- Initial masses of individual components of the liquid mixture in the tank;
- Initial temperature of the mixture;
- Initial pressure in the tank.

If user-defined value of initial pressure exceeds 0, mass fraction of components of the gas mixture in the gas region must be entered.

If zero value of initial pressure is entered, two cases of initial conditions in the gas region might be considered:

Equilibrium conditions in the gas region:

- Pressure in tank is the equilibrium vapor pressure at current initial temperature in the tank or temperature in tank is the equilibrium boiling temperature at current initial pressure.
- The composition of gas mixture is the composition of equilibrium vapor at current initial temperature of the liquid in the tank.

Notation.

- A - area
- a_j - Degree of conversion of j-th reaction
- c_{f_i} or c_{l_i} - Mass fraction of j-th component of liquid mixture
- C_p - Specific heat capacity at constant pressure
- c_{s_i} - Mass fraction of j-th component of equilibrium vapor mixture
- d - Absolute differential operator
- ∂ - partial differential operator
- f(x) - function of x
- W or G - Mass flow rate kg/s
- W_s - vapor generation rate due to boiling of liquid
- g - Mass flux kg/s/m²
- W_v - Vent mass flow rate kg/s
- g_0 - Gravitational acceleration
- H - Enthalpy
- M - Mass of the tank contents, kg
- m_j - Molecular mass of j-th component of mixture
- N_l - Number of components of liquid mixture
- N_g - Number of components of gas mixture
- N_r - Number of reactions
- P - Pressure
- T - Temperature, K
- X_{g0}, X_v - Weight-flow fraction of insoluble gas and vapor, respectively, in two-phase flow
- Y_{l_i} - Mole fraction of i-th component of liquid mixture
- Y_{sb} - Total mole fraction of vapor in bubble zone in reaction mixture
- Y_{s_i} - Mole fraction of i-th component of equilibrium vapor mixture
- α - Volume fraction of gas phase
- $\beta_P \equiv \left. \frac{\partial \ln(\rho)}{\partial P} \right|_{\substack{T=\text{Const} \\ c_i=\text{Const}}} \quad \text{Coefficient of compressibility at constant temperature and composition}$
- $\beta_T \equiv - \left. \frac{\partial \ln(\rho)}{\partial T} \right|_{\substack{P=\text{Const} \\ c_i=\text{Const}}} \quad \text{Thermal coefficient of expansion at constant pressure and composition}$
- μ - Dynamic viscosity
- V_{gf} - The difference of gas and fluid specific volumes, m³/kg
- ρ - Density (without subscript - density of mixture, otherwise see Subscripts)

Subscripts

b -	Gas phase in bubbles in reaction mixture (bubble region)
e -	Equilibrium
ext -	External
f or l	Liquid
fs -	Free surface of liquid
g -	Gas phase or tank vapor space
0 -	rate of changing of parameter when $W_s = 0$
mix -	Reaction mixture
react-	Linked with chemical reaction
sb-	Vapor in bubble zone
s-	Equilibrium (saturated) vapor at current state parameters
tank-	Elements of tank construction
v-	Vapor of the liquid mixture

References

1. DIERS."DIERS Project Manual", Ney York, 1992.
2. J. S. Duffield and R.Nijsing "Computer Simulations Describing the Emergency Pressure Relief of Hybrid and Gassy Systems", , ICHEM SYMPOSIUM SERIES No. 134.
3. J.C.Leung "Simplified Vent Sizing Equations for Emergency Relief Requirements in Reactors and Storage Vessel" AIChE JOURNAL, October 1986
4. J.A. Hare Problem Specification for Round Robin on Chemical Reactor Relief System Models (Vapor Pressure System), Contract no: JR05.086
5. Morris, S., "DIERS-JRC Contract Large Scale Test Results – Dracula and Columbus Test Facilities", Minutes of 22th DIERS Users Group Meeting, Charlestone, South Carolina, October, 1998
6. D.A. Shaw.,Validation of SAFIRE Computer Programm for ERS Design., International Symposium on Runaway Reactions, Pressure Relief Design, and Effluent Handling. March 11—13, 1998, Louisiana, New Orleans American Institute of Chemical Engineers N.Y., 1998, pp. 461—481
7. Chevassus,V., Emballement Thermiques. Comparison des Logicies de Simulation: SAFIRE, RELIEF and GRICHCA, Rhone-Poulenc Industrialization
8. Batch Stirred Tank. Relief System Design Software, Version 4.06,USER'S GUIDE, St-Petersburg, 2007

Appendix 1 Examples

Project "Cl2". Blowdown of Liquid Chlorine out of a Tank Car

Project comments: Horizontal cylinder. Chlorine valve problem. Blowdown. Bottom based venting.
 Demonstrates a good agreement with the "Safire" calculations.
 Components data: Chlorine (Cl₂), molar mass 70.91

Vent System type: Rupture Disk
 Vent Position: Bottom
 Actuation Conditions: Pressure 1 Bar

Entrance Tube

Parameter	Units	Value
Length	m	2.5
Elevation	m	2.5
Diameter	m	0.025
Inclination	deg	90
Entrance Loss Factor	-	0

Nozzle

Back Pressure	Bar	1
---------------	-----	---

Tail tube

Length	m	0.25
Elevation	m	0
Diameter	m	0.025
Inclination	deg	0
Entrance Loss Factor	-	0

Tank Data

Parameter	Units	Value
Shape		Horizontal Cylinder
Volume	m ³	60
H1/Htank	-	1
H/Htank	-	-
Maximum Allowed Pressure	Bar	10
Heat Capacity of Empty Tank	J/K	13854423
Initial Mass of Mixture	kg	20580
Initial Filling of Tank	-	-
Initial Tank Temperature	C	7
Initial Tank Pressure	Bar	-
Radius	m	1.25
Length	m	12.2231

Tank Results Graphics

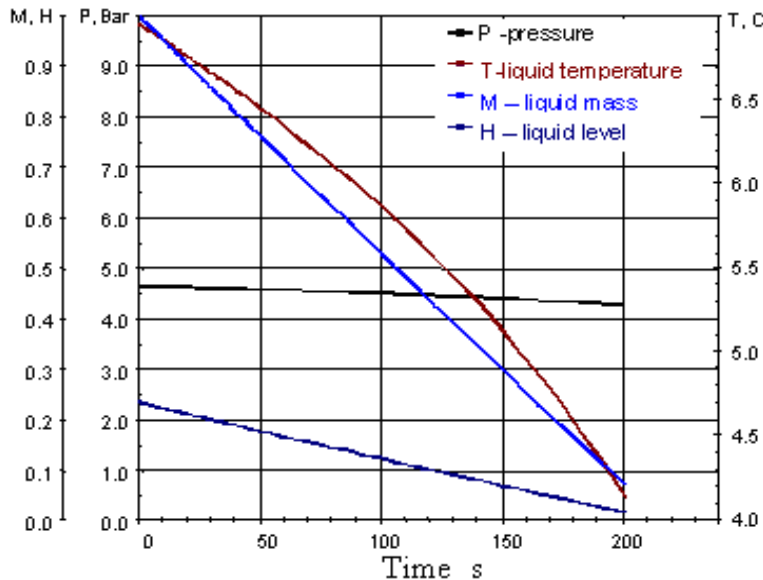


Fig. A1-1. Time dependence of pressure, mass flux, mass fraction of liquid and liquid level

NOTE: BST 4 uses new enhanced Mixture software that provides more precise calculation of physical properties. Therefore results of simulation of demo examples may slightly differ from the results presented in this document.

Project "H2O2Fe_d".

Simulation of Thermal Explosion in an Adiabatic Well-Stirred Batch Tank for Hydrogen Peroxide Decomposition (75%H2O, 25%H2O2 +Fe).

This task simulates an adiabatic explosion of hydrogen peroxide solution in a laboratory reactor. The reactor parameters are specified in [2]

Simulation task: Vent sizing

Reaction: 2*hydrogen peroxide → 2*water + oxygen

Kinetics: descriptive model DESK $r = K_0 \cdot \exp(-E/RT) \cdot [\text{hydrogene_peroxide}]^n$

Rates of species concentration variation

$d[\text{hydrogene_peroxide}]/dt = -2 \cdot r$

$d[\text{oxygen}]/dt = r$; $d[\text{water}]/dt = 2 \cdot r$

Kinetic Parameters:

Substances

Parameter	Units	Value	Short Name	Mole Mass	Comments
ln(k0)	ln((kmol/m ³) ^{0.00} /s)	27.34	H2O	18.01	Water (liquid)
E	kJ/mol	106.697	H2O2	34.0	Hydrogen Peroxide (liquid)
n	-	1.0	O2	32.0	Oxygen (gas)
Q	kJ/mol	189.720			
G	Mol/mol	1.0			

DESK - MIXTURE Synchronization

MIXTURE\DESK	Hydrogene peroxide	oxygen	water
H2O			#
H2O2	#		
O2		#	

Tank Data

Parameter	Units	Value
V_tank	m ³	1.178
M_liq_0	kg	907.0
Filling	-	0
cliq(1)	-	.75
cliq(2)	-	.25

Parameter	Units	Value
Cp_tank	J/K	0
T00	K	323.150
P00	Bar	0
MAWP	bar	4.49450

Task Options

Parameter	Value
Disengagement model	CHURN-TURBULENT
Co	1.50000
Flow model	Homogeneous equilibrium model for nozzle (ideal gas)
Formula for Fanning factor	0.0035+0.254/Re ^{0.42}
Calculating mode	VENT SIZING

Vent Data

Parameter	Units	Value
Type of device	-	Rupture Disk
Vent location	-	TOP
Set Pressure	bar	1.35845
Reset Pressure	bar	1.42637
Set Temperature	bar	.000000

Vent Sizing Result

Step	Nozzle Area (m2)	Diameter(m)	Overpressure	Resume
1	0.23894E-02	0.55153E-01	3.1428	6195.64 s; Pressure > MAWP :Program automatically goes to next step.
2	0.47781E-02	0.77998E-01	-0.8686E-05	7844.56 s; Next Step (User's command)
3	0.32491E-02	0.64318E-01	-0.4315E-05	6915.50 s; Next Step (User's command)
4	0.26987E-02	0.58618E-01	0.8348E-01	7189.89 s; Next Step (User's command)
5	0.25005E-02	0.56425E-01	0.30354	6372.08 s; Pressure dropped down to back pressure: BST automatically goes to next step.
6	0.24292E-02	0.55614E-01	1.2276	6327.72 s; Pressure dropped down to back pressure: BST automatically goes to next step.
7	0.24035E-02	0.55319E-01	3.0320	6307.02 s; Pressure dropped down to back pressure: BST automatically goes to next step.
8	0.23942E-02	0.55213E-01	3.1205	6201.50 s; Pressure > MAWP :BST automatically goes to next step.
9	0.23976E-02	0.55251E-01	3.1518	6206.38 s; Pressure > MAWP :BST automatically goes to next step.
10	0.239970E-02	0.55276E-01	3.1247	6211.02 s; Pressure > MAWP :BST automatically goes to next step.
11	0.24035E-02	0.55319E-01	3.0320	6307.02 s; Pressure dropped down to back pressure: BST automatically goes to next step.

Successful end of vent sizing:

Parameter	Units	Value
Area of nozzle throat	square meters	0.240349E-02
Diameter of nozzle throat	meters	0.553192E-01

Inference: A good agreement by temporal characteristics is observed. However, nozzle cross section calculation results differ greatly. This may occur because the work [3] doesn't take into account the possibility of the inverse transformation from two-phase into one-phase flow when the quantity of liquid in the tank is decreased. The time-dependencies of liquid mass in the tank, that are presented in [3], do not show any changes in curve behavior when the gas cushion is formed and after transformation into gas flow occurs. Thus, the liquid effluent out of the tank during the process according to the work [3] is considerably higher than according to BST

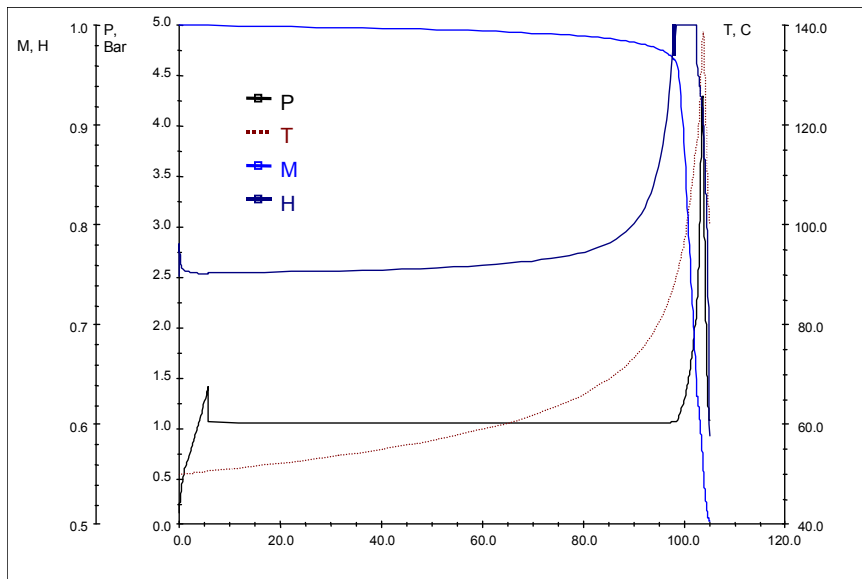


Fig. A1-5. Time dependence of pressure, mass flux and mass fraction of liquid

Project "Ph_forml"

Comparison with data of British Plastics Federation report taken from [3].

Demonstrates a satisfactory agreement with [3].

Kinetics:

formal kinetic model (Fork) of the N-order type $A \rightarrow B$:

$$d\alpha/dt = K_0 \exp(-E/RT) (1 - \alpha)^n$$

where α denotes conversion degree

Kinetic parameters

Parameter	Units	Value
ln(k0)	ln(1/sec)	25.7350
E	kJ/mol	103.0
n	-	2.0
Q	kJ/kg	270.85

Components data (liquids)

Short Name	Mole Mass	Comments
CH2O	30.03	formaldehyde_
C6H6O	94.11	phenol
H2O	18.01	water

Kinetics-Composition Relationship

Name\Stage	A→B
CH2O	0.0
C6H6O	0.0
H2O	0.0

Vent System

Vent System type: Rupture Disk

Vent Position: Top

Actuation Conditions: Pressure 2 Bar

Nozzle: Back Pressure: 1 Bar

Parameter	Units	Value
Area	m ²	0.070684
Diameter	m	0.3
Discharge Coefficient	-	1
Roughness	-	0

Tank Data – Sphere

Parameter	Units	Value
Padius	m	1.0272
V_tank	m ³	4.54
M_liq_init	kg	3268
Filling	-	.000000

Parameter	Units	Value
Mal allowed P	bar	2.5
Cp_tank	J/K	-
T ₀	C	120
P ₀	Bar	-

Task Options

Parameter	Value
Disengagement model	CHURN-TURBULENT
Flow model	Homogeneous equilibrium model for nozzle (ideal gas)
Calculating mode	auto

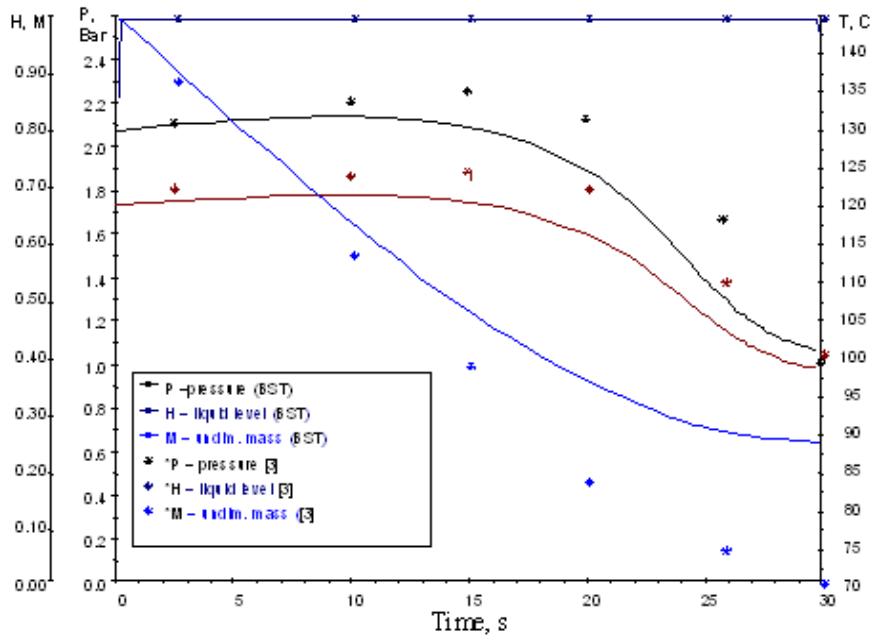


Fig. A1-3 6. Time dependence of reactor parameters

Project "Test_V32W1"

Comparison with DIERS manual [1], chapter III, page 209. Water blowdown.

Good agreements with reported data.

Simulation Results:

Reaction - No

Tank Data

Parameter	Units	Value
V_tank	m ³	.032
M_liq_0	kg	.000000
Filling	-	.980000
cliq(1)	-	1.00000

Parameter	Units	Value
Cp_tank	J/K	1536.00
T00	K	273.150
P00	Bar	5.63580
MAWP	bar	6.06000

Task Options

Parameter	Value
Disengagement model	CHURN-TURBULENT
Co	1.50000
Flow model	Homogeneous equilibrium model for nozzle (ideal gas)
Formula for Fanning factor	0.0035+0.254/Re ^{0.42}
Calculating mode	AUTO

Vent Data

Parameter	Units	Value
Type of device	-	Rupture Disk
Vent location	-	TOP
Set Pressure	bar	1.01
Reset Pressure	bar	1.0605
Set Temperature	bar	0

Parameter	Units	Value	Comment
Set Pressure	bar	1.01	
Reset Pressure	bar	1.06050	AUTO
Calculating mode	-	BLOWDOWN SIMULATING	Automatic choice of task mode
Initial temperature in tank	K	429.593	Reset initial temperature due to equilibrium condition
Initial pressure in tank	Pa	563580	Initial temperature reset due to equilibrium conditions (O
Initial mass of liquid in tank	kg	28.1942	
Initial density of liquid in tank	kg/m3	899.051	

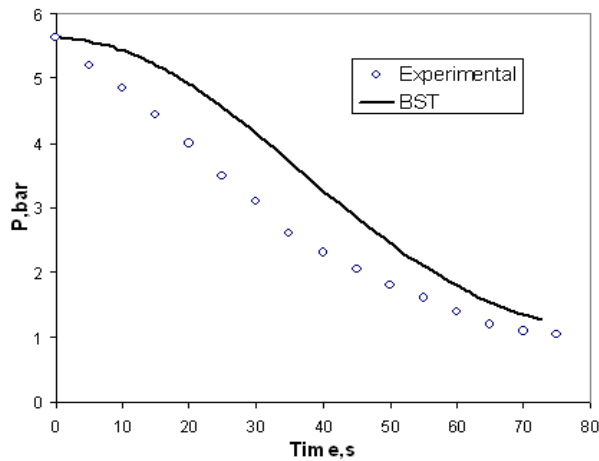


Fig. A1-4. Time dependence of reactor parameters

Project "H2O2vs".

Determination of Critical Diameter of Rupture Disk during Thermal Explosion

Project comments: Isopropyl method of H2O2 synthesis. Side reaction.

Demonstration of Vent Sizing task. Short nozzle.

Kinetics:

formal kinetic model (Fork) of the N-order type A → B:

$$d\alpha/dt = K_0 \exp(-E/RT) (1 - \alpha)^n$$

where α denotes conversion degree

Kinetic parameters

Parameter	Units	Value
ln(k0)	ln(1/sec)	20.986
E	kJ/mol	98.81
n	-	0
Q	kJ/kg	923.0

Components data ()

Short Name	Mole Mass	Comments
C3H6O	58.08	Acetone (liquid)
O2	32.0	Oxygen (gas)

Kinetics-Composition Relationship

Name\Stage	A→B
C3H6O	0.0
O2	0.0

Vent System type: Rupture Disk; **Vent Position:** Top; **Actuation:** Pressure 12 Bar; **Back Pressure:** 1 Bar

Tank Data – Vertical cylinder

Parameter	Units	Value
Radius	m	1.5
Height	m	22
Volume	m ³	155.59
H1/Htank	-	-
H/Htank	-	-
Maximum Allowed Pressure	Bar	15

Parameter	Units	Value
Heat Capacity of Empty Tank	J/K	5000000
Initial Mass of Mixture	kg	-
Initial Filling of Tank	-	0.7
Initial Tank Temperature	C	100
Initial Tank Pressure	Bar	11

Initial composition: liquid in a tank – C3H6 (mass fraction=1); gas in the void volume – O2 (mass fr.=1).

Vent Sizing

Step	Nozzle Area, m ²	Diameter, m	Overpressure	Resume
1	.314150E-01	.1999	.281055E-02	34382.9 s; Next Step (User's command)
2	.000000	.0000	3.25518	1626.52 s; Pressure > MAWP :Program automatically goes to next step.
3	.157075E-01	.14142	.495162E-02	3140.16 s; Next Step (User's command)
4	.565470E-02	.84853E-01	4.44446	1791.31 s; Pressure > MAWP :Program automatically goes to next step.
5	.927371E-02	.1086	3.51597	1819.63 s; Pressure > MAWP :Program automatically goes to next step.
6	.115899E-01	.12148	3.10532	1879.75 s; Pressure > MAWP :Program automatically goes to next step.
7	.130722E-01	.12901	3.14138	2057.94 s; Pressure > MAWP :Program automatically goes to next step.
8	.140209E-01	.13361	3.10622	2207.58 s; Pressure > MAWP :Program automatically goes to next step.
9	.146281E-01	.13647	.521282E-03	30784.0 s; Next Step (User's command)
10	.142395E-01	.13465	.905960E-03	3766.70 s; Next Step (User's command)
11	.140996E-01	.13399	3.11248	2216.15 s; Pressure > MAWP :Program automatically goes to next step.
12	.142395E-01	.13465	.905960E-03	2956.94 s; Next Step (User's command)

Vent Sizing Results

Vent sizing has been finished successfully

Parameter	Units	Value
Area of nozzle throat	m ²	.142395E-01
Diameter of nozzle throat	m	.134649

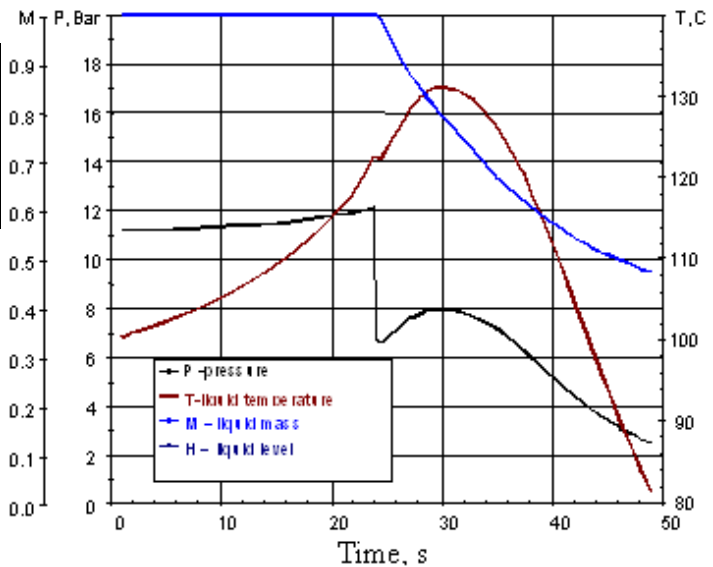


Fig. A1-5. Time dependence of reactor parameters

HSE Round-Robin Test

BST was used for modeling pilot scale reaction venting experiment performed by HSE [4] for the exothermic equimolar etherification reaction between propionic anhydride and isopropanol catalyzed by 188.8 ppm of sulfuric acid.

The following simplifications were made:

- Since BST simulates only three-sectional vent systems, the real vent system was simplified.
- The reactor shape was simplified too (vertical cylinder).
- The catch tank was ignored.

The exothermic equimolar etherification reaction between propionic anhydride and isopropanol catalyzed by sulfuric acid was simulated.

Kinetics has been evaluated on the basis of Phi-tech adiabatic data provided by HSE.

The DesK software was used for creation of the descriptive concentration-based model. The ForK software was used for creation of the formal model based on conversions as state variables.

The following notation is used below for reagents and reaction products:

IP – isopropanol (C3H8O); PA – propionic anhydride (C6H10O3)
 PAc – propionic acid (C3H6O2); IPA – isopropyl propionate (C6H12O2); N₂ – nitrogen¹⁷.

Descriptive kinetics, Kinetic Scheme



$$r_1 = K_0 \cdot e^{-E/RT} \cdot [IP]^{n11} \cdot [PA]^{n12}$$

$$r_2 = K_0 \cdot e^{-E/RT} \cdot [IP]^{n21} \cdot [PA]^{n22} \cdot [PAc]^{n23}$$

Parameters:

Parameter	Units	Value
ln(k ₀)	Ln((kmol/m ³) ^{-1.72} /s)	16.058
E	kJ/mol	74.633
n11	-	0.938
n12	-	1.780
Q	kJ/mol	47.706

Parameter	Units	Value
ln(k ₀)	Ln((kmol/m ³) ^{-2.86} /s)	16.818
E	kJ/mol	75.770
n ₂₁	-	1.268
n ₂₂	-	1.406
n ₂₃	-	1.189
Q	kJ/mol	84.223

Rates of species concentration variation:

$$d[IP]/dt = -r_1 - r_2; \quad d[IPA]/dt = r_1 + r_2 \quad d[PA]/dt = -r_1 - r_2 \quad d[PAc]/dt = r_1 - r_2 + 2 \cdot r_2$$

Formal kinetics. Kinetic Model



where z stands for the autocatalytic constant

Kinetic Parameters:

Parameter	Units	Value
ln(K ₀)	ln(1/sec)	19.1560
E	kJ/mol	72.4429
n1	-	1.7998
n2	-	0.5270
Z	-	0.1111
Q	kJ/kg	360.9858

Kinetics-Composition Relationship $A_{K,ij}$

Name\Stage	A→B
C3H6O2	0.389
C3H8O	-0.316
C6H12O2	0.611
C6H10O3	-0.684
N2	0.0

¹⁷ We assume that pressure in the tank before the start of the experiment is equal to the atmospheric pressure due to presence of insoluble gas.

Physical properties of the components

Properties of isopropanol and propionic acid¹⁸ were already stored in the main database of the MIXTURE software.

Properties of propionic anhydride and isopropyl propionate were added to the temporary database of the MIXTURE software, using the initial data presented by Dr. J. A. Hare [2]. Missing data on viscosity of liquid isopropyl propionate were evaluated by using the method of Van Velzen, Cardozo, and Langecamp [3].

Since propionic anhydride contains some groups not presented in the modified UNIFAC method, we couldn't use this method for evaluation of non-ideality of the mixture.

Vent System

Vent System type: Valve; **Vent Position:** Top; **Roughness:** 0.000029 m

Actuation Conditions: Pressure 1.5 Bar; **Overpressure** 5%; **Back Pressure:** 1 Bar

Entrance			Tube Nozzle			Tail Tube		
Parameter	Units	Value	Parameter	Units	Value	Parameter	Units	Value
Length	m	3.635	Area	m ²	0.003848	Length	m	1.18
Elevation	m	1.162	Diameter	m	0.07	Elevation	m	-1.18
Diameter	m	0.07	Discharge Coeff.	-	1	Diameter	m	0.08
Inclination	deg	18.6436				Inclination	deg	-90
Entr. Loss Factor	-	1.245				Entr. Loss Factor	-	0.64

Tank Data:

Parameter	Units	Value	Parameter	Units	Value
Shape		Vertical Cylinder	Maximum Allowed Pressure	Bar	7
Radius	m	0.34	Heat Capacity of Empty Tank	J/K	109000
Height	m	0.9362055	Initial Mass of Mixture	kg	185.8
Volume	m ³	0.34	Initial Filling of Tank	-	-
H1/Htank	-	1	Initial Tank Temperature	C	65
H/Htank	-	0	Initial Tank Pressure	Bar	1

Initial Composition of liquid (mass fraction).

Parameter	Units	Value
C3H6O2	-	0
C3H8O	-	0.31588
C6H12O2	-	0
C6H10O3	-	0.68412

Heat Exchange

Time (sec)	q ₀ (W/m ²)	α (W/(m ² *K))	T _e (C)
0.0	0.0	270.0	75.0
1000.0	0.0	270.0	75.0

Effective emissivity factor: 0.0.

Disengagement Parameters

Flow Model: Bubble with C₀=1.1

¹⁸ Without considering vapor dimerisation

Simulation Results

Events:

Parameter	Units	Value	Comment
Time	sec	290.985	Vent flow transforms into two phase regime
time	sec	319.649	Vent flow transforms into one phase regime

Results

Parameter	Units	Value
Maximum pressure reached in pilot-scale reactor	Bar	2.25
Maximum temperature reached in pilot-scale reactor	°C	143
Mass remaining in pilot-scale reactor	kg	75.3

Tank Results based on descriptive kinetics, vapor dimerisation is neglected

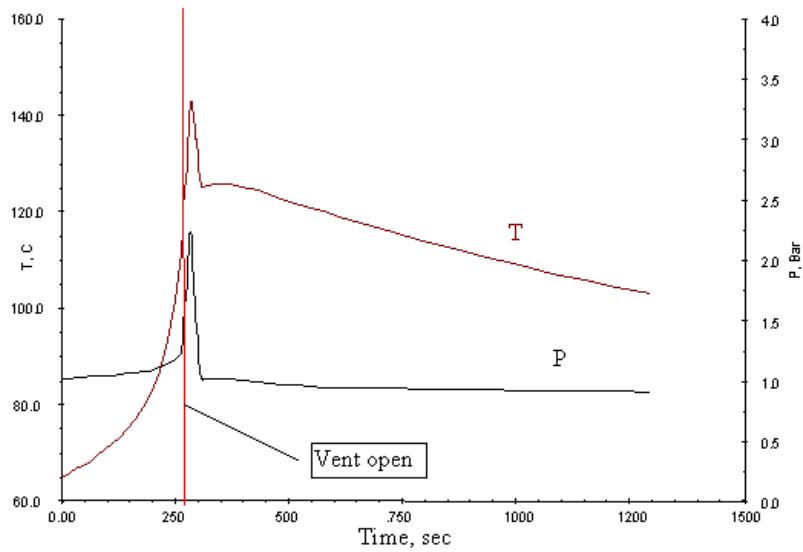


Fig. A1-6. Pressure (P), Liquid temperature (T) and dimensionless mass of liquid in tank

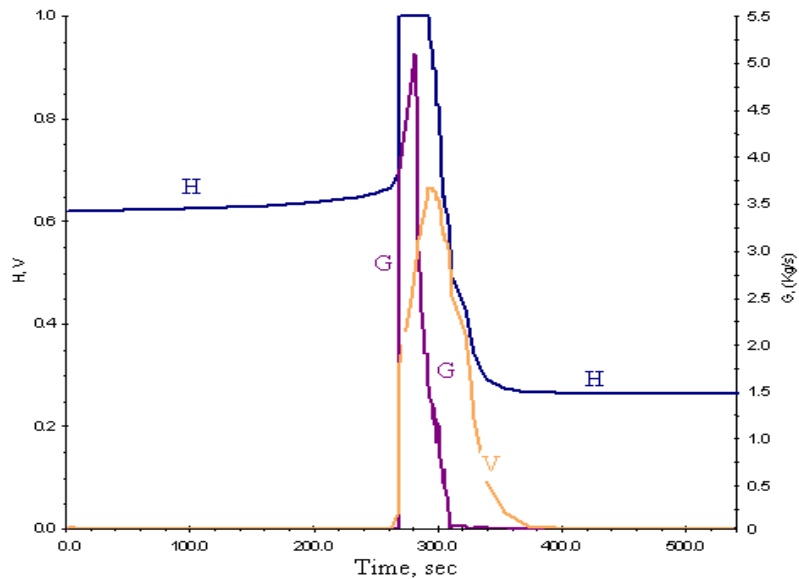


Fig. A1-7. Pressure (P), dimensionless liquid level in reactor (H), vent mass flux (G) and average void fraction in reactor(V)

Comparison of the results based on formal and descriptive kinetics

When used formal kinetics we approximated the change of liquid composition during the chemical reaction by the following relation:

$$G_{IR_i} \equiv M_1 \cdot \sum_{j=1}^{N_j} A_{K_{ij}} \cdot \frac{da_j}{dt}$$

Here G_{IR_i} is the rate of mass changing for i-th liquid component, M_1 is the mass of the liquid, $\frac{da_j}{dt}$ is the rate of conversion for j-th formal reaction, $A_{K_{ij}}$ is a constant matrix (see .p. 31)

When one of the source reagents disappears due to evaporation, the reaction is forced to stop though conversion is not complete yet. In and one can see the difference between the DESK and FORK results.

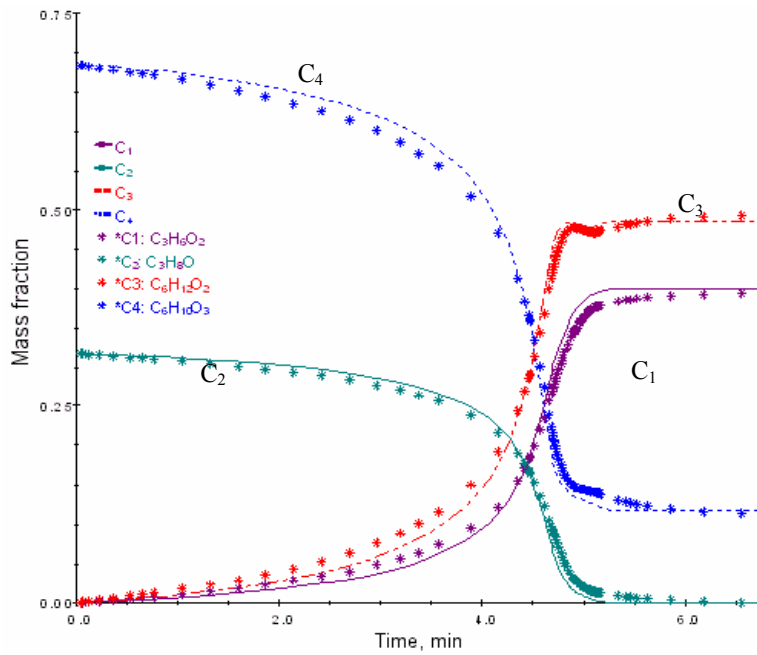


Fig. A1-8 Difference between FORK (Solid lines) and DESK (asterisks). Mass fractions (C_i)

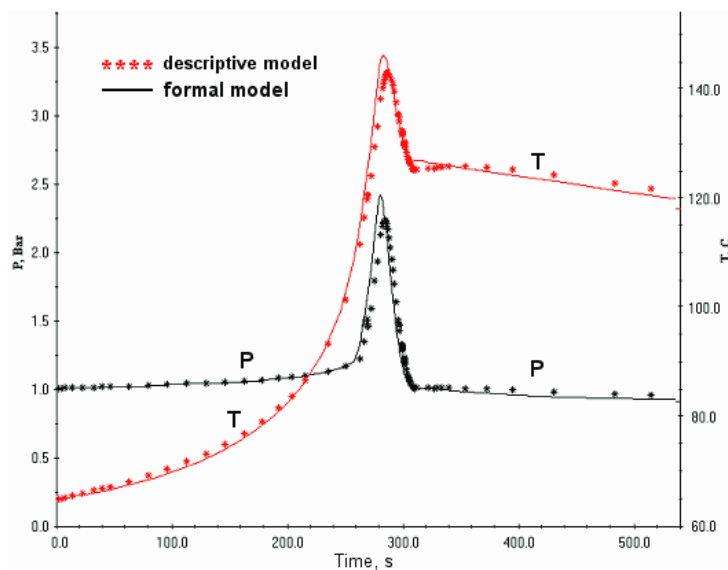


Fig. A1-9 Difference between FORK (Solid lines) and DESK (asterisks).. Pressure(P) and temperature (T).

Because of less accuracy of calculation of changing composition for the formal kinetics the formal reaction model is slightly more intensive and is completed earlier than that for descriptive kinetics. The way the formal kinetics considers dependence of the chemical reaction rate on composition factors (i.e. selective vaporization of the isopropanol) does not provide adequate results. Therefore in this terms reaction proceeds faster and stops earlier. That causes continuous temperature rise after the pressure is relieved for the formal model (see, 310-350 sec.)

Correspondingly, the peak pressure, calculated for Fork is greater and occurs earlier than one calculated for DESK.

Comparison with the experimental results of Round Robin Test.

The heat sensors in reactor indicate that temperature drops below the initial one at first 80-100 seconds of the process. This is caused by stirring of the components of the initial mixture taking place in this space. If not consider this interval, behavior of the simulated curves is in satisfactory agreement with experimental data.

Fig. 2 shows both data simulated with BST (DESK kinetics) and experimental data on pressure and liquid temperature in reactor.

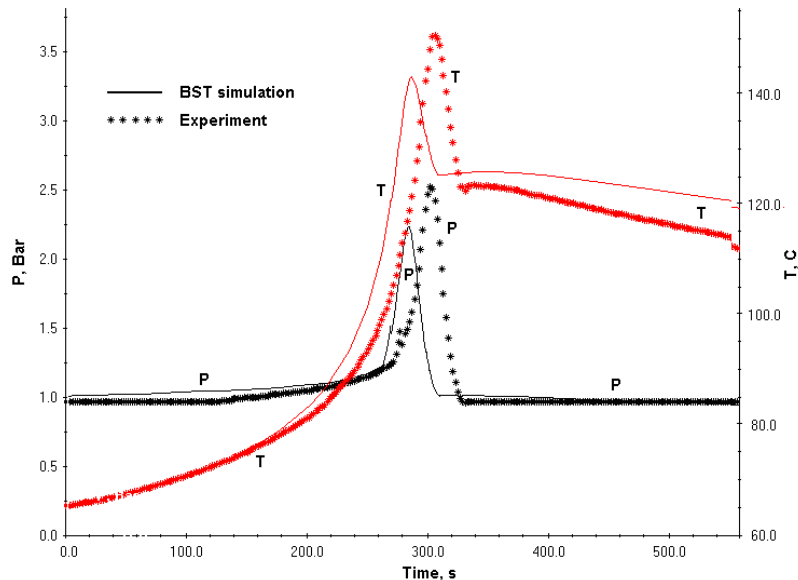


Fig. A1-10. Comparison of experimental and simulated data on temperature (T) and pressure (P). Descriptive kinetic. Solid lines -= BST, asterisks – experiment.

It should be noted that correlation between experimental and simulated data is still satisfactory although simulated peak pressure is 0.25 bar less than experimental one.

All the results adduced are obtained by using the Bubble disengagement model with $C_0 = 1.1$. The final mass of the liquid in reactor is 78.5 kg for descriptive kinetics and 73.4 kg for formal kinetics while the experimental value is 82.8 kg. Applying Churn-turbulent model leads to improper results.

Conclusions:

- BST properly simulates the processes in a batch well-stirred reactor as well as the vent system activity
- For this system the best simulation results are attained when using Bubble disengagement model with $C_0=1.1$ until the void fraction value is less than 0.5. Using Churn Turbulent model (including substituting the Bubble one at void fraction $> 0.25-0.3$) leads to significant understatement of the peak pressure value, so this model is non-conservative.

DRACULA project

This is a project from [5].

Vessel	Insulated iron top-vented vertical cylinder with torrespherical heads ¹⁹ and 0.03 m thick walls, inside diameter is 1.594 m, length of the strait side is 2.54 m
Vent system	Rupture disk of 0.076 m diameter and 0.9 discharge coefficient ²⁰
Mixture	Water
Initial filling	0.941
Initial pressure	5 bar
Agitation	No
Flow	Churn-turbulent

Here the simulated data meets experimental one. *BST* approximates the behavior of the experimental curve properly.

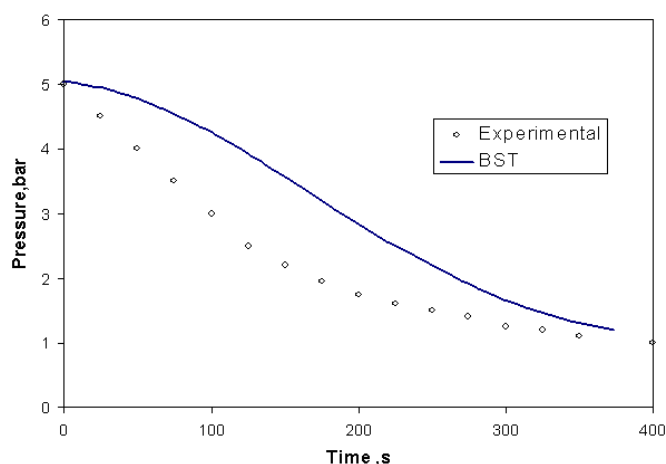


Fig. A1-11. Comparison of the results on DRACULA project with the experimental data

In this project, a good agreement with experimental data takes place. For *BST*, the less velocity of pressure relief is caused by applying homogeneous model for the two-phase flow that gives a conservative estimate of discharge.

T4a project

This is a project from [5] *DIERS Phase III Large Scale Integral Tests* (p.142). The initial data are:

Vessel	Insulated iron top-vented vertical cylinder with hemispherical heads ²¹ and 0.024 m thick walls, inside diameter is 0.914 m, length of the strait side is 3.05 m
Vent system	Single pipe of 31.8 m length and 0.053 m diameter
Mixture	Water
Initial filling	0.941
Initial pressure	5.1 bar
Agitation	Yes
Flow	Churn-turbulent

¹⁹ It was approximated with a vertical cylinder of the same volume in *BST*.

²⁰ The original problem considers some tubes, but it has been demonstrated by computational experiments that they can be neglected.

²¹ It was approximated with a vertical cylinder of the same volume in *BST*.

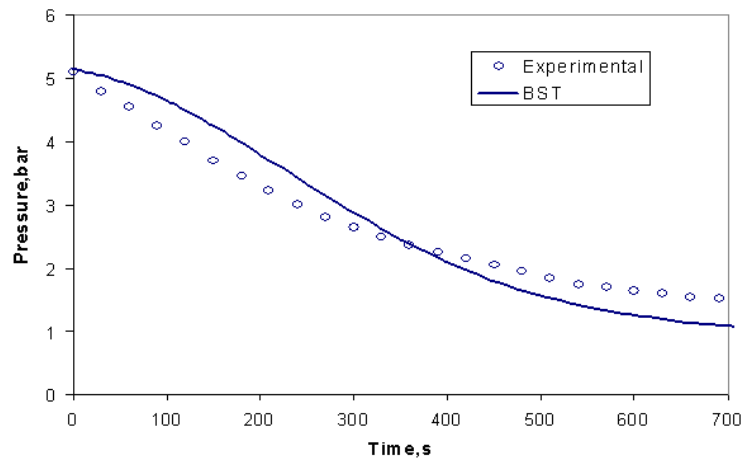


Fig. A1-12 Comparison of the results on T4a project with the experimental data

T5a project

This is a project from [5] *DIERS Phase III Large Scale Integral Tests* (p.142). The initial data are:

Vessel	Insulated iron top-vented vertical cylinder with hemispherical heads ²² and 0.0254 m thick walls, inside diameter is 0.914 m, length of the strait side is 3.05 m
Vent system	Single pipe of 31.2 m length and 0.078 m diameter
Mixture	Water
Initial filling	0.947
Initial pressure	5.6 bar
Agitation	No
Flow	Churn-turbulent

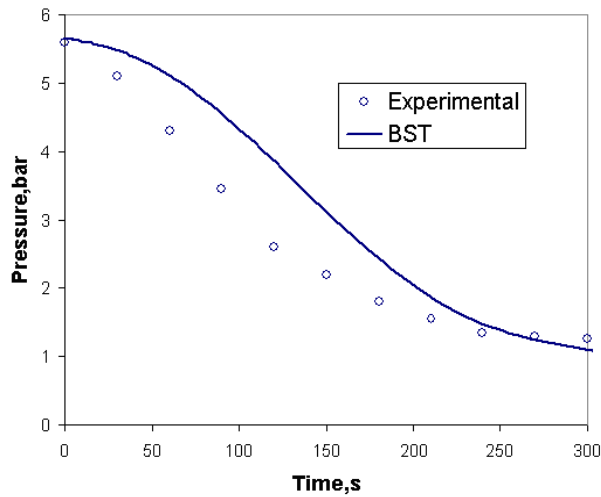


Fig. A1-14. Comparison of the results on T5a project with the experimental data

As one can see, a good agreement between experimental and simulated data takes place. As for the difference between the experimental results and simulated ones in the *T4a* and *T5a* projects, it may be caused by that there was a catch tank in experiments while *BST* cannot simulate it.

²² It was approximated with a vertical cylinder of the same volume in *BST*.

BENCHMARK 6 project

This is a project from [6].

Vessel	Insulated iron bottom-vented vertical cylinder with 2:1 elliptical heads ²³ and 0.03 m thick walls, inside diameter is 1.07 m, length of the strait side is 0.5 m
Vent system	Various horizontal pipes
Mixture	Water
Initial filling	0.99
Initial pressure	9.3 bar
Agitation	No
Flow	Churn-Turbulent

The water runaway was simulated for three pipes of various lengths (all 0.0508 m diameter). Here we adduce mass flow rates (kg/s) at the 8th second of the process simulated with Safire [3], BST and the experimental data.

Pipe length	Experimental	Safire	BST
5 m	33.1	29.9	28
50 m	5.24	4.56	4.4
500 m	0.44	0.39	0.378

VALERY project

V. Chevassus from Rhone-Poulenc carried out the comparison of modeling by using SIFIRE and BST the blowdown of flashing water[7].

Vessel	Insulated iron top-vented vertical cylinder with negligibly thick walls, inside diameter is 0.6 m, length of the strait side is 0.99 m
Vent system	Horizontal pipe of 6 m length and 0.04 m diameter
Mixture	Water
Initial filling	0.99
Initial pressure	8 bar
Agitation	No
Flow	Churn-Turbulent

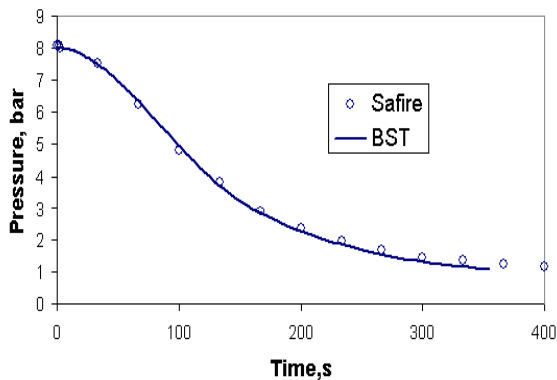


Fig. A1-15. VALERY project. Pressure

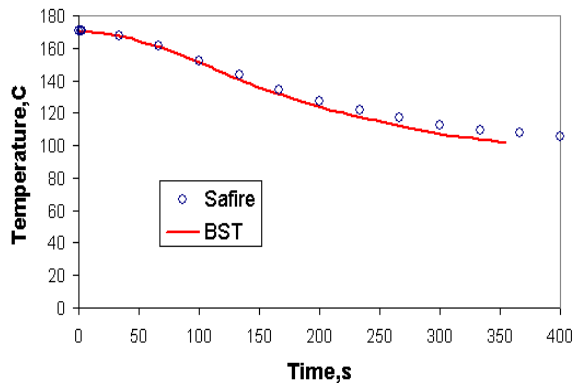


Fig. A1-16. VALERY project. Temperature

BST demonstrated satisfactory agreement with experimental data and excellent agreement with SIFIRE data.

²³ It was approximated with a vertical cylinder of the same volume in *BST*.