



Sustainable Bioenergy
Solutions for Tomorrow

RESEARCH REPORT
NO D4.2-2
HELSINKI 2016

Leena Fagernäs
Kirsi Korpijärvi
Eija Alakangas

Overview of health and safety issues in the logistics of wood and torrefied pellets



Solution Architect for Global
Bioeconomy & Cleantech Opportunities



Sustainable Bioenergy
Solutions for Tomorrow

Overview of health and safety issues in
the logistics of wood and torrefied pellets
Fagernäs, L., Korpijärvi, K. & Alakangas, E.

22.11.2016



CLIC INNOVATION OY
ETELÄRANTA 10
P.O. BOX 10
FI-00131 HELSINKI,
FINLAND
CLICINNOVATION.FI

ISBN 978-952-7205-09-9



CUSTOMER REPORT


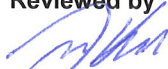

VTT-CR-5782-15 | 4.12.2015



Overview of health and safety issues in the logistics of wood and torrefied pellets

Authors: Leena Fagernäs, Kirsi Korpijärvi and Eija Alakangas

Confidentiality: Restricted

Report's title		
Overview of health and safety issues in the logistics of wood and torrefied pellets		
Customer, contact person, address		Order reference
Helen Oy Jussi Kukkonen Kampinkuja 2, Helsinki 00090 HELEN		Tilausnumero 151111887
Project name		Project number/Short name
Biohiililogistiikan HSE-selvitys SECTOR-kokeisiin liittyen		105427 HSESECTOR
Summary		
<p>The aim was to compile the recent studies on the health and safety issues in the logistics of wood and torrefied pellets. The work was connected to the studies of Helen Oy on the EC 7th FP project "SECTOR" and to the BEST research program coordinated by CLIC Innovation Ltd.</p> <p>The biomass materials are susceptible to heat generating processes from microbiological growth, chemical oxidation and moisture absorption and are thus prone to self-heating and spontaneous ignition. During storage of pellets, microbial decomposition is considered to be a minor factor unless the pellets have relatively high moisture content such as $\geq 12-15\%$. Off-gassing refers to the emission of different volatile compounds by wood pellets along the supply chain, from manufacturing to customers use. The pellet raw material, its treatment prior to production, and the pellets manufacturing conditions influence the off-gassing. Chemical oxidation has been presented the dominant mechanism for off-gassing of wood pellets. The main off-gas emissions are hexanal, monoterpenes, CO, CO₂ and CH₄. The knowledge of safety-technical properties of biomass fuels related to self-heating, self-ignition and dust explosions is of essential significance.</p> <p>During transportation of pellets occupational hazards can occur. In truck transportation the health risks result mainly during loading and unloading where high dust concentrations may result in a risk of dust explosions and human exposure to dust and microspores. A large proportion of wood pellets are shipped by ocean vessels. Cargo holds are sealed during the voyage which results in very fast oxygen depletion and generation of CO, CO₂, CH₄ and some H₂. Entry into cargo holds and communicating spaces are prohibited unless the spaces have been thoroughly ventilated and the gas concentration has been verified by a combination of oxygen and CO measurements.</p> <p>The supply chain of torrefied biomass is generally the same as for regular wood pellets logistics. From a safety perspective conveying, storage, loading and unloading, milling and feeding operations of torrefied biomass are the most relevant points. Potential safety issues along the value chain for torrefied pellets are mainly related to self-heating, dust emissions, off-gassing and oxygen depletion. Severe dusting during the unloading and conveying of torrefied pellets has been observed. Due to a very fine particle size and almost zero moisture content, the torrefied dust may ignite more easily and thus create a larger dust explosion risk than conventional biomass dusts and coal dust. The most significant difference between regular pellets and torrefied pellets is the explosibility characteristics of dust. The torrefied wood chips have been found to emit less off-gases when compared with wood pellets and untreated wood chips. Controlling dust emissions when conveying, loading and unloading at the power plant site has been mentioned by several end-users as an important issue. The main health and safety risks, their effects and protective measures against them in the supply and utilization chain of torrefied pellets were compiled in the report.</p>		
Jyväskylä 4.12.2015		
Written by	Reviewed by	Accepted by
		
Kirsi Korpijärvi, Research Scientist	Janne Kärki, Research Team Leader	Jani Lehto, Head of Research area
VTT's contact address		
PL 1603, FI-40101 Jyväskylä		
Distribution (customer and VTT)		
Helen and VTT. BEST consortium by permission of Helen.		
<p><i>The use of the name of VTT Technical Research Centre of Finland Ltd in advertising or publishing of a part of this report is only permissible with written authorisation from VTT Technical Research Centre of Finland Ltd.</i></p>		

Preface

This report is a literature review of the health and safety issues in the logistics of wood and torrefied pellets. The research work “Biohiililogistiikan HSE-selvitys SECTOR-kokeisiin liittyen” was ordered by Helen Oy on February 18, 2015 from VTT Technical Research Centre of Finland Ltd. The work is connected to the studies of Helen Oy on the occupational hygiene of the logistics chain of torrefied pellets produced by Topell in the EC 7th FP project “Production of solid sustainable energy carriers from biomass by means of torrefaction (SECTOR)”. The pellets were transported in February 2015 from the Netherlands to Helsinki to Helen Oy for combustion tests involved also in the SECTOR project. The contact persons of Helen Oy within the work have been Tea Erätuuli and Jussi Kukkonen.

The research work is also included in the Sustainable Bioenergy Solutions for Tomorrow (BEST) research program coordinated by CLIC Innovation Ltd. (former CLEEN Ltd. & FIBIC Ltd.). One of the BEST program’s research groups is the Health, Safety and Environment (HSE) group, which focuses on studying health and safety issues in the bioenergy supply chain, for example on the storage of densified bioproducts prior to co-firing in urban environment. The goal is to develop guidelines for safe delivery and handling of solid biofuels at existing power plants and new power plants to be constructed.

The work was carried out at VTT during the period between February 2015 and December 2015. The authors of the report were Leena Fagernäs, Kirsi Korpijärvi and Eija Alakangas.

Jyväskylä, December 2015

Authors

Contents

Preface.....	2
Definitions of terms used.....	4
1. Introduction.....	6
2. Health and safety factors of biomass fuels.....	7
2.1 Biological agents.....	7
2.2 Chemical agents.....	8
2.3 Self-heating, off-gassing and dust explosions.....	9
3. Health hazards in production of wood and torrefied pellets.....	10
3.1 Storage of pellet raw material.....	10
3.2 Drying of raw material.....	11
3.3 Pellet production plant and pelletizing process.....	13
4. Health hazards in storage and transportation of wood and torrefied pellets.....	15
4.1 Risks and fatal incidents.....	15
4.2 Investigations on off-gassing.....	16
4.3 Exposure effects and occupational limit values of off-gases.....	24
4.4 Other properties and analyses related to storage of pellets.....	26
5. Safety-technical characteristics of biomass fuels.....	28
5.1 Self-heating.....	28
5.2 Self-ignition and dust explosion.....	29
5.3 EU Project “Safe handling of renewable fuels and fuel mixtures”.....	31
5.4 Torrefaction project within Tekes/BioRefine Programme.....	32
6. Regulations and guidelines on health and safety issues of wood pellets and torrefied biomass.....	36
6.1 MSDS of Wood Pellet Association of Canada.....	36
6.2 Development of MSDS for torrefied biomass.....	38
6.3 Transportation of wood pellets.....	39
6.4 Development of ISO standards for safety issues of wood pellets.....	40
7. Logistics and utilisation of torrefied biomass.....	42
8. Comparison of torrefied pellets to wood pellets.....	45
9. Summary.....	50
References.....	54

Definitions of terms used

Bioaerosol	Aerosol or particulate matter of microbial, plant or animal origin
Deflagration Index K_{st}	Constant expressing the maximum pressure increase per time unit, if an explosion was to take place in a fixed volume of 1 m^3
Explosion	Violent event emitting sound and light and often immediately followed by fire
Emission factor	Milligrams of off-gas emitted per kilogram of biomass
Hydrothermal moisture migration	Cyclical vaporization and condensation of moisture on the surface of the pellets during storage in large bulk
Headspace ratio	The relative size of storage headspace in an enclosed space
Inhalable dust	Airborne particles of $100 \mu\text{m}$ diameter (AED) or less which can enter the nose and mouth during normal breathing
Limiting Oxygen Concentration LOC	Indicates in inertial cases at which maximum ambient oxygen content an explosion is prevented
Lower Explosion Limit LEL	The minimum concentration of the dust in a dust cloud which may generate an explosion
Maximum Explosion Pressure Rate dP/dT_{max} , $K_{max} = K_{St}$, Deflagration Index	
Minimum Explosible Concentration MEC (LEL)	The minimum concentration of the dust in a dust cloud which may generate an explosion
Minimum Ignition Energy MIE	The lowest energy stored in a capacitor which upon discharge is sufficient to produce ignition of the most easily ignitable dust mixture with air under specified test conditions
Minimum Ignition Temperature MIT	The lowest temperature at which the ignition of a sample occurs
Off-gassing	Spontaneous emission of condensable and non-condensable gases from biomass, the emission of volatile compounds by wood pellets along the supply chain
Respirable dust	Particles of less than $2.5 \mu\text{m}$ that will penetrate the gas exchange region of the lungs
Self-Ignition Temperature T_{St}	The highest temperature at which a given volume of dust will not ignite
Thoracic dust	Particles of $10 \mu\text{m}$ diameter or less that will pass through the nose and throat and reach the lungs

Torrefaction

Thermochemical treatment where a biomass feedstock is heated at 200 to 300 °C for about 30 minutes under atmospheric pressure and in the absence of oxygen

1. Introduction

Biomass as an organic material can cause health and safety risks during handling, processing, and storage of the material. Related health and safety factors are biological agents, chemical agents, physical factors (e.g. noise and vibration), self-heating, off-gassing, self-ignition and dust explosion.

The pellet production and logistics chain includes storing, crushing, grinding, drying, and milling of biomass raw material, pelletizing process itself, and cooling, screening and storing of the pellets, as well as transportation of the pellets to the customer. The torrefied pellets production chain includes in addition to these the torrefaction process step after drying. Wood pellets are made generally of sawdust, but also wood chips, forest chips and bark can be used as raw materials. The wet sawdust and the other raw materials are generally dried in a thermal dryer from about 50-55 w-% moisture content to 8-12 wt-%.

The wood raw material and its pretreatment affect the pelletizing process, quality of pellets, and also the health and safety of workers in pellet production plants and during storage and transportation of pellets. Occupational health hazards and fatal incidents during the supply chain of wood pellets have been detected during the 2000s. Hence several investigations on the risks have been carried out and reported during over the last ten years. So far the health and safety aspects of torrefied pellets have been studied and published only very restrictedly.

The aim of the report was to compile the recent studies on the health and safety issues in the logistics of wood and torrefied pellets. The main focus was on the storage, handling and transportation of the pellets. The report includes also shortly the health hazards in the production of wood pellets, because the pretreatment and pelletizing of raw material affect the health and safety issues during storage, transportation, and use of pellets. The report is based on the published literature, the earlier VTT projects, the current BEST and SECTOR projects, and the work underway in the ISO/TC 238/WG7 safety group. Especially, torrefied pellets were aimed to be compared with wood pellets.

2. Health and safety factors of biomass fuels

The health and safety factors biological agents, chemical agents, self-heating, off-gassing, self-ignition, and dust explosions related to biomass processing and the health effects when exposed to them has been presented in the literature review by the HSE group (Fagernäs *et al.* 2014) within the BEST project. Based on this review these factors will be shortly described in the following.

2.1 Biological agents

Handling, storage and processing of biomass produces organic dust, which is defined as a dust containing plant or animal origin particles. Another often synonymously used term for organic dust is bioaerosols, which can be defined as aerosols or particulate matter of microbial, plant or animal origin (Douwes *et al.* 2003). Heavy processes as chipping and crushing wood may be significant sources of airborne bioaerosols. According to Finnish legislation (Ammattitautiasetus 1347/1988), organic dusts such as from plants (e.g. wood) and animals are classified to chemical agents. Micro-organisms such as bacteria, viruses, fungi and parasites are biological agents.

In most biomass fuel environments dust will be the most significant risk factor. The health risks are affected by the biomass properties and the size of the particle coming from biomass. The hazard is greater the smaller the particles are and the further into the lung they can travel. Bioaerosols have a particle size of 0.02-100 µm. Depending on size, aerosol particles easily deposit in various parts of our airways. The size of a particle is determined by means of Aerodynamic Equivalent Diameter (AED) and relates to the density and form factor (shape) of the particle (Koppejan *et al.* 2013). The dusts are classified by AED as follows:

- Inhalable dust (PM100): Airborne particles of 100 µm diameter or less which can enter the nose and mouth during normal breathing.
- Thoracic dust (PM10): Particles of 10 µm diameter or less that will pass through the nose and throat and reach the lungs.
- Respirable dust (PM2.5): Particles of less than 2.5 µm that will penetrate into the gas exchange region of the lungs.

Biological agents may consist of pathogenic or saprophytic, live and dead micro-organisms or their fragments. The most common routes of entry for biological agents are inhalation of airborne micro-organisms and their fragments or through direct contact with organic material. Direct contact includes absorption through mucous membranes (eyes, nose and mouth) or chapped, sheared or any other broken skin. The greatest hazard for workers is usually caused by irritation of the mucous membrane and by toxic or allergenic effects after inhalation of large number of microorganisms and their fragments. (Douwes *et al.* 2003)

The microbiological health effects of infectious diseases are derived from pathogenic viable organisms (viruses, bacteria, fungi, or parasites) entering the host, then propagating within the body, and resulting in disease. Mycosis is a disease, which may arise from inhalation of fungal spores in handling decaying matter. For example a common fungus *Aspergillus fumigatus* in woodchip piles can cause this kind of mycosis, aspergillosis.

Allergic respiratory diseases are extrinsic allergic alveolitis (EAA), asthma and allergic rhinitis, and non-allergic respiratory diseases are organic dust toxic syndrome (ODTS), chronic bronchitis, and chronic obstructive pulmonary disease (COPD). Fungi such as moulds and yeasts may be the causative agents for these respiratory diseases together with bacteria. Mesophilic and thermophilic actinobacteria and *Aspergillus fumigatus* fungi have

found to be abundant at wood-chip plants (Madsen 2004). This may be due to self-heating of wood chips causing growth of thermophilic and thermotolerant micro-organisms.

In the wood-processing industry, dose–response relationships have been found between personal exposure to fungi and bacterial endotoxin, and work-related symptoms. All gram-negative bacteria in the organic material include endotoxin which is a fragment of their cell walls. Endotoxins are pulmonary immunotoxicants. They can cause acute systemic and respiratory symptoms (dry cough, shortness of breath, fever, shivering, and joint pain) and acute lung function changes. Chronic effect of endotoxin may be an accelerated decline in lung function and increased bronchial reactivity, which can lead to COPD. The Nordic and Dutch Expert Group (2011) has concluded that adverse health effects are expected after chronic occupational exposure at approximately 90 EU/m³ (EU=endotoxin unit, 0.1 ng). Additionally, endotoxin may have adjuvant effects on reactions to allergens. They may synergistically enhance the release of allergic mediators and increase the production of antibodies.

2.2 Chemical agents

Wood dust is composed mainly of cellulose, polyoses (hemicelluloses) and lignin and a large and variable number of substances of lower relative molecular mass which may significantly affect the properties of the wood. These include non-polar organic extractives (fatty acids, resin acids, waxes, alcohols, terpenes, sterols, steryl esters and glycerols), polar organic extractives (tannins, flavonoids, quinones and lignans) and water-soluble extractives (carbohydrates, alkaloids, proteins and inorganic material) (WHO 1995). In addition, pure wood dust might contain natural wood impurities like sand and chemical impurities, such as biocides, pesticides, insecticides, and herbicides.

Spruce, pine, and birch dusts are found commonly in forestry, woodworking industry, paper and pulp industry, pellet production and power production (Directive 90/394/EEC, Vna 716/2000, Kemikaalit ja työ 2005, Ahonen and Liukkonen 2008, HTP-arvot 2014). Workers in the solid biofuel supply chain can expose to softwood dust in the beginning of the supply chain during the chipping of wood, in the middle during transportation of the fuel to the power plant and especially in the end during reception of the fuel into the bio power plants. Hardwoods tend to be denser and have a higher content of polar extractives than softwoods (WHO 1995). Hardwood dusts such as oak and beech dusts are classified to carcinogenic to humans by EU (Directive 90/394/EEC). Most of the wood dust found in work environments has a mean aerodynamic diameter of more than 5 µm.

General knowledge of particle size indicates that wood dust can be deposited in human upper and lower airways, the deposition pattern depending partly on particle size. Heavy exposure to wood dust may result in decreased mucociliary clearance and, sometimes, in mucostasis. Exposure to wood dust may cause cellular changes in the nasal epithelium. Increased frequencies of cuboidal metaplasia and dysplasia were found in some studies of workers exposed to dust from both hardwood and softwood. These changes can potentially progress to nasal carcinoma. Impaired respiratory function and increased prevalence of pulmonary symptoms and asthma have also been found in workers exposed to wood dust (WHO 1995).

In addition to wood dust, workers can be exposed to gaseous and particular phase of diesel exhausts in different parts of bioenergy supply chain. These exhausts include carbon monoxide, hydrocarbons, nitric oxide, nitrogen dioxide, sulfur compounds, aldehydes, aromatic compounds (e.g. benzene and toluene), many of which are known or potential carcinogens. The particles contain aldehydes, alkanes, alkenes, hydrocarbons, and polycyclic aromatic hydrocarbons (PAHs) and PAHs derivatives. Other exposing chemical agents in bioenergy supply chain include ammonia, methane, carbon dioxide, carbon monoxide and reduced sulfur compounds. Exposing gases can be irritating, asphyxiant and anesthetic. Volatile organic compounds (VOCs) of wood are alcohols, ketones, aldehydes,

terpenes and organic acids. VOCs can cause irritation in eyes and respiratory system when inhaled and are flammable and harmful to humans in high concentrations. Monoterpenes are irritating to the skin, eyes and mucous membranes and can cause both non-allergic and allergic contact dermatitis (Edman 2003).

2.3 Self-heating, off-gassing and dust explosions

Self-heating is a well-known phenomenon for biomass. Traditionally the research has been devoted to understanding self-heating in biomass raw material. However, the potential for self-heating in wood pellets has been a concern for the pellets industry already many years and has been monitored during large scale storage as well as during ocean transportation (Melin 2013a).

The materials are susceptible to heat generating processes from biological metabolic reactions (microbiological growth), exothermic chemical reactions (chemical oxidation) and heat-producing physical processes (e.g. moisture absorption) and are thus prone to self-heating and spontaneous ignition. These processes can act alone or in combination, where the dominating process depends on the conditions, e.g. temperature and moisture content (Koppejan *et al.* 2013). Cell respiration can continue for some time after harvesting, as an exothermic process. Oxidation of fatty acids in sawdust and other moist fuels is accelerated by microbial activity with mesophilic bacteria and fungi up to approximately 40 °C and by thermophilic bacteria up to approximately 70 °C. Above this temperature chemical oxidation becomes dominant and further raises the temperature. (Lönnermark 2008)

Off-gassing is an important phenomenon, which refers to the emission of different volatile compounds by wood pellets along the supply chain, from manufacturing to customers use. The pellet raw material, its treatment prior to production, and the pellets manufacturing conditions influence the off-gassing. Oxidation takes place above 5 °C and generates heat, non-condensable gases and a number of condensable compounds. (Kuang *et al.* 2008, Koppejan *et al.* 2013)

In addition, absorption of moisture in pellets is an exothermic process and generates heat. When pellets with propensity to exhibit one or more of the heat generating processes are stored in a large volume, the temperature will increase within the pile, which may lead to spontaneous ignition in pellet storage facilities. (Koppejan *et al.* 2013)

Self-heating can be seen as the first step in a process that might result in spontaneous combustion. Babrauskas (2003) defines these steps as: 1) self-heating: an increase in temperature due to exothermal reactions in the fuel, 2) thermal runaway: self-heating, which rapidly accelerates to high temperatures, and 3) spontaneous combustion: visible smouldering or flaming by thermal runaway. (Koppejan *et al.* 2013)

Spontaneous heating and ignition phenomena are especially hazardous in storage bins and process equipment, as smouldering material deposits are potential sources of more extensive fire and dust explosions. When storing and handling biomass and other fuels, the tendency to spontaneous ignition and the temperature required for ignition should be known. Primarily four factors contribute to spontaneous ignition: oxidation tendency, ambient temperature, amount and characteristics of the material, and shape of the material storage vessel. The ambient temperature and the amount and form of the stored material are of significance, as heat generation typically occurs in proportion to volume and heat losses occur through the surface. As the volume increases according to the third power and the surface area according to the second one, there is a critical amount of material in which the generated heat is able to escape through the surface relatively quickly to prevent the temperature within the material from reaching the ignition point. Dust explosions are always an actual risk in handling biomass fuels. The dusty nature and high reactivity of biofuels, combined with generally needed thermal drying stage emphasise the hazards of dust explosions. (Wilén *et al.* 1999)

3. Health hazards in production of wood and torrefied pellets

3.1 Storage of pellet raw material

Prior to pelletizing, the wood raw materials are generally stored, and then crushed, ground and dried. The pellets are produced mainly from sawmill by-products: sawdust or cutter shavings. The supply of dry sawdust is limited and other raw materials are or will also be used, such as wet sawdust, wood chips, bark, and stem wood. Investigations have shown that storing the raw material for some time will increase pellet quality and also pellet mill capacity. Thus, it is a common practice to store fresh pellet raw material for up to several months at pellet plants. Also, logistics, transport issues and yearly harvesting conditions may require the manufacturers to store the raw material. The most common storage method at pellet plants is to stockpile the wet raw material in large piles as chips or sawdust. (Filbakk *et al.* 2011, Koppejan *et al.* 2013)

During storage, wood fuels are subject to biological and chemical reactions and decomposition caused by fungi. Moist biomass releases heat, different humidity zones are formed in the storage and mean moisture content of the fuel can be changed. The most factors causing problems are heat development with a possible risk of self-ignition, losses of dry matter and calorific value, and potential health hazard from airborne microspores. Many fungi require oxygen, moisture content above 20 w-%, and certain nutrients for their growth. Different microorganisms have different requirements for optimal growth and sporulation. The various species of moulds can grow at a very wide range of temperatures between 5 and 55 °C. The most frequent microorganisms associated with the storage of wood chips are moulds and actinomycetes. The inhalation of organic particles of bacteria, spores of actinomycete and moulds is associated with various forms of respiratory diseases such as ODS and allergic alveolitis. (Jirjis 1996)

Microbiological properties during storage of forest residues have been reported in many studies, e.g. by Törnqvist and Jirjis (1990), Jirjis and Theander (1990), Alvarez de Davila and Bengtsson (1993), and Jirjis (1996).

Storage can alter the composition of the wood material, and affect the pelletizing process and the quality of the pellets. These relationships depend on storage time and methods as well as on the moisture content of the stored material. The effect of the storage on the physical properties of wood pellets has been studied for example by Lehtikangas (2001) and Arshadi *et al.* (2008). The pellets made of stored pine fraction have higher bulk densities and better durability properties than pellets made of fresh pine sawdust. The wood pellet industry generally believes that a blend of fresh and stored (mature) sawdust is the best raw material for pellet production. It will improve the durability of pellets and also lower the power consumption in the pelletizing. (Arshadi *et al.* 2008)

In storing, extractives in sawdust are reduced and modified by microbiological activities and chemical reactions. Arshadi *et al.* (2007) carried out an experiment on the industrial storage of pine and spruce sawdust over a period of 16 weeks. The aim was to investigate how the chemical and physical properties of pine and spruce sawdust changed during large-scale outdoor storage. Samples were taken out every week and all samples were analysed by visible-near infrared (vis-NIR) spectroscopy or by gas chromatography-mass spectrometry (GC-MS) combined with extraction and derivatisation for their composition of fatty acids and resin acids. The resulting data were subjected to multivariate data analysis. Both the methods showed that aging takes place and the process is different for pine and spruce. The oxidation of fatty acids and resin acids was the main effect of the aging of sawdust. Also changes in the colour and moisture were important for monitoring maturity. Most of the changes in the amounts of fatty and resin acids occurred in the fresh pine sawdust during the weeks from six to twelve. The sawdust was mature after twelve weeks. As a fast and

inexpensive method for monitoring the aging process and determining the optimum storage time for sawdust, vis-NIR spectroscopy was considered potential to become useful in the pellet industry.

Furthermore, Nielsen (2009) studied the effect of storage on surface extractives of the raw material to investigate the storage effect on the raw material and the possibilities for accelerating the effect. The analysis showed that the extractive concentrations of the surface material were initially high and that they further increased during storage. The concentrations of triterpenoid and steroidal structures increased during the storage, whereas the concentrations of fatty acids and diterpenoid structures decreased, which reflected oxidation and polymerization reactions of the fatty acids and diterpenoid structures.

According to Tumuluru *et al.* (2010) the storage issues like off-gassing and self-heating may be very low in torrefied biomass as most of the solid, liquid, and gaseous products, which are chemically and microbiologically active, are removed during the torrefaction process. Some studies conducted by researchers at the University of British Columbia (UBC), Vancouver, Canada on off-gassing from torrefied wood chips, indicated that CO and CO₂ emissions were very low, nearly one third of the emissions from regular wood chips.

Kymäläinen *et al.* (2014) investigated the ability of different fungi to degrade and utilize torrefied wood (spruce and birch). Torrefaction changes the wood raw material to hydrophobic and thus makes the storage easier. As decaying agents require minimum 15-20% moisture content, torrefied wood should be inert to biodegradation. In addition, the heat-induced caramelization process degrades low-molecular carbohydrates, which lose water and become more aromatic. Torrefied wood should therefore also be less suitable for mould fungi. However, there are several bacteria and fungi that can also modify and decompose dry and seemingly unfavorable materials. Hence, several microorganisms are potential utilizers of torrefied wood in storage. Two experiments were conducted including a controlled laboratory fungal growth experiment with four different wood utilizing fungi and a preliminary field experiment with uncontrolled conditions. The growth of the fungi was evaluated by visual assessment, measuring the carbon, nitrogen and moisture contents, calculating the dry matter loss and through field emission scanning electron microscopy (FE-SEM) images. The experiments showed that in storage, torrefied wood is subjected to biological degradation and dry matter losses. In favorable conditions, the fungi used can utilize the carbon and nitrogen components of torrefied wood. Fungal growth increased the moisture contents of samples. Thus torrefied wood seemed to not have full resistance towards fungal degradation. This has to be taken into account when planning the supply chain of the material, as outside storage may not be advisable. However, more studies were required to quantify the biological deterioration.

3.2 Drying of raw material

Drying of the raw material is an important part of the pelletising process. In drying of wood and biomass materials, different organic compounds are released as a result of volatilization, steam distillation and thermal destruction and cause emissions to the environment, into the air or wastewaters. The emissions are affected by raw material, type of dryer, drying temperature, drying medium and residence time. The compounds emitted in wood drying have been categorized into VOCs and condensable compounds. Studies on the emissions have been reported, for example, in references of Fagernäs *et al.* (1992, 1996, 2007, 2010), Bridgwater *et al.* (1995), Björk and Rasmuson (1995), Granström *et al.* (2003), Rupar and Sanati (2003), Ståhl *et al.* (2004), and Banerjee *et al.* (2006).

The raw material is thermally dried at 100-400 °C. The dryers used are classified usually to indirect or direct dryers. The drying media used are hot air, flue gas or steam. Directly heated atmospheric gas dryers are common. In these the drying temperature is relatively high and the organic compounds released are diluted in the flue gas and emitted through the chimney, if flue gas condensation after the dryer is not utilized. The thermal destruction of wood

materials starts at about 150 °C with destruction of hemicelluloses. Alcohols, carboxylic acids and aldehydes are released. Also lipophilic fatty acids and resin acids are released. Thermal decomposition increases with the temperature rise. Presently relatively low temperatures are preferred in biomass drying, partly due to the high emissions of high temperature dryers. (Fagernäs *et al.* 2010)

Steam dryers are often used in integrated processes where heat recovery through condensing the waste steam from the dryers is utilized. The organic compounds released can be found in the condenser as inert gases, dissolved in the condensed water and as tar, floating on the condensed water. Volatile hydrocarbons may contribute to air pollution and hydrocarbons in the condensed water may contribute to eutrophication. The condensates can also cause problem for the de-nitrification process of sewage plants. To avoid this, the condensate can be treated by precipitation and biological oxidation before being led to a recipient. The non-condensable gases can be destructed in an existing boiler. (Fagernäs *et al.* 2010)

At low drying temperatures the compounds emitted consist mainly of terpenes. Monoterpenes (C₅H₈)₂ and sesquiterpenes (C₅H₈)₃ are volatilized easily at reasonable temperatures. Also, triterpenes (C₅H₈)₆ and oxygen containing terpenoids are released. The composition and concentration of terpenes in wood vary between different species. The content of monoterpenes in stemwood of Norway spruce is ~0.1% and in wood of Scots pine ~0.6% of dry wood, concerning round wood and chips from sawmills (Back and Allen 2000). Rupar and Sanati (2003) dried green pine and spruce wood chips with a circulated fluidized bed dryer with hot air and steam at 140, 170 and 200 °C to moisture contents below 10%. The main components of the emitted compounds were monoterpenes and sesquiterpenes, while the emission of diterpenes was negligible.

In the drying experiments at VTT (Fagernäs *et al.* 2007) with a laboratory fixed-bed batch dryer at 100-180 °C to about 10 w-% moisture content the non-condensing compounds were also mainly monoterpenes, for sawdust and pine bark α -pinene and Δ -3-carene, for spruce bark α -pinene and β -pinene and for forest chips α -pinene, β -pinene and Δ -3-carene. In addition, condensable compounds including low-molecular mass alcohols, carboxylic acids, aldehydes and ketones were quantitatively measured. It was found that it is possible to carry out the drying without emitting harmful amount of organic compounds to the environment. Prerequisites were e.g. that drying occurs in a bed, the inlet drying gas temperature is not higher than 180 °C and the steam formed is not condensed. The steam released prevents over-drying as long as a part of the material in the bed is still moist. The amount of organics released was 0.2-0.8 w-% of the feed.

Likewise, according to Otwell *et al.* (2000) the VOCs can be reduced by drying the wood to final moistures of 5% or more. Hazardous Air Pollutants (HAPs) evolved from drying pine flakes surged sharply at 5-10% moisture content during drying at 130-160 °C. Emissions of methanol, formaldehyde, pentanal, and hexanal all begin simultaneously, with the release of methanol and formaldehyde being the most sensitive to dryer temperature. Banerjee *et al.* (2006) showed that particles smaller than about 400 μ m will thermally degrade under typical dryer conditions and give rise to disproportionately high HAPs methanol, formaldehyde and acetaldehyde. They presented that screening out the fine particles below 500 μ m should reduce emissions by up to 70%. A further reduction could be taken by reducing dryer inlet temperatures.

The amount of volatile terpenes left in sawdust after drying varies with drying technique. The emissions of terpenes are higher in dryers with long residence times. In steam dryers sawdust keeps more terpenes than in rotary drum dryers. Sawdust dried in steam dryers lost 48% and 71% of the initial terpene content, while sawdust dried in rotary drum dryers lost about 80%. However, the terpenes not released during drying escape to a large part during pelletizing. (Ståhl *et al.* 2004, Granström 2003)

The VOC emissions are of environmental concern since ground-level ozone is formed by a chemical reaction between VOCs and nitrogen oxides in the presence of sunlight. Photo-oxidants are also harmful to humans, as they cause irritation in the respiratory tract and in sensitive parts of the lungs. Low emissions mean less air pollution, which benefits the work environment and the environment in the surroundings of the dryers.

Storing dried wood in stockpiles may also lead to self-heating and associated ignition problems. Thermal drying usually destroys the natural bacteria culture of the fuel and makes it even more accessible to outside attacks from microbes in the surrounding air and soil. A suitable moisture content of 20 wt% or more may lead to a rapid biological activity. Self-heating and hot spots are usually found at some distance from the surface of the stockpile. Boundary layers between dry and wet sections of the fuel storage are also known to be susceptible to self-heating. Therefore protecting dry fuel storages from water and moisture access is of great importance.

A dryer fire or explosion can arise from ignition of a dust cloud if substantial amounts of fines are present, or from ignition of combustible gases released from the drying material. Both causes of ignition require the presence of sufficient oxygen and either a sufficiently high temperature or some other source of ignition. In most dryers, the risk of fire or explosion becomes significant if the drying medium has an oxygen concentration over ~ 10% (vol.). The most important measure of precaution is to maintain a sufficiently inert atmosphere in the dryer during operation and especially during start-up and shut-down. Carbon monoxide together with dust creates a risk of hybrid explosion, which is very violent. The oxygen level should then be kept below 8% (10% minus 2% safety margin), with an alarm at 8% and possible interlocking to extinguishing water at 10-11%. (Fagernäs *et al.* 2010)

Crushing of coarse wood residue material is usually performed before the drying step. After drying the raw material is milled to the appropriate particle size. This is usually done by a fast rotating hammer mill. The milling of the pellet raw material opens up the cell structure and exposes the cellulose, hemicelluloses, lignin and the extractives to oxidation. This generates heat and off-gases. The higher the temperature is, the higher the rate of off-gassing becomes. (Koppejan *et al.* 2013)

3.3 Pellet production plant and pelletizing process

During production of wood pellets, exposure of workers to wood dusts, microorganisms or monoterpenes has been studied by Alvarez de Davila (1999), Edman *et al.* (2003), Madsen *et al.* (2004), Ståhl *et al.* (2004) and Granström (2005). In addition, Hagström *et al.* (2008) studied exposure to wood dust, resin acids, and volatile organic compounds.

In pelletizing, the dried wood material is pressed at 100 °C through the holes of a steel die to form cylindrical pellets. The warm pellets are then transported through a cooling tower to bagging or storage or for transportation with trucks or by ships. In the production of torrefied pellets, the dried biomass feedstock will be led to the torrefaction process, where it is heated at 200 to 300 °C for about 30 minutes under atmospheric pressure and in the absence of oxygen.

Edman *et al.* (2003) carried out measurements at six Swedish pellet producers. For 24 workers, personal exposure to monoterpenes was low and to wood dust high, compared with the Swedish occupational exposure limit (OEL) and previous studies in Swedish woodwork industries. The personal exposure to monoterpenes ranged from 0.64 to 28 mg/m³. Levels of monoterpenes were higher when fresher raw material instead of stored material was used. The OEL in Sweden was 150 mg/m³ for either individual monoterpenes or their sum. The personal exposure to wood dust varied between 0.16 and 19 mg/m³ and for 10 participants it exceeded the Swedish OEL for wood dust 2 mg/m³ measured as total dust. Inhalable dust is defined as the total amount of airborne particles that can be inhaled through the mouth and nose. Total dust is defined as dust measured on a filter in an open-faced cassette with a

diameter of 37 or 25 mm. The personal wood dust measurements showed considerable variation within and between workers, which was explained by differences in working tasks and/or differences in working routines. The air levels obtained by static sampling for monoterpenes was highest at the press and ranged from <0.84 to 74 mg/m³. Low levels of monoterpenes were measured at the grinder (range 0.60-2.4 mg/m³). The wood dust levels were at the press <0.10-2.2 mg/m³ and at the grinder 0.64-0.78 mg/m³.

Emissions of monoterpenes from pellets production was also studied by Ståhl *et al.* (2004) and by Granström (2005). Most of the terpenes were emitted during the drying step. During the production of pellets, 68-95% of the terpene content remaining in the dried sawdust was released. The higher the moisture content of the sawdust, the higher percentage losses occurred. After the sawdust has been both dried and pelleted, almost all the volatile terpenes have been emitted. Consequently, sawdust with higher terpene content caused higher emissions during pelleting.

Exposure to wood dust, monoterpenes, and resin acids, and as an indicator of diesel exhaust to nitrogen oxide were measured at four wood pellet production plants during a period of one year by Hagström *et al.* (2008). The participated 44 workers represented several working categories. Personal exposure levels to wood dust were high, and a third of the measured levels of inhalable dust exceeded the Swedish OEL. Exposure levels for resin acids approached 74% of the British OEL for colophony, set at 50 µg/m³. The resin acids analysed were 7-oxo-dehydroabietic acid, dehydroabietic acid, abietic acid, and pimaric acid. Exposure to the resin acids was found a potential concern with respect to workers' health. Personal exposure levels to monoterpenes and nitrogen dioxide were low. Area measurements at the pellet press ranged for total dust <0.10-28 mg/m³, for resin acids <0.29-59 µg/m³, for α-pinene <0.25-26 mg/m³, for nitrogen dioxide 13-83 µg/m³ and for TVOC 0.67-23 mg/m³. Carbon monoxide levels were under the detection limit in all area measurements. To reduce exposure to wood dust, suggestions for the changes were presented to the plants, such as increasing automation, improving local ventilation, and implementing good housekeeping practices. Reducing the manual handling of raw material by automating the transportation of sawdust from the storage sites to the production sites could reduce exposure levels substantially. Also it would be preferable to using central vacuum cleaners for cleaning, instead of sweeping and cleaning with compressed air.

The temperature of the pellets when leaving the pellet press is high, even 80-100 °C. Cooling is performed generally in vertical cooling towers or on belt type cooling conveyers. During an efficient cooling process the moisture content of the pellets decreases by 2-3 percentage units. Cooling of the pellet stream is highly important with regard to safe storage of the product. After cooling the pellets will be screened. If the product stream after the pellet press contains large amounts of fines, these fines may pass the cooling step without proper cooling due to bad air penetration. Without an efficient screening phase these fines may end up in the product. Warm and humid fines can then destroy the product and cause a risk of self-heating.

4. Health hazards in storage and transportation of wood and torrefied pellets

4.1 Risks and fatal incidents

Dry wood pellets require protected storage to keep the structure and low moisture content of the pellets (Koppejan *et al.* 2013). They are stored either in silos or flatbeds or packaged in large bags. During storage self-heating of pellets occurs, mainly in large-scale storage, but also in smaller piles.

The three mechanisms involved in self-heating are microbial decomposition, chemical oxidation and hydrothermal moisture migration (see section 2.3) (Melin 2011). Due to the low moisture content of pellets, and normally high temperatures in drying and in pelletizing, microbial activities should be very limited in pellets during storage (Lönnermark *et al.* 2008). Storage of wood pellets is different from the storage of sawdust, as the pellet process kills parenchyma cells and the low moisture content of pellets hinders the growth of microorganisms, so self-heating would be due primarily to chemical oxidation processes (Granström 2014).

The hydrothermal moisture migration is present when pellets are stored in large bulk, particularly in an environment when fluctuations in the ambient thermal conditions causes cyclical vaporization and condensation of moisture on the surface of the pellets, with moisture constantly moving upwards in a pile. The accumulation of significant moisture concentrations in the upper levels of large storages in combination with convection heat moving upwards promotes microbial growth which in turn initiates self-heating and off-gassing. (Melin 2011)

Torrefied material is considered easy to store even outside owing to its hydrophobicity and stability. The recent results of Kymäläinen *et al.* (2015) do not support this. Biological degradation and changes in moisture content and composition were recorded in five-month storage trials with covered and uncovered storages for both torrefied pellets and steam-explosion pellets. It was considered that torrefied material must be stored in a covered setting, but silos do not seem necessary. Unlike untreated pellets, which require closed containers to maintain their quality, torrefied and steam-exploded pellets were not found to suffer from covered storage.

For wood pellets, the tendency for self-heating seems to vary between different qualities of pellets and is most pronounced relatively shortly after production. The temperature can vary, depending on the raw material and most often is around 60 and 65 °C. The temperature increase can sometimes be higher (up to 90 °C), but at such temperatures the risk of a run-away temperature resulting in a spontaneous ignition will increase, especially, if the volume of the pile is large or the pellets are stored in a silo. If the pellets are not cooled enough, the temperature in the storage can increase rapidly.

Serious incidents of self-heating and spontaneous ignition of wood pellets in storage have occurred. Examples of fires occurred in Sweden and Denmark and caused by self-heating have been reviewed by Koppejan *et al.* (2013). The fires have occurred both in silos and flat storages.

The self-ignition and explosions in the pellets has been investigated at the SP Technical Research Institute of Sweden during several years (e.g. Persson *et al.* 2006, Lönnermark *et al.* 2008). The focus has been *a.o.* to increase the knowledge on fire development, detection and extinction technique in silo fires and to develop guidelines regarding firefighting of silo fires. One aim of fire extinguishing research has been to develop the inertation technique using nitrogen injection.

The main risks resulting from the self-heating process of stored pellets are: release of asphyxiating [e.g. carbon monoxide (CO)] and irritating gases (e.g. aldehydes and terpenes), spontaneous ignition resulting in pyrolysis of bulk material and release of pyrolysis/combustion gases, gas and/or dust explosion, and surface fire and spread of fire, typically as a result of an explosion in a silo (Koppejan *et al.* 2013). The pellets and off-gassing can pose a safety and health threat for workers involved with handling the product in large bulk.

.A number of serious accidents has occurred during ocean transportation of wood pellets (Svedberg *et al.* 2008, Lönnermark *et al.* 2008, Pa and Bi 2010). In 2002, the ocean vessel MV Weaver Arrow loaded in Vancouver with wood pellets was discharging pellets in the Port of Rotterdam when one stevedore was killed and two other workers were severely injured as a result of exposure to CO when entering one of the cargo holds. In 2006, a similar fatal accident on board MV Saga Spray vessel in the Port of Helsingborg, Sweden, occurred, when unloading wood pellets from British Columbia (BC), Canada. One seaman was killed, a stevedore was seriously injured and several rescue workers were slightly injured after entering an unventilated staircase next to a cargo hold due to the lack of oxygen (O₂) and the emission of CO. Collected data indicated that the stairway environment had an abnormally low O₂ concentration of about 15%. In addition, CO concentration in the stairway exceeded the hygiene limit by at least 10 times. Carbon dioxide (CO₂) concentration in the stairway was also >50 times higher than the 15-min exposure limit.

Several other fatal accidents have also been reported in Europe. In transport and storage of pellets a few persons have died in Finland. In 2008, a maintenance man perished in CO formed in a wood pellet silo (TVL 2008). He had worked alone and descended to the bottom of the silo. After four days he was found dead. A few accidents in Germany and Austria have also been reported and the risk with residential storage of pellets has been verified. Gauthier *et al.* (2012) reported two deaths that occurred in wood pellet storerooms of private households in German and Austria and were investigated by forensic medical teams. Both victims died of CO poisoning. Other accidents have occurred in Denmark, Ireland and Switzerland (Melin 2010). Since 2002, according to Fan and Bi (2013) there have been more than eight fatal accidents resulting from off-gas emissions from stored wood pellets in ocean vessels and storage areas and a significant oxygen-deficit atmosphere leading to the death of nine people and the permanent injury of three people.

Gauthier *et al.* (2012) carried out a series of experiments in order to confirm CO production by wood pellets. Thirty kg of freshly produced pellets from two different manufacturers were stored for 16 days in ten airtight containers (60 L) at 26 °C with different relative humidities. CO concentrations between 3100 and 4700 ppm were measured in all containers. There were no notable differences between the wood pellet products or storage at different humidities. They showed that significant CO concentrations can build up even when the rooms are ventilated in accordance with the regulations and that such levels may cause the death of healthy persons.

4.2 Investigations on off-gassing

After the fatal accidents with wood pellet shipment, industry and research institutions started to do in depth investigation of wood pellets properties that included off-gassing, and the influence of storage parameters on it (Melin 2011). The studies on off-gassing have mainly been conducted in Canada and Sweden. Wood Pellet Association of Canada (WPAC) has studied production of toxic emissions during ocean transportation of wood pellets (Lönnermark *et al.* 2008, Svedberg *et al.* 2008). WPAC together with University of British Columbia (UBC) agreed to develop a deeper understanding of the quantitative aspect of off-gassing using laboratory reactors to simulate storage conditions for pellets (Melin 2010). Research has been conducted to quantify the emission factors for CO, CO₂ and methane (CH₄) in combination with oxygen depletion. It has focused on self-heating as a chemical

process and kinetic modelling of off-gassing to establish a prediction model to be used by industry. Biomass and Bioenergy Research Group (BBRG) was formed at UBC.

Investigations on measurements of off-gases, both condensable compounds and non-condensable gases, in real storages and in laboratory experiments as well as kinetic studies of off-gas emissions will be reviewed in the following.

Investigations in real storages and in laboratory

Off-gas emissions has been investigated and published for example by Svedberg *et al.* (2004, 2008), Arshadi and Gref (2005), Arshadi *et al.* (2009), and Granström (2010, 2014).

Earlier, Svedberg *et al.* (2004) investigated the emissions of volatile compounds, particularly hexanal and carbon monoxide, from large- and small-scale storage of wood pellets. Air sampling was performed with Fourier transform infrared spectroscopy (FTIR) and adsorbent sampling in pellet warehouses, domestic storage rooms, and experimental set-ups. Pentanal, methanol, acetone and formic acid were identified and quantified by the FTIR method, Monoterpenes, other aldehydes and organic acids were found in substantially lower levels and required adsorbent sampling and GC-MS analysis for detection. Inside the warehouses, the dominant organic compounds were aldehydes, acetone and methanol. Hexanal was the predominant aldehyde found in the organic volatiles. In addition, high CO concentrations were found. The monoterpene concentrations in the warehouses were low. Hexanal was presented to be probably formed by the oxidative degradation of natural lipids present in the wood. This was the first time when the low temperature emission of CO from wood products such as pellets was reported. CO was postulated to be formed due to auto-oxidative degradation of residual fats and fatty acids in the pellets. They concluded that high levels of hexanal and CO were strongly associated with storage of wood pellets and may constitute an occupational and domestic health hazard.

After the accident on board MV Saga Spray vessel (see section 4.1), Svedberg *et al.* (2008) initiated an investigation on five ocean vessels for the characterization and quantification of gaseous compounds emitted during ocean transportation of wood pellets in closed cargo hatches from Canada to Sweden. Air sampling was done during transport and immediately before discharge in the undisturbed headspace air above the wood pellets and in the staircase adjacent to each hatch. The samples were analysed with FTIR and direct reading instruments. The concentration ranges of CO, CO₂ and CH₄ were 1460-14650, 2960-21570 and 80-956 ppm, respectively, which were well above the safety threshold values. The oxygen levels were low and varied from 0.8 to 16.9%. The aldehyde concentrations were much lower than in previous findings in pellet warehouses. The concentrations in the staircases were almost as high as in the cargo hatches, indicating a fairly free passage of air between the two spaces. A potentially dangerous atmosphere was reached within a week from loading. They concluded that ocean transportation of wood pellets in confined spaces may produce an oxygen deficient atmosphere and lethal levels of CO which may leak into adjacent access spaces.

Also earlier Arshadi and Gref (2005) investigated the emission of VOCs from fuel pellets made from fresh and stored Norway spruce and Scots pine sawdust. Measurements were done by head-space (HS) and GC-MS methods. It was found that pellets emit high levels of VOCs, especially volatile aldehydes but that the drying temperatures of sawdust and self-heating of stored pellets affect the amount and composition of the emitted compounds. In pellets with a pungent smell, high levels of hexanal and pentanal together with minor amounts of other aldehydes were detected. The odour was most probably due to a synergistic effect of many VOCs. The lipid content of sawdust seemed to be a good maturation indicator for sawdust. Spruce and stored pine sawdust contains lower amounts of unsaturated fatty acids than fresh pine sawdust and thus should generate lower amounts of aldehydes. From an emission point of view, spruce sawdust or stored (mature) pine sawdust

should be the preferred raw material. It might be possible to reduce VOC emissions of pellets by optimizing the drying temperature and other process parameters in pellet production.

Later on, Arshadi *et al.* (2009) investigated the influence of the raw material and the process parameters on fatty/resin acids composition in pellets and the emission of aldehydes/ketones from fresh and stored pellets. The study was carried out in an industrial production plant using an experimental design and multivariate data analysis. The fatty/resin acids were determined by GC-MS and the aldehydes/ketones by high performance liquid chromatography for both newly produced pellets and those after 2 and 4 weeks of storage.

For both the fatty/resin acids and aldehydes/ketones, substantial decreases over time of the average levels were noted over 4 weeks. The amount of fatty/resin acids decreased about 40% in the studied 11 piles and that of emitted aldehydes/ketones generally decreased by 45% during storage. The content of pine and drying gas temperature were the two factors that had a positive effect on the formation of all aldehydes detected. The amounts of dienoic and trienoic unsaturated fatty acids in pellets were lower compared to fresh wood, which confirms that these acids are more sensitive to oxidation than monoenoic fatty acids (Back and Allen 2000). The main resin acids in the pellets were dehydroabietic acid and 7-oxo-dehydroabietic acid which were in greater amounts compared to typical fresh pine and spruce wood.

In the piles of pellets made of pine, the temperature evolved over storage time. The decrease in dehydroabietic acid corresponded to an increased content of 7-oxo-dehydroabietic acid. So the accumulation of 7-oxo-dehydroabietic acid could be used as an indicator of pellet maturity. The oxidation of unsaturated fatty acids gives rise to aldehyde/ketone emissions from pellets. In pellets made from spruce, the emissions of aldehydes and ketones are significantly lower than in pellets made from pine. Emissions of aldehydes/ketones cause unpleasant odours in storage rooms. A high drying gas temperature used for drying the sawdust leads to higher emissions of aldehydes/ketones after production and during storage of pellets. By choosing the optimal raw material mixture of pine and spruce and process parameters, it should be possible to reduce the amount of the aldehydes during storage of wood pellets and also any possible risk to the health of workers in the pellets industry and users in the households.

Granström (2010) studied the emission of monoterpenes and the formation of hexanal during storage of undried sawdust, dried sawdust, and wood pellets. The measurements were done in a controlled laboratory setting with Scots pine pellet raw material. The emission of volatiles was analyzed with static headspace gas chromatography (SHS-GC).

In both dried and undried sawdust terpenes were emitted rapidly during the first 10 days. During this time there were no aldehyde emissions. As terpene emissions decreased, hexanal emissions increased. After 1.5 months, the hexanal in undried and dried sawdust peaked. In undried sawdust, the amount of hexanal at its highest concentration was about equal to the remaining terpene content. In dried sawdust, the amount of hexanal at this time was about twice the amount of terpenes. The terpene levels in the pellets were very low (Figure 1). The only terpenes present in measurable amounts were α -pinene and 3-carene. Terpenes were still being emitted, however, as the amount of terpenes decreased even more during storage.

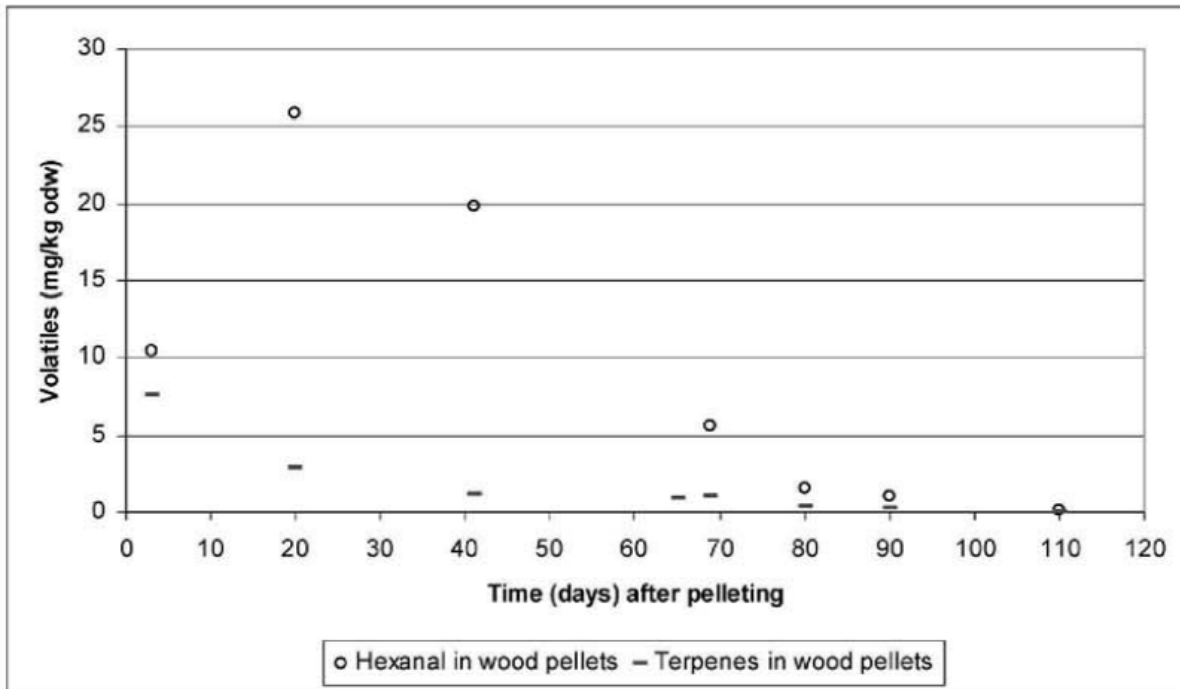


Figure 1. Monoterpenes and hexanal in pellets during storage (Granström 2010).

Hexanal was found only a few days of pellets storage, which is a more rapid progression than in sawdust. The process of drying and pelleting hastens hexanal formation. The faster formation in pellets may be due to an accumulation of semistable fatty acid hydroperoxides during the propagation stage of auto-oxidation. When sawdust has been dried and pelleted, the extractives have been exposed to both oxygen and high temperatures and are likely to contain fatty acid hydroperoxides as well as unsaturated fatty acids. The hexanal content in the pellets increased quickly to reach a maximum (26 mg/kg) after about one month (Figure 1).

The wood was low emitting regarding both terpenes and hexanal after 2 months for undried sawdust, 2.5 months for dried sawdust, and about 3 months for pellets. The risk of odors from wood pellets is likely to be highest about 1 month after drying. The risk of spontaneous ignition is greatest when relatively fresh pellets (1 to 6 weeks old) are stored in large silos.

Granström (2014) has described the principle path of fatty acids auto-oxidation and hexanal formation (Figure 2). Triglycerides (esterified fatty acids) in wood can hydrolyze to form free unsaturated fatty acids. Oxidation of unsaturated fatty acids is a complex self-catalyzing free radical chain reaction started by free radicals. The radicals cause free fatty acids to become hydroperoxides. The hydroperoxides are unstable and start to decompose soon after they are formed. Hydroperoxides break down to one alkoxy radical and one hydroxyl radical. When the oxidation has started, it self-catalyzes and continues until all the radicals have been neutralized. One of the most notable compounds emitted from the oxidizing of fat is hexanal.

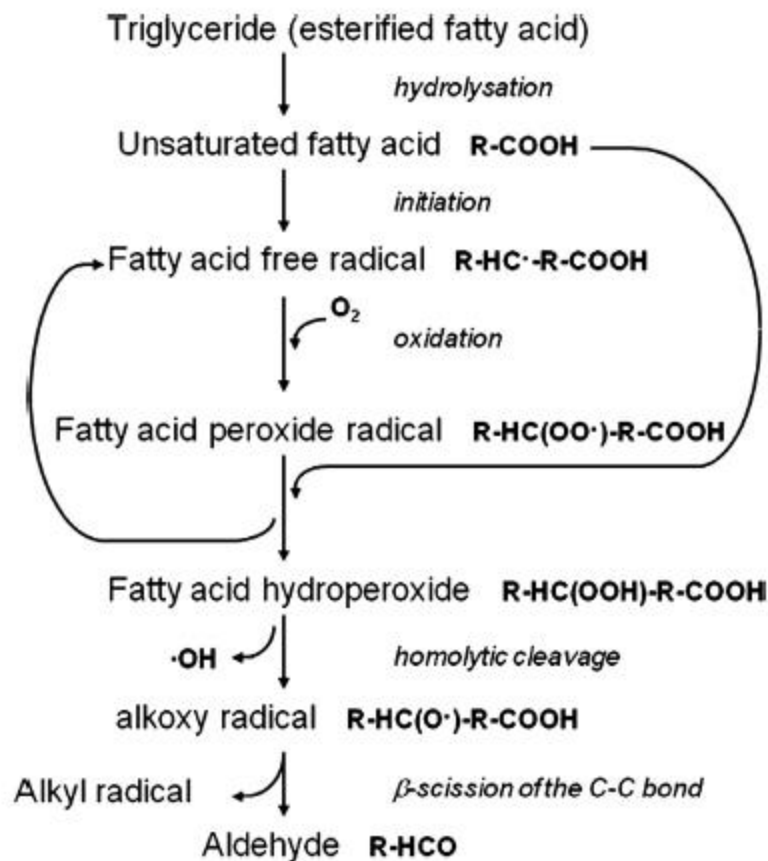


Figure 2. Principle path of fatty acids auto-oxidation and hexanal formation (Granström 2014).

Furthermore, Granström (2014) investigated the effect of the age of the pelletized sawdust on the amount of oxidation, measured as produced hexanal. Pellets were produced from Scots pine sawdust that was either freshly sawn or had been stored for 4 months. The pellets were then stored at either 18 °C or at 40 °C. The formation of hexanal in the samples was analyzed with SHS-GC.

Pellets made from fresh sawdust were low-emitting after 80 days, whereas pellets made from aged sawdust did not reach the same low level until 190 days after production. The pellets made from aged sawdust emitted thus considerably more hexanal, and over a longer time period than pellets made from fresh sawdust, which was a finding consistent with the higher level of extractives typically found in aged sawdust. When a low level of aldehyde emissions is required during storage, the pellets should be produced of sawdust that is freshly sawn. These results were in contradiction with the investigations of Arshadi and Gref (2005), who suggested that pellets made from stored sawdust might generate less VOCs than pellets made from fresh sawdust. The fresh pellets stored at 18 °C reached maximum emissions after 20 days, whereas fresh pellets stored at 40 °C peaked shortly after production. Storage at an elevated temperature thus hastened the oxidation process in pellets made from fresh sawdust but not in pellets made from aged sawdust. Hexanal was found a reliable indicator of lipid oxidation.

A field study on exposure to CO from off-gassing of bulk stored wood pellets used in different typical U.S. storage systems in New York State, including in-use bins in schools, work places, and a residence was recently carried out by Soto-Garcia *et al.* (2015). The results presented for the six different small-scale pellet storage bins during a period of a year showed, in general, that all the concentrations were below 200 ppm. The study demonstrated that there is off-gassing of sufficient CO from stored pellets to represent a hazard that needs

to be adequately addressed. Concentrations above levels set as exposure guidelines of 35 ppm in occupational settings and 9 ppm in homes were exceeded, especially immediately after pellet delivery. The results raise a safety question regarding how pellets storage bins are designed and sited. In energy efficient homes with low air exchange rates, unacceptable CO concentrations could occur. Pellet aging clearly reduced the amount of observed CO. Higher temperatures produced higher off-gassing production. Thus, bin temperatures need to be considered when designing or choosing a pellet storage bin.

Kinetic studies of off-gas emissions

Kinetic studies of off-gas emissions from wood pellets have been conducted mainly by Kuang *et al.* (2008, 2009a, 2009b), Tumuluru *et al.* (2010), Pa and Bi (2010), and Fan and Bi (2013).

Kuang *et al.* (2008) characterized emissions of CO, CO₂, and CH₄ from wood pellets in an enclosed storage space and developed a first-order kinetic equation for predicting the evolution of emission rate factors at different storage temperatures. Five 45-L metal containers were used to study the temperature effect on the off-gas emissions of wood pellets. Ten 2-L aluminium canisters were used to study the gas emissions as a function of storage time and storage temperature for switchgrass, wood pellets made in BC, wood pellets made in Europe and torrefied woodchips made in Europe. Gas samples were drawn from the containers and canisters by a syringe daily. The composition of the sampled gas was analysed by the GC methods using hydrogen flame ionization (FID) and thermal conductivity (TC) detectors.

Storage temperature was one of the critical factors that affected the off-gassing from stored wood pellets. Higher peak emission factors and faster emission rates were associated with higher temperatures. The concentrations of CO, CO₂ and CH₄ in the sealed space of the reactor increased over time. As the storage temperature increased from 20 to 55 °C, the emission rate increased significantly. First-order reaction kinetics fitted the data well. The maximum concentration and the time it takes for the build-up of gas concentrations can be predicted using kinetic equations. The results suggest that chemical decomposition of wood pellets could be the dominant mechanism for off-gassing CO, CO₂, and CH₄ within the temperature ranges of 20-55 °C. The quantity of O₂ in a sealed container affected the generation of the off-gases. There was strong correlation between the build-up of CO and CO₂ concentrations and decrease in O₂ concentration in the containers.

A large increase in emission concentrations of CO₂, CH₄ and CO for different biomass materials was found as the storage temperature increased from 20 to 40 °C (Table 1). The European wood pellets were very sensitive to the temperature increases. Torrefied woodchips, on the other hand, were less sensitive to temperature increases, emitting the highest amount of CO₂ at 20 °C of all materials, but the least at 40 °C. The removal of VOCs during the torrefaction process is a likely explanation why emission of gases from torrefied wood is less sensitive to the temperature. Switchgrass and torrefied woodchips generally emit less gas at 40 °C.

Table 1. Plateau (peak) concentrations of CO₂, CO and CH₄ for five different woody materials stored in 2-L containers at two temperatures (Kuang *et al.* 2008).

Material	Storage time (days)	CO ₂ (ppm) 20 °C	CO ₂ (ppm) 40 °C	CH ₄ (ppm) 20 °C	CH ₄ (ppm) 40 °C	CO (ppm) 20 °C	CO (ppm) 40 °C
Switchgrass	56	1878	43104	3	17	367	8914
Fines of BC* wood pellets	56	5434	38327	169	1665	7662	15086
BC* wood pellets	56	5128	36210	138	1029	5510	14334
European wood pellets	42	2156	30547	7	310	335	13973
European torrefied woodchips	27	12446	25084	3	7	259	4833

*BC = British Columbia

The peak concentrations of CO₂, CO and CH₄ emitted from BC wood pellets in 45-L containers for 20-55 °C were comparable with those measured in closed cargo ship hatches reported by Svedberg *et al.* (2008) and well above their respective threshold limit value-time weighted average (TLV-TWA) values. Kuang *et al.* (2008) presented that future study incorporating the real temperature and ventilation data from specific storage and shipping vessels and the emission factor data from their study should provide useful safety guidelines.

Recently Tumuluru *et al.* (2015) tested wood chips, torrefied wood chips, ground switchgrass, and wood pellets for off-gas emissions during storage at 20 and at 40 °C for an 11-day storage period. Further emission-concentration data was used to calculate an emission factor (milligrams of off-gas emitted per kilogram of biomass). Commercially-produced wood pellets yielded the highest CO emissions at both 20 and 40 °C (1600 and 13000 ppmv), whereas torrefied wood chips emitted the lowest of about <200 and <2000 ppmv. CO₂ emissions from wood pellets were 3000 ppmv and 42000 ppmv, whereas torrefied wood chips registered at about 2000 and 25000 ppmv, at 20 and 40 °C at the end of 11 days of storage. The results indicate that torrefied wood chip emits less CO, CO₂, and CH₄ when compared to wood pellets, untreated wood chips, and ground switchgrass. At 40 °C, the off-gases CO and CO₂ increase to levels where they could produce fatal accidents within short exposure times. CO emission factors calculated were lowest for ground switchgrass and torrefied wood chips (2.68 and 4.86 mg/kg) whereas wood pellets had the highest CO of about 10.60 mg/kg, respectively, at 40 °C after 11 days of storage. CO₂ emission factors were 55.46 mg/kg for wood pellets and 123.50 and 118.68 mg/kg for wood chips and torrefied wood chips, respectively, at the end of the storage at 40 °C. CH₄ was negligible for all feedstocks except for wood pellets at the end of storage at 40 °C.

Furthermore, Kuang *et al.* (2009a) investigated the effects of temperature, moisture, and the relative size of storage headspace on emissions from wood pellets in an enclosed space (10-L plastic containers). The sampled gas was analysed by GC-FID and TCD to quantify concentrations of CO, CO₂, CH₄, O₂, and N₂. The results showed that emissions of CO₂, CO and CH₄ from stored wood pellets are more sensitive to storage temperature (10-45 °C) than to relative humidity RH (low, high) and the relative volume of headspace (25, 50 and 75%). Higher peak emission factors were associated with higher temperatures. Increased headspace volume ratio increased peak off-gas emissions because of the availability of oxygen for pellet decomposition. Increased humidity in the headspace in the container increased the emissions of CO₂, CO, and CH₄. Hence the control methods such as restricting the storage temperature, RH, or choosing an appropriate headspace ratio in a contained

storage space could be effective in reducing the off-gas emissions from wood pellets in order to protect the workers' health.

In the study of Kuang *et al.* (2009b) on the effects of headspace and oxygen level on off-gas emissions the purpose was to provide data on the concentrations, emission factors, and emission rate factors of CO₂, CO and CH₄ from wood pellets stored with different headspace to container volume ratios with different initial oxygen levels. Metal containers of 45 L were used in the study. The composition of the sampled gas was analyzed using GC-TCD and GC-FID. TCD was used for the determination of CO, CO₂, and CH₄ and FID was used for O₂ and N₂. The previously developed first-order kinetic model (Kuang *et al.* 2008) for evolution of gas emissions was used to fit the data of each gas species. Headspace to the container volume ratio was one of the critical factors that affect the off-gas emissions from wood pellets. Higher peak emission factors and faster emission rates were associated with higher headspace ratios. The oxygen level determines the emission rate of CO₂ and CO from wood pellets. Lower oxygen levels generate lower emissions of CO₂ and CO at room temperature, whereas CH₄ emission is insensitive to the oxygen level.

Tumuluru *et al.* (2010) developed three sealed containers to investigate the concentration of off-gases accumulated in the headspace and also changes in some of the physical properties of wood pellets during storage. Pellets occupied 75% of the container volume leaving 25% headspace. The off-gases were collected and analyzed using micro-GC. The emissions of CO (5000 ppmv) and CO₂ (10000 ppmv) were relatively high at room temperature (22 °C) for a storage period of 24 days. These accumulations increased sharply at storage temperatures >30 °C. At 50 °C, the maximum measured concentration of CO, CO₂ and CH₄ was about 17 000, 70 000 and 3000 ppmv, respectively.

In modeling of off-gas emissions from wood pellets during marine transportation Pa and Bi (2010) developed a two-compartment model for the first time to predict the concentrations of CO, CO₂, CH₄ and O₂ inside the cargo ship and the time and rate of forced ventilation required before the safe entry into the stairway adjacent to the storage hatch. They applied the kinetic equations of Kuang *et al.* (2008) in a two-compartment reactor model to simulate the buildup of off-gases in ocean storage vessels of wood pellets during marine transportation from Vancouver to the Netherlands. The hatch and stairway were treated as two perfectly mixed tanks. The model was applied to predict the effect of ocean temperature on the off-gas emissions and the buildup of concentrations in the hatch and stairway. The predicted concentrations at the end of the ocean journey were then compared with the measured final concentrations of CO, CO₂, CH₄, and O₂ in the stairway of the storage system. It was found that the parameters need to be scaled in order to reproduce the magnitude of pollutant concentrations observed onboard. It was also noted that in the models, the predicted oxygen levels were much higher than the measured values. For safe entry to the cargo ship, the model predicted that a minimal ventilation rate of 4.4 hr⁻¹ is required for the stairway's CO concentration to lower to a safe concentration of 25 ppmv. At 4.4 hr⁻¹, 10 min of ventilation time is required for the safe entry into the stairway studied. Being able to predict off-gas concentrations and understand the factors controlling the emission rates will allow the industry to devise ways to minimize emissions or to manage the safe handling, storage, and unloading of wood pellets during marine transportation operations.

To consider the effect of oxygen, Fan and Bi (2012) developed a new kinetic model based on available experimental data (Kuang *et al.* 2009a, 2009b) at different container headspaces or initial amount of O₂, storage temperatures, initial O₂ concentrations, and relative humidity. A lumped three-reaction kinetic model for off-gas emissions of stored wood pellets in sealed containers was developed, accounting for the formation of CO and CO₂ and the depletion of O₂. CO and CO₂ emissions were directly related to the consumption of O₂. Two typical sets of experimental data and the fitted kinetic model are presented in Figure 3. This simple model with kinetic parameters fitted with reported experimental data showed improved agreement compared with the previous models without the consideration of O₂ effect. With

properly estimated model parameters, this new kinetic model can be used to predict off-gas emissions, oxygen depletion, and the buildup of toxic air pollutants in wood pellet storage containers/vessels.

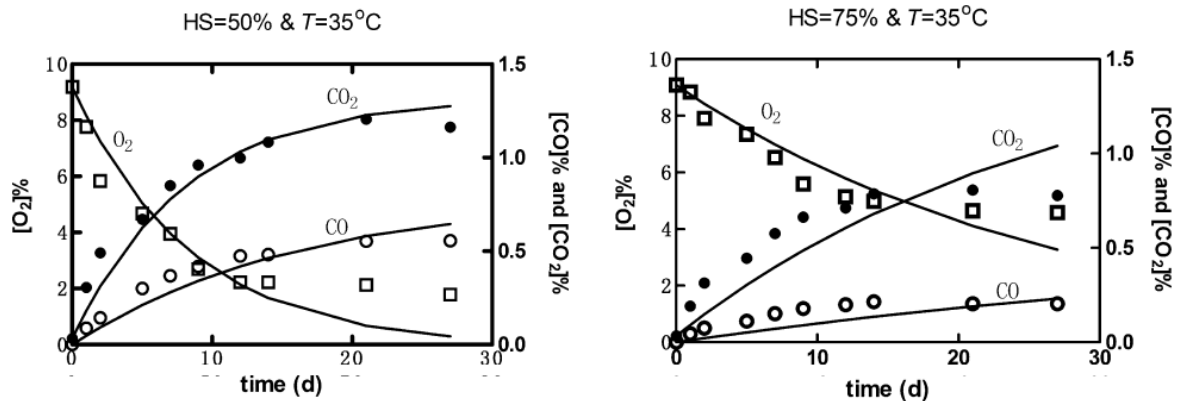


Figure 3. Comparison between fitted and experimental data for two typical sets of data. The gas concentrations in %volume (Fan and Bi 2012).

The mass balance calculations conducted do not fully explain where the oxygen goes and further analysis may disclose the potential existence of adsorption or conversion of oxygen to solid oxides (Melin 2011). Adsorption in the pellets of CO and CO₂ has also been observed. The adsorption of CO₂ was tested at +40 °C for regular white pellets, torrefied pellets and steam explosion pellets. The results indicated that torrefied pellets adsorb about twice as much gas as steam explosion pellets, most likely as a consequence of the porous characteristics of torrefied wood. The adsorption for white regular pellets was between the torrefied pellets and the steam explosion pellets. Adsorption increases with temperature and is reversely lowering as the temperature is decreasing. Additional work will be done to explore the adsorption of CO which appears to be excessive, perhaps due to a higher reactivity.

4.3 Exposure effects and occupational limit values of off-gases

The main off-gas emissions found in the investigations were hexanal, monoterpenes, CO, CO₂ and CH₄. Other compounds found were pentanal, methanol, acetone, and formic acid. The occupational exposure limit values (OEL) established for these compounds by Finnish Ministry of Social Affairs and Health (STM 2014) are presented in Table 2. The OEL values include the maximum average concentrations of a chemical in air to which workers can be exposed during a normal 8-hour working day and 40-hour week, and the maximum average concentrations to which workers can be exposed for a short period (15 minutes). Exceeding of these values in the occupational measurements at the work place means instant requirement for the employer to improve working conditions with technical measures. If these actions are not capable to reduce exposure level under OEL values, workers have to use personal protective equipment at the workplace. (Korpijärvi *et al.* 2014)

The concentration of oxygen should not decrease below 18%, otherwise the workers may start to suffer lack of oxygen (STM 2014). Finnish Institute of Occupational Health has established for total volatile organic compounds (TVOC) a reference value, which should not be exceeded in good industrial environment. The recommended value is 3000 µg/m³. For the high quality environments the established target value is 300 µg/m³. (Korpijärvi *et al.* 2014). For wood dust the OEL value has been 2 mg/m³, but concerning the new and modernized plants the value is 1 mg/m³ (STM 2014).

Koppejan *et al.* (2013) has collected examples of typical national and international dust limits. General dust level limits exist in most countries based on occupational exposure levels.

Table 2. Occupational exposure limit values (OEL) for the off-gas compounds (STM 2014).

Compound	OEL _{8 hours} ppm	OEL _{8 hours} mg/m ³	OEL _{15 min} ppm	OEL _{15 min} mg/m ³
Acetone	500	1200	630	1500
Formic acid	3	5	10	19
Hexanal			10	42
Methanol	200	270	250	330
Pentanal				
Terpenes	25	140	50	280
Carbon monoxide	30	35	75	87
Carbon dioxide	5000	9100		
Methane	1000			

Terpenes and hexanal have adverse health effects. Monoterpenes irritate mucous membranes, affecting the eyes and the respiratory systems. A hexanal exposure of 10 ppm causes ocular and nasal discomfort and results in headaches. The occupational exposure limit for terpenes is 25 ppm in Sweden, Norway, Denmark, and Finland, and 100 ppm in The United States. The released compounds also have an environmental impact - in the presence of nitrogen oxides both terpenes and aldehydes contribute to the formation of ground-level ozone and other photochemical oxidants, which disturb plant photosynthesis. (Granström 2010)

Concerning the health effects of the gases, a CO₂ concentration >15000 ppm in the air starts to cause headaches and dizziness, increases the heart rate and blood pressure and induce coma. The TLV-TWA for 8 h exposure is set at 5000 ppm in most jurisdictions. (Kuang *et al.* 2008)

The toxic effects of CO result from the formation of carboxyhemoglobin in the blood stream. CO prevents the uptake of oxygen by the hemoglobin of the red blood cells and thereby prevents the blood cells from carrying the required oxygen to the brain and other parts of the body. The TLV-TWA for 8 h exposure is between 25 and 50 ppm in most jurisdictions. Exposure to CO concentration above the threshold level can lead to dizziness and headaches, and concentrations greater than 800 ppm can result in fatal accidents. (Kuang *et al.* 2008, Tumuluru *et al.* 2010) In addition, CO is ototoxic and can affect the ear by impairing the sense of hearing (STM 2014, Nies 2012).

The dangerous combination of extremely high levels of CO and reduced oxygen produces a fast-acting toxic combination (Svedberg *et al.* 2008).

In addition to asphyxiation by replacing oxygen, accumulation of high concentrations of CH₄ in the storage bins could lead to explosions and fires (Tumuluru *et al.* 2010).

Wood dust from pine and spruce causes irritation in the eyes and upper airways at air levels between 0.1 and 6.3 mg/m³. Wood dust levels around 1 mg/m³ may cause reduced lung function. (Edman 2003)

Prevention of fatal accidents on board a vessel Svedberg *et al.* (2008) presented that measurement of both CO and oxygen levels is essential prior to entry into spaces with air communication with a cargo of wood pellets. Forced ventilation of staircases prior to entry is necessary in order to achieve safe entry conditions within a reasonable time. The provision of proper gas monitoring instruments and training and education of crews are of vital importance as well as the proper design, labelling and locking of access doors leading to confined spaces.

Replacing oxygen with inert gases in the storage space is a potentially effective method to reduce the biomass degradation and toxic off-gas emissions (Kuang *et al.* 2009b). The proper ventilation of the storage space can also be used to maintain a high oxygen level and low concentrations of toxic off-gassing compounds in the storage space, which is especially useful during the loading and unloading operations to control the hazards associated with the storage and transportation of wood pellets. (Kuang *et al.* 2009b)

In addition, Gauthier *et al.* (2012) recommended urgent revision of the safety regulations of wood pellets storerooms of private households. The continuous ventilation of the storerooms is needed to be ensured. Also, warning signs should be obligatory, not just recommended, and affixed to both the outside and the inside of the main door. A protective mesh should be provided across the doorway and the CO and O₂ levels measured with an appropriate device before entering the room.

4.4 Other properties and analyses related to storage of pellets

In addition to off-gassing characteristics, several other parameters and pellet properties related to the health and safety in the storage of pellets have been studied. A large research reactor (LRR) with a volume of approximately 3 m³ was installed at UBC to study the off-gassing characteristics under controlled conditions, including different types of ventilation, implanted disturbances in terms of material stratification and asymmetric external heating (Melin 2010). Fundamental parameters such as thermal conductivity, permeability, temperature rate increases, heat front velocity as well as quantification of gas evolution and oxygen depletion are now much better understood. Prediction models have been developed to assist the industry with recommendations for safe design and operation of facilities for storage and handling of pellets in large bulk. (Melin 2011)

Preventive measures are necessary to avoid storage fire. It is important to maintain the stored pellets under cool and dry conditions, and uniform temperature to prevent migration and localized accumulation of moisture. Forced ventilation is a management tool to reduce excessive concentration of toxic gases such as CO, CO₂ and CH₄ and to prevent possibility of spontaneous combustion. (Yazdanpanah *et al.* 2011). The permeability of pellets in bulk is a critical parameter when designing ventilation systems since it determines the size of fans required and the design of plenum for distribution of the ventilation air. BBRG has conducted experiments to establish resistance to air flow for pellets with different length, specific density and moisture content. In the laboratory setup compressed air was forced through a plenum at the bottom of a vessel filled with the wood pellets. The pressure of the air was monitored as well as the vertical pressure drop over the bed of pellets. (Melin 2011)

In the study of Yazdanpanah *et al.* (2011), bulk wood pellets manufactured from sawdust in BC were subjected to airflow in laboratory tests. Pressure drops versus airflows were measured for several sizes of cylindrical pellets. Experimental airflow rates ranged from 0.014 to 0.8 m³/s m². The corresponding measured static pressures ranged from 2 to 2550 Pa/m. The pressure drop was observed to increase with airflow rate and such increases became more profound for higher airflows. Smaller wood pellets had the highest resistance to airflow. Increasing the size of wood pellets or using a mixture of different sizes decreased the resistance.

Furthermore, the pressure drop increased with an increase in fines content (Yazdanpanah *et al.* 2010). By increasing the percent fines content from 0% to 10%, and then from 10% to 20%, the pressure drop was observed to increase by 2.1-2.7 times, depending on the airflow rate. The airflow rates used in the experiment ranged from 0.004 to 0.357 m/s. The corresponding pressure drop ranged from 1.9 to 271 Pa/m for clean pellets, from 4.8 to 1100 Pa/m for 10% fines content, and from 7.9 to 1800 Pa/m for 20% fines content.

The thermal conductivity of wood pellets is an important inherent characteristic affecting the heat transfer from one area to another in large storages. Thermal conductivity also has a

direct impact on the propensity for self-heating in pellets and the promotion of microbial decomposition, chemical oxidation and hydro-thermal moisture migration. The major factor impacting the thermal conductivity is the moisture content of individual pellets and to a much lesser degree the bulk density of the material. The heat convection transfer co-efficient was also established as 5 to 20 W/m²K at air velocities from 1 to 5 m/s. Both thermal conductivity and heat convection transfer co-efficient are of fundamental importance for proper design of safe storage facilities for pellets in bulk. (Melin 2011)

While measurement of wood pellet porosity is central in the design of storage silos and bunkers, and transportation containers, the porosity also influences the heat and mass transfer during combustion, and off-gas emissions. A novel simplified stereometric measurement method for determining the macro-porosity of wood pellets through geometrical approach was successfully developed and tested by Igathinathane *et al.* (2010). Actual wood pellets overall macro-porosity was determined as $41.0 \pm 2.5\%$ and $35.5 \pm 2.7\%$, and classified as "Class-3:Medium" and "Class-3&4:Medium to Low" for loose and tapped fills, respectively. The developed method can be used as a handy inexpensive laboratory procedure to estimate the macro-porosity of different types and makes of wood pellets.

5. Safety-technical characteristics of biomass fuels

The knowledge of safety-technical basic characteristics of biomass fuels is of essential significance when planning safety measures and instructions, handling, storage and feeding equipment, and evaluating fire and explosion hazards. Several safety-technical properties of the fuels with respect to their behaviour on hot surfaces and as dust clouds can be determined.

5.1 Self-heating

Self-heating potential and self-ignition of materials are determined experimentally often with calorimetric methods performed at small scale giving results from which kinetic parameters such as the heat of reaction (Q) and the activation energy (E) can be calculated. The kinetic parameters obtained are then extrapolated using the Frank-Kamenetskii theory to predict self-heating potential at larger scale. For determination of kinetic parameters can for example following small scale tests be used: 1) Oven basket test – FRS method, 2) Oven basket test – Crossing Point method, 3) Isothermal calorimetry, 4) Thermogravimetry, and 5) Differential Scanning Calorimeter. (Koppejan *et al.* 2013)

The International Maritime Organization (IMO) is the United Nations' specialist agency responsible for the safety and security of shipping and the prevention of marine pollution by ships. It stipulates certain requirements for allowing commodities to be transported in bulk in the International Maritime Solid Bulk Cargoes (IMSBC) Code. The Test 4.2 methodology in the UN Manual of Tests and Criteria (MTC) shall be used for determining the criticality of self-heating. The test determines if the material is allowed to be shipped in bulk in ocean vessels or if the product needs to be packaged to limit the risk for exothermic run-away conditions during transportation. The criterion for a non-self-heating substance is characterized by temperature escalation below 60 °C within 24 hours starting at 140 °C. (Melin 2013a)

The criticality of self-heating when storing wood pellets was determined at UBC by Guo by a method based on the Crossing Point method using test samples of various sizes (100, 160, 200 mm cubes) heated in an oven to temperatures reaching 200 °C. The result and validated by other research (e.g. Svedberg *et al.* 2008) as well as live tests in ocean vessel on large scale clearly indicated that wood pellets for the purpose of criticality of self-heating pass the Class 4.2 test and can be shipped in bulk and do not have to be packaged. (Melin 2013a)

Recently Guo *et al.* (2014) reported on the measurements of wood pellets self-heating kinetic parameters using isothermal calorimetry. A TAM air isothermal calorimeter was used to measure the rate of heat release by bulk pellets at temperatures of 30-50 °C. The heat release rate reached a peak value (0.33 mW/g at 50 °C and 0.04 mW/g at 30 °C) very quickly at the beginning of the test and slowly decreased with time after the peak reached due to the decrease in the oxygen concentration. Heat release rate from decomposition of stored wood pellets strongly depended on the storage temperature and the age of the pellets. It increased as the storage temperature increased, but was not sensitive to pellets moisture content. The activation energy of fresh wood pellets determined from this study ranged from 50 to 60 kJ/mol and increased with the age of the pellets. A kinetic model equation for self-heating heat release rate, which accounts for both oxygen-dependent and independent reactions, was developed from the experimental data. The model can be applied to simulate the self-heating process in pellets storage containers at different storage temperatures and age of stored pellets.

5.2 Self-ignition and dust explosion

Airborne dust from wood pellets is the cause of many fires and explosions when exposed to ignition source or heat and often results in substantial damage and injuries. Particles of combustible materials smaller than 425 μm (screen 40) are classified by the Occupational Safety and Health Administration (OSHA) as explosible dust. The size of a particle is determined by means of Aerodynamic Equivalent Diameter (AED) and relates to the density and form factor (shape) of the particle. The concept of AED is a way to relate the particle characteristics to the sedimentation speed at normal temperature and atmospheric pressure (NTP). (Melin 2013b)

The airborne dust generated during handling of wood pellets ranges in size from 500 to a few μm . The smaller the particle is the larger the relative surface area, which means increased exposure to the oxygen in the air. The larger the oxygen exposure is of combustible material the higher the risk is for open flame combustion in the presence of an igniting source or a source of heat. (Melin 2013b)

Explosion is used as a general characterization of a violent event emitting sound and light and often immediately followed by fire. Explosions occur in dust suspended in air as well as dust sediments on hot surfaces. The explosibility is a function of particle concentration, oxygen concentration, energy of the ignition source or the temperature of the heat exerted on the dust.

Standard tests are conducted on dust clouds as well as dust layers. The result of the tests generates a dust classification which is used as a guideline for how the product generating the dust should be handled and how the handling facility should be designed. The smaller the particle is the higher the explosibility. The particle size of the dust used in the testing varies between the different standards. For example in the ASTM standards sub 200 screen materials (particles 75 μm or less) are used. The ISO 6184-1 Standard recommends $\leq 63 \mu\text{m}$ as the norm for testing, ASTM E 1226 is stipulating 95% of the particles $<75 \mu\text{m}$ and a moisture content of $<5\%$, and EN 14034 Standards is recommending testing sample as received. (Koppejan *et al.* 2013)

Table 3 summarizes the standard tests and parameters of dust explosibility. The table is based on ASTM standards. There are also corresponding EN testing standards, which are used in Europe for dust. The ASTM test methods have been described by Melin (2013b). The methods were used in 2008 for testing dust from softwood and hardwood pellets. The result from the softwood dust collected in BC, Canada was the basis for the data documented in the MSDS developed by WPAC (see Section 6.1).

The Kst (Deflagration Index) is the basis for dust explosibility classification in three ranges: Kst [$\text{bar}\cdot\text{m/s}$] $>0-200$ (St 1), $201-300$ (St 2) and >300 (St 3). There are also other classifications. The US National Materials Advisory Board NMAB 353-3-80 Classification of Combustible Dusts in Accordance with the National Electrical Code defines dusts having Ignition Sensitivity (IS) ≥ 0.2 , or Explosion Severity (ES) ≥ 0.5 to be appreciable explosion hazards requiring electrical equipment for Class II locations. For dusts from white pellets manufactured in BC and bark pellets manufactured in Nova Scotia ES values of 1.40 and 1.61, respectively, were obtained. Consequently installations exposed to these dusts require equipment classified as Class II compatible. (Melin 2013b)

Table 3. Standard tests and parameters of dust explosibility (Melin 2013b).

Test Mode	Test parameter (dust 95% sub 75 μm), <5% moisture	Measure	Testing Standards
Dust cloud	Auto-Ignition Temp (Godbert-Greenwald) T_c	$^{\circ}\text{C}$	ASTM E1491
	Min Ignition Energy MIE	mJoule	ASTM E2019
	Max Explosion Pressure P_{max}	bar	ASTM E1226
	Max Explosion Pressure Rate dP/dt_{max}	bar/sec	ASTM E1226
	Deflagration Index K_{St}	bar.m/sec	ASTM E1226
	Min Explosible Concentration MEC	g/m^3	ASTM E1515
	Limiting Oxygen Concentration LOC	%	ASTM E1515 mod
	Dust Layer	Hot Surface Ignition Temp (5 mm) T_s	$^{\circ}\text{C}$
Hot Surface Ignition Temp (19 mm) T_s		$^{\circ}\text{C}$	ASTM E2021
Auto-ignition Temp T_L		$^{\circ}\text{C}$	USBM (Bureau of Mines) RI 5624
Dust Class (> 0 to 200 bar*m/sec)			ASTM E1226
Dust Class (Explosion Severity ES > 0.5)			OSHA CPL 03-00-06
Explosion severity			OSHA CPL 03-00-07
Ignition sensitivity			OSHA CPL 03-00-08
Volume resistivity & volume resistance		ohm-cm	ASTM D257
Bulk density		kg/m^3	ASTM D1895A

With the IMO 4.1 Flammability test of the UN MTC, it is established if the material under test shall be classified as flammable or not. A material burning a distance of 200 mm of a mould in 2 minutes or less is classified as flammable. The material in one end of the mould (Figure 4) is heated by a torch until it ignites and the time for burning to the opposite end of the mould is clocked. For dusts from white pellets and bark pellets the burning rate obtained in the test was 20 mm/2 min and 22 mm/2 min, respectively. Thus these two dusts were not classified as flammable. (Melin 2013b)

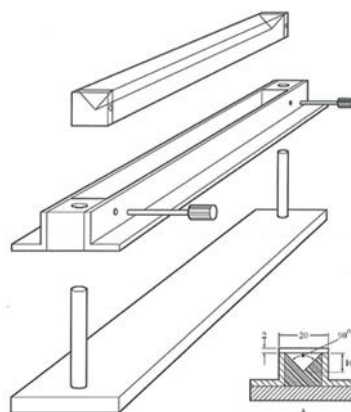


Figure 4. Mould and accessories for the IMO 4.1 Flammability test (Courtesy UN Manual of Tests and Criteria, rev. 3, 2000).

5.3 EU Project “Safe handling of renewable fuels and fuel mixtures”

Earlier, VTT participated as a coordinator in the EU project “Safe handling of renewable fuels and fuel mixtures” (JOR3-CT95-0032) within the framework Joule 3 Programme. In the project, new data on the safety-technical characteristics of renewable fuels (wood fuels and wood wastes, agricultural residues and energy crops), low-rank coals and mixtures of these, was created. The study included reactivity analyses, self-ignition tests and dust explosion tests. The results were published by Wilén *et al.* (1999).

The reactivity of the combustible dusts was characterized by thermal analysis employing a Differential Thermal Analysis (DTA) and a Thermo-Gravimetric Analysis (TGA). The objective was to rank the fuel samples according to their tendency to self-ignition. The tests at ambient pressure were carried out by Institut National de l'Environnement Industriel et des Risques (INERIS) and analyses at elevated pressure by VTT. Classification of the dust samples indicated that the low-grade coals are clearly more reactive than the biomass samples. The mixtures also showed a higher reactivity than the pure biomass fuels. Increasing the pressure leads to a higher oxygen partial pressure, increasing the aggressiveness of the oxidation. This resulted in a higher reactivity of the sample at elevated pressures. Thermoanalysis appeared to be a fast and convenient means of classifying fuels according to their reactivity.

The minimum ignition temperature of a biomass layer was between 300 and 340 °C and a little lower, 230-240 °C, for lignites. Corresponding ignition temperature of a dust cloud was higher, 400-460 °C for both biomasses and lignites. The ignition sensibility was evaluated through the determination of minimum ignition temperature (MIT) and minimum ignition energy (MIE). MIT is the lowest temperature at which the ignition of a sample occurs. The test may be conducted using a sample in the form of a cloud (MIT_c) or a layer (MIT_l). MIE is the lowest energy stored in a capacitor which upon discharge is sufficient to produce ignition of the most easily ignitable dust mixture with air under specified test conditions. The self-ignition temperature is defined as the highest temperature at which a given volume of dust will not ignite.

The self-ignition temperature of a dust deposit is a function of the size of the deposit; i.e. the self-ignition temperature falls when the size of the deposit (or storage volume) increases. The aim of the experiments in isothermal ovens was to determine the self-ignition temperature of the pulverised sample in volumes of varying sizes. Self-ignition properties of the fuels were studied at normal and elevated pressures (1-25 bar) by VTT and INERIS. The results were mainly in line with the reactivity tests carried out on DTA-TGA. The lignites were the most reactive fuels both at ambient and elevated pressure. The pure wood fuels, wood and Spanish pine, were least reactive with regard to spontaneous ignition. The wood wastes, bark and forest residues were more reactive than the agricultural straw residues. The elevated pressure had a significant effect on the self-ignition temperature of all fuel samples: increasing the pressure decreased the self-ignition temperature. Partial inerting i.e. decreasing the oxygen concentration of the ambient air atmosphere, increased the self-ignition temperature, but to a rather low degree. To establish significantly safer conditions in fuel storage, an inert atmosphere with an oxygen content well below 7% is required.

Dust explosion tests were performed in 1 m³ vessels and 20 litre spheres. The tests were performed both in normal conditions and at elevated temperature and pressure. Dust explosion parameters, maximum explosion pressure P_{max}, rate of pressure rise K_{st}-value, and lower oxygen concentration LOC were determined. The P_{max} was directly proportional to the initial pressure and fell for all fuels in the same order of magnitude. The values measured for the K_{st}-value were more scattered. Most differences can probably be associated with diverse turbulence conditions inside the explosion vessel. In most cases, and clearly for wood, the LOC slightly increased with increasing initial pressure. It was suggested that for most cases safe conditions can be obtained by decreasing the oxygen content of the surrounding atmosphere to a level of approximately 11-15 vol%. In practice a safety margin

of 2 percentage units is usually recommended. The LOC decreased with increasing initial temperature, around 1-3 vol% per 100 °C temperature rise.

Suppression systems are frequently used in industry as a measure of explosion protection. The explosion suppression tests were conducted in the heatable 1 m³ vessel. Increasing the temperature makes the suppression of the dust explosion more demanding. Use of partly inert atmosphere, e.g. by reducing the oxygen concentration from 21% to 17%, led to an increased efficiency of the explosion suppression system.

The dust explosion indices are essential for the design of protective measures. Generally very little information existed earlier in the literature regarding explosion properties of biomass fuels and especially of explosion indices measured at elevated conditions. Therefore the knowledge created within this project was considered unique.

5.4 Torrefaction project within Tekes/BioRefine Programme

The research project “Torrefaction of woody and agro biomasses as energy carriers for the European markets” coordinated by VTT was carried out within the BioRefine Programme of Tekes – the Finnish Funding Agency for Innovation during the years 2010-2012 (Wilén *et al.* 2013). It was found that hardly any information was available on the ignition and explosion properties of torrefied biomass fuels. Therefore, a limited study on dust explosion and self-ignition characteristics of torrefied wood was carried out at the Laboratorio Oficial J.M. Madariaga (LOM) in Spain (Torrent 2011, Wilén *et al.* 2013). The test material was torrefied pellets produced from whole tree wood chips at 245 °C in the PATRIG pilot rig of Energy research Centre of the Netherlands (ECN). The samples were a pellet sample for the self-ignition tests and a dust sample milled from the same pellets for the dust explosion and flammability tests.

Explosion severity

A dust explosion can be characterised as combustion of a dust cloud that results in a rapid build-up of pressure or in uncontrolled expansion effects. The generation of a dust explosion requires the simultaneous occurrence of three particular conditions: combustible dust, dispersive air (oxygen) and an ignition source. The explosion severity is usually expressed in terms of maximum explosion over pressure P_{max} and maximum rate of pressure rise (dP/dt)_{max} or K_{max}. These indices are the main ones influencing the assessment and design of different kinds of explosion relief venting and suppression. The Limiting Oxygen Concentration LOC in inertial cases indicates at which maximum ambient oxygen content an explosion is prevented. Lower Explosion Limit LEL describes the minimum concentration of the dust in a dust cloud which may generate an explosion. (Wilén *et al.* 2013)

The dust explosion tests were carried out in a 20 litre sphere (Figure 5) and conducted over a dust concentration range (explosive range) of 125-2250 g/m³. The optimum dust concentration was found to be 1250 g/m³. The tests performed were P_{max} (EN 14034-1), K_{max} (EN 14034-2), LOC (EN 14034-4), and LEL (EN 14034-3). Table 4 shows the results obtained in these tests and as a comparison corresponding values measured earlier for other fuel dusts (Wilén *et al.* 1999). The torrefied wood dust was classified as a St1 dust (K_{max} value ≤ 200 m*bar/s, explosion severity normal or low), as most fuel dusts. (Wilén *et al.* 2013)



Figure 5. A 20-L sphere used for dust explosion measurements (Wilén et al. 2013).
Photo: TNO.

Table 4. Explosion parameters of different dusts (Wilén et al. 2013).

Sample	Explosion pressure P _{max} (bar g)	Rate of pressure rise K _{max} (m ³ bar/s)	Limiting Oxygen Concentration LOC (%)
Torrefied wood dust	9.0	150	11
Wood dust	9.1-10.0	57-100	10-12
Peat dust	9.1-11.9	120-157	13.5
Lignite dust	9.4-11.0	90-176	13-15
Coal dust	8.9-10.0	37-86	14

Thermal stability

The flammability and spontaneous ignition tests performed are listed in Table 5. The flammability parameters of torrefied wood dust and other fuel dusts are presented in Table 6. The MIE of a dust cloud measured for torrefied wood dust was 160 mJ, which is of the same magnitude as that of other biomass dusts. Coal dust usually has an MIE to the order of >1000 mJ. Generally it can be concluded that the torrefied wood dust is more sensitive to ignition due to elevated temperatures or e.g. electrical sparks than coal dust.

Table 5. Flammability and spontaneous ignition tests (Wilén et al. 2013).

Parameter	Applied standard	Test device	Uncertainty
Minimum Ignition Temperature on a layer, MIT-l	EN 50281-2-1:1999	Flat oven (plate)	5 K
Minimum Ignition Temperature in a cloud, MIT-c	EN 50281-2-1:1999	Vertical oven	5 K
Minimum Ignition Energy, MIE	EN 13821:2003	MIKE3	1 mJ
Self-ignition Temperature, T _{SI}	EN 15188:2008	Isothermal oven	5 K

Table 6. Flammability parameters for fuel dusts (Wilén et al. 2013).

Material	Minimum Ignition Temperature in a dust cloud (°C)	Minimum Ignition Temperature on a layer (°C)
Torrefied wood dust	460	330
Wood dust	420	340
Peat dust	470-590	305-340
Lignite dust	410-450	230-250
Coal dust	590-760	270-450

The self-ignition tests were carried out with torrefied wood pellets. Table 7 presents the self-ignition temperatures and induction times obtained with different cylindrical cell sizes.

Table 7. Results of self-ignition tests in the isothermal oven for torrefied wood pellets (Wilén et al. 2013).

Cell size (cm ³)	Lower temp. resulting in ignition (°C)	Higher temp. without ignition (°C)	Ignition temperature T _{SI} (°C)	Induction time (min)
50	190	185	187.5	54
150	170	165	167.5	71
350	160	155	157.5	130
1500	145	140	142.5	317

Table 8 summarizes the interdependence between the size of storage bin (cubic), storage temperature and induction time. Given the experimental features of the test method and this interpretation of results through a process of extrapolation, these values should be viewed with caution.

Table 8. The influence of (cubic) storage size, temperature and time on the self-ignition behaviour of torrefied wood pellets (Wilén et al. 2013).

Storage size (m ³)	Temperature (°C)	Induction time
100	41.0	3.4 months
10	57.6	28 days
1	75.9	7.8 days
0.1	96.4	2.2 days

IMO test the transportation of dangerous goods

The IMO 4.1 flammability and IMO 4.2 self-heating tests were carried out by TNO on crushed torrefied wood pellets according to the UN MTC (United Nations 2009). Crushed pellet samples were used because it may simulate a certain degree of disintegration occurring in handling and shipping operations. Based on the results (Mak 2011), it was concluded that the investigated sample of crushed torrefied wood pellets is not flammable and has no self-heating properties. Consequently the material does not need to be classified as a flammable solid or as a self-heating substance.

Conclusions

As with most of the dusts generated during biomass handling, pre-treatment and processing steps, dust and dust layers of torrefied biomass are susceptible to dust explosions and self-ignition. The safety-technical characteristics of the torrefied dust do not differ significantly from those of normal biomass dust, but are clearly more reactive than coal dust. Torrefied wood pellets are drier and more brittle than conventional wood pellets. Severe dusting during the unloading and conveying of torrefied pellets has been observed. Due to a very fine particle size and almost zero moisture content, the torrefied dust may ignite more easily and thus create a larger dust explosion risk than conventional biomass dusts and coal dust. The elimination of dust formation and ignition sources is therefore critical in the whole utilisation chain. The self-heating and spontaneous ignition behaviour of the torrefied wood pellets is more difficult to predict, partly because of the long time span these reactions require, but these hazards cannot be neglected in the large-scale storage of the fuel.

6. Regulations and guidelines on health and safety issues of wood pellets and torrefied biomass

6.1 MSDS of Wood Pellet Association of Canada

Material Safety Data Sheets (MSDS) for wood pellets in bulk and for wood pellets in bags have been developed by the Wood Pellet Association of Canada (WPAC) and BBRG at UBC. The latest MSDS for wood pellets in bulk has been dated in January, 2014 (Melin 2014). The MSDS for wood pellets in bags is meant for wood pellets packaged in bag smaller than 25 kg (Melin 2009^a).

The MSDS has been done for regular pellets including wood pellets, fuel pellets, whitewood pellets, softwood pellets, hardwood pellets, and bark pellets. The use of pellet product comprises fuel for conversion to energy, animal bedding and adsorbent. Draft of a Safety Data Sheet (SDS) for wood pellets is now underway to replace the current MSDS for wood pellets. It will be based on the UN Globally Harmonised System (GHS) guidelines. An MSDS or SDS for torrefied materials does not exist yet (Melin 2015).

In comparison to the older one (Melin 2009^b), the latest MSDS for wood pellets in bulk (Melin 2014) contains as modifications an introduction of the MARPOL classification and in definition of dust explosibility a change of particle size from 63 µm to 95% sub 200 (<75 µm). According to the MARPOL classification the material is not considered harmful to the marine environment or to animals or humans.

The MSDS for wood pellets in bulk contains information and regulations on product identification and use, composition and physical properties, health hazard data, first aid procedures, fire and explosion measures, accidental release measures, safe handling and storage, exposure control and personal protection, stability and reactivity data, and exposure and toxicological data. In the following the sections III-X will be shortly reviewed.

The basis for the Health hazard data (Section III) is as follows: Wood Pellets emit dust and gaseous invisible substances during handling and storage as part of the normal degradation of all biological materials. Ambient oxygen is typically depleted during such degradation. The sizes of the particulate matter range from crumbs to extremely fine airborne dust. The dust normally settles on surfaces over time. The emitted gases are immediately diluted by the air in the containment and escape with the ventilation air. If the wood pellets are stored in a containment which is not ventilated (naturally or forced) the concentration of emitted gases, or the oxygen depletion, may pose a health threat for humans present in the containment and the containment should be ventilated and precautions should be taken as specified in this MSDS. Section IX prescribes a method of estimating the concentration of gases. The gases emitted at normal indoor temperature include CO, CO₂, CH₄ and hydrocarbons. Their Permissible Exposure Levels (PEL) and symptoms are presented.

First aid procedures (Section IV): Wood pellets are considered a benign product for most people. However, individuals with a propensity for allergic reactions may experience reactions and should contact their physician to establish the best remedial action to take if reaction occurs.

In case wood pellets are not handled or stored in accordance with recommendations in Section VII the risk of harmful exposure increases, particularly exposure to concentration of CO higher than stipulated PEL in Section III. In case of exposure it is important to quickly remove the victim from the contaminated area. Unconscious persons should immediately be given oxygen and artificial respiration. The administration of oxygen at an elevated pressure has shown to be beneficial, as has treatment in a hyperbaric chamber. The physician should

be informed that the patient has inhaled toxic quantities of carbon monoxide. Rescue personnel should be equipped with self-contained breathing apparatus when entering enclosed spaces with gas.

CO is highly toxic by means of binding with the hemoglobin in the blood to form carboxy-hemoglobin, which cannot take part in normal oxygen transport, greatly reducing the blood's ability to transport oxygen to vital organs such as the brain. Asphyxiating gases like CO₂ and CH₄ are primarily hazardous by means of replacing the air and thereby depriving the space of oxygen. Person exposed to oxygen depleted conditions should be treated the same as a person exposed to CO.

Fire and explosion measures (Section V): Wood pellet is a fuel and by nature is prone to catch fire when exposed to heat or fire. During handling of wood pellets there are three phases with various levels of stability, reactivity and decomposition products: solid intact wood pellets, crumbs or dust, and non-condensable (primarily CO, CO₂ and CH₄) and condensable gases (primarily aldehydes, acetone, methanol, formic acid). For extinguishing a fire in wood pellets to be successful special methods are required and presented.

Accidental release measures (Section VI): If wood pellets are released in a populated area, the material should be removed by sweeping or vacuuming as soon as possible. Wood pellets are a fuel and should preferably be disposed of by means of burning. Deposition of wood pellets or related dust should be such that gas from the material does not accumulate. A protective mask should be worn to prevent inhaling of dust during cleanup.

Safe handling and storage (Section VII): Precautionary measures are recommended to avoid hazardous conditions by the reactivity as outlined in Section IX from developing when handling wood pellets.

Exposure control and personal protection (Section VIII): Precautionary measures shall be taken for personal protection

Stability and reactivity data (Section IX): The stability and reactivity properties of wood pellets are presented. Concerning off-gassing, emission of CO, CO₂ and CH₄ from wood pellets contained in a space is a function of temperature, ambient air pressure, bulk density, void in wood pellets, access to oxygen, relative humidity in air (if ventilated) as well as the age and composition of the raw material. The emission rate in grams (g) of off-gassing per tonne of stored wood pellets given are from measurements of gas generated within a sealed containment filled with wood pellets at approximately constant pressure without ventilation over a period of >20 days. The emission factors values are only valid for sealed containment without sufficient oxygen available to support oxidation of the wood pellets. The numbers should not at any time be substituted for actual measurements. Examples are given to illustrate how the emission factors can be used for estimating a rough order of magnitude of the gas concentration in a non-ventilated as well as a ventilated containment with wood pellets, assuming the ambient air pressure is constant.

Concerning oxidization, it is believed that a combination of microbial decomposition of biological material, chemical oxidation of fatty acids contained in the woody material and thermo-dynamic moisture migration are the primary causes for depletion of oxygen and emission of gas species as exemplified above during storage of wood pellets or related dust. The depletion ratio is a function of temperature, pressure, bulk density, void in wood pellets, relative humidity in air (if ventilated) as well as the age and composition of the raw material. The numbers given are from measurements of gas generated within the space of the wood pellets at approximately constant pressure. The numbers should not at any time be substituted for actual measurements.

Exposure and toxicological data (Section X): The feedstock is the basis of the toxicological characteristics of wood pellets. The available data does not make a clear distinction between

whitewood and bark material. The toxicological data applies primarily to the material in form of dust. Respirable dust means particles with an AED < 10 µm capable of deposition in nasal, thoracic and respiratory regions.

Dust from certain hardwoods has been identified by International Agency for Research on Cancer (IARC) as a positive human carcinogen. An excess risk of nasal adeno-carcinoma has been reported mainly in those workers in the industry exposed to wood dusts. Some studies suggest workers in the sawmilling, pulp and paper and secondary wood industries may have an increased incidence of nasal cancers and Hodgkin's disease. However, IARC concludes that the epidemiological data does not permit a definite assessment. Dust from Western Red Cedar is considered a "Nuisance Dust" [=containing less than 1% silicates (OSHA)] with no documented respiratory carcinogenic health effects by American Conference of Governmental Industrial Hygienists (ACGIH). Cedar oil is a skin and respiratory irritant.

6.2 Development of MSDS for torrefied biomass

Within the SECTOR project a general material safety data sheet (MSDS) for torrefied biomass as fuel based on the European Regulation (EC) No. 1907/2006 of the European Parliament and of the Council (2006) was drafted. The Deliverable D8.6 (Ziegler *et al.* 2015) is the result of collaboration between members of the project, supported by the International Biomass Torrefaction Council. It aimed to highlight existing gaps in the knowledge about torrefied material. The deliverable consists of three parts:

- Part I: General description and additional information about the development of an MSDS.
- Part II: Detailed characterization of the MSDS for torrefied biomass according to the requirements for the compilation of safety data sheets (2006).
- Part III. Template made for MSDS users. Companies have to modify it according to their own specific product.

Due to the thermo-chemical production process and its porous fine particle structure of torrefied biomass a safety data sheet (SDS) is needed for distribution on the market. SDSs should be produced for all substances and mixtures which meet the harmonized criteria for physical, health or environmental hazards under the GHS and for all mixtures which contain substances that meet the criteria for carcinogenic, toxic to reproduction or target organ systemic toxicity in concentrations exceeding the cut-off limits for SDS specified by the criteria for mixtures. Therefore the document according to the European regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) was developed.

Whether a registration under REACH for torrefied material is required cannot be determined unequivocally at the present time. The biomass feedstock does not require it, neither from lignocellulose plants nor agriculture residues. By subjecting the biomass to a heat treatment in an oxygen deficient environment the resulting product is more comparable to coal, which is not under the obligation to register and is covered by the regulation in Annex V/7. The question is if the heat treatment can be considered as a chemical treatment or not, the torrefaction process tends to modify the natural occurring substance somewhat by mainly removing water, and weakening the strength of the hemicelluloses.

In spite of the question whether a registration is necessary or not, an MSDS facilitates safe trading between different countries and business partners. The document compiled provides a template for the independent development of an MSDS. Clear identification of the substance or mixture is a pre-condition to most of the REACH processes. If the substance or mixture has any hazards, no matter if it is from a chemical or natural compound, information

on toxic effects concerning human, physiochemical or environmental hazards should be provided by the manufacturer or importer.

The original requirements of REACH for SDS have been further adapted to take into account the rules for safety data sheets of the GHS of Classification and Labelling of Chemicals and the implementation of other elements of the GHS into EU legislation that were introduced by Regulation (EC) No 1272/2008 (CLP Regulation) via an update to Annex II of REACH.

In part II the requirements according to REACH and connected regulations are given and a suggestion how this possibly can be solved for already produced torrefied material regarding currently available scientific knowledge. As a guideline the requirements for the compilation of safety data sheets (Annex II in European Regulation 2006) is used.

In part III the suggestion for an individual MSDS is given. This version comprises necessary information and gives decision suggestions for potential MSDS users to adapt it on their product.

Information given in the MSDS is partially based on experiences and empirical values gained by dealing with torrefied material within and beyond the SECTOR project. A round of experts from several companies and institutions (e.g. Topell Energy, ECN, CENER, OFI, AEBIOM) discussed the sections to collect profound knowledge to ensure the protection of human health and safety at the workplace as well as the protection of the environment.

As a conclusion it was stated that torrefied biomass is in a stage of development regarding its production technology and its optimal feedstock and process parameters (Ziegler *et al.* 2015). Currently first commercial plants enter the market with torrefied wood pellets. Against this background a possibly needed REACH registration has not been done yet. Several issues have still to be examined. Studies on different issues, e.g. toxicological information, have to be made in future to collect a broad database for a potential classification and registration of torrefied biomass to accomplish the requirements given by REACH. Altogether it can be stated that despite some open questions a safety data sheet for torrefied biomass can be generated by the use of the available knowledge to ensure an SDS with the required information in most parts.

6.3 Transportation of wood pellets

During transportation of pellets occupational hazards can occur. The size, shape, moisture content and type of raw material influence the transport, handling and storage properties of a solid biofuel. Koppejan *et al.* (2013) has dealt with occupational hazards in transporting solid biofuels by truck, ship and train, which will be reviewed in the following. Truck transport of wood pellets includes mainly transport of pellets from producer/harbour to an intermediate storage or end user. The health risks result mainly during loading and unloading where high dust concentrations may result in a risk of dust explosions and human exposure to dust and microspores. There are two types of trucks for transport of pellets: tank trucks that pneumatically blow the pellets to the customer, and trucks with flatbed for unloading by rear tipping. Loading of flatbed trucks is done with frontend loaders or conveyor belt and can cause heavy dust exposure to buildings, equipment and personnel. There are instructions for the driver to keep distance and use breathing mask if necessary. An indoor loading facility for pellets using frontend loader caused a heavy dust explosion in a Danish pellet factory in 2010. Static electricity can cause dust explosion during unloading if the hose from the truck to the storage is rubber and not metal. Exposure value limits recommended by various regulatory bodies have been given in the MSDS for wood pellets (Melin 2014).

A large proportion of the wood pellets produced worldwide are shipped by ocean vessels. The safety in ship transport regulated by IMO includes significant safety issues onboard vessels, in terminal storage and during handling. Cargo holds are sealed during ocean voyage which results in very fast oxygen depletion and generation of CO, CO₂, CH₄ and

some H₂. Entry into cargo holds and communicating spaces are prohibited unless the spaces have been thoroughly ventilated and the gas concentration has been verified by a combination of oxygen and CO measurements. An appropriate instrument for measuring shall be provided together with detailed instructions for its use. The shipper has to provide a Shipper Cargo Information Sheet to the master of the ocean vessel about the properties of the cargo. Material Hazardous in Bulk (MHB) includes for example wood pellets. Such products are subject to restrictions in handling, storage and segregation, ventilation and emergency actions in case of fire. The current safety code for transportation of wood pellets in the IMSBC Code have a conditional requirement stipulating that carriage should be done onboard vessels with fixed gas fire extinguishing equipment since the schedule for wood pellets says that wood pellets may emit flammable gases. Recent research (Melin 2013) has however proven that the gas mixture emitted, even if the pellets are damaged by water up to 15% or higher and stored in temperature up to +60 °C, does not reach flammable concentrations. Application has been done by WPAC to re-classify wood pellets and allow carriage in regular vessels. An additional requirement, MTC 4.2 Test (see section 5.1) has been added as a condition regarding self-heating for all cargoes carried in ocean vessels. Recent research (Melin 2013a) has clearly indicated that it can be shipped in bulk.

In train transport, pellets are transported by tank or grain cars with a capacity ranging from 60 to 110 tons in large volumes from pellet plants to power plants or to shipping ports. It is crucial to make sure the pellets are cool (below 30 °C) before leaving the pellet plant in order to avoid overheating during transportation during summertime. When a rail car is exposed to the hot sun the temperature inside is known to reach +50 °C or even 65 °C. At this temperature the air can hold a lot of moisture. When a cycle of heating and cooling is repeated a number of times it creates an ideal condition for microbial growth followed by self-heating. There are several instructions how the pellets must be transported in rail cars. During discharge of pellets from rail cars substantial amounts of gas is entrained in the flow and will accumulate in the pit in which the pellets are dumped.

6.4 Development of ISO standards for safety issues of wood pellets

A new working group for safety issues within ISO TC 238 Solid biofuels was established in 2014. The working group “WG 7 – Safety of solid biofuels” will develop new standards on safety issues for wood pellets. The standards under development are listed in Table 9. For the development of the standards a list of relevant documents and articles on analysis of off-gassing products from pelletized biofuels has been collected. This list has been reviewed in this report.

Table 9. The standards that are under development in the working group WG7 – Safety of solid biofuels.

Standard	Contents
ISO/AWI 20023 Solid biofuels – Safety of solid biofuel pellets – Safe handling and storage of wood pellets in residential and other small scale applications	Will include the supply chain from loading the truck at pellet plant up to filling the end-user storage. It is targeted also for planning and construction.
ISO/AWI 20024-1 Solid biofuels – Safe handling and storage of solid biofuel pellets in commercial and industrial applications – Part 1: General	Will provide principles and requirements for safe handling and storage of solid biofuel pellets in commercial and industrial applications.
ISO/AWI 20024-2 Solid biofuels – Safe handling and storage of solid biofuel pellets in commercial and industrial applications – Part 2: Detection, suppression and management of fire and explosion	Will give specific guidance on detection and suppression systems and preparatory measures to enable safe and efficient firefighting operations.
ISO/AWI 20048 Solid biofuels – Determination of off-gassing and oxygen depletion	Will present analytical methods for the determination of off-gassing from and oxygen depletion by solid biofuel pellets. Special procedures for sampling and sample handling of solid biofuel pellets prior to the analysis are established.
ISO/AWI 20049 Solid biofuels – Determination of self-heating	Will present analytical methods for determination of the self-heating.

7. Logistics and utilisation of torrefied biomass

Torrefaction is a thermochemical treatment where a biomass feedstock is heated at 200 to 300 °C for about 30 minutes under atmospheric pressure and in the absence of oxygen. The main objective is to use the torrefied biomass (“biocoal”) as a fuel, especially as a pellet, with similar grinding properties and storability as coal, for co-firing at pulverized coal power plants.

The supply chain of torrefied biomass (Figure 6) is generally the same as for wood pellets logistics. From a safety perspective conveying, storage, loading and unloading, milling and feeding operations of torrefied biomass are the most relevant points. Potential safety issues along the value chain are similar as for wood pellets, and mainly related to self-heating, dust emissions, off-gassing and oxygen depletion. Proper handling and monitoring are required to minimize the risk for damage and financial losses. (Stelte 2014)

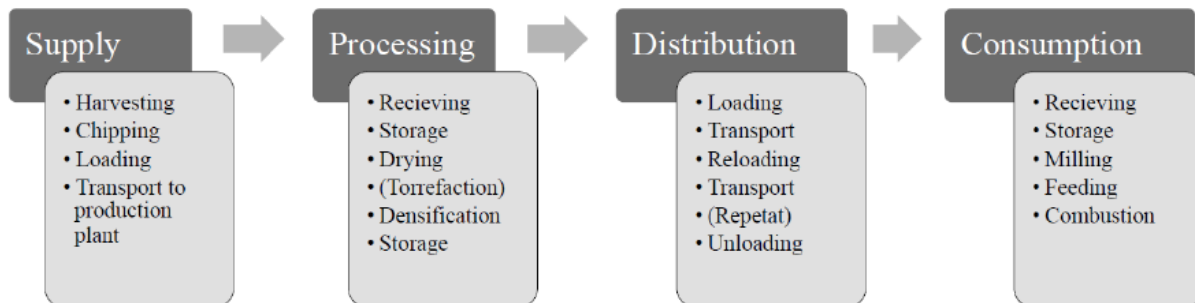


Figure 6. Value chain of energy carriers made from torrefied biomass (in Stelte 2014).

The most cost efficient method for long distance shipping of torrefied biomass, i.e. from North America to Europe is ocean shipping, preferably in bulk carriers similar to the ones used for wood pellets today. Currently torrefied material does not have a safety classification under IMO yet and can therefore not be transported by ocean vessels without special permission since it has similarities with charcoal, which is prohibited to be transported in bulk. Short distance transport of torrefied biomass is made by train, truck and boats similar as for wood pellets. The torrefaction industry is currently working on the safety classification of energy carriers made from torrefied materials to ease transportation formalities and connected insurance issues. (Stelte 2014)

The utilization of torrefied biomass in coal-fired power plants has been tested by European power producers. Within the SECTOR project, existing handling and storage facilities at the existing five coal-fired power plants of RWE, EON and Vattenfall were described. On the basis of this description and the experiences with co-firing biomass (and in some cases also thermally pre-treated biomass) the critical logistic steps were identified when switching from coal to torrefied biomass. (Zwart *et al.* 2012)

Although the plants evaluated applied different coals (both lignite and hard coal) and/or conversion technology (both pulverized coal combustion and entrained flow gasification) the existing handling and storage facilities were not that different, and as such the issues foreseen in handling and storing (torrefied) biomass were rather similar. In the handling and storage, a distinction can be made between (i) supply to the power plant, (ii) the handling and (iii) the storage at the power plant and (iv) the end-use in the power plant. The specific issues related to these four sections and some possible requirements to deal with them are presented in Table 10. However, it should be determined by means of tests if all these foreseen issues are indeed relevant. In all steps considerations must be taken regarding

safety, workplace environment and health aspects, emissions to air and consequences on fuel properties affecting the plant performance.

Table 10. The specific issues and specific requirements foreseen in handling and storage of (torrefied) biomass (Zwart et al. 2012).

System	Specific issues	Specific requirements
Supply (delivery and un-loading)	Durability in relation to moisture content and dusting problem Parameters for dust explosion	Solution to avoid / minimize effect of dusting are needed Safety measures connected to dust explosion must be applied
Handling (transportation & transition station)	Durability in relation to moisture content and dusting problem Parameters for dust explosion Transportability due to shape of pellets (or briquettes) Odour Delivery and removal from bunkers	Solution to avoid / minimize effect of dusting are needed Safety measures connected to dust explosion must be applied Keep equipment and surfaces free from dust Avoid pellets fall off from the conveyor or backwards due to high inclination Evacuation system may be needed to avoid odour Modify existing excavators Modify existing scrapers
Storage (coal yard and boiler bunkers)	Durability in relation to moisture content and dusting problem Bulk density Biodegradation Weather resistance properties Height of outdoor stock piles Self-heating and ignition Odour Off-gassing Eluate properties	System for smooth feeding into silo may be needed to avoid fines In case of outdoor storage use of front loaders might be limited Safety protection system to avoid self-ignition will be needed Evacuation system may be needed to deal with odour and off-gassing System for handling of eluate will be needed
End-use (mixing, drying, grinding & feeding)	Effects on homogeneity of the fuel Decision on mixing point Effect on milling capacity & energy Parameters for dust explosion Risk of drying with hot flue gas	Control of feeding rate Extra mill supervision for optimal operation Either co-milling in existing mills or dedicated milling in new mills Safety measures connected to dust explosion must be applied

The key fuel properties identified were (i) the durability of the pellets in relation to the actual moisture content and the consequent dusting problem, (ii) self-ignition and consequential safety measures that must be applied and (iii) odour and consequential safety aspects and possibility to use the fuel in residential areas.

Dusting has been identified as a particularly critical issue connected to handling of thermally treated biomass and there is a crucial need for a method for quantifying dusting properties. Pellet breakage and fines generation were higher in the torrefied pellet than in a reference white wood pellet sample in SECTOR project handling tests (Weatherstone *et al.* 2015). This indicates higher material loss of torrefied than wood pellets in supply chain, and dust management strategies within the plant would need to be reviewed. Controlling dust emissions when conveying, loading and un-loading at the power plant site has also been mentioned by several end-users as an important issue. Conveying of torrefied biomass at the plant site has been reported un-problematic. Coal conveyors can be used for torrefied biomass.




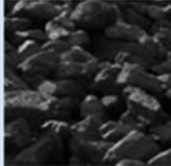
Outside storage of torrefied pellets at a coal yard exposes them to sun, rain, wind and frost that can alter the product and result in emissions such as dust or leachate. Risks for self-heating, ignition and degradation during outside storage are currently under investigation and depend on multiple factors such as climate, pile size and shape as well as pellet quality. Safety measures valid for coal yards should be applicable to torrefied biomass pellets. Degradation of torrefied pellets due to climatic effects increases the risk for dust formation for subsequent conveying operations.

The outdoor stockpile tests of the SECTOR project indicated that the torrefied pellets are not suitable for long-term storage outside (Weatherstone *et al.* 2015). Pellets absorbed moisture and lost their mechanical durability on exposure to rain. Moisture absorption leads to decreased net calorific value, and a decrease in durability causes more dusting during the handling steps. However, the rate of this deterioration in quality occurred more slowly than that of white pellets. During the first weeks of storage tests only surfaces of the pellets piles showed significant deterioration which suggests that torrefied pellets could survive temporary storage outside to e.g. facilitate ship loading. It may be possible to extend storage periods through the use of sheeting or simple covers to prevent direct rain exposure (Thrän *et al.* 2015). Outdoor storage as covered was also suggested after small scale handling and storage tests (Korpijärvi *et al.* 2014). Storage as uncovered can increase the pellets moisture content up to a level suitable for fungal degradation (Kymäläinen 2015).

8. Comparison of torrefied pellets to wood pellets

Torrefied pellets have a number of characteristics that offer clear advantages compared with conventional wood-based fuels, such as low moisture content, low uptake of moisture, high energy content, resistance against biological degradation, and good grindability in coal mills. In Table 11 characteristics of torrefied pellets in comparison with wood chips, wood pellets and coal are presented.

Table 11. Characteristics of torrefied pellets, wood pellets and coal (Thr n et al. 2015, Alakangas et al. 2015).

	Wood chips	Wood pellets	Torrefied wood pellets	Coal
Moisture content (w%)	30 – 55	7 – 10	1 – 10	10 – 15
Net calorific value (Q) (MJ/kg) <i>as received</i>	7 – 12	15 – 17	17 – 24	23 – 28
Volatile matter (VM) (w%, dry basis)	70 – 84	75 – 84	55 – 80	15 – 30
Fixed carbon (C _f) (w%, dry basis)	16 – 25	16 – 25	22 – 35	50 – 55
Bulk density (BD) (kg/m ³)	200 – 300	550 – 650	550 – 800	800 – 850
Energy density (E) (MWh/m ³)	0.4 – 1.0	2.2 – 3.1	3.3 – 5.3	5.0 – 6.7
Hygroscopic properties	hydrophilic	hydrophilic	moderately hydrophobic	hydrophobic
Biological degradation	fast	fast	slow	none
Milling requirements	special	special	standard (feedstock-specific)	standard
Product consistency	limited	high	high	high
wt% = weight percentage	 © Kay Schaubach / DBFZ	 © Thomas Siepmann / pixelio.de	 © Kay Schaubach / DBFZ	 © Gabi Sch�nemann / pixelio.de

In the studies of J rvinen and Agar (2014) storage and handling properties of pellets made of torrefied pine, logging residues and beech were compared with wood pellets. The measured properties included calorific value, bulk density, durability, hardness and equilibrium moisture content. Superior properties of torrefied pellets to conventional wood pellets included higher calorific value (4-10%), greater energy density (max 11%), lower equilibrium moisture content, and resistance to moisture. Mechanical durability of torrefied pellets was found to be inferior ranging from 80% to 92%. The hardness of all torrefied pellets was less than for conventional pellets. Based on the results, the feedstock choice had a strong influence on properties of torrefied pellets. Outdoor heap storage of torrefied pellets was not recommended. In addition, logging residues did not seem to be an optimal feedstock for torrefied pellets.

During torrefaction, the biomass loses some of the low-volatile components and extractives resulting in a hydrophobic product low in moisture content. Torrefaction temperatures >200 °C result in breakage of inter- and intra-molecular, hydrogen, C–O, and C–C bonds. Breaking chemical bonds leads to the emission of hydrophilic and oxygenated compounds. Also, the destruction of OH groups during torrefaction makes biomass hydrophobic and increases storage stability. (Tumuluru *et al.* 2015) Based on the immersion tests of Järvinen and Agar (2014) higher torrefaction temperature resulted in a more water-resistant pellet.

The comparisons between wood and torrefied pellets presented above in this report will be compiled in the following. The supply chain of torrefied biomass is generally the same as for wood pellets logistics. Potential safety issues along the value chain are similar as for wood pellets, and mainly related to self-heating, dust emissions, off-gassing and oxygen depletion. (Stelte 2014)

During storage, microbial decomposition is generally low in wood pellets because of their low moisture content and normally high temperatures in drying and in pelletizing. Emissions from torrefied biomass in the investigations of Tumuluru *et al.* (2015) indicated that microbial degradation may not be the reason for off-gas emission, because torrefied biomass has less moisture and adsorbs little moisture during storage (Tumuluru *et al.* 2015). It has however been shown experimentally that in storage torrefied wood can be subjected to biological degradation and thus seem to not have full resistance towards fungal degradation (Kymäläinen *et al.* 2014). Biological degradation and changes in moisture content and composition were recorded in five-month storage trials with covered and uncovered storages for torrefied pellets and steam–explosion pellets (Kymäläinen *et al.* 2015). The pellets showed varying responses to storage in terms of durability and moisture absorption with the steam-explosion pellets possessing more favorable properties than torrefied and untreated pellets. It was considered that torrefied material must be stored in a covered setting, but silos do not seem necessary. Unlike untreated pellets, which require closed containers to maintain their quality, torrefied and steam-exploded pellets were not found to suffer from covered storage.

The investigations of Tumuluru *et al.* (2015) indicated that torrefied wood chip emits less CO, CO₂, and CH₄ when compared to wood pellets, untreated wood chips, and ground switchgrass. At 20 and 40 °C, wood pellets recorded the maximum CO concentrations of 1600 and 13 000 ppmv, whereas torrefied wood chips emitted less than 200 and 2000 ppmv (Figures 7 and 8). CH₄ was negligible for all feedstocks except for wood pellets at the end of storage at 40 °C. According to Kuang *et al.* (2008) European wood pellets were found very sensitive to the temperature increases within the ranges of 20-55 °C. Torrefied woodchips, on the other hand, were less sensitive to temperature increases (Table 1). The removal of VOCs during the torrefaction process was suggested a likely explanation why emission of gases from torrefied wood is less sensitive to the temperature.

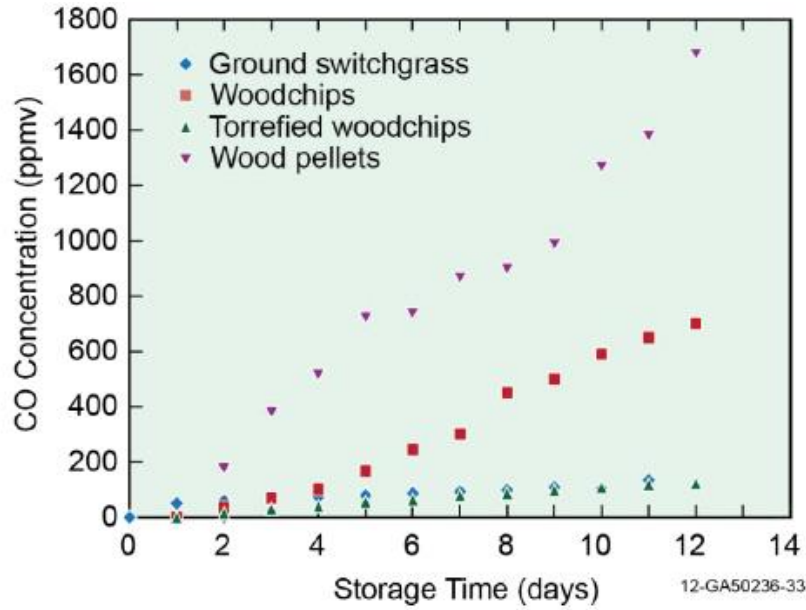


Figure 7. Emission level of CO from different biomass samples at 20 °C storage temperature (Tumuluru et al. 2015).

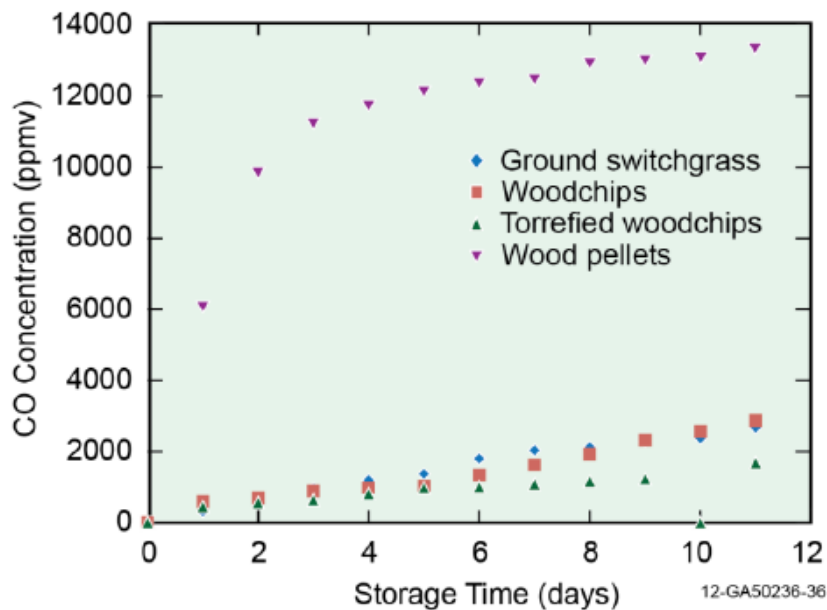


Figure 8. Emission level of CO from different biomass samples at 40 °C storage temperature (Tumuluru et al. 2015).

Concerning adsorption of CO and CO₂ in the pellets, torrefied pellets has found to adsorb about twice as much gas as steam explosion pellets, most likely as a consequence of the porous characteristics of torrefied wood. The adsorption for white regular pellets was between the torrefied pellets and the steam explosion pellets. Adsorption was increased with temperature. (Melin 2011)

The safety-technical characteristics of the torrefied dust do not differ significantly from those of normal biomass dust, but torrefied dust is clearly more reactive than coal dust. Torrefied wood pellets are drier and more brittle than conventional wood pellets. Severe dusting during

the unloading and conveying of torrefied pellets has been observed. Due to a very fine particle size and almost zero moisture content, the torrefied dust may ignite more easily and thus create a larger dust explosion risk than conventional biomass dusts and coal dust. Explosion pressure and pressure rise indices also indicate more severe explosion behaviour of torrefied wood dust compared to most coal dusts (Wilén *et al.* 2013).

According to Melin the most significant difference between regular pellets and torrefied pellets is the explosibility characteristics of dust. The minimum ignition energy for regular pellets dust is 17 mJ. The equivalent number for torrefied material has been found to be 3-30 mJ depending on degree of torrefaction. The minimum explosible concentration is 70 g/m³ for regular pellet dust and only 30-60 g/m³ for torrefied material. (Melin 2015, Melin 2014)

The results obtained in the IMO flammability and self-heating tests have shown that the white pellets, bark pellets and torrefied pellets do not need to be classified as flammable solids or as self-heating substances (Melin 2013a, Melin 2013b, Wilén *et al.* 2013). Therefore they can be shipped in bulk. Currently torrefied material does not, however, have a safety classification under IMO yet and can therefore not be transported by ocean vessels without special permission since it has similarities with charcoal, which is prohibited to be transported in bulk. Short distance transport of torrefied biomass is made by train, truck and boats similar as for wood pellets. (Stelte 2014)

Torrefaction increases the reactivity such as self-heating although specific numbers have not been established yet since the degree of torrefaction significantly impacts the self-heating. The reactivity is directly proportional to the exposure to oxygen and the concern is primarily for shipments in bulk. For transportation of torrefied material a new SDS needs to include characterization of reactivity such as self-heating and gas flammability.

To conclude the main health and safety risks, their effects and protective measures against them in the supply and utilization chain of torrefied pellets are compiled in Table 12.

Table 12. The main health and safety risks, their effects and protective measures in the supply and utilization chain of torrefied pellets.

Risk	Likelihood	Effects	Protective measures
Dusting - in loading, unloading and conveying of pellets	High	Irritation in the eyes and upper and airways, impaired respiratory functions, asthma Increased reactivity of dust Spontaneous ignition Dust explosion	Dust classification with standard tests Controlling dust emissions Elimination of dust formation and ignition sources in the whole utilisation chain, keeping equipment and surfaces free from dusts Central vacuum cleaners Automation Ventilation
Self-heating in storage due to - absorption of moisture in pellets - microbiological growth in pellets	Medium	Spontaneous ignition Dust explosion Health hazard from airborne microspores: moulds, actinomycetes, OTDS, allergic alveolitis	Protected storage (covered) Storage under cool and dry conditions and at uniform temperature Homogeneity of the fuel Temperature and moisture measurements Safety protection system
Off-gassing (chemical oxidation of fatty acids) - in storages and stairways in ocean vessels - in manufacturing (drying, milling, pelletizing) - in residential storages	Low	Release of non-condensable gases (CO, CO ₂ , CH ₄) and condensable compounds (e.g. hexanal) harmful and toxic for humans causing serious and fatal accidents Odour (ketones, aldehydes) Oxygen depletion Release of heat, self-heating, spontaneous ignition	Measurement of CO and O ₂ prior to entry, proper gas monitoring equipment, warning signs Forced ventilation of staircases Education of crews Replacing O ₂ with inert gases Optimal raw material blend (age, composition) and process parameters (storing, drying, milling, cooling) Restricting of temperature and relative humidity, appropriate headspace ratio in storage Evacuation system to deal with odour and off-gases

9. Summary

Biomass as an organic material can cause health and safety risks during handling, processing, and storage of the material. Related health and safety factors are biological agents, chemical agents, physical factors, self-heating, off-gassing, self-ignition and dust explosion. The pellet production and logistics chain includes storing, crushing, grinding, drying, and milling of biomass raw material, pelletizing, and cooling, screening and storing of the pellets, as well as transportation of the pellets to the customer. The torrefied pellets production chain includes in addition to these the torrefaction process step after drying. Occupational health hazards and fatal incidents during the supply chain of wood pellets have been detected during the 2000s. Hence several investigations on the risks have been carried out and reported. So far these aspects for torrefied pellets have been studied and published only very restrictedly. The aim of the report was to compile the recent studies on the health and safety issues in the logistics of wood and torrefied pellets.

The biomass materials are susceptible to heat generating processes from biological metabolic reactions (microbiological growth), exothermic chemical reactions (chemical oxidation) and heat-producing physical processes (e.g. moisture absorption) and are thus prone to self-heating and spontaneous ignition.

It is a common practice to store fresh pellet raw material for up to several months at pellet plants. The most common storage method at pellet plants is to stockpile the wet raw material in large piles as chips or sawdust. Moist biomass releases heat, different humidity zones are formed in the storage and mean moisture content of the fuel can be changed. The most factors causing problems are heat development with a possible risk of self-ignition, losses of dry matter and calorific value, and potential health hazard from airborne microspores. Storage can alter the composition of the wood material, and affect the pelletizing process and the quality of the pellets. The wood pellet industry generally believes that a blend of fresh and stored (mature) sawdust is the best raw material for pellet production.

Drying of the wood raw material is an important part of the pelletizing process. In drying different organic compounds are released. The emissions are affected e.g. by raw material, type of dryer, and drying temperature. The compounds emitted in wood drying have been categorized into volatile organic compounds and condensable compounds. At low drying temperatures the compounds consist mainly of terpenes. Most of the wood terpenes are emitted during the drying step. Storing dried wood in stockpiles may lead to self-heating and associated ignition problems. Protecting dry fuel storages from water and moisture access is of great importance. Likewise important is to maintain a sufficiently inert atmosphere in the dryer during operation and especially during start-up and shut-down. The oxygen level should then be kept below 8%.

At pelletizing plants personal exposure to wood dust has been found high and to monoterpenes low. Exposure to resin acids has also been found a potential concern with respect to workers' health. The air levels obtained by static sampling for monoterpenes were highest at the press and low at the grinder. CO levels were under the detection limit in the area measurements. The cooling of the pellet stream is extremely important with regard to safe storage of the product. Dry wood pellets require protected storage to keep the structure and low moisture content of the pellets.

During storage self-heating of pellets occurs, mainly in large-scale storage, but also in smaller piles. A number of serious incidents of self-heating and spontaneous ignition of wood pellets in storage have occurred. The three mechanisms involved in self-heating of pellets are microbial decomposition, chemical oxidation and hydrothermal moisture migration. Microbial decomposition is generally considered to be a minor factor unless the pellets have relatively high moisture content such as 12-15% or higher.

Off-gassing is an important phenomenon, which refers to the emission of different volatile compounds by wood pellets along the supply chain, from manufacturing to customers use. The pellet raw material, its treatment prior to production, and the pellets manufacturing conditions influence the off-gassing. Chemical oxidation of wood pellets has been presented the dominant mechanism for off-gassing. The fatty acids in pellets are oxidized to aldehydes and ketones, accompanied by the generation of heat. Further oxidation will produce low molecular carboxylic acids. The main off-gas emissions are hexanal, monoterpenes, CO, CO₂ and CH₄. Other compounds found are pentanal, methanol, acetone, and formic acid. The pellets and off-gassing can pose a safety and health threat for workers involved with handling the product in large bulk. For the main compounds emitted occupational exposure limit values have been established. Exceeding these values causes different health effects for the workers.

The drying temperatures and self-heating of stored pellets affect the amount and composition of the emitted compounds. By choosing the optimal raw material mixture of pine and spruce and process parameters, it should be possible to reduce the amount of aldehydes during storage of wood pellets. The wood was found low emitting regarding both terpenes and hexanal after about 3 months for pellets.

Storage temperature is a critical factor that affects the off-gassing from stored wood pellets. Higher peak emission factors and faster emission rates have been associated with higher temperatures. As the storage temperature increased from 20 to 55 °C, the emission rate increased significantly. A strong correlation was found between the build-up of CO and CO₂ concentrations and decrease in O₂ concentration in the containers. The studies have also shown that emissions of CO₂, CO and CH₄ are more sensitive to storage temperature (10-45 °C) than to relative humidity (low, high) and the relative volume of headspace (25, 50 and 75%). Increased headspace volume ratio increased peak off-gas emissions because of the availability of oxygen for pellet decomposition. Increased humidity in the headspace in the container increased the emissions of CO₂, CO, and CH₄. Hence the control methods such as restricting the storage temperature, relative humidity, or choosing an appropriate headspace ratio in a contained storage space could be effective in reducing the off-gas emissions from wood pellets in order to protect the workers' health. Lower oxygen levels generate lower emissions of CO₂ and CO at room temperature, whereas CH₄ emission is insensitive to the oxygen level.

Off-gassing and self-heating may be very low in torrefied biomass as most of the solid, liquid, and gaseous products, which are chemically and microbiologically active, are removed during the torrefaction process. Torrefaction changes the wood raw material to hydrophobic and thus makes the storage easier. The emission studies have indicated that torrefied wood chip emits less CO, CO₂, and CH₄ when compared to wood pellets, untreated wood chips, and ground switchgrass. At 20 and 40 °C, wood pellets recorded the maximum CO concentrations of 1600 and 13 000 ppmv, whereas torrefied wood chips emitted less than 200 and 2000 ppmv. CH₄ was negligible for all feedstocks except for wood pellets at the end of storage at 40 °C.

In addition, absorption of moisture in pellets is an exothermic process and generates heat. When pellets with propensity to exhibit one or more of the heat generating processes are stored in a large volume, the temperature will increase within the pile, which may lead to spontaneous ignition in pellet storage facilities.

The knowledge of safety-technical basic characteristics of biomass fuels is of essential significance when planning safety measures and instructions, handling, storage and feeding equipment, and evaluating fire and explosion hazards. Several safety-technical properties of the fuels related to self-heating, self-ignition and dust explosions can be determined. Standard tests are conducted on dust clouds as well as dust layers. The result of the tests generates a dust classification which is used as a guideline for how the product generating the dust should be handled and how the handling facility should be designed.

Within two VTT projects, dust explosion and self-ignition characteristics were determined for renewable fuels and torrefied wood. The safety-technical characteristics of the torrefied dust did not differ significantly from those of normal biomass dust, but are clearly more reactive than coal dust. Due to a very fine particle size and almost zero moisture content, the torrefied dust may ignite more easily and thus create a larger dust explosion risk than conventional biomass dusts and coal dust. The elimination of dust formation and ignition sources is therefore critical in the whole utilisation chain. The torrefied wood dust was classified as a St1 dust (explosion severity normal or low), as most fuel dusts studied.

The most significant difference between regular pellets and torrefied pellets is the explosibility characteristics of dust. The minimum ignition energy for regular pellets dust is 17 mJ. The equivalent number for torrefied material has been found to be 3-30 mJ depending on degree of torrefaction. The minimum explosible concentration is 70 g/m³ for regular pellet dust and only 30-60 g/m³ for torrefied material. The results obtained in the IMO flammability and self-heating tests have shown that the white pellets, bark pellets and torrefied pellets do not need to be classified as a flammable solid or as a self-heating substance. Therefore they can be shipped in bulk.

Material Safety Data Sheets (MSDS) for wood pellets in bulk and for wood pellets in bags have been developed by the Wood Pellet Association of Canada and the University of British Columbia. The MSDS for wood pellets in bulk contains information and regulations on product identification and use, composition and physical properties, health hazard data, first aid procedures, fire and explosion measures, accidental release measures, safe handling and storage, exposure control and personal protection, stability and reactivity data, and exposure and toxicological data. In the work the results of the investigations on off-gas and dust emissions were utilized.

Within the SECTOR project a general MSDS for torrefied biomass as fuel based on European Regulation concerning REACH has been drafted. It was stated that torrefied biomass is in a stage of development regarding its production technology and its optimal feedstock and process parameters. A possibly needed REACH registration has not been done yet. Studies on different issues, e.g. toxicological information, have to be made in future to collect a broad database for a potential classification and registration of torrefied biomass to accomplish the requirements given by REACH. Altogether it can be stated that despite some open questions a safety data sheet for torrefied biomass can be generated by the use of the available knowledge to ensure an SDS with the required information in most parts.

A new working group for safety issues within ISO TC 238 Solid biofuels was established in 2014. The working group "WG 7 – Safety of solid biofuels" will develop new standards on safety issues for wood pellets.

During transportation of pellets occupational hazards can occur. The size, shape, moisture content and type of raw material influence the transport, handling and storage properties of a solid biofuel. An important health and safety risk in handling and transporting is connected to inhaling dust. The harm from dust depends on chemical composition, dust concentration and particle size and shape. Truck transport of wood pellets includes mainly transport of pellets from producer/harbour to an intermediate storage or end user. The health risks result mainly during loading and unloading where high dust concentrations may result in a risk of dust explosions and human exposure to dust and microspores.

A large proportion of the wood pellets produced worldwide are shipped by ocean vessels. The safety in ship transport is regulated by IMO and there are significant safety issues onboard vessels, in terminal storage and during handling. Several fatal accidents happened have been recorded, which have resulted from exposure to harmful gas emissions. Cargo holds are sealed during ocean voyage which results in very fast oxygen depletion and generation of CO, CO₂, CH₄ and some H₂. Entry into cargo holds and communicating spaces are prohibited unless the spaces have been thoroughly ventilated and the gas concentration

has been verified by a combination of oxygen and CO measurements. The shipper has to provide a Shipper Cargo Information Sheet to the master of the ocean vessel about the properties of the cargo. Material Hazardous in Bulk (MHB) includes for example wood pellets. Such products are subject to restrictions in handling, storage and segregation, ventilation and emergency actions in case of fire.

Currently torrefied material does not have a safety classification under IMO yet and can therefore not be transported by ocean vessels without special permission since it has similarities with charcoal, which is prohibited to be transported in bulk. Short distance transport of torrefied biomass is made by train, truck and boats similar as for wood pellets.

The supply chain of torrefied biomass is generally the same as for wood pellets logistics. From a safety perspective conveying, storage, loading and unloading, milling and feeding operations of torrefied biomass are the most relevant points. Potential safety issues along the value chain are similar as for wood pellets, and mainly related to self-heating, dust emissions, off-gassing and oxygen depletion. Proper handling and monitoring are required to minimize the risk for damage and financial losses.

The utilization of torrefied biomass in coal-fired power plants has been tested by European power producers. Within the SECTOR project, existing handling and storage facilities at the existing five coal-fired power plants were described. On the basis of this description and the experiences with co-firing biomass (and in some cases also thermally pre-treated biomass) the critical logistic steps were identified when switching from coal to torrefied biomass. The key fuel properties identified were the durability of the pellets in relation to the actual moisture content and the consequent dusting problem, self-ignition and consequential safety measures that must be applied, and odour and consequential safety aspects and possibility to use the fuel in residential areas. Dusting was identified as a particularly critical issue connected to handling of thermally treated biomass and there is a crucial need for a method for quantifying dusting properties. Controlling dust emissions when conveying, loading and un-loading at the power plant site has been mentioned by several end-users as an important issue.

References

- Ahonen, I., Liukkonen, T. Pellettivaraston ilman epäpuhtaudet ja niiden aiheuttamien vaarojen ehkäiseminen. Työympäristötutkimuksen raporttisarja 32. Työterveyslaitos, 2008. (In Finnish)
- Alakangas, E., Arpiainen, V., Korpijärvi, K. Biohiilen tuotanto ja käyttö, SECTOR-projektin tuloksia (Production and use of biochar, Results from the SECTOR project). Presentation in ForestEnergy 2020 seminar, Joensuu, Finland, 7 October 2015. Available at www.forestenergy2020.org (in Finnish)
- Alvarez de Davila, E., Bengtsson, L. Arbetsmiljön vid hantering av träbränsle och torv för energiproduktion. (Working environment during handling of wood fuel and peat for energy production). IVL Rapport B 1088. Stockholm 1993. 30 p. + app. 20 p. (In Swedish)
- Alvarez de Davila, E. Arbetsmiljön vid hantering av träpellets för energiproduktion samt arbetsmiljöerfarenheter vid eldning av olivkross och halm. (Working environment during handling of wood pellets for energy production and working environment experiences during burning of olive crush and straw). IVL Rapport B 1315. Stockholm 1999. 23 p. + app. 26 p. (In Swedish)
- Arshadi, M., Gref, R. Emission of volatile organic compounds from softwood pellets during storage. *Forest Products Journal* 55(2005)132-135.
- Arshadi, M., Nilsson, D., Geladi, P. Monitoring chemical changes for stored sawdust from pine and spruce using gas chromatography-mass spectrometry and visible-near infrared spectroscopy. *J. Near Infrared Spectrosc.* 15(2007)379-386.
- Arshadi, M., Gref, R., Geladi, P., Dahlqvist, S.A., Lestander, T. The influence of raw material characteristics on the industrial pelletizing process and pellet quality. *Fuel Processing Technology* 89(2008)1442-1447.
- Arshadi, M., Geladi, P., Gref, R., Fjällström, P. Emission of volatile aldehydes and ketones from wood pellets under controlled conditions. *Ann. Occup. Hyg.* 53(2009)797-805.
- Babrauskas, V. Ignition Handbook. Issaquah, WA, USA, 2003, Fire Science Publishers.
- Back, E.L., Allen, L.H. (Eds.) Pitch control, wood resin and deresination. Tappi Press, Atlanta, 2000. 392 p.
- Banerjee, S., Pendyala, K., Buchanan, M., Yang, R., Abu-Daabes, M. Process-based control of HAPs emissions from drying wood flakes. *Environ. Sci. Technol.* 40(2006)2438-2441.
- Björk, H., Rasmuson, A. Moisture equilibrium of wood and bark chips in superheated steam. *Fuel* 74(1995)1887-90.
- Bridgwater, T., Elliott, D.C., Fagernäs, L., Gifford, J.S., Mackie, K.L., Toft, A.J. The nature and control of solid, liquid and gaseous emissions from the thermochemical processing of biomass. *Biomass and Bioenergy* 9(1995)325-341.
- Council Directive 90/394/EEC of 28 June 1990 on the protection of workers from the risks related to exposure to carcinogens at work (Sixth individual Directive within the meaning of Article 16 (1) of Directive 89/391/EEC.

- Douwes, J., Thorne, P., Pearce, N., Heederik, D. Bioaerosol Health effects and exposure assessment: progress and prospects. *Ann. Occup. Hyg.* 47(2003)187-200.
- Edman, K., Löfstedt, H., Berg, P., Eriksson, K., Axelsson, S., Bryngelsson, I., Fedeli, C. Exposure Assessment to α - and β -pinene, Δ^3 -carene and wood dust in industrial production of wood pellets. *Ann. Occup. Hyg.* 47(2003)219-226.
- European Regulation (EC) No 1907/2006 of The European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC (Text with EEA relevance), European Parliament (2011).
- Fagernäs, L. Peat and bark extractives and their behavior in drying processes. Espoo: Technical Research Centre of Finland, VTT Publications 121, 1992. 51 p. + app. 95 p. Doctoral thesis.
- Fagernäs, L., Sipilä, K. Emissions of biomass drying. In: Proc. Developments in Thermochemical Biomass Conversion. Bridgwater, A.V., Boocock, D.G.B. (Eds.). Intl. Conf., Banff, Canada, 20-24 May, 1996. p. 783-797.
- Fagernäs, McKeough, P., Impola, R. Behaviour and emissions of forest fuels during storage and drying. In: Proc. 15th European Biomass Conference, from research to market deployment, Intl Conf., Berlin, Germany, 7-11 May, 2007. ETA-Renewable Energies, 2007. Pp. 613-617.
- Fagernäs, L., Brammer, J., Wilén, C., Lauer, M., Verhoeff, F. Drying of biomass for second generation synfuel production. *Biomass and Bioenergy* 34(2010)1267-1277.
- Fagernäs, L., Ojanen, K., Jokiniemi, J., Korpinen, L. Health Issues in Bioenergy Production and Use. Cleen/Best, Research report D4.4.9, Cleen Oy, Helsinki 2014. 66 p. (Confidential report)
- Fan, C., Bi, X.T. Development of off-gas emission kinetics for stored wood pellets. *Ann. Occup. Hyg.* 57(2013)115-124.
- Filbakk, T., Skjevraak, G., Høibø, O., Dibdiakova, J., Jirjis, R. The influence of storage and drying methods for Scots pine raw material on mechanical pellet properties and production parameters. *Fuel Processing Technology* 92(2011)871-878.
- Gauthier, S., Grass, H., Lory, M., Krämer, T., Thali, M., Bartsch, C. Lethal carbon monoxide poisoning in wood pellet storerooms-two cases and a review of the literature. *Ann. Occup. Hyg.* 56(2012)755-763.
- Globally Harmonized System of Classification and Labelling of Chemicals (GHS). Fifth revised edition. Aufl. New York and Geneva, 2013 – ISBN 978-92-117067-2.
- Granström, K.M., Berghel, J., Renström, R., Ståhl, M. Steam drying of sawdust for pellets production – medium scale. In: Proc. Bioenergy 2003, Intl Nordic Bioenergy Conf., Jyväskylä, Finland, 2-5 September, 2003. Pp. 476-479.
- Granström, K. Emissions of volatile organic compounds from wood. Karlstad University Studies, 2005:6. Dissertation.
- Granström, K.M. Emissions of hexanal and terpenes during storage of solid wood fuels. *Forest Products Journal* 60(2010)27-32.

- Granström, K.M. Sawdust age affect aldehyde emissions in wood pellets. *Fuel* 126(2014)219-223.
- Guo, W., Trischuk, K., Bi, X., Lim, J., Sokhansanj, S. Measurements of wood pellets self-heating kinetic parameters using isothermal calorimetry. *Biomass and Bioenergy* 63(2014)1-9.
- Hagström, K., Axelsson, S., Arvidsson, H., Bryngelsson, I.-L., Lundholm, C., Eriksson, K. Exposure to wood dust, resin acids, and volatile organic compounds during production of wood pellets. *Journal of Occupational and Environmental Hygiene* 5(2008)296-304.
- Igathinathane, C., Tumuluru, J.S., Sokhansanj, S., Bi, X., Lim, C.J., Melin, S. Simple and inexpensive method of wood pellets macro-porosity measurement. *Bioresource Technology* 101(2010)6528-6537.
- Jirjis, R. Health risks associated with the storage of wood fuels. IEA Bioenergy Task XII, Feedstock preparation and quality, Workshop, 1996. Pp. 9-17.
- Järvinen, T., Agar, D. Experimentally determined storage and handling properties of fuel pellets made from torrefied whole-tree pine chips, logging residues and beech stem wood. *Fuel* 129(2014)330-339.
- Kemikaalit ja työ, Selvitys työympäristön kemikaaliriskeistä. Työterveyslaitos, Vammalan kirjapaino Oy, Vammala. 2005. (In Finnish)
- Koppejan, J., Lönnermark, A., Persson, H., Larsson, I., Blomqvist, P., Arshadi, M., Valencia-Reyes, E. et al. Health and safety aspects of solid biomass storage, transportation and feeding. IEA Bioenergy Report, May 2013. 86 p.
- Korpijärvi, K., Alakangas, E., Taipale, R., Kaipainen, H. Comparison of torrefied and wood pellet storage behaviour. Book of proceedings, Bioenergy from Forest 2014, Benet Oy, Helsinki 2014 96-103.
- Korpijärvi, K., Fagernäs, L., Laitinen, S., Laitinen, J., Aatamila, M., Jumpponen, M., Ojanen, K., Koponen, H., Tissari, J., Karhunen, T., Sippula, O., Jokiniemi, J., Korpinen, L. Occupational hygiene measurements at power plant sites. Cleen/Best, Research report D4.4.9, Cleen Oy, Helsinki 2015. 79 p. (Confidential report)
- Kuang, X., Tumuluru, J.S., Bi, X.T., Sokhansanj, S., Lim, C.J., Melin, S. Characterization and kinetics study of off-gas emissions from stored wood pellets. *Ann. Occup. Hyg.* 52(2008)8, 675-683.
- Kuang, X., Tumuluru, J.S., T.J., Bi, X.T., Lim, C.J., Sokhansanj, S., Melin, S. 2009a. Rate and peak concentrations of off-gas emissions in stored wood pellets—Sensitivities to temperature, relative humidity, and headspace volume. *Ann. Occup. Hyg.* 53(2009)789-796.
- Kuang, X., Tumuluru, J.S., Sokhansanj, S., Lim, C.J., Bi, X.T., Melin, S. 2009b. Effects of headspace and oxygen level on off-gas emissions from wood pellets in storage. *Ann. Occup. Hyg.* 53(2009)807-813.
- Kymäläinen, M., Havimo, M., Keriö, S., Kemell, M., Solio, J. Biological degradation of torrefied wood and charcoal. *Biomass and Bioenergy* 71(2014)170-177.
- Kymäläinen, M. Moisture sorption properties and fungal degradation of torrefied wood in storage. Dissertation. Forestales 206, 2015. 58 p.

- Kymäläinen, M., Mäkelä, M.R., Hildén, K., Kukkonen, J. Fungal colonisation and moisture uptake of torrefied wood, charcoal, and thermally treated pellets during storage. *Eur. J. Wood Prod.* 73(2015)709-717.
- Lehtikangas, P. Quality properties of pelletised sawdust, logging residues and bark. *Biomass and Bioenergy* 20(2001)351-360.
- Lönnermark, A., Persson, H., Blomqvist, P., Hogland, W. Biobränslen och avfall – Brandsäkerhet i samband med lagring. SP Sveriges Tekniska Forskningsinstitut, Borås, Sweden. SP Rapport 2008:51. 80 p. (In Swedish)
- Madsen, A. M., Mårtensson, L., Schneider, T., Larsson, L. Microbial dustiness and particle release of different biofuels. *Ann. Occup. Hyg.* 48(2004)327-338.
- Mak, W.A. Flammability and self-heating properties of a sample of crushed torrefied wood pellets. TNO report TNO-DV 2011 C266. September 2011. Not published.
- Melin, S. 2009a. Material Safety Data Sheet for wood pellets in bags. Wood Pellet Association of Canada. 2009.
- Melin, S. 2009b. Material Safety Data Sheet for wood pellets in bulk. Wood Pellet Association of Canada. 2009. 13 p.
- Melin, S. Review of off-gassing from wood pellets, a Canadian perspective. February 26, 2010. 6 p.
- Melin, S. Research on off-gassing and self-heating in wood pellets during bulk storage. Wood Pellet Association of Canada. A report prepared for Ethanol BC. November 11, 2011. 22 p.
- Melin, S. 2013a. Classification of self-heating in wood pellets in accordance with the UN MTC Test 4.2 Criteria. Wood Pellet Association of Canada, 2013. 6 p.
- Melin, S. 2013b. Testing of explosibility and flammability of airborne dust from wood pellets. Wood Pellet Association of Canada, 2013. 19 p.
- Melin, S. Material Safety Data Sheet for wood pellets in bulk. Wood Pellet Association of Canada. 2014. 12 p.
- Melin, S. Personal comment, February 17, 2015.
- Nielsen, N.P.K., Nørgaard, L., Strobel, B.W., Felby, C. Effect of storage on extractives from particle surfaces of softwood and hardwood raw materials for wood pellets. *Eur. J. Wood Prod.* 67(2009)19-26.
- Nies, E. Ototoxic substances at the workplace: A brief update. *Arh Hig Rada Toksikol* 63(2012)147-152.
- Otwell, L.P., Hittmeier, M.E., Hooda, U., Yan, H., Su, W., Banerjee, S. HAPs release from wood drying. *Environ. Sci. Technol.* 34(2000)2280-2283.
- Pa, A., Bi, X.T. Modeling of off-gas emissions from wood pellets during marine transportation. *Ann. Occup. Hyg.* 54(2010)833-841.
- Persson, H., Blomqvist, P., Yan, Z. Brand och brandsläckning i siloanläggningar – En Experimentell studie, SP Report 2006:47, Borås 2006. (In Swedish)

- Rupar, K., Sanati, M. The release of organic compounds during biomass drying depends upon the feedstock and/or altering drying heating medium. *Biomass and Bioenergy* 25(2003)615-622.
- Soto-Garcia, L., Huang, X., Thimmaiah, D., Rossner, A., Hopke, P.K. Exposures to carbon monoxide from off-gassing of bulk stored wood pellets. *Energy Fuels* 29(2015)218-226.
- Stelte, W. Logistics and storage of torrefied biomass. Safety aspects. Resultat-Kontrakt (RK) Report. Danish Technological Institute, Taastrup, Denmark, 2015. 9 p.
- STM. HTP-arvot, Haitallisiksi tunnetut pitoisuudet, Sosiaali- ja terveysministeriön julkaisuja 2014:2, Sosiaali- ja terveysministeriö. Suomen Yliopistopaino Oy. Tampere 2014. 97 s. (In Finnish) <http://urn.fi/URN:ISBN:978-952-00-3749-5>
- Ståhl, M., Granström, K., Berghel, J., Renström, R. Industrial processes for biomass drying and their effects on the quality properties of wood pellets. *Biomass and Bioenergy* 27(2004)621-628.
- Svedberg, U., 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.* 48(2004)4, 339-349.
- Svedberg, U., Samuelsson, J., Melin, S. Hazardous off-gassing of carbon monoxide and oxygen depletion during ocean transportation of wood pellets. *Ann. Occup. Hyg.* 52 (2008)4, 259-266.
- Svedberg, U., Petrini, C., Johanson, G. Oxygen depletion and formation of toxic gases following sea transportation of logs and wood chips. *Ann. Occup. Hyg.* 8(2009)779-787.
- The Nordic Expert Group for Criteria Documentation of Health Risks from Chemical and the Dutch Expert Committee on Occupational Safety. 144. Endotoxins. 2011. Available at: <http://hdl.handle.net/2077/26596>
- Thrän, D., Witt, J., Schaubach, K., Kiel, J., Carbo, M., Maier, J., Ndibe, C., Koppejan, J., Alakangas, E., Majer, S., Schipfer, F. Technical, economic and environmental improvements of the overall torrefaction supply chain through the SECTOR project. Submitted to *Biomass and Bioenergy*, autumn 2015.
- Thörnqvist, T., Jirjis, R. Bränsleflisens förändring över tiden - vid lagring i stora stackar. (Changes in fuel chips during storage in large piles). Uppsala 1990. Sveriges Lantbruksuniversitet, Institutionen för virkeslära, Rapport nr 219, 49 p. + app. (In Swedish)
- Torrent, J. Test report on characterization of flammable solids, torrefied wood fuel. Laboratorio Oficial J.M. Madariaga. October 2011. Not published.
- Tumuluru, J.S., Kuang, X., Sokhansanj, S., Lim, C.J., Bi, X.T., Melin, S. Development of laboratory studies on the off-gassing of wood pellets. *Canadian Biosystems Engineering* 52(2010) 8.1-8.9.
- Tumuluru, J.S., Lim, C.J., Bi, X.T., Melin, S., Kuang, X., Melin, S., Yazdanpanah, F., Sokhansanj, S. Analysis on storage off-gas emissions from woody, herbaceous, and torrefied biomass. *Energies* 8(2015)1745-1759.

- TVL. Kinteistönhoitaja menehtyi puupellettisiiloon syntyneeseen häkään. (A maintenance man perished in carbon monoxide formed in a wood pellet silo). TVL, 2008. TOT-Tutkinta. YTOT 2/08. 13 s. (In Finnish) Available at: <http://totti.tvl.fi> (Visited 27.7.2015)
- United Nations Recommendations on the transport of dangerous goods, Manual of tests and criteria, fifth revised edition. United Nations, New York and Geneva, 2009. 456 p.
- Valtioneuvoston asetus työhön liittyvän syöpävaaran torjunnasta, Vna 716/2000, Sosiaali- ja terveysministeriö, 2000.
- Weatherstone, S., Simonsson, N., Karlsson, G., Padban, N., Adell, A., Abelha, P., Carbo, M. Final report on bulk tests in existing storage and handling facilities. Deliverable No. D6.7. Production of Solid Sustainable Energy Carriers from Biomass by Means of Torrefaction (SECTOR) –EU-project, 2015. 98 p.
- WHO, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans Wood Dust and Formaldehyde, Summary of Data Reported and Evaluation. Vol. 62, 1995. IARC, Lyon, France.
- Wilén, C., Moilanen, A., Rautalin, A., Torrent, J., Conde, E., Lödel, R., Carson, D., Timmers, P., Brehm, K. Safe handling of renewable fuels and fuel mixtures. Espoo 1999. VTT Publications 394. 117 p. + app. 8 p.
- Wilén, C., Jukola, P., Järvinen, T., Sipilä, K., Verhoeff, F., Kiel, J. Wood torrefaction – pilot tests and utilisation prospects. Espoo 2013. VTT Technology 122. 73 p.
- Ziegler, D., Hoeft, M., Witt, J., Pommer, L., Lemus, J., Janssen, A., Carbo, M. General Material Safety Data Sheet. Deliverable No. D8.6. Production of Solid Sustainable Energy Carriers from Biomass by Means of Torrefaction (SECTOR) EU project, 2015. 36 p.
- Zwart, R., Quick, W., Weatherstone, S., Theobald, K., Kollberg, K., Hinderson, A., Karlsson, G., Padban, N., Quak, R., Khodayari, R. Description of existing handling and storage facilities and the associated issues. SECTOR-Production of solid sustainable energy carriers from biomass by means of torrefaction, Deliverable No. D6.1, 30.09.2012. 28 p.
- Yazdanpanah, F., Sokhansanj, S., Lau, A.K., Lim, C.J., Bi, X., Melin, S., Afzal, M. Permeability of wood pellets in the presence of fines. *Bioresource Technology* 101(2010)5565-5570.
- Yazdanpanah, F., Sokhansanj, S., Lau, A.K., Lim, C.J., Bi, X., Melin, S. Airflow versus pressure drop for bulk wood pellets. *Biomass and Bioenergy* 35(2011)1960-1966.