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D6.1 - Relation between off-gassing and self-heating

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1 Background

Pellets are the most advantageous solid biofuel. This is due to its higher energy density and better defined qualities compared to other solid biofuels. So far, the largest share of the production is made from virgin wood sources. With the rapidly growing demand also recycled wood assortments and non wood resources will be used for pellets production.

However, this increase in production may also lead to an increase in risks from the phenomena of off-gassing and self-heating from biomass pellets and thereby could result in an increase in accidents related to each of the two phenomena. Up to now dedicated methods to assess the off-gassing and/or self-heating potential of biomass pellets were not available.

The origins and quantification of both, (1) off-gassing of CO, CO₂, CH₄ and VOCs from and (2) self-heating and spontaneous ignition of wood pellets, are not fully clear yet.

1.1 The off-gassing phenomenon

Wooden biomass is known to emit a broad spectrum of off-gasses during thermal treatments such as drying but also during storage, especially, when stored in form of chips, sawdust or pellets. Dependent on the kind of thermal treatment and on the form of the biomass the off-gassing spectrum changes in composition and shifts with respect to its major components. For example, off-gassing from wood chips and sawdust has been investigated in several studies [Rupar 2003, Rupar 2005, Banerjee 2006, Granström 2005, Granström 2008, Larsen 2000]. Reported off-gasses from wood chips and sawdust include mono-, sesqui-, and diterpenes [Englund 2000, Rupar 2003, Rupar 2005, Granström 2009] along with CO₂, CO and CH₄ [Meijer2004, Svedberg 2009], formaldehyde and methanol [Marutzky 1977, Otwell 2000, Banerjee 2006], whereas pellets are also reported to emit a broad spectrum of aldehydes, most prominent amongst them hexanal and pentanal [Svedberg 2004, Arshadi 2005, Granström 2010] and other volatile organic compounds such as acetone [Hagström 2008].

In the study by Arshadi and Gref 2005 [Arshadi 2005], the off-gassing characteristics for different types of sawdust (pine, spruce, fresh and mature) were investigated yielding the result that very high levels of emitted VOCs were produced. Above all, the substances pentanal and hexanal were measured in comparable volumes. Moreover, it could be determined that the lipid content of sawdust was reduced with longer storage time, a result that was subsequently evaluated as evidence for the decomposition of fatty acids in wood through autoxidation. The lipid content of the wood was furthermore suggested as indicator for the maturity of the sawdust. The findings were then taken up in follow up studies [Arshadi 2007, Arshadi 2008] with the goal to predict the expected pellets quality as well as the required energy costs associated with pellet production. For this purpose, the moisture content of the raw material was determined online by means of near infrared spectroscopy and correlated with the quality of the pellets. In doing so, the moisture content of the pellets was ascertained to be a crucial factor. A



correlation between the lipid content in the raw material and the pellets quality could, however, not be determined with certainty.

The off-gassing behavior of wood pellets became the focus of intensive research after a series of tragic accidents on board of two pellet bulk carrier ships, the "Weaver Arrow" in May 2002 in Rotterdam and the "Saga Spray" in November 2006 in Helsingborg, which were reported in Svedberg et al 2008 [Svedberg 2008] and Melin et al 2008 [Melin2008]. The studies provided a clear sign that the formation of CO from wood pellets is a phenomenon, which does not result exclusively from elevated temperatures. Also data was provided on the effect of O₂ depletion, a parallel effect occurring simultaneously to the off-gassing effect and proven to be one of the contributing factors in the fatal accidents on-board the pellet bulk carrier ships. The fact that CO is released during the storage of wood pellets was, however, first reported some years earlier in the study by Svedberg et al 2004 [Sve2004], which deals with the characteristics of released emissions from wood pellets production facilities. In this publication, special attention was placed on the measurement of CO and hexanal, whereby the measured mean concentration of each compound in the storage containers were found to be 56 mg/m³ (value above the Swedish permissible exposure level during 8 h exposure of 40 mg/m³ and 360 mg/m³ (no maximum allowable value exists), respectively. It could be determined that these emissions were produced before the pelletizing process as well as generally from the decomposition of wood. Moreover, this is the first publication in which it was suggested that the autoxidation of fatty acids was responsible for the formation of CO from wood pellets. The formation of CO from hydrocarbons in general, however, has been reported prior to that in the work of Levitt et al as early as 1995 [Levitt 1995]. The authors Svedberg et al 2004 also illustrate that the decomposition of fatty acids is the most accountable mechanisms for the formation of the identified organic compounds in the overseas transportation of wood pellets. These suggestions, based on the released knowledge in Back and Allen 2000 [Back 2000], also state that hexanal is the main principal decomposition component released from the oxidization of linoleic acid and linoleic acid esters. A fact, which is also supported by a second earlier study published in 1991 by Koelsch et al [Koelsch1991].

In recent years many publications on the topic of off-gassing from stored wood pellets were provided by researchers from the University of British Columbia [Tumuluru 2007, Kuang 2008, Kuang 2009a, Kuang 2009b, Kuang 2011, Yazdanpanah 2014a, Yazdanpanah 2014b]. In the studies by Kuang et al [Kuang 2008, Kuang 2009a, Kuang 2009b, Kuang 2011] and Fan and Bi 2013 [Fan2013] the authors concentrated on the measurement of CO, CO₂ and CH₄ emitted from wood pellets in sealed, air tight containers with a capacity of 45 liters. With the obtained data a kinetic model for the formation of these gases was created. The results showed that the recurrent concentrations, according to the definition, behave as a first order chemical reaction and therefore an autoxidative fat-degradation reaction is essential as the most dominant causal agent. The impact of temperature, oxygen level and relative humidity on the rate of emission as well as the peak concentration for each gas was also looked into. It could be established that

temperature is a key parameter affecting the peak off-gassing emission factors for stored wood pellets significantly.

Yazdanpanah et al 2014 [Yazdanpanah2014b] have shown that the CO₂ and CO off-gassing behavior of wood pellets is also strongly influenced by the moisture content. For this purpose the concentration of emitted gases from wood pellets were investigated in an enclosed space at variable moisture content (from 4-50%) and high temperature (from 20-60°C). In line with results previously reported [Kuang 2009a] CO₂ and CO concentrations rose with rising temperature, however, with rising moisture content (<15%) CO emissions were decreasing. Also oxygen depletion was hampered with rising moisture content, but accelerated with rising temperature. It has also been reported that high temperature storage causes deterioration of wood pellet durability [Tumuluru 2013].

Although, the number of publications on parameters influential to the off-gassing phenomenon are steadily growing, little has been published on possible reaction pathways responsible for the release of emissions, and of CO in particular. In fact only one study published in 2012 by a group of researcher from the University of Newcastle has suggested a possible complete formation mechanism for the oxidation of linolenic acid and the subsequent formation of CO [Juita2012]. The group investigated a pathway for the autoxidation of linseed oil, which is a common ingredient in paints, varnishes and wood treatment agents. It consists mainly of linoleic, linolenic, palmitic and oleic acid, all of which constituents typically found in the extractive content of wooden biomass samples. In wood samples linolenic acid is only present at very low concentrations, however, it is reasonable to assume that if the degradation of this acid yields CO emissions also the degradation of other unsaturated fatty acids such as oleic, palmitic and linoleic acid will result in CO formation.

Due to the fact, that autoxidation of the extractives contained in the wooden biomass is responsible for the release of off-gassing emissions, the extractive content is also regarded to be of significant impact to the off-gassing behavior. The extractive content of wood sawdust is also a key factor when it comes to the pelletizing process and has, thus, been in the focus of research regarding pelletizing properties of wood raw materials [Nielsen 2009, Nielsen2010]. The studies provided by Nielsen et al [Nielsen 2009, Nielsen 2010] report on the effect of age on the extractive concentrations of the surface materials of pelletizing raw materials. They were found to be initially high and to increase even further during storage. However, a more in depth analysis revealed, that only the concentrations of triterpenoid and steroidal structures increased, whereas fatty acid and diterpenoid structures decreased over time. Polymerization reactions of the fatty acids and diterpenoid structures were suggested as underlying mechanisms to explain these findings. Whether the effect of storage with respect to particle surface accumulation of extractives is of significant importance when compared with the total amount of extractives in the raw material, was, however, not conclusively established. In Fengel and Wegener [Fengel 2003] and Arshadi et al 2007 [Arshadi 2007] it has been reported, that the extractive content of wooden biomass is decreasing with time. A fact that is also supported by literature presenting data on the storage of fresh wooden biomass and the gaseous emissions released during its



storage in combination with the related dry matter losses [Wihersaari 2005a, Wihersaari 2005b, He 2012}. To give an example, in the study presented by He et al 2012 [He 2012] dry matter losses during the storage of fresh Douglas fir (*Pseudotsuga menziesii*) branches were estimated between 0.78 - 2.0% over a period of 35 days and increasing with storage temperature.

A more recent study provided by Granström in 2014 [Granström 2014] reported on the effect of the age of the raw material on the release of aldehyde emissions from oxidation processes from wood pellets. In this study, pellets made from fresh sawdust were reported to show low-emitting levels after 80 days of storage, whereas pellets made from aged sawdust did not reach the same low level until 190 days after production. A key conclusion of that study was that when a low level of aldehyde emissions is required during storage, the pellets should be produced from sawdust that is freshly sawn. Furthermore, previous studies also support suggestions to rather produce pellets from fresh sawdust from an economic point of view, as it has been shown that it requires less energy in production. This has been attributed to increased friction in the matrix caused by the loss of extractives in the case of aged sawdust [Nielsen 2009, Filbakk 2011].

An interesting point is made in the study by Arshadi et al 2012 [Arshadi 2012]. By the removal of fatty and resin acids from pine sawdust utilizing supercritical extraction with carbon dioxide, it is suggested that the potential for uncontrolled autoxidation processes can be reduced significantly. The study revealed that the calorific value of the pelletized sawdust was not significantly affected by the extraction process. However, whether the extracted pellets also showed reduced off-gassing behavior was not investigated in that study.

Whilst the emission of CO₂ and CO from wood pellets has generally been attributed to the autoxidative degradation of fatty acids, the release of these gases from non-thermally processed forest products such as logs and chips are usually attributed to microbiological activities [Svedberg 2004, Svedberg 2009, Meijer 2004]. The extent to which microbial activity in wood contributes to the release of CO and VOCs during storage was primarily investigated in correlation with the theme of self-heating and spontaneous ignition of wood [Blanchard 2007, Rupar-Gadd 2004]. In Meijer 2004 [Meijer 2004], the authors reported about the release of CO₂ in early phases in which microorganisms triggered biological self-heating whereas they attributed the formation of CO to a chemical oxidation process to a later time with higher temperatures (>70°C). In this study, the phenomenon of the formation of CO by lower temperatures was not observed and as such, the detection of instantaneous CO was linked to the danger of the spontaneous ignition of wood. In Rupar-Gadd 2004 [Rupar-Gadd 2004], the influencing factors of relative humidity and different storage temperatures were named as the most crucial for the variable growth of microorganisms. It could also be determined that pellets containing bark exhibit higher microbial activity than pellets without. Evidence that CO can be generated as a direct decomposition product through microbial activity was not found.

1.2 Self-heating phenomenon

Questions concerning the formation of off-gassing emissions and the associated mechanisms were also examined from a further significant standpoint, namely, the phenomenon of the self-heating and the spontaneous ignition of stored biomass. In Blomqvist et al 2007 [Blomqvist 2007] experiments are described in very small volumes (1 dm^3) as well as in larger volumes (up to 4 m^3) conducted with the goal of obtaining kinetic data of the exothermic reaction characteristics in wood pellets during the self-heating process. Primarily, the oxidation mechanisms in wood due to temperatures exceeding 80°C were investigated, whereby the O_2 , CO_2 , CO and VOC gases were analyzed. It appears that in the interior of the pellets pile, CO_2 and CO as well as VOCs (above all terpenes, pentanal and hexanal) emerge very slowly thereby hindering the early detection of the emerging gases. The method applied for determination of the kinetic parameters in self-heating substances is commonly referred to as the "crossing-point temperature method". It involves the periphery heating of an initially exothermic material being subjected to a hot environment with a constant temperature. When the center temperature exceeds the temperature measured a small distance from the center, that point at that temperature is defined as the "crossing-point temperature" [Blomqvist 2003].

In Blomqvist and Persson 2003 [Blomqvist 2003] it is pointed out that the largest risk for spontaneous ignition would be in storages of moist biofuel such as wood chips and sawdust, as these provide suitable conditions for growth of bacteria and fungi. They in turn produce heat in the low temperature regime, which is usually a prerequisite for attaining the temperature regime where oxidative processes commence. Dry refined wood fuels such as wood pellets and briquettes are considered to be at low risk for spontaneous ignition, if stored properly. However, self-ignition of wood pellets is not an unheard of phenomenon and there are several documented cases [Persson2013].

In Larsson et al 2012 [Larsson 2012] six large scale silos for wood pellets were monitored over a period of 7 months. The temperature profiles recorded within the silos showed an increase where temperature increased over time and by increasing height. A fact that is supported by the work conducted by Guo 2013 [Guo 2013], where data is presented from industrial wood pellet silo sites that shows temperatures of up to 60°C measured in the silos

Hydrocarbon oxidation is named as the dominant source of heat responsible for self-heating of biomass aided by various other exothermic 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 [Blomqvist 2003]. Therefore, the phenomena of off-gassing and of self-heating of biomass are believed to be closely connected.



2 Objectives and approach

The objective of this work is to assess a possible link between the propensity for off-gassing and self-heating exhibited by wood pellets. To this extent different types of biomass pellets were tested utilizing various methods for the determination of the off-gassing of the self-heating activity of pellets. A comparison of the results from the individual methods with respect to their activity shall provide insight into the question whether pellets, who show a high off-gassing activity also exhibit a high self-heating activity.

The experiments leading to the results discussed in this report have been derived in the work packages 3 and 4 of the SafePellets project and were carried out by the scientific partners Sveriges Lantbruksuniversitet [SLU] , SP Sveriges Tekniska Forskningsinstitut [SP], the Dansk Technologisk Institut [DTI] and BIOENERGY 2020+ GmbH [BE2020] in cooperation with the Deutsches Biomasseforschungszentrum [DBFZ].

3 Materials & methods

3.1 Pellet samples

Table 3-1 lists the pellet samples used in the characterization experiments. Due to the distinctly different behavior of non-woody pellets in the off-gassing and self-heating experiments it was decided that a comparison between the methods should only be carried out with wood pellet samples. The 13 chosen pellet samples were partly produced using laboratory pelletizing equipment and were partly supplied by commercial pellet producers. The table below lists their composition in terms of raw material source (pine, spruce or a mixture of both) as well as the pellet diameter.

Table 3-1: Pellet samples used in the characterization experiments

SafePellets Batch numb.	Pine/spruce ratio	Production	Description	Diameter
1	100/0	Laboratory	Grinded material stored for 4 days in big bag climatized at 20 °C	6
2	0/100	Laboratory	Grinded material stored for 8 days in big bag at climatized 20 °C	6
3	100/0	Laboratory	Material pelletized immediately after grinding	6
4	0/100	Laboratory	Material pelletized immediately after grinding	6
5	100/0	Commercial	Pellets obtained from a German pelletizing company straight from the production	6
6	20/80	Commercial	Pellets obtained from a Swedish pelletizing company straight from the production	8
8	0/100	Commercial	Pellets obtained from a German pelletizing company straight from the production	6
9	40/60	Commercial	Pellets obtained from Swedish pelletizing company straight from the production	6
10	60/40	Commercial	Pellets obtained from a Swedish pelletizing company straight from the production	8
12	50/50	Commercial	Pellets obtained from Swedish pelletizing company straight from the production	8
15	100/0	Laboratory	Sawdust pelletized in a flat-die press	6
16	100/0	Laboratory	Same sawdust as pelletized in batch 15 but pelletized in a ring-die press	6
18	80/20	Commercial	Pellets obtained from a German pelletizing company straight from the production	6



3.2 Analytical methods

In this section a brief description of each analytical method for the determination of the off-gassing or self-heating activity of the pellet samples is given.

3.2.1 Fatty and resin acids performed by SLU

The content of fatty and resin acids in the various pellet batches investigated were performed as follows.

Triplicates of 3 gram of each pellet samples to be investigated were crushed using a porcelain mortar, extracted in a Soxhlet apparatus using a mixture (90/10 % v/v) of petroleum ether and acetone. After solvent evaporation heptadecanoic acid was added as derivatisation control and internal standard.

Saponification of the triglycerides was performed by KOH hydrolysis in methanol by dissolving the extracted material in 10 ml of an ethanolic (90 %) 0.4 M KOH solution and heating the resulting mixture to 70 °C for 4 hours. After neutralisation the fatty and resin acids were then extracted with petroleum ether and silanized using BSTFA/TMCS before solvent change to dichloromethane and analysis by gas chromatography-mass spectrometry (GC-MS). (Örså and Holmbom 1994)

GC-MS analyses were performed using a quadrupole GC-MS instrument and a standard capillary column. Separation was accomplished by temperature programming. Recorded mass spectra were used and compared to a NIST spectra library for the identification of the fatty and resin acids in the sample. Quantitation was made using the internal standard added during sample preparation (see above).

Data evaluation

The obtained results from the GC-MS obtained in µg/ml are converted into µg compound/g pellet to be able to compare different samples. The total concentration of all fatty acids and resin acids found in the sample is used.

3.2.2 Determination of aldehydes performed by SLU

Experimental Setup

Determination of the tendency for the various pellet batches to emit aldehydes (and ketones) was determined using a laboratory set-up. In addition, emissions of aldehydes and ketones were performed in large scale experiments in industry locations.

The general experimental set-up described by Samuelsson et al. (Samuelsson et al., 2006) was used in the laboratory, with some modifications, see Figure 1.

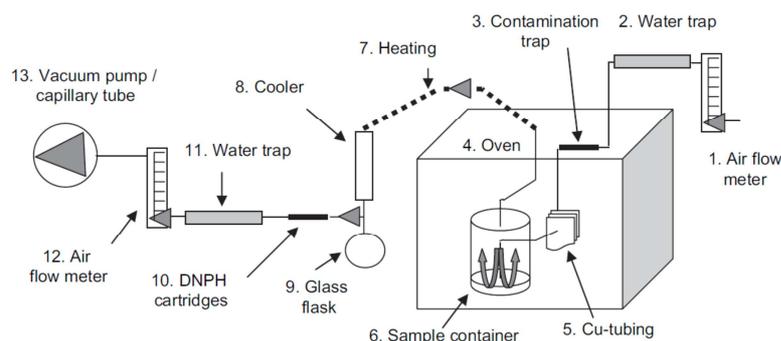


Figure 1: Scheme of the laboratory setup used for heating pellets and sampling of the emitted aldehydes and ketones

Analyses of 10 g pellet samples were performed in triplicate. Pellets were placed in sample containers maintained at 60 °C. Atmospheric (filtered) air was pumped through the system and aldehydes and ketones were sampled on 2,4-dinitrophenylhydrazine impregnated adsorbent tubes (commercially available). When adsorbed the aldehydes and ketones are directly derivatized to their corresponding stable 2,4-dinitrophenylhydrazone hydrazone derivatives. These derivatives are then extracted using dichloromethane and analysed by HPLC.

For the HPLC-analysis a reversed phase column was used and for detection a UV-detector operating at 365 nm, was used. Identification and quantification of the aldehydes were made using a set of relevant reference compounds.

Experimental procedure

For determination of aldehydes and ketones during storage in small and industrial scale the same basic sampling principle was used. For practical reasons a diffusion sampling equipment was used instead on the active sapling tubes used for the laboratory experiments. However, the methods work by the same principle i.e. reaction with 2,4-dinitrophenyl hydrazine as described above. Analysis was mad in the same way.

Data evaluation

The obtained results from the HPLC obtained in µg/ml are converted into µg compound/g pellet to be able to compare different samples. The total concentration of aldehydes measured over a period of 48h is used in the ranking.



3.2.3 Determination of CO, CO₂ and CH₄ emissions during of-gassing experiments performed by SLU (Off-gassing 1)

Experimental setup and procedure

Two sealed 19 dm³ plexi-glass containers were used as models for silo storage (see Figure 2).



Figure 2: Setup for measuring the off-gassing of CO, CO₂ and CH₄.

The containers were filled with wood pellets to 70 % of their volume capacity. In each experiment, one container was maintained at room temperature and the other container where surrounded by a heating mantel set at 60 °C. Gas emissions (CO, CO₂ and CH₄) were measured using a gas analyzer that uses a combination of electrochemical and infrared (IR) sensors. Off-gassing emissions were measured 9 times over a period of 48 hours for each sample and the time averaged emission data were calculated.

Data evaluation

The values obtained from the off-gassing experiments (concentration of gas in percent or ppm) are converted to volume gas produced over a period of 48h in the containers.

3.2.4 Determination of CO, O₂, and VOC's performed by BE2020 (Off-gassing 2)

Experimental setup and procedure

For the determination of emitted concentrations of CO, CO₂ and volatile organic compounds (VOC) the pellet samples were stored in 5-liter glass bottles (see Figure 3). Each measurement was carried out with two bottles per pellet sample and the results were calculated from mean averages of the two measurements. Approximately 2.4 kilograms of pellets were filled into the bottles, which corresponds to a filling level of between 60 to 70%. Then the glass-bottles were closed air tight. At trial start the water content was determined according to the method

presented in ÖNORM EN 14 774-2. Two samples of 100 g at minimum of each pellet type were dried at (105 ± 2) °C until constant weight.



Figure 3: Storage experiments for pellets in 5-liter glass bottles

The glass-bottles were stored for five days in dark at 22°C. For the measurement of CO and CO₂ concentrations a gas analyzer (Emerson, NGA 2000) and for the VOC concentrations a flame ionization detector (M&A, Thermo-FID PT63FH/LT) were used. At the start of the measurements the polypropylene-cap of the flask was removed and replaced by a cap similar measurement head. It was equipped with two openings for simultaneous inlet and outlet of gases in separate channels. The time for substituting the cap was kept as short as possible. The outlet of the glass bottles and the gas analyzers were connected with a silicone tube. The CO, CO₂ and VOC concentrations were measured in ppm. The sample gas in each bottle was ingested and measured for a duration of 10 minutes. The peak concentrations of the measured gases were noted down.

Data evaluation

The received values of the measurements were ppm concentrations of CO, CO₂ and VOC. The gas measurement was carried out for approximately 10 minutes. The peak concentrations were typically measured during the first two minutes and noted down. The concentration values were then converted into a rate of gas release in mg gas per kg pellets_{drybasis} per day.

3.2.5 Micro calorimetry performed by SP

Experimental setup

Screening tests have been performed with a micro calorimeter instrument. The method used is often called micro calorimetry, but the more general and describing term is isothermal calorimetry. The isothermal calorimeter is used to very accurately (mW-scale) measure the heat of reaction and by that self-heating caused by oxidation processes in the pellets.



For the experiment, an eight channel TAM Air 3116-2 isothermal calorimeter was used (see Figure 4). The instrument has a temperature range between 5 °C and 90 °C. For each channel a test ampoule of 20 mL is used. The sample is put in the ampoule, which is sealed. For each of the eight channels there is a reference. The ampoule is in contact with a heat flow sensor, which is also in contact with a heat sink. This means that when heat is produced inside the ampoule, a temperature gradient is developed across the sensor. The voltage, which thereby is generated, is then measured. The voltage signal is proportional to the heat flow across the sensor and thereby to the rate of the process taking place in the sample ampoule. This gives time-resolved results.



Figure 4: The eight channel TAM Air 3116-2 isothermal calorimeter

Experimental procedure

Each pellet batch (5 kg) was delivered to SP from DBFZ in an air tight plastic bag. The pellet batches were put in a freezer at arrival and defrosted in time for testing. The screening tests were performed on 4 g of pellets at a temperature of 60 °C. Previous work by SP has shown that this method is suitable to test the reactivity of a pellet. Minimum duplicate tests were performed on each pellet type.

Data evaluation

The results from micro calorimeter tests are derived in heat release rates in mW/g. The higher the amount of heat released from the sample is, the higher is (usually) the self-heating activity of the pellet sample.

3.2.6 Oxipres method performed by DTI

Experimental setup

The Oxipres™ (MikroLab Aarhus A/S, Denmark) measures the decline in oxygen pressure over time in a closed volume containing the sample and 5 bar 100% oxygen at elevated temperature. 50,0 g pellets is placed in the Oxipres sample container, and the air in the container is hereafter replaced with 5 bar 100% oxygen. The container is equipped with a pressure gauge and immediately placed in the Oxipres apparatus. The container is heated to a target temperature (T) and the pressure is then monitored through 8 hours. Initially, the pressure increases due to the heating of the container, but starts to decline after 1-2 hours. The time of the maximum pressure point is defined $t_{P_{max}}$, and the pressure and pressure decline is quantified in bar and mbar/min. The sample can be characterized by the pressure decline in given intervals after $t_{P_{max}}$. In the present trials, T were 40°C and 100°C, and the samples have been characterized using the pressure decline in the intervals for 40°C: [$t_{P_{max}}$, ($t_{P_{max}}+120$ min)], and for 100°C: [($t_{P_{max}}+60$ min), ($t_{P_{max}}+180$ min)].

Experimental procedure

In order to rank the “reactivity” of pellets, the Oxipres method was applied, which originally was developed for investigating oxidation and stability of fat in food. The method investigates the potential of oxygen consumption by analysing the pressure decline in closed containers with the samples exposed to pure oxygen at elevated temperature. The test is made by applying 50 g of pellets in a closed glass container (Figure 5) applying a 5 bar excess pressure of 99.9% oxygen. The container is placed in a temperature controlled heating block at 40 to 100 C, equipped with a pressure monitor (Figure 6).



Figure 5: Sample containers for the Oxipres method



Figure 6: Oxipres equipment

The pressure in the container is monitored for 6 to 12 hours and the change in the pressure curve reveals the speed of sample oxidation.

Data evaluation

In the Danish LUBA project a screening, based on a visual interpretation of the pressure curves, revealed that the method had good repeatability and was able to distinguish between pellets known as reactive and much less reactive pellets. Within SafePellets a visual qualitative evaluation of the pressure curves show the same ability to distinguish.

To be able to rank the pellets in an objective and unambiguous manner, a quantitative interpretation of the pressure curves was needed. The following interpretation approach was developed by DTI:

- Normalize all pressure measurements to $P_{max} = 1$
- For $T = 40\text{ }^{\circ}\text{C}$ read the pressure 2 hours after reaching P_{max}
- For $T = 100\text{ }^{\circ}\text{C}$ read the pressure 1 and 3 hours after reaching P_{max}
- "Reactivity" = $1000 * (\text{Pressure}_1 - \text{Pressure}_2) / 2$

In the development of the interpretation procedure, results based on different time intervals were compared with the ranking from a number of other laboratory methods applied within SafePellets WP3. The best fit between the combined ranking of other methods and the Oxipres was achieved with the above stated time intervals. It is important to notice that the best correlation between Oxipres and the other methods is obtained by applying a combined ranking based on pressure curves from both 40 and 100 °C.

4 Results – Ranking according to activity of the pellet samples

In this section, the results from each individual method are listed as normalized values. This method of data representation was chosen to allow the scientific partners in the project to publish the results of the experiment in scientific journals, without running the risk of copyright infringement. All data are normalized to the sample with the highest value and sorted from highest to lowest activity observed in the experiments. Data are presented in percentage.

4.1.1 Fatty and resin acids

Table 4-1: Normalized results from fatty and resin acid analysis

Batch number	Normalized value for fatty and resin acid content
15	100
16	83
12	55
3	46
5	43
6	33
8	29
4	21
10	17
18	16
2	16
9	15
1	12



4.1.2 Aldehydes

Table 4-2: Normalized results from determination of aldehyde emissions

Batch number	Normalized value of aldehyde emissions
12	100
9	29
16	28
15	28
6	24
5	19
10	19
18	13
2	11
1	11
8	11
3	9
4	8

4.1.3 Off-gassing part 1

Table 4-3: Normalized results from method off-gassing 1

Batch number	Normalized values of gases emitted at 23°C			Normalized values of gases emitted at 60°C			Sum of normalized values
	CO	CO ₂	CH ₄	CO	CO ₂	CH ₄	
12	100	69	100	92	59	100	520
9	41	100	43	100	100	31	415
6	22	43	16	95	95	31	301
10	12	22	7	86	80	15	223
18	22	18	6	65	62	11	184
15	9	19	8	23	40	7	106
16	10	12	5	22	37	6	92
5	6	12	3	31	29	8	89
8	2	0	2	26	28	6	64
2	3	11	2	10	16	2	45
3	4	0	1	14	14	2	35
4	2	0	1	10	15	2	29
1	2	0	1	12	12	1	28

4.1.4 Off-gassing Part 2

Table 4-4: Normalized results from method off-gassing 2

Batch number	Normalized values of emitted gases at 22°C			Sum of normalized values
	CO	CO ₂	VOC	
12	100	100	100	300
9	31	94	12	137
6	12	56	9	77
10	11	48	1	60
16	20	35	3	58
18	9	30	7	46
15	17	24	1	42
5	7	25	3	35
8	2	14	1	17
2	3	13	0	16
1	4	10	0	14

*Pellet batches 3 and 4 were not analyzed with this method

4.1.5 Micro calorimetry

Table 4-5: Normalized results from micro calorimetry experiments

Batch number	Normalized values of heat release
9	100
6	85
12	76
10	38
18	34
5	32
16	18
15	15
8	15
1	12
2	10

*Pellet batches 3 and 4 were not analyzed with this method



4.1.6 Oxipres method

Table 4-6: Normalized results from Oxipres method

Batch number	Normalized values from Oxipres method
12	100
9	74
6	51
2	45
15	43
10	41
16	41
18	38
8	37
3	35
4	33
5	31
1	29

5 Discussion

A comparison of the results from the individual methods reveals that with each method one sample could clearly be identified as the one with the highest activity according to each test method. However, some of the presented methods show a more or less evenly distributed activity amongst the samples (e.g. the analysis of fatty and resin acids), whereas other methods show one or two sample with activities much higher than the rest of the samples (e.g. the determination of emitted aldehydes, the method Off-gassing 2 or the Oxipres method).

It is possible in with most method to identify a kind of 3-part grouping amongst the samples, with one group of high activity pellets, one group with medium activity and one group of low activity pellets. For example when taking a closer look on the results from the micro calorimetry, pellet batches 9, 6 and 12 represent the high activity group, followed by 10, 18 and 5 with medium activity and the rest of the batches fall into the low activity group. Also the results from the method Off-gassing 1 can be grouped in such a way, with the samples 12, 9 and 6 in the high activity group, followed by 10 and 18 with medium activity and the rest of the tested batches in the low reactivity group. The method Off-gassing 2 has only two samples, batches 12 and 9, in the high activity group, 3 samples with medium activity, batches 10, 16 and 18, and the remaining 8 samples in the low activity group.

The fatty and resin acid content determination revealed two samples with high activity, batches 15 and 16 and three samples with medium activity, batches 12, 3 and 5. And finally, the determination of aldehydes revealed only one sample with high activity, batch 12, compared to the rest of the tested batches. A summary view of the ranking of the individual pellet batches with each individual method is given in Table 5-1. The table also includes the overall result of the ranking of the pellet batches based on all methods.

The picture that presents itself shows that, with the exception of the determination of fatty and resin acids, all tested methods give an overall similar result for the relative reactivity of the pellet samples ranked from highest to lowest. Aside from minor deviations in the individual positioning of the samples, overall, pellet batches 12, 9 and 6 were identified as the three samples with highest activity by 4 out of the 6 utilized methods. Only the determination of emitted aldehydes identified batch number 16 as more reactive than batch number 6. The reasons behind the low correlation of the results from the fatty and resin acid determination with the results from the other methods, despite the fact that literature has reported a clear tendency that wood species with higher extractive content tend to show higher off-gassing propensity, remains unclear. It can, however, be clearly stated, that there seems to be no direct correlation between fatty and resin acid content and high off-gassing or self-heating activity.

A closer look on the raw material composition of the tested pellet samples reveals that the three pellet batches with the highest activity are all batches made from mixtures of pine and spruce sawdust. In the medium activity range pellet batches made from 100% pine sawdust, as well as further batches made from mixed pine/spruce sawdust can be found, whereas all pellet batches



made from 100% spruce sawdust can be found in the low activity range of the ranking. Interestingly, the sample with the overall lowest activity is again a sample produced from 100% pine sawdust. This result is surprising, since data reported from previous literature always identified pine pellets as by far more active as spruce pellets. It was therefore expected, that pellets produced from mixtures of pine and spruce would have an activity in-between pure spruce and pure pine pellets. However, these results indicate, that there either might be some kind of “positive” interaction between the wood species to enhance the activity of the mixed pellets or that there might be other factors, apart from the mere choice in raw material, responsible for the activity of a pellet batch, which were not part of this investigation (e.g. influence of production parameters such a press condition, raw material pre-treatment etc.).

Table 5-1: Summary table of the ranking of the pellet batches with each individual method from highest to lowest active sample

Ranking	Fatty and resin acids	Aldehydes	Off-gassing 1	Off-gassing 2	Micro calorimetry	Oxipres	Overall (based on all methods)
1	15	12	12	12	9	12	12
2	16	9	9	9	6	9	9
3	12	16	6	6	12	6	6
4	3	15	10	10	10	2	16
5	5	6	18	16	18	15	15
6	6	5	15	18	5	10	10
7	8	10	16	15	16	16	18
8	4	18	5	5	15	18	5
9	10	2	8	8	8	8	3
10	18	1	2	2	1	3	8
11	2	8	3	1	2	4	2
12	9	3	4			5	4
13	1	4	1			1	1

*Pellet batches 3 and 4 were not analyzed with the methods Off-gassing 2 and micro calorimetry



6 Conclusions

Based on the results from the comparison of different methods to characterize the activity of wood pellets in terms of off-gassing and self-heating propensity it could be established, that a link between the two phenomena is very likely. The consistency of the results from the activity ranking of the individual pellet samples is too strong to be coincidental. A “classic” method to determine the self-heating characteristic of a pellet sample is micro calorimetry and the result from micro calorimetry is very well correlated to the result from the methods from off-gassing. The very same reactions responsible for the depletion of oxygen in the surrounding atmosphere of pellets and the release of off-gasses from wood pellets are most likely also a source of heat generated by the pellet batches. It is partly dependent on the fact that autoxidation reactions are exothermic reactions (i.e. generate heat). Thus, pellets with high off-gassing activity, will also be more likely to have high self-heating activity.

The results also allow concluding that fatty and resin acid determination is not a suitable tool to predict the off-gassing or self-heating activity of a sample. The reason may be the fact that degradation of fatty/resin acids occur slowly (during several weeks from pellets production time) compared to off-gassing and self-heating that are measured either later or earlier than the oxidation process completed. In another word more systematic analyses of fatty/resin acids needs to be done in order to reveal possible correlation of autoxidation of fatty/resin acids (and also the content of other reactive species) with off-gassing and self-heating.

More data is still needed to investigate why the pellet batches produced from mixtures of spruce and pine sawdust were much more reactive than the pure pine pellet samples. Further investigations should be carried out to determine, whether there exists some kind of “positive” interaction between the wood species (i.e. synergic effect of two species) to enhance the activity of the mixed pellets or whether there might be other factors, apart from the mere choice in raw material, responsible for the activity of a pellet batch (e.g. influence of production parameters such a press condition, raw material pre-treatment etc.).

In the future studies monitoring of process parameters and sampling from different productions sites may be needed to be able to see how the raw material and pellets in different stages will be changed. Then it will be possible to give practical solutions to the problem.

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