Slutrapport
Självantändning vid lagring av biobränsle och biogent avfall

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Spontaneous ignition in stored biofuel and biological waste
Göran Holmstedt

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Sökord: spontan antändning, självantändning, lagring, biobränsle, avfall, kalorimetri, modellering, experiment
Keywords: spontaneous ignition, self-ignition, storage, biofuel, waste, calorimetry, modelling, experiment

Abstract: The aim of this research proposal is to develop a tool for the evaluation of waste material that needs to be stored in anticipation of material or energy recycling. This system would enable users to determine the correct method of storage to minimise the risk for self-ignition.

Subproject 1 Biological and chemical activity
The heat released from the biological and chemical activity in different biofuels stored under various conditions has been investigated with an isothermal calorimeter (TAM Air), The biofuels investigated were aged sawdust (stored outdoors for three months), pellets made of wood and bark and dried sawdust mix before it was pressed into pellets.An anacysis of how the reaction rate depends on on the oxygen pressure and addition of iron and copper ions has beed performed

Subproject 2 Models of heat and mass transfer in flammable waste.
A comprehensive three-dimensional finite volume CFD code SMAFS (Smoke Movement and Flame Spread) based on numerical solution of a set of governing equations including the continuity equation, extended Darcy momentum equations, energy conservation equations for both gas and solid phases, and mass conservation equations for different chemical species has been developed in the program. Numerical results were compared with small scale experimental measurements, showing excellent agreement.

Validation of the CFD-code.
Spontaneous ignition experiments in small and medium scale have been carried out. The main equipments used for the experiments were temperature-controlled ovens and with re-circulating air. The size of the pellets baskets of biofuel in the ovens were 1dm^3 and 1 m^3 respectively.

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Förord

Projektet *Självantändning vid lagring av biobränsle och biogent avfall* har bedrivits under tiden 1juli 2002 till 30 juni 2005. Projektet omfattar tre organisationer med fem deltagande avdelningar:

1. Lunds Tekniska högskola :Brandteknik, Byggnadsmaterial, Byggnadskonstruktion
2. Växjö Universitet: Teknik och Design
3. Sveriges Provnings- och Forskningsinstitut: Brandteknik

Projektet har finansierats av Statens Energimyndighet via CECOST, BRANDFORSK (projekt nr 705-02102, 701-031) och Statens Räddningsverk.

Till projektet har en referensgrupp varit knuten med följande externa representanter:

- Baeling, Peter, Lantmännen
- Bygberg, Henrik, Dask Brand- och Sikringsteknisk Institut
- Erlandsson, Ulf, Statens Räddningsverk
- Gierow, Martin, ÅF-Konsult
- Källström, Kjell-Åke, Räddningstjänsten Höga Kusten - Ådalen
- Larsson, Lars, Lantmännen
- Pauner, Martin, Dask Brand- och Sikringsteknisk Institut
- Wikmer, Hans, Trygg-Hansa

Projektet har redovisats i artikelform i vetenskapliga tidskrifter, i institutionsrapporter och som presentationer vid internationella konferenser.

Innehållsförteckning:

Chapter

Chapter 1: Summary

1. Project: Spontaneous Ignition

Sub-project leader: prof. Göran Holmstedt, Fire and Safety Engineering, LTH
Participants: prof. Göran Holmstedt, MSc Ulf Göransson, Doc. Lars Wadsö and Dr. Zhenghua Yan,, LTH
Prof. Mehri Sanati and Lic. Katarina Rupar-Gadd, Växjö Universitet
Dr. Patrick van Hees and Lic. Per Blomqvist, Swedish National Testing and Research Institute

1.1.1 Background

Spontaneous combustion of long-term storage is a long-standing practical problem that, in spite of extensive and intensive studies, has proved to be so intractable that there is still need for a definitive-working model capable of prediction of ignition behaviour with accuracy. An accurate prediction of fire risk requires an adequate description of the initiation and development of a fire.
The problem is compounded by the uncertain physical and chemical behaviour involved at ambient conditions and presents difficulties of practical control to restrict the temperature increase in storage.
The dominant source of heat is the hydrocarbon oxidation governed essentially by the rates of diffusion and convection of air from outside, however there can also be significant influence of heat of wetting from adsorption of the inherent moisture.
Various exotermic processes such as low temperature oxidation, microbial metabolism, the adsorption-desorption of water due to the difference between real and equilibrium moisture concentration in a storage and air and oxidation of volatile and reactive compounds can contribute to self heating of materials in storage and spontaneous combustion.

1.1.2 Objective

The aim of this research proposal is to develop a tool for the evaluation of waste material that needs to be stored in anticipation of material or energy recycling. This system would enable users to determine the correct method of storage to minimise the risk for self-ignition.

1.1.3 Scientific achievements

1.1.3.1 Low temperature biological reactivity

Self-ignition in stored materials is a problem that will probably increase in the future due to the increase of storing of biological materials. The heat released from the biological activity in different biofuels stored under various conditions has been investigated with an isothermal calorimeter (TAM Air), see Figure 1. The biofuels investigated were aged sawdust (stored outdoors for three months), pellets 8 mm and the dried sawdust mix before it was pressed into pellets (Dry Mix), sample size was approximately 2 grams. The storage temperatures were 20,50,55 and 60°C. Optimal storage temperature for maximum heat release was 50-55 °C s. There was an increase in the heat release after 10-30 days, after that the level decreased to a low constant value for up to 74 days. Metals were added to observe

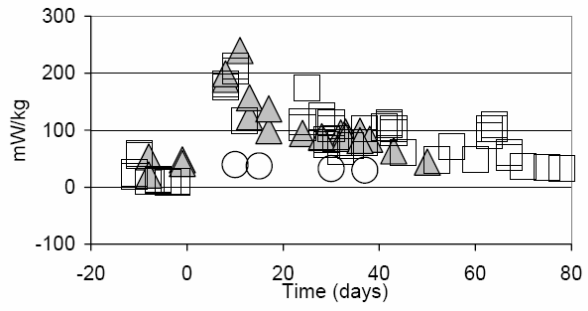

Figure 1. Rate of heat release, mW/kg, of different wooden material stored at 50 C, circles: aged sawdust, triangles: dry mix, squares: pellets 8 mm.

catalytic effects, the metals added were MnO2, Fe2O3, C6H5FeO7*5H2O , Cu2O and Cu(NO3)*3H2O. Addition of metals to the samples gave an increasing effect, the peak values in 50°C and 55°C after 10-30 days increased with up to 220 percent, with copper giving the highest effect.

Low temperature chemical activity

Biofuels are commonly stored in large stacks that may heat up and self-ignite from microbiological and chemical heat production. In the project it has been shown how isothermal calorimetry can be used to measure to measure heat production rates of biofuels at relative low temperatures close to where self-heating starts to be a problem. A problem with this type of measurements is that the heat production is influenced by many factors, for example vaporization of volatile degradation products and vaporization/condensation of water. We have now developed a measurement protocol that gives reproducible results:

Measurements can be made to assess how the reaction rate is a function of such factors as temperature, extent of reaction, oxygen pressure, water content and the presence of catalytic compounds. Measurements have been made on pellets made of wood and bark together with an analysis of how reaction rate of bark pellets depends on the oxygen pressure. It is also shown that 1% iron or copper ions increased the reaction rate of wood pellets by a factor three, see Figure 2.

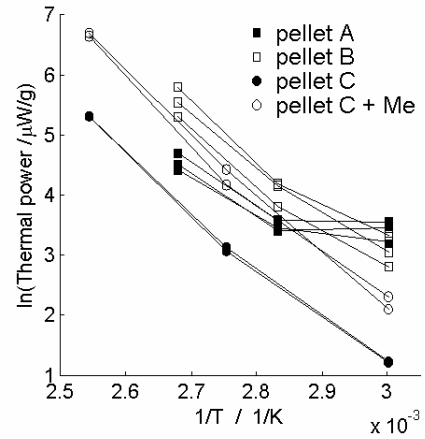

Figure 2. Rate of heat release as a function of inverted temperature.

1.1.3.2 Models of heat and mass transfer in flammable waste

A comprehensive three-dimensional finite volume CFD code SMAFS (Smoke Movement and Flame Spread) based on numerical solution of a set of governing equations including the continuity equation, extended Darcy momentum equations, energy conservation equations for both gas and solid phases, and mass conservation equations for different chemical species has been developed in the program. Consideration was given to a series of essential physical and chemical processes, including convection and diffusion in porous media, evaporation, condensation and heat generation which is mainly due to chemical oxidation. With reliable material properties input data provided by separate measurements, it simulates the temporal state evolution inside the biomass fuel storage. Numerical results were compared with small scale experimental measurements, showing excellent agreement, see **Fel! Hittar inte referenskälla.**.

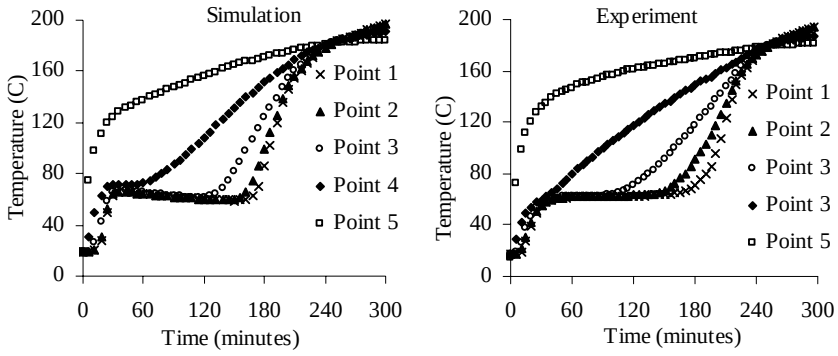

Figure 3. Comparison between simulated and measured temperatures in a 1dm^3 basket test.

1.1.3.3 Validation of the CFD-code

Spontaneous ignition experiments in small and medium scale have been carried out. The main equipments used for the experiments were temperature-controlled ovens and with re-circulating air, see Figure 4. The size of the pellets baskets of biofuel in the ovens were 1dm^3 and 1 m^3 respectively. In order to trigger and speedup the spontaneous ignition process the oven was heated up and maintained to have a temperature of 180 C for the sawdust case and 200 C for the wood pellets case in the 1dm^3 experiment and 100 C for the wood pellets case and in the 1 m^3 experiment. In order to carry out the CFD simulations, reliable input data on the material's properties is needed. The needed input data covers fuel storage's permeability, porosity, moisture content of the concerned biomass fuel, the compact density of the solid fuel, fuel's overall reaction rate, and the thermal properties of the solid fuel including its specific heat and heat conductivity. Measurements were conducted to provide the necessary material properties. The permeability tests were performed in an ad hoc set-up consisting of a standing cylinder of 0.9 meter in height and 0.55 m in diameter and measurements of the temperature dependence of c_p and λ were conducted using the transient plane source technique (TPS).

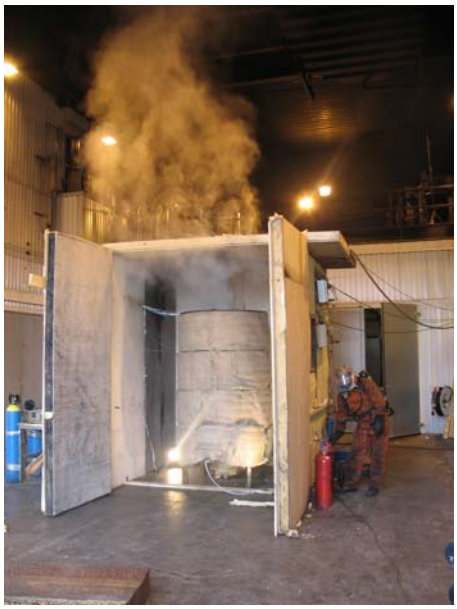

Figure 4. 1 m^3 basket test (oven after the pellets had ignited spontaneously).

1.1.4 Input and coupling to other CECOST-projects and industry

During the project a number of non intrusive measurement techniques that can improve the understanding of the spontaneous ignition phenomena have been discussed with the Combustion Physics Division. To develop new non intrusive techniques for measurement of O_2, CO_2, CO, organic compounds and temperature, adapted to fixed fuel beds are of special importance.

A number of project meetings have taken place and access to the project on a web-site has been given. During the project contacts have been established with the Danish Institute of Fire and Security Technology (DIFT). DIFT has contributed to the project with small scale experiments. A number of members of pellets manufacturer (Lantmännen), thermal power station (Öresundskraft), consultants (ÅF, Öresafety) and authorities (SRV, local fire departments) have taken part in the projects meetings. A thermal power station has ordered measurements on new types of pellets that includes different amounts of wood, bark, peat and waste.

1.1.5 List of publications

1. Per Blomqvist and Bror Persson "Spontaneous Ignition of Biofuels- A Literature Survey of Theoretical and Experimental Methods,", SP AR 2003:18, Fire Technology, Borås 2003.
2. Katarina Rupar, Licentiate Degree "A parameter Study of Drying and Storage of Biomass", ISBN: 91-7636-374-0, June 2003.
3. Katarina Rupar-Gadd[1], Lars Wadsö[2], Göran Holmstedt[2], Bror Persson[3], Per Blomqvist[3], and Mehri Sanati[1], "Spontaneous Combustion of Biofuels caused by Microbial Activity,[1] Växjö University, [2] Lund University, [3] SP Swedish National Testing and Research Institute, The International Society for Biological Calorimetry (ISBC) XIIIth Conference Würzburg, Germany, September 27-October 01, 2003.
4. Katarina Rupar-Gadd[1], Lars Wadsö[2], Göran Holmstedt[2], Bror Persson[3], Per Blomqvist[3] and Mehri Sanati[1], "Biomass resources Spontaneous Combustion of Biofuels caused by Microbial Activity", [1] Växjö University, [2] Lund University, [3] SP Swedish National Testing

and Research Institute 2nd World Conference and TechnologyExhibition on Biomass for Energy, Industry and Climate Protection, 10-14 Maj 2004, Rom, Italien, www.etaflorence.it, www.conference-biomass.com/abstracts.
5. Katarina Rupar, Mehri Sanat, “The release of terpenes during storage of biomass”, Biomass and Bioenergy 28 (2005) 29–34
6. Zhenghua Yan[1], Per Blomqvist[2], Ulf Göransson[1], Göran Holmstedt[1], Lars Wadsö[1], Mehri Sanati[3] and Patrick Van Hees[2].”Validation of CFD Model for Simulation of Spontaneous Ignition in Bio-mass Fuel Storage”, [1] Lund University, [2] SP Swedish National Testing and Research Institute, [3] Växjö University, Accepted for publication at 8th IAFSS 2005 , Peking September 2005.
7. Katarina Rupar-Gadd[1], Lars Wadsö[2], Jonas Widuch[1], Patrick van Hees[3], Göran Holmstedt[2], and Mehri Sanati[1], “Parameter Study of the Contribution of Heat released from Microbial Activity to the Self-heating of Stored Biofuels”, [1] Växjö University, [2] Lund University, [3] SP Swedish National Testing and Research Institute, Submitted to Fire and Material June 2005.
8. Lars Wadsö, ”Measuring chemical heat production rates of biofuels by isothermal calorimetry for hazardous evaluation of large storages”, Submitted to Fire and Material June 2005.
9. Jonas Widuch, “Spontaneous Combustion of Biofuels caused by Microbial activity”, Växjö februari 2005 Avdelningen förTeknik och Design,Växjö University
10. Extract from“Determination of Material Properties for Fire Modelling” Ulf Göransson Department of Fire Safety Engineering Lund University, Sweden Doctoral Thesis, Lund October 20, 2005

1.1.6 Generated PhD- or Licentiate degrees

Licentiate	Katarina Rupar, ISBN: 91-7636-374-0, June 2003.
Ph.D	Ulf Göransson LUTVDG/TVBB-1034-SE, 2005 (part)
Ph.D	Per Blomqvist LUTVDG/TVBB-1030-SE, 2005 (part)