CHEMICAL ENGINEERING TRANSACTIONS
VOL. 48, 2016

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Eddy de Rademaeker, Peter Schmelzer

ISBN 978-88-95608-39-6; **ISSN** 2283-9216
DOI: 10.3303/CET1648039

Self-Ignition Caused by Solar Radiation

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Transportation of goods is carried out by railroad tank cars or by tank trucks or by sea containers. Transport of dangerous goods has to be in agreement with international codes like "UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 5th rev. ed., United Nations, New York and Geneva 2009".
Unfortunately the international codes do not take into account the influence of solar radiation on the self-ignition of chemical reactive substances during transport and storage. The thermal behavior of the chemical substances is regarded only under the influence of the ambient temperature. Thermal loading by solar radiation is neglected. This is a deficiency in all the codes.
This paper will explain the importance of taking solar radiation into account. Solar radiation means that package and substance are exposed to an external diurnal heat flux. Depending on the kinetic properties of the substance sooner or later runaway may occur. That is why the induction period of the material in consideration has to be known. Transportation and storage time is only one part of the induction time.
A practical example serves to demonstrate the importance of taking external heat flux into account. The thermal behavior of hard coal dust is investigated packed in paper bags and piled up on a palette. It is demonstrated that the runaway process is influenced by solar radiation. If the boundary conditions imply this external heat flux the hard coal dust suffers from runaway after 14 days. If the boundary conditions are governed by ambient temperature only the external heat flux is missing and no thermal explosion will occur.
Transportation and storage time has to be significantly less than the induction period of 14 days. How this can be managed is discussed in the last chapter of this paper.

1. Introduction

Auto-ignition defined in international codes combines effects of ambient temperature, kinetic parameters of the chemical reactive substance, package shape and size, physical parameters of the substance and heat transfer properties of the package. No word is mentioned for instance in the UN Test Series (2009 and 2013) about external heat fluxes that may act as additional temperature loading.
In this paper we regard a palette loaded with hard coal dust that is assumed to be stored outside in ambient air and exposed to solar radiation for a certain time. In this case a permanent external heat flux causes an additional temperature loading. The surfaces that are facing the sun are not able to transport the internal produced exothermic heat to the outer boundary. On the contrary external heat flux is transported into the volume.
Practical observation reveals that the above mentioned package is susceptible to auto-ignition. This is especially the case if the palette is transported and stored in climatic regions that are hot and dry. To investigate the effect of solar radiation two numerical simulations were performed here. One simulation takes external heat flux into account. The other one ignores external heat flux. This is the only difference. All other boundary- and initial conditions remain the same.
Runaway happens after a certain induction time. At the end of the induction time thermal explosion is unavoidable. The induction period may be divided into two parts. The first part is called quenching or extinguishing time according to Frank-Kamenetzkii. Runaway is suppressed by decreasing ambient temperature and/or shadowing the package. The second part is the ignition time. In this period thermal explosion can be prevented only by emergency actions.

Please cite this article as: Krause G., 2016, Self-ignition caused by solar radiation, Chemical Engineering Transactions, 48, 229-234
DOI:10.3303/CET1648039

The conclusion to be drawn is that transport and storage time altogether has to be less than the quenching time. Packages like the hard coal dust palette are transported around the world and stored after unloading somewhere. Therefore it is necessary to know all the facts about extinguishing-, ignition- and induction periods.

2. Temperature Loading due to Solar Radiation

It is certain that the sun appears in the east in the morning and disappears in the west in the evening. The sun describes an apparent path at the celestial sphere - see figure 1.
It is adopted that the declination angle of the sun is the greatest one during the year. That means the months June and July govern solar radiation. The zenith angle of the sun is calculated according to the relationship, shown by Iqbal (1983) – figure 1.

$$\cos\Theta_z = \sin\delta \cdot \sin\varphi + \cos\delta \cdot \cos\varphi \cdot \cos\omega \qquad (1)$$

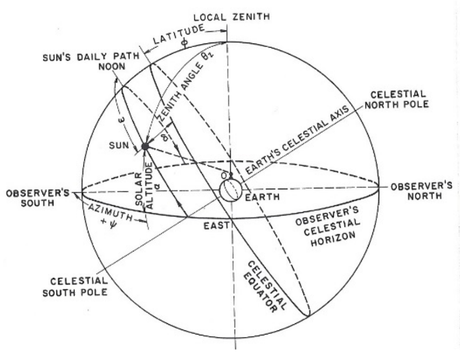

Figure 1: Apparent path of the sun at the celestial sphere according to Iqbal (1983)

Table 1: Definitions of the angles

Angle	Description
Θ_z	Zenith angle or distance in degrees
δ	Declination angle of the sun in degrees
φ	Geographic latitude in degrees
ω	Hour angle. At noon zero. Morning positive. It holds: 1 hour comes up to 15 degrees.

In summer time, June and July: $\delta \approx 23.5°$. The geographic latitude is adopted to be: $\varphi = 30°$.

STANAG 2895, NATO Standardization Agreement (1990) defines world-wide climatic conditions. Climatic region A2 means hot and dry climatic conditions during summer time.

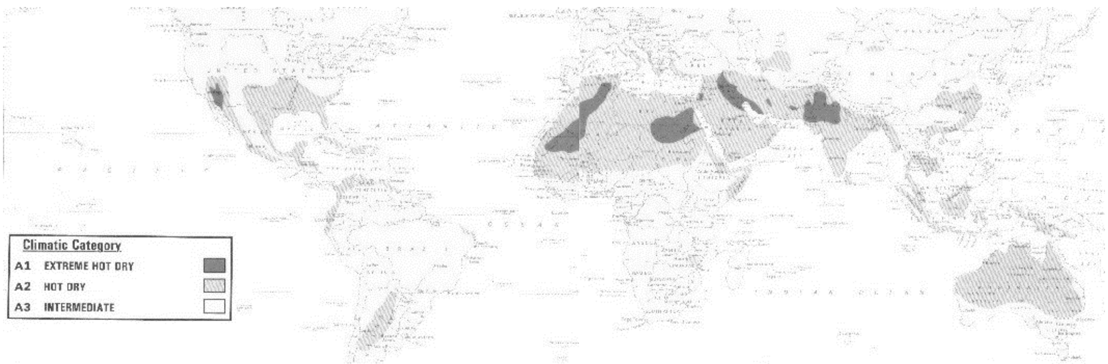

Figure 2: Climatic Regions according to STANAG 2895 (1990)

The diurnal temperature in climatic region A2 ranges from 30° C to 44° C within 24 hours.

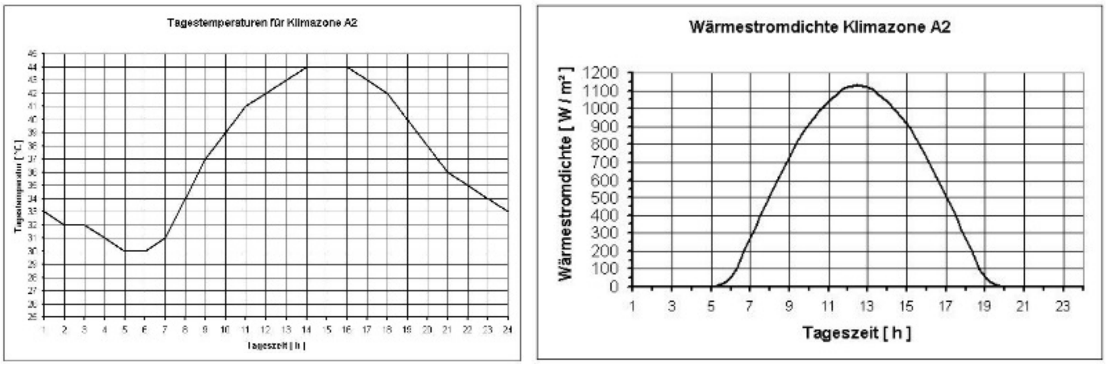

Figure 3: Diurnal Temperatures and Heat Flux in the Climatic Region A2

3. Material, Geometry and Shape of the Palette, Heat Transfer Coefficients

3.1 Material and kinetic parameters

The kinetic and physical parameters refer to hard coal dust.

Table 2: Material and kinetic parameters

Parameter	Unit	Description
$\frac{E}{R} = 7800.$	[K]	Apparent activation energy
$Q_0 = 1.0 \cdot 10^6$	[K / s]	Arrhenius rate
$\rho = 800.0$	[kg / m³]	Density
$\lambda = 0.10$	[W / m K]	Thermal conductivity

Table 2: Material and kinetic parameters

Parameter	Unit	Description
$c_p = 1000.0$	[J / kg K]	Specific heat capacity
$a = 1.20 \cdot 10^{-7}$	[m² / s]	Thermal diffusivity
$c_p \approx 1009.$	[J / kg K]	Specific heat capacity of ambient air
$\lambda \approx 0.029$	[W / m K]	Thermal conductivity
$\rho \approx 1.0452$	[kg / m³]	Density

3.2 Geometrical data

The technical data of the palette are given as follows.

Table 3: Geometrical data

Parameter	Unit	Description
$H = 1.44$	[m]	Height
$W = 1.0$	[m]	Width
$L = 1.2$	[m]	Length
$t_{Fiber} = 0.001$	[m]	Wall thickness packing
$\lambda_{Fiber} \approx 0.1$	[W / m K]	Thermal conductivity of fiberglass

3.3 Heat transfer coefficients

Figure 4: Palette of Transport Loaded with Paper Bags Containing Hard Coal Dust

The before mentioned data serve to calculate heat transfer coefficients. It holds the general expression

$$\frac{1}{\alpha} = \frac{1}{\alpha_{\mathrm{Air}}} + \frac{1}{\alpha_{\mathrm{Palette}}} \tag{2}$$

The air heat transfer coefficient is estimated to be $\alpha_{\mathrm{Air}} \approx 7.5$ [W / m² K] and the heat transfer coefficient of the palette can be derived by

$$\alpha_{\mathrm{Palette}} = \frac{\lambda_{\mathrm{Fiber}}}{t_{\mathrm{Fiber}}} \tag{3}$$

Using appropriate numbers the overall heat transfer coefficient α should be greater than 1.0 [W / m² K].

4. Numerical Simulation

The thermal behavior of the hard coal dust in the paper bags stored on the palette is analyzed by a numerical, transient temperature field simulation under the influence of climatic conditions A2 either with solar radiation or without as desired. All numerical calculation were performed with the software program ISAFEM/3D, developed by Krause (2013).
The finite element model represents the hard coal dust (left) and the air cushions (right). The total FE model consists of 19141 finite elements and 17331 nodes.

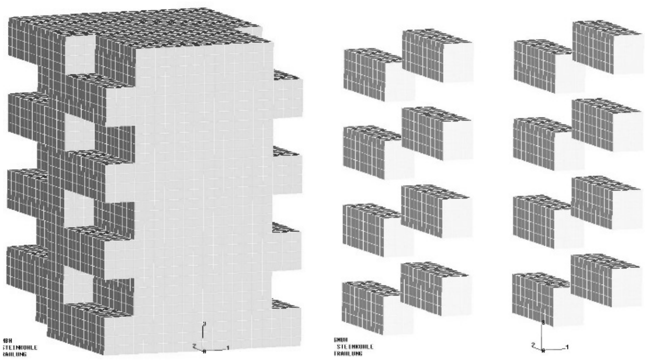

Figure 5: Finite Element Model of Hard Coal Dust and Air Cushions

All the material and the kinetic parameters that are used in the FE analysis are given in section 3 together with the shape of the palette. These data form the basis of the numerical simulation.
The initial temperature of the hard coal dust in the paper bags is set to 40° C because the material is assumed to be heated up by the ambient temperature already. Boundary conditions are equivalent to the ambient

temperature due to figure 6. The ambient heat flux is in accordance with figure 6. These boundary conditions hold every day.
The results of the analysis depend on the absorptivity of the palette surface. The absorptivity is assumed to be 0.4 in the case regarded here. Absorptivity = 0.0 means that solar radiation is of no importance. The radiation is reflected totally. Absorptivity = 1.0 means that all the radiation is absorbed. No heat flux is reflected.
From the physical point of view it seems to be clear that after a certain induction time the chemical reaction may run away. This is due to the fact that permanently energy is transported into the palette by solar radiation.

4.1 Auto-Ignition initiated by Solar Radiation

Firstly we consider the case that ambient temperatures as well as solar radiation due to climatic region A2 act as temperature loading on the palette. For sake of simplicity a reaction of zero order is adopted.

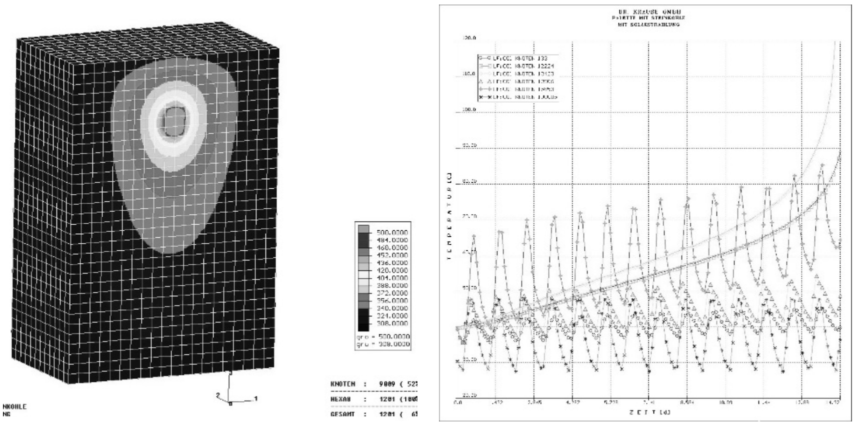

Figure 6: Temperature Field and Time Histories at Selected Grid Points with Solar Radiation included

After initial- and boundary conditions as well as material parameters have been defined the finite element analysis is started. The numerical simulation comes out with the result that the hot spot appears in the top layers of the palette. The hot spot leads to thermal explosion at the end.
The adopted initial and boundary conditions as well as the climatic region A2 lead to a runaway of the hard coal dust stored in the paper bags after an induction time of 14 days.

4.2 Neglecting Solar Radiation

The same analysis is repeated once more but now the influence of solar radiation is denied, i.e. the external heat flux according to figure 3 is neglected. Nevertheless this is in accordance with international rules.
The temperature field in the palette differs significantly from the first case. It is now symmetrically. The temperatures in the hot spot area converge to 49° C after 52 days. The temperature increase in the centre amounts to 14° C. No runaway will occur.

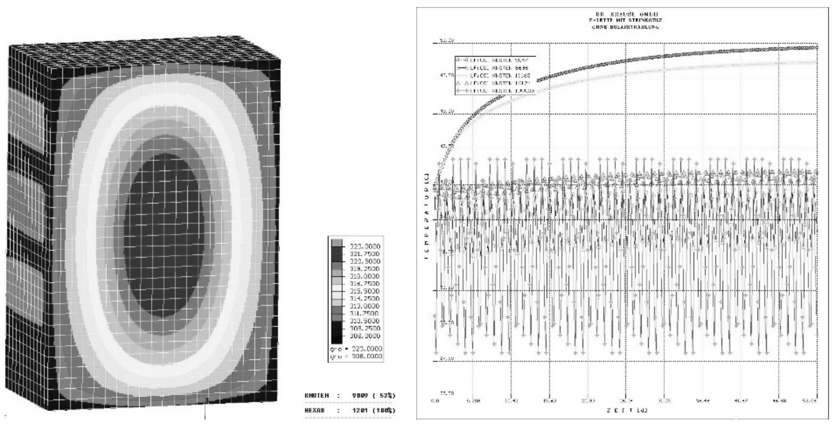

Figure 7: Temperature Field and Time Histories at Selected Grid Points with Ambient Temperatures A2 only

5. Transportation and Storage Times

In the following we assume that the temperature of transport and storage is above the critical ambient temperature level of the chemical reactive material that is volume dependent. Otherwise the following considerations make no sense.
First of all the temperature of transport and storage has to be defined. This is supposed to be the mean value of diurnal temperatures at a certain site in a specific climatic region.
Secondly we define the time of standstill. This concerns loading- and unloading-time plus storage time of the package that contains the substance. Time of standstill is supplemented by the time of transport. This is the driving time plus waiting period during carriage.
The induction period of the substance plays an important role. This is the adiabatic induction period (TMR) in simple cases. Even better the physical induction period is taken that is found by the numerical analysis. The induction period consists of two parts. One part is the quenching or extinction time. The second part is the ignition time.
The quenching time is the ultimate moment that allows to prevent runaway of the material by decreasing the ambient temperature below the critical ambient temperature in such a way that the ambient temperature becomes now below the critical temperature in the same difference as it was above before. The knowledge of the quenching time is important and necessary if protections of health and safety standards have to be considered.
The time lack between quenching time and induction period is called ignition time. If the quenching time is surpassed the ignition time starts. During this period emergency precautions have to work. Runaway can only be avoided by suddenly emptying a tank, spreading out a compact volume to a thin layer, inserting stoppers into a fluid, etc.
Now the admissible time of transportation has to be clarified. We require that the time of transport has to be less than a certain safety-factor times the induction period. The safety-factor must be less than one because the maximum admissible time of transport is prescribed by the quenching time.
A safety factor of one half is adopted. If this is regarded to be safe enough this leads in the present example to a time of transport of 7 days or one week for the palette loaded with hard coal dust. At least after one week the paper bags have to be unloaded from the palette and stored separately. Health and safety protections are now fulfilled.

6. Conclusions

The palette loaded with hard coal dust in paper bags runs away after 14 days if external heat flux is incorporated in the numerical analysis. The physical induction time serves to give a safe prediction for the transport time. The proposal is to use one half of the physical induction period.
This is in contrast to temporary international codes that do not take solar radiation into account. These rules suggest that the hot spot temperature converges to 49° C. The induction period becomes infinite.

References

Krause G., 2015, ISAFEM/3D. Dr. Krause GmbH <www.isafem.de>, Potsdam, Germany.

Iqbal M., 1983, An Introduction to Solar Radiation, ISBN 0-12-373750-8. Academic Press Canada, Ontario, Canada.

NATO, 1990, Extreme Climatic Conditions. VERLAG, New York, USA and Geneva, Switzerland.

United Nations, 2009, UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 5th rev. ed. New York, USA and Geneva, Switzerland.

United Nations, 2013, UN Recommendations on the Transport of Dangerous Goods, Model Regulations, 18th rev. ed. New York, USA and Geneva, Switzerland.