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Doctoral Thesis

Emissions from Wood Pellets during Storage

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Abstract

Wood pellets have been reported to emit various gases like carbon monoxide (CO), carbon dioxide (CO₂) and a variety of volatile organic compounds (VOC) during storage. Increased concentrations of these gases in storages cause the environment to become toxic to those who operate in and around these storages. To investigate this phenomenon on a broad basis the research described in this thesis was carried out dealing with the topic from three different perspectives.

The first perspective deals with the investigation of the formation mechanism of the above mentioned emissions, especially the formation of CO gas from wood pellets, as this odorless and highly toxic component represents the highest immediate danger to people entering pellet storages. To this end, a series of storage experiments were conducted, in which off-gassing from various biomass raw material and pellet samples were investigated. The influence of storage related parameters such as storage temperature, time and atmosphere as well as of pellet related parameters such as wood species, raw material fraction and pelletizing conditions has been studied. The parameters which proved to be of the greatest impact on the off-gassing rates for CO, CO₂ and VOC proved to be the wood species, followed by storage temperature and storage time. Furthermore, off-gassing experiments with pure linoleic acid were carried out to gain insight on the chemical processes relevant to the off-gassing phenomenon. In the course of the experiments it could be determined that CO is released in the autoxidation reactions of linoleic acid at room temperature and the highest detectable CO off-gassing rate was determined at $78 \text{ mg/kg linoleic acid}$ in 24 hours.

The second perspective discussed in this work deals with the relevance of the off-gassing issue for small-scale pellet storages. Data from CO emission monitoring experiment in 26 small-scale pellet storages (below 20 t of storage capacity) in Austria was collected and evaluated based on storage situation, storage time and development of CO levels within the storages. It could be determined that also in small-scale pellet storages CO build-up can reach levels harmful and potentially lethal to humans. The peak CO concentrations within the storages were typically reached within one week after delivery of new pellets but subsequently decreased in every monitored storage situation. Furthermore, it could be observed that the CO off-gassing activity for all freshly delivered pellets was very high, even though the pellets production age varied significantly.

The third and final perspective deals with the assessment of technical solutions for ventilation of small-scale pellet storages to control the off-gassing issue, with respect to CO in particular. Experiments on various types of commonly used small-scale pellet storage systems have been carried out to test the effectiveness of ventilation solutions utilizing natural as well as forced ventilation. Also the influences of the size of the ventilation opening, temperature differences as well as the implementation of a chimney on the achievable air exchange rate were investigated. Results show that all investigated natural ventilation solutions are operating with fluctuating air exchange rates, due to their dependence on temperature fluctuations. Therefore, natural ventilation can only be recommended as a safety measures for pellet storages with a capacity of no more than 10 t, where only small volumes of air need to be exchanged. Pellet storages of a larger capacity should only be entered after some form of CO concentration measurement has taken place and should only be entered when the CO concentration is below 60 ppm (accepted STEL). Forced ventilation solutions were found to be the best solution for pellet storages with a storage capacity of no more than 10 t as they have the big advantage, that the necessary ventilation rate at a specific point in time can be controlled. However, the experiments have also shown, that with any type of ventilation solution it is paramount that the equipment is installed properly in order for it to work effectively. The goal is to achieve the highest possible degree of ventilation, which can only be guaranteed if a corresponding cross ventilation supplies fresh air.

The work presented in this thesis has been influential during the development of guidelines and recommendation for safe handling and storage of wood pellets. The data presented provided useful information in the decision making process during the development of the ÖNORM M 7137 and of the VDI 3464 guidelines, both dealing with the requirements for pellet storage rooms.

Kurzfassung

Es wurde festgestellt, dass Holzpellets bei der Lagerung verschiedene Gase, unter anderem Kohlenmonoxid (CO), Kohlendioxid (CO₂) und eine Vielzahl anderer flüchtiger organischer Verbindungen (VOCs) emittieren. Erhöhte Konzentrationen dieser Gase in der Atmosphäre eines Lagers können toxisch auf Personen wirken, welche sich im oder in der Nähe eines Pelletlagers aufhalten. Um dieses Ausgasungsphänomen möglichst vielschichtig zu untersuchen wurde das Thema in dieser Arbeit hinsichtlich dreier unterschiedlicher Aspekte untersucht.

Der erste Aspekt behandelt Untersuchungen hinsichtlich des Bildungsmechanismus der oben genannten Emissionen, im Besonderen der CO Bildung aus Holzpellets, da von dieser geruchlosen und hochtoxischen Verbindung das größte Sicherheitsrisiko für Personen ausgeht, welche einen Pelletlagerraum betreten. Zu diesem Zweck wurden eine Vielzahl von Lagerversuchen ausgeführt, in welchen das Ausgasungsverhalten verschiedener biogener Rohstoffsortimente und Pelletproben untersucht wurden. Der Einfluß von lagerungsbedingten Parametern, z.B. Lagertemperatur, Lagerdauer und Lageratmosphäre, wurde dabei ebenso untersucht wie Parameter, welche abhängig von der Pelletprobe sind, z.B. Holzsorte, Rohstofffraktion und Pelletierbedingungen. Von größter Bedeutung zeigte sich dabei der Einfluß der Holzsorte, gefolgt von der Lagertemperatur, der Lageratmosphäre und der Lagerdauer auf die Ausgasungsraten von CO, CO₂ und VOC. Desweiteren wurden Ausgasungsexperimente mit reiner Linolsäure durchgeführt, welche Aufschluß über die zugrundeliegenden chemischen Prozesse des Ausgasungsphänomens liefern sollten. Dabei konnte eindeutig festgestellt werden, dass CO tatsächlich durch Autoxidationsreaktionen von Linolsäure mit Luftsauerstoff bei Raumtemperatur freigesetzt wird. Die höchste gemessene Ausgasungsrate betrug 78 *mg/kg Linolsäure* pro Tag.

Der zweite Aspekt diente der Untersuchung der Relevanz der Ausgasungsproblematik in für Österreich typischen kleinen Endkundinnenlagern für Holzpellets. Dazu wurden Daten eines Monitoringprojektes, durchgeführt in 26 Endkundinnenlagern (mit einer Lagerkapazität kleiner 20 t), gesammelt und ausgewertet. Die Auswertung erfolgte hinsichtlich der konkreten Lagersituation, der Lagerdauer und der Entwicklung der CO Konzentration im Lager. Das Ergebnis der Untersuchung zeigte, dass auch bei der Lagerung geringer Mengen Holzpellets eine Anreicherung der Lageratmosphäre mit gefährlich hohen und potenziell tödlichen Konzentrationen an CO möglich ist. Die Höchstwerte der CO Konzentrationen wurden dabei in der Regel innerhalb der ersten Woche nach der Befüllung des Lagers mit frischen Pellets gemessen und nahmen

dann kontinuierlich ab. Zusätzlich konnte festgestellt werden, dass die CO Ausgasungsaktivität bei frisch ausgelieferten Pellets besonders hoch war, unabhängig vom Produktionsalter der Pellets.

Der dritte Aspekt schließlich, befasst sich mit der Bewertung von technischen Belüftungslösungen für Endkundinnenlager mit kleiner Lagerkapazität mit dem Ziel der Kontrolle der CO Emissionen im Lager. Hierzu wurden Experimente an verschiedenen, in Österreich häufig vorkommenden, Holzpelletlagertypen durchgeführt, um die Effektivität verschiedener natürlicher und mechanischer Ventilationsmaßnahmen zu testen. Dabei wurde der Einfluß der Parameter Größe der Lüftungsquerschnittsfläche, Temperaturunterschiede und Einbau eines Kamins auf die erreichbaren Luftwechselraten bestimmt. Die Ergebnisse zeigen, dass natürliche Belüftung, bedingt durch die temperaturabhängigen Schwankungen der Luftwechselraten, nur bei Lagern mit kleinen Volumina (Lagerkapazität < 10 t) empfohlen werden kann. Größere Lager sollten nicht ohne vorherige Bestimmung der CO Konzentration im Lager betreten werden und nur wenn die gemessene Konzentration unterhalb 60 ppm beträgt (akzeptierter Kurzzeitgrenzwert). Mechanische Belüftung wurde als beste Sicherheitsmaßnahme für größere Pelletlager identifiziert, da sie über den großen Vorteil verfügt konstante Luftwechselraten gewährleisten zu können. Jedoch konnte auch festgestellt werden, dass auf sachgerechte Installation der Lüftungsmaßnahme in jedem Fall äußerster Wert gelegt werden muss, um die gewünschte Leistung zu erzielen. Das Ziel einer größt möglichen Luftwechselrate kann nur durch Sicherstellung von Querlüftung mit Frischluft erreicht werden.

Die in dieser Arbeit präsentierten Ergebnisse bildeten eine wichtige Grundlage für die Entwicklung von Standards und Richtlinien zum sicheren Umgang und Lagerung von Holzpellets. Die Daten dienten als Basis zur Entscheidungsfindung in der Erstellung der ÖNORM M 7137 und der VDI Richtlinie 3464, welche sich mit den Anforderungen an Holzpelletlagerräume beschäftigen.

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Abbreviations, symbols and indices

List of abbreviations	
ab. gr.	above ground level
BE2020	BIOENERGY2020+ GmbH
BR	basement room
CH ₄	methane
CO	carbon monoxide
CO ₂	carbon dioxide
COHb	carboxyhaemoglobin
CSA	cross-sectional area
EU	European Union
EU-27	European Union member countries in 2012
FID	flame ionization detector
GC	gas chromatograph
H ₂	hydrogen
H ₂ O	water
HC	hydrocarbons
HS	headspace
ID	identification number
LD-PE	low density polyethylene
LOD	limit of detection
LOQ	limit of quantification
MC	moisture content
MP	measurement point
MS	mass spectrometry
N ₂	nitrogen
NaOH	sodium hydrate
NDIR	non dispersive infrared
O ₂	oxygen
OEL	occupational exposure limit
ppm	parts per million
REG	regression
RH	relative humidity
SAVF	specific air volume flow
SPME	solid phase micro extraction
STEL	short-term exposure level
TCD	thermal conductivity detector
VOC	volatile organic compound
vol%	volume percent
wt%	weight percent

List of symbols

A	area	$[m^1]$
b	slope factor	
c	concentration	$[ppm]$
$C_E(t)$	average exhaust gas concentration at time "t"	$[m^3/m^3]$
$C(t)$	concentration of tracer gas at time "t"	$[m^3/m^3]$
$C(x, t)$	concentration at time "t" and position "x"	$[m^3/m^3]$
d	diameter	$[m]$
D_U	mechanical durability	
h	height	$[m]$
k	constant	
k_0	pollutant concentration at time t=0	$[cm^3/m^3 \approx ppm]$
k_a	pollutant concentration in the ventilation air	$[cm^3/m^3]$
k_i	admissible pollutant concentration	$[cm^3/m^3]$
$k(t)$	time dependent development of the pollutant concentration	$[cm^3/m^3]$
\dot{K}	pollutant volume flow	$[m^3/h]$
m	mass	$[kg]$
\dot{m}	mass flow	
M	molar mass	$[g/mol]$
n	molar amount	
\bar{N}	time-averaged specific air volume flow	$[1/h]$
$Q_V(t)$	exchange rate at time "t"	$[m^3/h]$
s_e	standard deviation of the noise function e	
s_f	standard deviation of the function f	
p	pressure	$[Pa]$
R	ideal gas constant	
t	time	$[s, h \text{ or } day]$
T	temperature	$[K]$
V	volume	$[m^3]$
\dot{V}	volume flow	$[m^3/h]$
$V_{gas}(t)$	total volume of the tracer gas at the time "t" ($= \iiint_E C(x, t) \cdot dV$)	$[m^3]$
w_i	weighting factor for the concentration of component i	

Greek symbols

$\alpha(T)$	dependent drop function	
Δ	temperature difference	
ρ	density	$[kg/m^3]$
σ_{ci}^2	variance of the concentration value of component i	

List of indices	
<hr/>	
0	start of experiment condition
$a1 - a3$	ambient temperatures
<i>at</i>	after treatment
<i>atmos</i>	atmospheric gas
<i>atro</i>	dry basis
<i>bt</i>	before treatment
<i>bulk</i>	bulk
<i>CO</i>	carbon monoxide
<i>cons</i>	consumed
<i>emit</i>	emitted
<i>emz</i>	effective mixed zone
<i>flask</i>	flask
<i>gas</i>	gas
<i>i</i>	component i
<i>ideal</i>	ideal gas
<i>in</i>	inlet
<i>iw</i>	initial weight
<i>dm</i>	current day of measurement
$dm - 1$	day before the current day of measurement
<i>out</i>	outlet
<i>PE</i>	value after the pressure equalization
<i>pellet</i>	pellet
<i>sample</i>	sample
<i>solid</i>	gross volume
$t1 - t6$	measurement point temperatures
<i>t.c.</i>	trial condition
<i>total</i>	over the whole experiment
<i>VOC</i>	volatile organic compounds
x_1	variable x_1

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I. Background

1. Biomass pellet markets

The global wood energy market continues to grow, motivated and driven by public policies that have set ambitious targets for renewable energy. Biomass plays a major role to fulfill the European Unions (EU) energy targets for 2020 [1]. The EU's 20-20-20 targets aim for a 20 % reduction of greenhouse gas emissions from energy, a 20 % increase in efficiency and a 20% increase of renewable energy sources in energy consumption by 2020 compared to 1990 levels. In Europe these targets are among the predominant drivers of growth in wood energy consumption. In 2012, total wood pellet production in all European Union member countries (EU-27) was estimated at about 11 million tons, and EU-27 wood pellet consumption exceeded 15.1 million t. Early estimates suggest it reached 19 million t in 2013 [2]. According to some forecasts, European pellet consumption will reach even 35 million tons by 2020 [3]. This means that the growing demand will have to be met from both outside and within Europe.

Within renewable energy resources, wood pellets are predestined for long distance transportation due to their high energy density, storage properties and flexible utilization options. In 2011 most imports to Europe came from Canada and USA with each more than 1 million t pellets. Another 0.5 million t were imported from Russia and from Eastern European neighboring countries. Other pellet exporting countries are South Africa with 43.000 t, New Zealand with 30.000 t and, finally, Australia with 14.000 t imports to Europe in 2011 [4]. Most pellet imports to the EU are destined for co-firing in coal power plants [5], where they are pulverized and co-combusted with pulverized coal. The robustness of the industrial process allows the use of lower quality pellets with higher ash content and higher impurity and content of fines. Typically, they are classified as B quality according to the European standard EN 14961-2 [6]. However, an increasing import of premium pellets into the EU can also be noted due to the increasing demand in the residential heating market. In the segment of residential heating the main drivers for market expansion are often indirect support measures for the installation of pellet stoves and boilers as well as the low and stable prices of wood pellets compared to fossil fuels such as heating oil and natural gas. Especially in rural areas that are not connected to the gas grids it is a cost efficient alternative. In this market segment Italy, Austria, Sweden, Germany and Denmark are among the main consumers (see Table I.1).

Table I.1.: European pellet demand in tons according to [7].

	2011	2015	2020
Italy	1.900.000	3.100.000	4.250.000
Germany	1.400.000	1.900.000	3.500.000
Sweden	1.000.000	1.200.000	1.400.000
Austria	710.000	1.490.000	3.500.000
Denmark	700.000	1.000.000	1.250.000
France	560.000	1.400.000	2.500.000
Switzerland	160.000	250.000	400.000
Spain	150.000	450.000	1.150.000
Belgium	100.000	150.000	200.000
Finland	70.000	150.000	450.000
UK	50.000	500.000	1.250.000
Ireland	40.000	60.000	70.000
Other	1.100.000	1.600.000	2.200.000
Total	7.940.000	13.250.000	22.120.000

2. Wood pellet storages

A high degree of user comfort of pellet heating systems and the increased awareness towards climatic issues has led to a steady increase in the number of homes heated by wood pellets. In Germany alone more than 195.000 homes were heated with pellets in the year 2012 according to the German Wood Fuel & Pellet Association [8]. More than 96 % of those have a heating capacity below 50 kW and are mainly used to supply energy to single family homes and residential developments. The preparatory study for the implementation of ecodesign measures for solid fuel small-scale combustion installations published by the European Commission DG TREN (2009) estimated a total stock of 634 900 units of pellet stoves within the EU-27 in the year 2009 [9]. More recent numbers on the development of pellet boiler and stove units sold all of the EU-27 countries are hard to obtain, however, individual European countries have statistics on boiler and stove sales number also from the recent past. For example in Austria, out of the total of 3.647 million homes, in 2012 20.3 % were heated by biomass [10]. From 1997 to 2013 a total of 111.622 wood pellet central heating systems have been installed according to Haneder and Furtner [11]. More than 90 % of those are smaller than 30 kW with an average of 18 kW. The number of sold pellet stove units by the end of 2013 was estimated around 40.000 units [12]. In Table I.2 data on the situation in other European countries is presented.

Table I.2.: Pellet boiler and stoves units below 50 kW installed in selected European countries by 2013 according to [12].

	Pellet boilers	Pellet stoves
Germany	213.350	100.900
Spain	10.325	73.591
France	39.400	280.785
Italy	52.533	1.900.000
Finland	25.650	1.600
Switzerland	13.600	9.800

Typical small scale users are private households. Such residential buildings use pellets as the primary or secondary heating source in pellet boilers or pellet stoves. The typical boiler size in this sector is approximately 25 kW. The equipment is not able to handle pellets with high ash content. Therefore, only high quality wood pellets should be used, such as ENplus or DINplus certified pellets. This material guaranties low ash content of below 1 % and ensures minimized operational problems. Pellets are usually delivered as bulk pellets or in bags of 15-25 kg. When delivered in bulk, they are usually stored in closed storage rooms in the cellar of the end user and as close to the furnace as possible. Such storage rooms are in most cases built by the house owner according to regional building regulations. Most often, the rooms are equipped with a plastic baffle plate opposite the filling and return pipe for the filling-up of the pellet stock and a fuel supply system, most often an auger, to supply the pellets from the storage to the heating unit of the building set at the bottom of a slanted floor to ensure a complete emptying of the storage. However, other pellet storage types are used in residential heating as well such as underground pellet storage tanks and pre-fabricated storage tanks made from fabric or steel, which are set up indoors (for more details see [13]). According to ÖNORM M 7137 [14], the fuel demand per heating period lies around 0.6 to 0.7 m³ per kW heating load. For a building with a heat demand of 10 kW that would amount to 6-7 m³ of pellets (equivalent with 3.9 - 4.5 t of pellets) per heating period.

3. Toxicity of off-gassing emissions

Wooden biomass is known to emit off-gasses during thermal treatments such as drying but also during storage, especially, when stored in form of chips, sawdust or pellets. Dependent on the kind of thermal treatment and on the form of biomass the off-gassing spectrum changes in composition and shifts with respect to its major components. A detailed introduction to the most relevant literature on the phenomenon is given in section II.1. In the following section a brief overview on the most relevant off-gasses in relation to the storage of wood pellets is given together with important information on the toxicity of the individual gases.

Carbon monoxide (CO)

Carbon monoxide is a colorless, odorless gas that can be poisonous to humans. It is formed most often as a byproduct of incomplete combustion of carbon-containing fuels, but is also produced by natural processes. The health effects of carbon monoxide are largely the result of the formation of carboxyhaemoglobin (COHb), which impairs the oxygen carrying capacity of the blood. In biology, carbon monoxide is naturally produced during hemoglobin breakdown. This process produces a certain amount of carboxyhaemoglobin in normal persons, even if they do not breathe any carbon monoxide. When exposed to additional carbon monoxide the human body will experience subtle symptoms of poisoning such as dizziness and nausea and exposure to higher levels can result in death. An overview on the toxic effects of CO on the human body is given in Figure I.1.

A healthy human will have a COHb value of 0.5 %, a smoker will be around 3 % COHb and a traffic policeman might show a value of up to 10 % COHb in his blood. However, up to this level typically a person will not present any symptoms of CO poisoning. The occupational exposure level (OEL), which gives the upper limit on the acceptable concentration of a hazardous substance in workplace air for a particular material or class of materials, for CO is set at 30 ppm CO. The short time exposure limit (STEL), which is the acceptable average exposure over a short period of time, usually 15 minutes as long as the time weighted average is not exceeded, for CO is set at 60 ppm [15]. Concentrations greater than 800 ppm can result in fatal accidents [16].

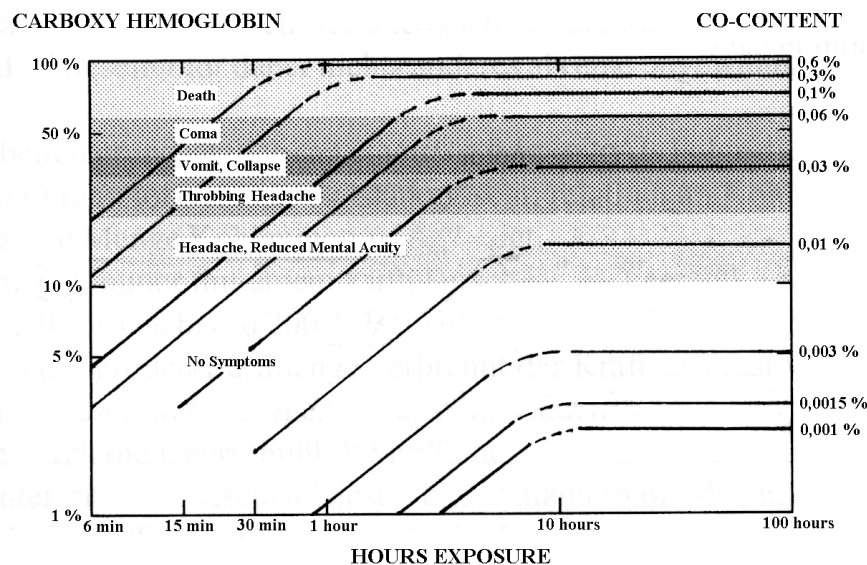


Figure I.1.: Toxic effects of carbon monoxide dependent on concentration and exposure according to [17].

The frequency of health problems associated with sub-lethal levels of CO is difficult to quantify. The risk of exposure to dangerous levels of CO can be anticipated for example near traffic intersections, in congested traffic or in poorly ventilated areas such as parking garages and tunnels. Indoors, CO concentrations in the workplace and in homes with faulty or unvented combustion appliances or downdrafts and back-drafts, have been measured in excess of 100 ppm, which is estimated to result in COHb levels of greater than 10 % after 8 h of exposure [18].

Carbon dioxide (CO₂)

CO₂ is an ubiquitous gas which occurs in the ambient air in a concentration of about 0.03 %. It is a colorless gas with a slight acidic smell and taste. It is produced during the respiration of all aerobic organisms and is exhaled in the breath of air-breathing land animals, including humans. Furthermore, it is formed during the processes of decay of organic materials and the fermentation of sugars in beer and wine making and by combustion of wood, carbohydrates and major carbon- and hydrocarbon-rich fossil fuels such as coal, peat, petroleum and natural gas. It is emitted from volcanoes, hot springs and geysers and is freed from carbonate rocks by dissolution in water and acids. CO₂ is found in lakes, at depth under the sea and commingled with oil and gas deposits.

CO₂ is 1.5 times heavier than air and therefore it accumulates on the ground. It is also well known as fermentation gas at vine production. The concentration in humans' breath is normally 4 vol% when breathing out. CO₂ concentrations of the one digit percent range already leads to negative health effects. Inhalation of pure CO₂ leads to fast asphyxiation, due to the absence of O₂. The OEL level for CO₂ is set at 5000 ppm and the STEL is set at 10000 ppm [15]. According to the literature, the effects of CO₂ play a less important role relating to the intoxication due to pellets.

Volatile organic compounds (VOC)

According to a European directive VOCs are defined as: "Volatile organic compound (VOC) shall mean any organic compound having at 293.15 K a vapor pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use. For the purpose of this Directive, the fraction of creosote which exceeds this value of vapor pressure at 293.15 K shall be considered as a VOC" [19].

A normal concentration of VOC in ambient air ranges between 0.25-0.5 mg/m³. The effects of raised levels of VOC on human health and welfare are various. They range from odors and irritation to toxic effects resulting in chronic injuries. Because of the high variance in composition of VOC it is not possible to create appropriate concentration thresholds [20]. In literature some publications were found which reported on VOC emissions of specific compounds. An overview is given in Table I.3.

Table I.3.: Individual VOC components found in off-gassing emissions.

Component	Source
<ul style="list-style-type: none"> • Hexanal • Pentanal • Acetone • Methanol • Formic acid • Caproic acid 	[21–23]

Methane (CH₄)

Methane is the simplest alkane and the main component of natural gas. In high concentrations (>5 vol%) it could cause asphyxiation by displacing oxygen in the blood. Naturally occurring methane is mainly produced by the process of methanogenesis. This multistep process is used by microorganisms as an energy

source. Methanogenesis is a form of anaerobic respiration used by organisms that occupy landfill and ruminants (e.g. cattle).

4. Thesis outline

Wood pellets are a relatively new type of fuel and only limited information on its off-gassing properties is available in literature. Autoxidation processes are considered as the main reason for the release of off-gases from wood pellets and factors such as high temperature and high fatty acid content are thought to be main influential parameters of high off-gassing activity in pellets. As a result of high off-gassing activity accidents might occur due to CO intoxication, but also exposure to other off-gassing components could prove harmful to health in the long run.

This thesis deals with the topic of off-gassing from wood pellets during storage from three different perspectives. In part II the mechanisms behind the off-gassing phenomenon are investigated. An overview of the state of the art knowledge on the topic is given and several experimental methods are presented to determine off-gassing rates of individual gaseous emissions, as well as extractive content and composition of the investigated biomass samples. Furthermore, the effects of storage related parameters such as storage temperature and storage atmosphere on the development of off-gassing rates for CO, CO₂, VOC and in some cases CH₄ are investigated and discussed. Additionally, pellet related parameters such as the influence of different wood species, the raw material, the production parameters and the production age on the off-gassing behavior is presented. Moreover, results from mechanistic experiments on the off-gassing behavior of pure linoleic acid are given.

The second perspective on the relevance of the off-gassing issue for small-scale pellet storages is dealt with in part III. In this part results from CO emission monitoring in 26 small-scale pellet storages in Austria is presented. The utilized equipment for the monitoring experiments is described as well as the individual storage system parameters for all monitored pellet storages. In the course of the monitoring the effect of implementing defined ventilation openings, which allow for natural air exchange to occur between the pellet storage and the ambient, on the monitored CO levels in the storages is documented and discussed. Additionally, parameters such as user behavior, operation of the heating system and the filling of the pellet storage with fresh pellets and their effects on the CO levels within the storages are investigated.

The third and final perspective discussed in part IV deals with technical solutions to safely handle off-gassing in pellet storages by means of ventilation. Experiments on various types of pellet storage systems have been carried out to test the effectiveness of various types of technical solutions utilizing natural as well as forced ventilation. The influences of the size of the ventilation opening, temperature differences as well as the implementation of a chimney on the achievable air exchange rate is presented and discussed. Furthermore, characteristic curves for the necessary air exchange rates dependent on the off-gassing rates of the pellets and the degree of filling of the pellet storage are calculated. From these results safety recommendations on handling of wood pellets in storages are derived. In part V the work presented in this thesis is summarized. Finally, in part VI, an outlook on future fields of investigation is provided.

II. Off-gassing phenomenon - Investigation of the mechanism and influential parameters

1. Introduction

1.1. Off-gassing phenomenon

Wooden biomass is known to emit a broad spectrum of off-gasses during thermal treatments such as drying but also during storage, especially, when stored in form of chips, sawdust or pellets. Dependent on the kind of thermal treatment and on the form of the biomass the off-gassing spectrum changes in composition and shifts with respect to its major components. For example, off-gassing from wood chips and sawdust has been investigated in several studies [24–29]. Reported off-gasses from wood chips and sawdust include mono-, sesqui-, and diterpenes [24, 25, 30, 31] along with CO₂, CO and CH₄ [32, 33], formaldehyde and methanol [26, 34, 35], whereas pellets are also reported to emit a broad spectrum of aldehydes, most prominent amongst them hexanal and pentanal [21, 22, 36] and other volatile organic compounds such as acetone [37].

In the study by Arshadi and Gref 2005 [22], the off-gassing characteristics for different types of sawdust (pine, spruce, fresh and mature) were investigated yielding the result that very high levels of emitted VOCs were produced. Above all, the substances pentanal and hexanal were measured in comparable volumes. Moreover, it could be determined that the lipid content of sawdust was reduced with longer storage time, a result that was subsequently evaluated as evidence for the decomposition of fatty acids in wood through autoxidation. The lipid content of the wood was furthermore suggested as indicator for the maturity of the sawdust. The findings were then taken up in follow up studies [38, 39] with the goal to predict the expected pellets quality as well as the required energy costs associated with pellet production. For this purpose, the moisture content of the raw material was determined online by means of near infrared spectroscopy and correlated with the quality of the pellets. In doing so, the moisture content of the pellets was ascertained to be a crucial factor. A correlation between the lipid content in the raw material and the pellets quality could, however, not be determined with certainty.

The off-gassing behavior of wood pellets became the focus of intensive research after a series of tragic accidents on board of two pellet bulk carrier ships, the "Weaver Arrow" in May 2002 in Rotterdam and the "Saga Spray" in November 2006 in Helsingburg, which were reported in Svedberg *et al* 2008 [40] and Melin *et al* 2008 [41]. The studies provided a clear sign that the formation of CO from wood pellets is a phenomenon, which does not result exclusively from elevated temperatures. Also data was provided on the effect of O₂ depletion, a parallel effect occurring simultaneously to the off-gassing effect and proven to

be one of the contributing factors in the fatal accidents on-board the pellet bulk carrier ships. The fact that CO is released during the storage of wood pellets was, however, first reported some years earlier in the study by Svedberg *et al* 2004 [21], which deals with the characteristics of released emissions from wood pellets production facilities. In this publication, special attention was placed on the measurement of CO and hexanal, whereby the measured mean concentration of each compound in the storage containers were found to be 56 mg/m^3 (value above the Swedish permissible exposure level of 40 mg/m^3 and 360 mg/m^3 (no maximum allowable value exists), respectively. It could be determined that these emissions were produced before the pelletizing process as well as generally from the decomposition of wood. Moreover, this is the first publication in which it was suggested that the autoxidation of fatty acids was responsible for the formation of CO from wood pellets. The formation of CO from hydrocarbons in general, however, has been reported prior to that in the work of Levitt *et al* as early as 1995 [42]. The authors Svedberg *et al* 2004 also illustrate that the decomposition of fatty acids is the most accountable mechanisms for the formation of the identified organic compounds in the overseas transportation of wood pellets. These suggestions, based on the released knowledge in Back and Allen 2000 [43], also state that hexanal is the main principal decomposition component released from the oxidization of linoleic acid and linoleic acid esters. A fact, which is also supported by a second earlier study published in 1991 by Koelsch *et al* [44].

In recent years many publications on the topic of off-gassing from stored wood pellets were provided by researchers from the University of British Columbia [45–51]. In the studies by Kuang *et al* [46–49] and Fan and Bi 2013 [52] the authors concentrated on the measurement of CO, CO₂ and CH₄ emitted from wood pellets in sealed, air tight containers with a capacity of 45 liters. With the obtained data a kinetic model for the formation of these gases was created. The results showed that the recurrent concentrations, according to the definition, behave as a first order chemical reaction and therefore an autoxidative fat-degradation reaction is essential as the most dominant causal agent. The impact of temperature, oxygen level and relative humidity on the rate of emission as well as the peak concentration for each gas was also looked into. It could be established that temperature is a key parameter affecting the peak off-gassing emission factors for stored wood pellets significantly.

Yazdanpanah *et al* 2014 [50] have shown that the CO₂ and CO off-gassing behavior of wood pellets is also strongly influenced by the moisture content. For this purpose the concentration of emitted gases from wood pellets were investigated in an enclosed space at variable moisture content (from 4-50 %) and high temperature (from 20-60 °C). In line with results previously reported [47] CO₂ and CO concentrations rose with rising temperature, however, with rising moisture content (>15 %) CO emissions were decreasing. Also oxygen depletion was hampered with rising moisture content, but accelerated with rising temperature. It has also been reported that high temperature storage causes deterioration of wood pellet durability [53].

Although, the number of publications on parameters influential to the off-gassing phenomenon are steadily growing, little has been published on possible reaction pathways responsible for the release of emissions, and of CO in particular. In fact only one study published in 2012 by a group of researcher from the University of Newcastle has suggested a possible complete formation mechanism for the oxidation of linolenic acid and the subsequent formation of CO [54]. The group investigated a pathway for the autoxidation of linseed oil, which is a common ingredient in paints, varnishes and wood treatment agents. It consists mainly of linoleic, linolenic, palmitic and oleic acid, all of which constituents typically found in the extractive content of wooden biomass samples. Figure II.1 depicts the complex mechanism of the formation of various volatile

organic emissions and of CO as suggested by literature. In wood samples linolenic acid is only present at very low concentrations, however, it is reasonable to assume that if the degradation of this acid yields CO emissions also the degradation of other unsaturated fatty acids such as oleic, palmitic and linoleic acid will result in CO formation.

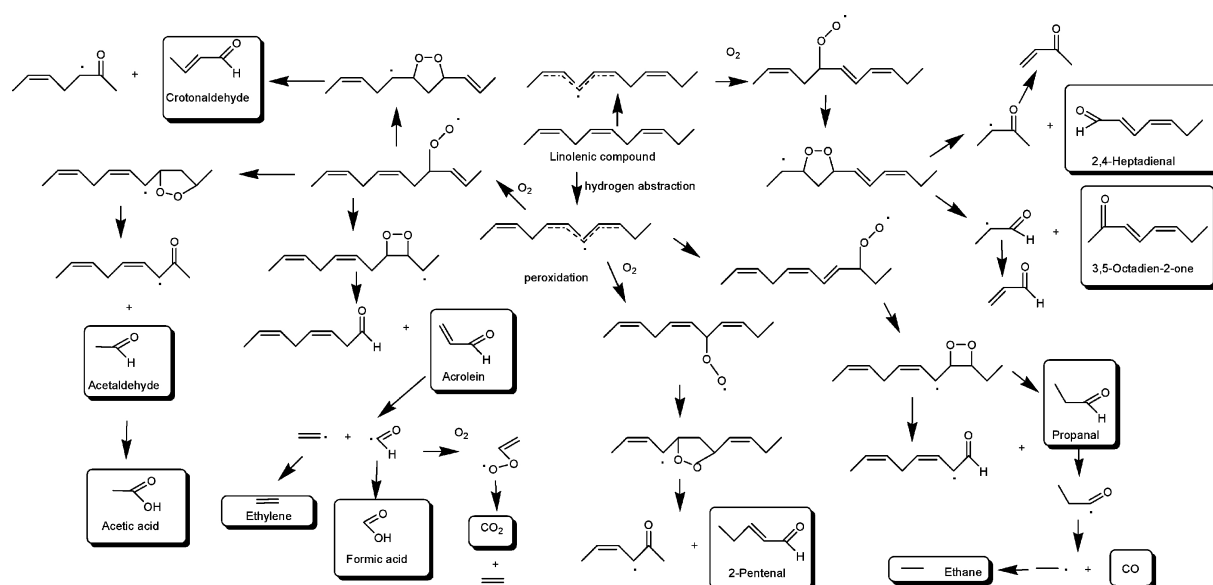


Figure II.1.: Proposed mechanism for product emission from the linolenic compound according to [54].

Due to the fact, that autoxidation of the extractives contained in the wooden biomass is responsible for the release of off-gassing emissions, the extractive content is also regarded to be of significant impact to the off-gassing behavior. The extractive content of wood sawdust is also a key factor when it comes to the pelletizing process and has, thus, been in the focus of research regarding pelletizing properties of wood raw materials [55, 56]. The studies provided by Nielsen *et al* [55, 56] report on the effect of age on the extractive concentrations of the surface materials of pelletizing raw materials. They were found to be initially high and to increase even further during storage. However, a more in depth analysis revealed, that only the concentrations of triterpenoid and steroidal structures increased, whereas fatty acid and diterpenoid structures decreased over time. Polymerization reactions of the fatty acids and diterpenoid structures were suggested as underlying mechanisms to explain these findings. Whether the effect of storage with respect to particle surface accumulation of extractives is of significant importance when compared with the total amount of extractives in the raw material, was, however, not conclusively established. In Fengel and Wegener [57], Arshadi *et al* 2007 [38] and a more recent study released in 2012 by the German Pellet Association (Deutscher Energieholz- und Pellet-Verband e.V.) [58] it has been reported, that the extractive content of wooden biomass is decreasing with time. A fact that is also supported by literature presenting data on the storage of fresh wooden biomass and the gaseous emissions released during its storage in combination with the related dry matter losses [59–61]. To give an example, in the study presented by He *et al* 2012 [61] dry matter losses during the storage of fresh Douglas fir (*Pseudotsuga menziesii*) branches were estimated between 0.78 - 2.0 % over a period of 35 days and increasing with storage temperature.

A more recent study provided by Granström in 2014 [62] reported on the effect of the age of the raw material on the release of aldehyde emissions from oxidation processes from wood pellets. In this study, pellets made from fresh sawdust were reported to show low-emitting levels after 80 days of storage, whereas pellets made from aged sawdust did not reach the same low level until 190 days after production. A key conclusion of that study was that when a low level of aldehyde emissions is required during storage, the pellets should be produced from sawdust that is freshly sawn. Furthermore, previous studies also support suggestions to rather produce pellets from fresh sawdust from an economic point of view, as it has been shown that it requires less energy in production. This has been attributed to increased friction in the matrix caused by the loss of extractives in the case of aged sawdust [55, 63].

An interesting point is made in the study by Arshadi *et al* 2012 [64]. By the removal of fatty and resin acids from pine sawdust utilizing supercritical extraction with carbon dioxide, it is suggested that the potential for uncontrolled autoxidation processes can be reduced significantly. The study revealed, that the calorific value of the pelletized sawdust was not significantly affected by the extraction process. However, whether the extracted pellets also showed reduced off-gassing behavior was not investigated in this study.

Whilst the emission of CO₂ and CO from wood pellets has generally been attributed to the autoxidative degradation of fatty acids, the release of these gases from non-thermally processed forest products such as logs and chips are usually attributed to microbiological activities [21, 32, 33]. The extent to which microbial activity in wood contributes to the release of CO and VOCs during storage was primarily investigated in correlation with the theme of self-heating and spontaneous ignition of wood [65, 66]. In Meijer 2004 [32], the authors reported about the release of CO₂ in early phases in which microorganisms triggered biological self-heating whereas they attributed the formation of CO to a chemical oxidation process to a later time with higher temperatures ($>70^{\circ}\text{C}$). In this study, the phenomenon of the formation of CO by lower temperatures was not observed and as such, the detection of instantaneous CO was linked to the danger of the spontaneous ignition of wood. In Rupar-Gadd 2004 [66], the influencing factors of relative humidity and different storage temperatures were named as the most crucial for the variable growth of microorganisms. It could also be determined that pellets containing bark exhibit higher microbial activity than pellets without. Evidence that CO can be generated as a direct decomposition product through microbial activity was not found.

1.2. Self-heating phenomenon

Questions concerning the formation of off-gassing emissions and the associated mechanisms were also examined from a further significant standpoint, namely, the phenomenon of the self-heating and the spontaneous ignition of stored biomass. In Blomqvist *et al* 2007 [67] experiments are described in very small volumes (1 dm³) as well as in larger volumes (up to 4 m³) conducted with the goal of obtaining kinetic data of the exothermic reaction characteristics in wood pellets during the self-heating process. Primarily, the oxidation mechanisms in wood due to temperatures exceeding 80 °C were investigated, whereby the O₂, CO₂, CO and VOC gases were analyzed. It appears that in the interior of the pellets pile, CO₂ and CO as well as VOCs (above all terpenes, pentanal and hexanal) emerge very slowly thereby hindering the early detection of the emerging gases. The method applied for determination of the kinetic parameters in self-heating substances

is commonly referred to as the "crossing-point temperature method". It involves the periphery heating of an initially exothermic material being subjected to a hot environment with a constant temperature. When the center temperature exceeds the temperature measured a small distance from the center, that point at that temperature is defined as the "crossing-point temperature" [68].

In Blomqvist and Persson 2003 [68] it is pointed out that the largest risk for spontaneous ignition would be in storages of moist biofuel such as wood chips and sawdust, as these provide suitable conditions for growth of bacteria and fungi. They in turn produce heat in the low temperature regime, which is usually a prerequisite for attaining the temperature regime where oxidative processes commence. Dry refined wood fuels such as wood pellets and briquettes are considered to be at low risk for spontaneous ignition, if stored properly. However, self-ignition of wood pellets is not an unheard of phenomenon and there are several documented cases [69]. In Larsson *et al* 2012 [70] six large scale silos for wood pellets were monitored over a period of 7 months. The temperature profiles recorded within the silos showed an increase where temperature increased over time and by increasing height. A fact that is supported by the work conducted by Guo 2013 [71], where data is presented from industrial wood pellet silo sites that shows temperatures of up to 60°C measured in the silos.

Hydrocarbon oxidation is named as the dominant source of heat responsible for self-heating of biomass aided by various other exothermic processes such as low temperature oxidation, microbial metabolism, the adsorption-desorption of water due to the difference between real and equilibrium moisture concentration in a storage [68]. Therefore, the phenomena of off-gassing and of self-heating of biomass are believed to be closely connected.

2. Objectives & approach

The main goal of this thesis is to study and quantify off-gassing behavior, with a major focus on CO_2 , CO and VOC emissions, of biomass pellets during storage. The influence of parameters related to the storage situation such as storage temperature, storage atmosphere and degree of filling, or headspace ratio, are investigated. Additionally, parameters related to the pellet material e.g. type of wood/biomass species, history of raw material, pelletizing process and pellet production age are characterized and quantified. These investigations include a series of pelletizing and off-gassing experiments, where different types of pellets were stored at changing temperature and storages atmospheres. The off-gassing emissions were monitored throughout the experiments and used to draw conclusion on the off-gassing activity of various types of biomass in specific storage situations. Furthermore, the thesis aims to explore the underlying mechanism responsible for the occurrence of the off-gassing phenomenon. For this purpose an experiment was carried out studying the off-gassing behavior of pure linoleic acid, a material inherently present in wooden biomass and an important constituent within the extractive fraction of wood.

The biomass pellet market is also confronted with the emerging of new and advanced treatments of biomass, amongst which torrefaction of biomass has become a more and more widespread phenomenon. Therefore, this study's third objective is to give data on the off-gassing behavior of torrefied biomass pellets. Finally, this work aims to provide data on the off-gassing behavior of various agricultural biomass fuels, for both chipped as well as pelletized samples.

3. Materials & methods

The experimental work described in this thesis was carried out in the context of several different project and over a duration of six years. In the course of time and based on the experience gained in the course of the projects a continuous development of some of the methods took place. In the following section an overview of all used materials and methods is provided.

3.1. Raw material and pellet samples

The overview given in Table II.1 and Table II.3 shows the complete set of raw material and pellet samples investigated within this thesis. In the subsequent result chapters the samples are referenced using the sample identification numbers (ID) indicated in the Tables in the following section.

Raw material samples

Information on the type of raw material, the moisture content (MC) and the density of the samples (ρ_{sample}) is given in Table II.1. The tested raw materials include wooden as well as agricultural biomass and one sample of torrefied biomass.

Table II.1.: Summary Table of all analyzed raw material samples

ID	Raw material	Botanical name	MC %	ρ_{sample} kg/m^3
RM01	spruce sawdust	<i>picea abies</i>	13.8	460 ¹
RM02	spruce sawdust	<i>picea abies</i>	13.9	460 ¹
RM03	spruce sawdust	<i>picea abies</i>	14.2	460 ¹
RM04	spruce sawdust	<i>picea abies</i>	20.0	460 ¹
RM05	spruce shavings	<i>picea abies</i>	8.8	460 ¹
RM06	pine chips	<i>pinus taeda</i>	16.5	458 ²
RM07	pine chips	<i>pinus silvestris</i>	49.5	520 ¹
RM08	larch chips	<i>larix decidua</i>	8.6	600 ³
RM09	ash chips	<i>fraxinus excelsior</i>	12.5	700 ¹
RM10	hardwood sawdust	-	24.3	600 ¹
RM11	straw granulate	-	10.3	1124 ⁴
RM12	miscanthus chips	-	9.7	300 ⁵
RM13	torrefied spruce chips	<i>picea abies</i>	7.2	300 ⁴

¹ data according to DIN 68364 [72]

² data according to Isik *et al* 2008 [73]

³ data is an assumed value, exact wood species unknown

⁴ data according to determination at BE2020

⁵ data according to El Bassam and Huismann 2001 [74]

Pellet samples

A similar list is given for the investigated pellet samples. It includes data on the types of raw material used in pellet production and information on whether the pellet was produced commercially (Comm.) or whether it was produced on a laboratory pellet press (Lab.). Furthermore, data on the MC, particle density of the pellets (ρ_{pellet}), mechanical durability (D_U) and (if available) information on the applied production standard (Prod. stand.) is given. Since 2014 an ISO standard describing fuel specifications and classes for different types of biomass pellets is available in form of the ISO EN 17225-2 [75]. Even though this standard has already replaced former European and national standards such as the EN 14961-2 [6] and the ÖNORM M 7135 [76], they are shown because some of the investigated samples were produced according to their requirements. In Table II.2 an overview on the different requirements from the different standards is provided. In Table II.3 a list of the investigated pellet samples is provided.

Table II.2.: Specifications of wood pellet qualities according to ISO EN 17225-2 and previous standards and quality labels for selected countries (according to [77]).

	World ISO EN 17225-2 A1	Europe EN 14961-2 A1	Austria ÖNORM M 7135 HP 1	Germany Dinplus	Sweden SS 187120 Group
Diameter in mm	6 (± 1) or 8 (± 1)	6 (± 1) or 8 (± 1)	$4 \leq D$ and $D < 10$	$4 \leq D$ and $D < 10$	n.d.
Length in mm	≥ 3.15 ; ≤ 40	≥ 3.15 ; ≤ 40	$\leq 5 \cdot D$	$\leq 5 \cdot D$	$\leq 4 \cdot D$
Density in kg/dm^3	n.d.	n.d.	≥ 1.12	≥ 1.12	n.d.
Bulk density in kg/m^3	≥ 600	≥ 600	n.d.	n.d.	≥ 600
Water content in %	≤ 10	≤ 10	≤ 10	≤ 10	≤ 10
Ash content in %	≤ 0.7	≤ 0.7	≤ 0.5	≤ 0.5	≤ 0.7
Additives in %	≤ 2	≤ 2	≤ 2	≤ 2	no limit
Fines in %	≤ 1	≤ 1	n.d. ¹	n.d. ¹	≤ 0.8
D_U in %	≥ 97.5	≥ 97.5	≥ 97.7	≥ 97.7	n.d.

n.d. not defined

¹ Fines have to be removed

Again, the sample identification indicated in Table II.3 will be used as a sample reference in the following result chapters. The list of samples includes pellets produced from wooden, agricultural and torrefied biomass. The investigated spruce and pine pellet samples, as well as pellets produced from a mixture of both, were all produced from the European wood species *picea abies* and *pinus silvestris*, respectively. The same is true for the pellet samples produced from torrefied wood.

ID	Raw material	Mix ratio %	Ø mm	Source	MC %	ρ_{pellet} kg/m ³	D _U %	Prod. stand.
P40	spruce/pine	40/60	8	Comm.	6.0	1225	98.2	SS 187120
P41	spruce/pine	40/60	8	Comm.	5.1	1214	n.d.	SS 187120
P42	spruce/pine	30/70	6	Comm.	7.1	1200*	n.d.	Dinplus
P43	spruce/pine	20/80	6	Comm.	7.2	1200*	n.d.	Dinplus
P44	spruce/pine	unknown	6	Comm.	8.1	1225	n.d.	Dinplus
P45	larch	100	6	Comm.	5.2	1301	n.d.	ÖNORM M 7135
P46	larch	100	6	Lab.	8.7	1326	n.d.	–
P47	spruce/ douglas fir	85/15	6	Comm.	9.3	1200*	n.d.	Dinplus
P48	pine/larch/fir	75/rest	8	Comm.	8.7	1274	99.3	unknown
P49	hardwood	100	6	Comm.	8.7	1280	n.d.	unknown
Agricultural pellets								
P50	straw	100	8	Comm.	9.8	1116	95.9	unknown
P51	straw	100	6	Comm.	9.1	1180	n.d.	unknown
P52	straw/seed residue/spruce	83/11/6	8	Comm.	7.3	1183	96.1	unknown
P53	eucalyptus	100	6	Lab.	10.0	1211	98.4	–
P54	eucalyptus	100	6	Lab.	5.3	1290	93.6	–
P55	vine pruning/ pomace	50/50	6	Lab.	10.1	1324	98.2	–
P56	miscanthus/straw	90/10	6	Comm.	9.1	1266	n.d.	unknown
P57	miscanthus/maize/ wheat straw	33/33/33	6	Comm.	5.9	1307	n.d.	unknown
Torrefied pellets								
P58	torrefied spruce	100	6	Lab.	7.1	1198	n.d.	–
P59	torrefied mix ¹	100	8	Comm.	8.5	1235	n.d.	–
P60	torrefied pine	100	8	Lab.	1.9	1259	80.6	–
P61	torrefied pine	100	8	Lab.	3.2	1177	85.8	–

*assumed values

¹ mix of spruce with leaves, bark and branches

n.d. not determined

3.2. Characterization of material properties

3.2.1. Determination of moisture content

The determination of the moisture content of the samples is carried out according to the ÖNORM EN 14774-2 [78] at the beginning of the experiment. The samples are dried in a laboratory oven at a drying temperature of $105 \pm 2^\circ\text{C}$ until a constant mass is measured.

3.2.2. Particle density of the pellets

The particle density of the pellet samples (ρ_{pellet}) was determined using a stereometric method of volume determination. The volume of 15 randomly chosen pellets was calculated after measuring length and width on the basis of the ÖNORM EN 16127 [79]. In preparation of the determination the fractured areas on both ends of the pellets were carefully smoothed out using abrasive paper until pellets with a cylindrical shape could be obtained. Next the lengths and widths of the pellets were determined using a sliding caliper. Afterwards, the weight of the pellets was determined on a precision balance Sartorius ME235P (manufacturer: Sartorius). Next, the volume of the pellet was calculated based on the formula for a cylindrical body:

$$V = \pi \cdot \left(\frac{d}{2}\right)^2 \cdot h \quad (\text{II.1})$$

The particle density of the pellet was calculated using the equation below:

$$\rho_{\text{pellet}} = \frac{m_{\text{pellet}}}{V_{\text{pellet}}} \quad (\text{II.2})$$

The particle density was derived from the arithmetic mean value of 15 consecutive particle density measurements.

3.2.3. Mechanical durability of the pellets

The determination of the mechanical durability of the pellet samples is carried out according to the ÖNORM EN 15210-1 [80]. In which, after having removed the fines, a pellet sample is filled in the testing chamber of a tumbler and rotated at 50 ± 2 revolutions per minute. After 500 rotations the fine material is sieved again and the remaining wood pellets are weighed. The mechanical durability is then determined using the following formula:

$$D_U = \frac{m_{bt}}{m_{at}} \cdot 100 \quad (\text{II.3})$$

3.3. Determination of extractive content

The determination of the extractive content of the biomass sample was done via Soxhlet extraction. The methodology used in this work has first been described in the master thesis of Schmutzer-Roseneder 2012 [81]. As extraction solvent a mixture of acetone and distilled water ($96/4$ vol%) was used. Prior to the extraction roughly 10 g of sample are milled using an analytical mill (manufacturer: IKA) and the grinded sample is then weighed in a dry extraction thimble. The weight of the sample is determined with an accuracy of 10 ± 0.100 g. Afterwards the extraction thimble is placed into the main chamber of the Soxhlet extractor. The Soxhlet extractor is then placed onto a flask containing 400 ml of extraction solvent and a condenser is connected on top of the Soxhlet extractor. The solvent is afterwards heated to reflux and the extraction process is maintained for six hours. In Figure II.2 a photograph of the extraction apparatus is depicted.



Figure II.2.: Soxhlet extractor with extraction thimble placed inside.

When the extraction has finished and the solvent has cooled down ≈ 50 g of sodium sulfate are added to the solvent and the mixture is placed into a refrigerator for at least 12 hours to remove all water from the solution. As a next step the dry and cooled solution is filtered to remove the drying agent. The filter cake is washed with acetone and is united with the filtered solution.

Next, the solvent is placed in a 1.000 ml separating funnel and 100 ml of distilled water. As second solvent 60 ml n-hexane are used in the subsequent liquid-liquid extraction, which is carried out twice. The remaining acetone/ H_2O fraction contains the organic extractives and is transferred into a dried and weighed 500 ml round bottom flask. Subsequently, the solvent is removed using a Rotavapor [manufacturer: Büchi] operated at a pressure of 700 mbar at a temperature of 70°C . Once all the solvent is removed, the organic extractive content is determined by weighing the round bottom flask once more and subtracting the tare weight of the flask. The calculation of the extractive content is carried out in four steps. First, the loss of extractives due to retention of organic compounds in the n-hexane phase is calculated. For this the masses of acetone and distilled H_2O used for the liquid-liquid extraction are summed up. The difference from the added n-hexane phase and the recovered n-hexane phase is compared. From the comparison the mass of the acetone/ H_2O fraction retained in the n-hexane phase is derived. This mass is now converted into a mass percentage of the recovered n-hexane phase.

In a second step the dry mass of the sample is calculated according to the equation below:

$$m_{atro} = m_{iw} \frac{100}{100 - MC} \quad (\text{II.4})$$

In a third step, the amount of organic extractive content is calculated by subtracting the weight of the empty round bottom flask from the weight of the round bottom flask after the solvent has been evaporated. The recovered amount of extract is then expanded by the amount retained in the n-hexane phase after liquid-liquid extraction. Finally, in the fourth step, the organic extractive content is converted into a mass percentage based on the dry matter of the sample.

Every sample has thus been determined three times and an arithmetic mean value of the three determinations is given as extractive content of the sample. The three determinations had to fit within a confidence interval of $\pm 15\%$ of the arithmetic mean, otherwise another three determinations were carried out.

3.4. Determination of extractive composition

To determine the extractive composition of the wood samples 700 mg of sample material are grinded and methanolic NaOH is added. The material is then heated up to 80 °C and esterified using methanolic boron trifluoride (10 %). As extractive agents distilled water and n-heptane are used. The organic phase is subsequently separated using a gas chromatograph and the different fatty acids are quantified via flame ionization detection (Manufacturer: HP5890 series II, equipped with a polar GC capillary: WAX, 30 m x 0.25 mm x 0.25 μ m). Using a commercial standard solution for fatty acids (Manufacturer: Nu-Check Prep, GLC68C), the fatty acids determined with this method are listed in Table II.4.

Table II.4.: List of extractive components detected via an extractive method using a GC/FID system for identification and quantification.

C atoms:# double bonds	Name	Molecular formula
C8:0	caprylic acid	C ₈ H ₁₆ O ₂
C10:0	capric acid	C ₁₀ H ₂₀ O ₂
C11:0	methyl undecanoate*	C ₁₂ H ₂₄ O ₂
C12:0	lauric acid	C ₁₂ H ₂₄ O ₂
C14:0	myristic acid	C ₁₄ H ₂₈ O ₂
C14:1	myristoleic acid	C ₁₄ H ₂₆ O ₂
C16:0	palmitic acid	C ₁₆ H ₃₂ O ₂
C16:1	palmitoleic acid	C ₁₆ H ₃₀ O ₂
C18:0	stearic acid	C ₁₈ H ₃₆ O ₂
C18:1	oleic acid	C ₁₈ H ₃₄ O ₂
C18:2	linoleic acid	C ₁₈ H ₃₂ O ₂
C18:3	linolenic acid	C ₁₈ H ₃₀ O ₂
C20:0	arachidic acid	C ₂₀ H ₄₀ O ₂
C20:1	paullinic acid	C ₂₀ H ₃₈ O ₂
C20:2	eicosadienoic acid	C ₂₀ H ₃₆ O ₂
C20:3	mead acid	C ₂₀ H ₃₄ O ₂
C20:4	arachidonic acid	C ₂₀ H ₃₂ O ₂
C22:0	behenic acid	C ₂₂ H ₄₄ O ₂
C22:1	erucic acid	C ₂₂ H ₄₂ O ₂
C24:0	lignoceric acid	C ₂₄ H ₄₈ O ₂
C22:6 & C24:1	docosahexaenoic & nervonic acid	C ₂₂ H ₃₂ O ₂ & C ₂₄ H ₄₆ O ₂

*internal standard

3.5. Determination of off-gasses: SPME-HS-GC-MS

Utilizing a system working with solid phase micro extraction - headspace - gas chromatography - mass spectrometry (SPME-HS-GC-MS) the group of VOC can be analyzed according to individual gaseous species, which accumulate in the headspace above a pellet sample stored within a sample vial. Subsequently these gaseous compounds are separated using a gas chromatographic system and identified with a mass spectrometer (Manufacturer: Agilent, Agilent 7890 GC/MS). The benefit of this sample preparation technique lies within the solvent-free method of sample collection. The sample was collected on "Stable Flex fiber" (50/30 μm DVB/Carboxen/PDMS) of a length of 2 cm. The individual VOC components detected by this method are listed in Appendix A Table A.1.

3.6. Determination of off-gasses: Glass flask method

For measuring CO and VOC emissions of biomass pellets during storage the glass flask method, modeled after the design first described in Kuang *et al* 2008 [46], has been developed and has been described earlier in the master theses of Schmutzer-Roseneder 2012 [81] and Trinkel 2012 [82].

3.6.1. Sample preparation and post-experimental treatment

At the start of the experiment typically between 1 and 2.4 kg of the biomass sample are filled into 5-liter glass flasks, which are then sealed using gas-tight screw caps. Parallel to the filling process a sample is taken to determine the moisture content of the biomass at the start of the experiment. Thereafter, the starting time of the experiment is noted and the glass flasks are stored in an air-conditioned room, at $\approx 22^\circ\text{C}$, protected from direct sunlight. Gas concentration measurements are carried out every 3 to 4 days.

After the final gas concentration measurements, on the last day of the experiment, the glass flask is opened and the sample material is removed. Again, the moisture content of the sample is determined. The average moisture content from start until the end of the experiment is used for the calculations of the off-gassing rates based on the dry matter of the biomass sample. As a last step, the glass flask is cleaned and ready for the next sample.

3.6.2. Equipment description

For the measurements of the CO and O₂ concentrations a NGA2000 (manufacturer: Rosemount) gas analyzer was used. The determination of the VOC concentration was carried out with a flame ionization detector (FID, manufacturer: Horiba). In Table II.5 the measurement ranges and specifications for each component used are given.

Table II.5.: Gas measurement equipment and specifications - glass flask method.

System	Species	Meas. principle	Range	Accuracy
NGA2000	CO	NDIR ¹	0 - 5.000 ppm	≤ 1 % rel.
	CO ₂	NDIR ¹	0-25 %	≤ 0.5 % rel.
	O ₂	paramagnetic	0-25 %	≤ 1 % rel.
FID/Horiba	VOC	FID	0 - 10.000 ppm	≤ 4 % rel

¹ non dispersive infrared

To connect the glass flask with the gas analyzer a specially designed measurement adapter is mounted on top of the glass flask and connected with the gas analyzer via a flexible silicon tube. The exchange of the screw cap of the bottle to the measurement adapter must be carried out quickly to insure that the gas exchange of the atmosphere in the bottle with the environment is as small as possible. The measurement adapter allows the gas for the gas concentration measurements to be taken from the headspace of the glass flask, while, simultaneously, directing fresh air to the bottom of the flask to prevent a speedy mixing of the storage atmosphere with the fresh air during the first few minutes of the concentration measurement. The principle of the measurement adapter is shown in Figure II.3.

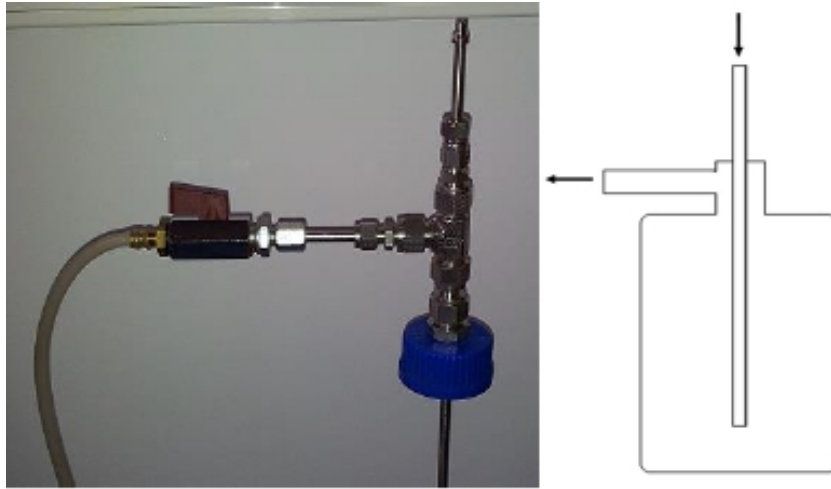


Figure II.3.: Photograph of the measurement adapter for the glass flask and schematic of the measurement principle for the glass flask method.

3.6.3. Testing procedure

The 5-liter glass flasks are filled with the biomass sample and afterwards sealed and stored in an air conditioned room at a temperature of approximately 22 °C during the storage experiment. The measurements of CO concentrations within the atmosphere of the flask are subsequently undertaken in 3 to 4 day intervals. At the end of a measurement the flask is purged with pressurized air for 10 to 15 minutes and afterwards resealed until the next measurement takes place. At the end of the storage experiment the

moisture content of the sample is determined for a second time and the average moisture content from start until the end of the experiment is used for the calculation of off-gassing rates based on the dry matter of the sample.

3.6.4. Processing of data

Figure II.4 depicts the typical development of the CO curve during a measurement point. Due to the steady dilution of the gas volume within the glass flask, the result of the inflow of fresh air into the glass flask during the measurement process, only a 3-minute interval at the beginning of each measurement was chosen for data evaluation. The CO value of the measurement was determined from the arithmetic mean value of CO during this interval.

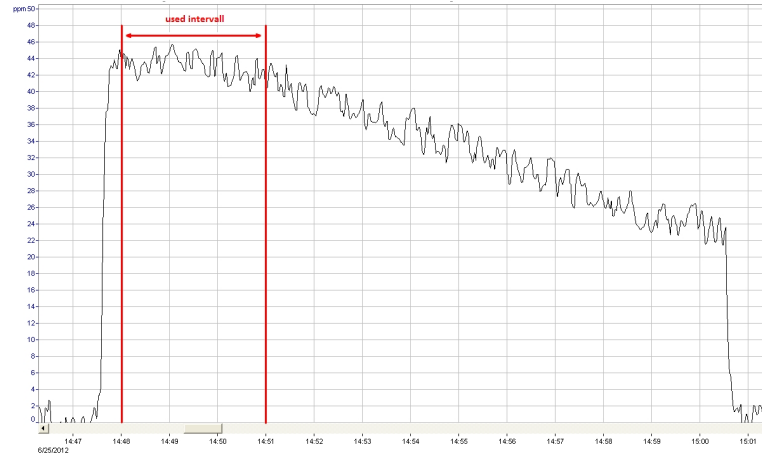


Figure II.4.: Typical CO measurement curve from a sample measured with the glass flask method, the marked interval was used to determine the average CO concentration of the measurement point.

The calculation for the determination of the CO off-gassing rate in $mg/kg_{fuel_{atmo}}$ in 24 hours from the measured CO concentration in ppm was carried out as follows. First of all, the gross volume of the pellets V_{solid} within the laboratory bottle was calculated.

$$V_{solid} = \frac{m_{sample}}{\rho_{pellet}} \quad (II.5)$$

Next, the volume of atmospheric gas within the glass flask is calculated.

$$V_{atmos} = V_{flask} - V_{solid} \quad (II.6)$$

With the values for V_{atmos} and the average concentration (c) value of CO (in ppm) the volume of CO gas within the bottle can be determined.

$$V_{CO} = \frac{c_{CO} \cdot V_{atmos}}{10^6} \quad (II.7)$$

Next, the mass of the CO gas (in kg) within the flask was derived on the basis of the ideal gas law ($V_{ideal} = 22.414 \text{ l/mol}$) and the molar mass of CO ($M_{CO}=28 \text{ g/mol}$).

$$m_{CO} = \frac{V_{CO}}{V_{ideal}} \cdot M_{CO} \quad (\text{II.8})$$

Subsequently, the mass flow of CO gas (in mg/kg fuel) within 24 hours was determined, by dividing the measured amount of CO gas by the duration of the storage period (in days) times the mass of the biomass sample.

$$\dot{m}_{CO} = \frac{m_{CO}}{t \cdot m_{pellets}} \cdot 1000 \quad (\text{II.9})$$

Finally, the CO off-gassing rate (in mg/kg fuel_{atro}) for the dry pellet sample was determined as follows:

$$\dot{m}_{CO,atro} = \dot{m}_{CO} \frac{100}{100 - MC} \quad (\text{II.10})$$

The calculation for the VOC off-gassing rate, $\dot{m}_{VOC,atro}$ [mg/kg fuel_{atro} in 24 hours], was carried out similarly. In this case the molar mass from propane was used as reference molar mass.

3.7. Determination of off-gasses: Pellet tank method

For measuring emissions of biomass pellets during storage a lab-scale pellet tank was designed especially for this purpose and described earlier in the master theses of Trinkel 2012 [82] and Meier 2014 [83].

3.7.1. Sample preparation and post-experimental treatment

Upon the samples arrival, typically two sealed polyethylene sample bags were delivered each containing roughly eight kg of pellets, the bags are stored in an air conditioned room at a temperature of approximately 22°C protected from direct sunlight. Typically within four weeks after arrival one bag is opened and a determination of the off-gasses with the glass flask method (details on the method see section II.3.6) is carried out. At this time the determination of the pellet density of the pellet sample is also carried out together with a photographic documentation of the sample. The second bag is kept in storage at the conditions mentioned before until the time the determination of off-gasses with the pellet tank method is carried out.

After the final concentration measurements, on the last day of the experiment, the tank is opened and the sample material is removed. Again, the moisture content of the sample is determined. The average moisture content from start until the end of the experiment is used for the calculations based on the dry matter of the biomass sample. As a last step, the tank is cleaned and prepared for the next sample.

3.7.2. Equipment description

Pellet tank

The apparatus is a cylindrical vessel and consists of stainless steel and is gas-tight. The inner volume is 31 liters. Both, gas inlet and outlet, are controlled with a magnetic valve allowing for controlled flow in automatic operation. The stream from the gas bottle is controlled by the inlet valve and the stream to the detection system is controlled by the outlet valve. Additionally, a membrane pump is installed to generate atmospheric circulation within the pellet tank to establish a high degree of mixing of the atmosphere to prevent possible gas stratification effects and, subsequently, imprecise gas measurements.

On top of the tank a pressure cell, a pressure control valve and a sensor for measuring relative humidity combined with a temperature sensor are located. Furthermore, a total of six additional temperature sensors are positioned along the walls of the tank in different heights. Their position within the tank can be adjusted according to the experimental requirements and objectives. The exact positioning of the measurement points (MP) utilized in the course of the experiments described in this thesis is depicted in Figure II.5 below. A photograph of the pellet tank is presented in Figure II.6. Inside, on the bottom of the tank a perforated plate is fixed, which allows the reaction gas to pass but also keeps the pellets away from the gas inlet device. For a controlled gas input a mass flow controller is used. The transfer of data from the sensors to the computer is implemented utilizing a profiMessage device, which is controlled with the program "Busmanager Version 3.66", a configuration and communication software. Thus, an autarkic data acquisition with universal contact possibilities is provided. Also the programming of the automatic procedure of the measurement was done with the Busmanager. Both, the profiMessage device and the Busmanager, were acquired from Delphin Technology AG.

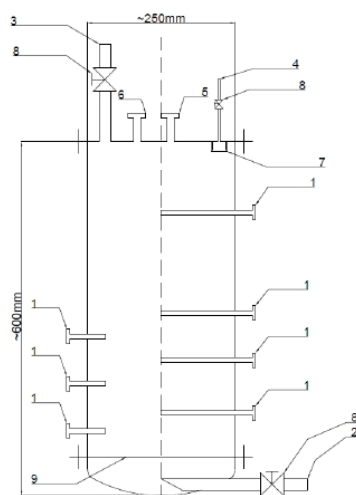


Figure II.5.: Drawing of the designed pellet tank: 1 - MPs for temperatures, 2 - inlet of reactor, 3 - outlet of reactor, 4 - measurement port for GC, 5 - MP for humidity and temperature, 6 - MP for pressure, 7 - filter for GC, 8 - plug, 9 - perforated plate.

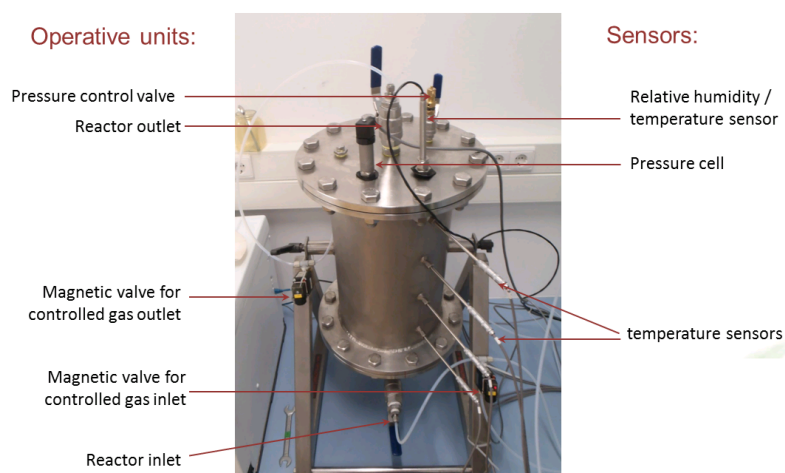


Figure II.6.: Photograph of the pellet tank.

Gas chromatograph

For the determination of the concentrations of the emitted gases a Perkin Elmer Clarus 580 gas chromatograph (GC) a modified model "Arnel 4016PPC" is used. This analyzer is equipped with an additional methanizer and a secondary FID connected in series with a primary thermal conductivity detector (TCD). Through special circuitry, consisting of an additional gas sampling valve and a restrictor column, the analysis of VOC by FID is enabled. Furthermore, the system is designed to quantify O_2 , N_2 , CO_2 , CO , CH_4 and VOC. Separation of the compounds of the gas phase is accomplished in two independent channels. In the first channel the gases O_2 , N_2 , CO_2 , CH_4 and CO can be detected. Going through two columns at a temperature of $175^\circ C$ the gases are separated. The first column, a HayeSep[®] column, separates CO_2 . The second column, a molecular sieve 13x, separates O_2 , N_2 , CH_4 and CO .

The TCD is a universal and non-destructive detector, which allows that the sample gas concentration can be redetermined by the FID in a secondary step of analysis. Before the sample reaches the FID it is injected in the methanizer, which converts the CO and CO_2 to methane by catalytic hydrogenation. Injection temperature to the methanizer is set at $400^\circ C$, which is required in order for the hydrogenation to take place. The VOCs are separated in a second channel. The sample passes through a restrictor and then the concentration is determined by the FID. One GC run is completed within 13 minutes. Technical descriptions of the components are presented in Table II.6. The software "TotalChrom Workstation Version 6.3" is used for operating the GC-FID/TCD. The gases He , H_2 , synthetic air and N_2 of specific quality are required for the application of the GC (see Table II.7). A photograph of the completely assembled measurement system is given in Figure II.7.

Table II.6.: System components of GC-FID/TCD and detection ranges for the gas measurements.

Component	Technical data/Detection ranges
Flame ionization detector (FID) Company: Perkin Elmer	CO ₂ : 1 ppm - 10 vol% CO: 1 ppm - 10 vol% VOC: 1 ppm - 5 vol% CH ₄ : 1 ppm - 10 vol%
Thermal conductivity detector (TCD) Company: Perkin Elmer	CO ₂ : 0.01-100 vol% CO: 0.01 - 100 vol% O ₂ : 0.01 - 100 vol% N ₂ : 0.01 - 100 vol% CH ₄ : 0.01 - 100 vol%
HayeSep [®] column type D Company: Vici	Length: 10 inch Inner diameter: 0.125 inch Mesh: 80 - 100 Material: Divinylbenzene
Molecular sieve 13x Company: Perkin Elmer	Length: 9 inch Inner diameter: 0.125 inch Mesh: 45 - 60 Material: Zeolithe

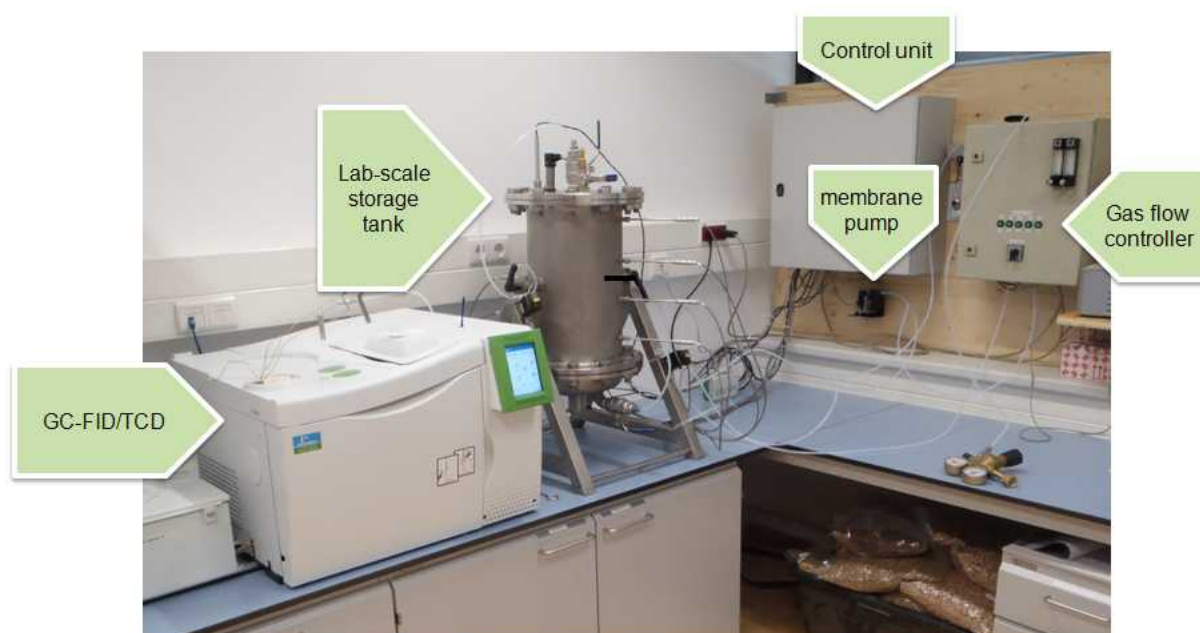


Figure II.7.: Photograph of the assembled experimental setup for the pellet tank method.

Table II.7.: Description of operation gases for the GC-FID/TCD, quality of gases according to data sheets provided by the producer Linde Gas GmbH.

Gas	Function	Requirements	Characteristics
Helium	Carrier gas	Purity: $\geq 99.999\%$	Purity $\geq 99.999\%$ ≤ 2 ppm O_2 ≤ 3 ppm N_2 ≤ 3 ppm H_2O ≤ 0.2 ppm hydrocarbons
Hydrogen	Fuel for FID flame	Hydrocarbon free	Purity $\geq 99.999\%$ ≤ 5 ppm H_2O ≤ 3 ppm N_2 ≤ 2 ppm O_2 ≤ 0.5 ppm hydrocarbons
Synthetic air	Fuel for FID flame	Hydrocarbon free	Class 2 according to ISO 6141 Hydrocarbon free
Nitrogen	Pneumatic regulation of valves	Dry, oil free	Purity $\geq 99.999\%$

3.7.3. Calibration of the GC

The calibration of the GC measurements was carried out utilizing the gas mixtures listed in Table II.8. After an initial calibration, every week during testing two to three calibration gases were redetermined, having all gases controlled within a period of four weeks. Later acquired measurement values were compared with initial values, to control measurement quality. Using the statistical program SAS a linear or a polymeric trend was defined and the accordant formula (see Table II.10) was used for converting the peak area value into a concentration value. The measurements of the calibration gases were conducted in alphabetic order according to the internal names of the gases presented in Table II.8. In this order concentration of the required compound was in no case lower than in the previous calibrations gas. The impact of higher concentrated component residues was avoided thereby.

Table II.8.: Calibration gases used for the GC.

Notation	Gas compositions					
	CO	CO ₂	C ₃ H ₈	CH ₄	O ₂	N ₂
0						100 %
A	50 ppm	2 %			2 %	Residual
B			50 ppm			Residual SA *
C	179 ppm	54 ppm				Residual
D	845 ppm	11 %				Residual
E					20 %	80 %
F	0.498 %	5.98 %	199 ppm			Residual
G					35 %	65 %
H				15 ppm		Residual

*SA synthetic air(20 % O₂ and 80 % N₂)

Error calculation

Absolute errors of assessed values were calculated using the method of the Gaussian error propagation. A confidence interval of 95 % was chosen. Calculation of errors derived from concentration measurements with GC-FID/TCD were calculated automatically with the statistical program SAS. Error values of the individual equipments are given in Table II.9.

$$s_f = \sqrt{\left(\frac{df}{dx_1}\right)^2 \cdot s_{x_1}^2 + \left(\frac{df}{dx_2}\right)^2 \cdot s_{x_2}^2 + \left(\frac{df}{dx_3}\right)^2 \cdot s_{x_3}^2 + \dots} \quad (\text{II.11})$$

Table II.9.: Error values of sensor equipment of the pellet tank.

Sensor	Error
Temperature 1-6 (PT 100)	at 20 °C = ± 0.4 °C
Temperature 7 (PT 1000)	at 20 °C = ± 0.2 °C
Pressure	0.5 % of full scale = ± 800 Pa

Limit of quantification

The limits of quantification (LOQs) were determined according to the flash estimation method in DIN 32645 [84]. The noise ranges of the blank values of the investigated substances on the chromatograms were ascertained. Presuming Gaussian distribution within the noise signals implies that a sixth of the range comprising all amplitudes in both directions corresponds standard deviation (s_e) of noise. The highest value of each determined noise ranges was used for the calculation of each substance. The LOQ was calculated as presented in the equation below. The variable b stands for the slope of the linear relation between zero point and the lowest concentration of the substance in the available calibration gas. The evaluated peaks of the respective gas compounds, which were higher than LOQ were assessed as quantifiable peaks.

$$LOQ = 6 \cdot \frac{s_e}{b} \quad (\text{II.12})$$

The limits of detection (LOD) were not determined because the LOQs were already very low. Values below the LOQ were not of interest.

3.7.4. Testing procedure

Before the pellets are filled into the tank, possibly occurring emission gases from previous storage have to be removed. This is done by filling the pellet bulk three times into a bucket, enabling gas exchange with ambient air. Thus, residual emission gases trapped in the pellet bulk are removed. The weighed sample is then filled into the tank, which is vacuum cleaned before, to assure that any remaining emission gases from previous experiments are removed. Afterwards, the lid of the pellet tank is closed and the tank is flushed with the gas mixture chosen as starting atmosphere for the experiment for at least 15 min with a volume flow of 5 l/min using the inlet and outlet valve. Thus, the requested gas atmosphere is adjusted.

During the experiment the determination of gas concentrations are carried out in a 24-hour rhythm. The measurements are executed with an automatic program, which has been designed in course of the master thesis of Meier 2014 [83]. The single steps of the measurement program are described as follows:

- Gas input: At first a slight overpressure was induced due to injection of gas. The type of input gas was chosen dependent on the experimental setup and experimental storage atmosphere. Due to the fact, that during pellet storage in tight containers negative pressure can develop [85], the pressure level vary before each measurement. To ensure similar measurement conditions and to enable gas injection into the GC at constant values slight overpressure is applied to the system before the measurement can start. Therefore, the pressure level before the measurement is raised to 1.03 bar each day.
- Mixing: Next, a peripherally installed membrane pump starts to mix the reaction gas with a flow rate of 5 l/min . This ensures that all gas components are mixed homogeneously and that atmosphere composition in the pellet bulk and in the headspace are equal. The initial mixing period before sampling lasts 20 minutes. The pump runs continuously until pressure equalization at the end of the measurement procedure is reached.
- Sampling: The connection valve between the pellet tank and the GC is opened and gas from the pellet tank flows through the lines to the GC due to the overpressure induced in the tank. Before the first of four measurements takes place, the GC-FID/TCD is flushed 15 minutes to remove any residual gases from previous measurements. In between the remaining three more determinations the line is flushed for another five minutes each time.
- Pressure equalization: After each flushing interval it takes about twelve seconds to reach pressure equalization within the GC system, after which the actual measurement is initiated.

- **Measurement:** Then the GC-FID/TCD starts to measure the constitution of the sample gas. A single determination takes 13 minutes. For each determination a total of four measurements are carried out.
- **Pressure reduction:** After the fourth measurement is completed the magnetic valve from the tank outlet to the GC-FID/TCD is opened again for 90 minutes to reduce the induced overpressure in the tank to the level of ambient pressure within the laboratory. After this step the pellet sample in the tank meets ambient pressure conditions for the next reaction period.

Overall, the procedure for determining concentrations of the sample gas including the pressure equalization lasts about 2.5 hours. In Figure II.8 the measurement procedure is presented using the pressure curve.

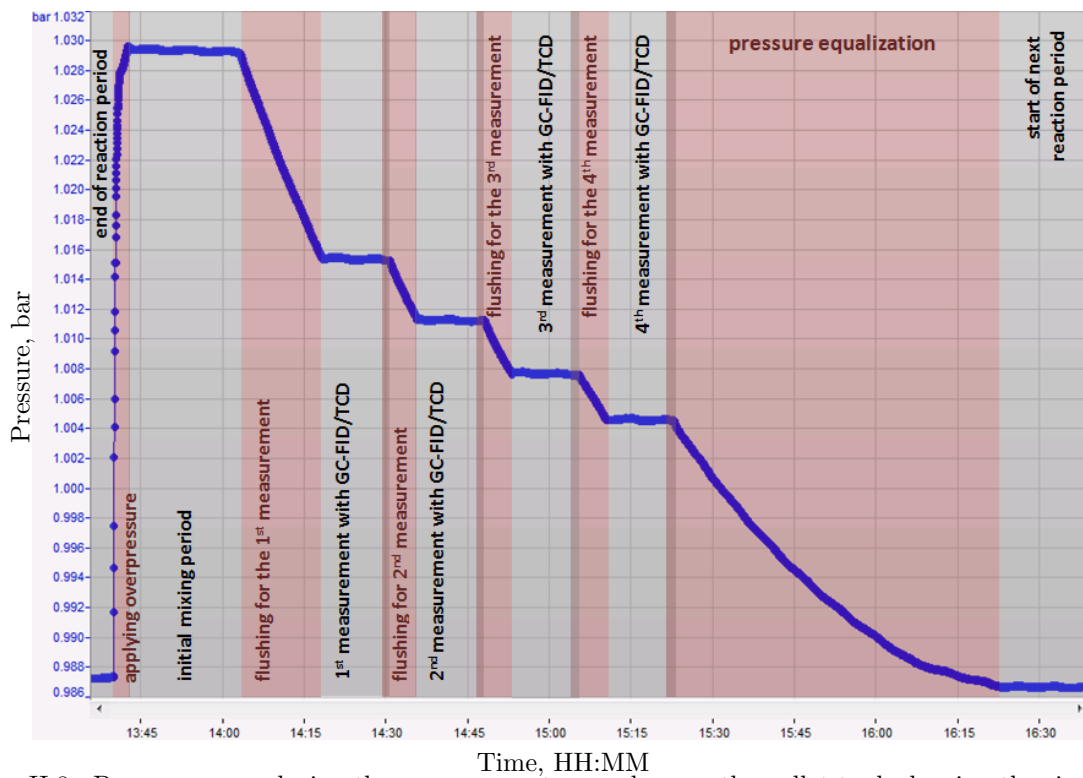


Figure II.8.: Pressure curve during the measurement procedure on the pellet tank showing the single steps of measurement.

Between determinations of gas concentrations the tank is sealed. Using the data logging system variances of pressure, temperature and relative humidity are monitored. The temperature around and in the tank is kept in a range between 21.5 and 23.5 °C throughout the storage experiment. After the final concentration measurements, on the last day of the experiment, the tank is opened and the sample material is removed. Again, the moisture content of the sample is determined and the tank is cleaned and prepared for the next sample.

3.7.5. Processing of data

Gas amounts are always expressed in volume at 22 °C and 1 bar, which is defined as the typical trial conditions (t.c.). Slight changes in temperature and pressure led to significant influences on the results. Therefore, the real gas volumes had to be corrected accordingly for 295.15 K and 100000 Pa. Because the volume of the gas, the current temperature and the current pressure had been determined, the volume at these conditions could be calculated using the following equation:

$$V_{t.c.} = \frac{p \cdot V}{T} \cdot \frac{T_{t.c.}}{p_{t.c.}} \quad (\text{II.13})$$

Subsequently, the given volumes are always considered at trial conditions. This will not be designated anymore. For converting peak areas of GC-FID/TCD into concentration values of the investigated substances an appropriate model was required. For this purpose the statistical program SAS was used. For each substance a quadratic or linear regression model based on the calibration gas measurements was accomplished. For each substance the standard deviation increased with higher concentration. As a consequence of this behavior, the method of the weighted least square regression was applied. Each peak area value of the calibration gas measurements was multiplied with the weighting factor of the respective concentration (w_i), which is the reciprocal value of the variance (σ_{ci}^2) thereof [86].

$$w_i = \frac{1}{\sigma_{ci}^2} \quad (\text{II.14})$$

A prediction interval of 95 % was chosen. Correlation models of the presented format were created and are presented in Table II.10. In the cases for CO, VOC, O₂ and N₂ the regression curves were forced through the zero point. Consequently, no intercept is given. For CO₂ the linear model including an intercept resulted in a better fit. In case of CH₄ only one calibration gas was available. Therefore, it was not possible to build an interpolation curve. However, the values acquired from the calibration gas measurements of one concentration and the zero point for CH₄ were interpolated. The prediction interval, which was determined of the available calibration gas concentration, of 15 ppm was assumed for all values of CH₄. Since this is not accordant to correct laboratory practice, all determined values of CH₄ in this work are considered best estimated values. The free volume at start ($V_{\text{atmos},0}$) can be derived by subtracting the volume of the pellet sample from the volume of the tank (V_{tank}).

$$V_{\text{atmos},0} = V_{\text{tank}} - m_{\text{pellet}} \cdot \rho_{\text{pellet}} \quad (\text{II.15})$$

As the pressure had been increased before the concentration measurement was conducted, the larger gas amount inside the tank has to be taken into account when converting the measured volumes into volumes at trial conditions. The higher pressure during the measurement resulted in a higher calculated gas volume at a pressure of 100000 Pa. The volume of the respective gas compound (V_i) was calculated by multiplying the concentration value [in %] with the total gas volume (V_{gas}), determined simultaneously along with the concentration determination.

$$V_i = \frac{c_i}{100} \cdot V_{\text{gas}} \quad (\text{II.16})$$

Table II.10.: Regression models and applied SAS procedures.

Substance(s)	Model	SAS procedure	Procedure adjustments
CO, VOC, O ₂ , N ₂	peak area = $k_1 \cdot c^2 + k_2 \cdot c$	GLM (Generalized linear models) procedure	<ul style="list-style-type: none"> • No Intercept • Distribution: normal • Predicted values: Confidence level 95 %
CO ₂	peak area = $k \cdot c + a$	REG(Regression) procedure	<ul style="list-style-type: none"> • Include Intercept • Confidence Limits for parameters estimates: Confidence level 95 % • Full model fitted
CH ₄	peak area = $k \cdot c$	REG procedure	<ul style="list-style-type: none"> • Include Intercept • Confidence Limits for parameters estimates: Confidence level 95 % • Full model fitted

Determination of CO, CO₂, CH₄ and VOC

The concentrations of emission gases were determined every 24 hours. Since gas was released for pressure equalization at every determination, a loss of the respective compounds occurred. Therefore, the released volume of the respective gas after measurement on the day before had to be subtracted from the complete volume of this gas from the day before (dm-1). The newly emitted gas volumes of CO, CO₂, CH₄ and VOC on the current day (dm) were calculated as presented in the following equation:

$$V_{i,emit,dm} = V_{i,dm} - (V_{i,(dm-1)} - V_{i,PE,(dm-1)}) \quad (II.17)$$

Determination of O₂

In contrast to the emitted gases O₂ was consumed during the experiment. Therefore, the calculations had to be adapted accordingly. The current O₂ volume and the O₂ volume, which was lost at pressure equalization on the day before, had to be subtracted from the present volume of O₂ on the day before. The result is the consumed O₂ volume, which was consumed in between the two concentration measurements.

$$V_{O_2,cons,dm} = V_{O_2,(dm-1)} - V_{O_2,PE,(dm-1)} - V_{O_2,dm} \quad (II.18)$$

Analogue to the calculation for the emitted gases, the sum of all consumed O₂ volumes had to be subtracted from the O₂ volume, which was present at trial start, to determine the overall O₂ consumption.

$$V_{O_2,cons,total} = V_{O_2,0} - \sum_{j=1}^{dm} V_{O_2,cons,j} \quad (II.19)$$

Emission/Consumption rates

For the determination of emission and consumption rates it was necessary to relate the emitted gas volumes to the emitted gas masses. This could be achieved by , first, converting the volumes into molar amounts of the respective compound.

$$n_{i,emit/cons,dm} = \frac{p \cdot V_{i,emit/cons,dm}}{R \cdot T} \quad (\text{II.20})$$

The conversion into emitted gas masses now only requires a multiplication of the molar amounts with the molar mass of the respective compound.

$$m_{i,emit/cons,dm} = n_{i,emit/cons,dm} \cdot M_i \quad (\text{II.21})$$

With the help of equations II.9 and II.10 the emission/consumption rates ($\dot{m}_{i,emit/cons,atro}$ [$mg/kg_{fuel_{atro}}$ in 24 h]) of the gases can be calculated.

$$\dot{m}_{i,emit/cons,atro} = \frac{m_{i,emit/cons,dm} \cdot 1000}{m - \frac{MC}{100}} \quad (\text{II.22})$$

Emission/Consumption factors

The emission/consumption factors [$mg/kg_{fuel_{atro}}$] of the respective gas compounds were calculated by summarizing the emitted/consumed gas volumes released during the experiment. The total amount of emitted gas volumes for the individual compounds was calculated by summarizing all newly formed gas volumes from the first to the last day of measurements.

$$f_{i,emit/cons} = \sum_{j=1}^{dm} \dot{m}_{i,emit/cons,atro,j} \quad (\text{II.23})$$

4. Results & discussion

The experimental work described in this thesis was carried out in the context of several different projects focusing on different aspects of the off-gassing topic. In order to structure the experiments in a thematic grouping the results were clustered according to the the following five topics:

1. Storage related influential parameters
2. Pellet material related influential paramters
3. Investigations into the off-gassing mechanism
4. Off-gassing properties of agricultural and torrefied biomass
5. Supplementary investigations

4.1. Storage related influential parameters

4.1.1. Headspace ratio

The headspace (HS) ratio is defined according to equation II.24, with the bulk volume of the filled pellets (V_{bulk}) being calculated by dividing the weight of the pellets (m_{pellet}) by the pellet bulk density (ρ_{bulk}).

$$HS\ ratio = \frac{V - V_{bulk}}{V} \quad (II.24)$$

The effects of oxygen content and HS ratio on the off-gassing behavior of wood pellets in sealed container storage have been investigated by Kuang *et al* 2009 [48]. The scientist found that with decreasing HS ratio the peak emission rate factors as well as the slopes of the emission factor curves for the investigated off-gassing emissions decreased. This was attributed to the fact that less oxygen was available for the oxidative reaction in the reactors containing more pellets.

However, the differences in the experimental setup described in this work, where the glass-flasks used for determination of off-gassing rates are ventilated on a regular basis (method description see section II.3.6) thereby eliminating the hampering effect of limited oxygen availability, make it necessary to carry out a similar experiment. To determine, whether the headspace ratio is influential on the development of the off-gassing rates for CO, CO₂ and VOC in this particular experimental setup a storage experiment was carried out. Six 5-liter glass flask were filled with spruce pellets (sample P01). Three flasks contained roughly 1 kg of pellets and the other three were filled with 2.4 kg of pellets each. This resulted in a headspace of 70, respectively, 25 %. The flasks were subsequently stored for 1 week and measurements were carried out on day 3 and day 7 of the storage period.

The results given in Table II.11 reveal that whilst in this setup relatively stable oxygen levels can be maintained throughout the storage experiments a headspace influence on the off-gassing rates, especially for CO₂ could still be detected. For all three investigated emissions a higher amount of off-gassing with a larger HS ratio could be observed. At this point there is no satisfactory explanation for these results.

Therefore, in the following experiments this fact was taken into consideration and results are compared at similar headspace ratios if possible, otherwise the HS ratio is clearly indicated.

Table II.11.: Influence of headspace ratio on off-gassing rates of CO, CO₂ and VOC (sample P01).

HS ratio	Storage time	Off-gassing rates			O ₂
		CO	CO ₂	VOC	
%	days	mg/kg fuel _{atro}		in 24 h	%
70	3	0.36	4.00	0.154	20.1
25	3	0.31	1.79	0.092	19.2
70	7	0.29	3.32	0.125	20.3
25	7	0.24	1.33	0.068	19.9

4.1.2. Storage temperature

In the course of this experiment six 5-liter glass flasks were each filled with roughly 2.4 kg of commercially produced spruce pellets (sample P02). Afterwards, three of the six bottles were flushed with nitrogen gas for a time span of 20 minutes in order to create a close to oxygen free environment during storage. Next, the pressure within each bottle was measured using a pressure sensor JUMO dTRANS p30 404366 (manufacturer: JUMO) with a range from 0 - 1.6 bar. Subsequently, two glass flasks were stored at 7, 20 and 50 °C, respectively, each set consisting of one flask with nitrogen atmosphere and one with air as start atmosphere (see Figure II.9). The flasks were thus stored for one week and after that period all six flasks were kept at 20 °C for two hours to equilibrate. After equilibration the pressure within each flask was determined and subsequently the gas atmosphere composition was determined utilizing the equipment described earlier in section II.3.6.2. The results of these measurements are presented in Table II.12.



Figure II.9.: Experimental setup for the investigation on the influence of storage temperature and storage atmosphere, from left to right depicting the storage at 7, 20 and 50 °C.

The data presented in Table II.12 clearly depicts the temperature influence on the off-gassing rates for the gases CO, CO₂ and VOC independent of the storage atmosphere. For both storage atmospheres, nitrogen and air, it could be shown that with rising temperatures the off-gassing rates are increasing. Furthermore, the increase is not linear but rather exponential.

A closer look on the off-gassing rates for the individual components reveals that the release of VOC seems to be more or less independent of the storage atmosphere and to be only influenced by storage temperature. The influence of the storage atmosphere is most apparent for the off-gassing rates of CO₂ resulting in much lower off-gassing rates when stored under nitrogen atmosphere than compared to storage with air atmosphere. The same behavior is also observed by the CO off-gassing rates, but it is less pronounced. The question as to where the oxygen for the formation of CO₂ and CO is coming from in a close to zero oxygen storage atmosphere can be answered when considering that, first, the nitrogen storage atmosphere is not completely free of oxygen and that some residual oxygen after the nitrogen flushing procedure was still available for reactions.

Secondly, it can also be assumed that some of the oxygen for the off-gassing products is also coming from the biomass itself. This hypothesis is supported by the increased pressure levels measured for the glass flasks with nitrogen atmosphere stored at 7 °C and at 20 °C, as the increase in pressure means an increase in gaseous components due to the conversion of solid matter to gaseous matter. The trend, however, is not sustained at 50 °C where the measured pressure level inside the flask has dropped due to a decrease of gaseous matter because of adsorption or chemical reaction of gaseous components effectively binding them to the biomass. For the glass flasks with an initial storage atmosphere of air, this drop in pressure levels can be observed for all storage temperatures and is also mirrored in the drop of the measured oxygen levels, which far exceeds the increase of gaseous components from CO, CO₂ and VOC combined. This leads to the conclusion that while gaseous components are released from the stored biomass a far greater amount of oxygen is at the same time taken up by the biomass.

4.1.3. Storage atmosphere - Oxygen content

In these experiments the emissions of CO, CO₂, VOC and CH₄ of commercially produced spruce pellets (sample P24) were investigated for three storage scenarios differing in the availability of O₂ during storage. All experiments were carried out under ventilated storage conditions, the difference was only in the oxygen concentrations of the storage atmospheres chosen. The chosen storage atmospheres were:

1. 0 % O₂, 100 % N₂
2. 20 % O₂, 80 % N₂
3. 35 % O₂, 65 % N₂

Close to constant O₂ concentrations throughout the experiments were accomplished by flushing the tank with the gases with the chosen atmospheric gas at the start of the experiment. Later on the chosen atmospheric gas was used for the over-pressurization just before the injection of measurement gas into the GC equipment (details see section II.3.7.4), thus providing fresh atmospheric gas every 24 hours and thereby creating ventilated storage conditions. The actual O₂ concentrations during the testing ranged between 0.1-0.8 %, 18.7-17.3 % and 33.1-30.4 % for the three atmospheres over the course of the three week storage experiments. The aim of these experiments is to investigate the time-dependent development of the emission rates of CO, CO₂, VOC and CH₄ without the possibly limiting effect of decreasing O₂ concentrations on the emission rates. Previous studies carried out by Kuang *et. al.* in 2009 [47, 48] so far have only reported off-gassing rates and emission factors for pine pellets stored in sealed container experiments with a naturally decreasing availability of oxygen over storage time. The results of these experiments are presented in Figure II.10.

A first look at the development of the off-gassing rates for all detected off-gasses shows a very similar overall trend throughout all three storage experiments. CO₂ is the dominating off-gas in each storage situation, followed by CO, VOC and lastly CH₄. Over the course of the 20 days storage time the off-gassing rates for CO₂ and CO are clearly dropping more or less continuously, the drop is less significant for the off-gassing rates of VOC and least noticeable for CH₄. The development of the emission factors shows an increase of the release of CO₂ and CO with rising O₂ content in the storage atmosphere while at the same time the emission factors of VOC and CH₄ are decreasing with rising O₂ values. The results for storage in close to zero O₂ content for this experiment and the experiment described in section II.4.1.2 also prove to be very similar. Once more the picture that presents itself shows that, although CO₂ and CO off-gassing is somewhat diminished under these storage conditions, they are by no means stopped.

Interestingly, the consumption of O₂ is on average about double as high for the storage experiment at 35% oxygen content in the storage atmosphere than for the storage at 20 % O₂. However, the release of CO₂ and CO, though higher at 35 % O₂ than at 20 % O₂, does not reflect that same fact. Again, similar to what could be seen in the experiment in section II.4.1.2, a far greater amount of gaseous oxygen is taken up by the biomass, than consumed to promote the release of CO₂, CO and VOC.

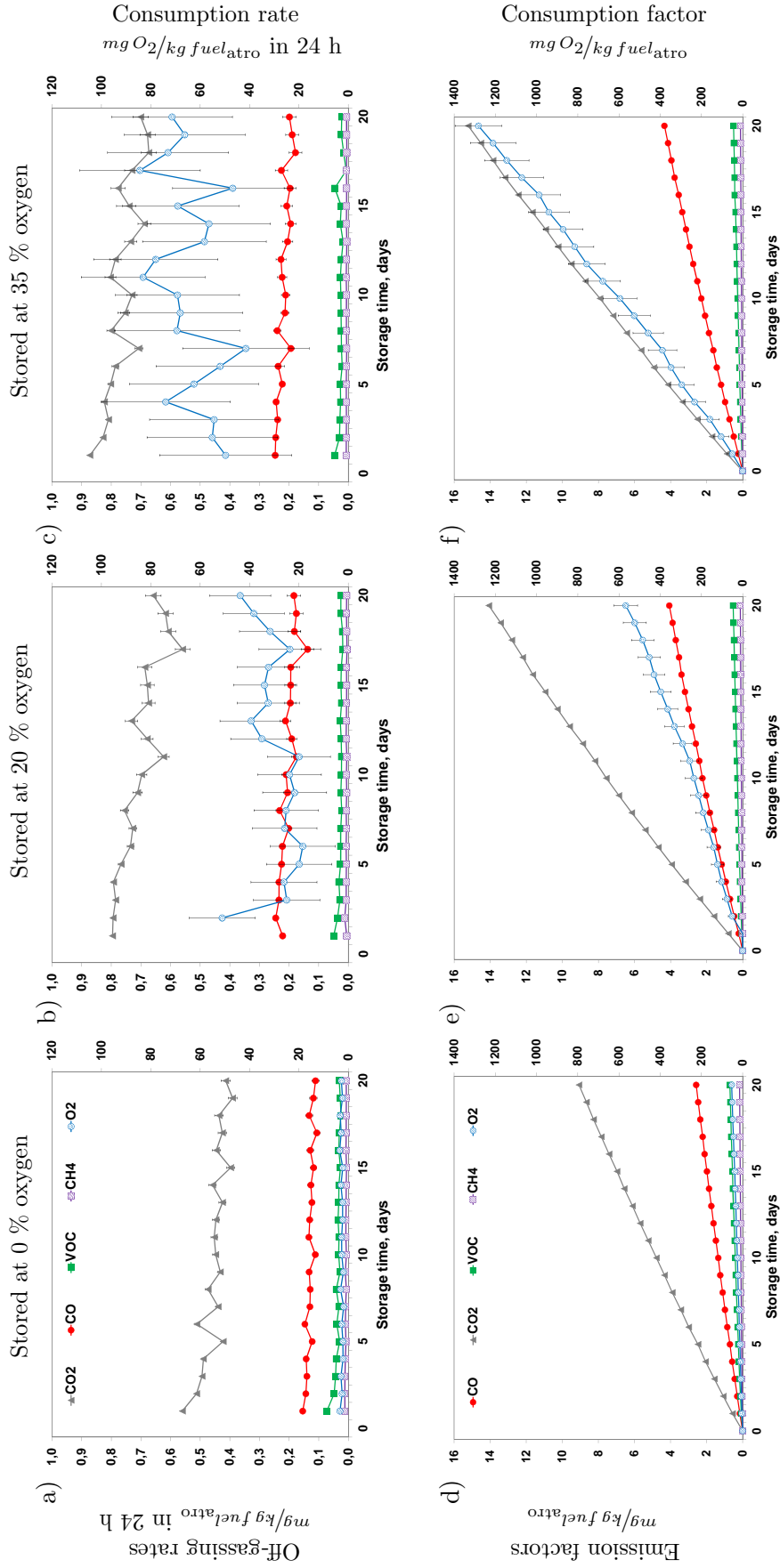


Figure II.10.: Off-gassing/consumption rates dependent on the oxygen content of the storage atmosphere (sample P24) a) at 0 % b) at 20 % and c) at 35 % O_2 ; Emission/consumption factors d) at 0 % and e) at 20 % and f) at 35 % O_2 . The values of the O_2 consumption rates and factors are to be read from the secondary y-axis.

In order to see just how much more gaseous oxygen is taken up rather than released in the forms of CO₂, CO and VOC a simplistic comparative mass balance calculation is carried out. Assuming that the total released VOC fraction is released as pentanal, a compound with one oxygen atom incorporated, the O₂ mass balance calculation revealed that after 20 days of storage only 15.68, 2.25 and 1.07 % of the consumed O₂ can be found within the determined off-gassing emissions in the cases of storage experiments at 0, 20 and 35 % of initial O₂ concentration, respectively.

For a better evaluation of the results a comparison with some of the results from the studies of Kuang *et. al.* in 2009 [47, 48] is presented in Table II.13. The literature values for the emission factors after 20 days of storage of CO₂, CO and CH₄ as well as the vol% values for the oxygen concentrations have been determined using a simple graphical method from the Figures provided in the journal articles. For better comparability only the results from storage experiments carried out at room temperature were chosen for the overview. Furthermore, all literature data was converted into $mg/kg\ fuel_{atro}$ and corrected according to a corrigendum concerning the above mentioned articles published in 2011 [49].

First of all, it has to be mentioned that a comparison between off-gassing rates from pine and spruce materials needs to be done on the basic understanding that pine material is typically more reactive than spruce material. Therefore, quantitative differences in the amounts of released off-gasses need to be interpreted with that fact in mind. The literature data show that the range of reported off-gassing rates for CO₂, CO and CH₄ for pine samples is considerable. This illustrates the fact, that even though some wood species have a tendency to be more reactive in terms of off-gassing than others, it is still difficult to predict the reactivity of an individual sample without testing.

The closest overlap with the data presented in this work is between the pellets from charge C and the new data from the spruce pellets. For the literature data from charge C pellets stored at an initial O₂ content of 20 % at a HS ratio of 50 % and the spruce pellets stored at 20 % O₂ the values on all measured emission factors are actually almost identical. However, whilst the development of the emission factors taken from literature are already leveling off and are approaching maximum plateau values after 20 days of storage, this is not the case for the data gained from the new experiments. The stable availability of oxygen throughout the storage experiment has influenced the changes in the development of the off-gassing rates by stabilizing the off-gassing rates for CO₂ and CO over a longer period of time and slowing their decrease.

Table II.13.: Comparison between literature data from sealed storage experiments and new data from ventilated storage experiments on the emission factors for the off-gasses CO₂, CO, VOC and CH₄.

Source	Data set	Storage conditions	CO ₂	CO <i>mg/kg fuel_{atro}</i>	CH ₄	VOC	O ₂ vol%
[48]	4.5 kg pine pellets (charge A)	sealed, 0 % initial O ₂ , 85 % HS	50.0	15.0	0.26	n.a.	3.5
	4.5 kg pine pellets (charge A)	sealed, 20 % initial O ₂ , 85 % HS	124.0	30.0	0.36	n.a.	15
	25.5 kg pine pellets (charge B)	sealed, 20 % initial O ₂ , 25 % HS	10.5	11.0	0.19	n.a.	1.5
	17.0 kg pine pellets (charge B)	sealed, 20 % initial O ₂ , 50 % HS	22.0	20.0	0.21	n.a.	6.8
	8.5 kg pine pellets (charge B)	sealed, 20 % initial O ₂ , 75 % HS	46.0	30.0	0.24	n.a.	8.2
[47]	5.25 kg pine pellets (charge C)	sealed, 20 % initial O ₂ , 25 % HS	8	3 ⁺	0.08 ⁺	n.a.	18.2
	3.5 kg pine pellets (charge C)	sealed, 20 % initial O ₂ , 50 % HS	11.3	3 ⁺	0.08 ⁺	n.a.	17.8
	1.75 kg pine pellets (charge C)	sealed, 20 % initial O ₂ , 75 % HS	16	4.8	0.08 ⁺	n.a.	15.8
Sample P24	7.0 kg spruce pellets	ventilated, 0 % O ₂ , 65 % HS	9.1	2.6	0.17	0.71	<1
	7.0 kg spruce pellets	ventilated, 20 % O ₂ , 65 % HS	14.1	4.1	0.13	0.53	≈ 18
	7.0 kg spruce pellets	ventilated, 35 % O ₂ , 65 % HS	15.2	4.3	0.12	0.51	≈ 33

n.a. data not available

⁺data source did not allow a more accurate reading of the values

4.2. Influential parameters related to the pellet material

4.2.1. Wood species

The off-gassing behavior exhibited by wood pellets spans a broad spectrum of values for the off-gassing rates of the emitted volatile compounds. One influential parameter on the off-gassing behavior related to the pellet material has been reported to be the type of wood species chosen for the pellet production. As explained in more detail in section II.1, it is a well established fact that wood pellets produced from pine have a tendency to exhibit higher off-gassing rates than wood pellets produced from spruce. However, it is difficult to estimate the off-gassing rates or rather the bandwidths of off-gassing rates for any given wood pellet sample based on the very few data points available in literature, today. Furthermore, the published values focus on wood species utilized in North America ([45–51]) and, therefore, might not be reliable to estimate values for off-gassing behavior of wood species common to Europe.

In Table II.14 a list of 49 pellet samples is presented. For each sample a determination of the off-gassing rates for CO₂, CO and VOC was performed utilizing the glass flask method described in section II.3.6. The samples were stored for 72 hours, after which the off-gassing rates were determined. The Table contains information on the raw material used for the pellet production and (if available) information of the pellets age since production.

Table II.14.: Summary Table of off-gassing rates for all analyzed wood pellet samples.

#	Raw material	Mix ratio %	Ø mm	CO ₂ <i>mg/kg fuel_{atro}</i>	CO <i>in 24 h</i>	VOC <i>in 24 h</i>	Prod. time weeks
P01	spruce	100	6	1.35	0.24	0.068	unknown
P02	spruce	100	6	0.35	0.12	0.030	unknown
P03	spruce	100	6	2.24	0.80	0.057	1
P04	spruce	100	6	0.92	0.14	0.067	1
P05	spruce	100	6	2.03	0.07	0.009	1
P06	spruce	100	6	2.26	0.08	0.008	1
P07	spruce	100	6	1.56	0.08	0.008	1
P08	spruce	100	6	2.79	0.99	0.150	1
P09	spruce	100	6	0.59	0.06	0.009	12
P10	spruce	100	6	0.61	0.05	0.031	7
P11	spruce	100	6	n.d.	0.06	0.009	unknown
P12	spruce	100	6	0.68	0.10	0.012	unknown
P13	spruce	100	6	n.d.	0.02	0.005	unknown
P14	spruce	100	6	0.88	0.24	0.030	unknown
P15	spruce	100	6	n.d.	0.02	0.006	unknown
P16	spruce	100	6	2.84	0.49	0.110	unknown
P17	spruce	100	6	1.52	0.60	0.153	unknown
P18	spruce	100	6	1.74	0.41	0.097	unknown

Continued

#	Raw material	Mix ratio %	Ø mm	CO ₂ <i>mg/kg fuel_{atro}</i>	CO <i>in 24 h</i>	VOC <i>in 24 h</i>	Prod. time weeks
P19	spruce	100	6	0.89	0.16	0.042	unknown
P20	spruce	100	6	0.38	0.02	0.003	unknown
P21	spruce	100	6	2.02	0.06	0.048	unknown
P25	pine	100	6	1.26	0.25	0.054	2
P26	pine	100	6	1.14	0.46	0.053	1
P27	pine	100	6	0.46	0.06	0.005	12
P28	pine	100	6	1.12	0.13	0.076	10
P29	pine	100	6	n.d.	0.60	0.122	2
P30	pine	100	6	1.07	0.31	0.037	1
P31	pine	100	6	1.55	0.37	0.085	2
P32	pine	100	8	1.91	0.31	0.062	13
P33	pine	100	6	6.10	3.41	1.114	1
P34	pine	100	6	0.65	0.09	0.012	>12
P35	pine	100	6	3.64	0.21	0.177	unknown
P36	spruce/pine	80/20	8	2.48	0.22	0.229	7
P37	spruce/pine	80/20	6	1.35	0.16	0.177	8
P38	spruce/pine	60/40	6	4.23	0.56	0.309	3
P39	spruce/pine	50/50	8	4.47	1.83	2.545	3
P40	spruce/pine	40/60	8	2.14	0.19	0.035	5
P41	spruce/pine	40/60	8	0.34	0.05	0.011	13
P42	spruce/pine	30/70	6	1.62	0.05	0.045	unknown
P43	spruce/pine	20/80	6	1.87	0.06	0.065	unknown
P44	spruce/pine	unknown	6	1.65	0.51	0.121	8
P45	larch	100	6	0.89	0.34	0.041	>3
P46	larch	100	6	0.46	0.03	0.003	1
P47	spruce/douglas fir	85/15	6	2.14	0.10	0.072	unknown
P48	pine/larch/fir	75/rest	8	0.43	0.04	0.014	9
P49	hardwood	100	6	1.48	0.13	0.003	>12

For a better graphical presentation of the results compiled in the Table above the average and range of the off-gassing rate measurements for the pellet samples produced from spruce, pine and a mixture of both have been summarized in a box-and-whiskers plot or boxplot (see Figure II.11). To begin with, the results from the boxplot diagrams highlight, that over a significant range of off-gassing values the results for the three wood species groups overlap. This result demonstrates, that no clear distinction between the off-gassing behavior of the three groups of pellet samples does exist. It is possible to find both high and low value off-gassing rates of equal amounts within each of the three groups of pellet samples. However, a comparison of the individual medians of the off-gassing rates shows trends in accordance with literature findings. In the case of CO off-gassing rates, for example, presented in Figure II.11.b, the average CO off-gassing rate for pine pellets is about three times as high as for spruce pellets and about 33 % higher than for mixed

pellets. Also for average VOC off-gassing rates the pine pellets prove twice as reactive as the spruce pellets, the mixed pellets, on the other hand, prove twice as reactive as the pine pellets.

The analysis of the range of values, represented by the length of the whiskers in the boxplot, also supports the previous literature findings [46–48] on the higher off-gassing reactivity of pine pellets over spruce pellets. Both, in case of CO_2 and CO , the highest off-gassing rates could be found for pine pellet samples. Furthermore, the off-set between the highest values for the spruce pellets and the mixed pellets in relation to the pine pellets is significant. Only the measured VOC off-gassing values do not follow that trend. Here the highest measured value was exhibited by a mixed pellet sample, followed by pine and spruce. However, this is not in conflict with literature values on VOC off-gassing rates, as there are practically no existing reported values for VOC off-gassing available.

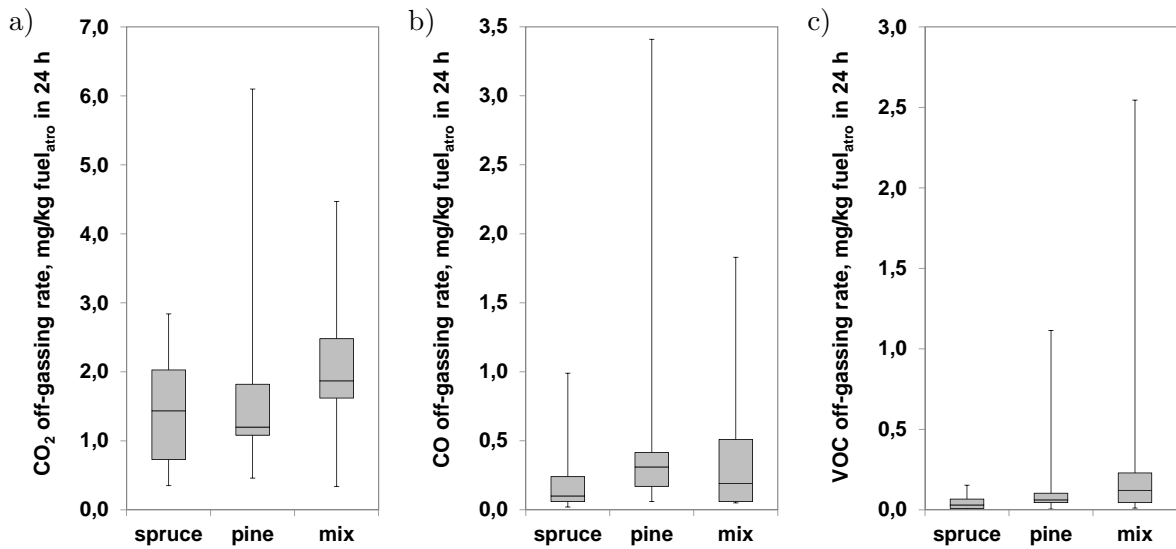


Figure II.11.: Boxplots for the off-gassing rates of pellets made from spruce, pine and mixtures of both wood species for a) CO_2 , b) CO and c) VOC emissions.

Whilst the boxplot presentation gives a good overview on the statistical distribution of off-gassing values from the investigated pellet samples, some of the depth of information available for the data is lost. Most importantly the information on the ages of the pellet samples since production is lost in the presentation of averaged data. The importance of this parameter is discussed in more detail in section II.4.2.4. For now, it is sufficient to mention that the development of the off-gassing rates for all investigated emission gases, but especially for CO , is strongly dependent on the age of the pellet and decreases with time.

In order to see if there is a correlation between the investigated off-gassing rates for the gases CO_2 , CO and VOC with each other two-dimensional plots were created, which plotted the off-gassing rates of two emission gases dependent on each other, e.g. off-gassing rates for CO_2 versus off-gassing rates for CO . Including all data points used also for the creation of the boxplot diagrams proved to be not ideal due to the aforementioned strong influence of the pellets ages since production. As a result, only data points with a known sample age of ≤ 5 weeks have been included in the plots depicted in Figure II.12.

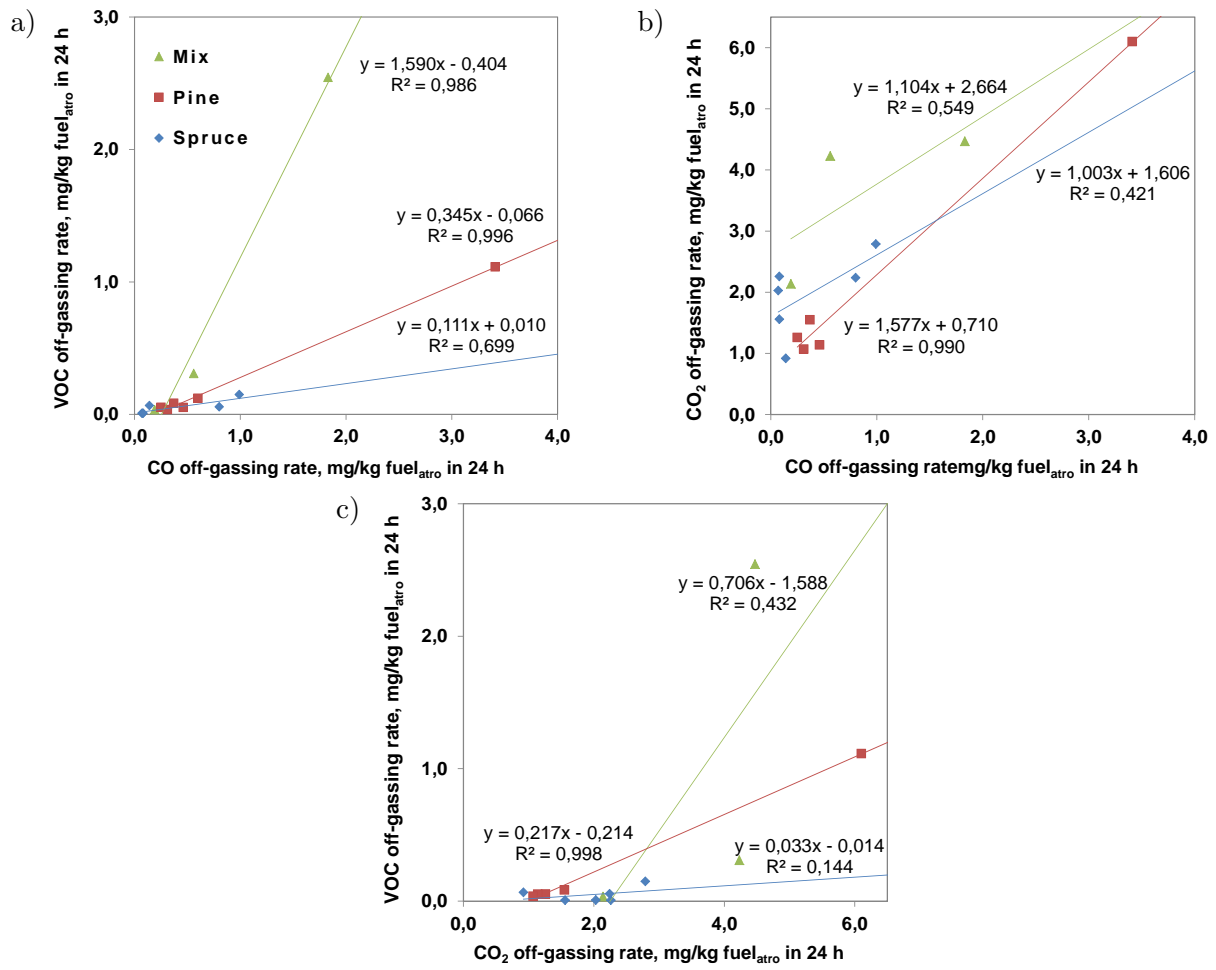


Figure II.12.: Correlation plots for off-gassing emissions of pellet samples from spruce, pine and a mixture of both wood species. The green data points and trend lines correspond to the mixed pellet samples, the red and the blue data corresponds to pine and spruce samples, respectively.

Based on the distribution of data points within the two-dimensional plots a linear correlation model was chosen and based on the values for the coefficient of determination of the linear correlation the applicability of the model is evaluated. The results show, that a linear correlation exists for all three of the investigated gases only within the group of pine pellet samples. Here, however, the correlation is in all three plots distinctly visible.

For the mixed pellet sample a quite good correlation can also be seen between the VOC off-gassing rates and the CO off-gassing rates with a high coefficient of determination on the linear regression equation for this data set. However, it has to be mentioned that this set includes only three data points and, therefore, more data points would be necessary to strengthen this result. In the case of the spruce pellet samples, however, no satisfactory evidence of linear correlation between any of the three investigated off-gassing emissions can be seen. An explanation as to why the pellet samples from the different wood species behave so differently from each other can not be offered at this point and will have to be the topic of future research work.

4.2.2. Raw material fraction

The off-gassing phenomenon has been reported to originate from autoxidation reactions of woods own fatty acids (more details see section II.1). Therefore, an experiment was designed to investigate the possible influence of extractive content on the release of emissions from off-gassing wood samples. The objective was to choose samples, which were on one hand very similar to each other, yet had a distinctly different extractive content. This could be achieved by choosing wood samples of the same wood species, but from different raw material fractions. It was decided that a comparison between spruce sawdust (sample RM01) and spruce shavings (sample RM05) would provide the ideal parameters for such an experiment. In this test the sawdust sample represents a sample with high extractive content, that can furthermore be considered as a fresh sample, whereas the shavings sample represents low extractive content and is considered a mature sample. Additionally, pellets were made from both raw materials, spruce sawdust and spruce shavings (P03 & P04, respectively) to study the influence of the pelletizing process on the extractive content, extractive composition and off-gassing behavior of the samples.

The raw materials were obtained directly from a pellet production facility and pelletized on a laboratory scale pellet press with a capacity between 5 to 10 kg/h , without the use of binding agents. For the determination of the off-gassing rates the sample materials were stored in sealed glass flasks with a volume of five liters. In the case of the shavings and sawdust samples roughly 1 kg of material was stored, in the case of the pellet samples around 2.4 kg of material were stored. For better reliability three parallel storage series were conducted and an arithmetic average for the off-gassing rates of the samples were determined. The storage experiment was carried out for a series of five days and measurements of gas concentrations within the flasks were conducted after three and after five days of storage. Based on measured values of gas concentrations, known sample volumes and volumes of the storage containers the off-gassing rates in $mg/kg_{fuel_{atro}}$ in 24 hours were calculated. An overview on the results is given in Figure II.13.

A comparison of the fresh sawdust sample with the mature shavings sample delivers the hypothesized result that the mature sample exhibits less off-gassing than the fresh sawdust sample. The difference is clearly visible in the determined CO_2 and CO off-gassing rates and present, although less pronounced, also in the VOC off-gassing rates. Interestingly, the extractive content of the two samples, given in Table II.15, is very similar and does not follow the predicted trend of being significantly diminished in the case of the shavings sample. A change can be observed though in a shift in the ratio of saturated to unsaturated fatty acids. For the fresh sawdust sample the ratio is very close to 1:4, whereas for the mature shavings sample the ratio is basically 1:3. This means, that the mature sample contains a lower amount of unsaturated fatty acids, which would be the reactands in an autoxidation process.

The pelletized samples differ from the raw material samples in that CO_2 off-gassing rate are significantly lowered in the pelletized samples. The CO off-gassing rates, on the other hand, do not show a similarly consistent trend, in one sample (P03) the rate is increased after pelletizing, while in the other sample (P04) the rate is slightly decreased. Both pellet samples, moreover, exhibit higher VOC off-gassing than the corresponding raw material samples.

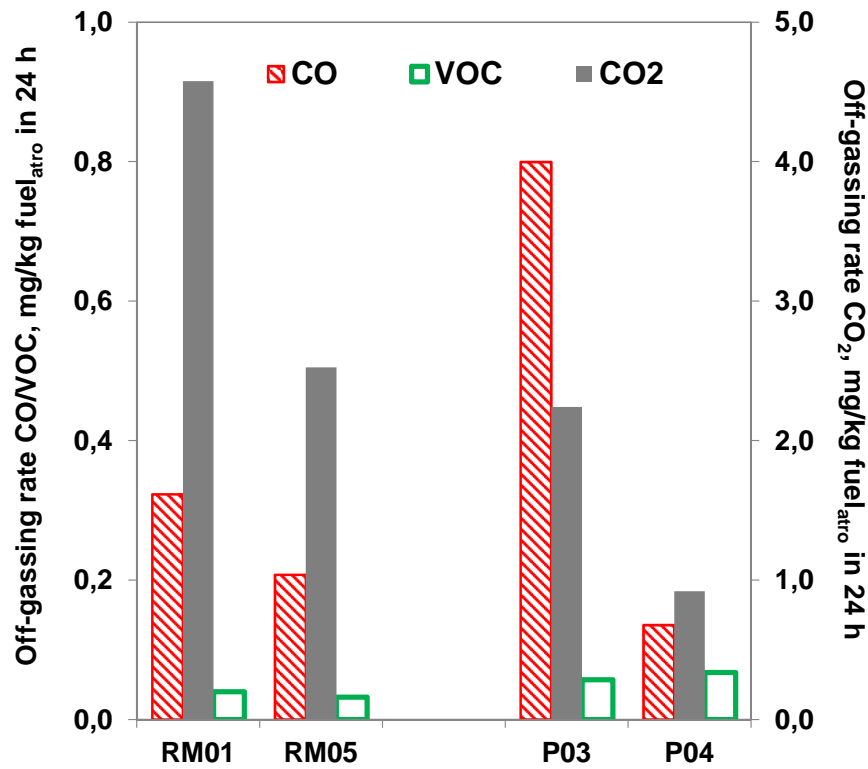


Figure II.13.: Influence of raw material history on the off-gassing rates for CO₂, CO and VOC for samples RM01 (spruce sawdust), RM05 (spruce shavings) and pellet samples produced from these raw materials, P03 and P04, respectively. The CO₂ off-gassing rates need to be read from the secondary y-axis.

Relating the findings for the off-gassing behavior with the analysis of the extractive content and composition further accentuates the differences between raw material and pellet samples, see Table II.15. As a result of the pelletizing process the overall extractive content of the pellet samples has been reduced by half, yet a similar reduction for the off-gassing rates can only be observed in the case of CO₂. CO and VOC emission, on the other hand, have instead been increasing. The only exception to this is the CO off-gassing rate for the shavings pellet sample, which is lowered, but only by $\approx 25\%$. The ratio of saturated to unsaturated fatty acids in the pellet samples remains through the pelletizing process very close to the original ratios determined for the raw material samples. However, a slight shift from higher hydrocarbons to lower hydrocarbons takes place.

Table II.15.: Influence of raw material fraction on extractive content and composition for samples RM01 (spruce sawdust), RM04 (spruce shavings) and pellet samples produced from these raw materials, P03 and P04, respectively.

	RM01	RM05	P03	P04
Extractive content $mg/kg_{fuel_{atro}}$	879	775	399	275
Shares of individual extractive components				
C8:0	1.67	1.96	2.73	4.12
C10:0	1.39	0.28	0.76	1.06
C12:0	0.42	1.60	0.38	0.73
C14:0	0.49	0.29	0.59	1.19
C14:1	0.48	0.27	0.59	0.91
C16:0	4.42	8.84	12.82	12.74
C16:1	0.56	0.57	1.35	1.75
C18:0	1.85	4.41	4.06	8.40
C18:1	13.38	24.39	28.23	22.04
C18:2	36.34	28.19	29.23	27.54
C18:3	1.71	1.21	1.29	3.22
C20:0	1.54	1.62	2.24	3.10
C20:1	0.59	1.55	3.09	2.43
C20:2	9.94	1.58	1.85	1.88
C20:3	2.86	1.67	0.59	0.61
C20:4	2.10	3.23	1.15	0.84
C22:0	8.05	8.18	1.12	0.66
C22:1	1.68	1.99	3.46	1.36
C24:0	6.32	6.57	2.96	3.25
C22:6 & C24:1	4.23	1.61	1.52	2.17
Sum saturated	26.14	33.74	27.66	35.26
Sum unsaturated	73.86	66.26	72.34	64.74

The results suggest, that the maturity of the raw material plays a significant role in the off-gassing behavior of the pellet sample. The pellet sample produced from spruce shavings exhibited the lowest off-gassing rates for CO₂ as well as for CO out of all four investigated samples, raw materials and pellets alike. Whilst the pelletizing process seems to have a decreasing effect on the off-gassing behavior of the shavings pellet sample, it has just the opposite effect on the sawdust pellet sample, at least with respect to the CO off-gassing rates. For this particular sample the CO off-gassing is more than doubled for the pellet sample with respect to the sawdust sample. From the data obtained so far it can not be properly explained why, despite the fact that the pelletizing process resulted in a decrease of the extractive content of the material in both cases, it had such a different effect on off-gassing behavior of the pellet samples. The influence of the pelletizing process on the off-gassing is dealt with in more detail in the following section.

4.2.3. Pelletizing process - press conditions

For the determination of a possible influence of the pelletizing process on the development of CO₂, CO and VOC off-gassing rates the following experimental design was chosen. Two spruce tree trunks of similar age were purchased from a local farmer located in the vicinity of Wieselburg (Lower Austria). At the time of purchase the tree trunks had been stored to dry for roughly six months. Next, the trunks were debarked and afterwards the trunks were chipped with a straw cutter and the wood chips were collected separately and given the designations batch A and B. As a next step, the relatively moist wood chips were left to dry until a moisture content of roughly 15 % was reached. Subsequently, the wood chips were grinded further using a cutting mill (manufacturer: Retsch) to a particle size below 4 mm.

Next, about 50 kg of shavings from batch A and about 100 kg of shavings from batch B were prepared for a pelletizing experiment. First, the shavings were conditioned to a moisture content between 18 - 20%. Then, the shavings from batch B were divided into two equal parts (B and B2). At this point 4 kg of sample of each of the three shavings piles were collected and provided the material used for the investigations on the off-gassing rates for the samples shavings. The samples, RM02, RM03 and RM04, were given the alternative designations shavings A ("sha. A"), B ("sha. B") and B2 ("sha. B2"), respectively, to indicate the source tree of each sample. Afterwards, the shavings from batch A and from batch B were pelletized under the same pelletizing conditions and without additional binding agents. The resulting pellet sample (P05 and P06) were also given alternative designations, namely pellets A ("pel. A") and B ("pel. B"), respectively. Finally, the remaining shavings from batch B2 were also pelletized keeping all pressing parameters on the same settings as before except for the raw material throughput through the pellet press, which was lowered by half. The reduction of the raw material throughput lead to a prolonged retention time of the pelletizing material within the pellet press, which also resulted in a prolonged thermal treatment of the material during pelletizing. The resulting pellet sample was designated "pel. B2" (P07).

For the determination of the CO and VOC off-gassing rates six 5-liter glass flask were each filled with roughly 2.4 kg of pellets, two for each pellet sample, and another six 2-liter glass flasks were each filled with roughly 0.4 kg of shavings, again two for each shavings sample. The bottles were stored for a period of two weeks and the off-gassing rates for CO and VOC were determined 5 times within this period in intervals of 3 to 4 days. After each determination, the bottles were flushed with pressurized air for a period of ≈ 10 minutes to replace the storage atmosphere with fresh air and to remove all off-gasses from the previous storage interval. In Figure II.14 the results of this experiment are presented.

While the development of the CO and VOC off-gassing rates of the shavings samples, depicted in Figure II.14.b, experiences strong similarities, the pellet samples, depicted in Figure II.14.a, show a clear difference between the behavior recorded for the samples "pel. A" and "pel. B" compared to sample "pel. B2". The fact that both shaving samples from spruce B ("sha. B" and "sha. B2") show similar behavior while the two pellet samples "pel. B" and "pel. B2" show differences in behavior indicates that the small change in the pressing conditions is responsible for the increased off-gassing rates of sample "pel. B2". Sample "pel. A", although produced from a different stock of raw material, shows very similar off-gassing rates to sample "pel. B". This is further indication for the hypothesis that similar pressing conditions result in similar CO off-gassing rates for pellets.

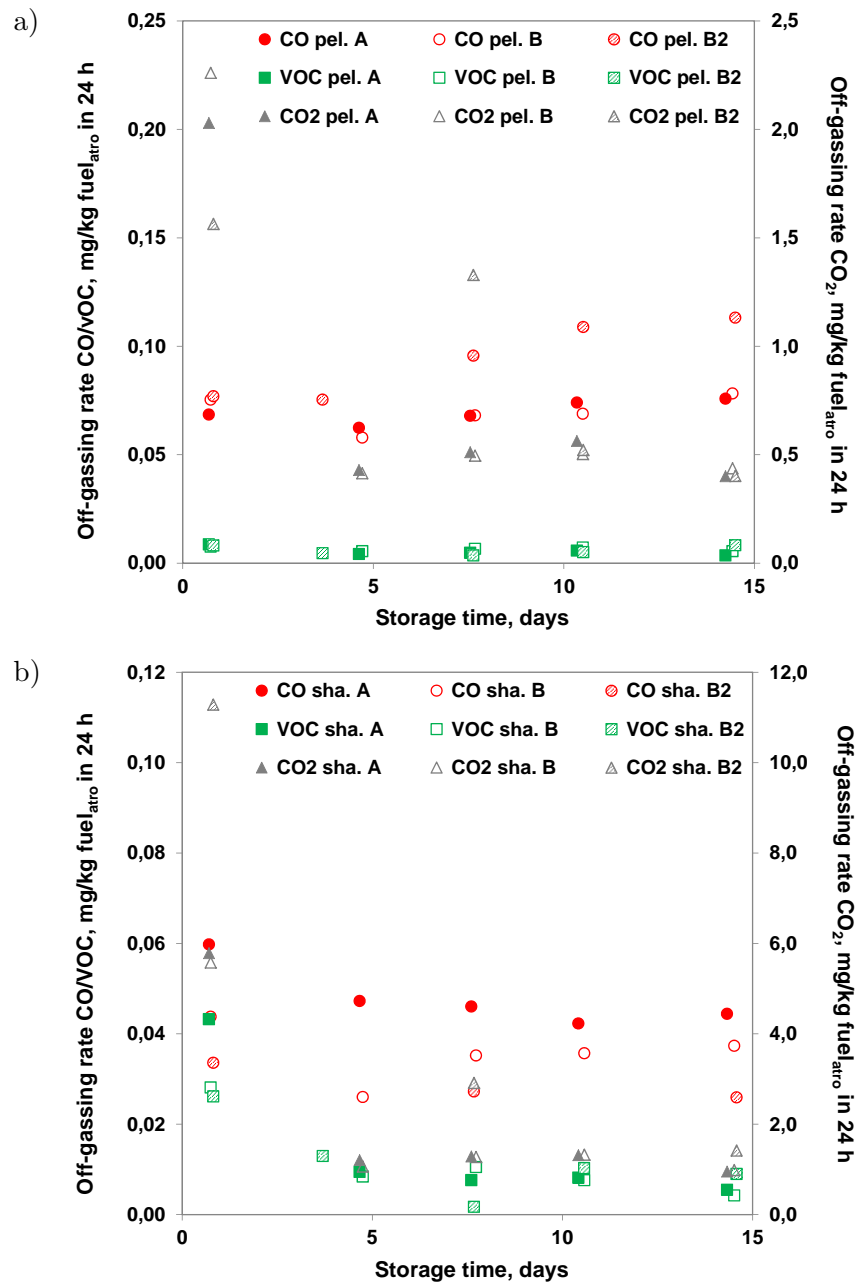


Figure II.14.: Influence of pelletizing process on the development of CO₂, CO and VOC off-gassing rates.

a) spruce pellet samples A, B and B2 (P05, P06 and P07) b) spruce shavings samples A, B and B2 (RM02, RM03 and RM04). The CO₂ off-gassing rates need to be read from the secondary y-axis.

Sample "pel. B2" exhibits a slight increase of the CO off-gassing rates in the course of the two weeks storage interval reaching a maximum value of almost $0.12 \text{ mg/kg fuel}_{\text{atro}}$ in 24 hours at the end of the storage experiment. In comparison, the samples "pel. A" and "pel. B" start at very similar values for the CO off-gassing rates but in the course of the experiment they exhibit only a very slight increase of the CO

off-gassing rates resulting in maximum values close to $0.075 \text{ mg/kg fuel}_{\text{atro}}$ in 24 hours, which are fairly close to the starting values. The development of the VOC off-gassing rates shows a very stable behavior over the two week storage period for all three pellet samples without significant differences between the individual samples.

A comparison between the shavings and the respective pellet samples highlights the heightened CO off-gassing rates as a result of the pelletizing process. Whats more, the CO off-gassing rates from the pellet samples further increased over the storage period, while the CO off-gassing from the shaving samples decreased with time. Contrary to the stable VOC off-gassing rates throughout the storage experiment from the pellet samples, the shavings samples show a decline in the VOC off-gassing rates with increased storage time. Also the starting VOC off-gassing rates are between 3 and 4 times higher for the shavings samples than for the pellet samples. The values at the end of the experiment, however, are very similar for both the shavings and the pellet samples.

The behavior of the off-gassing rates for CO_2 for shaving samples versus pellet samples present the same trends, which could be observed for the off-gassing rates for VOC only on a larger scale. For example, the initial CO_2 off-gassing rates for the shavings samples are on average 3 to 4 times larger than for the pellet samples. Furthermore, the CO_2 off-gassing rates, for both shavings and pellet samples, are marked by a very step decrease of the measured rates between the first and the second measurement point before leveling out at relatively stable values at the end of the 14 days storage experiment. This can be seen in particular for the shavings sample "sha. B2" in Figure II.14.b, which starts with an initial CO_2 off-gassing rate of $11.5 \text{ mg/kg fuel}_{\text{atro}}$ in 24 hours and levels off to a value around $1.5 \text{ mg/kg fuel}_{\text{atro}}$ in 24 hours by the time of the third measurement point. While the initial CO_2 off-gassing values are between 100 and 200 times larger than the initial off-gassing rate for CO, the final off-gassing rates are only larger by an average factor around 30. For the pellet samples the initial CO_2 off-gassing values start at $\approx 1 \text{ mg/kg fuel}_{\text{atro}}$ in 24 hours (a factor of 20 to 30 larger than for CO) and stabilize at a lower CO_2 off-gassing rate of approximately $0.5 \text{ mg/kg fuel}_{\text{atro}}$ in 24 hours (a factor of 10 when compared with CO).

Simultaneously to the off-gassing experiments a monitoring of the changes in the extractive profile of the pellet samples was carried out (method description see section II.3.4). Not only have the overall extractive contents of the samples been determined, but also the changes for the individual components. In Figure II.15 the extractive profiles for the three investigated pellet samples over the course of the 14 days storage experiment are depicted. The most prominent difference is certainly the significantly lower extractive content of sample "pel. B2" with respect to the other two samples. Indeed a determination of the average extractive content for the three pellet samples over the course of the storage experiment resulted in 242, 281 and only 181 $\text{mg extractives/kg fuel}_{\text{atro}}$ for samples "pel. A", "pel. B" and "pel. B2", respectively. Considering that the raw materials basis for samples "pel. B" and "pel. B2" is identical, this means a reduction of the overall extractive content by 35.8 % in the case of sample "pel. B2" due to the changes in the pelletizing process. The profiles further reveal the overwhelming similarities between the composition of the extractives of samples "pel. A" and "pel. B". A closer look on the profiles also shows that there is basically no decrease in the measured amount of the individual extractive components over the course of time with the exception of C18:2 (linoleic acid). The amount of linoleic acid is visibly decreasing during the storage experiment in all three pellet samples.

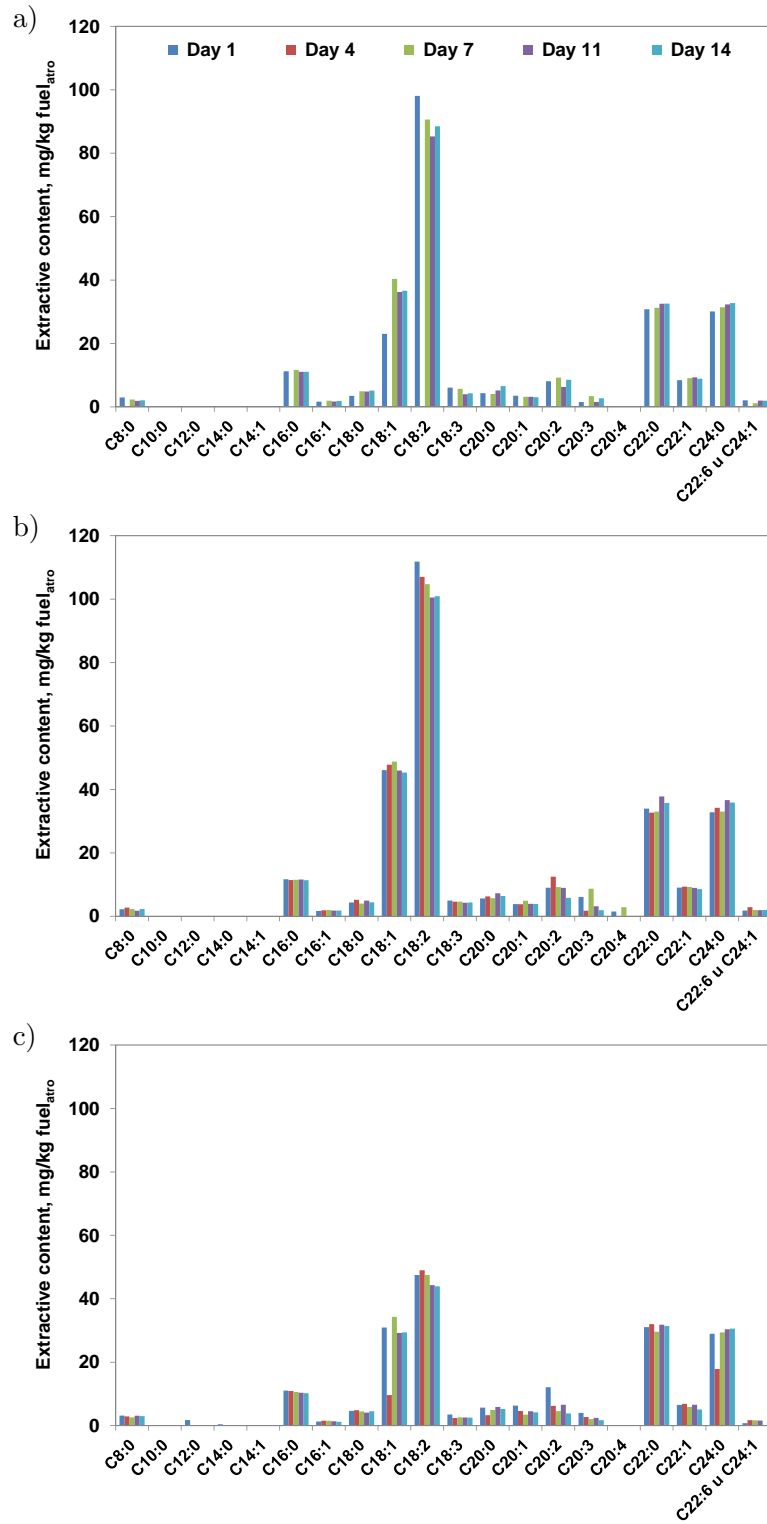


Figure II.15.: Extractive profiles over the course of a 14 days storage period. a) "pel. A" (P05, data for day 4 is not available) b) "pel. B" (P06) and c) "pel. B2" (P07).

Apart from the overall reduction of extractive content determined in sample "pel. B2" compared to sample "pel. B", one can also see distinct changes in the extractive composition between the samples. In Figure II.16 an overview for the shares of individual extractive components for the three pellet samples is given. Once again the samples "pel. A" and "pel. B" show a high degree of similarity, whereas in sample "pel. B2" the relative reduction in the share of linoleic acid in the overall extractive content is clearly the most distinct difference. Compared to sample "pel. B", where linoleic acid makes for roughly 37.3 % of the extractives, in sample "pel. B2" its share has dropped to 25.7 %. A similar, though much less distinct, trend can also be observed for oleic acid (C18:1), where the share for sample "pel. B" is at 16.6 % and for sample "pel. B2" only at 14.8 %. Overall this also results in shift of the ratio between saturated and unsaturated extractive components for the three samples. While the ratio saturated/unsaturated components is at 1:1.8 and 1:2 for samples "pel. A" and "pel. B", respectively, for sample "pel. B2" it is 1:1.2.

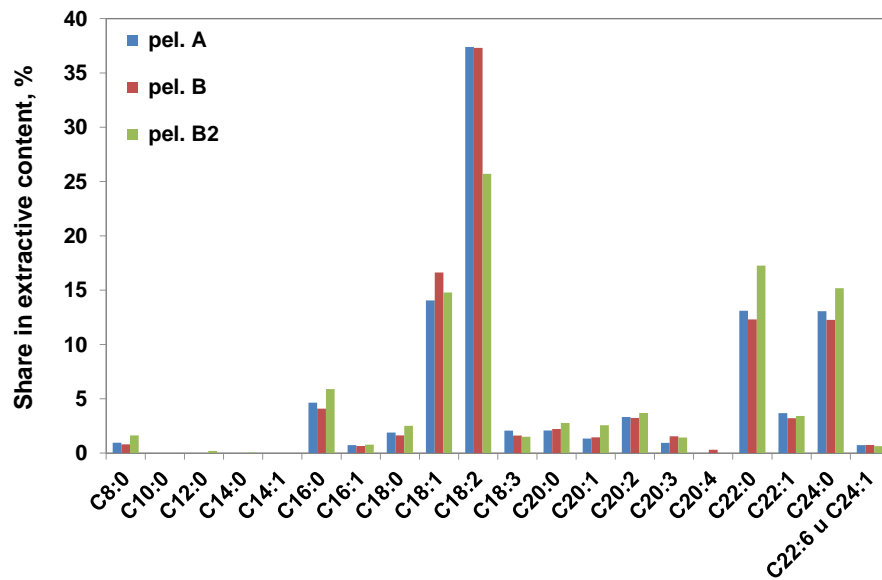


Figure II.16.: Comparison of the shares of individual extractive components in the overall composition for the samples "pel. A" (P05), "pel. B" (P06) and "pel. B2" (P07).

Relating these findings with the off-gassing data one can observe that the changes in the pelletizing process have effected the sample "pel. B2" not only in its off-gassing behavior, but also the chemical composition of the extractive components within the wood. As indicated in previous studies ([56, 87–89]) changes in moisture content and extractive content impact on the pelletizing pressure. It can, therefore, be concluded that changes in the pelletizing process and the resulting changes in the moisture and extractive content of the pellet also imply that this pellet has experienced a different pressure regime during pelletizing. However, the extent of that influence on the pellet sample remains yet to be investigated further. The fact remains that the reduction of the raw material throughput during the pelletizing of sample "pel. B2" and the resulting prolonged retention time of the pelletizing material within the pellet press as well as the prolonged thermal treatment of the material during pelletizing have lowered the extractive content of the sample "pel. B2" and also resulted in its increased off-gassing behavior.

4.2.4. Production age

To study the development of CO₂, CO and VOC off-gassing rates over time, a sample of freshly produced spruce pellets was stored only 24 hours after production. Subsequently, CO₂, CO and VOC off-gassing rates were determined over the course of 11 weeks approximately every 3 to 4 days. For the experiment three 5-liter glass flasks were each filled with around 2.4 kg of spruce pellets (P08), which were produced by an Austrian pellets producer according to the ÖNORM M7135 [76]. After each determination, the bottles were flushed with pressurized air for a period of ≈ 10 minutes to replace the storage atmosphere with fresh air and to remove all off-gasses from the previous storage interval. This treatment ensures that the storage atmosphere throughout the experiment is never saturated with CO₂, CO or VOC off-gasses. Furthermore, due to this treatment the availability of oxygen is not an inhibiting factor in the off-gassing development.

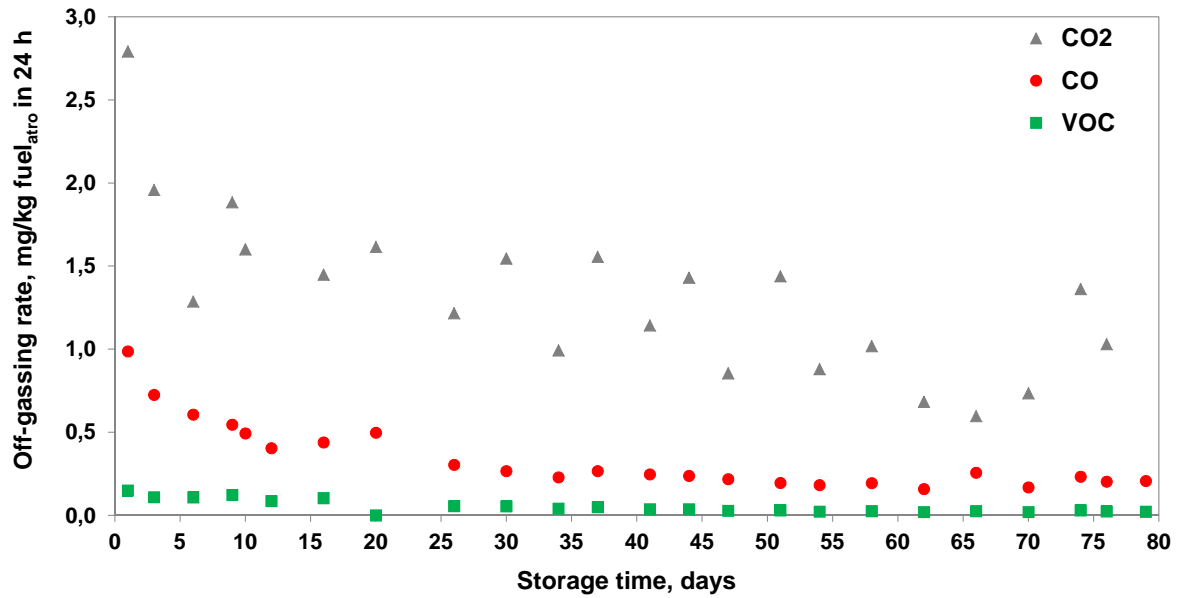


Figure II.17.: Development of CO₂, CO and VOC off-gassing from freshly produced spruce pellets over the course of 11 weeks (P08).

At the start of the storage experiment the off-gassing rate for CO₂ is initially at about $2.8 \text{ mg/kg fuel}_{\text{atro}}$ in 24 hours. Over the course of time the development of the CO₂ off-gassing rate exhibits an overall drop to a much lower rate of roughly $1 \text{ mg/kg fuel}_{\text{atro}}$ in 24 hours, with the measurement points distribution scattered instead of the evenly drop obtained for the other two measured off-gasses CO and VOC.

For CO the initial off-gassing rate of $1 \text{ mg/kg fuel}_{\text{atro}}$ in 24 hours was reduced by half after 10-20 days of storage and dropped to about $0.3 \text{ mg/kg fuel}_{\text{atro}}$ in 24 hours after one month. After a storage period of 40 days the rate reached a very stable value of around $0.2 \text{ mg/kg fuel}_{\text{atro}}$ in 24 hours and did not drop any further during the end of the 80 days of storage. VOC started out at an off-gassing rate of just above $0.1 \text{ mg/kg fuel}_{\text{atro}}$ in 24 hours and similar to CO dropped by half within the first 10 to 20 days of

storage. From then on the rates dropped very slowly but continuously resulting in a VOC off-gassing rate of $0.02 \text{ mg/kg fuel}_{\text{atro}}$ in 24 hours at the end of the storage experiment.

From these results it can be concluded, that whilst the off-gassing rates for all investigated emissions are decreasing with time, the actual drop rates for individual gases are different. The fastest drop in off-gassing rates with time can be seen for CO, followed by CO₂ and finally VOC. This knowledge is of great importance in the assessment of technical solutions against off-gassing emissions in wood pellet storages, which are discussed in detail in part IV.

4.3. Investigations of the off-gassing mechanism

A similar setup to the glass flask method (see section II.3.6) was chosen for an experiment to determine the off-gassing rates of CO and VOC from linoleic acid. Unfortunately, it was not possible to also determine CO₂ off-gassing rates due to an equipment malfunction of the gas analyzer used during the experiment. In preparation for the storage experiment 12 2-liter glass flasks were each filled with roughly 1 kg of filling material. The filling material consisted of pieces of LD-PE tubes with a length between 2-4 cm and an inner and outer diameter of 6 and 8 mm, respectively (see Figure II.18), and provided a high surface area for the homogeneous dispersion of the linoleic acid. In a next step, between 1 and 2 mg of linoleic acid, procured from SIGMA ALDRICH with a purity of 99.5 % (CAS 60-33-3), was dispersed into the glass flasks with the help of a spray bottle. By weighing the spray bottle before and after each application the exact amount of linoleic acid in each flask was determined. Finally, the glass flasks were sealed and stored at room temperature over a period of 1 to 6 days.



Figure II.18.: On the left a picture of the LD-PE filling material and to the right the 2-liter glass flasks with the filling material.

Similar to the procedure with the biomass samples the rates of CO and VOC off-gassing from linoleic acid

were calculated in $\text{mg/kg linoleic acid}$ in 24 hours. Parallel to the concentrations of the off-gasses also the oxygen content in the bottles were measured and recorded. The development of the CO and the VOC formation rates over the course of the five day storage experiment is depicted in Figure II.19.

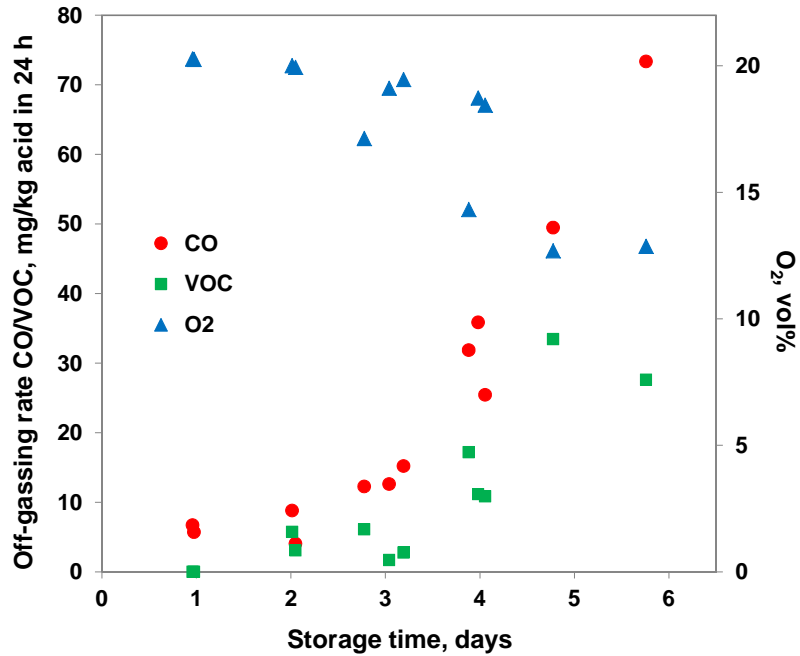


Figure II.19.: Development of CO and VOC off-gassing from pure linoleic acid during 5 days of storage; the O₂ content in the flasks is displayed on the secondary y-axis.

During the course of the experiment the observed off-gassing rates for CO as well as for VOC are increasing with increasing storage time. A maximum rate of CO off-gassing around $78 \text{ mg/kg linoleic acid}$ in 24 hours after 5 days could be reached. The maximum rate of VOC off-gassing was reached at roughly $30 \text{ mg/kg linoleic acid}$ in 24 hours after 5 days of storage. At that time the oxygen content in the glass flasks was only around 13 vol%.

With this experiment it could undoubtedly be proven, that CO formation takes place as a result of degradation of linoleic acid. Due to the lack of information on the off-gassing of CO₂ it was, unfortunately, not possible to calculate an O₂ mass balance similar to the one discussed in section II.4.1.3. However, even with the limited information for the released CO and VOC amounts, it can safely be assumed that a large share of the consumed O₂ is not converted to CO₂, CO or VOC off-gassing emissions alone, similar to the results discussed in section II 4.1.2 and II 4.1.3. This is supported by a study, which was already published as early as 1945, in which the author suggests that oxygen absorbed by linoleic acid is mainly bound in the form of highly reactive peroxidic groups [90]. This illustrates the great potential of the fatty acids inherent to biomass to act as O₂ traps and may be the main reason also for the oxygen depletion witnessed whenever biomass is stored under sealed conditions.

4.4. Off-gassing properties of agricultural and torrefied biomass

In the following section off-gassing experiments carried out on various types of agricultural biomass pellets as well as test on a small number of torrefied biomass pellets are presented.

4.4.1. Off-gassing from agricultural biomass

As nowadays the resource wood is getting more scarce caused by the growing demand in material and the energetic use, alternative solid biofuels, like miscanthus, straw or eucalyptus, are experiencing growing interest for energetic use. So far very little literature data is available on agricultural biomass, values for switchgrass are reported in Kuang *et al* 2008 [46] and for miscanthus in Trinkel 2012 [82]. In this section off-gassing rates for 8 biomass pellet samples produced from agricultural biomass such as straw, miscanthus, eucalyptus and vine prunings have been determined. The results are presented in Table II.16.

Table II.16.: Off-gassing rates for agricultural pellet samples.

#	Raw material	Mix ratio %	Ø mm	CO ₂	CO	VOC	Prod. time weeks
P50	straw	100	8	1.16	0.03	0.005	>24
P51	straw	100	6	0.48	0.03	0.001	unknown
P52	straw/seed residue/spruce	83/11/6	8	2.10	0.06	0.008	7
P53	eucalyptus	100	6	0.83	0.03	0.012	>52
P54	eucalyptus	100	6	1.16	0.04	0.002	5
P55	vine pruning/ vine pomace	50/50	6	1.92	0.04	0.053	3
P56	miscanthus/straw	90/10	6	0.45	0.03	0.007	>12
P57	miscanthus/maize/ wheat straw	33/33/33	6	0.52	0.05	0.005	>12

The off-gassing results obtained in the test with the agricultural biomass pellets show very low activity in terms of CO off-gassing and only average to low activity for CO₂ and VOC off-gassing compared to wood pellets. This behavior is in accordance with previously reported values for off-gassing of alternative solid biofuels [46, 82].

4.4.2. Off-gassing from torrefied biomass

The torrefaction process is typically described as a mild form of pyrolysis and will convert the utilized biomass into a fuel with higher energy density and other advantageous properties (e.g. higher hydrophobicity and lower risk for biological activity). An overview of the process as well as on technologies utilized is given in the review article by Nhuchhen *et al* 2014 [91]. The aim of this investigation is to find out whether torrefied solid biofuels also exhibit off-gassing behavior and if so, to what extend.

The four investigated torrefied biomass pellet samples have been provided by different suppliers and hence the torrefaction parameters have also been different. In Table II.18 a short summary of some of the production parameters is given according to information provided by the individual suppliers. The results of the off-gassing tests on the torrefied biomass pellet samples are presented in Table II.18.

Table II.17.: Torrefaction parameters.

ID	Torrefaction temperature °C	Residence time min.
P58	308	12
P59	315	12
P60	280	35-40
P61	250-300	< 5

The torrefied samples showed moderate off-gassing activity for CO₂, CO and VOC comparable to moderately reactive wood pellet samples. In this case, the biomass used in the torrefaction was wood. The question arises as to which parameter is of larger influence on the off-gassing activity of the thusly treated biomass, the torrefaction parameters or the properties of the utilized biomass? It has been suggested in the work of Kuang *et al* 2008 [46] that off-gassing rates from torrefied materials are less sensitive to temperature increases during storage due to the removal of VOCs during the torrefaction, thereby indicating the significant impact of the torrefaction process on the off-gassing properties of the material. However, lack of data on the off-gassing properties of non-wooden biomass make it impossible to come to a conclusion on the influence of the utilized biomass on the off-gassing properties of torrefied biomass as of yet. Further research on this topic would allow an assessment of whether similar risks to the handling of wooden biomass pellets also need to be considered when handling torrefied biomass pellets.

Table II.18.: Off-gassing rates for torrefied pellet samples.

#	Raw material	Mix ratio %	Ø mm	CO ₂	CO	VOC	Prod. time weeks
				<i>mg/kg fuel_{atro}</i>			
P58	torrefied spruce	100	6	1.70	0.30	0.003	2
P59	torrefied mix ⁺	100	8	3.40	0.22	0.009	>4
P60	torrefied pine	100	8	0.95	0.18	0.003	7
P61	torrefied pine	100	8	1.17	0.26	0.013	7

⁺ mix of spruce with leaves, bark and branches

4.5. Supplementary investigations

In the course of the different projects which contributed to the work described in this thesis supplementary data to the topic of off-gassing from biomass could be collected. On one hand, this data contains information on the extractive composition of various wooden biomass samples, both raw material and pelletized samples. On the other hand, results from a study on the changes in the VOC profiles emitted from various wood pellet samples dependent on storage temperature and time are presented. Although this data could not be connected conclusively with the previously presented results it may provide a useful point of reference for future investigations into the off-gassing topic and, therefore, is presented within this thesis.

4.5.1. Extractive composition of biomass raw materials and pellet samples

The results presented in this section give an overview on the extractive composition of seven raw material and nine pellet samples and will highlight some key differences between the two types of samples. Utilizing the method described in section II.3.4 21 different extractive components as well as the extractive content of the chosen samples have been determined. To densify this large set of data out of the 21 components only the ones for which at least one sample showed a share of $\geq 10\%$ in the overall extractive content were selected. This results in a decreased set of only 11 extractive components, which, for all investigated samples, represent a share of at least 87 % of the the overall extractive content. Table II.19 gives an overview on the extractive contents determined for the individual samples, as well as a representation of the shares of the 11 selected extractive components.

For the spruce and larch samples the largest share is made up by C18:2 (linoleic acid) and second largest by C18:1 (oleic acid), in case of the pine samples the order is reversed. Generally, these two fatty acids together account for between 32-72 % of the extractive content in the case of the raw materials with an average value of 55 % and 29-70 % in the case of the pellet samples with an average of 50 %. It could also be observed, that the pellet samples have an overall slightly lower extractive content, than the raw material samples of the same wood species. This indicates, that the pelletizing process has a diminishing effect on the extractive content of the pelletized material.

A more detailed analysis of the results reveal that a comparison of the extractive composition of the raw material and the pellet samples shows an decrease of the unsaturated extractive components (C18:1, C18:2, C18:3, C20:1 and C20:3) in favor of the saturated components (C8:0, C16:0, C22:0 and C24:0) by an average of 10 % of the overall extractive content in the case of pellet samples. This shift is most likely also a byproduct of the pelletizing process. Moreover, another shift can be noticed between the raw material and the pellet samples namely one from larger hydrocarbons to lower hydrocarbons. For the raw material samples between 40-84 % of the extractive content is made up by the C8:0-C18:3 fractions, with an average of 66 %. In the case of the pellet samples this shift to 50-88 %, with an average of 75 %.

Table II.19.: Extractive composition and content of various raw material and pellet samples

Wood species	C 8:0		C 16:0		C 18:0		C 18:1		C 18:2		C 18:3		C 20:1		C 20:2		C 20:3		C 22:0		C 24:0		Sum of shares %	Extractive content $mg/kg\ fuel_{atro}$	
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%				
Raw material samples																									
RM01	spruce	2	4	2	13	36	2	1	10	3	8	6	87	879											
RM02	spruce	1	4	2	5	49	2	0	11	2	15	4	95	164											
RM03	spruce	1	3	2	7	25	1	13	8	12	8	7	88	236											
RM05	spruce	2	9	4	24	28	1	2	2	2	8	7	89	775											
RM06	pine	1	6	3	38	23	1	3	2	7	1	2	87	1393											
RM07	pine	0	7	3	45	27	1	1	1	1	1	3	92	1227											
RM08	larch	0	7	2	26	35	3	1	3	2	6	5	89	1611											
Wood pellet samples																									
P03	spruce	3	13	4	28	29	1	3	2	1	1	3	88	399											
P04	spruce	4	13	8	22	28	3	2	2	1	1	3	87	275											
P05	spruce	1	5	1	10	42	3	1	3	1	13	13	93	235											
P06	spruce	1	4	2	16	39	2	1	3	2	12	11	93	287											
P07	spruce	2	6	2	15	24	2	3	6	2	16	15	92	200											
P33	pine	11	30	9	22	8	1	3	1	1	2	1	90	808											
P34	pine	6	29	14	33	6	0	4	0	0	0	1	93	1160											
P45	larch	1	14	4	28	31	7	2	0	1	1	3	91	729											
P46	larch	0	7	3	29	41	7	1	1	1	0	4	94	1310											

4.5.2. VOC profiles of biomass pellets dependent on storage temperature and time

Over the course of a four-week storage experiment the development of individual VOC components was measured for four individual pellet samples, which were produced on a laboratory pellet press specifically for these tests, stored at three different temperatures. The tests were carried out to gain knowledge on the differences in VOC emissions of pellets made from different wood species, in this case spruce, pine and larch as well as on their behavior dependent on changing temperature conditions and over the course of time. Additionally, it was investigated whether the blending of the additive maize starch, a commonly used pelletizing aid, would result in a changed off-gassing behavior in this case for pelletized spruce material.

The four tested types of pellet samples include pellets made from spruce, pine and larch as well as one sample of spruce material mixed with 2 wt% of maize starch. Smaller samples were taken and from each pellet batch roughly 150 g of material were stored openly at 18, 30 and 50 °C. At the start of the experiment and at the end of each week samples of 20 g were taken of which 8 g were kept as a reserve sample and the remaining 12 g were grinded. Of the grinded material 5 times 0.3 g, for each of the 4 pellet batches, were filled in a glass vial and sealed. For the determination of the initial VOC concentration in the vial headspace via solid phase micro extraction (equipment details see section II.3.5) the vials were heated to 40 °C. Next, the extraction fiber was inserted through the vial septum in the headspace over the sample and exposed for 20 minutes. In a second automated step the fiber was transferred to the GC-MS equipment, where a thermal desorption procedure was initiated and the injection and subsequent separation of the gaseous components took place. A more detailed description of the method can be found in Reinisch 2014 [92]). Out of the five determinations for each component an average value is calculated as arithmetic mean.

As the data material generated by this experiment is rather extensive, it is necessary to shrink down the data sets to a more manageable size in order to compare the results in a simple 2-dimensional graphic. Thus, the detectable VOC components have been clustered into four groups aldehydes, acids, terpenes and other VOCs. Out of those the first three can be considered most important since they comprise the proportionally largest shares of components compared to the total sum. For each group one to two lead components have been chosen that are representative in their behavior for the other components in that group. In case of the aldehydes group pentanal and hexanal were chosen, for the acids the lead component is caproic acid and for the terpenes α -pinene was chosen. A complete Table of the results for all components is listed in Appendix B in Table B.

In Figure II.20 the development of the lead VOC components of the three groups aldehydes, acids and terpenes, represented by the selected lead components, over the course of 4-week trial is depicted. One of the most obvious results is the clearly visible difference in VOC off-gassing behavior exhibited by the pellet samples according to the wood species. Overall, the pellet batch showing the highest concentrations of components was pine followed by larch and, finally, spruce. Broken down to the individual groups the results are less straight forward. For the aldehyde concentrations the order of the samples is pine > spruce > larch. For the acid group the pine sample is again emitting the highest concentrations by a factor of ≈ 6 , followed by larch and spruce at a very similar level. For the terpene group, finally, the order is pine > larch > spruce, whereby both pine and larch exceed the values of spruce on average by a factor of 3 and 2, respectively.

It should also be noticed, that in the total sum over all three classes of components a significant increase in emitted VOC components could be observed when the storage temperature was raised from 18 to 30 °C, whereas the increase from 30 to 50 °C lead to no significant change in the amounts of emitted VOC components. The overall similarity in the results of the spruce and the spruce with additive pellet batches lead to the conclusion, that adding 2 % of maize starch did not influence the off-gassing behavior of the pellets significantly.

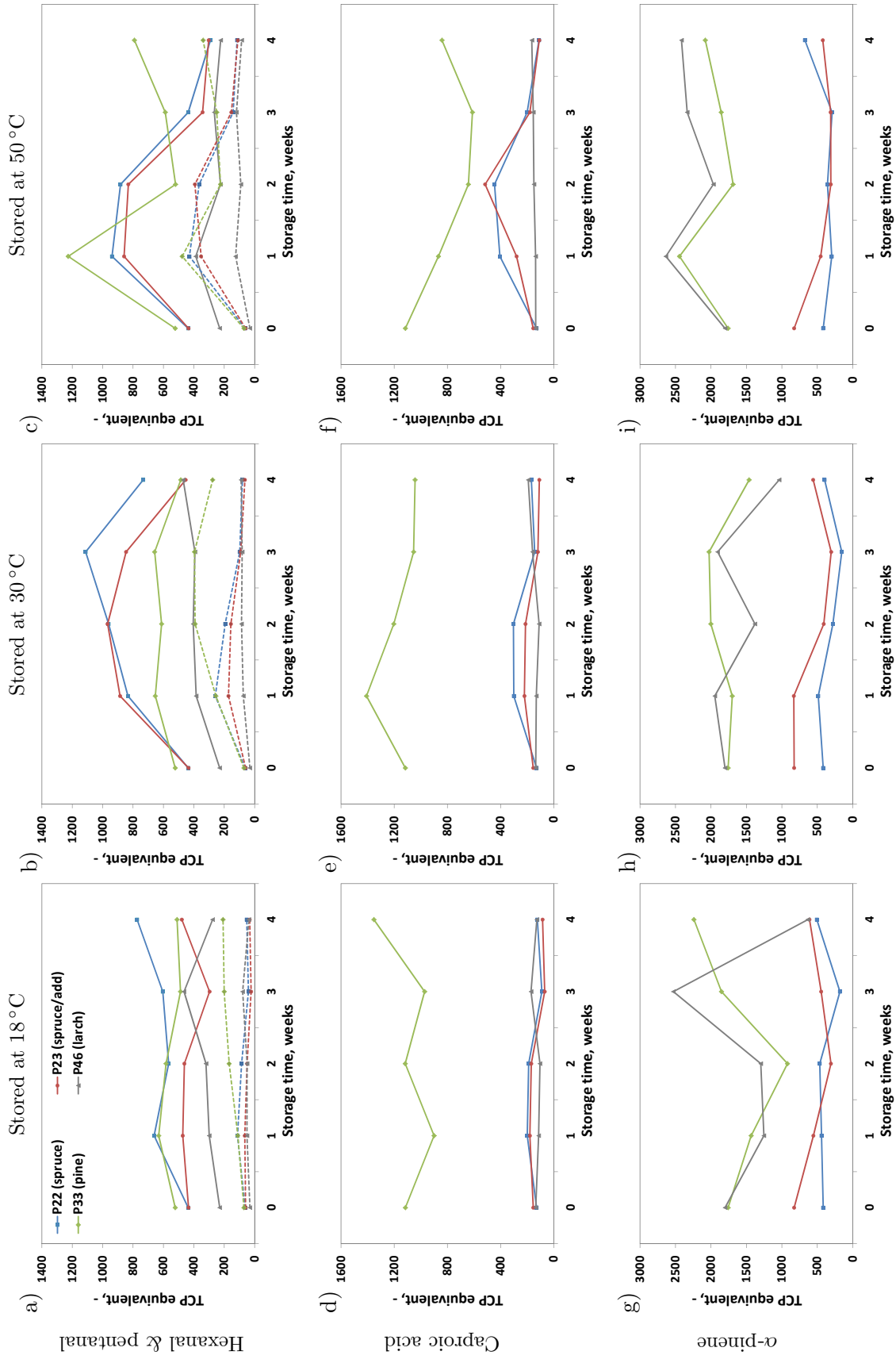


Figure II-20.: VOC emissions from biomass pellets dependent on temperature and storage time. From left to right the results are sorted with ascending storage temperature. In the case of the two lead components for the aldehyde group the dashed line represents pentanal concentrations and the solid line the hexanal concentrations.

5. Conclusions

Off-gassing behavior dependent on storage related parameters

The outcome of the experiments on the three investigated storage related parameters headspace ratio, storage temperature and storage atmosphere clearly revealed that the storage temperature is the most important parameter to influence the off-gassing behavior of the stored biomass pellets. This result is in good agreement with previous literature. However, the investigations also revealed storage atmosphere to be the second most influential parameter on the off-gassing behavior. It could, moreover, be demonstrated, that removal of oxygen from the storage atmosphere is not sufficient to stop off-gassing emissions from being released, completely. In fact, storing wooden biomass pellets at 20 °C at close to 0 % oxygen atmosphere still results in more than 50 % of the off-gassing emissions measured at the same temperature at a 20 % oxygen atmosphere. An explanation for this, at first glance odd result, could be related to the pellets ability to store large quantities of oxygen. The O₂, which according to literature could be bound in the form of highly reactive peroxidic groups as a result of oxidation processes of the extractives inherent to the biomass samples, may be the source of the oxygen found mainly in the CO and CO₂ emissions.

It was also detected, that there is an influence of the headspace ratio on the off-gassing behavior of stored biomass pellets under ventilated storage conditions, such as existing in the described glass flask method. With increasing headspace ratio an increase in detected off-gassing emissions was measured over the course of storage interval of one week. A similar effect was reported earlier for storage studies utilizing sealed storage containers. It was, therefore, unclear whether the effect was only induced by gradually lowered O₂ availability and resulting potentially restricting storage atmospheres to the off-gassing activities of the stored biomass. However, as a similar, although less pronounced, effect was also noticed in non-sealed storage conditions the headspace ratio is influential to the off-gassing behavior and needs to be considered when setting up an off-gassing experiment or comparing results from off-gassing determinations. Whether this effect is the result of reactions driven by a sort of concentration dependent chemical equilibrium between specific gas phase and/or solid phase components needs to be investigated further.

Off-gassing behavior dependent on parameters related to the pellet material

Whilst the parameters relating to the storage conditions are applicable to all types of biomass pellets, there are also differences to be noticed between pellets produced from different types of biomass. But equally important, it was found that there are also a number of influential parameters pertaining to the production, more precisely to the pelletizing process, which prove to be of significant impact on the off-gassing behavior later to be exhibited by the biomass pellet sample. With respect to the differences between the off-gassing behavior of various wood species, it could be determined that on average pine pellets are more reactive than larch pellets and spruce pellets, in that order. Pellets produced from a mix of pine and spruce raw materials on average rank in between pine and spruce pellets. However, it could also be demonstrated, that individual samples may very well exhibit much higher off-gassing activity than the average values calculated for that species. In fact, the spread of values covers a broad range and seems to be dependent on other parameters than the wood species alone.

One such parameter is the age of the pellet sample, with respect to the time that has passed since its production. It could be demonstrated in several experiments, that the off-gassing activity of the pellets is significantly declining with the time. The most reactive off-gassing period was found to be within the first couple of weeks after production, with a significant loss of activity already after one week of storage and a much slower decrease in activity after a time span of weeks after storage. At this point it has to be mentioned, that not all freshly produced pellet samples exhibited a particularly high off-gassing activity in the first place, but for all samples, the activity dropped over time.

Finally, the pellet production process and the condition of the specific raw material (fresh or mature sawdust) also influences the off-gassing behavior of the resulting pellet sample. Slight changes in the pelletizing parameters of the pellet press were found to have a more significant influence on the pellet samples than small variations in the raw material provided. In fact, different batches of raw materials could be turned into pellets with very similar off-gassing behavior, when pelletized with the same production parameters. It also implies, that the prediction of the off-gassing activity of a specific pellet batch is likely to exhibit can not be based solely on the investigation of the raw material used in the production, at least not without deeper knowledge into how the process itself is going to influence the product. Contrary to results published in earlier literature, pellets produced from more mature raw material, in the case of this study it was pellets made from shavings in comparison with pellets made from fresh sawdust, showed less off-gassing activity for CO and CO₂ than in the case of the fresh raw material. However, the literature, which presented the contradictory findings, only investigated pellets made from sawdust material of varying maturity levels and did not consider other types of raw materials such as shavings.

Investigation of the off-gassing mechanism

As a result of the experiments on the off-gassing behavior of pure linoleic acid it could be established, that CO, CO₂ and VOCs are released from autoxidation processes of the fatty acid. Furthermore, just as observed with biomass pellet samples, a large amount of oxygen is absorbed by the acid and bound in some form, possibly as peroxidic groups, on the surface. As peroxidic groups are highly reactive, this uptake of oxygen might be one of the kinetically most relevant steps in the reactions, which subsequently lead to the release of CO.

Off-gassing from agricultural and torrefied biomass

Due to the growing interest in converting non-renewable fuels to renewable energy sources and the resulting growing interest in all kinds of biomass suitable for thermal utilization, agricultural biomass fuels based are in growing demand. As these types of fuels become of more importance it has also become necessary to understand, if the same risks for off-gassing associated with wood pellets are also to be respected when handling agricultural pellets. In this work it was found that the off-gassing behavior of the investigated miscanthus, straw, eucalyptus and vine pruning residue pellets showed very little off-gassing activity when stored at room temperature. Their off-gassing behavior in general is clearly different from the behavior exhibited by wooden biomass pellets and due to the very low amounts of released CO during the storage experiments the risks for off-gassing during storage of agricultural biomass pellets can be categorized as very low in comparison to wooden biomass.

The evaluation of the off-gassing behavior of torrefied wood pellet samples revealed a picture similar to the one presented for the investigated wood pellets. At this point it seems most logical to conclude that the torrefied pellet samples would behave similar to the pellet samples from the same raw material and thus

need to be treated with the same risk awareness and risk management protocols applied also to regular wood pellets. Whether torrefied pellets made from agricultural biomass present a similar low-risk off-gassing behavior than regular agricultural pellets has so far not been investigated.

Supplementary Investigations

In the course of this thesis some results indicated that samples with a higher extractive content also exhibited higher off-gassing activity. However, attempts to correlate this relation proved unsuccessful. Moreover, more detailed attempts to correlate the ratio between saturated and unsaturated extractive components or just the amounts of individual extractive components with the off-gassing activity were also fruitless. Whilst the generalized statement that overall biomass samples with higher extractive content are more likely to exhibit higher off-gassing activity can still be regarded as true, individual pellet samples may exhibit off-gassing activity within a broad spectrum of values dependent on several influential parameters such as time since production, production parameters or storage history.

III. Emission monitoring in small-scale pellet storages

1. Introduction

With the growing emphasis on using biomass for energy utilization it is becoming more and more obvious that there is a growing need to understand the behavior of biomass in storage and transport. Typically, whenever wood pellets are produced, they will be stored on-site at the production plant for some time before being transported to be delivered to the consumer. The transport can entail one or a series of logistical steps from direct packing of pellets into small bags ready to be used by an end consumer, delivery via pellet trucks into consumer storages or longer routes involving transport on ocean transporters or bulk containers transported with trains [13]. Whenever pellets are shipped in large volumes, they are classified as hazardous material due to the potential for off-gassing and self-heating. However, even in small volumes there is a risk, especially from CO off-gassing, that hazardous amounts of gases can be accumulated in pellet storages. Table III.1 contains an overview listing several documented accidents related to pellet transport and storage, which have occurred since 2002. The data provided highlights the significant risks involved in the transportation of large volumes in enclosed spaces, which are typical on ocean transport vessels. Nonetheless, the reported accidents in pellet storages have occurred also in situations where much smaller volumes of pellets had been stored indicating a risk of poisoning of toxic gases can also occur in a small-scale pellet storage. Nevertheless, it can also be assumed that many cases remain unreported, especially if the outcome of the accident was regarded harmless, and therefore the data collected do not necessarily give the full picture of the situation. Up to now only little data has been published on the development of CO concentrations in real pellet storages [93, 94].

Table III.1.: Accidents due to off-gassing related to wood pellet transportation and storage.

Year	Location	# people hurt(killed)		Description	Source
2002	Rotterdam, The Netherlands	3 (1)	T	1 person collapsed and dies in a stairway between two cargo holds containing pellets - vessel "Arrow Weaver"	[95]
2006	Helsingborg, Sweden	1 (1)	T	1 sailor enters a stairway between two cargo holds containing pellets and dies - vessel "Saga Spray"	[95]
2007	Finland	1 (1)	S	1 person dies after entering a 10 t pellet storage	[96]
2008	Finland	1 (1)	S	1 person dies after entering a 10 t pellet storage	[96]
2009	Bornholm, Denmark	2 (2)	T	2 sailors collapse and die in a stairway leading down to a cargo hold containing pellets - vessel "Amirante"	[96]
2010	Remscheid, Germany	2 (1)	S	1 engineer dies in pellet storage of 150 tons capacity	[97]
2010	Ireland	1 (1)	S	1 person dies a pellet storage with 10 tonnes	[96]
2011	Horwer, Switzerland	1 (1)	S	1 pregnant woman dies in a pellet storage of 100 tons capacity	[98]
2012	Senden, Germany	2 (0)	S	1 maintenance worker passes out after entering a pellet storage of unknown size	[99]
2014	Floby, Sweden	3 (1)	S	1 Worker dies after entering a pellet silo of unknown size	[100]
2014	Fredricia, Denmark	5 (1)	T	1 sailor dies after collapsing in a stairway down to the cargo hold containing pellets - vessel "Lady Irina"	[101]
2014	Goole Docks, United Kingdom	3 (3)	T	3 sailors collapse and die in a stairway down to the cargo hold containing pellets - vessel "Suntis"	[102]

T... transport
S... storage

2. Objectives & approach

The aim of the investigation is to collect a data basis on CO development in real small-scale pellet storages, which are typical for the Austrian wood pellet heating sector. The data shall be used as basis to support decisions on guidelines and recommendations on how best to handle the wood pellets at end consumer storages. Furthermore, the monitoring of a selected number of storages for a longer period in time will help to identify key influential parameter on the off-gassing behavior of pellets, which are related to the storage conditions rather than to the stored wood pellets.

3. Materials & methods

The pellet storage monitoring experiment was carried out in cooperation with a pellet production and supply company. The company was vital in the connection of pellet storage owners with the team conducting the monitoring experiment. It was possible for a team member to accompany pellet delivery truck drivers

on their delivery route and to equip the freshly filled storages with the monitoring sensors. With the help of the volunteer participants of the monitoring study a detailed documentation of the monitored pellet storages was conducted. The storages were typically monitored over the course of at least 7 days, beginning immediately after a delivery of fresh pellets.

3.1. Sensory equipment

During the monitoring period every pellet storage system was equipped with two types of data loggers, one logger to record the levels of temperature and relative humidity (RH) within the storages and a second logger to record the CO concentration. In Table III.2 the specifications of the utilized sensory equipment is given.

Table III.2.: Specifications of the sensory equipment used in the pellet storage monitoring.

Manufacturer	Sensor	Range	Uncertainty	Measurement interval
Lascar electronics	temperature/ humidity	-35 to 80°C 0 to 100 % RH	$\pm 2^\circ\text{C}$ $\pm 6\% \text{ RH}$	every 10 min
Lascar electronics	CO	0 to 1000 ppm	$\pm 6 \text{ ppm}$	every 5 min

The sensors were installed immediately after the delivery of fresh pellets. As soon as the pellet dust, which is inevitably created during the filling process, had settled, the sensors, which were mounted on a regular welding rod, were placed inside the pellet storages in the headspace above the pellet bulk. In Figure III.1 a photograph of the utilized data loggers is shown, as well as an example a logger mounted on a welding rod and installed in one of the monitored storages.

In the case of the pellet storage with the identification number 16 (see Table III.3 ID 16) a different measurement equipment to monitor CO levels was installed. The measuring device, an ECOM J2KN pro (manufacturer: Ecom), allowed simultaneous CO and O₂. Its specification are listed in Table IV.2.

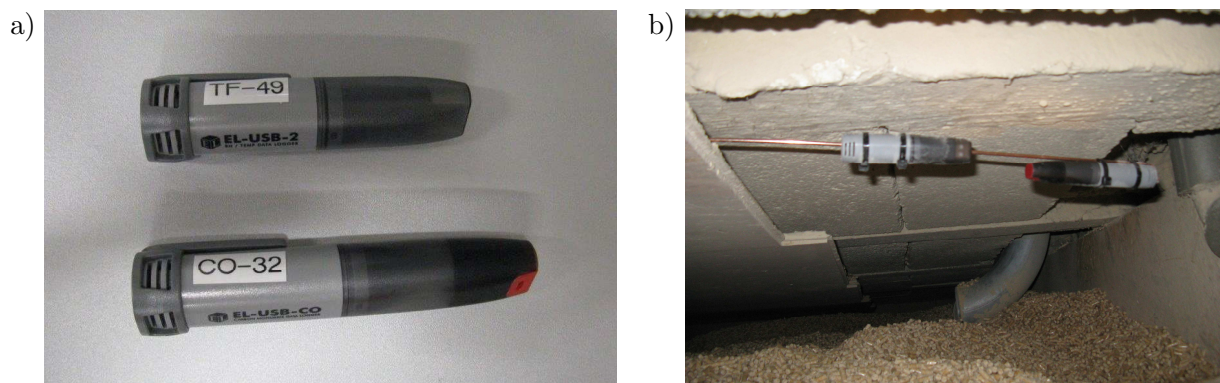


Figure III.1.: Photographs of the data loggers (on the left) and their positioning in a monitored storage (on the right).

3.2. Monitored storages

Overall, 24 pellet storages were monitored in autumn of 2010. The storages differed in size, type of storage as well as positioning of the filling pipes, preexisting filling levels as well as tightness. Tightness in this case can be understood as the degree at which air exchange from the pellet storage to its surroundings is possible. This last parameter can differ significantly dependent on the type of pellet storage and the specific design of the individual storage. Moreover, this parameter additionally is influenced by temperature fluctuations and changes in ambient pressure, which makes it difficult to determine. Therefore, it was only possible to carry out a qualitative assessment of the degree of tightness for each monitored storage. A value was assigned the form of a star symbols (*). The tighter the storage is classified the more * symbols it is given, with the highest possible class represented by four * symbols. The classification was based on the on-site assessment of the storage type and specific design, e.g. underground storage systems are typically constructed from a one piece shell and, therefore, extremely tight. A basement storage room with large opening, e.g. a regular size entrance door, and unplastered walls is considerably less tight than a similar room with smaller openings and plastered walls. It was possible to monitor indoor pellet storage rooms, the most widespread type of pellet storage in Austria, underground pellet tanks, prefabricated pellet storage systems such as sheet steel tanks and fabric silos, as well as outdoor pellet storages. An overview on all monitored storages is given in Table III.3.

With the help of the pellet delivery company the production age, the time elapsed since pellet production, of the delivered pellets could also be estimated. The raw material in the pellet production was, in all cases, spruce sawdust and all delivered pellets were produced in the same pelletizing plant, with the exception of storages 23 and 24, which were supplied by a different producer at an earlier time.

3.3. Ventilation equipment

In the course of the monitoring 8 out of the 24 monitored storages were equipped with special ventilated caps, which are constructed to fit a standard Storz A coupling. Storz A couplings are a type of hose coupling that connect using interlocking hooks and flanges. In addition to its common use at the connection point between the pellet storage and the pellet delivery truck, this type of coupling has been widely employed on fire hoses in firefighting applications and is the standard coupling on fire hoses in many European countries. The cap, once implemented on the outside end of the filling pipes of the pellet storage, serves as ventilation opening and allows a certain degree of air exchange between the pellet storage and its surrounding. The air exchange at any given time is dependent on temperature changes between the inside and outside temperature of the pellet storage as well as changes in ambient pressure (e.g. due to operation of the attached combustion system or automated fuel supply systems) and user behavior. A photograph of the cap is given in Figure III.2. It is constructed with eight holes for ventilation and its special design prevents splash water from entering the pellet storage. By allowing air exchange with the surrounding of the pellet storage, toxic CO off-gassing emissions as well as other off-gasses such as CO₂ and VOCs can be ventilated out of the pellet storage. To avoid the risk of possible accumulation of such toxic gases in other parts of the houses containing the pellet storages, the ventilated caps were only installed on filling pipes ending outside of the house.

Table III.3.: Description of the monitored pellet storages.

ID	Delivered amount t	Estimated residual pellets amount t	Storage capacity t	Pellet production age weeks	Description	Tightness
1	3	1	5	1	Indoor wood construction	**
2	5	1	7	1	BR - brick-built and plastered	***
3	6	0	6	1	BR - brick-built and plastered	***
4	8	2	11	1	BR - 3 sides brick-built and plastered, 1 side half brick-built half wood construction	***
5	3.5	0	3.5	1	Fabric silo in comparatively large room	*
6	5	5	10	1	BR- brick-built and plastered	***
7	4.5	5	10	1	BR - brick-built and plastered	***
8	2.3	2	4.5	2	Storage shed, brick-built with wooden roof	*
9	5.4	0	6	2	Underground plastic tank	*****
10	9.4	0	10	2	BR - brick-built and plastered	***
11	8	1	9	2	BR - 3 sides brick-built and plastered, 1 side wood construction with a regular door opening 90*200 cm	**
12	5	1	6.5	2	BR - brick-built and plastered without fuel extraction system	**
13	6.6	0	7	2	BR - brick-built and plastered and tightly sealed	****
14	2.9	4	7	2	Underground plastic tank	****
15	3.5	4.5	10	2	BR - brick-built and plastered with door 90*200 cm	**
16	3	0	3.5	3	Indoors, sheet steel tank, tightly sealed	*****
17	7.6	0.5	9	1	BR - brick-built	**
18	1.4	4	6	1	BR - brick-built and plastered	***
19	4	3.5	8	1	BR - brick-built and plastered	***
20	8	0	8	1	BR - brick-built and plastered	***
21	5	2.5	8	1	BR - 3 sides brick-built and plastered, 1 side plasterboard	**
22	7	0	7	1	BR - brick-built and plastered	***
23	11	0	12	>17 ¹	BR - brick-built	**
24	5	0	6	>17 ¹	BR - brick-built	**

BR Basement room

¹ these pellets were delivered 17 weeks prior to the start of the monitoring



Figure III.2.: Photograph of the ventilated cap used in the storage monitoring trials.

4. Results & discussion

In autumn of 2010 a total of 24 pellet storages were monitored to gain insight on typical development of CO concentrations in real existing storage situations. All pellet storages were monitored for a minimum of 7 days, most were monitored over a period between 2-4 weeks. Table III.4 gives an summary overview on the monitoring data collected for the first week of storage for all 24 storages. In the Table data on the filling level of the storage, the qualitative assessment of the tightness of the storages, the peak CO concentration within the 7 day storage experiment as well as the CO concentration after exactly one week of storage is given along with average temperature and humidity values. The ratio of fresh pellets gives information on the amount of freshly delivered pellets in comparison to pellets from earlier pellet deliveries, which are considerably older and less reactive in terms of off-gassing. Out of the 24 storages eight storages were chosen to be monitored under ventilated storage conditions. This was achieved by implementing special ventilated caps fitted on the end of the filling pipes of the storages leading to the outside, thus, enabling a certain degree of continuous natural ventilation.

What could be observed in all monitored pellet storages, ventilated as well as non-ventilated, was that the development of the CO concentrations reached a peak concentration, typically within the first 2-4 days, and subsequently CO levels would begin to drop. However, the actual height of the peak concentration as well as the speed of decay of the CO concentration varied significantly from one storage to the next. When sorted according to the measured peak CO concentration out of the 10 storages, which showed the highest CO levels, 9 storages had not been equipped with the ventilation caps. The highest recorded value for a non-ventilated storage system was 2500 ppm CO, a value recorded at the top of the detection range of the utilized measurement equipment. The actual value can be assumed to have been even higher. In the case of the ventilated storage systems the highest recorded value was at 271 ppm CO. Analyzing the monitored CO development, in general, good agreement could be noticed between the assessment of the tightness of the storages and the measured CO peak concentrations.

Table III.4.: Results of the pellet storage monitoring

ID	Storage capacity t	Filling level %	Ratio of fresh pellets	Pellet production age weeks	Tightness	CO peak ppm	CO level after 1 week ppm	Arithmetic mean Temperature °C	rel. Humidity %
1	5	80	0.75	1	**	67	20	20	60
2	7	86	0.83	1	***	316	190	20	40
3	8	100	1.00	1	***	357	175	21	50
4	11	91	0.80	1	***	507	285	20	52
5	3.5	100	1.00	1	*	62	24	19	43
6	10	100	0.50	1	***	266	135	22	46
7	10	95	0.47	1	***	217	115	19	47
8	4.5	96	0.53	2	*	165	6	10	66
9	6	90	1.00	2	****	516	123	11	65
10	10	94	1.00	2	***	182	80	17	55
11	9	100	0.89	2	**	632	277	18	50
12	6.5	92	0.83	2	**	480	475	11	80
13	7	94	1.00	2	****	1333 ¹	1075	16	49
14	7	99	0.42	2	****	871	209	11	48
15	10	90	0.44	2	**	167	159	17	44
16	3.5	86	1.00	3	****	>2500 ²	1987	22	50
17	9	90	0.94	1	**	153	58	22	55
18	6	90	0.26	1	***	93	27	32	40
19	8	94	0.53	1	***	93	25	22	51
20	8	100	1.00	1	***	271	134	18	52
21	8	94	0.67	1	**	43	26	21	51
22	7	100	1.00	1	***	258	140	17	65
23	12	92	0.00	>17 ³	**	10	0	12	70
24	6	83	0.00	>17 ³	**	18	1	17	57

¹ CO concentration exceeded detection range of sensor² CO concentration exceeded detection range of sensor³ these pellets had already been stored for 17 weeks prior to the start of the monitoring

The monitoring of the storages with the older pellets, ID 23 and 24, showed, that these pellets exhibited virtually no CO off-gassing activity during the monitoring period. It could be established, that by ventilating the storages with the special caps, the off-gassing activity was not increased, or rather that the naturally occurring ventilation provided by the cap did in any case counteract any possible increase as a result of the ventilation. Such an increase could be the result of higher moisture content of the pellets due to the additional air exchange.

All pellet storages supplied with fresh pellets were recorded to exceed the maximum occupational exposure limit (OEL) of 30 ppm CO, at some time during the 7 days storage period. At the end of the 7 days only 19% of the non-ventilated storages showed CO levels below the OEL, whereas in the ventilated storages 50% of the storages showed CO levels below 30 ppm. Three out of the 16 non-ventilated pellet storages showed potentially life threatening concentrations of CO even after one week of storage at levels of 1987, 1075 and 475 ppm CO, respectively.

The monitoring study further revealed some examples on how the different influences such as boiler operation, changes in temperature and tightness of the storage can influence the CO development within the individual storage. In Figure III.3.a an example of how user operations are influential on the CO concentration is given. The very sharp drops in CO concentrations visible in this example are caused by short intervals in which owner of the pellet storage (ID 12) entered the storage to extract roughly 20 kg of pellets for the daily hopper of the pellet oven. These sharp drops in concentration are only short lived and within just a couple of hours the CO concentration is back to the same level as before. By opening the pellet storage, the CO concentration is lowered by 300 ppm in a matter of just 10 minutes of ventilation and after closure of the door starts to rise again to the previous levels over the course of the next 3-4 hours. The pellet storage also seems to have hardly any air exchange with its surroundings, which can be gleaned by the very smooth appearance of the CO curve and the fact that the peak CO levels are stable for a comparatively long time after. In fact, over a storage period of 3 weeks the CO levels had hardly dropped from the peak concentration of 480 ppm to only around 430 ppm.

Figure III.3.b depicts an example typical for pellet storages with a very low degree of tightness as was the case with this outdoor storage shed (ID 8). The CO development in this storage showed a very sharp increase of CO within the first hour after filling to a peak concentration of 165 ppm, which subsequently dropped rapidly to levels below the OEL within just a few hours. A secondary beneficial factor in the relatively mild CO development curve might also be the very low ambient temperature in the shed, which on average was only around 10 °C.

A comparison between Figure III.3.c and III.3.d also highlights some interesting findings. Both monitored storages were filled with pellets from the same pellet batch, by the same delivery truck at the same day. Additionally, both storages were filled with about the same amount of fresh pellets and were classified with the same degree of tightness. One of the two storages (ID 22) was equipped with the ventilated caps while the second one (ID 4) was not ventilated during the monitoring. The non-ventilated storage showed a steep rise in CO concentration over the course of 48 hours and a subsequent slow decrease to ≈ 300 ppm within one week. The CO development curve again shows a smooth appearance and only small fluctuations.

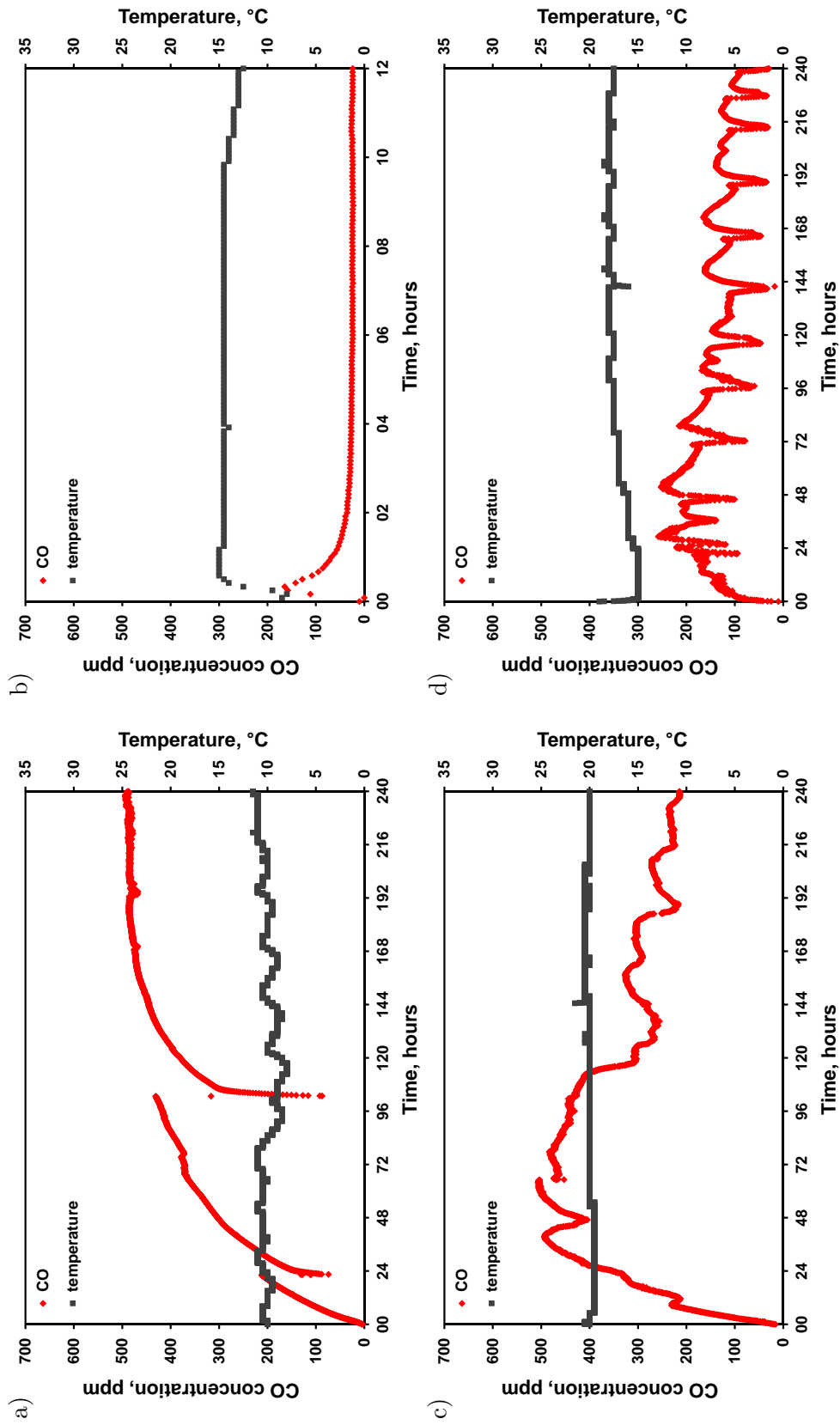


Figure III.3.: Examples for CO development in the monitored pellet storages, a) user influence on CO concentration (storage ID 12), b) influence of low degree of tightness (storage ID 8), c) non-ventilated 10 ton pellet storage room with a tightness of *** (storage ID 4), d) ventilated 7 ton pellet storage with a tightness of *** (storage ID 22)

The CO development in storage 22, however, shows a significantly different behavior. The curve depicted in III.3.d is essentially a result of two influential parameters. First of all, the sharp reductions in CO concentrations, which occur with a high level of regularity every 24 hours are most likely due to an automated fuel supply systems, which delivers fuel to the daily hopper of the heating system. Similar to the example given in III.3.a these drops in CO levels quickly recover and CO concentrations increase again within a couple of hours. The second influential parameter, however, is the implemented continuous ventilation. The ventilated caps allow for a continuous air exchange between the pellet storage and its surroundings enabling additional reduction of CO levels by dilution with fresh air. As this dilution takes effect immediately after the filling process is finished, the peak CO levels in the pellet storages are naturally lowered and the reduction of the CO levels over time is further positively affected.

It was possible, in the course of the monitoring experiments, to measure additional data on the development of O₂ concentrations in one particular pellet storage (ID 16), a prefabricated sheet steel tank of small volume and with a particular high degree of tightness. The visual representation of the concentration curves for this experiment is given in Figure III.4.

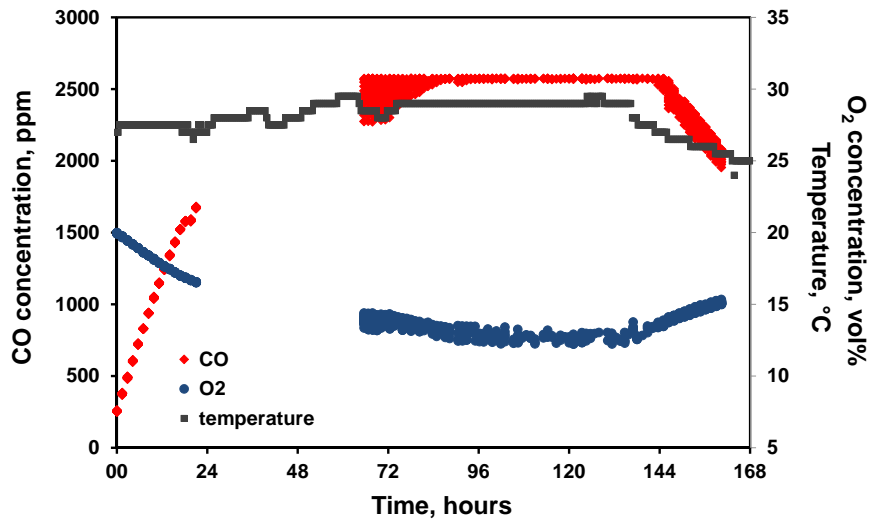


Figure III.4.: O₂ and CO development pellet storage ID 16, O₂ and temperature values are to be read from the secondary y-axis. Due to failure of the measurement equipment there are time gaps in the recorded data.

The most striking result of this experiment is the mirrored curve shape of the CO and O₂ development within the pellet storage. At CO levels well above 2500 ppm the recorded O₂ level is at only 12.5 vol%. As the CO levels decrease with increasing time, the oxygen levels simultaneously rise. Even in this comparatively tight pellet storage, the CO levels reach the peak concentration with in only a few days before starting to continuously drop to lower levels. This indicates that, although, no specific means of ventilation has been added to the pellet storage the storage itself is not 100% sealed from its surroundings. As the CO off-gassing activity decreases with time this air exchange becomes large enough to allow the O₂ levels to rise again and to dilute the high CO concentrations. However, at the observed rate it would take more than a month to lower CO levels in this storage below harmful levels.

5. Conclusions

The development of CO concentrations from wood pellets have been studied in a monitoring program covering 24 small-scale pellet storages. The focus of the study was to determine characteristic patterns of CO build-up and decrease over time dependent also on various parameters associated with the specific storage situation. A summary of the major findings is as follows:

- CO build-up in small-scale pellet storages can reach levels harmful and potentially lethal to humans
- pellet storages, which are built in a particularly tight way, are especially prone to show a fast increase in CO concentrations and are more likely to keep the CO concentrations at a high level
- peak CO concentrations are typically reached within one week after delivery of new pellets
- even in the tightest pellet storages CO concentrations decrease with time, as there is always some air exchange with the surrounding
- increasing air exchange, e.g. by implementing ventilated caps, always has a positive effect to decrease CO concentrations
- the time immediately after a fresh pellet delivery is the most dangerous time to enter a pellet storage due to potentially high levels of CO and low levels of O₂

Furthermore, it could be observed that the CO off-gassing activity for all freshly delivered pellets was very high, even though the pellets production age varied between 1 and 3 weeks. This leads to the conclusion that the delivery process itself could have significant influence on the off-gassing behavior a pellet is going to exhibit in the storages. Heat input from hot pressurized air used when the pellets are blown into the storage as well as the mechanical strains from friction during the delivery process could cause the pellets to exhibit heightened off-gassing activity.

As buildings are refurbished with better thermal insulation their shells also become tighter. In the future this could cause more pellet storages to become prone to the risks of high CO build-up and O₂ depletion. Implementing artificial leakages, e.g. by implementing ventilation openings in pellet storages, can counteract such unwanted implications of otherwise very positive energy efficiency measures.

It could also be established, that, although, there have been reported and documented cases of lethal accidents due to CO poisoning in pellet storages at end consumers only very little effort has been made by pellet industry to warn the general public about the risks, their causes and possible safety measure to avoid the risks. Press articles such as one published in Autumn of 2014 [103] are living proof that a large gap still exists between the knowledge available on the topic of off-gassing and the potential risks involved and the level of information of the general population on these topics. Although some guidelines and recommendations have been released to warn about off-gassing (for details see section IV.1), no special information campaigns have been started to educate boiler installers, chimney sweeps or fire-fighters on that topic. Despite the fact, that these professionals are quite often the first to be contacted when the users become aware of any signs of trouble within their pellet storages. In the future, special attention should be paid and an extra effort should be made to ensure that these professionals are appropriately trained to respond adequately when called upon for help.

IV. Ventilation of small-scale pellet storages

1. Introduction

Dating back to the year 2004, when the first publication, written in English, on off-gassing from wood pellets on emissions of hexanal and carbon monoxide from storage of wood pellets was published [21], the issues of occupational health and safety for workers along pellet production and supply chains have been raised. However, it wasn't until 2006, when the first fatal accident due to carbon monoxide poisoning was reported. The accident occurred onboard a vessel in the Port of Helsingborg, Sweden, while the vessel was discharging wood pellets from Canada [95]. In the wake of this tragic event investigations into the off-gassing phenomenon were made (for more details see section II.1) and over time more and more detailed safety measures have been suggested for the safe loading and unloading of cargo ships transporting wood pellets [33, 40, 41, 104]. It has nowadays become a common safety procedure to lock access doors leading to confined spaces on the vessels during the voyage and to label access doors with warnings signs about low oxygen content, toxic atmosphere, or the skull and crossbones symbol, visible both when the door is open and closed. Furthermore, the oxygen level is to be measured before anyone enters a confined space with suspected air communication with a cargo hold where wood products are stored or have just recently been stored. Also wearing a personal oxygen monitor has become obligatory when entering such a confined space. An extensive list on safety requirements for cargo ships was compiled by the International Maritime Organization in the "IMSBC Code - International Maritime Solid Bulk Cargoes Code and supplement" [105].

Compared to the development of safety regulations for the unloading of cargo ships, the development of safety regulations for pellet storages has been less fast-paced. The reasons for this are manifold and suffice it to say that the topic of pellet storage, aside from the relatively narrow field of transportation on a cargo ship, covers a broad variety of storage systems and requirements for workers and end users along the pellet production and supply chains and, naturally, many restrictions and requirements have to be met. Nonetheless, a series of recommendations and guidelines have recently been published focusing mainly on pellet storage for the domestic application in small- and medium-scale pellet storages below 100 tons of storage capacity. For example, both, the Austrian standard (ÖNORM M7137) on requirements for storage of pellets at the ultimate consumer [14] and the German guideline (VDI 3464) on storage of wood pellets at the end user [106], provide instructions on safety measures for the handling of off-gasses from wood pellets during storage. Similar recommendations from less prominent institutions have also been published during the year 2013, e.g. a guideline titled "Recommendations for the storage of wood pellets" from the German Wood Fuel and Pellet Association [107] as well as a report from the Saxon State Ministry for Economic Affairs, Labor and Transport on the storage of wood pellets and related safety hazards [108]. A detailed overview on other safety and health related issues with the storage and handling of biomass,

including off-gassing but also other topics such as dust exposure and fire safety, is given in "The Pellet Handbook" along with the most comprehensive list of references on production and thermal utilization of pellets existing to date [13].

While the development of safety measures is certainly a big step in the right direction, there is still some way to go before all safety related issues dealing with the storage of wood pellets have been properly investigated and understood. Only recently, in the work of Yazdanpanah et al. [51, 109] results from investigations on the stratification of off-gases and the effectiveness of purging on the gas emissions in wood pellet silo storage has been presented. However, with respect to the effectiveness of ventilation measures in small-scale pellet storages in general, and non-silo types in particular, only incomplete work has been presented up until now (e.g. in Emhofer and Aigenbauer 2012 [94]).

2. Objectives & approach

This study aims to improve the knowledge on safety issues related to the accumulation of hazardous emissions from CO off-gassing from wood pellets during storage. As CO represents the off-gassing emission with the highest hazardous potential to human safety all methods described in the following sections are tested with respect to their suitability to keep CO levels in pellet storages at a risk-free level. CO₂ and VOC level development due to ventilation is not investigated in particular, but can be assumed to also be lowered whenever CO levels are successfully managed. The main focus of this work is thus to test the effectiveness of various ventilation measures on typical small-scale pellet storage systems and to assess their suitability for different areas of application.

In addition, the aim of the investigations is to gain a better understanding of the influence of the parameters temperature difference, cross-ventilation, implementation of a chimney and size of cross-sectional area on ventilation and to determine, which are the ones with the highest impact on the effectiveness of ventilation solutions based on continuous natural ventilation of pellet storages.

As the main focus of this work is based on small-scale pellet storages, it is of particular importance to determine the strengths and weaknesses, or rather the utility and the limitations of commonly recommended ventilation measures, which are not clearly defined and strongly dependent on a specific storage situation as is the case with the "open hatch" ventilation. Finally, a determination of the minimum requirements of necessary specific air volume flow to constantly stay below a desired specific CO concentration in a pellet storage is undertaken.

The approach to reach these objectives combine experimental studies to test the effectiveness of the various ventilation measures on four different nowadays typical storage systems for small-scale pellet storage and mathematical calculations to quantify and determine the impact of the influential parameters on the air exchange rates for ventilation.

3. Materials & methods

3.1. Pellet storages

3.1.1. Plastic tanks

As experimental storages two plastic pellet tanks with a height of 2.9 and a diameter of 3.3 meters were utilized. Each tank has a volume of approximately $V = 8 \text{ m}^3$ and is fabricated from a special strengthened plastic material. At the top of the tank two coupling connections with a diameter of DN100 ending in Storz A connectors, for the filling with pellets, and two coupling connections with a diameter of DN50, for the extraction of pellets with a suction system, are located. The tubes for pellet extraction reach to the inclined bottom of the tank. In the center of one of these steel tubes a vertical screw is fitted, which helps to convey the pellets up to the interconnection point where the pneumatic pellet suction system then takes over the transportation of the pellets to the boiler unit. The propulsion engine for the screw is mounted outside on top of the tank. The plastic tank is also equipped with a service opening located at the top of the tank with a cross section opening of $A = 0.26 \text{ m}^2$. A schematic of the tanks dimensions is indicated in Figure IV.1 according to the producer [110] and in Figure IV.2 the various positions of measurement points for the ventilation experiments are indicated. At measurement points 1 to 3 both CO concentration as well as temperature measurements were taken. The exact positions are directly in line with the position of one of the DN100 filling pipes at a height of 0.5, 1.2 and 2.1 m, respectively, measured above floor level of the installation room, in which the tanks have been positioned. Furthermore, the ambient temperature in the installation room was measured in close proximity to the tanks at a height of 1 m above floor level (MP7). The two plastic tanks have been placed next to each other and have been designated tank A and tank B. The positions of measurement points 1 to 3 have been mirrored for the second tank and are referred to as MP1B to MP3B. The installation room had the dimensions of 8.22 x 5.98 x 7.16 m (length x width x height), the tanks were placed next to each other on the long side of the room.

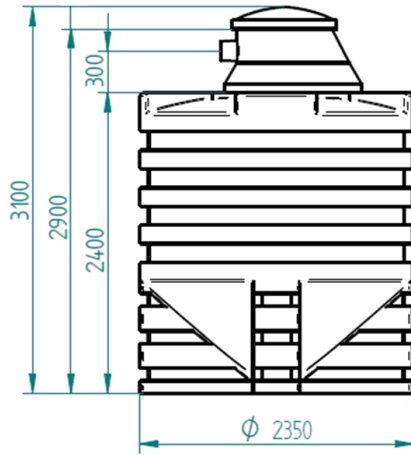


Figure IV.1.: Schematic of the plastic pellet storage tank used in the experiments according to [110], all dimensions are given in cm.

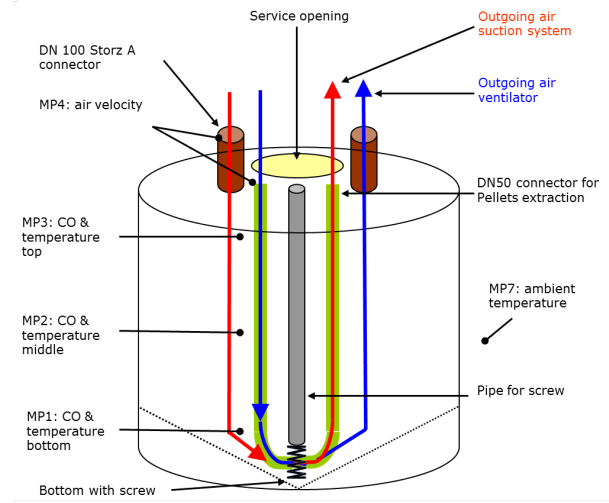


Figure IV.2.: Schematic of the measurement positions used in the ventilation experiments with the plastic tank.

3.1.2. Concrete tank

Experiments have been performed with a two-part pellet storage tank made of reinforced concrete, with a total volume of $V = 6.5 \text{ m}^3$ and a useable volume of $V = 5.85 \text{ m}^3$. The tanks main body is designed as a cylinder and its top has the shape of an irregular truncated cone. The overall height of the tank is 2.65 meters and its diameter is 2.5 meters. The discharge system for the pellets, which is based on a pneumatic system from the top of the tank, was dismantled from the tank for the course of the experiments. All openings used for the ventilation experiments are located on the top of the tank as indicated in Figure IV.3. The tank is equipped with two pipes of a diameter of 0.11 m, whose openings end in Storz A connectors. These pipes are typically used for filling the tank with wood pellets from a pellet delivery truck. Furthermore, the tank is also equipped with a service opening, which remained closed during all ventilation experiments. Figure IV.3 also depicts the positions of the various measurement points, which were used during the experiments. At measurement points 1 to 3 both CO concentration as well as temperature measurements were taken. The exact positions are directly in line with the position of one of the filling pipes at a height of 0.1, 1.0 and 1.83 m, respectively, measured above tank bottom level. Measurement point 4 is located directly below one of the Storz A connectors, at which the temperature at the air inlet into the tank is measured. The tank was positioned inside a storage depot for the duration of the experiments to avoid the influence of wind or other weather conditions on the outcome of the experiments. The storage depot was neither heated nor cooled and the temperatures within were continuously recorded throughout the experiments. In Figure IV.4 a photograph of the concrete tank inside the storage depot is shown. The temperatures inside the storage depot were measured at three measurement points in close proximity to the concrete tank at a height of 0.1, 1.0 and 3.3 m above floor level of the storage depot, respectively and are summarized in Table IV.1.

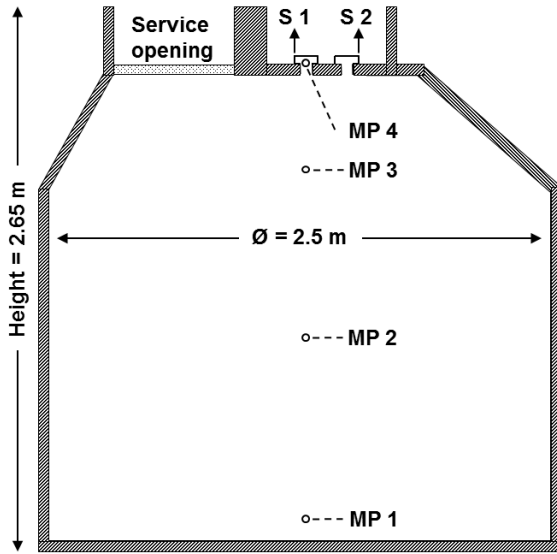


Figure IV.3.: Schematic of the concrete tank used in the experiments. MP indicates the positions of the measurement points.



Figure IV.4.: Experimental setup of the concrete tank in the storage depot. In front of the tank the gas analyzer and the switch board for the measurement cycle can be seen.

Table IV.1.: Measured quantities and positions (see figs. IV.3 and IV.9 for position of the measurement points MP1 to MP6 (ab.gr. = above ground level) within the concrete tank.

Symbol	Measured variable and position
c_1	CO concentration in the tank, 0.10 m ab.gr. (MP1),
c_2	CO concentration in the tank, 1.00 m ab.gr. (MP2),
c_3	CO concentration in the tank, 1.83 m ab.gr. (MP3);
T_{t1}	temperature in the tank at MP1,
T_{t2}	temperature in the tank at MP2,
T_{t3}	temperature in the tank at MP3,
T_{t4}	temperature in the tank at MP4, 2.35 m ab.gr.,
T_{t5}	temperature in chimney at MP5 (only for control),
T_{t6}	temperature in chimney at MP6, 3.15 m ab.gr.;
T_{a1}	ambient temperature, 3.3 m ab.gr.,
T_{a2}	ambient temperature, 1.00 m ab.gr.,
T_{a3}	ambient temperature, 0.10 m ab.gr.

3.1.3. Pellet storage room

The pellet storage room used for the ventilation experiments was designed to resemble a typical pellet storage located in the cellar of a residential house. The room was constructed according to the requirements of the ÖNORM M 7137 [14] and was designed as a cube with a side length of 2.5 meters resulting in a total volume of $V = 15.63 \text{ m}^3$ and a useable volume of roughly $V = 10 \text{ m}^3$. As building material plywood was used. A 50 cm x 80 cm hatch was installed on one side of the storage room, the filling pipes with a nominal diameter of DN100 were installed on the front of the storage as depicted in Figure IV.5. On the inside wall opposite of the filling pipes a plastic baffle plate was installed to minimize the breaking of pellets into smaller pieces during the process of filling of the pellet storage. Additionally, the storage room was built with an inclined bottom with an angle of 40° . Pellet extraction from the storage worked utilizing two suction probes installed at the bottom of the storage. To enable a dust-free filling of the storage room the joints between the plywood boards were sealed using a synthetic tape with vapor seal properties. The storage room was equipped with a number of measurement points, whose positions are indicated in Figure IV.5. Measurement points 1 to 3 were used for both CO concentration as well as temperature measurements. The exact coordinates for MP1 were 2.3, 0.1 and 0.5 m, for MP2 0.1, 0.6 and 1.25 m and for MP3 0.7, 1.4 and 2.4 m, in x, y and z direction, respectively.

The storage room was erected inside a larger room at the testing site at "BIOENERGY2020+ GmbH" (BE2020) for the duration of the experiments. The ambient temperature in the installation room was also measured in close proximity to the storage room at a height of 1.0 m above floor level. The installation room had the dimensions of 6.15 x 5.27 x 3.36 m (length x width x height) and the storage room was erected in one corner of the room with a gap of roughly 0.2 m between the walls of the room and the walls of the storage.

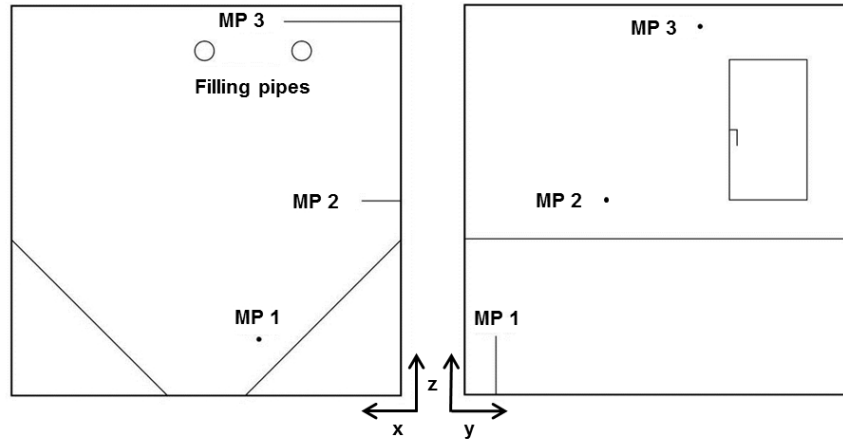


Figure IV.5.: Schematic of the pellet storage room constructed for the experiments. MP indicates the positions of the measurement points. On the right the side view with the position of the hatch and on the left the front with the position of the filling pipes is depicted.

3.1.4. Sheet steel tank

The two sheet steel tanks used for the ventilation experiments were made from galvanized steel sheets, which were delivered in individual components and put together at the testing site at BE2020. The construction is a closed, self-supporting design that is easy to assemble and designed especially for usage in premises with small entrance doors. After assembling the tanks sheets had to be sealed using strong adhesive tape to ensure dust-tightness in accordance with the enclosed manual for installation [111]. The tanks had a squared base of $A = 2.25 \text{ m}^2$ and a height of 2.2 m. The bottom of the tanks were constructed with an inclined floor resulting in a total volume of roughly $V = 3.66 \text{ m}^3$. The pellet storage capacity of the tank is approximately 2.8 tons according to the producer [111]. Pellet extraction from the storage worked using two suction probes installed at the bottom of the storage. The sheet steel tank was fully equipped with two filling pipes as well as a service hatch with the dimension of 50 x 80 cm as can be seen in Figure IV.6. On the inside wall opposite of the filling pipes a plastic baffle plate was installed to minimize dust formation during the process of filling of the pellet tank. The storage tanks was equipped with a series of measurement points, whose positions are indicated in Figure IV.7. Measurement points 1 to 3 were used for both CO concentration as well as temperature measurements. The exact coordinates for MP1 were 0.25, 0.75 and 0.2 m, for MP2 0.4, 0.75 and 0.9 m and for MP3 0.75, 0.5 and 2.1 m, in x, y and z direction, respectively. The position of the measurement points was mirrored for the tank B to be in the same position as in tank A. The ambient temperature in the installation room was also measured in close proximity to the sheet steel tanks at a height of 1.0 meter above floor level. The installation room had the dimensions of 6.15 x 5.27 x 3.36 meters and the tanks were placed next to each other on the long side of the room.



Figure IV.6.: Photograph of the installed sheet steel tank.

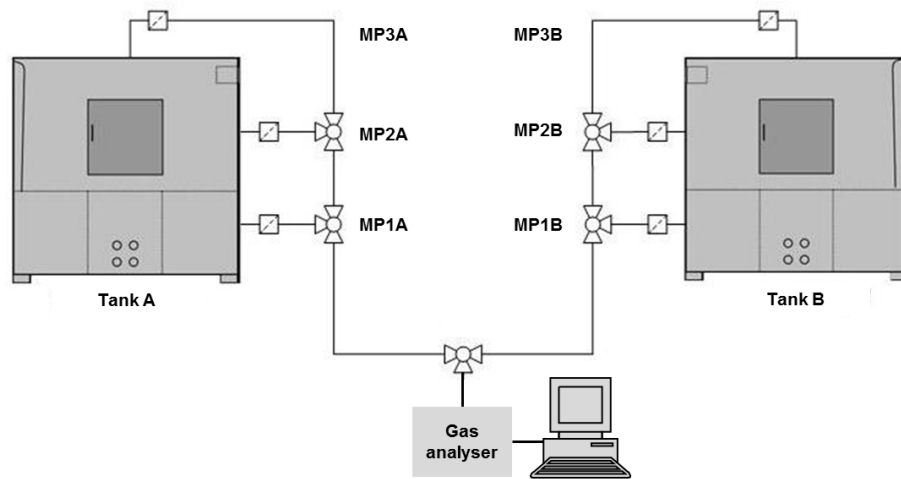


Figure IV.7.: Schematic of the sheet steel tanks set up for the ventilation experiments. MP indicates the positions of the measurement points.

3.2. Measurement equipment

3.2.1. Temperature measurement

For the measurement of ambient temperature and surface temperatures type K (NiCr-Ni) thermocouples were used. Their inherently simple design allows them to withstand high levels of mechanical shock and vibration. Their small size provides nearly immediate response to small temperature changes [112]. They are inexpensive and have an operating range from -40°C to 1000°C . The uncertainty tolerance is $\pm 1.5\text{ K}$ in the operating range from -40°C and 375°C .

3.2.2. Gas measurements

For different experimental setups various measuring devices for the CO and O_2 measurements were in use, such as a Varioplus Industrial (manufacturer: MRU), a NGA2000 (manufacturer: Rosemount) and an ECOM J2KN pro (manufacturer: Ecom). In Table IV.2 the measurement ranges and specifications for each system used are given.

Table IV.2.: Gas measurement equipment and specifications.

System	Species	Meas. principle	Range	Accuracy
NGA2000	CO	non dispersive infrared	0 - 5000 ppm	≤ 1 % rel.
	O ₂	paramagnetic	0 - 25 %	≤ 1 % rel.
ECOM J2KN	CO	electrochemical	0 - 2500 ppm	± 3 % rel.
	O ₂	electrochemical	0 - 21 %	≤ 5 % rel.
Varioplus Industrial	CO	non dispersive infrared	0 - 2000 ppm	± 10 ppm

3.2.3. Synthetic gases

The initial CO concentrations established at the start of the ventilation experiments described in chapter 4 were obtained by mixing pure CO gas with synthetic air and flushing the used storage system until the desired CO concentration could be established. The specifications of the used gases are described below.

Carbon monoxide 4.7

The gas was purchased from the company Linde AG. The specifications according to the producer are listed in Table IV.3.

Table IV.3.: Gas specifications (based on ideal gas volumes) of the technical carbon monoxide gas used during the ventilation experiments.

Component	Specifications (mole/mole)
CO	≥ 99.997 %
H ₂ O	≤ 5 ppm
O ₂	≤ 5 ppm
N ₂	≤ 10 ppm
Ar	≤ 15 ppm
H ₂	≤ 1 ppm
HC	≤ 2 ppm

Synthetic air

The gas was purchased from the company Linde AG. The specifications (based on ideal gas volumes) are 80 % N₂ and 20 % O₂ according to the product information sheet.

3.3. Ventilation equipment

3.3.1. Natural ventilation

Openings

The effect of ventilation by utilizing existing openings available for the different storage types on the CO concentration levels was investigated in several experiments. A list of the openings used along with their specific cross-sectional areas (CSAs) and the information on which storage systems they were tested can be found in Table IV.4.

Table IV.4.: Overview on the openings used in the ventilation experiments and the used storage systems.

	CSA m ²	Storage
Service opening	0.257	plastic tank
Storz A	0.0095	concrete tank/plastic tank
A	0.0012	concrete tank/plastic tank
Cap B	0.0022	concrete tank/plastic tank
C	0.0033	concrete tank/plastic tank
Service hatch	0.25*	sheet steel tank/pellet storage room

*the CSA of the fully opened hatch is 0.4 m² but was reduced to the smaller size

The exact positioning of the service opening as well as of the Storz A openings on the plastic tank can be found in the manufacturer manual [110] for the plastic tank, as well as in Figure IV.3 for the concrete tank. The fully opened service hatch has a dimension of 0.5 x 0.8 m and was implemented in the sheet steel tank as well as in the pellet storage room. Its respective positioning can be seen in Figures IV.6 and IV.5. For the ventilation experiments the hatches size was reduced to the smaller size of 0.5 x 0.5 m by implementing three metallic boards, which typically prevent the pellets from falling out of the storage when opening the hatch of a filled storage.

The ventilated caps are all constructed to fit a standard Storz A coupling and are implemented on the filling pipes of the pellet storages. A photographic documentation of the caps is given in Figure IV.8. Whilst cap B and cap C are fairly similar in design with a circular ventilation opening capped by a splash guard, cap A is constructed differently with four distinct holes for ventilation and a different way of preventing splash water from entering the pellet storage.

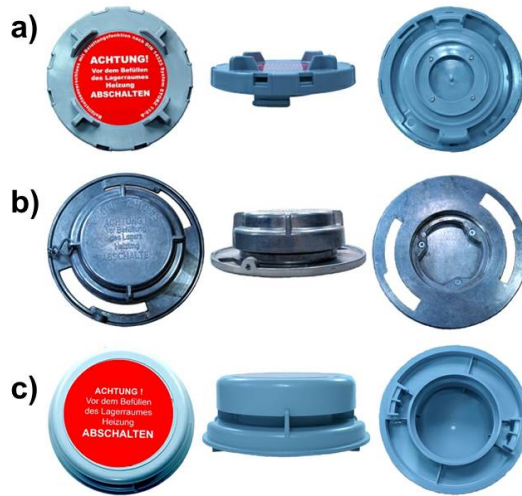


Figure IV.8.: Photographs of the ventilated caps and their respective CSAs used in the ventilation experiments, (a) ventilated cap A (0.0012 m^2), (b) ventilated cap B (0.0022 m^2), (c) ventilated cap C (0.0033 m^2).

Chimney

Additionally, the effect of adding a chimney to support ventilation was studied under varying temperature conditions. A schematic of the two chimneys used in the experiments is given in Figure IV.9. The variation in temperature was achieved by heating and cooling the chimney. Heating was carried out by applying a heating band (400 watt power) and cooling with a mix of ice and salt water.

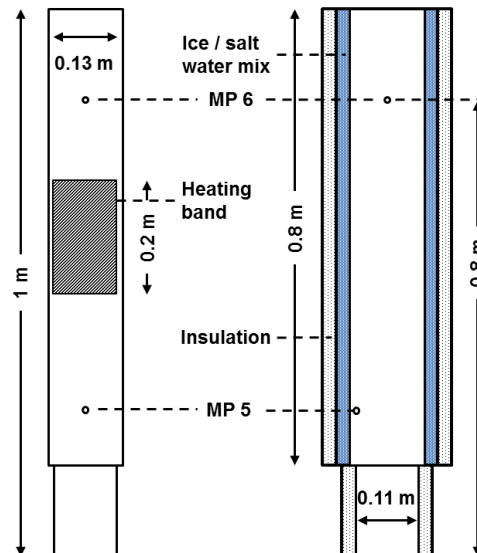


Figure IV.9.: Illustration of the two chimneys used, the left chimney was used for the setup "chimney" and "heated", the right chimney was used for the setup "cooled". MP indicates the positions of the temperature measurement points.

3.3.2. Forced ventilation

For testing the effectiveness of forced ventilation in decreasing the CO concentration within a pellet storage two types of ventilators were tested, which are described below.

Suction system

The suction system is a ventilator with 100 watt power, which was connected to the pellet storage by a flexible pipe leading to one of the filling pipes of the pellet storage system. During the experiments the second filling pipe opening was closed with a ventilated cap A to allow fresh air to flow into the storage.

Ventilator

The used ventilator has a power of 12 watt. A picture of a similar model is depicted in Figure IV.10. The ventilator was incorporated in a pipe positioned to form an extension of one of the filling pipes. It was operated to create under pressure in the pellet storage. Again the second filling pipe opening was closed with a ventilated cap A to allow air to flow into the storage during the experiments.



Figure IV.10.: Photograph of the 12 watt ventilator used in the experiments with forced ventilation.

3.4. Calculation of air exchange rates

3.4.1. Air exchange rates according to ÖNORM EN ISO 12569

The calculation of the given air exchange rates was carried out according to the international standard ÖNORM EN ISO 12569 "Thermal performance of buildings and materials - Determination of specific airflow rate in buildings - Tracer gas dilution method" [113]. The tracer gas used in the ventilation experiment was CO, as it mixes uniformly with air due to its similar molar weight and can easily be detected utilizing standard gas measurement equipments. The equipment used in the experiments is described in Table IV.2. The measurement method used was the 2-point concentration decay method which can be utilized if the following conditions are fulfilled:

1. the concentration of the measured agent can be expected to be uniformly distributed in the measured space
2. a limited measurement duration of several hours

The method principle can be described as follows. At the beginning of the measurement the tracer gas is injected in the measurement zone and the air exchange rate or the specific air volume flow (SAVF) are determined on the basis of the concentration decay of the tracer gas. The underlying basic equation is:

$$\frac{dV_{gas}(t)}{dt} = -C_E(t) \cdot Q_V(t) \quad (IV.1)$$

If the concentration in an effective mixed zone is continuously uniform the time-averaged air exchange rate from start to end point of the measurement can be calculated. The specific air flow volume does not need to be constant during the measurement. Subsequently the following equations can be derived:

$$V_{gas}(t) = V_{emz} \cdot C(t) \quad (IV.2)$$

$$C_E(t) = C(t) \quad (IV.3)$$

Equations IV.1, IV.2 and IV.3 result in equation IV.4 from which equation IV.5 can be derived.

$$\int_{t_1}^{t_2} \frac{dC}{C(t)} = - \int_{t_1}^{t_2} \frac{Q(t)}{V_{emz}} dt \quad (IV.4)$$

$$\bar{N} = \frac{1}{t_2 - t_1} \cdot \log_e \frac{C(t_1)}{C(t_2)} \quad (IV.5)$$

On the basis of two concentration measurements of the tracer gas at two separate points in time the time averaged specific air volume flow is calculated for this period. The concentration difference between start (t_1) and end point (t_2) has to be above the error span of the concentration measurement equipment.

Error calculation

Absolute errors of assessed values were calculated using the method of the Gaussian error propagation (see also equation II.11. A confidence interval of 95 % was chosen. Error values of the individual equipments are given in the descriptions of the specific equipments.

3.4.2. Air exchange rates dependent on temperature differences

In the most simple case of a constant ventilation rate, the carbon monoxide concentration would be governed by the differential equation:

$$\dot{C} = -\alpha \cdot C \quad (IV.6)$$

with $\alpha > 0$. For the initial condition $C(0) = C_0$ the solution is the exponential drop:

$$C(t) = C_0 \cdot e^{-\alpha t}. \quad (IV.7)$$

In a semilogarithmic plot, this corresponds to a straight line. As shown in Figure IV.11.a, such a behavior is indeed found for some experiments. For other experiments, however, this is only true for limited periods of time. As shown in Figure IV.11.b, during different stages of the ventilation experiment, pieces of straight lines with significantly different slopes yield a reasonable description of the data.

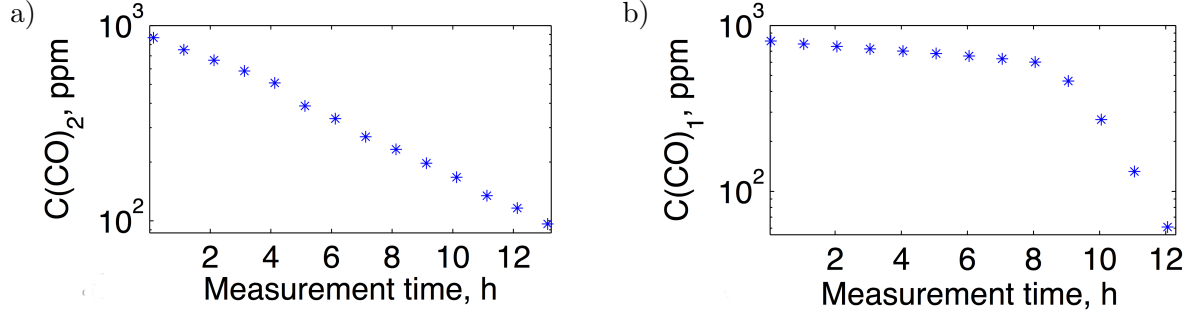


Figure IV.11.: Semilogarithmic CO concentration plots (for more details see section IV.4.2), a) data obtained by sensor C_2 for setup "heated/closed"; b) data obtained by sensor C_1 for setup "chimney/open".

This makes clear that equation (IV.7) with constant α does not describe the general case. A reasonable generalization is to assume a dependence of the drop rate on the temperatures,

$$\alpha = \alpha(T_{t1}, \dots, T_{tx}). \quad (\text{IV.8})$$

A simple, yet plausible relation is to assume the dependence on one characteristic temperature difference

$$\alpha = \alpha(T_{in} - T_{out}) \quad (\text{IV.9})$$

with two characteristic temperatures T_{in} and T_{out} inside the storage and outside of it. In order to check the hypothesis expressed in equation (IV.9), time-dependent drop rates have been determined from the concentration data as

$$\alpha_i(t) = \frac{1}{\Delta t} \cdot \ln \frac{C_i(t - \Delta t)}{C_i(t)} \quad i = 1, 2, 3 \quad (\text{IV.10})$$

and, using the volume V of the storage, further converted to a ventilation or air exchange rate. A discussion of error propagation is given in Appendix C.

$$\dot{V}(t) = \alpha(t) \cdot V \quad (\text{IV.11})$$

For these air exchange rates correlation plots of \dot{V} vs. a characteristic temperature difference ΔT can be created. Temperature differences have the form $\Delta T = T_{in} - T_{out}$ with T_{in} typically representing a temperature inside the pellet storage and T_{out} representing a temperature outside the pellet storage.

3.4.3. Calculation of the specific air volume flow based on formulas from ventilation and air-conditioning technology

The calculation of the specific air volume flows (SAVF) given in section IV.4.5 was carried out according to the formulas given in the "Handbook on heating and air conditioning technology" [114]. The necessary volume flow to maintain a specific level of air purity can be calculated if the source of the pollution is known. It can be determined utilizing the following equation:

$$\dot{V} = \frac{\dot{K}}{k_i - k_a} \quad (\text{IV.12})$$

By dividing the calculated necessary volume flow by the volume, which is to be ventilated, the specific air volume flow for ventilation is obtained:

$$\bar{N} = \frac{\dot{V}}{V} \quad (\text{IV.13})$$

If the air used for ventilation and/or if the volume, which is to be ventilated, are already contaminated with the pollutant before the ventilation has started, then the temporal plot for the pollutant concentration can be calculated using the equation below:

$$k(t) = k_a + (k_0 - k_a) \cdot e^{\bar{N} \cdot t} + \frac{\dot{K}}{\bar{N} V} \cdot (1 - e^{\bar{N} \cdot t}) \quad (\text{IV.14})$$

4. Results and discussion

In the first section of this chapter three parameters and their influence on the air exchange rates for continuous natural ventilation of pellet storages are presented. The parameters investigated are:

- Size of cross-sectional area,
- temperature differences,
- existence of cross-ventilation and
- implementation of a chimney

In the second part of this section an evaluation of the effectiveness of two ventilation measures, namely "open hatch" ventilation and forced ventilation, using two ventilators of different electric power, in reducing CO concentration levels within pellet storages in a given time span has been investigated. Finally, based on formulas for heating- and air conditioning systems characteristic sets of curves to determine required air exchanges rates for storages are presented.

4.1. Size of cross-sectional area

For the investigation of the influence of the size of the cross-sectional area (CSA) on the ventilation rates two plastic storage tanks (setup described in section IV.3.1.1) were utilized. At the beginning of the experiment the two otherwise empty tanks were flushed with a mixture of CO gas in synthetic air until all concentration measurement points recorded that a CO concentration of roughly 600 ppm had been reached. Afterwards all tank openings were sealed for three hours to allow the CO gas to distribute evenly in the tank. At the end of the equilibration phase a control measurement was made to check whether an even distribution had been reached. If the concentration measurement at the three MPs deviated by ≤ 5 ppm the measurement was started, otherwise the system was allowed to equilibrate for another hour after which the CO distribution in the tank was checked again until the distribution criterion was fulfilled.

The measurement was then started by opening the tank and measuring the drop in CO concentration over time. For the measurements of the CO concentrations in the tank a gas analyzer using an NDIR based measurement principle (type: NGA2000) was used. During one 30 minutes measurement cycle at each of the three measurement points MP1 to MP3 gas was sampled for 4 minutes, the rest of the time the lines were flushed with ambient air. The CO concentration values were recorded as 5-seconds mean values. The temperature measurements were also continuously recorded as 5-seconds mean values using type K thermocouples. The resulting air exchange rates $Q(t)$ were calculated using the method described in section IV.3.4 according to ÖNORM EN ISO 12569 [113] based on the recorded start and end concentrations of the experiment and the experiments duration. All results are given in Table IV.5. Measurement error calculation was carried out based on the given accuracy data of the measurement equipment using the method of the Gaussian error propagation described in section IV.3.4.1.

Table IV.5.: Average air exchange rates dependent on the size of the ventilated cross-sectional area and the associated experimental data.

	CSA m ²	CO conc. ppm		Exp. duration h	Q(t) m ³ /h	Error %
		Start	End			
Service opening	0.257	597	32	22.1	1.0514	<1
Storz A	2x0.0095	590	60	17.5	1.0403	<1
A	2x0.0012	622	156	163.2	0.0672	1
Cap B	2x0.0022	632	310	92.4	0.0615	2
C	2x0.0033	603	131	165.6	0.0856	1

At first glance the results show a significant increase in the air exchange rates only when switching from the smaller CSAs of the ventilated caps to the larger openings by a factor of roughly 15, whereas, in between the three types of ventilated caps the obtained air exchange rates do not follow the expected trend of increasing $Q(t)$ with increasing CSAs. Also, when comparing the results between the service and the Storz A opening, one can not see a significant increase in $Q(t)$ even though the CSA of the service opening is more than a hundred times bigger than that of the Storz A openings.

A closer look on further time-resolved results is given in Figure IV.12 for the experiments with the ventilated caps A and C as an example. In this Figure the air exchange rates have been calculated not from start to end of the experiment but rather as 24 hour sliding averages from start till end of the experiment. Although, this is increasing the error margin for the calculated results, the data clearly indicates that whilst in the case with cap A the ventilation rate has been almost constant, this was not so in the experiment with cap C. Especially, in the first half of the experiment with cap C the air exchange rates have been almost twice as high as in the second half, where the air exchange rates for both experiments are almost identical. The air exchange rates for the individual experiments have, therefore, been calculated a second time using adequate intervals of sliding averages and the arithmetic mean average from these calculations as well as the minimum and maximum values for $Q(t)$ and are summarized in Table IV.6.

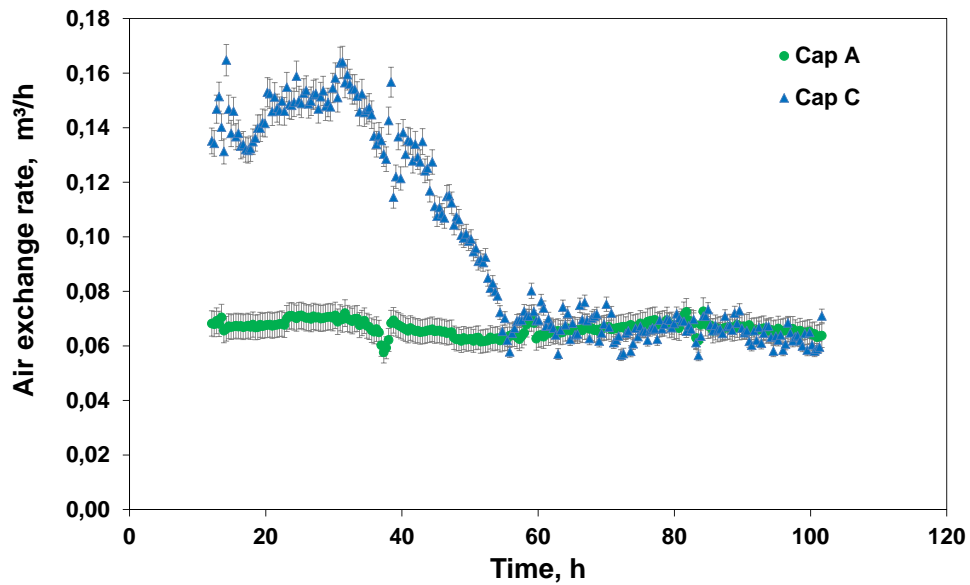


Figure IV.12.: Detailed results for changes in air exchange rates for the two ventilated caps A and C.

The analysis of the minimum and maximum value for $Q(t)$ show a high variation of the air exchange rates over the course of the experiments. The variations suggest the existence of at least on more influential parameter superimposing the influence of the parameter cross-sectional area significantly. Assuming that the influence of variations of the CSAs is the least affected by other influences at the minimum levels of $Q(t)$ determined, the results suggest that there is no significant increase in $Q(t)$ within the three investigated ventilated caps. Furthermore, there is no significant difference in $Q(t)$ between the service opening and the Storz A opening. Nevertheless, there is an increase in $Q(t)$ between the ventilated caps and the larger Storz A and service opening, respectively, by a factor > 10 .

Table IV.6.: Averaged time-resolved air exchange rates dependent on the size of the ventilated cross-sectional area and corresponding error margins.

		Interval h	Q(t) m^3/h			Error %
			average	min.	max.	
Service opening		6	1.1040	0.5818	1.3585	2
Storz A		6	1.0812	0.5946	1.6628	2
	A	24	0.0665	0.0577	0.0727	7
Cap	B	24	0.0609	0.0492	0.0729	7.7
	C	24	0.0976	0.0565	0.1648	5.5

It can be concluded that there is a positive correlation between size of CSA and $Q(t)$. However, the actual impact of the effect is of much less significance to the absolute value of $Q(t)$ than other influential parameters, such as temperature differences between the tank and the ambient air, which were investigated in a different experimental setup and will be described in the next section.

4.2. Temperature differences, cross-ventilation and implementation of a chimney - Multivariate correlation analysis

In the course of the experiments three influential parameters on the level of air exchange rate from a pellet storage system have been investigated. The three parameters investigated were:

- Temperature differences between the storage and the surroundings,
- existence of cross-ventilation and
- implementation of a chimney

For the ventilation experiments the storage system used was the concrete tank described in section IV.3.1.2. The setup was chosen because it provided an airtight system, where the utilized ventilation measures could be investigated independently and with a high degree of resolution.

The opening labeled **S1** (see Figure IV.3) was used as ventilation opening in all experiments. Its cross-sectional area was reduced by capping with a cap A cover (see Table IV.4). The opening labeled **S2** was only used in the experiments where the effect of cross-ventilation was studied, otherwise it remained closed. For the cross-ventilation experiments the **S2** opening was capped with the same type of cover also used on the **S1** opening.

Additionally, the effect of adding a chimney to support ventilation was studied under varying temperature conditions. A schematic of the two chimneys used in the experiments is illustrated in Figure IV.9. The variation in temperature conditions were achieved by heating and cooling the chimney by applying a heating band (400 watt power) and a mixture of ice and salt water, respectively. The heating or cooling was continuously put in place during the ventilation experiment. The temperatures measured at measurement point 5 (control temperature) were around 403 K in the case of the heated chimney and around 270 K in case of the ice-cooled chimney throughout the experiment. Finally, the effect of adding a chimney without artificial heating or cooling has also been studied.

At the beginning of each experiment the empty tank has been filled with a premixed flow of air and CO gas which corresponds to an initial concentration of CO of approximately 800 ppm. Once the CO concentrations at all three measurement points inside the tank had reached a stable value, the gas flow was stopped and the subsequent drop of the CO concentration in the tank was monitored. Each ventilation experiment was stopped with the first measured CO concentration below a threshold of 200 ppm, but latest after a time span of about 44 hours. In the course of the experimental part, eight different setups have been studied, for an overview see Table IV.7. The four general possibilities investigated were each combined with either a **closed** or an **open** second opening S 2.

Table IV.7.: Overview over experimental setup for the multivariat parameter investigation on level of air exchange rate of a concrete tank

Experiment setup	Means of ventilation	Cross-ventilation
opening/closed	capped filling tube (S 1 in Figure IV.3)	no
opening/open	capped filling tube (S 1)	yes
chimney/closed	chimney	no
chimney/open	chimney	yes
heated/closed	heated chimney	no
heated/open	heated chimney	yes
cooled/closed	ice-cooled chimney	no
cooled/open	ice-cooled chimney	yes

For the measurements of the CO concentrations in the tank a gas analyzer using an NDIR based measurement principle (type: Varioplus Industrial, manufacturer: MRU) was used. During one 30 minutes measurement cycle, at each of the three measurement points C_1 - C_3 , gas was sampled for 4 minutes, the rest of the time the gas analyzer was flushed with ambient air. The CO concentration values were recorded as 5-seconds mean values. The temperature measurements were also continuously recorded as 5-seconds mean values using type K thermocouples.

The individual start and end concentrations for all experiments as well as their duration are given in Table IV.8.

Table IV.8.: CO start/end concentrations and duration for the ventilation experiments. Experiments 9 and 10 are essentially repetitions of experiments 3 and 4.

Exp.#	Setup	C(CO), ppm		Duration
		start	end	
1	opening/closed	807	463	44 h 00 min
2	opening/open	856	190	9 h 05 min
3	chimney/closed	847	199	38 h 10 min
4	chimney/open	806	130	11 h 05 min
5	heated/closed	875	175	10 h 10 min
6	heated/open	850	170	2 h 20 min
7	cooled/closed	866	199	25 h 10 min
8	cooled/open	846	167	2 h 10 min
9	chimney/closed	860	318	44 h 00 min
10	chimney/open	838	174	5 h 40 min

Utilizing the calculation method described in section IV.3.4.2, for air exchange rates dependent on temperature differences, it turns out that for most possible temperature differences in the chosen setup there is either no or no simple dependency of the air exchange rate on them. The plots, which exhibit a characteristic dependence, are typically quite similar to each other, so it is sufficient to pick one characteristic correlation plot for each of the setups. This is shown in more detail in Appendix D.

For most setups the characteristic dependence on ΔT seems to be piecewise affine linear,

$$\dot{V} = \begin{cases} -k_- \Delta T + d_- & \text{for } \Delta T < 0, \\ k_+ \Delta T + d_+ & \text{for } \Delta T > 0 \end{cases} \quad (\text{IV.15})$$

with $k_- > 0$, $k_+ > 0$ and $d_- \approx d_+ > 0$.

This functional form has a simple physical interpretation: For $\Delta T \approx 0$ only diffusion is relevant, the ventilation rate is minimal and given by $\dot{V} \approx d_- \approx d_+$. If the air inside the tank is either cooler or warmer than the ambient, convection sets in and leads to additional air exchange approximately proportional to the driving influence, i.e. ΔT . Since the convection mechanisms differ for $\Delta T < 0$ and $\Delta T > 0$ there is no reason to expect $k_- \approx k_+ > 0$, and indeed, these slopes are significantly different in most cases. (Details on implementation and evaluation of the piecewise linear fit are given in Appendix E.)

The form (IV.15) can be generalized to

$$\dot{V} = \begin{cases} -k_- \Delta T + d_- & \text{for } \Delta T < \Delta T_0, \\ k_+ \Delta T + d_+ & \text{for } \Delta T > \Delta T_0 \end{cases} \quad (\text{IV.16})$$

with a constant ΔT_0 . This takes into account that the temperatures accessible for measurements might be shifted by a systematic offset to the ones most relevant for the air exchange rate.

The results of the correlation analysis for the ventilation experiments described in Table IV.8 are presented as parameters for the piecewise linear fit given in Table IV.9. In general, the analysis is significantly less reliable for "open" setups (Exp. # 2,4,6,8 and 10), since the gas exchange is much faster, there are fewer data points than in the "closed" cases. For a better comparability of the effectiveness of the different experimental settings the calculated air exchange rates are given, whenever possible, at values of $\Delta T = \pm 4$ K, also given in Table IV.9.

Table IV.9.: Resulting fit parameters for equation IV.16 and characteristic air exchange rates $\dot{V}_{-4} := \dot{V}(\Delta T_0 - 4 \text{ K})$ und $\dot{V}_{+4} := \dot{V}(\Delta T_0 + 4 \text{ K})$ for the experiments listed in Table IV.8. The reference values $\Delta T = \Delta T_0 \pm 4 \text{ K}$ are significantly outside the fit range for the "heated" configurations and for "cooled/open", therefore, they require extrapolation and are not reliable. The fit for "heated/open" can not be considered to be reliable at all due to the poor data basis.

exp. #	ΔT	$\Delta T_0 [\text{K}]$	$k_- [\text{m}^3/\text{h K}]$	$d_- [\text{m}^3/\text{h}]$	$k_+ [\text{m}^3/\text{h K}]$	$d_+ [\text{m}^3/\text{h}]$	$\dot{V}_{-4} [\text{m}^3/\text{h}]$	$\dot{V}_{+4} [\text{m}^3/\text{h}]$
1	$T_{t3} - T_{a1}$	0.005	-0.044	0.058	0.114	0.051	0.235	0.507
2	$T_{t3} - T_{a1}$	-0.149	-0.029	0.257	0.719	0.352	0.378	3.122
3	$T_{t3} - T_{a1}$	-0.224	-0.0242	0.075	0.092	0.094	0.177	0.443
4	$T_{t3} - T_{a1}$	-0.303	0.012	0.459	2.018	1.092	0.409	8.554
5	$T_{t3} - T_{t4}$	-4.472	0.256	2.571	0.192	2.299	0.405	2.208
6	$T_{t3} - T_{t4}$	-2.629	–	–	10.130	22.910	–	36.801
7	$T_{t4} - T_{a1}$	-1.170	-0.062	0.018	0.096	0.210	0.338	0.480
8	$T_{t4} - T_{a1}$	-6.677	-0.331	4.959	0.133	8.363	8.496	8.006
9	$T_{t3} - T_{a1}$	-1.259	-0.057	-0.034	0.064	0.120	0.263	0.294
10	$T_{t3} - T_{a1}$	-0.735	0.022	0.525	1.875	1.810	0.422	7.930

Setups opening and chimney

The most significant correlation plots for setups "opening/closed", "opening/open", "chimney/closed" and "chimney/open" are shown in fig. IV.13. For the "opening/open" case the calculated air exchange rates for $\Delta T = T_{t3} - T_{a1} = +4 \text{ K}$ is in the range of $\dot{V} = 3.122 \text{ m}^3/\text{h}$. This rate is by a factor of six larger than the one obtained for the "opening/closed" case for the same value of ΔT . As was to be expected the air exchange rates for both cases ("open" and "closed") are lowest for temperature values of ΔT close to 0. Furthermore, it could be shown that although an increase in the absolute value of ΔT always resulted in an increased air exchange rate, the increase was even higher when the temperature inside the tank was higher than the reference temperature outside of the tank. Thus the air exchange rate in the case "opening/closed" more than doubled from a $\dot{V} = 0.235 \text{ m}^3/\text{h}$ for a $\Delta T = -4 \text{ K}$ to a $\dot{V} = 0.507 \text{ m}^3/\text{h}$ for a $\Delta T = +4 \text{ K}$. The increase was even more pronounced in the case opening/open where the air exchange rate for $\Delta T = +4 \text{ K}$ was more than eight times higher than for a $\Delta T = -4 \text{ K}$.

A comparison between the results for the cases "chimney/closed" and "opening/closed" show a high degree of resemblance with similar air exchange rates for similar values of ΔT . However, the results for the case "chimney/open" differ significantly from the case "opening/open". While the calculated air exchange rate for the experiment "chimney/open" result in a $\dot{V} = 8.554 \text{ m}^3/\text{h}$ for a value of $\Delta T = +4$, the experiment "opening/open" resulted in the smaller value of $\dot{V} = 3.122 \text{ m}^3/\text{h}$ for the same value of ΔT . However, looking at the air exchange rates for negative values of ΔT , when the temperature inside the tank was lower than the reference temperature outside of the tank, the setups "chimney/open" and "opening/open" result in much more similar air exchange rates for similar values of ΔT .

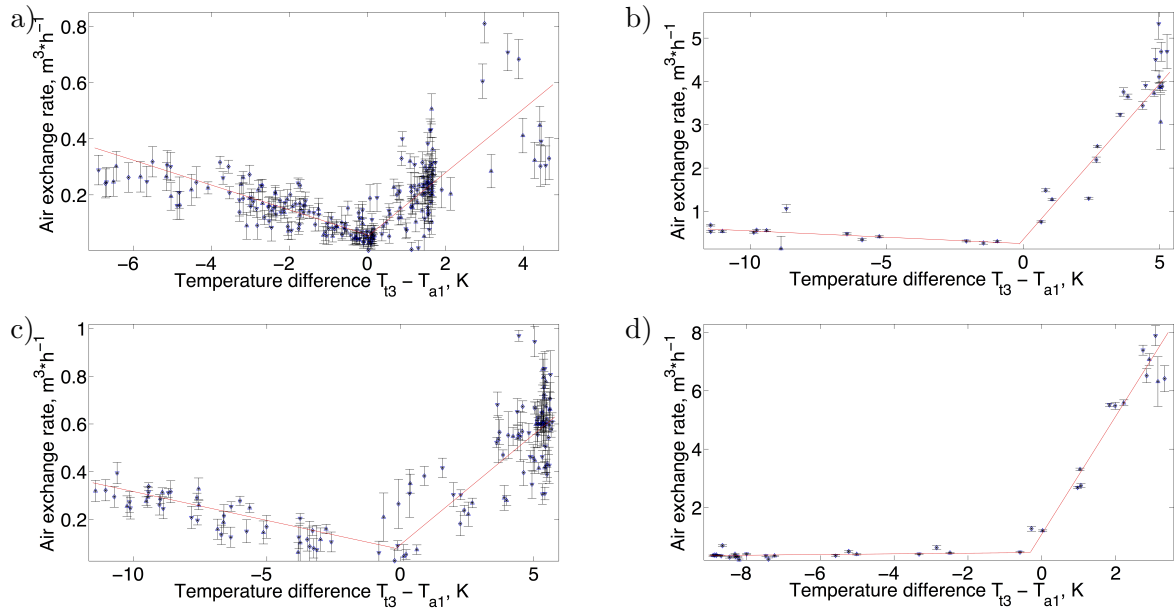


Figure IV.13.: Correlation plot for the setups a) opening/closed (experiment #1), b) opening/open (experiment #2), c) chimney/closed (experiment #3) and d) chimney/open (experiment #4). Beware of the changes in scaling.

Setups heated and cooled chimney

Some general remarks have to be made before taking a closer look on the results for the experiments with the heated chimney. First of all, it has to be mentioned, that it proved to be extremely difficult to choose a reference temperature for the heated chimney due to the fact, that the temperature profile along the air column inside the chimney was very inhomogeneous. During the experiments the temperatures measured at the measurements points 4, 5 and 6 averaged around 293, 403 and 353 K, respectively. Finally, measurement point 4 was used as a correlation point, with full awareness, that the resulting values for the calculation of ΔT would not serve as representative values of ΔT along the air column of the heated chimney. Therefore, all following evaluation of results for the heated chimney setup can only be understood as qualitative assessment of the effectiveness of such a setup. Furthermore, due to the relatively short experimental duration and the subsequent small number of measured values, the given reference values for $\Delta T = \Delta T_0 \pm 4 \text{ K}$ (given in tab. IV.9) are significantly outside the fit range and, therefore, they require extrapolation and are not reliable.

The highest calculated air exchange rates for measured data points were between approximately 2 and $2.5 \text{ m}^3/\text{h}$ in the case "heated/closed" and up to a value of around $\dot{V} = 6 \text{ m}^3/\text{h}$ "heated/open" (see Figure IV.15.e and f). Based on the available temperature values there is, however, no way to relate these air exchange rates with reasonable values of ΔT . Finally, just looking at the decrease of CO concentrations in time for the two setups "heated/closed" and "heated/open" allow to deduct that the average air exchange rate in the "heated/open" must be higher than for the setup "heated/closed".

In the setups with the cooled chimney the temperatures with the highest degree of correlation were in fact the temperatures T_{t4} (bottom end of the chimney) and T_{a1} (ambient temperature close to the top end of the chimney), shown in Figure IV.14.b for experiment #7, both outside the pellet storage. The usual temperature couple relating inside storage temperature to an outside temperature (shown in Figure IV.14.a) showed no correlation, contrary to all other setups. This is attributed to the fact, that in the chosen experimental setup the influence of a warm layer of air above the cooled chimney is superimposing the effect of warm air in the pellet tank below the cooled chimney. In the setup "cooled/closed" the obtained air exchange rates for values of $\Delta T \sim 4 \text{ K}$ are very similar to the results from the cases "opening/closed" and "chimney/closed". The results for the setup "cooled/open" show a relatively stable and also quite high air exchange rate of around $7.5 \text{ m}^3/\text{h}$ over a range of values of ΔT from -5 K to -8 K .

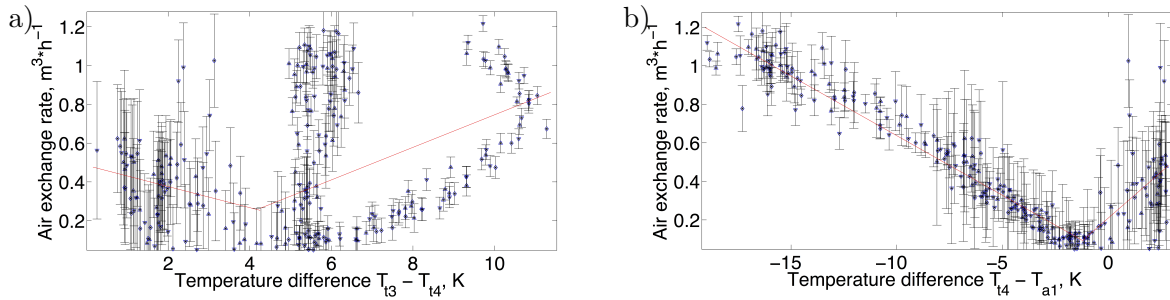


Figure IV.14.: Correlation plots for setup cooled/closed (experiment #7) a) using temperatures T_{t3} and T_{t4} and b) using temperatures T_{t4} and T_{a1} . Beware of the changes in scaling.

Comparison of all setups

The correlation plots in Figure IV.15 (for better comparability they are all shown on the same scale) show that the hypothesis expressed in equation (IV.9) seems to be correct in most cases: The ventilation rate mainly depends in a piecewise linear relation on a characteristic temperature difference.

Furthermore, in some cases a distinct change in the air exchange rates can be observed when the sign of this temperature difference changes. A characteristic example is depicted in Figure IV.15.d (experiment #4), where the air exchange rates for negative values of ΔT are relatively small and stable (around $0.4 \text{ m}^3/\text{h}$), whereas for positive values of ΔT the air exchange rates rise directly proportional with larger values ΔT and reach amounts of up to $8 \text{ m}^3/\text{h}$. This example as well as other results suggest that a temperature difference, where the temperature inside the tank is higher than the reference temperature outside of the tank is more beneficial to the obtained air exchange than vice versa.

The introduction of a chimney to enhance air exchange rates proved only successful under the condition "open" in all setups. This leads to the conclusion that the installation of a chimney alone does not lead to an

effective enhancement of air exchange rates. A "stack-effect" could only be observed when cross-ventilation through a second opening was possible, in these cases, however, at least a doubling of the air exchange rates could be observed. Also, the effects of temperature differences are much more significant in cases where the second opening of the tank is "open" resulting in air exchange rates about twice as high as for the "closed" setups. In the course of the experiments the highest air exchange rates were obtained for the setups "chimney/open" and "cooled/open". A more extensive discussion on the results and a more detailed description of the experiments has been published by Emhofer *et al* 2014 [115].

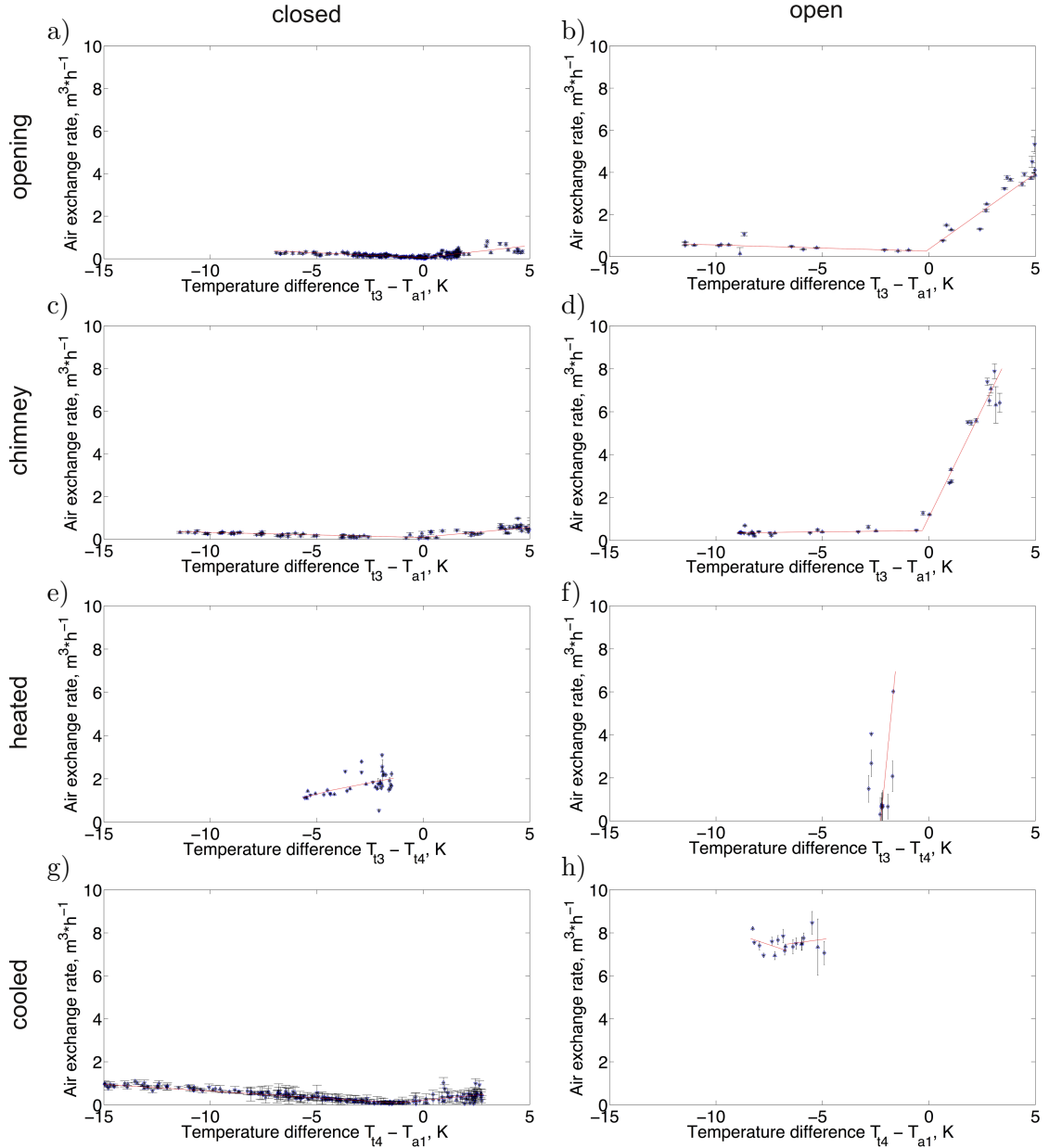


Figure IV.15.: Correlation plots for all configurations on uniform scale both for temperature and air exchange rates.

4.3. "Open hatch" ventilation

As explained in more detail in section IV.1, it is currently common practice to warn pellet consumers that a pellet storage may only be entered after a sufficiently long ventilation period, prior to entering, with a duration of at least 15 minutes. As appropriate ventilation measure the opening of the pellet storage door or access hatch is suggested [107].

For the two experimental storage types sheet steel tank and storage room (for details on the systems see section IV.3.1) the effectiveness of this recommendation was evaluated. Following a majority of regulations governing car-parks and the CO threshold concentrations therein, the criterion for successful and effective ventilation was set at a CO level of ≤ 100 ppm, which needed to be reached in the headspace of the storage at the end of the ventilation interval. In accordance with the VDI guideline 2053 "Air treatment systems for car parks" [116] a second, more ambitious, success criterion was set at a CO level of ≤ 60 ppm. However, as the area of application for the VDI guidelines is a continuously ventilated volume and the storage systems used in the experiments are ventilated on the spot, the second criterion shall serve only as a mark of excellence, whereas the first criterion shall serve as a mark of success.

In preparation for the experiments the two storage systems sheet steel tank and storage room have been filled with 1900 kg and 4900 kg of spruce pellets, respectively, resulting in a filling level of $\frac{2}{3}$ for the sheet steel tank and $\frac{3}{4}$ for the storage room. At the start of the experiment the storages were flushed with a premixed gas flow of synthetic air and CO gas to reach stable initial concentrations of CO. Afterwards the implemented service hatches (details see Table IV.4) of the systems were opened and then the subsequent drop of the CO concentration in the storages was monitored. At the end of the ventilation interval the hatch was closed again and the development of CO concentration within the storages was monitored for another hour to investigate the development of the CO concentration after the initial ventilation. An overview of the experiments and the experimental conditions is given in Table IV.10.

Table IV.10.: Experimental conditions of ventilation experiments on the effectiveness of open service hatches.

Storage system	Initial CO conc. ppm	Ventilation interval min	No. of measurements
sheet steel tank	≈ 300	15	2
sheet steel tank	≈ 300	30	2
sheet steel tank	≈ 600	15	2
sheet steel tank	≈ 600	30	2
pellet storage room	≈ 600	15	2
pellet storage room	≈ 600	30	2

In both storage systems the measurement points labeled with the number 3 were located in the top volume of the storages, which were in the headspace above the pellet bulk, whilst the MPs labeled with the numbers 1 and 2 were located within the pellet bulk. Due to the relatively short duration of the experiment, less than three hours, and the fact that the pellets used in the experiment were not freshly produced and had

been stored for some time prior to the experiment, the pellet bulk as a source of additional CO gas was neglected during data evaluation.

In Figure IV.16 two examples of the typical progress of CO development over the course of the experiments are given. A closer look on Figure IV.16.a shows an early fast drop in CO concentration from 315 to ≈ 100 ppm CO at MP3A. At the end of the ventilation interval of 30 min, when the service hatch was closed again, a subsequent rise in CO concentration measured at MP3A can be observed. The CO concentrations measured at MP1A and MP2A, located within the pellet bulk, show a much slower but continuous decrease of CO levels also during the time the service hatch had been closed again. All three curves level out at a CO concentration of ≈ 160 ppm, one hour after the closing of the service hatch. The same is true for the second run of the experiment. Figure IV.16.b in comparison shows overall a similar progression for the development of CO for the MPs 1 to 3. However, the curves do not level out as fast as in the previous experiment. In fact, an equilibrated CO level within the storage system had not been reached at the end of the experiment, more than three hours after the closing of the service hatch.

The results from the "open hatch" ventilation experiments show that ventilating the storage using a service hatch can lead to significant reduction of CO concentration in the headspace of the two tested storages in a short time. Nonetheless, CO concentrations will increase steadily and fast as soon as the service hatch is shut again. Moreover, within the ventilation interval of 15 minutes CO concentrations could not be lowered to values below 100 ppm in every experiment. In fact, only in 50 % of the experiments the first criterion condition for successful ventilation was reached, regardless of the duration of the ventilation interval and the storage type. The second criterion for successful ventilation was reached only in 25 % of the experiments, all of which on the sheet steel tank.

The ventilation utilizing a same size of the service hatch, is less effective for ventilating the larger volume storage system, the storage room. While the CO concentration levels at the headspace measurement position in the storage room drop to similar values as in the sheet steel tank during ventilation, the CO levels rise faster and higher in the storage room, once the hatch is closed again. Due to the storage rooms larger volume, which is almost three times bigger than that of the sheet steel tank, the remaining CO gas volume within the pellet bulk, which is hardly affected by the ventilation procedure, is also much larger causing the different development of CO concentrations once the ventilation is stopped. A complete overview on the experimental results for the "open hatch" ventilation experiments is given in Table IV.11. Overall, the results do not show a significant improvement in the CO levels, when the ventilation interval is extended from 15 to 30 minutes. In the case of the storage room the results even show a much higher CO concentration after 30 minutes of ventilation than for the shorter ventilation period. This clearly indicates that the effectiveness of the "open hatch" ventilation not only depends on the air exchange between the storage space and the adjacent room, but also, on the air exchange between the adjacent room and the building. Unfortunately, this parameter could not be determined in the course of the experiments and can, therefore, not be quantified or properly discussed.

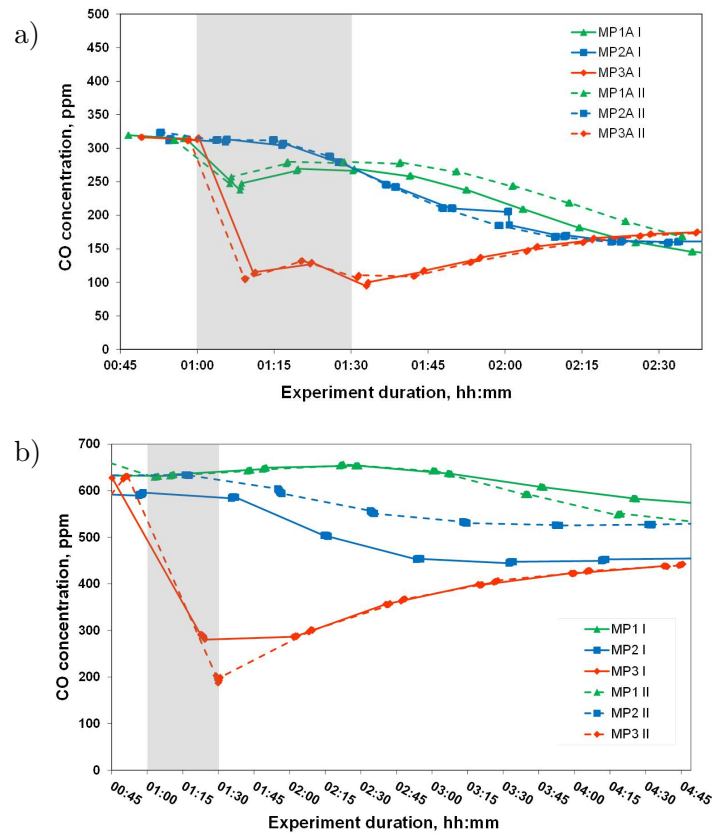


Figure IV.16.: CO levels in the "open hatch" experiments. The gray shaded areas represent the time the hatch was opened (continuous line - 1. run; dashed line - 2. run). a) Sheet steel tank, ≈ 300 ppm CO, 30 min of ventilation; b) Storage room, ≈ 600 ppm CO, 30 min of ventilation.

Table IV.11.: Results for the CO concentrations during the "open hatch" experiments.

Exp.#		CO concentration at MP3, ppm				
		Start	15 min vent.	30 min vent.	30 min closed	60 min closed
Sheet steel tank	300-15 I	330	100	-	120	140
	300-15 II	330	50	-	90	115
	600-15 I	600	130	-	200	225
	600-15 II	610	130	-	200	220
	300-30 I	315	-	110	145	170
	300-30 II	315	-	110	145	170
	600-30 I	600	-	50	105	130
	600-30 II	600	-	40	140	170
Stor. room	600-15 I	640	80	-	469	480
	600-15 II	630	70	-	470	490
	600-30 I	610	-	210	280	340
	600-30 II	610	-	190	295	340

4.4. Forced ventilation

Utilizing the very same experimental setups as described in section IV.4.3 the two storage systems, sheet steel tank and storage room, also served to test the effectiveness of two forced ventilation systems, a 12 watt ventilator and a 100 watt suction system (details see section IV.3.3.2). In Figure IV.17 the development of the CO concentrations throughout the storage systems is depicted. Although the chosen ventilation intervals for the experiments with forced ventilation are of a different length than in the "open hatch" experiments, some comparisons with the previous experiments can be made. The most significant difference between the "open hatch" and the forced ventilation is the simultaneous decrease of CO concentration measured for all three measurement points in the experiments with forced ventilation. Whilst in the "open hatch" experiments the CO levels at MP2 and MP3 stayed more or less close to the initial CO levels before ventilation, in the forced ventilation experiments the CO gas levels within the pellet bulk also seem to be lowered by the ventilation procedure. Furthermore, CO levels at MP3, above the pellet bulk, could be lowered to values below 100 ppm much faster when using the suction systems compared to the ventilator or the "open hatch" ventilation and also within a time frame of 15 minutes.

Applying the same criteria of effectiveness as defined in section IV.4.3 with 100 and 60 ppm CO, respectively, at the end of the ventilation interval, the appraisal of the tested forced ventilation systems is done according to the individual storage system. For the sheet steel tank both ventilation systems, the ventilator and the suction system, prove very effective and could manage to reach not only the first but also the second CO level criteria within the first 15, respectively, 30 minutes of ventilation. Thus, the implemented forced ventilation systems provide effective ventilation for the investigated storage system, sheet steel tank.

However, for the storage room the results from the experiment with the ventilator show, that the CO level of 100 ppm could not be reached within the first 30 minutes of ventilation while in the experiments with the suction system at least the first criterion could be reached within 30 minutes. Nonetheless, the implemented forced ventilation, although generating a larger air exchange rate than the natural ventilation, also needs to be improved upon in order to ensure sufficiently low CO levels prior to entering the storage room.

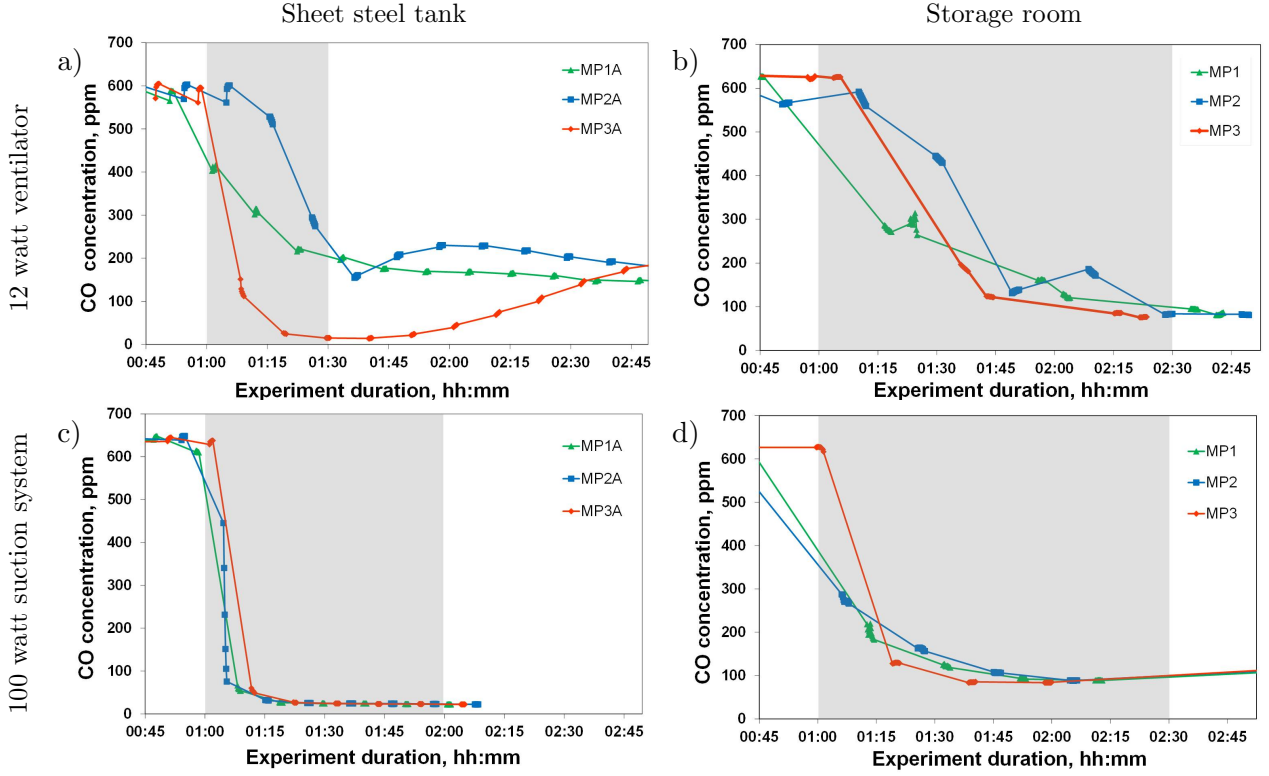


Figure IV.17.: Development of CO concentrations for the forced ventilation experiments. The gray shaded areas represent the times the ventilator was operating. a) Sheet steel tank, ≈ 600 ppm CO, 30 min 12 watt ventilation; b) Storage room, ≈ 600 ppm CO, 90 min 12 watt ventilation; c) Sheet steel tank, ≈ 600 ppm CO, 60 min 100 watt ventilation; d) Storage room, ≈ 600 ppm CO, 90 min 100 watt ventilation.

4.5. Calculation of a characteristic set of curves for ventilation of storages

In order to know how much air exchange is necessary to ventilate a pellet storage sufficiently to always stay below a specific threshold value of CO concentration one can apply some simple calculations under certain assumptions. Assuming that the CO off-gassing rate is known and constant and that the volume to be ventilated is also constant, the calculation of the specific air volume flows (SAVF) can be carried out according to the formulas given in the "Handbook on heating and air conditioning technology" [114] described in section IV.3.4.3. In Figure IV.18 a characteristic set of curves is shown, which can be used to determine the necessary specific air volume flow to constantly stay below the specific CO concentrations of 30 ppm and 100 ppm, respectively, dependent on first, the ratio of $V_{\text{solid}}:V_{\text{air}}$ and secondly, the CO off-gassing rate. All values for the calculated SAVFs are normalized to the volume of the entire storage ($V_{\text{solid}}+V_{\text{air}}$) and take the changing levels of V_{air} into account. The chosen values for the CO off-gassing rate, 1 and 3 $\text{mg/kg fuel}_{\text{atro}}$ in 24 hours, represent typical worst case off-gassing rates from freshly produced spruce and pine pellets, respectively (more details see section II.4.2.1).

The ratio $V_{\text{solid}}:V_{\text{air}}$ describes the proportional relationship between the gross volume of pellets within a pellet storage and the air volume within the same storage. V_{solid} should not be mistaken for the bulk volume V_{bulk} of pellets, which includes the gross volume and the air in between the individual pellets.

Similarly, V_{air} is the sum of the air volume surrounding the pellet bulk plus the air within the pellet bulk. A few examples for storages that represent a certain ratio of $V_{\text{solid}}:V_{\text{air}}$ are given in Table IV.12. The same examples have been used in the calculations to generate Figure IV.18.

Table IV.12.: Examples of storages with specific ratios for $V_{\text{solid}}:V_{\text{air}}$.

V_{pellets}	:	V_{air}	Filling level	Storage example
1	:	1	full	plastic tank
1	:	2	full	storage room
1	:	3	$\frac{3}{4}$ full	storage room
1	:	15	full	bag silo in a heating room

In Figure IV.18 the necessary SAVF dependent on the CO off-gassing rate for storages with a specific ratio of $V_{\text{solid}}:V_{\text{air}}$ to constantly stay below a specific CO concentration, in this case 30 or 100 ppm, can be derived. One obvious result is that the higher the off-gassing rate is the higher the necessary SAVF becomes to keep a certain CO level. Furthermore, the graphic illustrates that with an increasing ratio $V_{\text{solid}}:V_{\text{air}}$ the necessary SAVF to keep a certain CO level is rising fast. Whilst it is possible to maintain a CO level of 100 ppm in all 4 discussed storage examples at a SAVF of $0.215 \text{ } 1/h$ the SAVF needs to be raised to $0.716 \text{ } 1/h$ when the target CO level is lowered to 30 ppm (assuming a CO off-gassing rate of $1 \text{ } mg/kg \text{ } fuel_{\text{atro}}$).

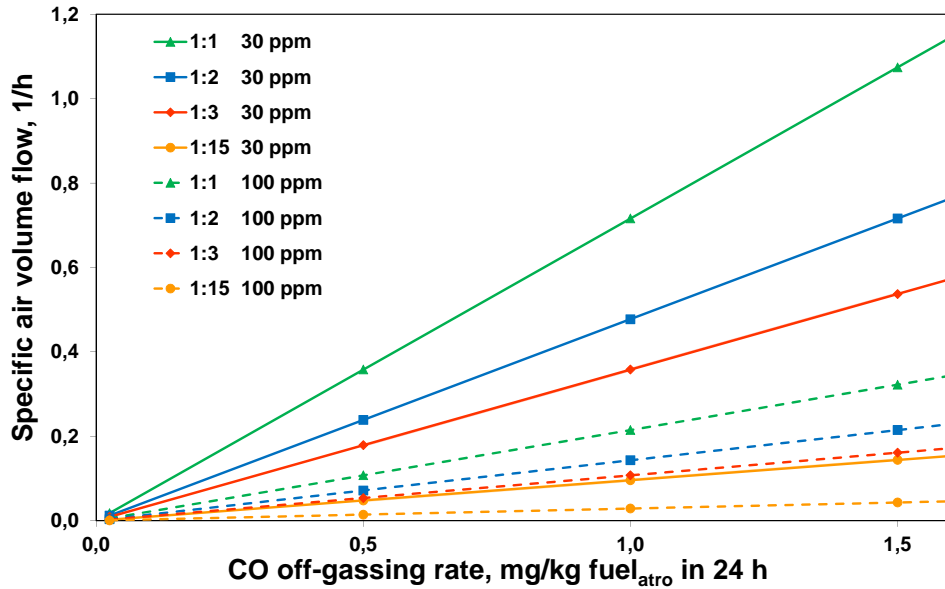


Figure IV.18.: Characteristic map to determine the necessary specific air volume flow to constantly stay below the specific CO concentrations of 30 ppm (continuous lines) and 100 ppm (dashed lines) dependent on the ratio of $V_{\text{solid}}:V_{\text{air}}$ and the CO off-gassing rate.

A similar approach can also be taken to calculate the development of CO concentrations within a pellet storage at a given specific air volume flow. This calculation proves very useful, when determining whether a certain air exchange is large enough to ventilate an already CO contaminated pellet storage, e.g. for a storage that is not permanently ventilated and in which a certain CO level has already been reached. In Figure IV.19 such calculations have been shown for the storage examples described earlier, assuming again two different CO off-gassing rates and six different SAVFs. Also, in each case a preexisting contamination of the storage with a CO level of 500 ppm has been assumed.

The presented examples illustrate, that if a storage room with a preexisting CO contamination needs to be ventilated quickly, very large SAVFs, of at least $2 \text{ }^1/h$, are necessary to properly ventilate a room in within 30 to 60 minutes of time to an acceptable level of CO concentration (below 100 ppm). The necessity of such high ventilation rates suggest the utilization of forced ventilation, whenever a storage room with a preexisting CO contamination needs to be entered.

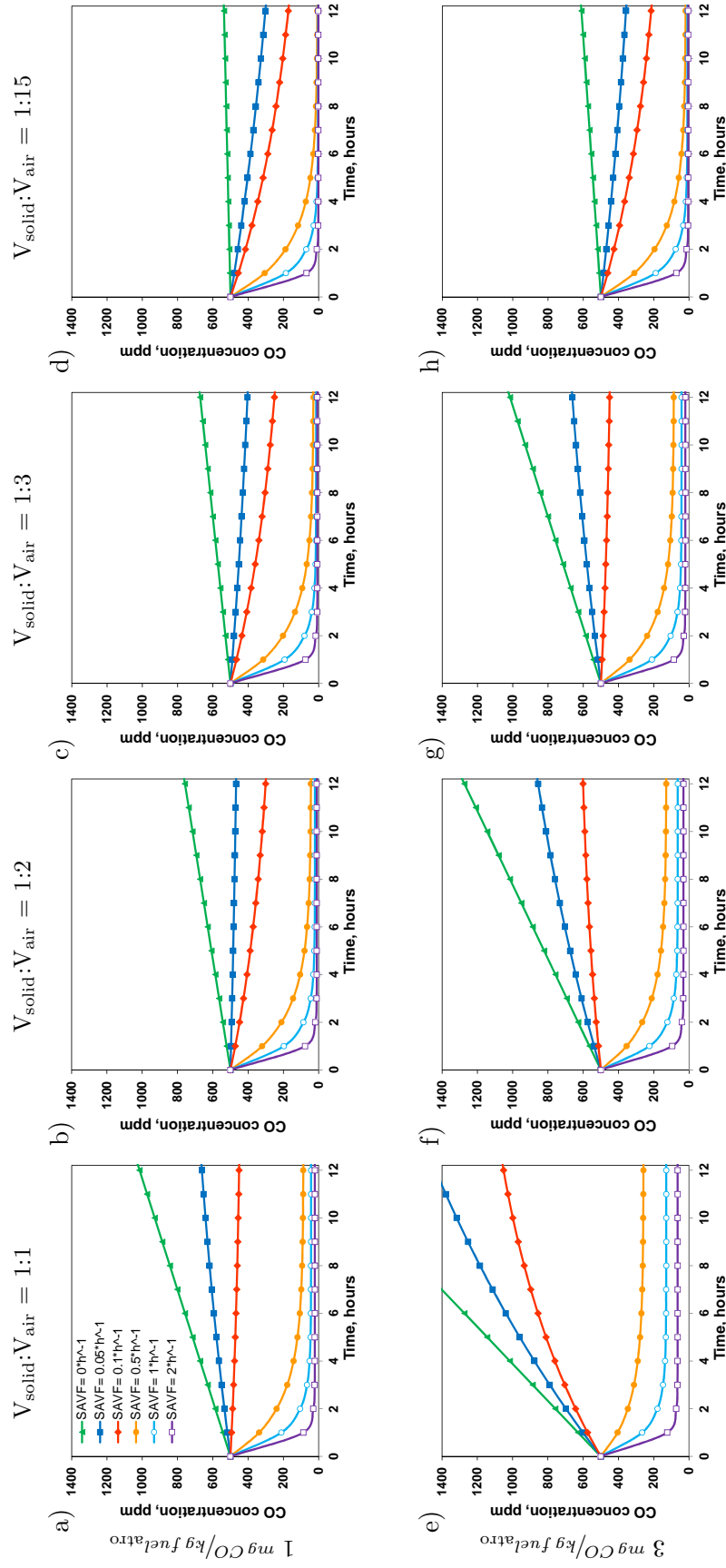


Figure IV.19.: Development of the CO concentration in ventilated storages dependent on the specific air volume flow, the ratio of $V_{\text{solid}}:V_{\text{air}}$ and the CO off-gassing rate. An initial CO concentration of 500 ppm before ventilation is started is assumed. a-d) CO off-gassing rate of $1 \text{ mg/kg fuel}_{\text{atro}}$ in 24 hours, e-h) CO off-gassing rate of $3 \text{ mg/kg fuel}_{\text{atro}}$ in 24 hours.

5. Conclusions

Natural ventilation - Determination of the impact of various influential parameters

In the course of the ventilation experiments it could be established that the ventilation of small-scale pellet storages utilizing natural ventilation solutions, such as ventilation caps, openings and chimneys, is a possible measure to enhance safety from CO emissions, but not one without limitations. Whilst under certain conditions the ventilation rates that could be achieved in the various experimental setups were relatively high, at other times, they were close to zero. Moreover, the actual value for the ventilation rate at a specific point in time can not be predicted with accuracy, making it difficult to know if the ventilation is effective at all times. Nonetheless, it was possible to determine the level of influence for certain parameters on the effectiveness of natural ventilation.

Temperature differences between the storage and surroundings are by far the most influential parameter on the ventilation rates for natural ventilation. Whenever the ΔT was close to zero, the ventilation rates were close to zero, too. However, even very small temperature differences lead to a slow but steady decrease of CO concentration within a storage and will in time alleviate the safety situation within the storage.

The introduction of a chimney to enhance air exchange rates proved only successful, when cross-ventilation was possible during the experiment. This leads to the conclusion that the installation of a chimney alone does not lead to an effective enhancement of air exchange rates and that the existence of cross-ventilation is the second most influential parameter on the effectiveness of natural ventilation equipment.

The size of the cross-sectional ventilation area proved to be an influential parameter of only minor importance. Whilst in general terms, the rule of thumb "bigger is better" holds true when the areas increase by a significant factor, in the experiments this could be observed when the size of the CSA was increased by a factor of > 10 , no such influence could be determined for areas that were of more similar size, e.g. different areas by a factor of 2. In those cases other influential parameters, such as the temperature difference between storage and surroundings, were superimposing on the influence of the cross-sectional area.

Despite the fact that natural ventilation is capable of providing sufficiently high air exchange rates for effective ventilation of a pellet storage, when implemented in a storage system without the additional presence of a CO detection system, its area of application should be confined only to small-scale pellet storages below a storage capacity of < 10 tons. Due to the possible high variance in the actual value for the ventilation rate at a specific point in time, ventilating larger storage spaces by means of unchecked natural ventilation would provide to great a risk for human safety.

"Open hatch" ventilation - Utility and limitations

"Open hatch" ventilation is also a means of natural ventilation and is recommended in guidelines and standards for wood pellet storages as an additional safety measure prior to the entering of a small-scale pellet storage. While the results from the "open hatch" ventilation experiments show that ventilating the storage using a service hatch can lead to significant reduction of CO concentration in the headspace of the two tested storages in a short time, only in 50 % of the experiments the targeted CO concentration of ≤ 100 ppm could be attained. Furthermore, the increase in the ventilation interval from 15 to 30 minutes did not lead to significantly better results. Therefore, it is concluded, that "open hatch" ventilation should only be considered as an additional safety measure and certainly not as only safety measure before entering a pellet storage. Furthermore, as with all other safety measures based on natural ventilation solutions, its area of application should be confined only to small-scale pellet storages below a storage capacity of < 10 tons. For storages with a larger storage volume either the implementation of a CO detection system or of a ventilation system based on forced ventilation is considered necessary.

Forced ventilation - Utility and limitations

Contrary to natural ventilation, forced ventilation, in the course of the experiments, has proven to also be capable of ventilating some of the CO gas from the pellet bulk and not only from the headspace of the pellet storage. This means that overall more of the accumulated CO can be transported out of the pellet storage in the same ventilation interval. However, the experiments have also shown, that implementing a forced ventilation solution does not necessarily guarantee a large enough reduction of the CO levels within the pellet storage to reach a certain "safe" CO concentration. Nonetheless, great care must be taken to install the equipment in such a way, that the highest possible degree of ventilation can be reached, e.g. by implementing cross-ventilation. Overall, forced ventilation has the big advantage, that the ventilation rate at a specific point in time is known and constant.

Determination of the minimum requirements of necessary specific air volume flow

A characteristic set of curves could be presented, which can be used to determine the minimum requirements of necessary specific air volume flow to constantly stay below a specified CO concentration within a pellet storage. The parameters taken into account include the ratio of $V_{\text{solid}}:V_{\text{air}}$, or rather the holding capacity of the pellet storage, and the CO off-gassing rate and provide a solid recommendation for the planning of ventilation systems for pellet storages.

Recommendations - An extension to existing guidelines for storages based on new knowledge

As already mentioned in the introduction to this chapter, standards and guidelines on safety issue related to hazardous gases in pellet storages already exist [14, 106, 107]. The work done in the course of this thesis has partly influenced the development of these guidelines and helped to promote the implementation of these documents. However, some aspects of ventilation of pellet storages, that had not been considered earlier, have been investigated only recently and based on these results some additions to the existing guidelines are suggested.

First of all, the recommendations given in "VDI 3464 Storage of wood pellets at the end user - Requirements on the storage room as well as on pellet production and delivery regarding health and safety aspects - DRAFT" [106] can be considered the most advanced and provide a sensible set of rules that ensure a high degree of safety within a pellet storage. Based on the aforementioned VDI guideline some

additional recommendations are suggested, which could be derived from the results presented in this thesis:

For storages with a capacity ≤ 10 tons

- Do not enter the pellet storage within the first four weeks after a pellet delivery.
- If you have to enter the pellet storage within this time frame, only enter after carrying out a CO measurement and making sure that CO levels are below 60 ppm.
- If the pellet storage is a silo storage system, always carrying out a CO measurement and make sure that CO levels are below 60 ppm, before entering.
- While staying in the pellet storage the wearing of a portable CO detection sensor, with an alert threshold at 60 ppm, on the body is recommended. Once the threshold signal is set off, the storage needs to be exited.
- During a stay in the pellet storage ventilation of the storage must be maintained.

For storages with a capacity > 10 tons

- Only enter the pellet storage after carrying out a CO measurement and making sure that CO levels are below 60 ppm.
- While staying in the pellet storage the wearing of a portable CO detection sensor, with an alert threshold at 60 ppm, on the body is recommended. Once the threshold signal is set off, the storage needs to be exited.
- During a stay in the pellet storage ventilation of the storage must be maintained.
- If the storage is ventilated by forced ventilation only, the function of the ventilation fan needs to be coupled with the door mechanism. This shall ensure the operation of the fan only when the door is open.

V. Executive Summary

Wood pellets are known to emit off-gasses during production, transportation and storage. Among the broad spectrum of individual gas components to be emitted from biomass CO emissions represent the greatest immediate risk to human health. During production and transportation emissions from wood pellets are primarily a work environment issue. However, when stored directly at the consumer (on-site) it becomes an issue that affects workers, at industrial plants, as well as private individuals such as home owner. As the likelihood of CO concentrations accumulating to high levels is particularly high during pellet storage, this very real threat has to be covered in some form of risk management. In order to implement proper safety guidelines and recommendations it is vital to understand which parameters are responsible and/ or influential in the release of off-gassing emissions and what is their impact. Furthermore, it is necessary to understand the requirements for technical solutions to effectively control emission levels in pellet storages and to understand possible limitations on the applicability of individual technologies.

Off-gassing phenomenon - Investigation of the mechanism and influential parameters

The investigations of the most influential parameters responsible for the level of off-gassing activity exhibited by an individual pellet sample revealed the parameters storage temperature to be the most influential followed at a distance by storage atmosphere and lastly by available headspace ratio. The removal of oxygen from the storage atmosphere is not sufficient to stop off-gassing emissions from being released. In fact, pellets have the ability to take up large quantities of oxygen, which might act as source for the oxygen emitted in the form of CO, CO₂ and oxygen containing VOCs during the storage experiments in N₂ atmosphere.

It could also be established, that there is a difference to the off-gassing activity to be noticed between pellets produced from different types of biomass. It was possible to determine that on average pine pellets are more reactive than larch pellets and spruce pellets, in that order. However, individual samples may very well exhibit much higher off-gassing activity than the average values typical for that specific wood species. In fact, the spread of values covers a broad range and seems to be dependent on other parameters than the wood species alone. For instance it could be shown that the history of the raw material (fresh or mature) and the actual pelletizing parameters contribute to the off-gassing activity exhibited by the final pellet product.

One major point - all investigated pellet samples had in common - was, that the most reactive off-gassing period was found to be within the first couple of weeks after production, with a significant loss of activity already after one week of storage and a much slower decrease in activity after a time span of weeks after storage. Not all freshly produced pellet samples exhibited a particularly high off-gassing activity in the first place, but for all samples the activity dropped over time.

To summarize, with all the parameters that influence off-gassing behavior - wood species, production parameters, age, storage time, storage temperature - each contributes to the specific off-gassing activity exhibited by the individual pellet sample. It is not a question if emissions will occur but only how much. The pellets chemical composition seems to represent a specific built in range for the off-gassing activity of a specific pellet sample. To what extent that range is exhibited in the final product, the pellet, depends on the formative processes and the environmental conditions the pellet experiences during production, transportation and storage.

Emission monitoring in small-scale pellet storages

A monitoring study investigating the CO development in 24 small-scale (< 20 t of capacity) pellet storages revealed the massive influence of design and construction of the pellet storage on the measured peak CO concentrations and the speed of decay of the CO levels within the pellet storages. Typically, the most dangerous period to enter a pellet storage, with respect to the dangers of CO intoxication, is within the first few weeks after pellet delivery. In all monitored pellet storages the peak CO concentration was recorded within the first week after pellet delivery, most often between 2-4 days after delivery. Subsequently, in all cases the CO levels started to drop. After a couple of weeks the CO off-gassing rate did eventually reach very low activity levels and the drop in activity did occur at a much lower pace. However, the actual height of the CO peak concentration as well as the speed of concentration decay varied significantly from one storage to the next. In general, good agreement could be noticed between the assessment of the tightness of the storages and the measured CO peak concentrations. Storages, which had been implemented with artificial leakages in the form of caps with ventilation openings, which were installed at the end of the filling pipes of the storages, on average, showed much lower peak CO concentrations than storages without additional ventilation.

The study also revealed that with the exception of one storage the STEL level of 60 ppm CO was exceeded within all monitored storages at least for a short period immediately after a filling operation of the storage. In 62.5 % of all cases the CO levels had not dropped to the STEL level within 7 days of the filling operation. The highest CO concentrations could be recorded in a prefabricated sheet steel pellet storage, which was extremely well sealed during build-up and has a very good ratio of useable volume to volume. The system can filled to almost 80 % of its volume, a regular storage room with a slanted floor utilizes around 65 % of its volume at a maximum.

The factors, which increase the risks of encountering high CO concentration within a pellet storage include:

- recent filling operation of the storage
- high tightness of the storage
- high useable volume of the storage

Although, there have been reported and documented cases of lethal accidents due to CO poisoning in pellet storages at end consumers very little has been done so far to inform the general public about the risk of CO off-gassing from pellets and possible safety measures to avoid them. Furthermore, efforts should be made to inform professionals such as boiler installers, chimney sweeps and firemen about the issues and appropriate

measures to act, when the consumers become aware of any signs of troubles with harmful emission levels within their pellet storages.

With increasingly better thermal insulation of houses the issue of tight pellet storages might become a more significant in the future. This could cause more pellet storages to become prone to the risks of high CO build-up and O₂ depletion. Implementing artificial leakages, e.g. by implementing ventilation openings in pellet storages, can counteract such unwanted implications and lower the risks of CO intoxication.

Ventilation of small-scale pellet storages

To overcome the risks associated with CO intoxication various ventilation solutions have been investigated, both natural and forced. For small-scale pellet storages the pellet industry favors natural ventilation solutions as they are typically cheaper to install and since they are usually low-tech, they have a lower probability of default and lower maintenance requirements. A big drawback of such systems is, that they are operating with fluctuating air exchange rates, due to their dependence on temperature fluctuations. While this is less a problem when only small volumes of air need to be exchanged, e.g. in pellet storages with small storage capacity, it becomes increasingly problematic with rising storage volumes. Due to this fact, natural ventilation in pellet storages with a capacity of more than 10 t should only be implemented in combination with some form of CO detection technology, which allows to determine CO concentration levels before entering the storage. A pellet storage should only be entered when the CO concentration is below 60 ppm (accepted STEL).

Forced ventilation solutions have the big advantage, that the necessary ventilation rate at a specific point in time can be controlled. Within a short interval large volumes of air can be exchanged and accumulated CO can effectively be transported out of the pellet storage. However, the experiments in this study have shown, that implementing a forced ventilation solution does not necessarily guarantee a large enough reduction of the CO levels within the pellet storage to reach a certain "safe" CO concentration. It is paramount, with any type of ventilation solution, that the equipment is installed properly. The goal is to achieve the highest possible degree of ventilation, which can only be guaranteed if a corresponding cross ventilation supplies fresh air.

"Open hatch" ventilation as a safety measure to lower CO concentrations prior to the entering of a small-scale pellet storage is on its own in many cases an insufficient solution. Without additional ventilation measures the air exchange rates, which can be achieved differ greatly dependent on the design and construction of the storage as well as the adjacent space. Therefore, it should only be considered as an additional safety measure and certainly not as only safety measure before entering a pellet storage. Furthermore, as with all other safety measures based on natural ventilation principles, its area of application should be confined to small-scale pellet storages below a storage capacity of < 10 tons.

To conclude a few words on the image of wood pellets drawn by wood pellet industry in the last two decades. Wood pellets have been presented as convenient and easy to handle fuel, which is an attractive renewable alternative to conventional heating sources such as oil and gas. Although all of this is true, pellet industry has failed to communicate the fact that wood pellets are a fuel. While it is obvious to the public that during handling of other types of fuel like gas, oil or coal certain risks need to be considered and safety requirements need to be fulfilled to ensure trouble-free operation, wood pellets, in the past, have

been viewed as non-dangerous. Some imagery even presented wood pellets as a plaything or as source of pleasant aromatic essential oils. This distorted and trivializing depiction of wood pellets must be stopped. Instead an image for wood pellets needs to be created, which promotes the positive qualities of this advanced renewable fuel with a healthy respect for the risks associated with its handling.

The work presented in this thesis has been influential during the development of guidelines and recommendation for safe handling and storage of wood pellets. The data presented provided useful information in the decision making process during the development of the ÖNORM M 7137 and of the VDI 3464 guidelines, both dealing with the requirements for pellet storage rooms.

VI. Outlook

This thesis dealt with the topic of off-gassing from wood pellets during storage from three distinct perspectives. New insights on the topics of in depth research on the the off-gassing phenomenon itself, as well as the related topics of emission build up in pellet storages and research on ventilation solutions to overcome the danger of accumulation of CO emission wihtin pellet storages were presented. However, the new data also lead to a series of new questions, which should be the topics of future work. In the following paragraphs the issues for further research are identified and summarizes according to the individual perspectives of the off-gassing research described in this thesis.

Off-gassing phenomenon

This work provides a large collection of data points of determinations of off-gassing activity for various types of wooden and agricultural biomass pellet and raw material samples. It could also provide rare data on the off-gassing behavior of pellets made from torrefied raw materials. However, all the data provided can only be regarded as first indications in the still largely unexplored field of off-gassing research. Some of the results gained in the course of this thesis have invariably led to further questions. As already indicated, the field of off-gassing from torrefied biomass is still largely unexplored. Studies on the long-term off-gassing behavior of torrefied biomass need to be conducted and data on torrefied agricultural biomass samples are missing to be equipped to assess the risks in storage and handling of these commodities. As the torrefaction process is a such largely not well defined, it would also be interesting to investigate in which way the thermal treatment might influence reactions which lead to off-gassing and/or self-heating of biomass pellets.

A great deal of clarification is also demanded on the impact of pelletizing parameters on the off-gassing behavior of the produced biomass pellets. The research in this work has demonstrated that there is great potential in increasing or decreasing the off-gassing activity of individual pellet samples due to small changes in the production parameters. A deeper investigation which factors are beneficial in the targeted production of pellets with low off-gassing activity could provide the most effective way in lowering the risks of off-gassing in general. Parameters that could be investigated are changes in the pelletizing press (e.g. lower or higher throughput, lower or higher residence time, etc.) or changes in the cooling process after production (e.g. fast cooling by temperature quenching right after production).

Finally, there are also more questions with respect to storage conditions of pellets and how they influence the off-gassing behavior of the pellets. In some pellet production plants it has become part of the regular safety procedure to store freshly produced biomass pellets in silos under permanent nitrogen atmosphere. Under these conditions the pellets will show limited off-gassing and self-heating behavior, however, what happens when that pellet is transferred out of the silo and is stored under ventilated storage conditions or regular atmospheric conditions is not yet clear. Usually a pellet will lose some of its off-gassing activity

over time, but as the pellet was only in limited contact with oxygen before, the off-gassing activity of a pellet with that storage history might be higher due to limited aging effects.

Emission monitoring

In the course of the monitoring experiments a data basis could be established to assess the risks of CO build-up to toxic levels in pellet storages. This data will serve in decision-making processes when safety guidelines and recommendations are discussed and approved. However, some questions need further investigation to be clarified. It is not clear, for example, how exactly the pellet delivery process is influencing the pellets off-gassing behavior. While there are strong indications, that the pellets off-gassing behavior is enhanced as a result of truck delivery a scientific study on this topic quantifying the effects of temperature and mechanical stress on the pellets could help to make pellet storages safer. Furthermore, the question whether it is actually beneficial to store the produced pellet for some time at the production site before delivery to lower off-gassing activity, or whether this measure is in fact not futile in reaching the anticipated result has not been answered yet.

Despite the fact that no evidence to the contrary was found in the course of this monitoring program, it has also not been established to which degree the mechanical durability of the pellets would be affected when stored in a continuously ventilated storage space. An experiment to investigate the long-term stability of the mechanical durability of wood pellets during long-term storage in ventilated storages could provide useful answers.

Ventilation of pellet storages

In the course of this thesis basic investigations on the effectiveness of ventilation solutions to enhance safety in pellet storages and to limit the risks from CO off-gassing from wood pellets have been carried out. However, it was also found, that there is need for further investigations as some of the results obtained in this work have led to new questions. Especially, possible influences on the values for air exchange rates from natural ventilation solutions from parameters, which were not included in the experiments described in this thesis need to be examined further and have been collected below:

- Influence of variations of length of filling pipes in the ventilation utilizing ventilated caps on the air exchange generated by these caps.
- Further studies to determine the best positioning of ventilation openings for natural and forced ventilation solutions (e.g. optimum distance between openings, positioning on top or bottom of the storage, etc.).
- Effectiveness of single opening natural ventilation solutions, possible influences of the larger cross-sectional areas and/or the maximum lengths of pipe on the air exchange rates generated.
- Further studies to investigate the influence of seasonal temperature changes and the influences of larger temperature differences between the inside of a pellet storage and the ambient temperatures outside the buildings on the values for air exchange rates.

Additionally, a need for further investigation in the topic of back-gassing of combustion gases from the combustion units into the associated pellet storages has been identified. Oftentimes, when incidents of CO poisoning in pellet storages are reported, it is not quite clear whether the source of the CO gas can be attributed solely to off-gassing or whether there has been an additional malfunction in the boiler system

leading to an accumulation of CO gas from incomplete combustion processes within the storage. While there exists a European standard on the requirements for heating boiler (ÖNORM EN 303-5) [117], which defines safety criteria to prohibit back-burning for automatically stoked boilers, a certain leakage of combustion gases back into the fuel line is admissible in accordance with the standards requirements. As long as the CO concentration in the fuel line never exceeds 1 vol% of CO_{atmo} caused by any operational status or failure of the system, the safety measures implemented in the boiler will not be activated. While in the standard it is mentioned that safety requirements regarding harmful gas concentrations need to be considered, it also states that since they depend strongly on the place of the installation and the fuel storage discharge system the fall outside of the scope of this standard. So far, no investigations have been carried out to determine how often and under which circumstances malfunctions leading to back-gassing of combustion gases into the fuel storage are likely to occur and what measures can be taken in order to avoid this phenomenon. Furthermore, it is unclear if boiler systems predating the most recent version of the ÖNORM EN 303-5 can fulfill the safety requirements stated therein or whether they might be more susceptible to operational failures and possible connected back-gassing incidents. Finally, a closer look into different fuel storage discharge systems and an assessment of their possible vulnerability to back-gassing should also be taken.

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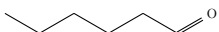
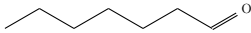
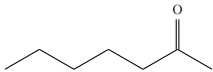
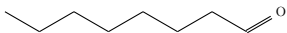
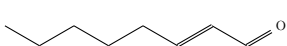
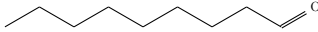

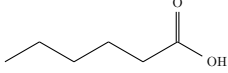
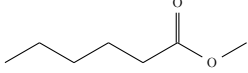
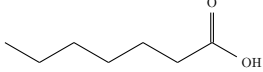
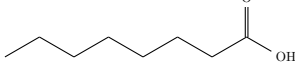
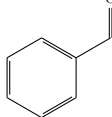
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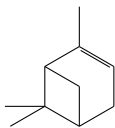
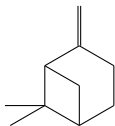
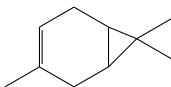
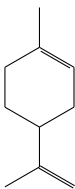
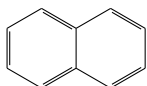
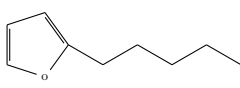
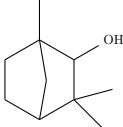
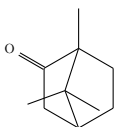
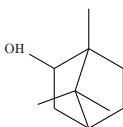
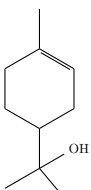
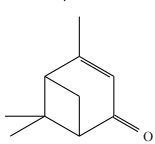
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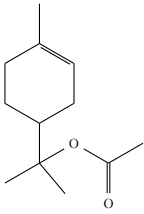
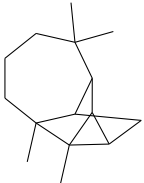
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Appendix A. List of volatile organic compounds detected via SPME-HS-GS-MS

Table A.1.: List of extractive components detected via an extractive method using a GC/FID system for identification and quantification.

Chemical structure	Name	Molecular formular
	pentanal	C ₅ H ₁₀ O
	hexanal	C ₆ H ₁₂ O
	heptanal	C ₇ H ₁₄ O
	2-heptenal	C ₇ H ₁₄ O
	octanal	C ₈ H ₁₆ O
	octenal	C ₈ H ₁₄ O
	nonanal	C ₉ H ₁₈ O
	decanal	C ₁₀ H ₂₀ O
	caproic acid	C ₆ H ₁₂ O ₂
	caproic acid methyl ester	C ₇ H ₁₄ O ₂
	heptanoic acid	C ₇ H ₁₄ O ₂
	caprylic acid	C ₈ H ₁₆ O ₂
	benzaldehyde	C ₇ H ₆ O
Continued		

Chemical structure	Name	Molecular formular
	α -pinene	$C_{10}H_{16}$
	2- β -pinene	$C_{10}H_{16}$
	Δ -3-carene	$C_{10}H_{16}$
	d-limonene	$C_{10}H_{16}$
	naphthalene	$C_{10}H_8$
	2-pentylfuran	$C_9H_{14}O$
	fenchol	$C_{10}H_{18}O$
	camphor	$C_{10}H_{16}O$
	borneol	$C_{10}H_{18}O$
	α -terpineol	$C_{10}H_{18}O$
	l-verbonene	$C_{10}H_{14}O$
Continued		

Chemical structure	Name	Molecular formular
	α -terpineol acetate	C ₁₂ H ₂₀ O ₂
	longicyclene	C ₁₅ H ₂₄

Appendix B. Development of VOC components dependent on time, wood species and storage temperature

Appendix C. Discussion of errors for ventilation rates

For the calculation of drop rates, all data points within a single measurement interval (4 minutes) have been averaged, since on this timescale random fluctuations typically dominate the drop characteristic. The standard error of this mean value contributes to the total error, in addition to the device error, which is given as

$$\Delta C_{dev} = \begin{cases} 10 \text{ ppm} & \text{if } C < 100 \text{ ppm}, \\ 0.1 \cdot C & \text{if } 100 \text{ ppm} \leq C < 200 \text{ ppm}, \\ 20 \text{ ppm} & \text{if } 200 \text{ ppm} \leq C < 400 \text{ ppm}, \\ 0.05 \cdot C & \text{if } 400 \text{ ppm} \leq C < 2000 \text{ ppm}. \end{cases} \quad (\text{C.1})$$

The standard formalism for error propagation, applied to (IV.10) yields

$$\Delta \alpha_i = \frac{1}{\Delta t} \left(\frac{\Delta C_i(t - \Delta t)}{C_i(t - \Delta t)} + \frac{\Delta C_i(t)}{C_i(t)} \right). \quad (\text{C.2})$$

This expression tends to significantly overestimate the error, since it does not take into account the correlation between the measurement errors at different time steps. Since the exchange rate is calculated from a ratio of concentration values, systematic relative errors do not affect the result. [If, for examples, concentrations are systematically 5 % to high, this cancels out in the calculation of air exchange rates.]

In order to account for this, we have split the device error into a systematic relative and a remaining absolute error,

$$C_{measured} = (1 \pm r_{dev,syst}) C_{real} \pm \Delta C_{abs}. \quad (\text{C.3})$$

We have assumed that the systematic relative error $r_{dev,syst}$ varies only slowly and can thus be neglected for the calculation of ventilation rates from the ratio of subsequent (averaged) concentration values. From measurement data, we have estimated the remaining absolute error to be $\Delta C_{abs} \leq 5 \text{ ppm}$.

This is the maximum range of fluctuations when the concentration has dropped to almost zero. These errors are compatible with the position of other data points and in most cases with estimates of linear regression.

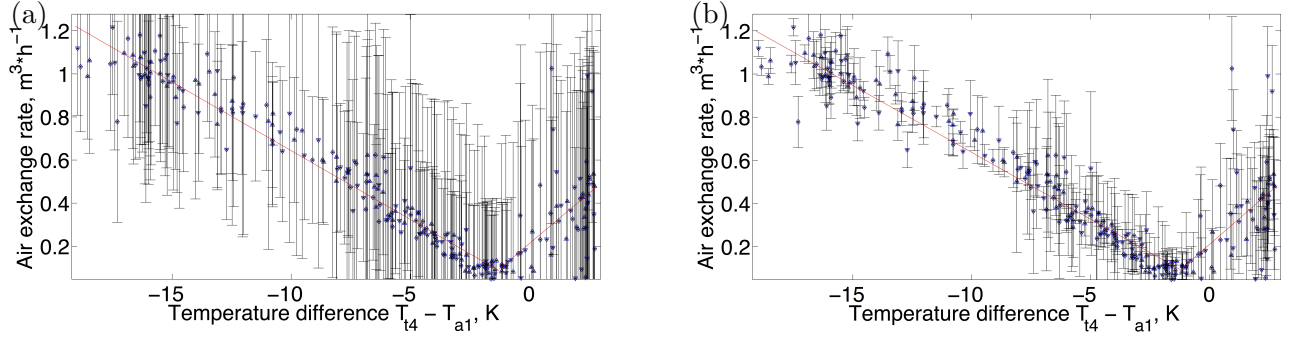


Figure C.1.: Characteristic correlation plots, including piecewise linear regression and error bars, for setup cooled/closed:

(a) plot employing the conservative error estimate (C.1), (b) plot with replacement $\Delta C_{dev} \rightarrow \Delta C_{abs} = 5$ ppm (same as in figure IV.14.b).

Therefore we have replaced the device error ΔC_{dev} by the estimate $\Delta C_{abs} = 5$ ppm. A comparison of error bar plots for the conservative and the refined error estimate is given in figure C.1.

Appendix D. A closer view on the correlation plots

Using the 8 significant temperatures listed in table IV.1 this leads to 28 independent temperature differences, corresponding to the $\frac{8 \cdot (8-1)}{2}$ independent entries of an antisymmetric $[8 \times 8]$ -matrix and thus to 28 different correlation plots, as depicted in figure D.1 for the setup `cooled/closed`. As already stated in section 3.4.2, there is either no or no simple dependency of the air exchange rate on most of these temperature differences. Those plots which exhibit a characteristic dependence are quite similar to each other.

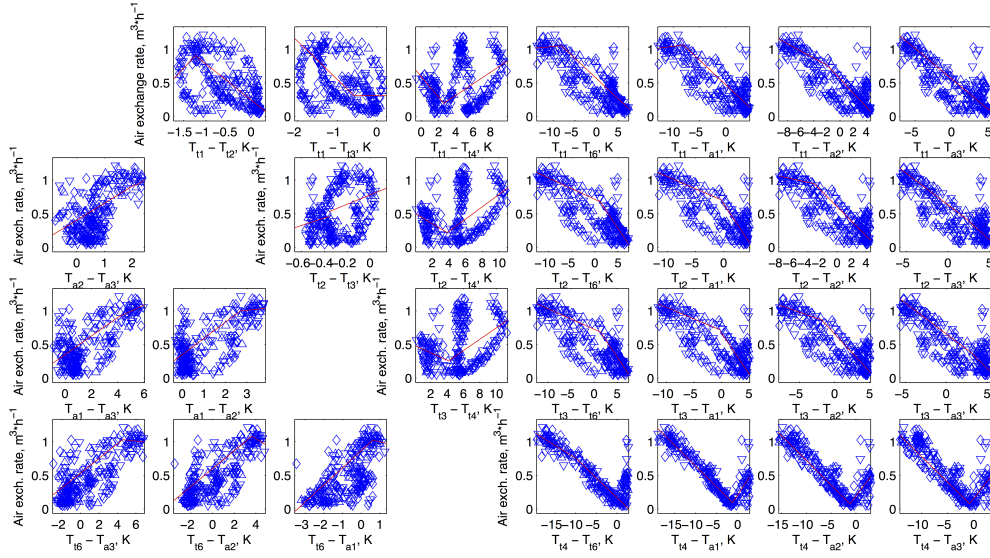


Figure D.1.: Correlation plots for setup `cooled/closed`. In all 28 cases we plot the ventilation rate \dot{V} vs. the specific temperature difference $\Delta T = T_{\text{in}} - T_{\text{out}}$.

Appendix E. Implementation and assessment of piecewise linear regression

There is no universal definition of the “best” piecewise linear regression for a given data set. In the present case, we have limited ourselves to a maximum of two regions with linear regression, separated by a threshold temperature difference ΔT_0 .

As candidates for the threshold ΔT_0 we have tested separately for each experiment and each possible definition of $\Delta T = T_{\text{in}} - T_{\text{out}}$ all values

$$\Delta T_0^{(\ell)} = \Delta T_{\text{min}} + \ell \cdot 0.1 \text{ K} \quad (\text{E.1})$$

with $\ell \in \{1, 2, 3, \dots\}$ and $\Delta T_0^{(\ell)} < \Delta T_{\text{max}}$. For each of these threshold values we have performed, if possible, a piecewise linear regression

$$\dot{V} = R = \begin{cases} -k_-^{(\ell)} \Delta T + d_-^{(\ell)} & \text{for } \Delta T < \Delta T_0^{(\ell)}, \\ k_+^{(\ell)} \Delta T + d_+^{(\ell)} & \text{for } \Delta T > \Delta T_0^{(\ell)} \end{cases} \quad (\text{E.2})$$

The quality of the regression has been assessed with a dimensionless cost function which is calculated from the quantities summarized in table E.1.

Table E.1.: Quantities employed in assessment of the piecewise linear regression

symbol	unit	quantity
ΔT_{min}	K	minimum value of $\Delta T = T_{in} - T_{out}$
ΔT_{max}	K	maximum value of ΔT
$\Delta T_0^{(\ell)}$	K	current threshold for ΔT
ΔT_i	K	temperature difference for data point i
R_i	m ³ /h	air exchange rate for data point i
σ_i	m ³ /h	estimated uncertainty of R_i
R_{min}	m ³ /h	minimum air exchange rate
R_{max}	m ³ /h	maximum air exchange rate
$N_-^{(\ell)}$	-	number of data points in $\left[\Delta T_{min}, \Delta T_0^{(\ell)} \right)$
$N_+^{(\ell)}$	-	number of data points in $\left(\Delta T_0^{(\ell)}, \Delta T_{max} \right]$
$\varepsilon(X)$	var.	error of fit parameter X

This cost function $\Delta^{(\ell)}$ is the sum of five terms which measure the quality of the fit or judge the plausibility of the parameters when taking into account the physical interpretation mentioned in section 3.4.2:

- Quality of the linear regression, determined by error estimates of regression parameters,

$$\Delta_1^{(\ell)} = \frac{\varepsilon(k_-^{(\ell)}) (\Delta T_0^{(\ell)} - \Delta T_{min}) + \varepsilon(d_-^{(\ell)})}{R_{max} - R_{min}} + \frac{\varepsilon(k_+^{(\ell)}) (\Delta T_{max} - \Delta T_0^{(\ell)}) + \varepsilon(d_+^{(\ell)})}{R_{max} - R_{min}}. \quad (E.3)$$

- Discontinuity at transition point,

$$\Delta_2^{(\ell)} = \frac{|k_+^{(\ell)} \Delta T_0^{(\ell)} + d_+^{(\ell)} - (-k_-^{(\ell)} \Delta T_0^{(\ell)} + d_-^{(\ell)})|}{R_{max} - R_{min}}. \quad (E.4)$$

The transition rate is expected to be a continuous function of ΔT , with a minimum given by purely diffusive transport. When working with experimental data, this equation can be expected to be fulfilled only approximately, but still a difference between the predicted values at the transition point is punished in the cost function.

- Weighted deviation between fit prediction and data,

$$\begin{aligned}
\Delta_3^{(\ell)} &= \sqrt{\frac{1}{N_-^{(\ell)}} \sum_{\Delta T_i < \Delta T_0^{(\ell)}}^{N_-^{(\ell)}} \frac{\left(R_i - \left(-k_-^{(\ell)} \Delta T_i + d_-^{(\ell)}\right)\right)^2}{\sigma_i^2}} \\
&+ \sqrt{\frac{1}{N_+^{(\ell)}} \sum_{\Delta T_i > \Delta T_0^{(\ell)}}^{N_+^{(\ell)}} \frac{\left(R_i - \left(k_+^{(\ell)} \Delta T_i + d_+^{(\ell)}\right)\right)^2}{\sigma_i^2}}
\end{aligned} \tag{E.5}$$

- positivity criterion for axis intercept,

$$\begin{aligned}
\Delta_4^{(\ell)} &= -\min \left\{ 0, k_+^{(\ell)} \Delta T_0^{(\ell)} + d_+^{(\ell)} \right\} \\
&\quad - \min \left\{ 0, -k_-^{(\ell)} \Delta T_0^{(\ell)} + d_-^{(\ell)} \right\}
\end{aligned} \tag{E.6}$$

- deviation of threshold from zero,

$$\Delta_5^{(\ell)} = \frac{|\Delta T_0^{(\ell)}|}{T_{\max} - T_{\min}}. \tag{E.7}$$

The total cost function

$$\Delta^{(\ell)} := \Delta_1^{(\ell)} + \Delta_2^{(\ell)} + \Delta_3^{(\ell)} + \Delta_4^{(\ell)} + \Delta_5^{(\ell)} \tag{E.8}$$

is minimized with respect to the choice of ℓ , which yields ℓ_{best} . This determines $\Delta T_0 := \Delta T_0^{(\ell_{\text{best}})}$, which separates the two regions for separate linear regression. If $\Delta T_0 \approx \Delta T_{\min}$ or $\Delta T_0 \approx \Delta T_{\max}$, only one linear fit has been performed.

Among all possible definitions of ΔT the most significant plot has been chosen (in some cases manually, in some cases based on an automated choice) as a representative of the situation. Significance has been judged by:

- a sufficiently large range of ΔT ,
- the quality of the regression, i.e. a small value of the cost function $\Delta^{(\ell)}$ for the optimized value of ℓ ,
- a strong dependence of the exchange rate on ΔT .

In most cases it is easy to judge whether a correlation plot can be considered as significant, and for each experiments the significant plots are rather similar.

Curriculum vitae

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2000-05	Matriculation examination (A-levels)
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1988 - 1992	Elementary school Volksschule Pergkirchen, Austria

Professional experience

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