



Water up-take in fuel pellets studied by Dynamic Vapour Sorption (DVS) analysis and its potential role in self-heating during storage

Calle Nilsson¹ · Henrik Ramebäck² · Callum Hill^{3,4} · Mehrdad Arshadi¹

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Abstract

The self-heating of wood fuel pellets is a well-recognised problem causing fire incidents in the storage of the pellets as well as severe intoxication of workers by elevated carbon monoxide and carbon dioxide levels and oxygen depletion. Possible factors contributing to the self-heating are considered to be autoxidation and microbiological activity, while the role and contribution to the temperature rise caused by the heat of condensation from water vapour condensing during fast changes in the relative air humidity is less investigated. Using Dynamic Vapour Sorption, the water uptake was measured at 25 °C when increasing the RH from 40 to 80% using 35 fuel pellet samples covering a broad variation in pellet raw materials and process equipment found in Europe (both pilot and industrial scale). The equilibrium total water uptake and speed of the uptake were determined. Total water uptake was 4.56% (range 3.69–6.86%) with no systematic difference found related to the scale of production (industry as compared to pilot plant). In addition, the variations within larger groups of raw material (pine, spruce and pine/spruce mixtures) were relatively small, and the mean water uptake did not differ significantly between these groups. An estimation of the overall potential heat release (when raising the RH% from 40 to 80%) made from the experimental results, taking the early fast water uptake process into consideration (2 h counting for half the total uptake), showed that a heat release of 47 kJ/kg of pellets (range 12–63 kJ/kg) and a potential temperature increase of 45 °C is possible. This estimation clearly demonstrates that the heat of condensation released during water condensation in a pellets silo or in a pellets pile should be expected to be a major contributing factor to initiating temperature rise incidents. In addition, such a temperature increase is expected to assist the initiation of, and to increase the speed of autoxidation of fatty acids and other compounds in the material that will further contribute to a temperature rise. Thus, the results in this study have the potential to improve the basis for modelling the self-heating process in pellet silos/storage and to predict the status of a certain pellet batch by presenting a broad basis for expected variation in the important parameters (specific heat capacity C_p and thermal conductivity λ_{eff}) influencing the process, and thus aid in taking preventive actions like venting or shifting the pellets to another silo/pile to reduce risk for self-heating and possible fire.

1 Introduction

Spontaneous self-heating in wood bio-fuel pellets during storage and transport (e.g., in silos and during bulk transportation by ship) has been reported to cause fire incidents, oxygen depletion and formation of carbon monoxide, carbon dioxide and volatile compounds (Fan and Bi 2013; Kuang et al. 2008, 2009a, b; Pa and Bi 2010; Koppejan et al. 2013; Ashman et al. 2018). Apart from the economic consequences of these large fires, the oxygen depletion and emission of toxic volatiles have caused several accidental deaths and severe incidents among workers exposed (Granström 2009, 2010; Hyttinen et al. 2010; Rupa-Gadd 2006; Arshadi et al. 2009; Arshadi and Gref 2005). The reason for self-heating is generally attributed to autoxidation and/or microbiological

✉ Mehrdad Arshadi
mehrddad.arshadi@slu.se

¹ Department of Forest Biomaterials and Technology, Swedish University of Agricultural Sciences (SLU), 901 83 Umeå, Sweden

² Swedish Defence Research Agency, CBRN Defence and Security (FOI), 901 82 Umeå, Sweden

³ Norwegian Institute of Bioeconomy Research, PO Box 115, 1431 Ås, Norway

⁴ Department of Architecture and Civil Engineering, University of Bath, Bath BA2 7AY, UK

activity (Larsson et al. 2012; Stratev et al. 2011; Arshadi et al. 2009; Arshadi and Gref 2005; Hemingway et al. 1971).

Autoxidation of fatty acids (triglycerides) is a well-known phenomenon resulting in a complex mixture of components such as shorter fatty acids, aldehydes (saturated and unsaturated) as well as carbon monoxide and dioxide (Svedberg et al. 2004, 2008, 2009). The fatty acid content in wood pellets is generally in the range of 1–2% (w/w). The autoxidation being an exothermic chain radical reaction can be considered a significant contributing factor in the self-heating process (Blomqvist and Persson 2003, 2008).

When it comes to the role of microbial activity (that is found, for example, in outdoor storage of wood chips for paper pulp production) (Jirjis 1995) this is less likely to be a major contributor to the self-heating of fuel pellets in storage since the material is relatively dry (wood pellets have a moisture content (MC) of 5–10% w.b.) (Oberberger and Thek 2010; Stelte et al. 2012). In addition, the pelleting process heats the material to 90–150 °C (Oberberger and Thek 2010), a temperature that is likely to kill most of the microorganisms that might be found in the raw material (Oberberger and Thek 2010; Filbakk et al. 2011).

However, heat of condensation/sorption and the role of water uptake caused by condensation during changes in relative air humidity seem to have received less attention when it comes to the area of storage of biofuel pellets. The self-heating of cellulose materials (wood, particleboard, etc.) has been discussed earlier in the literature. The adsorption rate of water vapour and temperature change of coal directly during coal storage and transportation have recently been investigated (Miura 2016). It has been shown that the heat released by an increase of a few percent in the moisture content in lignocellulosic material can raise the temperature of the material to a range where the oxidation rate increases sufficiently to lead to onset of carbonisation in the material and in the end possible auto-ignition (Back 1981/82; Back and Johanson 1990; Korber et al. 2010). Dynamic Vapour Sorption (DVS) is a technique based on the gravimetric determination of vapour (mostly water vapour) interactions with a sample. By varying the water vapour concentration (i.e., relative humidity, RH%) surrounding a sample and measuring the change in mass it produces, the rate of water sorption (adsorption and absorption) and quantity of sorbed water can be measured. This technique has been used, for example, in studies on wood behaviour (Xie et al. 2011a, b; Hill et al. 2010).

In order to estimate the role of water condensation as a contributing factor in these self-heating incidents, knowledge of how water vapour interacts with fuel pellets is required. This will contribute to vital information on estimating the role of heat of condensation in fuel-pellet storage facilities and the possible increase in temperature and self-heating incidents.

The main objective of the present study was to gain an estimation of the potential contribution to self-heating of fuel pellets caused by water condensation resulting from a fast change in the relative air humidity. Dynamic Vapour Sorption (DVS) experiments were used (during a change in RH from 40 to 80%) in order to measure the amount and speed of water uptake. Using the data, the heat of condensation formed and a maximum theoretical temperature rise were calculated. Further, the results are expected to aid in understanding the potential contribution of air humidity changes to self-heating incidents in pellet storages.

2 Materials and methods

2.1 Samples

When selecting pellet samples for the project, 35 batches from three pellet types generally commercially available in Europe were chosen for the study; (i) pellets that represent the current market, (ii) pellets that are expected to have an increased relevance in the future, and (iii) pellets, which can directly be related to self-heating and off-gassing incidents. The samples were collected and distributed as a part of the EU project SafePellets (SafePellets project, European project, grant agreement number 287,026). Samples used for the DVS analyses are listed in Table 1.

All samples (ca 5 kg each) were sealed in 15 L airtight polyethylene bags after production as in Table 1 and transported to the laboratory within 1–2 days from bagging. The samples were stored in the laboratory at 4 °C until DVS analysis. No binders were used in any of the batches. Batch number 34 was not included in the calculation since it was a new production of torrefied pellets as batch number 20 but the batch was not homogenous with high percent of fines and therefore, omitted from the calculations.

2.2 Dynamic vapour sorption analysis

2.2.1 Sample preparation

Samples (small single pellets, ca. 0.190 g, relative standard deviation (RSD) 7.5%) were randomly selected from the larger bagged sample batches described in Sect. 2.1 (Table 1). The samples were prepared for DVS analysis by conditioning in a constant humidity cabinet (Climacell 111, MMM-Medcenter Einrichtungen GmbH, Germany) at 40% RH and 25 °C for a minimum of 96 h. Triple samples were run to estimate the method variation using pellets from Batches 8 and 12.

Table 1 Composition and density of pellets of the samples used in the study (CP=Commercial plant, RP=Research plant)

Batch	Pellet raw material and treatment at production	Pelletizing Plant	Density of pellets (kg/m ³)
1	Pine 100%. Ground material stored 4 days in big bag at 20 °C before pelletizing	German, RP	1254
2	Spruce 100%. Ground material stored 8 days in big bag at 20 °C before pelletizing	German, RP	1258
3	Pine 100%. Pelletized immediately after grinding	German, RP	1254
4	Spruce 100%. Pelletized immediately after grinding	German, RP	1258
5	Pine 100%. Sample from ordinary production	German, CP 1	1213
6	Spruce 80%/Pine 20%. Sample straight from ordinary production	Swedish, CP 1	1217
7	83% straw, 11% seed residue, 6% spruce. Sample straight from ordinary production	Danish, CP 1	1183
8	Spruce 100%. Sample straight from ordinary production	German, CP 2	1180
9	Pine 40%/Spruce 60%. Sample from ordinary production	Swedish, CP 2	1212
10	Pine 60%/Spruce 40%. Sample from ordinary production	Swedish CP 3	1225
11	Eucalyptus 100%. Stored one year at the company	Spain CP 1	1211
12	Pine 50%/Spruce 50%. Sample straight from ordinary production	Swedish CP 4	1201
13	Vine pruning 50%/vine pomace 50%	German RP	1324
14	Pine 100%, scCO ₂ extracted (extracted at York, Swedish raw material), run 1	German RP	1191
15	Pine 100%	Austrian RP	1256
16	Pine 100%, RP (same raw material as in Batch 15 but different equipment with pelletizing)	German RP	1185
17	Straw pellets (100%). Stored in a flat storage for 6 months before delivery	Danish CP 2	1116
18	Spruce 80%/ Pine 20% - mixed pellets	German CP 3	1182
19	Pine 100%, torrefied at 308 °C, 12 min, pelletized after cooling	Swedish RP	1259
20	Pine 100%, torrefied at 315 °C, 12 min, pelletized after cooling	Swedish RP	1177
21	Obtained from pellet company after fire accident	Swedish CP 3	N/A
22	Eucalyptus 100%	German CP 4	1290
23	Pine 100%, reference to Batches 24, 25, 27, pelletized after cooling	Swedish RP	1243
24	Pine 100%, with TBHQ as antioxidant, pelletized after cooling	Swedish RP	1232
25	Pine 100%, with PG as antioxidant, pelletized after cooling	Swedish RP	1225
26	75% pine, 25% fir and larch	Danish CP 3	1274
27	Pine 95%, with 5% spruce bark	Swedish RP	1248
28	Spruce 100%. Flat storage trial in Denmark, sampling after 1 week	Danish CP	1252
29	Spruce 100%. Flat storage trial in Denmark, sampling right after production	Danish CP	1250
30	Obtained from pellet company after a fire accident	German CP 5	1225
31	100% pine, reference to Batch 14	German RP	1270
32	Pine 100%, scCO ₂ extracted (extracted at York, Swedish raw material, run 2) Attard et al. (2016)	German RP	1238
33	Reference to Batch 32. Attard et al. (2016)	German RP	1139
35	Pine 100%, with 0.5% additive	Swedish RP	1137
36	Reference to Batch 35	Swedish RP	1159

Density given as the mean pellet density calculated from 20 randomly chosen pellets from each batch respectively (Larsson and Samuelsson 2017)

2.2.2 Instrument

The instrument used was a Dynamic Vapour System instrument (DVS), model Advantage ET2 (Surface Measurement Systems, UK). The instrument has a sensitivity of 1.0 µg, dynamic range of 1 g, sample mass (max) of 5 g, a relative humidity (RH) range of 0–98% ±0.5% and a temperature range of 20–85 °C. The DVS instrument was operated using the following run-cycle (see Fig. 1):

1. Equilibration of sample at RH 40%: 5 h at 25 °C
2. Increase of RH to 80% which is held for 13 h
3. Drying step 5 h at 105 °C and RH 0% in order to determine the dry matter of the sample.

Due to the long analysis time for each sample, the same instrumental parameters were used during the whole study. This does not imply that a variation in conditions would not be of interest. On the contrary, from the results obtained in

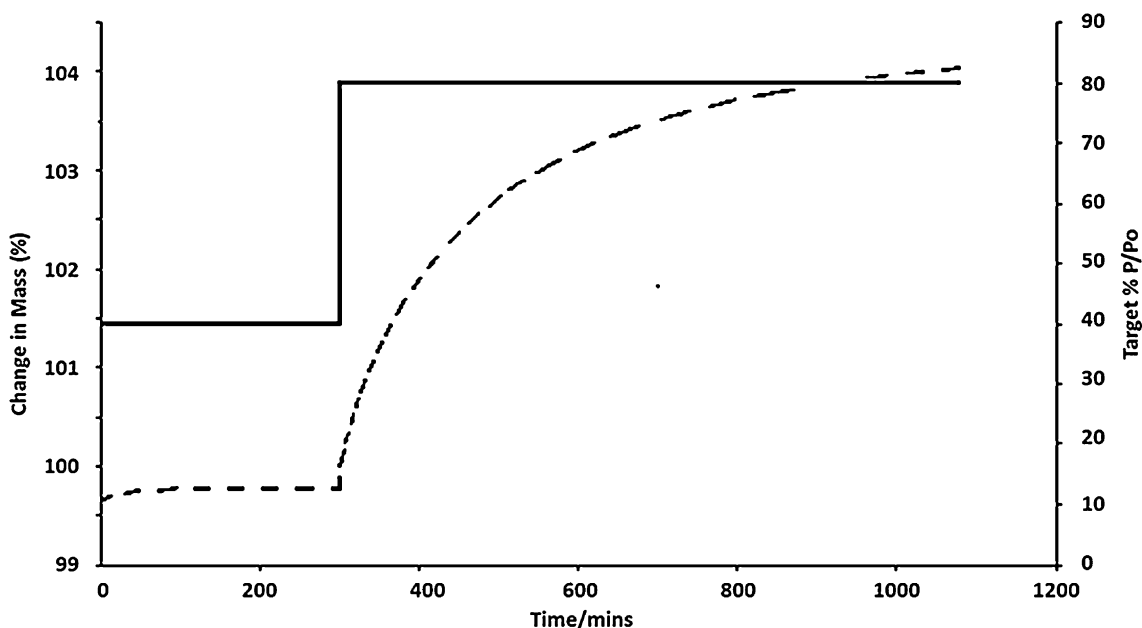


Fig. 1 DVS data registration from Batch 2. Solid line shows the DVS operating program. Dashed line shows registered weight-gain due to water uptake

this study, it is expected that additional valuable information can be gathered by DVS applying other sets of parameters.

2.3 Data collection and interpretation

For data collection and dm/dt calculations, the DVS instrument software was used. The weight-gain was measured to about 85–90% of the maximum weight-gain under the conditions used (13 h at RH 80%) with a sampling frequency of 3/min. Equilibrium water content at RH 80% was estimated by extrapolation to constant weight (more than 6 consecutive data points showing the same weight in g with 6 decimals) using the Excel Solver Add-in software (Microsoft Office). The Parallel Exponential Kinetics (PEK) model was applied to the modelling (Hill et al. 2010). The first 8 min of registration after the start of the RH 80% step were not taken into account since conditions are not stable then.

3 Results and discussion

3.1 General considerations and basis for interpretation

The experimental conditions in this study were chosen so as to model a fast change in the air RH in a pellet silo/storage. Starting conditions were set to an air RH of 40% at 25 °C, which is a typical lower air humidity level. The change to RH 80% was chosen to simulate, for example, a late summer/autumn situation where the RH% often increases fairly

quickly (to 70–90%) at the end of the day (Graham et al. 2017). In earlier studies typical temperatures during storage of fuel pellets were found to be in the range of 25–70 °C (Kuang et al. 2009a; Graham et al. 2016) and experiences from commercial silos (Larsson et al. 2012) verify these observations.

For modelling of the water vapour up-take process, the parallel exponential kinetics (PEK) model (Hill et al. 2010) was applied to the DVS data collected. It comprises two exponential functions describing two different processes that contribute to the total uptake as discussed by Hill et al. (2010). Thus, what is registered in an experiment by DVS is the sum of the two processes.

The model parameters were calculated by minimizing the weighted error square sum:

$$MC = MC_0 + MC_1 [1 - \exp(-t/t_1)] + MC_2 [1 - \exp(-t/t_2)] \quad (1)$$

MC Mass of water absorbed by the sample at infinite time (g), i.e. moisture content at infinite time. MC_0 Mass of sample at time 0 (i.e. when the RH 80% step starts), set to 0 g. MC_1 Portion of mass of absorbed water originating from fast process (g). MC_2 Portion of mass of absorbed water originating from slow process (g). t Time in process (min). t_1, t_2 Characteristic times for respective process (equation) (min).

The data from the analysis allows measuring or calculating the following parameters:

- Total water uptake for the pellet batch (%)

- Speed of water uptake (i.e. dm/dt)
- Calculated values of the parameters in the model equation that reflect the properties of water uptake for each batch individually (MC1 and MC2).

3.2 Measured data and method repeatability

It was observed that it is not reasonable to follow the water up-take process to equilibrium, which would take about 2 days (on average and maximum 6 days) as estimated by the Solver program. A typical result from a DVS run (Batch 2) is shown in Fig. 1. The chosen length of the RH 80% step (13 h) which is a reasonable time for practical application allows covering the weight-gain to about 90% of its maximum (infinite) weight-gain at the conditions used. This means that modelling of the remaining part of the process is required in order to determine the total weight gain for a specific pellet batch under the conditions used. The water uptake was measured when increasing the RH from 40 to 80% (as described above). The equilibrium water uptake was extrapolated to the time where the weight (g) remained constant (6 decimals) using the PEK model for estimation of the “infinite” water uptake. This modelling and extrapolation were made using the Solver program, and an overview of the DVS results are presented in Table 2. The calculated time when equilibrium water uptake was reached was 3000 min (mean) from start of the RH 80% step, but varied between 1800 and 5800 min (RSD 47%), which is also reflected in the differences observed in the water uptake rate as expressed by the derivative dm/dt (Table 2).

The method repeatability was determined by running two of the batches (Batch 8 and 12) in triplicate. The repeatability in total water uptake was 2.4% and 2.8% RSD of the mean (relative standard deviation of the mean) for the two batches respectively. The repeatability for the derivative of the water uptake was observed and found at 10, 30 and 60 min to be (3.7; 2.5), (3.7; 1.8) and (4.5; 2.7) for the two batches, respectively. This was regarded as adequate taking the expected batch sample homogeneity and the small sample size possible to use in the DVS experiments into consideration.

3.3 “Infinite” water uptake—influences of raw material and production

No systematic difference in total water up-take that was related to the production in industry as compared to pilot plants was found using T-test (Table 3). In addition, the variations within the larger groups of raw material (pine, spruce and pine/spruce mixtures) were relatively small (Table 3), and the mean water uptake did not differ significantly between these groups (T-test). However, batches made from wheat straw, wine prunings/pomace and torrefied pine did

differ more from the rest (Table 3), although the number of samples from these groups was small.

3.4 Modelling of the water up-take process

Modelling of the process using the Solver software generated parameters for the fitted PEK equation with a low or excellently low weighted error square sum (ESS) (Table 2). The equation and fitted model are shown in Fig. 2 for one of the samples. The PEK model, describing two different processes that contribute to the total uptake, are explained by Popescu et al. (2015) as a fast process being due to a physical diffusion process and a slow process as being due to a relaxation-limited process.

When separating the two equation components in the data of this study, it is observed (Fig. 2) that the fast process contributed less than the slow process to the total water uptake in all samples. However, the fast process has the largest influence in the first 2 h of water uptake and is thus likely to contribute most to a self-heating situation due to the quick rise in water uptake the first few hours after a change in RH% during pellet storage.

As discussed by Xie et al. (2011a), the reason for the differences in the allocation of moisture to the fast and slow processes is not fully revealed. However, the fast kinetic process was suggested to be related to a fast moisture sorption at “external” surfaces and “amorphous” regions, whereas the slow kinetic process was related to sorption onto the “inner” surfaces and “crystallites” (Morton and Hearle 1997; Okubayashi et al. 2004).

3.5 Rate of water up-take

The derivative for the water up-take over time is calculated by the software in the DVS instrument and is available for all data points. For the interpretation of the data and comparison of the various pellet batches, dm/dt at 10, 30 and 60 min were used. The reason for that choice is that the initial water uptake is fairly fast and is expected to contribute to the fast temperature rise observed in connection with the initiation of fire and heating incidents in pellets silos/storages (Larsson et al. 2012).

In Fig. 3, the water up-take rate (dm/dt) over time for four different batches is compared. These examples illustrate the wide variation in uptake rate, despite the total water uptake being almost the same for three of these samples. The reason for this behaviour might reflect differences in production parameters (e.g., pilot plant and industry scale production) but requires additional research in order to be explained. The production process in the pellet industry uses higher drying temperatures and a larger feedstock flow through the pellets press, also resulting in a higher temperature in the pellet die due to the continuous

Table 2 Overview of the results from DVS measurements

Batch	“Infinite” water uptake (%)	Solver solution parameters					dm/dt (g/min)		
		Water uptake (%) after 2 h	MC1	MC2	t1 (min)	t2 (min)	At 10 min	At 30 min	At 60 min
1	4.50	1.72	0.00184	0.00756	49.37	405.7	0.02954	0.01839	0.01306
2	4.32	2.10	0.00339	0.00533	78.46	342.9	0.03507	0.02343	0.01636
3	3.91	2.02	0.00189	0.00483	51.13	260.4	0.03650	0.02246	0.01541
4	4.62	2.37	0.00194	0.00628	46.33	247.7	0.03978	0.02654	0.01845
5	4.90	2.38	0.00254	0.00625	78.90	260.5	0.03538	0.02552	0.01943
6	4.20	2.32	0.00222	0.00609	46.40	221.2	0.04001	0.02689	0.01777
7	5.77	2.73	0.00250	0.00930	63.90	256.7	0.03986	0.02957	0.02223
8	4.20	1.80	0.00158	0.00676	47.11	316.4	0.02977	0.01952	0.01407
9	4.82	1.97	0.00146	0.00863	50.00	302.9	0.02964	0.02085	0.01585
10	4.68	2.03	0.00096	0.00842	38.77	246.2	0.02995	0.02169	0.01640
11	4.07	2.18	0.00231	0.00511	45.46	270.2	0.04005	0.02552	0.01643
12	4.92	1.98	0.00235	0.00640	60.67	235.6	0.03926	0.02795	0.02052
13	10.3	0.54	0.00190	0.01589	69.84	688.3	0.03202	0.02457	0.01954
14	4.10	2.28	0.00183	0.00583	42.96	207.7	0.04010	0.02624	0.01760
15	4.54	2.85	0.00177	0.00684	50.58	318.8	0.03277	0.02159	0.01535
16	3.81	2.45	0.00233	0.00419	46.25	178.7	0.04469	0.02909	0.01867
17	6.86	2.83	0.00210	0.00821	41.58	250.3	0.04536	0.03140	0.02226
18	3.92	1.75	0.00044	0.00709	8.66	225.3	0.03195	0.01601	0.01294
19	3.80	1.54	0.00085	0.00684	37.34	289.7	0.02453	0.01639	0.01214
20	3.96	2.26	0.00311	0.00467	57.77	258.8	0.03962	0.02626	0.01752
21	4.54	2.37	0.00239	0.00708	61.06	227.7	0.03688	0.02592	0.01885
22	5.83	2.09	0.00189	0.00956	60.74	395.8	0.03117	0.02229	0.01668
23	4.00	1.74	0.00135	0.00753	39.46	287.9	0.02887	0.01880	0.01345
24	4.37	2.33	0.00187	0.00701	50.39	210.7	0.03778	0.02563	0.01820
25	4.25	2.47	0.00243	0.00433	54.81	226.0	0.04324	0.02837	0.01914
26	4.35	2.07	0.00167	0.00619	49.69	268.7	0.03346	0.02292	0.01638
27	3.69	2.00	0.00089	0.00586	26.94	187.2	0.03546	0.02230	0.01530
28	4.97	2.22	0.00143	0.00775	60.55	258.6	0.03176	0.02357	0.01818
29	5.49	2.20	0.00158	0.00981	53.77	309.3	0.03166	0.02353	0.01790
30	4.32	1.82	0.00133	0.00641	45.70	314.4	0.02998	0.01958	0.01421
31	4.47	1.61	0.00135	0.00674	43.82	425.9	0.02828	0.01739	0.01216
32	5.06	1.98	0.00123	0.00786	46.68	326.1	0.03156	0.02058	0.01550
33	4.93	2.70	0.00154	0.00684	47.23	192.4	0.04325	0.02967	0.02154
35	4.41	2.07	0.00268	0.00617	68.62	322.0	0.03329	0.02259	0.01625
36	4.51	1.99	0.00167	0.00722	51.61	294.2	0.03113	0.02142	0.01585

Water uptake extrapolated to equilibrium (for explanation, see below in the section: Determination of “infinite” water uptake) using the Solver software and the PEK model

dm/dt derivative of weight gain

friction of the material with the steel. This harsh condition at industrial scale results in a lower MC in the pellets as compared to the pilot plant process, and these pellets are likely to reabsorb moisture faster than the pellets with higher initial moisture content. The initial rate of water up-take might be important in order to explain fast temperature increases in pellet storage.

3.6 Water uptake, heat of condensation and potential temperature rise

Thermal conductivity and specific heat capacity in wood pellets are important properties in estimating the temperature gain in wood pellets as a consequence of water condensation/absorption driven by changes in RH%, spread of the heat in the pellet bulk as well as modelling and understanding the

Table 3 Water uptake by pellet batches produced

Raw material	Mean (%)	sd	RSD	n
Pine (P)	4.36	0.41	9.4	14
Spruce (S)	4.66	0.45	9.6	6
Pine/spruce mix (PS)	4.48	0.31	6.9	8
Straw	6.32	–	–	2
Eucalyptus	4.95	0.88	17.8	2
Wine prunings/pomace	10.33	–	–	1
Torrefied pine	7.00	–	–	2
P+S+PS	4.61	0.63	13.7	28
All types	4.73	1.16	24.5	35
<i>Production</i>				
Industry	4.61	0.74	16.1	17
Pilot plant	4.84	1.44	29.7	18

Grouped according to raw materials used and production scale (industry/pilot plant)

self-heating processes in a pellet storage silo (Sjöström and Blomqvist 2014). In an investigation by Guo et al. (2013), three different pellet batches were studied with a MC ranging from 4.6 to 8.8 (Hartley and Wood 2008). From experimental data they estimated the values of the thermal conductivity and specific heat capacity of the pellets, from which they constructed the following model equation:

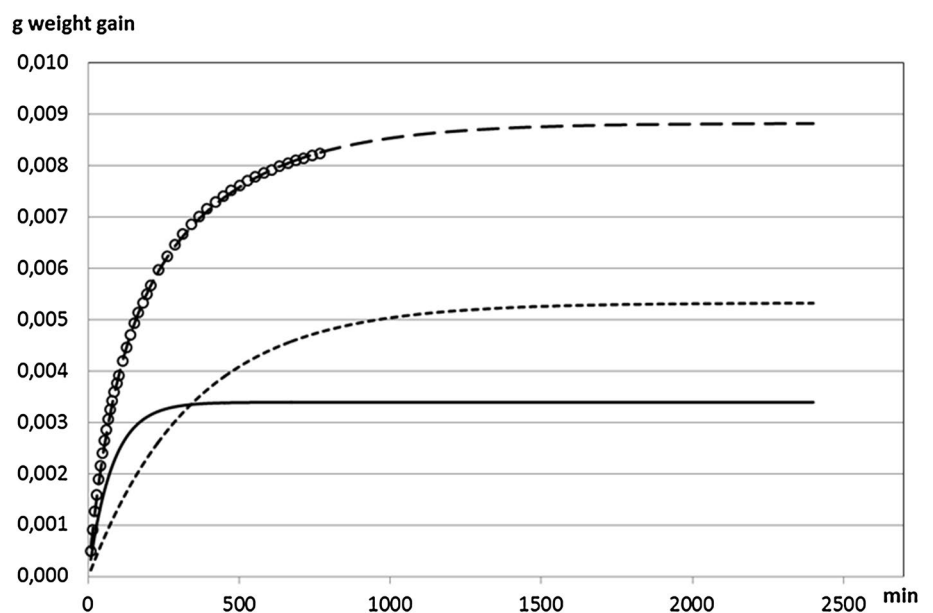
$$\lambda_{eff} = (0.219 + 0.01MC) \times (1 - \phi) + \phi \times 0.027 \quad (2)$$

where λ_{eff} is the effective thermal conductivity of the packed bed in W/(m K) and ϕ is the porosity in fraction; MC is the moisture content in percentage, wet based

and

$$C_p = 1.01 + 0.032MC \quad (3)$$

Fig. 2 Water uptake at 80 RH% for the sample of Batch 2, corresponding to 4.32% based on the sample weight at RH 40%. Observed DVS data (O), for clearness; at 0–100 min every 20th observation is shown, 100–200 min every 40th and at 200-min every 80th. Fitted PEK model equation (---), PEK equation separated in fast (—) and slow (●●●) processes



where C_p is the specific heat capacity for pellets in kJ/kg K and MC is the moisture content. The number 1.01 was their experimentally found mean for ($C_{P,dry}$) (Guo et al. 2013) and was used in the present study as a reasonable approximation.

In the present study, the following calculations were made for the various pellet batches (results from 34 samples were used, excluding Batch 13 as an outlier);

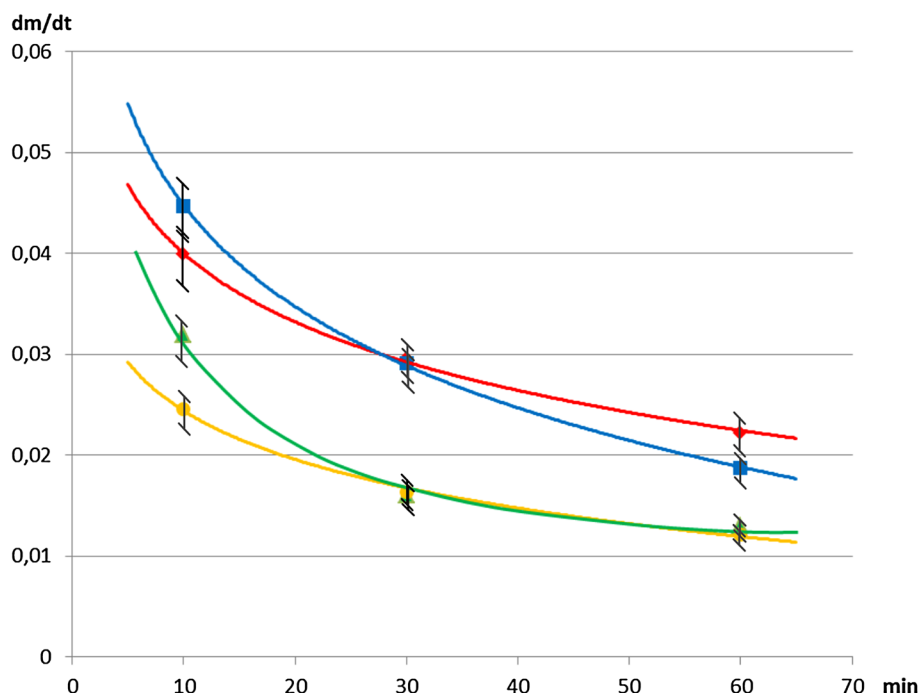
- the mean porosity ϕ (air space between the pellets in bulk) was calculated from pellet bulk density and single pellet density, to be 0.471 (range 0.415–0.557, RSD 6.4%), and
- the mean pellet MC at 40% RH was 7.53% (range 6.58–8.65%, RSD 6.52%).

These values were used to:

- calculate the effective thermal conductivity λ_{eff} (Eq. 2), using the DVS registered moisture uptake, to be 0.153 W/m·K (range 0.129–0.171 W/m·K, RSD 5.5%) over the MC range. This value is in the same range as was reported in the literature (0.146–0.192 W/m·K) (Guo et al. 2013).
- estimate the specific heat capacity C_p at RH 40% (Eq. 3), to be 1.16 kJ/kg K (range 1.13–1.23 kJ/kg K, RSD 1.8%, MC range 6.58–8.65% w.b.) as compared to the literature data (1.074–1.253 kJ/kg K, temp. range 25–50 °C, MC range 1.4–9.0% w.b.) (Guo et al. 2013).

In order to make an estimation of the potential heat release (when raising the RH% from 40 to 80%), the total water uptake was taken into account, 4.56% (Table 2, range 3.69–6.86%, RSD 14.3%) and an approximate heat

Fig. 3 Water uptake rate expressed as derivative of weight-gain (dm/dt) at 10, 30 and 60 min, (Confidence intervals are shown. For the method variation, see Sect. 3.2.) Batch 16 (square) pine. Total water uptake 3.81% (Industry); Batch 7 (diamond) wheat straw. Total water uptake 5.77% (Industry); Batch 18 (triangle) pine/spruce mixture. Total water uptake 3.92% (Pilot plant); Batch 19 (circle) torrefied pine. Total water uptake 3.80% (Pilot plant)



of condensation value of 2200 kJ/kg water was used. The slight change in C_p at different temperatures was not taken into account in this estimation.

- This (water uptake/heat of condensation) gives an estimation that a *heat release* of 100 kJ/kg pellets (range 81–151 kJ/kg, RSD 14.3%) would be possible and a potential temperature increase (heat release/ C_p) of 87 °C (range 72–169, RSD 12.2).

However, at the same time there will be loss of energy to the outside of the bulk as radiant heat on the surface and by conductivity in the bulk. The actual temperature increase will be balanced by these two effects. However, the first hours after an increase in RH% should be expected to be most critical if the first initial 2 h after a drastic change in RH% are included in the estimation and the loss of energy from the bulk is considered limited during this time. The water condensed is likely to re-volatilise due to the heat and after diffusion re-condense in cooler parts of the pellet bulk and thus, cause a “moving” heated zone as observed by pellet disintegration in the centre of the bulk after self-heating incidents (Oberberger and Thek 2010). This water transport will again lower the pellet humidity in parts of the storage closer to the outer parts of the bulk and make them sorb additional water from the air.

- Thus, the water uptake during the first 2 h at RH 80% was determined to be 2.15% (Table 2, range 1.54–2.85%, RDS 15.2%), corresponding to 48% of the infinite water

uptake at 80 RH%, resulting in a potential *heat release* of 47 kJ/kg (range 12–63 kJ/kg, RSD 15.2%) and *temperature rise* of 45 °C (range 12–58 °C, RSD 14%).

Even if this is a rough estimation, not taking all material properties (raw material, pellet size, etc.) into account and not including the dynamics in the process, it clearly demonstrates that the potential temperature rise is considerable and might cause self-heating problems during storage. As a comparison, temperature rise up to 55 °C in a ca. 12 tones pellets pile has been reported previously (Arshadi et al. 2009). The actual temperature reached in a silo locally and under specific conditions is however very complicated to calculate. Additional factors influencing the heat accumulation and potential risk of self-ignition are also depending on the physical surroundings affected by the construction of the silo/storage in question; size and insulation, ventilation, etc. on the temperature accumulation. The actual change in relative air humidity/temperature, ventilation, size and insulation of the storage are likely to play an important role; all factors contributing to make a full modelling very complicated.

In addition, the increase in temperature caused by condensation will also increase the reaction rate of the exothermal autoxidation of unsaturated fatty acids (Litwinienko 2001; Juita et al. 2012). The correlation between the autoxidation process and the produced gases during off-gassing from fuel-pellets mentioned above have recently been confirmed (Attard et al. 2016; Arshadi et al. 2009). This temperature increase will increase the autoxidation reaction rate and further add to the temperature rise. The combustible volatiles produced

(aldehydes/ketones, CO, CH₄) together with remaining terpenes and/or other combustible gases from the bulk will contribute to the potential for a self-heating incident to result in a fire.

4 Conclusion

The DVS technique applied to fuel pellet samples gives information on specific fuel pellet batches regarding their water uptake properties in air humidity/temperature conditions that cause condensation. From the results it can be concluded that:

- The heat of condensation released during water condensation in a pellet silo has a potential to considerably contribute to increasing the temperature, especially in a situation with a fast and/or large change in relative air humidity, and should be expected to be a major contributing factor to initiating temperature increase incidents. The correlation between water uptake and heat release of lignocellulosic material is a well-known process (Back and Johansson 1990; Back 1981). In addition, such a temperature rise can be expected to contribute to the initiation and acceleration of autoxidation.
- The water uptake between pellets made from pine, spruce and pine/spruce mixtures did not differ significantly but was higher for batches made from wine prunings/pomace, straw and torrefied pine (although these types of samples were few).
- The water uptake rate (dm/dt) in the initial part of the process gives an indication of the potential for a fast temperature rise associated with changes in air relative humidity and the following condensation in pellet storage. The uptake rate varies considerably between the pellet samples made from different raw materials.
- From the potential water uptake it is possible to calculate a heat release potential due to heat of condensation and to make an estimation of potential local temperature rise. In addition, this implies that the different batches have varying potential to release heat of condensation and initiate/accelerate a self-heating process in a silo.
- Thus, DVS analysis has the potential to complement other physical/chemical measurements on fuel pellets in predicting how the choice of fuel raw material and pellet processing parameters might influence the potential risk for self-heating, off-gassing and fire incidents.
- The results are based on a fairly large and representative number of fuel pellet batches on the European market and should provide a strong basis in modelling physical/chemical processes in pellet storage. Such further studies have the potential to give a tool to predict the self-heating potential of various pellet batches. Such a tool should

increase the possibility to reduce the risks associated with pellets storage/transportation and to avoid the conditions/situations involving highest risk for off-gassing, oxygen depletion and uncontrolled heat formation/fire.

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