

PLEASE NOTE! THIS IS PARALLEL PUBLISHED VERSION /
SELF-ARCHIVED VERSION OF THE OF THE ORIGINAL ARTICLE

This is an electronic reprint of the original article.
This version *may* differ from the original in pagination and typographic detail.

Author(s): Alakoski, Esa; Jämsén, Miia; Agar, David; Tampio, Elina; Wihersaari, Margareta

Title: From wood pellets to wood chips, risks of degradation and emissions from the storage of woody biomass : A short review

Version: final draft

Please cite the original version:

Alakoski, E., Jämsén, M., Agar, D., Tampio, E., & Wihersaari, M. (2016). From wood pellets to wood chips, risks of degradation and emissions from the storage of woody biomass – A short review. *Renewable and Sustainable Energy Reviews*, 54, 376-383.

DOI: 10.1016/j.rser.2015.10.021

URL: <https://doi.org/10.1016/j.rser.2015.10.021>

HUOM! TÄMÄ ON RINNAKKAISTALLENNE

Rinnakkaistallennettu versio *voi* erota alkuperäisestä julkaistusta sivunumeroiltaan ja ilmeeltään.

Tekijä(t): Alakoski, Esa; Jämsén, Miia; Agar, David; Tampio, Elina; Wihersaari, Margareta

Otsikko: From wood pellets to wood chips, risks of degradation and emissions from the storage of woody biomass : A short review

Versio: final draft

Käytä viittauksessa alkuperäistä lähdettä:

Alakoski, E., Jämsén, M., Agar, D., Tampio, E., & Wihersaari, M. (2016). From wood pellets to wood chips, risks of degradation and emissions from the storage of woody biomass – A short review. *Renewable and Sustainable Energy Reviews*, 54, 376-383.

DOI: 10.1016/j.rser.2015.10.021

URL: <https://doi.org/10.1016/j.rser.2015.10.021>

From wood pellets to wood chips - risks of degradation and emissions from the storage of woody biomass – a short review

Esa Alakoski^{*,a,b}, Miia Jämsén^{a,b}, David Agar^c, Elina Tampio^b, Margareta Wihersaari^{d,b}

^a JAMK University of Applied Sciences, Institute of Bioeconomy, Tuumalantie 17, FI-43130 Saarijärvi, Finland.

^b Department of Biological and Environmental Science, P.O.Box 35, 40014 University of Jyväskylä, Finland.

^c Department of Chemistry, P.O.Box 35, 40014 University of Jyväskylä, Finland.

^d Åbo Akademi University, Strandgatan 2, FI-65100 Vaasa, Finland.

***Corresponding author**

Esa Alakoski

Tel: +358 50 360 1968

Fax: +358 14 260 2321

Email: esa.alakoski@jamk.fi

Short title

Risks from emissions of wood chips vs. pellets

Abstract

The compounds in stored woody biomass degrade as a result of chemical and/or biological processes during storage. These processes produce gaseous emissions. Recent studies concerning gaseous emissions from wood pellet storages are reviewed herein. The applicability of the results from pellet research to wood chips is discussed. Thorough scientific understanding on the storage phenomena of wood chips is extremely important as the threat of climate change and the need to reduce greenhouse gas emissions have led to an increased need to large scale wood chip storage to ensure supply. Typically the gases produced from stored woody biomasses are carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), and other volatile hydrocarbons e.g. aldehydes and terpenes. CO₂ and CH₄ are greenhouse gases with high global warming potential. Chemical degradation via auto-oxidation of fats and fatty-acids seems to be the dominant mechanism for off-gassing from stored wood pellets, whereas biological processes are mainly responsible for the gaseous emission from wood chips. In confined storage spaces gaseous emissions may lead to oxygen depletion. Oxygen depletion together with a high CO concentration poses a serious health risk for those working in such conditions. The degradation processes also result in dry matter losses and in spontaneous heating and in the worst case, especially in large piles, spontaneous ignition of the stored material. Thorough and systematic scientific studies on degradation processes and their effects are needed in order to understand and minimise risks from large scale wood chips storage to human health, environment and property.

Keywords emissions, degradation, risks, biomass storage, wood pellets, wood chips

1 Introduction

The threat of climate change and the need to reduce greenhouse gas emissions have led to an increase in the demand and use of biomass in energy generation. In order to ensure supply, this means increasing in the amounts of biomass in storage for extended time periods. In areas with high heating demand during winter time e.g. in the northern coniferous forest belt this typically means woody biomass such as stem wood, wood chips and wood pellets.

Gaseous emissions are produced during storage of woody biomass [1-3]. The gases produced are typically greenhouse gases and present serious risks for people entering enclosed storages.

Chemical and biological degradation processes are responsible for these emissions. The processes leading to gaseous emissions also produce dry matter losses, deterioration of mechanical properties and spontaneous heating in the stored material [4-6]. These processes and their effects need to be thoroughly understood in order to minimise the risks produced.

During the last fifteen years wood pellet production, storage and use has seen a rapid increase. Some serious accidents with fatalities have also happened in pellet storages [7,8]. Preventing such accidents from happening has been the main motivation of several studies on gaseous emissions (off-gassing) from wood pellets [1,2,9]. On the other hand, similar studies on gaseous emission from stored wood chips are almost non-existent. Fears of fire hazards from spontaneous

heating in the stored material and of dry matter losses are currently the main factors limiting the storage of wood chips in large piles. Herein it is postulated that as both pellets and chips are produced from woody biomass the phenomenology during storage of both is similar and therefore significant insight to wood chip storage phenomena can be gained by considering pellet studies. This paper reviews pellet off-gassing studies and tries to reflect on the similarities in wood pellet and wood chip degradation phenomena. The purpose of this work is to provide a foundation for further research on the degradation processes on-going in wood chip storages. The ultimate goal of such experimental research is the development of new and safe methods to store wood chips in large piles for extended time periods.

2 Wood pellet storage

2.1 Storage halls and silos

Pellets are stored in halls and silos so that a year-round supply of fuel for consumers can be secured. Wood pellets are stored indoors in dry conditions as they absorb moisture rapidly. After production, pellets are stored at production facilities before transporting to customers for storage and use. Large-scale users, such as municipal heating companies and housing co-operatives, usually store their pellets in large silos. Small-scale users store pellets in their domestic storage rooms or smaller silos.

Storage time typically varies along with heating demand. In summer, when the heating demand is low, pellets are stored for longer times at production facilities and intermediate storages [10]. Longer storage times and the fact that the amount of gaseous emissions tends to be enhanced immediately after pellet production mean that the bulk of storage emission is produced in these locations. During winter the heavy heating demand leads to shorter storage times at production facilities and intermediate storages and increased emissions at user facilities [1]. One important growing industry with increasing interest in cheap and renewable energy heating systems in winter time is year around greenhouse farming [11].

Degradation processes induce heating in pellet piles during storage and produce gaseous emissions [2,3,9,12,13]. These processes may lead to reduction of pellet quality and dry-matter losses. At least two fatal accidents have occurred in pellet storages in Finland in recent years. In both cases a storage silo employee died from carbon monoxide poisoning [7]. In addition spontaneous heating resulting from degradation processes take place in pellet silos and this combined with the presence of wood dust can be a fire hazard [14,15].

2.2 Storage during transportation

Typically trucks are used for shorter distance and trains for longer distance land transportation of pellets [16]. Transportation distances e.g. in British Columbia, Canada are up to 150 km by truck from a pellet mill to a railhead and nearly 800 km by railway to port for overseas shipping [17]. Since 1997 pellets have been transported from Canada to Europe by using marine vessels. The

longest transportation distances are from the west coast of Canada via the Panama Canal and across the Atlantic Ocean to Sweden. The journey takes about seven to nine weeks. More than one third of the energy consumption of the pellet production and transportation process is caused by intercontinental transportation with marine vessels [17]. A rising new pellet market in the Far East is supplied from Canada via the Pacific Ocean. Shorter transportation distances lasting from 24 hours and upwards are used e.g. in the Baltic [8]. Typically long distance freighters have up to ten cargo holds per vessel and each of them can hold approximately 3000 tonnes of wood pellets. The cargo hatches are kept closed during sea voyages [18].

Off-gassing from pellets during transportation poses a serious occupational health hazard. The risks are high especially for people working with marine shipments as storage for extended periods in enclosed holds leads to accumulation of gases emitted from pellets. Typically accidents happen in ports during unloading of pellet shipments due to harmful gases that have leaked from cargo holds to adjacent access spaces [8,18]. For example, during a recent two-year period five fatalities and several injuries occurred in Swedish ports [8].

There are a few simple safety precautions for employee safety during pellet transportation and unloading. The degradation processes ongoing in the cargo consume oxygen. This leads to lowered oxygen levels in the cargo holds. Low oxygen concentration reduces the risk of fires in the cargo holds. Thus air conditioning is not recommended during sea transportation. However, access to cargo holds must be strictly forbidden during marine voyages. Cargo holds need to be ventilated well in harbours before employees enter passages and corridors, which is already

common practice in most harbours. Furthermore, marine vessels should be equipped with carbon monoxide and oxygen level analysers so that safe working conditions can be guaranteed [18].

3 Gases typically emitted from pellet storages, their effects and risks

3.1 Experimental methodology used in woody biomass storage studies

Typical experimental methodology for studying gaseous emissions from stored biomass is reviewed in depth in a recently submitted paper [19]. The paper focuses on methods suitable for field studies. Field studies are of importance, as some phenomena such as self-ignition of large piles are extremely difficult to simulate in a laboratory. In general pellet emission studies can be conducted either in the field or in the laboratory. The scales of experimental set-ups vary greatly, e.g. the University of British Columbia (UBC) uses a large research reactor (LRR) to conduct their pellet off-gassing studies [14]. The volume of LRR is 3 m³ and it is equipped with several hundred temperature sensors, humidity sensors and sampling ports for gas as well as for extraction of materials. Smaller airtight containers of 45 dm³ and 2 dm³ volume were used in a study by Kuang et al. [20]. In comparison, pellet piles of some 12 tonnes were studied in a field experiment at a large-scale pellet production plant [2]. The concentrations of emitted gases are typically analysed with gas chromatographic methods [2,9,20,21] or with Fourier Transform Infrared Spectroscopy (FTIR) [1,18]. However, there is apparent lack of scientific field studies on large scale wood chips piles. Therefore systematic and comparable measurement methodology will need to be developed for such studies in order to account for the larger scale of the storage in outdoor conditions. Important considerations for such studies are finding

representative gas sampling sites and procedures for collecting gas samples. As off-gassing may have temporal variation capability for on-line measurements is a must.

3.2 Gases emitted from wood pellet storage and their risks

3.2.1 Carbon monoxide (CO)

Carbon monoxide is colourless and odourless gas that is formed from incomplete combustion processes and also from sluggish decomposition of organic material [22].

It is an indirect greenhouse gas (GHG) with an atmospheric lifetime ranging from a few weeks to few months [23]. The GHG effects of CO are based on its reactions with atmospheric oxidants.

CO affects atmospheric GHG concentrations mainly in the following ways:

1. Carbon monoxide reactions and reaction chains produce CO₂ and ozone (O₃) [23].
2. The main reaction partner of CO in the lower atmosphere is hydroxyl radical (OH). OH radical is also responsible for the removal of CH₄. Increased amounts of CO leave less OH radicals available for reactions with CH₄ and are thought to lead to increased concentrations of CH₄ [24].

The health risks of carbon monoxide are well known. Carbon monoxide replaces oxygen from blood circulation by adhering to hemoglobin and forming carboxihemoglobin (COHb). Carbon monoxide adheres to hemoglobin over 200 times faster than oxygen [25]. This process

drastically reduces the oxygen supply of vital organs, e.g. the brain and heart. High carbon monoxide concentrations in blood induce damage to the central nervous system [26-28]. Death will follow when carbon monoxide concentration exceeds 5800 mg m^{-3} [27]. In Finland the ministry of social affairs and health defines the concentrations of impurities in workplace air known to be hazardous to men; the so-called occupational exposure limits (OEL). The OEL of carbon monoxide is set to 35 mg m^{-3} and 87 mg/m^3 for exposure periods of eight hours and 15 minutes, respectively [29]. For comparison, according to Svedberg et al. the measured carbon monoxide concentrations from pellet storages ranged from 1700 mgm^{-3} to 17000 mg m^{-3} [1].

3.2.2 Carbon dioxide (CO₂)

Carbon dioxide (CO₂) is colourless and odourless gas that is formed e.g. in thermal oxidation, aerobic biodegradation or anaerobic biodegradation of organic material. For example, cellular respiration produces CO₂ and water by consuming carbohydrates and oxygen [21]. CO₂ has a vital role for the cycle of life. It is the gas plants use for energy production in photosynthesis.

CO₂ is a significant greenhouse gas, with a long atmospheric lifetime, of approximately 100-200 years. No specific lifetime for carbon dioxide can be determined because it is continuously cycled between the atmosphere, oceans and land biosphere and its net removal from the atmosphere involves a range of processes with different time scales [23].

Term radiative forcing (RF) describes the ability of a gas to absorb infrared radiation from the Earth's crust. Increased amounts of gases with positive radiative forcing are considered as perturbation of Earth's atmospheric system that warms up the atmosphere. Radiative forcing is a cumulative measure of a gases ability to warm Earth's atmosphere. CO₂ has the most significant positive RF of the greenhouse gases [24]. A similar measure on a molecular level is the global warming potential (GWP). GWP is defined as the ability of a mass of gas to warm the Earth's atmosphere compared to similar mass of CO₂. GWP takes into account the atmospheric lifetime of a gas and it is typically calculated for 20, 100 and 500 year time-scales. The GWPs of gases with shorter life-times than CO₂ decrease as longer time-scales are considered. E.g. the GWP of Methane (CH₄) is 72 in 20 year time-scale and in 100 and 500 year scales 25 and 7.6 respectively. The atmospheric life-time on CH₄ is 12 years. The atmospheric life-times, RF values and GWPs of the most significant direct greenhouse gases CO₂, CH₄ and N₂O, emitted from storage and waste piles containing material of biological origin are summarised in Table 1.

{Table 1 here}

The current scientific consensus is that CO₂ concentration of the atmosphere has raised 180 mg m⁻³ within the last 250 years mainly due to human action. In 2010 the atmospheric CO₂ concentration was measured to be 580 mg m⁻³ [18,20,24].

CO₂ prevents oxygen from adhering to red blood cells and thus oxygen transportation to the brain and other parts of the body [20]. CO₂ concentration in air of approximately 5500 mg m⁻³

induces headache and breathing acceleration and more serious symptoms in higher concentrations of about $27\,000\text{ mg m}^{-3}$. The OEL of CO_2 is 9100 mg m^{-3} for eight-hour exposure [25,29]. The CO_2 concentrations in pellet storages can range between 1200 to 9300 mg m^{-3} [9]. CO_2 can also lead to suffocation in enclosed spaces due to oxygen deficiency [20,25]. Without proper ventilation CO_2 together with CO can cause serious accidents in pellet storages [1,9,14].

3.2.3 Methane (CH_4)

Methane (CH_4) is a simple hydrocarbon existing as an odourless gas at room temperature. CH_4 is released in anaerobic decomposition for instance in composts [30], landfills [31] and certain fertiliser induced soil types [32,33]. The largest natural sources of atmospheric methane are northern peat lands [34].

CH_4 differs from other volatile organic compounds because of its strong greenhouse gas potential [35]. It has a strong positive radiative forcing and it is, as mentioned earlier, on a per molecule basis significantly stronger greenhouse gas than CO_2 . Methane acts as a greenhouse gas, similarly as carbon dioxide, by absorbing infrared radiation emitted from the surface of the earth. Increased amounts of CH_4 in the atmosphere thus lead to warming of the atmosphere [24]. According to measurements made from air bubbles trapped in polar ice, the atmospheric CH_4 concentration has more than doubled since pre-industrial times [36].

In laboratory measurements from pellets stored in sealed vessels the CH₄ concentration was detected to vary between 6.7-110 mg m⁻³ at room temperature depending on the pellet quality [20]. CH₄ concentrations can increase over tenfold at a temperature of 40 °C. According to Svedberg et al. [18], CH₄ concentrations measured during ocean transportations of pellets ranged between 50-640 mg m⁻³. In very high concentrations methane can replace oxygen, and thus create hazards for storage employees [37]. There are no OEL values defined for CH₄.

3.2.4 Nitrous oxide (N₂O)

Nitrous oxide (N₂O) emissions are known to occur for example during composting of household wastes and storage of manure. The emitted N₂O is found to be the product of incomplete ammonium oxidation in aerobic conditions or the end product of incomplete denitrification in anaerobic conditions [38]. As can be seen from Table 1 N₂O is a greenhouse gas with a significant positive radiative forcing. At the molecular level N₂O is a still stronger greenhouse gas than CO₂ or CH₄ [24].

The OEL for N₂O in Finland is 180 mg m⁻³ for eight-hour exposure [29]. As the elemental nitrogen content of wood pellets is somewhat low, typically below 0.5% [39], the off-gassing of N₂O is probably not a serious employee safety issue.

Studies on N₂O emissions from stored pellets are not found in literature. However, because of its high GWP, the effect of changes in ambient conditions on the production of N₂O should be studied in detail when assessments on the environmental effects of pellet production are made.

3.2.5 Other volatile organic compounds

Volatile organic compounds, excluding CH₄, are called Non-Methanous Volatile Organic Compounds (NMVOC). NMVOCs are volatile hydrocarbons with maximum boiling point at 260 °C. This property also limits the size of these compounds to a maximum of 12 carbon atoms [40]. According to IPCC report NMVOCs are categorised as short-lived greenhouse gases, with positive radiative forcing [24]. NMVOCs have similar effects on the distributions and concentrations of CO₂, CH₄ and ozone as carbon monoxide. The GWPs of NMVOCs range from 0.5 to 5.5 in the 100 year scale [24].

Aldehydes, hexanal and pentanal are the most abundant NMVOCs emitted from pellet storages. Typically hexanal accounts for 80% of aldehydes emitted. The highest hexanal concentrations are measured from the top of the storage piles. Ahonen & Liukkonen measured a maximum hexanal peak value 200 mg m⁻³ from the top part of a pellet silo [9]. The OEL for hexanal for 15 minutes of exposure is 42 mg m⁻³ [29].

Monoterpenes are the dominant volatile organic compound emitted from fresh spruce and pine wood. However, according to measurements the concentration of monoterpenes in pellet storages

is low. The evident conclusion is that the greater part of the monoterpenes is emitted during the production of sawdust in sawmills and the following storage, grinding and drying processes, before pressing of the pellets [1,10]. The OEL limit value for turpentine (a mixture of terpenes) for eight-hour exposure is 140 mg m^{-3} [29].

NMVOCs can produce harmful odours [41] and induce, e.g. asthma-like respiratory tract symptoms [42]. Hexanal and other aldehydes can induce skin and mucous irritation, which are typical symptoms described by pellet storage employees [1].

4 Results from pellet off-gassing studies

The motivation behind this section is to compile existing quantitative and qualitative information on gases emitted from pellet storages. Also consideration is given to ambient conditions and other factors affecting off-gassing from storages. The results from pellet studies serve as a starting point on gases and factors that need to be considered when planning and conducting storage studies on wood chips. The ultimate goal of such studies is finding new ways of storing wood chips with reduced risks on human health, the environment and property.

4.1 Gas concentrations in pellet storages

The off-gassing of stored pellets has been studied from different types of pellet storages, at production sites, during transportation of pellets and at end-user storages. Also controlled laboratory studies have been conducted. The CO, CO₂, CH₄, cumulative aldehyde and terpene concentrations detected and typical conditions of different types of pellet storage off-gassing studies are compared in Table 2. The occupational exposure limits according to the Finnish ministry of social affairs and health are shown for comparison.

{Table 2 here}

In confined spaces the CO concentrations are typically several orders of magnitude higher than the occupational exposure limits. This applies to all types of storage facilities for wood pellets; at production sites, during transportation and at end-user facilities. Also CO₂ and aldehyde concentration often exceed the OEL. For aldehydes the OEL for hexanal is used; there is no cumulative OEL defined for aldehydes. Terpene levels at pellet storages are typically well below the OEL of turpentine.

In confined spaces without ventilation near complete oxygen depletion will occur. E.g. the lowest oxygen level measured during intercontinental marine transportations of pellets was 0.8% [18]. Results from laboratory experiments conducted in sealed containers give similar results [20]. Most of the oxygen is thought to be chemically bound in the oxidative degradation process of fatty acids and in other organic compounds present in the wood [12,8,20]. CO and CO₂

emissions and oxygen depletion are observed also during transportation of wood chips and logs [43].

4.2 Types of gases emitted from pellet storages and their safety data

A large variety of NMVOCs have been detected from different types of pellet storages. NMVOCs emitted from pellet storages can be e.g. alkanes, alkenes saturated, unsaturated and aromatic aldehydes, ketones, terpenes, alcohols and organic acids [1,9,18]. The compounds detected from pellet storages, their CAS numbers, and chemical classifications are given in Table 3.

{Table 3 here}

The concentrations of the compounds shown in table 3 vary several orders of magnitude depending e.g. on the compound, storage type and measurement location in the storage [1,9,18]. For simplicity the concentrations are omitted. According to their chemical safety data sheets, many of these compounds are classified as highly flammable and may thus play a role in the self ignition phenomenon. A systematic study is needed to clarify the role of gases in self ignition of stored material of biological origin. However, the large amount of different compounds detected illustrates the complexity of off-gassing from storage and the challenge of such studies. For comparison, according to a qualitative study by He et al.[44] the major chemical compounds

emitted from stored forest residues were alcohols, terpenes, aldehydes, acids, acetone, benzene, ethers and esters. No further details of the compounds emitted are given.

4.3 Factors affecting gaseous emissions from pellet storages

Several experimental observations have been made on off-gassing from stored pellets:

1. Storage temperature is a key factor affecting the gaseous emissions from wood pellets. An increase in ambient temperature and the temperature inside the storage piles enhances gaseous emissions, and has an effect on the relative amounts of the emitted gases. For example Kuang et al observed in a laboratory study conducted in temperatures ranging from 10°C to 45°C that the relative amount of CH₄ emitted compared to CO₂ increases as a function of increased temperature [20]. They also noted that CO₂ emissions are more sensitive to changes in temperature than CO emissions and this difference is more pronounced at higher temperatures.
2. Off-gassing from pellet storages seem to be a result predominantly of chemical processes. The monotonous increase of gas production Kuang et al observed as a function of increased temperature is an indication of this [20]. If microbial action would be responsible gas production there would be an increase to a certain level and then a decline as bacteria and fungi perish [45].
3. Auto-oxidative degradation of fats and fatty acids is postulated to be the principal process responsible for CO emissions from pellets [1,20]. Lower fatty acid content in the raw material leads to lower aldehyde and ketone emissions, e.g. these emissions are

significantly lower from spruce pellets than from pine pellets, as spruce typically contains less fatty acids than pine [46].

4. According to measurements by Svedberg et al. CO concentrations measured from wood chip and timber transportation are significantly lower than those measured from pellet transportation [43]. This is evidence of microbial action as microbial decomposition favours the production of CO₂ over CO. The results from microbial activity measurements in colony-forming units per gram of material confirm this. The bacterial and fungal activities in samples of dry or wet wood pellets were <13 cfu g⁻¹ and <13 cfu g⁻¹, respectively and in comparison in freshly produced wood chips 9.4x10⁵ cfu g⁻¹ and 7.1x10⁵ cfu g⁻¹, respectively [43]. The reason behind this drastically lower microbial activity in pellets is evidently the dehydration at high temperatures. High temperature and low humidity are environmental conditions that do not favour microbial activity [43,47].
5. An increase in ambient relative humidity increases emissions [20].
6. The availability of oxygen increases peak off-gas emissions [20].
7. Predominant VOCs emitted from freshly produced sawdust (the typical raw material used for pellet production) are terpenes. Most of the terpenes are emitted in the first few weeks of storage, and simultaneously hexanal production from sawdust starts to increase [10].
8. In pellets made from fresh sawdust Hexanal off-gassing peaks a few weeks after pellet production and starts to gradually diminish to low levels after a few months in storage [10, 48]. When aged sawdust is used as a raw material Hexanal production remains high up to half a year [48].

9. The physical handling of pellets e.g. repeated loading and unloading of pellets increases instantaneous emissions [8,18].

Considering the experimental results listed above important factors affecting also gaseous emissions from wood chips piles will in all likelihood be: raw material, storage time, ambient temperature and humidity, temperature inside the pile, availability of oxygen, microbial activity and physical handling of the pile. Systematic scientific studies on the effects of these factors on the gases emitted and their absolute and relative amounts from wood chip storage piles are needed.

5 Discussion

5.1 Storage of wood pellets compared to wood chips

There are several risks involved in the storage of materials of biological origin. Chemical and biological degradation in stored biomass leads to emission of volatile gases that introduce serious health risks for employees. The risks are especially high when biomass is stored in confined spaces. Storage in enclosed spaces leads to accumulation of emitted gases and oxygen depletion. The degradation processes may also lead to dry matter losses and spontaneous heating in the storage piles. The worst case scenario is self-ignition of the storage pile. When woody biomass is stored, the presence of wood dust constitutes an additional health risk and increases the risk of fires. In wood pellet storages there is also the added risk of catastrophic dust explosions as wood

pellets are hydrophilic and need to be stored in dry ambient conditions. However the pre-treatment stages during pellet production, especially dehydration at high temperature reduce the bacterial activity in pellets. This in turn reduces the risk of spontaneous heating and storage losses compared to wood chips. According to the studies reviewed here the main pathway to gaseous emissions and storage losses in pellets is a chemical process via auto-oxidation of fats and fatty acids whereas biological processes seem to play a more significant role in gaseous emissions from wood chips.

5.2 Factors and risks affecting large scale storage of wood chips

The material losses and the risk of fires due to spontaneous heating are significant with large-scale wood chip storage. There are several complicating factors affecting wood chip storages. Wood chips undergo no pre-treatments prior to chipping, except the natural drying of the raw material in outdoor conditions. Wood chips have a large surface area which facilitates microbial colonisation [47]. Forest residues and bark typically used as a raw material for chips contain high concentrations of minerals and inorganic elements that may enhance microbial activity. Storage outdoors in varying weather conditions may induce moisture and temperature gradients that probably affect the diffusion of oxygen and other gases in the pile. Storage outdoors also increases the risk of microbial colonisation from atmospheric deposition by rain, transportation by wind or immigration e.g. from the ground below the pile [47]. Considering the aforementioned factors it is evident that microbial activity plays a major role in degradation processes happening in a wood chip pile. Of course as chemical reactivity increases with increasing temperatures it is highly likely that chemical processes are enhanced as the

temperature inside the storage pile increases. The key inputs, factors and the risks produced during long term large-scale wood chip storage are summarised in Figure 1.

{Figure 1 here}

5.3 Risks from storage of wood chips to property

Degradation of material leads to storage losses but the worst case scenario for an owner of wood chips storage is spontaneous ignition of a storage pile. The fears of spontaneous fires are currently limiting the storage of wood chips in large piles. Fires of large piles are extremely costly as it is difficult to find their origin inside the pile and they are very difficult to put out. It can take several days or even weeks to get such a fire under control [49,50].

5.3.1 The effect of the pile size in spontaneous heating of storage piles

Due to their lower energy density and their use as a fuel in larger heating plants, wood chips need to be stored in much larger piles than pellets. Heat accumulation in a storage pile is proportional to the heat capacity of the pile which in turn is proportional to the pile radius (volume) to the third power [6]. On the other hand heat removal is proportional to second power of pile radius (surface area) [6]. This means that increasing the pile radius threefold e.g. from two to six metres increases the heat removal threefold while heat accumulation increases nine

fold. Thus, it is evident that the presence of a heat source, such as bacterial activity, will lead to accumulation of heat in sufficiently large material piles containing at least some biodegradables.

5.3.2 Factors affecting spontaneous ignition of large wood chips piles

There is good consensus among researchers that fermentation plays a significant role in spontaneous heating of large wood chips piles. However, heat accumulation and temperature development may at the beginning be very slow. It may in some cases take several months of storage time for the conditions inside the pile to become such that there is real risk of spontaneous ignition. This probably is the reason for cases of spontaneous ignition during winter in cold ambient conditions [49,50]. Although spontaneous heating due to bacterial action seems to be a precondition necessary for spontaneous ignition of wood chip piles, the actual mechanism of ignition is unknown. It probably is a complex physicochemical process and may involve some gases produced from the chemical and biological processes happening in the storage pile. It is a very difficult task to model spontaneous ignition process of large wood chip piles in laboratory-scale as two independent processes, chemical and biological are involved [6]. Moreover only large-scale wood chip piles are affected. No experimental field studies focusing on the ignition mechanism of a large-scale wood chip storage pile can be found in the literature. However, it is safe to conclude that eliminating microbial action inside the pile would also eliminate the risk of fires due to spontaneous ignition.

5.4 Health risks from storage of woody biomass

Gaseous compounds released from stored pellets pose a serious health risk for people working in pellet storages. CO and CO₂, and also CH₄ in high concentrations together with oxygen depletion can cause serious accidents. Volatile organic compounds released from stored pellets can produce harmful odour and induce asthma-like respiratory tract symptoms. Although the off-gassing mechanism may be different similar health risks arise from gases emitted from stored wood chips. As wood chips are typically stored outdoors oxygen depletion and high CO concentrations are probably serious risks in smaller scale storage of wood chips or storage during marine transportation in confined spaces. However, stored wood chips may contain significant concentrations of pathogenic micro-organisms [47]. It is important that this is taken into account when large-scale wood chips storage is planned.

5.5 Environmental risks from storage of woody biomass

The focus of pellet storage gas emission studies has been on CO, CO₂, CH₄ and NMVOC s, their effects on human health and related employee safety issues. Magelli et al. published a study on the environmental impact of greenhouse gas emissions from pellet production and transportation [17]. Their life-cycle emission assessment fails to include GHG emissions from storage. The most significant greenhouse gasses emitted from pellet storages are CO₂ and CH₄. No studies on N₂O emissions from pellet storages were found from literature. Of course compared to GHG emissions produced from transporting pellets from e.g. Canada to Europe the emissions from storage are bound to be insignificant as the fuel consumed in production and transportation corresponds up to 40% of energy content of the pellets being transported [17]. However, a simple way to make a clear reduction in the life-cycle emissions of pellets would be to use them

near the production sites. In such case reduced emissions from pellet transportation would increase the relative significance of GHG emissions from storage. This is especially so as some storage conditions may favour the production of CH₄ and N₂O, compounds with high GWPs. With long-duration storage of wood chips the emissions from storage are more important as wood chips cannot be transported in an economically viable way over long distances.

6 Conclusions

Due to the threat of climate change and with increasing oil prices there is need for increasing the use of biomasses for energy. With increasing use of biomasses for energy there comes also the increasing need for storage of woody fuels especially wood chips. However, there are apparent risks involved in large-scale storage of wood chips. These include; the risks of fires, due to spontaneous warming and ignition; risk of the reduction of fuel quality and dry matter losses; human health risks arising from gaseous emission produces and the presence of pathogenic microbes and environmental risks from the emissions of greenhouse gases. These risks arise from complex biological and physicochemical degradation processes ongoing in large wood chip storage piles. Currently there is an apparent lack of scientific understanding on factors affecting these processes. More research and a thorough understanding of these processes are needed for the development of new and safe storage procedures for large scale storage of wood chips.

Acknowledgements

The writing of this manuscript was supported in part by the BIOCLUS (FP7/Regions of

Knowledge/245438) -project, Fortum Foundation and The Foundation for Research of Natural Resources in Finland.

References

- [1] Svedberg URA, Högberg H-E, Högberg J, Galle, B. Emission of hexanal and carbon monoxide from storage of wood pellets, a potential occupational and domestic health hazard. *Ann Occup Hyg* 2004;48:339-349.
- [2] Arshadi M, Geladi P, Gref R, Fjällström P. Emission of volatile aldehydes and ketones from wood pellets under controlled conditions. *Ann Occup Hyg* 2009;53:97-805.
- [3] Lehtikangas P.. Storage effects on pelletised sawdust, logging residues and bark. *Biomass Bioenerg* 2000;19:287-293.
- [4] Bedane AH, Afzal MT, Sokhansanj S, Simulation of temperature and moisture changes during storage of woody biomass owing to weather variability, *Biomass Bioenerg* 2011;35:3147-51.
- [5] Ergül E, Ayrilmis N. Effect of outdoor storage conditions of wood chip pile on the technological properties of wood-based panel, *Biomass Bioenerg* 2014;61:66-72.
- [6] Li X-R, Koseki H, Momota M. Evaluation of danger from fermentation-induced spontaneous ignition of wood chips. *J Hazard Mater* 2006;A135:15-20.
- [7] YLE 29.7.2010. Pellettikuoleman selvittäminen päättyy. In Finnish. Finnish Broadcasting Company. Available from: http://yle.fi/alueet/pohjanmaa/2010/07/pellettikuoleman_selvittaminen_paattyy_1864939.html. Accessed in 22.2.2013.
- [8] Melin, S., Svedberg, U. & Samuelsson, J. 2008. Emissions from wood pellets during ocean transportation (EWDOT) – Research report. Available from: <http://www.pellet.org/linked/2008-01-16%20ewdot%20research%20report.pdf>. Accessed in 29.11.2012.
- [9] Ahonen I, Liukkonen, T. Pelettivarastojen ilman epäpuhtaudet ja niiden aiheuttamien vaarojen ehkäiseminen. In Finnish. Abstract in English. Air impurities of pellet storage and preventive measures for reducing health effects. Finnish Institute of Occupational Health: Work Environmental Research Report Series 2008;32:1-24.
- [10] Granström KM. Emissions of hexanal and terpenes during storage of solid wood fuels.– *Forest Prod J* 2010;60(1):27-32.
- [11] M. Esen, T. Yuksel, Experimental evaluation of using various renewable energy sources for heating a greenhouse, *Energy and Buildings* 2013;65:340-351.

- [12] Pa A, Bi XT. Modeling of off-gas emissions from wood pellets during marine transportation. *Ann Occup Hyg* 2010;54:833-841.
- [13] Guo W, Trischuk K, Bi X, Lim J, Sokhansanj S, Measurements of wood pellets self-heating kinetic parameters using isothermal calorimetry, *Biomass Bioenerg* 2014;63:1-9.
- [14] Melin, S. 2010. Review of off-gassing from wood pellets – a Canadian perspective. –Wood Pellet Association of Canada. Available from: <http://www.pellet.org/linked/2010-02-26%20review%20of%20off-gassing%20from%20wood%20pellets.pdf>. Accessed in 6.6.2012.
- [15] Holmstedt G. Självantändning vid lagring av bibränsle och biogent avfall. Slutrapport. Lunds universitet. In Swedish. Abstract in English. Project Final Report: Spontaneous ignition in stored biofuel and biological waste. University of Lund, Sweden.2005.
- [16] Laitila J, Leinonen A, Flyktman M, Virkkunen M, Asikainen A. Metsähakkeen hankinta- ja toimituslogistiikan haasteet ja kehittämistarpeet. In Finnish. VTT Tiedotteita – Research Notes 2564. VTT. Espoo, 2010.
- [17] Magelli F, Boucher K, Bi H, Melin S, Bonoli A. An environmental assessment of exported wood pellets from Canada to Europe *Biomass Bioenerg* 2009;33:434-441.
- [18] Svedberg, U., Samuelsson, J. & Melin, S. Hazardous off-gassing of carbon monoxide and oxygen depletion during ocean transportation of wood pellets. *Ann Occup Hyg* 2008;52:259-266.
- [19] Jämsén M, Agar D, Tampio E, Wihersaari M, Alakoski E. Measurement methodology for greenhouse gas emissions from storage of wood chips, submitted to *Biomass Bioenerg* 2012.
- [20] Kuang X, Shankar TJ, Bi XT, Sokhansanj S, Lim CJ, Melin S.. Characterization and kinetics study of off-gas emissions from stored wood pellets. *Ann Occup Hyg* 2008;52:675-683.
- [21] He X, Lau AK, Sokhansanj S, Lim C J, Bi XT, Melin S. Dry matter losses in combination with gaseous emissions during the storage of forest residues. *Fuel* 2012;95:662-4.
- [22] Curci MJ. Procurement, process and storage techniques for controlling off-gassing and pellet temperatures. Indeck Energy Biofuel Center. Available at http://pelletheat.org/wp-content/uploads/2010/08/Off_gassing_study_Curci_2010.pdf. Accessed in 4.6.2012.
- [23] Novelli PC, Masarie KA, Lang PM. Distributions and recent changes of carbon monoxide in the lower troposphere, *J Geophys Res* 1998;103:19015-19033.
- [24]: IPCC Fourth Assessment Report – Climate Change 2007. Intergovernmental Panel on Climate Change. IPCC 2007. Available from:

http://www.ipcc.ch/publications_and_data/publications_and_data_reports.htm, Accessed in 14.1.2012.

[25] OVA-ohjeet. Onnettomuuden vaaraa aiheuttavat aineet -turvallisuusohjeet. In Finnish. OVA 2011. Available from: <http://www.ttl.fi/ova/>, Accessed in 22.2.2013.

[26] Cho CH, Chiu NC, Ho CS, Peng CC. Carbon monoxide poisoning on children. *Pediatr Neonatol* 2008;49:121-5.

[27] Davis ML, Cornwell DA. 1998. Introduction to environmental engineering. 3rd ed.. WCB/McGraw-Hill. 1998.

[28] Raub JA. Health effects of exposure to ambient carbon monoxide. *Chemosphere* 1999;1: 331-351.

[29]. HTP-arvot 2009. Haitalliseksi tunnetut pitoisuudet. In Finnish. Summary in English. HTP Values 2009. Concentrations known to be harmful. Finnish ministry of social and health, 2009.

[30] Beck-Friis B, Pell M, Sonesson U, Jönsson H, Kirchmann H. Formation and emissions of N₂O and CH₄ from compost heaps of organic household waste. *Environ Monit Assess* 2000;62: 317-331.

[31] Amlinger F, Peyr S. Greenhouse gas emissions from composting and mechanical biological treatment. *Waste Manage Res* 2008;26:47-60.

[32] Chu H, Hosen Y, Yagi K. NO, N₂O and CO₂ fluxes in winter barley field of Japanese Andisol as affected by N fertilizer management. *Soil Biol Biochem* 2007;39:330-9.

[33] Jang I., Lee S, Zoh KD, Kang H. Methane concentrations and methanotrophic community structure influence the response of soil methane oxidation to nitrogen content in a temperate forest. *Soil Biol Biochem* 2011;43:620-7.

[34] Lai DYF. Methane dynamics in northern peatlands: A review. *Pedosphere* 2009;19(4): 409-421.

[35] Seinfeld JH. & Pandis, S.N. 2006. Atmospheric chemistry and physics – From air pollution to climate change. 2nd ed. John Wiley & Sons. New York. 2006.

[36] Wuebbles DJ, Hayhoe K. Atmospheric methane and global change, *Earth-Sci Rev* 2002;57: 177–210.

[37] Gendebien A, Pauwels M, Constant M, Lerdut-Damanet MJ, Nyns E-J, Willum HC et al. Landfill gas - From environment to energy. Commission of the European Communities, Contract No 88-B-7030-11-3-17 Final report. 1992.

- [38] Wihersaari M. Evaluation of greenhouse gas emission risks from storage of wood residue. *Biomass Bioenerg* 2005b;28:444-453.
- [39] Carrol, J.P. & Finnan J. 2012. Physical and chemical properties of pellets from energy crops and cereal straws, *Biosystems in Engineering* 112:151-9.
- [40] De Nevers. *Air pollution engineering*. Mc Graw-Hill. 1995.
- [41] Ling H-M, Liao C-M.. Modeling VOC-odor exposure risk in livestock buildings. *Chemosphere* 2007; 68:781-789.
- [42] Curtis L, Rea W, Smith-Willis P, Fenyves E, Pan Y. Adverse health effects of outdoor air pollutants. *Environ Int* 2006; 2:815-830.
- [43] Svedberg U, Petrini C, Johansson G. Oxygen depletion and formation of toxic gases following sea transportation of logs and wood chips. *Ann Occup Hyg* 2009;53:779-787.
- [44] He X, Lau AK, Sokhansanj SC, Lim CJ, Bi XT, Melin S. Dry matter losses in combination with gaseous emissions during the storage of forest residues. *Fuel* 2012; 95:662-4.
- [45] Agrios GN. *Plant pathology*. 5th ed. Academic Press. New York. 2004.
- [46] Arshadi M, Gref R. Emission of volatile organic compounds from softwood pellets during storage. *Forest Prod J* 2005;55:132-5.
- [47] Noll M, Jirjis R. Microbial communities in large-scale wood piles and their effects on wood quality and the environment, *Appl Microbiol Biotechnol* 2012;95:551-563.
- [48] Granström KM. Saw dust age affects aldehyde emissions in wood pellets. *Fuel* 2014;126:219-23.
- [49] Hyötypaperin palon sammutus jatkuu Valkealassa. In Finnish. Extinguishing the fire at Hyötypaperi in Valkeala continues. The local newspaper Kouvola sanomat 5.12.2011 Available from:
<http://www.kouvolansanomat.fi/Online/2011/12/05/Hy%C3%B6typaperin+palon+sammutus+jatkuu+Valkealassa/2011212527768/4>. Accessed in 20.2.2013.
- [50] Hakekasan sammutus voi jatkua päiviä, ilmanlaatu melko hyvä. In Finnish. Extinguishing the fire at the wood chip pile may continue for days. Air quality is reasonably good. Local newspaper Kouvola sanomat 8.3.2012. Available from:
<http://www.kouvolansanomat.fi/keskustelu/Keskustelua+uutisaiheista/Hakekasan+sammutus+voi+jatkua+p%C3%A4ivi%C3%A4,+ilmanlaatu+melko+hyv%C3%A4/61988/>. Accessed in 20.2.2013.

Figure caption

Figure 1: A scheme summarizing the key inputs and factors leading to risks on human health, the environment and property during long-term, large scale storage of wood chips.

Table captions

Table 1. Atmospheric life-times, global warming potentials (GWPs) and radiative forcing (RF) effects of CO₂, CH₄ and N₂O [24].

Table 2. CO, CO₂, CH₄, aldehyde and terpene concentrations measured from wood pellet storages

Table 3. Volatile organic compounds emitted from pellet storages and their classifications

Figure

<p>Biological input</p> <p>Fungal and bacterial action and respiration</p> <p>Aerobic and anaerobic degradation of wood constituents; cellulose, hemicellulose, lignin</p>	<p>Physical input</p> <p>Pile size</p> <p>Pile heat capacity</p> <p>Pile compactness</p> <p>Heat conduction</p> <p>Particle size</p> <p>Particle surface area</p>	<p>RISKS</p> <p>Emission of greenhouse and other hazardous gases, Oxygen depletion, Presence of pathogenic microbes</p> <p>Self heating and ignition, Dry matter loss, Reduced heating value, Increased ash content, Moisture changes</p>	<p>Chemical input</p> <p>Oxidation reactions</p> <p>Autooxidation of fats</p> <p>Exothermic reactions</p> <p>Availability of oxygen</p> <p>Mineral content</p> <p>pH</p>
		<p>Environmental input</p> <p>Ambient temperature</p> <p>Rainfall, Snowfall, Wind</p> <p>Transportation of microbes and material</p> <p>Pile base effects: soil/material type, slope, shape</p>	

Table

Gas	Lifetime (a)	GWP 20 a	GWP 100 a	GWP 500 a	RF (W m ⁻²)
CO ₂	100-200	1	1	1	+1.66
CH ₄	12	72	25	7.6	+0.48
N ₂ O	114	298	289	153	+0.16

Table

Compound	Storage time	T (°C)	Amount (g)	C (mg m ⁻³)	OEL 8h/15min (mg m ⁻³)	Environment	Additional information	Ref.
CO	8w ¹	20	800	640	35/87	Laboratory	Canadian pine	[15]
	8w	40	800	16700		Laboratory	Canadian pine	[15]
	6w	20	1200	400		Laboratory	European <i>pinus sylvestris</i>	[15]
	6w	40	1200	16300		Laboratory	European <i>pinus sylvestris</i>	[15]
	7-9w	5-25	3000M	1700-17000		Ocean vessels	Five intercontinental transportations	[13]
	?	?	30M	>900		Domestic	Conc. exceeded measurement range	[6]
	18h ²	?	6M	123 ± 10		Domestic		[1]
CO ₂	56d ³	20	800	9300	9100/-	Laboratory	Canadian pine	[15]
	56d	40	800	65900		Laboratory	Canadian pine	[15]
	42d	20	1200	3900		Laboratory	European <i>pinus sylvestris</i>	[15]
	42d	40	1200	55600		Laboratory	European <i>pinus sylvestris</i>	[15]
	7-9w	5-25	3000M	5400-31300		Ocean vessels	Five intercontinental transportations	[13]
	56d	20	800	90		Laboratory	Canadian pine	[15]
	56d	40	800	670		Laboratory	Canadian pine	[15]
CH ₄	42d	20	1200	5	no limit	Laboratory	European <i>pinus sylvestris</i>	[15]
	42d	40	1200	200		Laboratory	European <i>pinus sylvestris</i>	[15]
	7-9w	5-25	3000M	50-640		Ocean vessels	Five intercontinental transportations	[13]
	18h	?	?	111 ± 32		Industrial		[1]
	18h	?	6 M	98 ± 4		Domestic		[1]
	?	?	30M	309		Domestic		[6]
	3h	?	?	3.6		Industrial	Pile surface temperature 88°C	[1]
Terpenes	?	17-19	7000M	14.7-19.2	140/180 For turpentine	Industrial	Temperature 77°C at 1m depth	[6]
	?	?	30M	52		Domestic		[6]

¹ w=weeks, ² h=hours, ³ d=days

Table

Classification	Compound (CAS#)	Classification	Compound (CAS#)
Alkane	Pentane (109-66-0)	Aromatic aldehyde	Benzaldehyde (100-52-7)
Alkane	Heptane (142-82-5)	Ketone	Acetone (67-64-1)
Alkene	Ethene (74-85-1)	Alcohol	Methanol (67-56-1)
Alkene	Propene (115-07-1)	Alcohol	Butanol (75-65-0)
Aldehyde	Ethanal (75-07-0)	Alcohol	Isopropanol (67-63-0)
Aldehyde	Butanal (123-72-8)	Terpene	α -Pinene (2437-95-8)
Aldehyde	Pentanal (110-62-3)	Terpene	β -Pinene (-)
Aldehyde	Hexanal (66-25-1)	Terpene	Carene (13466-78-9)
Aldehyde	Heptanal (111-71-7)	Terpene	d-Limonene (5989-27-5)
Aldehyde	Nonanal (124-19-6)	Organic acid	Formic acid (64-18-6)
Aldehyde	Decanal (112-31-2)	Organic acid	Pentanoic acid (109-52-4)
Aldehyde	2-Ethylhexanal (123-05-7)	Organic acid	Hexanoic acid (109-52-4)
Unsaturated aldehyde	Acroleine (107-02-8)	Organic acid	Caproic acid (142-62-1)
Unsaturated aldehyde	Crotonaldehyde (4170-30-3)	Aromatic hydrocarbon	Toluene (108-88-3)
Unsaturated aldehyde	2-Heptenal (2463-63-0)	Aromatic hydrocarbon	Methyl-isopropylbenzene (99-87-6)