Self-ignition in structured packed columns, fundamentals of methodology development

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Sven Degenkolbe[*], Werner Witt

Brandenburg University of Technology Cottbus-Senftenberg, Burger Chaussee 2, 03044 Cottbus, Germany

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ABSTRACT

A combination of a residual film of flammable organic substance, air and structured packing may result in a fire during maintenance, at start up or after shut down. The self-ignition temperature depends on the substance (reactivity, volatility), construction and geometry of packing, heat loss conditions and accident scenario.

In this article a dynamic model to determine heat transfer data and a over-adiabatic model to determine formal reaction kinetic data for the system studied are presented. These data are used as a basis for SIT simulation. The simulation basis is described as well. Next, experimental heat transfer and formal reaction kinetic data and experimental SIT study results are documented for the system (LEX/LDX packing/fatty acid Ti05, a mixture of oleic acid (67%) and linoleic acid (13%)).

Comparison of simulated with experimental SIT data show acceptable agreement. As a conclusion of the studies a new and efficient procedure for SIT prediction in packing systems is proposed.

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1. Introduction

Organic liquid in contact with a porous material (e.g. insulation or structured packing) can result in a fire. Self-heating in insulation materials has been studied over several decades and several incidents are documented (Brindley et al., 2000; Mellin, 1991; Britton, 1991). Self-ignition in packed columns is a real industrial problem as well (Kister, 2003, 2011; Sachdeva and Todd, 2005; JST, 1988, 1991; Englund, 1995; Ender and Laird, 2003; FRI, 2007; Landucci et al., 2014). Kister (Kister, 2003, 2011) describes incidents which occurred during maintenance. Residual substances in the packing ignited after the contact with oxygen. Englund (Englund, 1995) reports a fire in a glycol recovery column after the column was opened. The high specific surface of the packing reduced the ignition temperature of the triethanolamine. Landucci (Landucci et al., 2014) describes an incident in a vegetable oil refinery. Residual fatty acids from vegetable oil ignited during maintenance of the column.

Although in both of the systems, insulation and packing, distributed organic chemicals may result in self-ignition, the scenarios are different. In insulation oxygen is available and contact with organic liquid, released from a leak, is the initiating event. In packing organic liquid is available and contact with air is now the initiating event. Little is known about the details of the self-ignition processes in wetted structured column packing. Only self-ignition processes caused by pyrophoric reactions were studied (Roberts et al., 2003; Plellis—Tsaltakis, 2012). First results about self-ignition studies of wetted column packing have been presented during Loss Prevention Symposium (Degenkolbe et al., 2010).

Advantages in description of self-ignition conditions are not only to support avoidance of fire hazards, but also reduction of operation time, e.g. start up time. The motivation of the studies presented in this article is directed to the development of a methodology able to predict and analyze self-ignition conditions in structured packed columns. Areas of a possible application of the new methodology are:

- Design/selection of inherent safe packing/construction
- Optimization of start up/shut down time
- Support of maintenance, definition of incident related procedures and risk analysis

2. Theoretical fundamentals

2.1. Self-ignition

The well known methods for determination of self-ignition temperatures (SITs) of dusts (Frank-Kamenetskii, 1959; Thomas, 1960) - based on the heat balance only — have already been

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extended for the determination of self-ignition analysis of insulation contaminated with organic liquids. In addition to the overall heat balance, now the consumption and loss of organic liquid, transport of organic vapor and transport and consumption of oxygen was necessary to consider (e.g. Brindley et al., 2000; Degenkolbe and Witt, 2015). Because of the high pressure drop, convective terms are not included in the balances (Brindley et al., 2000). Compared to insulation convection in packing is more likely. Specific surface area in insulation is much higher as in packing. Because of this, less organic liquid can be accumulated inside packing. Lower specific surface area and/or accumulated liquid mass results in much lower heat production rate in packing. On the other hand at the same liquid load heat loss in packing is greater. Both effects result in an increase of the SIT and reduction of maximum temperature at test conditions ($T_{max} < 250$ °C). Below this temperature level further reactions (decomposition of organic peroxides) will not be initiated or reaction rate is too small to compensate heat loss in standard laboratory scale experiments. As a result of this determination of the SIT is based on the temperature difference and not on the temperature criterion.

The constraints of self-ignition processes in packed columns depend on the scenario (open column, leak of air in vacuum column at stand by).

2.2. Balance equations for a finite cylinder

The self-ignition process can be described using the relevant energy balance and the mass balance equations. The model equations are based on Brindley's work (Brindley et al., 1999). Modifications to Brindley's model are described elsewhere (Degenkolbe and Witt, 2015).

It is assumed that movement of the liquid phase may take place only locally. In gas phase convection is considered only outside the packing.

Homogeneous distribution of liquid (L) and packing (S) are further assumptions.

I Energy balance

$$\bar{\rho}_\Sigma \cdot \bar{c}_p \cdot \frac{\partial T}{\partial t} = \bar{\bar{\lambda}}_\Sigma \cdot \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} \right) + \bar{\dot{q}}^L_{V,R} \cdot \varepsilon^L - \bar{\dot{q}}^L_{V,V} \cdot \varepsilon^G \qquad (1)$$

The heat release rate $\bar{\dot{q}}^L_{V,R}$ inside the packing is assumed to be the dominant heat source. Endothermic vaporization rate inside the packing is considered in $\bar{\dot{q}}^L_{V,V}$. Convection at the outer packing surface may intensify vaporization. This effect is considered with the integration in the boundary condition $\bar{\dot{q}}^L_{V,A}$. In case of convection inside the packing the gas phase has to be considered separately. This balance equation is based on the total volume.

II Mass balances of the liquid film (L)

The concentration and the reaction rate are based on the liquid volume.

$$\frac{\partial c^L_i(r,z,t)}{\partial t} = \dot{D}^L_i \cdot \left(\frac{\partial^2 c^L_i}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial c^L_i}{\partial r} + \frac{\partial^2 c^L_i}{\partial z^2} \right) - \dot{r}^L_{R,i} - \dot{m}^L_{V,V,i} \cdot \varepsilon^G / \varepsilon^L \qquad (2)$$

II a) Key components of fatty acid ($i = 1-3$) ($\upsilon_i = -1$)
II b) Product of first formal reaction ($i = 4$) without reaction
III Mass balances of gas phase (G)

The components considered up to now are:

III a) Key components of fatty acid ($i = 1-3$)
III b) Product of first formal reaction ($i = 4$)
III c) Oxygen ($i = 5$)

Because of large temperature differences during the simulation, the mass balance is realized using mass fractions. The gas phase concentration is calculated based on the local mass fraction $c^G_i = c^G_\Sigma(T) \cdot \zeta^G_i$ with the overall concentration $c^G_\Sigma(T) = \sum_i c^G_{FA,i} + c^G_{Prod} + c^G_{O2}$.

The concentration, specific rate of evaporation and reaction rate are based on the gas volume.

III a) Fatty acids

$$c^G_\Sigma(T) \cdot \frac{\partial \zeta^G_i}{\partial t} = \dot{D}^G_i \cdot c^G_\Sigma(T) \cdot \left(\frac{\partial^2 \zeta^G_i}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial \zeta^G_i}{\partial r} + \frac{\partial^2 \zeta^G_i}{\partial z^2} \right) + \dot{m}^G_{V,V,i} + \left[\dot{r}^G_{R,i} \right] \qquad (3)$$

In the mass balance equation gas phase reaction is not considered.

Evaporation is considered in $\dot{m}_{V,V,i}$. The reaction can be included into the calculation with $\dot{r}^G_{R,i}$ (not in this work). Both are based on the gas volume.

III b) Product of first formal reaction

$$c^G_\Sigma(T) \cdot \frac{\partial \zeta^G_i}{\partial t} = \dot{D}^G_i \cdot c^G_\Sigma(T) \cdot \left(\frac{\partial^2 \zeta^G_i}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial \zeta^G_i}{\partial r} + \frac{\partial^2 \zeta^G_i}{\partial z^2} \right) + \dot{m}^G_{V,V,i} \qquad (4)$$

Evaporation $\dot{m}_{V,V,i}$ is related to the gas volume.

III c) Oxygen

$$c^G_\Sigma(T) \cdot \frac{\partial \zeta^G_{O2}}{\partial t} = \dot{D}^G_i \cdot c^G_\Sigma(T) \cdot \left(\frac{\partial^2 \zeta^G_{O2}}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial \zeta^G_{O2}}{\partial r} + \frac{\partial^2 \zeta^G_{O2}}{\partial z^2} \right) + \dot{r}_{R,O2} \qquad (5)$$

For the oxygen balance a reaction is only considered in the liquid phase.

$$\dot{r}_{R,O2} = \tilde{M}_{O2} \cdot \left(\varepsilon^L / \varepsilon^G \right) \cdot \sum_i \left(\upsilon_{O2} \cdot \dot{r}^L_i / \tilde{M}_{FA,i} \right) < 0 \qquad (6)$$

2.3. Determination of heat transfer data ($\dot{\lambda}_\Sigma$, $\dot{h}^G_\Sigma$)

Determination of heat transfer data is based on comparison of experimental and simulated temperature profiles, obtained at surface and centre of the sample during the heat-up phase of an isoperibolic self-heating test. A more detailed description of this procedure can be found elsewhere (Degenkolbe and Witt, 2015). In the low temperatures region ($T < 70$ °C) the heat of reaction is small and the temperature rise inside the packing is caused mainly by heat conduction.

2.3.1. Heat conductivity
The heat conductivity of the structured packing included in