TECHNISCHE
UNIVERSITÄT
WIEN
Vienna | Austria

**Dissertation**

# How to reduce and cope with off-gassing of wood pellets during storage

carried out for the purpose of obtaining the degree of Doctor technicae (Dr. techn.)

submitted at the TU Wien, Faculty of Mechanical and Industrial Engineering

by

**Dipl.-Ing. Irene Sedlmayer M.Sc.**

Mat. Nr.: 00506044

under the supervision of

Univ. Prof. Dipl.-Ing. Dr. Hermann Hofbauer

Institute of Chemical, Environmental and Bioscience Engineering (E166)

and co-supervision of

Dipl.-Ing Dr. Elisabeth Wopienka

BEST - Bioenergy and Sustainable Technologies GmbH

Vienna, February 2023

Reviewed by

Univ.Prof. Dipl.-Ing. Dr.techn.
Christoph Pfeifer
BOKU - University of Natural Resources and
Life Sciences, Vienna
Institute of Chemical and Energy
Engineering
Muthgasse 107/I
1190 Vienna

Prof. Dr.-Ing. Martin Faulstich
TU Dortmund - Technical University of
Dortmund
Resource and Energy Systems

August - Schmidt - Str. 10
44227 Dortmund

# Affidavit

I, Irene Sedlmayer, declare in lieu of oath, that I wrote this thesis and performed the associated research myself, using only literature cited in this volume. If text passages from sources are used literally, they are marked as such.

I confirm that this work is original and has not been submitted elsewhere for any examination, nor is it currently under consideration for a thesis elsewhere.

I acknowledge that the submitted work will be checked electronically-technically using suitable and state-of-the-art means (plagiarism detection software). On the one hand, this ensures that the submitted work was prepared according to the high-quality standards within the applicable rules to ensure good scientific practice "Code of Conduct" at the TU Wien. On the other hand, a comparison with other student theses avoids violations of my personal copyright.

[redacted]

*City and Date*

[redacted]

*Signature*

# Kurzfassung

Holzpellets emittieren bei der Herstellung, dem Transport und bei der Lagerung Gase wie Kohlenstoffmonoxid (CO), Kohlenstoffdioxid ($CO_2$) und flüchtige organische Verbindungen (VOCs). Die gleichzeitige Abnahme des Sauerstoffgehaltes in der Luft führt zu einer toxischen Atmosphäre. Diese Arbeit befasst sich i) mit den Ausgasungsemissionen von gelagerten Pellets und deren Einflussfaktoren, ii) mit Maßnahmen zur Verringerung der Ausgasungsemissionen durch Modifizierung der Holzpelletsproduktion und iii) mit der Lagerung von Holzpellets und deren Belüftung.

Die bei der Lagerung von Holzpellets entstehenden Emissionen werden durch Oxidationsprozesse von holzeigenen Extraktstoffen initiiert. Die einzelnen Mechanismen und die Herkunft sämtlicher CO Emissionen sind nicht eindeutig geklärt. Zu Beginn dieser Arbeit wurden der Extraktstoffgehalt von Holzpellets und Rohstoffen sowie deren Ausgasungsverhalten gegenübergestellt. Der Pelletierprozess reduzierte den Extraktstoffgehalt, jedoch wurden höhere CO Emissionen bei den Pellets im Vergleich zu den Rohstoffen festgestellt. Zudem korrelierte das Ausgasungsverhalten von Holzpellets nicht mit dem zunehmenden Extraktstoffgehalt. Für die bei der Lagerung von Holzpellets auftretenden Gerüche sind VOCs verantwortlich. Geruchsaktive Holzpellets wiesen, im Vergleich zu unauffällig wahrgenommenen Holzpellets, keine höheren CO oder VOC Emissionen auf. Sowohl für die Ausgasung als auch für die Selbsterhitzung sind Oxidationsprozesse von Extraktstoffen die Ursache. Die simultane Untersuchung des Ausgasungs- und Selbsterhitzungsverhaltens zeigte, dass Pellets mit höherer Ausgasungstendenz auch als Pellets mit höherer Selbsterhitzungstendenz bewertet wurden. Untersuchungen zur Sauerstoffverfügbarkeit belegten einen deutlichen Anstieg der Emissionsbildung mit zunehmender Verfügbarkeit von $O_2$. Dies bekräftigt die Annahme, dass oxidative Prozesse für die Emissionsbildung verantwortlich sind. Zusätzlich wurden Pellets aus Biomasse wie Stroh oder Weinrebschnitte untersucht. Alle analysierten Biomassepellets emittierten CO, $CO_2$ und VOCs. Die sensorische Bewertung von Biomassepellets reichte von angenehm (krautig, süß) bis unangenehm (stechend, ranzig). Die wahrgenommenen Gerüche entsprachen den eingesetzten Rohstoffen. Das Geruchsspektrum ist auf die große Anzahl der gebildeten VOCs zurückzuführen. Wie bei Holzpellets, wurde bei allen untersuchten Biomassepellets Hexanal nachgewiesen. Hexanal ist ein bekanntes Abbauprodukt von Lipiden und lässt vermuten, dass auch bei der Lagerung dieser Biomassepellets, ähnlich der Lagerung von Holzpellets, oxidative Prozesse, stattfinden.

Maßnahmen in der Pelletsproduktion und deren Auswirkung auf das Ausgasungsverhalten von Holzpellets wurden untersucht. Dabei wurde der Fokus auf antioxidativ wirkende Substanzen gelegt. Natürliche und synthetische (antioxidative) Additive bewirkten eine signifikante Reduzierung von CO

Emissionen. Als weitere Maßnahme in der Pelletsproduktion wurde das Mischen von Rohstoffen zur Verringerung der CO Emissionen identifiziert. Sowohl die Beimischung von Seekieferrinde als auch von Eichensägemehl minimierten die CO Emissionen nachweislich. Die durch die Zugabe von Additiven und die Beimischung von Rohstoffen erzielte CO Reduktion beruht auf der antioxidativen Wirkung der Inhaltsstoffe. Als weitere Maßnahme zur CO Minderung wurde das Ende des Pelletierprozesses, der Kühlprozess, untersucht. Sowohl die Belüftungszeit als auch die Belüftungstechnik beeinflussten die CO Emissionen. Der Eingriff in den Kühlprozess führte jedoch zu einer geringeren Reduktion der Emissionen als der Einsatz von Additiven oder die Mischung von Rohstoffen.

CO ist bei der Lagerung von Holzpellets aufgrund seiner Toxizität und seiner geruchlosen Eigenschaft die bedeutendste Emission bei der Lagerung von Holzpellets. Die Einlagerung mehrerer Tonnen Holzpellets können zu hohen CO Konzentrationen führen, daher wurden reale Pelletslager bei Endverbrauchern gemonitort. Um den Einfluss der Belüftung auf die CO Abnahme in Pelletslagern zu beurteilen, wurden zusätzliche Lüftungsversuche durchgeführt. Die gleichzeitige Bestimmung der CO Emissionsraten der eingelagerten Holzpellets zeigte, dass zu Beginn der Holzpelletslagerung ein höherer Anstieg an CO Emissionen zu erwarten ist. Weitere Untersuchungen identifizierten die Querlüftung in Holzpelletslagern als geeignete Maßnahme zur CO Konzentrationsminderung. Die CO Reduktion wird durch eine zunehmende Querschnittsfläche der Belüftungsöffnungen begünstigt. Ein weiterer positiver Einfluss auf die CO Reduktion in Pelletslagern ist ein auftretender Temperaturunterschied zwischen dem Innen- und Außenbereich des Pelletslagers. Ein sorgsamer Umgang wird auch bei belüfteten Holzpelletslagern empfohlen.

# Abstract

Wood pellets emit gases like carbon monoxide (CO), carbon dioxide ($CO_2$) and volatile organic compounds (VOCs) during production, transportation and storage. Simultaneously, the atmospheric oxygen is depleted, leading to a toxic atmosphere for human health. This thesis deals i) with off-gassing emissions from stored pellets and their influencing factors, ii) with measures for reducing off-gassing emissions in wood pellets production and iii) with wood pellets storage facilities and their ventilation.

It is known, that formed emissions during the storage of wood pellets are caused by oxidation processes of wood extractives. The exact mechanisms and from where all the CO emissions originate is still unclear. The relation between the total extractive content and off-gassing emissions of raw materials and pellets was investigated. The total extractive content is not the decisive factor determining the formation of CO, $CO_2$ and VOC emissions. Although the pelletising process reduced the extractive content, the CO formation was increased at the same time. Furthermore, the formed off-gassing emissions of wood pellets did not correlate with increasing extractive content. A possible malodour can occur during storage of wood pellets. Again, the assumption is that degradation products of extractives are responsible for the formed VOCs and the resulting malodour. Wood pellets with a noticeable malodour do not necessarily have higher CO or VOC emissions than pellets perceived as pleasant. For both off-gassing and self-heating, the degradation of extractives is decisive. The application of different off-gassing and self-heating methods indicated that pellets with higher off-gassing reactivity were also evaluated as pellets with higher self-heating tendency. The investigation of the headspace ratio and the available oxygen ($O_2$) revealed a considerable increase in the formation of emissions with increasing availability of $O_2$. In addition to wood pellets, pellets from another biomass, likewise straw and grapevine, were investigated regarding their off-gassing behaviour. Results indicated the formation of CO, $CO_2$ and VOCs. The sensory evaluation of biomass pellets showed differently perceived odours ranging from pleasant (herbage, sweet) to unpleasant (pungent, rancid). As assumed, the odours correspond to the used raw materials. The odour spectrum is due to the large number of formed VOCs. As usual for wood pellets, hexanal was formed in all analysed biomass pellets batches. Hexanal is a known degradation product of lipids assuming that similar processes as in the storage of wood pellets, oxidative degradation process, also take place in the storage of other biomass pellets.

Within the framework of the thesis, the production process of wood pellets was modified. It becomes apparent that the usage of various antioxidative additives are useful measures to reduce CO emissions. In addition, the blending of raw material also proves to be a suitable measure for reducing

CO emissions. For instance, the blendings of maritime pine bark or oak sawdust without bark reduce CO emissions considerably. As a further measure for CO reduction, the end of the pelletising process and the cooling process are investigated. Both, the ventilation time and the ventilation technology demonstrated an influence on the formation of CO emissions. However, the ventilation measures indicate less effect than the usage of additives or the blending of raw materials.

Fact is, wood pellets form emissions during storage. CO is most relevant due to the toxicity of CO, its odourless property and the potential for formation. Even if the formation of CO can be reduced through suitable measures, several tonnes of wood pellets are nevertheless stored directly at the end user storage facility leading to possible high CO concentrations. In order to gain knowledge, real wood pellets storages are monitored at the end users. In addition, ventilation trials are carried out to estimate their influence on CO reduction. The simultaneous monitoring of wood pellets storages and the determination of CO emission rates of the wood pellets stored there, indicate that higher CO maxima are to be expected at the beginning of the storage. Moreover, cross ventilation is a suitable measure for CO reduction in wood pellets storage facilities. CO reduction is accelerated with increasing cross-sectional area of the ventilation openings. Another positive influence on CO reduction in wood pellets storages is an occurring temperature difference between the inside and outside of pellets storage facilities. Nevertheless, care should be taken when handling stored wood pellets.

# Acknowledgements

First of all, I want to acknowledge the Office of the Federal Government of Lower Austria, Department for Economy, Tourism and Technology for the financial support for the thesis (PellStore project AtheNoe No. 219).

The presented work was carried out in various research projects at BEST - Bioenergy and Sustainable Technologies GmbH. The research leading to these results received funding from

- the COMET program managed by the Austrian Research Promotion Agency
- the European Union Seventh Framework Programme (FP7/2007-2013)
- the Austrian Research Promotion Agency (Collective Research - Basisprogramm)

I would like to thank my supervisor Hermann Hofbauer for his pleasant guidance and assistance during the works for my thesis. I sincerely thank him for his extremely motivating words and support.

Many thanks go to Walter Haslinger, CEO at BEST - Bioenergy and Sustainable Technologies GmbH, who gave me the opportunity to do this thesis in the frame of my employment in the company.

My special thanks go to Elisabeth Wopienka from BEST who gave her support in many different fields of the work and encouraged me to seize the opportunity for doing a Dissertation. Thank you for the advice for the methodology, the thorough discussions about the results and the professional input for the publications.

Furthermore, I would like to express my special gratitude to all my colleagues from BEST for the pleasant working environment and the generous help whenever I asked for it. I'd especially like to mention Waltraud Bauer and Franziska Klauser for their support in the technical lab, Rita Sturmlechner for her inputs at data evaluation and Christoph Schmidl for his advice during publishing.

I would also like to thank Barbara Pöllinger-Zierler. She has accompanied me for years on the subject of off-gassing and has always had a sympathetic ear for me.

Appreciation is also extended to my parents Herbert and Ingrid Schmutzer-Roseneder for enabling me an academic education and for always believing in me.

Big thanks go to my babysitters, especially my mother and mother-in-law, who looked after my two children during my works for the thesis.

My greatest gratitude goes to my husband Jürgen who supported me in keeping it up. He is my motivator, resting place and optimist. Thanks for your encouragement.

# Table of contents

# List of peer-reviewed journal papers

The work presented in this thesis is based on five published peer-reviewed journal papers.

**Paper 1** Sedlmayer I, Arshadi M, Haslinger W, Hofbauer H, Larsson I, Lönnermark A, Nilsson C, Pollex A, Schmidl C, Stelte W, Wopienka E, Bauer-Emhofer W. Determination of off-gassing and self-heating potential of wood pellets - Method comparison and correlation analysis. Fuel. 2018;234:894–903.

**Paper 2** Meier F, Sedlmayer I, Emhofer W, Wopienka E, Schmidl C, Haslinger W, Hofbauer H. Influence of Oxygen Availability on off-Gassing Rates of Emissions from Stored Wood Pellets. Energy & Fuels. 2016;30:1006–1012.

**Paper 3** Pöllinger-Zierler B, Sedlmayer I, Reinisch C, Hofbauer H, Schmidl C, Kolb L, Wopienka E, Leitner E, Siegmund B. Interrelation of Volatile Organic Compounds and Sensory Properties of Alternative and Torrefied Wood Pellets. Energy & Fuels. 2019;33:5270–5281.

**Paper 4** Sedlmayer I, Bauer-Emhofer W, Haslinger W, Hofbauer H, Schmidl C, Wopienka E. Off-gassing reduction of stored wood pellets by adding acetylsalicylic acid. Fuel Processing Technology. 2020;198:106218.

**Paper 5** Emhofer E, Lichtenegger K, Haslinger W, Hofbauer H, Schmutzer-Roseneder I, Aigenbauer S, Lienhard M. Ventilation of Carbon Monoxide from a Biomass Pellet Storage Tank – A Study of the Effects of Variation of Temperature and Cross-ventilation on the Efficiency of Natural Ventilation. Annals of Occupational Hygiene. 2015;59:79-90.

# Author`s contribution

**Paper 1** The paper indicates a link between off-gassing and self-heating of stored wood pellets. Therefore, eleven wood pellets batches were investigated by using six different methods on their off-gassing or self-heating potential from five research institutions. The tests of one method were carried out by Irene Sedlmayer. The coordination of the paper, the data evaluation, the statistical analysis and the discussion were conducted by Irene Sedlmayer. Since Irene Sedlmayer wrote the greater part of the scientific paper, she became first author and acted as corresponding author.

**Paper 2** The impact of available oxygen on the formation of off-gassing emissions from stored wood pellets in the pellet tank reactor was studied. Irene Sedlmayer supported the development of the method and the planning of the experiments. Irene Sedlmayer was responsible for carrying out the experiments. She contributed to a large extent to the writing of the paper and was responsible for its submission and revision. Therefore, she received the second authorship and the corresponding author.

**Paper 3** Various biomass pellets were analysed concerning their formation of volatile organic compounds and sensory properties. Irene Sedlmayer prepared the concept of the paper together with the first author. The pellets to be investigated were selected by Irene Sedlmayer. Furthermore, she supported the process of writing and has composed some passages on her own. Irene Sedlmayer provided support for the correction as well as for submission and revision of the paper.

**Paper 4** In this paper the reduction potential on off-gassing emissions by adding the antioxidant acetyl salicylic acid in pellets production was investigated. Irene Sedlmayer together with industrial pelletising companies and other research institutions planned the experimental setup of the pellets production processes and the implementation. She supported the production of pellets in the field and developed the sampling procedure. Irene Sedlmayer carried out most of the off-gassing experiments and data evaluation. The majority of the work was written by her, making her first and corresponding author.

**Paper 5** The ventilation rates for a concrete small-scale pellet tank under characteristic temperature difference and varying opening settings were investigated. Irene Sedlmayer supported the set-up of the measuring equipment and the test procedures. She took over the performance of the ventilation tests.

# I. Introduction and background

## I.1. Wood pellets and pellets market

Wood pellets are a solid biofuel with a defined and consistent quality [1]. Wood pellets are cylindrically pressed from woody biomass with or without any additives and have broken ends. Usually, wood pellets are 3.15 to 40 mm long and have a diameter of approximately 6 or 8 mm. The product requirements of wood pellets for industrial and nonindustrial use of different classes are worldwide classified [2]. These include requirements on the raw material, type and quantity of impurities and foreign matter as well as fuel technology requirements. Moreover, quality characteristics like the defined moisture content, ash content, energy density, additives usage, mechanical durability, fines, density and homogeneous size and shape for nonindustrial usage are regulated. Further maximum limits for elemental contents of, for instance, nitrogen, sulphur, chlorine, arsenic, cadmium, chromium, copper, lead, and mercury are specified. This classification of wood pellets as solid biofuel should allow efficient and transparent trade and simplify communication between producers, traders and end users [3]. A further step towards ensuring pellets quality from production to the end users is enabled by two guidelines concerning safe handling and storage of solid biofuel pellets [4] [5].

The wood pellets market has shown considerable growth over the past two decades. In 2000, at the beginning of the records, almost 2 million tonnes of wood pellets were produced. A staggering 15 million tonnes of wood pellets were produced in 2010. And also, in the following years a large increase in the worldwide wood pellets production was achieved. More than 41 million tonnes were produced in 2020. The distribution of wood pellets production in 2020 is as follows: EU27 44%, other Europe 12%, North America 30%, South America 3% and Asia 11% [6]. However, the largest worldwide wood pellets producer is the United States with almost 8 million tonnes. The second greatest number of pellets is produced in Canada, followed by Germany. Even Austria is among the top 10 pellets producers worldwide in 2017 [7].

In terms of consumption, Europe is clearly ahead with 76%, with 49% in the EU27 and 27% in other Europe. In 2020, the consumption of wood pellets is 16% in Asia, 7% in North America and 2% in South America [6]. The largest consumer of pellets in the world is the United Kingdom with more than 7 million tonnes, followed by Italy and Denmark in 2017. Once again, Austria is represented in the top 10. Wood pellets are used in industrial, residential, and commercial appliances [1] [8].

Wood pellets are mainly used in the commercial and residential sectors for heat production. Furthermore, a large part is applied for energy production. The smallest part is utilised to generating heat and electricity in combined heat and power plants [7] [8]. In the residential and commercial sector more than 22 million tonnes of wood pellets were consumed which corresponds to 52% of used pellets worldwide. On the other hand, more than 20 million tonnes of wood pellets belong to the industrial sector (48%) [6].

## I.2. Off-gassing phenomenon

Chemical and biological processes are the cause of the degradation of wood components. These degradation processes in wood and other biomass lead to the formation of gaseous emissions [1] [9] [10] [11]. Off-gassing is the term used to describe the phenomenon of that release of emissions from wood pellets [1] [12] [13]. The formation of emissions is well known in the thermal treatment of wood [14] [15] [16] [17] [18] [19]. However, woody biomass also emits various gases during storage [20]. Carbon monoxide (CO), carbon dioxide ($CO_2$), volatile organic compounds (VOCs), methane ($CH_4$) with a simultaneous oxygen ($O_2$) deficiency occur during the storage of wood pellets [12] [21] [22] [23] [24] [25] [26] [27] [28] [29].

### Carbon monoxide

Carbon monoxide (CO) is a colourless, odourless, tasteless gas but toxic for humans. Due to the slightly lighter nature of carbon monoxide compared to air, CO distributes almost evenly in a room. Thus, when entering the room CO remains unnoticed. CO is formed during incomplete combustion of carbon-containing substances.

The danger of CO is that CO disrupts the respiration process in humans [30]. The toxicity of CO depends on the concentration and exposure time [31]. During respiration, the oxygen ($O_2$) usually binds to the iron in the haemoglobin and thus supplies the cells with oxygen [32]. The affinity of carbon monoxide to haemoglobin, compared to that of oxygen, is about 300 times higher [30]. When CO is present the binding to haemoglobin, forming carboxyhaemoglobin (COHb), is preferred. At a CO concentration of 0.3 %, already 75 % of the haemoglobin is present as COHb. This CO concentration can already lead to death at an exposure time of 15 minutes [32] [33]. The maximum working place concentration for CO is set at 30 ppm [30]. Higher concentrations than the 30 ppm can lead to headaches, dizziness, irritability, nausea and many other complaints [31]. Observed symptoms of CO content and the formation of COHb are summarised in Table 1.

**Table 1** CO occurrence, expected COHb values and resulting symptoms (adapted after Higgins [34] Winter and Miller [35]).

| CO in ppm | COHb in % | Symptoms |
|---|---|---|
| 70 | 10 | no appreciable effect except shortness of breath on vigorous exertion, possible tightness across forehead |
| 120 | 20 | shortness of breath on moderate exertion, occasional headache |
| 220 | 30 | headache, easily fatigued, judgement disturbed, dizziness, dimness of vision |
| 350-520 | 40-50 | headache, confusion, fainting, collapse |
| 800-1200 | 60-70 | unconsciousness, convulsions, respiratory failure, death if exposure continues |
| 1950 | 80 | immediately fatal |

### Carbon dioxide

Carbon dioxide ($CO_2$) is a colourless gas with a slight acidic smell and taste. $CO_2$ is ubiquitous and occurs in the air at more than 400 ppm. It is about 1.5 times heavier than air and therefore sinks to the ground. It is a natural product of cellular respiration in many living organisms and is also produced by combustion and fermentation. Concentration of 5% and more $CO_2$ can cause asphyxiation. Even higher concentration of 10% can lead to unconsciousness or death [36].

### Volatile organic compounds

Volatile organic compounds (VOCs) are a large and diverse group of gaseous compounds. According to the United States Environmental Protection Agency VOCs are: "Volatile organic compound (VOC) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions." [37] Moreover, the European definition for VOCs is: "Volatile organic compound (VOC) shall mean any organic compound having at 293.15 K a vapour 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 vapour pressure at 293.15 K shall be considered as a VOC." [38].

### Methane

Methane ($CH_4$) is a colourless and tasteless gas. At higher concentration (≥ 5%) a sweet oil type odour is perceived. $CH_4$ is flammable and can cause explosion at concentrations of 5% [39]. $CH_4$ is the simplest alkane. $CH_4$ at low concentration is not considered to be toxic for humans. However, higher concentrations (≥ 5%) can cause unconsciousness or asphyxia. $CH_4$ occurs naturally and is constantly being formed, for example during technical, geological or biological processes. Methanogenesis by microorganisms is mainly responsible for the presence of natural $CH_4$.

**Oxygen**

Dioxygen ($O_2$), two atoms of the element O, are formed at standard temperature and pressure. $O_2$ is a colourless and odourless gas. 20.95% of the Earth's atmosphere consists of $O_2$. $O_2$ is needed for combustion and aerobic respiration. According to the National Institute for Occupational Safety and Health an oxygen deficient atmosphere has a lower concentration of 19.5% $O_2$ at sea level. $O_2$ concentrations < 16%, influences the mental effectiveness, visual acuity, and muscular coordination. Unconsciousness can be caused by $O_2$ concentrations of 10%. Even lower concentration of $O_2$ (< 6%) are fatal [40].

## I.3. Self-heating phenomenon

In addition to the off-gassing phenomenon, self-heating during the storage of wood pellets is also well known topic [41] [42] [43]. According to Babrauskas, self-heating is an increase in temperature due to exothermal reactions in fuels. Self-heating occurs during the storage of many materials, that can decompose or can be oxidised [44]. Self-heating during biomass or wood pellets storage can be attributed to various sources. Biological metabolic reactions by bacteria, chemical oxidation reactions of wood own components (such as wood extractives) as well as physical transition reactions (e.g. water sorption) are causes for self-heating. These exothermal reactions, therefore, release heat. All of these reactions can occur individually or in combinations. If this released heat cannot be removed, this can lead to self-heating. The prevailing temperature during storage can then reach a thermal runaway, resulting in spontaneous combustion of the so-called self-ignition [45] [46]. However, microbial growth during wood pellets storage should be very low due to the low moisture content of stored wood pellets and high temperatures during wood pellets production (e.g.: during drying or pelletisation) [45].

## I.4. Structure of the work

This thesis is divided into five chapters. The research focus is dealt with in chapters II to IV. These chapters open with a short introduction to the actual topic and provides the relevant literature. In the next step, the used materials and applied methods are described. Then the results are presented and discussed. At the end of each of the three research chapters, a conclusion is provided.

Chapter I gives a general overview of wood pellets and the wood pellets market, as well as, of the two phenomena, off-gassing and self-heating. Furthermore, the structure of the thesis is described and the objectives and underlying research questions are outlined.

Chapter II deals with off-gassing analyses of stored wood and biomass pellets. Various relations and influencing factors on the off-gassing behaviour during wood pellets storages are investigated. In addition, studies are conducted on the odour of pellets.

Chapter III focuses on the wood pellets production. Various modifications are implemented in laboratory and industrial scale pellets production series. The addition of different additives, the blending of raw materials and changes in the cooling process are investigated.

Chapter IV examines pellets storage facilities and various ventilation measures. On the one hand, storage facilities in the field that are in real operation are monitored, while on the other hand, various ventilation scenarios in pellets storages are set up and investigated.

Chapter V contains the key findings and provides an outlook.

Moreover, the Appendix, lists the abbreviations, acronyms, indices and symbols. All used figures and tables are presented.

Furthermore, all used references are listed and cited in consecutive order.

All peer-reviewed journal papers on which this thesis is based on are listed.

Finally, the curriculum vitae of the author is attached.

## I.5. Aim of the work

The overall topic of this thesis is the profound investigation of the off-gassing phenomenon. For each research chapter (II - IV), an overarching research question was defined. Additional objectives are addressed in the respective chapters. Throughout this thesis the following research questions will be addressed and answered:

**Chapter II - Off-gassing of stored pellets*****: What characteristic off-gassing behaviour do pellets have?***

The first main focus in this thesis is on the off-gassing behaviour of wood and non-wood pellets. On the one hand, various relations with and influencing factors on the off-gassing of wood pellets are investigated. On the other hand, non-wood pellets are examined with regard to their off-gassing behaviour with particular emphasis on the presence of VOCs.

- What influence do wood characteristics have on the off-gassing behaviour of wood pellets and is there a link to other wood pellets storage properties?

- What influence do storage conditions have on the off-gassing behaviour of wood pellets during storage?
- What is the off-gassing behaviour of non-wood pellets?

**Chapter III - Effect of pellets production on off-gassing behaviour*****: Can the off-gassing behaviour of wood pellets be reduced by intervening in wood pellets production?***

Moreover, the pellets production of wood pellets itself is a further focus of the investigations. Thus, possible influencing variables through adaptations in production are being investigated aiming at the production of pellets with a lower off-gassing potential.

- Can the off-gassing formation of wood pellets, in particular CO, be reduced by adding additives in wood pellets production?
- Can the off-gassing formation of wood pellets, in particular CO, be reduced by blending with selected wood raw materials in pellets production?
- Can the off-gassing formation of wood pellets, in particular CO, be reduced by modifying the ventilation and cooling process immediately after pellets production?

**Chapter IV - Pellets storage*****: What influence do ventilation systems for pellets storage facilities have on carbon monoxide occurrence?***

The third research focus is on wood pellets storage. Real pellets storage facilities that are in operation are examined in combination with the stored pellets. In addition, different ventilation scenarios of pellets storage facilities are evaluated. These investigations should reveal further aspects of storage safety.

- What are the CO emission courses in real wood pellets storage facilities and are they influenced by ventilation?
- Does cross-ventilation affect the air exchange during wood pellets storage?

# II. Off-gassing of stored pellets

## II.1. Introduction

Wood pellets are known to emit various gases like CO, $CO_2$, VOCs and $CH_4$ during storage with a simultaneous decrease in atmospheric oxygen in the storage [12] [25] [26] [27] [29]. For the investigation of off-gassing emissions different laboratory methods have been used [12] [21] [26] [27] [47] [48]. All these methods analyse the gas in the headspace above the stored pellets. Therefore, pellets are stored in a closed defined container for a given period of time. However, these methods are executed differently which partly leads to the fact that the results are difficult to compare. In the meantime, the International Organization for Standardization has published a technical specification defining a laboratory method for measuring off-gassing emissions and $O_2$ depletion [49]. Moreover, a method for screening of carbon monoxide is available as final draft [50].

The off-gassing research on wood pellets of this thesis aims at, among other things, the investigation of off-gassing emissions of wood pellets in the context of different wood species and wood extractives [27] [28] [51]. Pine pellets tend to form higher emissions during storage than spruce pellets [21] [27]. Results have demonstrated that fatty and resin acids as well as the VOC emissions decrease with increasing storage time [27] [28]. However, no direct correlations have been identified between the content of organic extractives and off-gassing emissions yet.

Moreover, the formed VOCs during the storage of wood pellets are responsible for the odour in wood pellets storages [52]. However, it is not known whether pellets with a high odour also tend to produce a high amount of CO.

A further study has revealed that the initiator for off-gassing emission is the autoxidation of fatty acids and terpenes [53]. Furthermore, the degradation of extractives also plays an important role in the self-heating of pellets [45] [46]. Therefore, a relation between these two topics is assumed [42] although such a link has not been proven yet.

In addition to causal research on off-gassing emissions, various influencing factors on the off-gassing behaviour of wood pellets during storage were investigated. The formation of off-gassing emission decreases with increasing storage period [12] [21] [54]. Thus, freshly produced pellets cause higher danger during storage in terms of CO formation and possible $O_2$ depletion. In particular, the storage temperature of pellets has been identified as a very relevant influencing factor. The higher the storage temperature is, the higher are the formed emissions [21] [54] [55]. Previous studies have indicated that more emissions are formed with higher available $O_2$ during storage [21] [54] [55] [56]. The influence of a constant $O_2$ concentration, as with continuous ventilation, on emission formation is unknown.

Furthermore, the relative humidity of the storage atmosphere and its effect on the off-gassing behaviour were investigated. Results have indicated that with increasing relative humidity, $CO_2$, CO, and $CH_4$ emissions increase while oxygen is reduced. [54]. However, data on VOC emissions are not available. In order to validate and supplement the findings, investigations with different relative humidities are performed.

A large number of off-gassing studies of wood pellets were conducted in recent years [12] [21] [22] [27] [29]. Off-gassing data from other biomass pellets is rare. However, agricultural and torrefied pellets also emit CO, $CO_2$ and VOCs [21] [57]. Individual studies have identified various VOCs that occur during the storage of wood pellets. Aldehydes such as hexanal and also ketones occur during the storage of wood pellets [27] [28] [58] [59]. The effects from hexanal and pentanal on odour during wood pellets storage have been identified [27]. Since there is hardly any information about the off-gassing behaviour of biomass pellets, it is also obvious that there is hardly any information about individual VOCs of stored biomass pellets. However, a broad variety of VOCs were identified by off-gassing analyses of torrefied wood [60]. Increasing knowledge, extensive VOC emissions analyses and odour analyses of biomass pellets are carried out for the first time in this thesis.

## II.2. Objectives

The investigation of the off-gassing behaviour of wood and biomass pellets is the overall topic of chapter II. The following sections are based on the peer-reviewed journal papers number 1, 2 and 3. In the course of the research work many other interesting aspects regarding the off-gassing behaviour of wood pellets were investigated. The most important investigations are presented additionally. Within this chapter, several research questions are addressed. The overall aim is to provide further insights into the off-gassing topic. The individual objectives are outlined below.

**Off-gassing characteristics of wood pellets**

- The aim is to indicate relations between the extractive content and the off-gassing emissions of raw material, pellets or wood species.
- The aim is to identify a relation between the extractive content and off-gassing emissions.

- The aim is to show whether malodourous wood pellets form more off-gassing emissions than wood pellets perceived without malodour.
- The aim is the identification of relations between self-heating and off-gassing behaviour of stored wood pellets.

**Storage influencing factors on off-gassing emissions from stored wood pellets**

- The aim is to prove that the headspace, the amount of oxygen, has an influence on the emission formation during the storage of pellets.
- The aim is to show how the emission behaviour of pellets changes with different oxygen availability in the storage atmosphere.
- The aim is to show how the emission behaviour of pellets changes with different relative humidity.

**Off-gassing characteristics of biomass pellets**

- The aim is to show that non-wood pellets form emissions during storage.
- The aim is to determine the expected odours when storing non-wood pellets.
- The aim is to identify the most prevalent VOCs during the storage of torrefied wood and non-wood pellets.

# II.3. Materials and methods

## II.3.1. Raw material and pellets samples

An overview on the investigated wood raw materials, wood pellets and biomass pellets are given in Table 2, Table 3 and Table 4, respectively.

**Table 2** List of the investigated raw materials (RMs) and their characteristics.

| Batch | Raw material | Moisture content in % (m/m) | $\rho_{\text{raw material}}$ in kg m$^{-3}$ |
|---|---|---|---|
| RM 1 | spruce sawdust | 13.8 | 460[1] |
| RM 2 | pine sawdust | 16.5 | 520[1] |
| RM 3 | larch sawdust | 9.3 | 600[1] |
| RM 4 | hardwood sawdust | 24.3 | 600[1] |

[1] raw material density according to DIN 68364 [61]

**Table 3** List of the investigated wood pellets (WP) batches, the used raw material, the production and their characteristics. (LSPP stands for laboratory scale pellets production. ISPP stands for industrial scale pellets production.)

| Batch | Raw material | Production | d<br>in mm | Moisture content<br>in % (m/m) | $\rho_{pellets}$<br>in kg m$^{-3}$ |
|---|---|---|---|---|---|
| WP 1 | spruce sawdust | LSPP | 6 | 8.7 | 1281 |
| WP 2 | pine sawdust | LSPP | 6 | 16.5 | 1300 |
| WP 3 | larch sawdust | LSPP | 6 | 8.1 | 1326 |
| WP 4 | hardwood sawdust | LSPP | 6 | 9.3 | 1280 |
| WP 5 | unknown[1] | ISPP | 6 | 6.6 | 1200[2] |
| WP 6 | unknown[1] | ISPP | 6 | 6.1 | 1200[2] |
| WP 7 | unknown[1] | ISPP | 6 | 6.2 | 1200[2] |
| WP 8 | unknown[1] | ISPP | 6 | 6.6 | 1200[2] |
| WP 9 | unknown[1] | ISPP | 6 | 7.0 | 1200[2] |
| WP 10 | unknown[1] | ISPP | 6 | 9.0 | 1200[2] |
| WP 11 | unknown[1] | ISPP | 6 | 9.0 | 1200[2] |
| WP 12 | 100/0 pine/spruce | LSPP | 6 | 8.5 | 1254 |
| WP 13 | 0/100 pine/spruce | LSPP | 6 | 10.6 | 1258 |
| WP 14 | 100/0 pine/spruce | ISPP | 6 | 6.7 | 1213 |
| WP 15 | 20/80 pine/spruce | ISPP | 8 | 9.0 | 1217 |
| WP 16 | 0/100 pine/spruce | ISPP | 6 | 7.7 | 1180 |
| WP 17 | 40/60 pine/spruce | ISPP | 6 | 7.6 | 1212 |
| WP 18 | 60/40 pine/spruce | ISPP | 8 | 6.0 | 1225 |
| WP 19 | 50/50 pine/spruce | ISPP | 8 | 7.3 | 1201 |
| WP 20 | 100/0 pine/spruce | LSPP | 6 | 9.7 | 1256 |
| WP 21 | 100/0 pine/spruce | LSPP | 6 | 10.7 | 1185 |
| WP 22 | 20/80 pine/spruce | ISPP | 6 | 8.7 | 1182 |
| WP 27 | 50/50 pine/spruce | LSPP | 6 | 7.9 | 1257 |
| WP 26 | 50/50 pine/spruce | LSPP | 6 | 8.1 | 1262 |
| WP 28 | 50/50 pine/spruce | LSPP | 6 | 8.2 | 1262 |
| WP 29 | 50/50 pine/spruce | LSPP | 6 | 7.9 | 1277 |
| WP 25 | 50/50 pine/spruce | LSPP | 6 | 8.7 | 1263 |
| WP 23 | 50/50 pine/spruce | LSPP | 6 | 9.5 | 1259 |
| WP 24 | 50/50 pine/spruce | LSPP | 6 | 7.8 | 1246 |
| WP 30 | unknown[1] | ISPP | 6 | 5.2 | 1200[2] |
| WP 31 | 100/0 pine/spruce | ISPP | 6 | 3.5 | 1098 |

[1] purchased on the Austrian market; Pellets quality A1 according to ISO 17225 [2]

[2] assumed value

**Table 4** List of the investigated biomass pellets batches, the used raw material, the production and their characteristics. (LSPP stands for laboratory scale pellets production. ISPP stands for industrial scale pellets production.)

| Batch | Raw material | Production | d in mm | Moisture content in %(m/m) | $\rho_{pellets}$ in kg m$^{-3}$ |
|---|---|---|---|---|---|
| BP 1 | straw | ISPP | 8 | 7.3 | 1189 |
| BP 2 | eucalyptus | ISPP | 6 | 5.3 | 1250 |
| BP 3 | 50/50 vine pruning/vine pomace | LSPP | 6 | 10.1 | 1324 |
| BP 4 | torrefied spruce sawdust | LSPP | 6 | 3.2 | 1214 |
| BP5 | torrefied pine sawdust | LSPP | 6 | 6.4 | 1249 |
| BP 6 | miscanthus | LSPP | 6 | 8.2 | 1200[1] |
| BP 7 | dried distillers' grains with soluble | LSPP | 6 | 12.6 | 1200[1] |
| BP 8 | extracted rape seed | LSPP | 6 | 11.2 | 1200[1] |

[1] assumed value

## II.3.2. Methods

### II.3.2.1. Moisture content

The moisture content of the investigated raw material and pellets batches was determined according to ISO 18134-2 [62]. Therefore, the samples were dried in a laboratory drying cabinet at 105 ± 2 °C until constant mass was achieved.

### II.3.2.2. Particle density

The particle density of pellets batches was measured according to ISO 18847 [63]. The volume and the mass of the pellets batches were required. Therefore, height and diameter of 15 randomly chosen pellets of each batch was measured with a sliding calliper. For this purpose, the broken areas at both ends of the pellets were first carefully smoothed with sandpaper achieving pellets with a cylindrical shape. Then, the pellets were weighed on Sartorius ME 235P precision balance. Afterwards the particle density was determined and the arithmetic mean value of the 15 pellets samples was calculated.

### II.3.2.3. Extractive content

The extractive content of wood samples was determined using Soxhlet extraction with acetone/$H_2O_{distilled}$ in ratio of 96:4 (V/V). The method was described in detail in the diploma thesis by Schmutzer-Roseneder [51].

The ground sample was weighed in a dried extraction thimble. The thimble and the solvent were applied in the apparatus and the extraction lasted for 6 h. The cooled solvent was dried with $Na_2SO_4$ overnight. Afterwards the solvent was filtered and the filter cake was washed with acetone. Afterwards, the separatory funnel (1 L) was filled with the entire solvent and a volume of 0.1 L

$H_2O_{distilled}$ was added. The inorganic components were extracted twice with each 0.06 L of n-hexane. The organic fraction (remaining acetone and $H_2O_{distilled}$) was transferred to a weighed round bottom flask. The solvent was separated in two steps (acetone first) on the Buchi Rotavapor. After removal of the solvents the mass of the organic extractive content was determined. The quantitative organic extractive content was an arithmetic mean value of a threefold determination. The three single values had to be within the range of ± 15% of the mean value.

#### II.3.2.4. Off-gassing determination – glass flask method

The CO, $CO_2$ and $VOC_{tot}$ off-gassing emissions as well as the residual $O_2$ concentration of stored biomass were determined using the so-called glass flask method. The method was developed following the setup of Kuang *et al.* 2008 [12]. The method was first described in detail by Schmutzer-Roseneder 2012 [51]. The method was continuously adapted [21] [23] [57] and the last modifications were published in Sedlmayer *et al*. [64].

Using the glass flask method, the formed emissions of $CO_2$, CO, and $VOC_{tot}$ and the residual $O_2$ concentration were determined. 2.4 and 0.3 kg, respectively, of each pellets batch was filled in 5 L glass flasks (in duplicate or triplicate) and closed. The flasks were stored at 22 °C for 5 days avoiding exposure to sunlight.

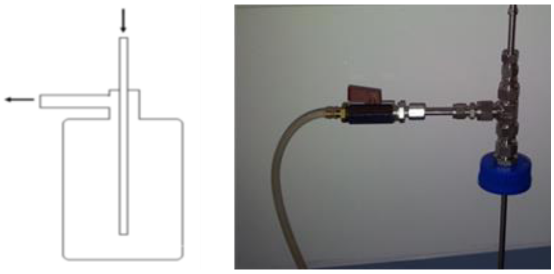


**Figure 1** a) Scheme of gas sampling and b) picture of the device for gas sampling used in the glass flask experiments.

The gas was sampled (Figure 1a)) by replacing the cap with the adapter (see Figure 1b)) which were connected to gas measurement systems. The concentration of CO, $CO_2$ and $O_2$ was detected by gas analyser (Emerson, NGA 2000) and $VOC_{tot}$ by flame ionization detector (M&A, Thermo FID PT63FH/LT). The measured CO, $CO_2$ and $VOC_{tot}$ concentration was converted into emission rates in mg of the specific gas component per kg of dry pellets per day (mg $kg^{-1}$ $pellets_{db}$ $day^{-1}$). The processing of data and the calculation were described in detail by Emhofer [21]. Therefore, pellets density, moisture content of the used pellets batch and actual storage duration within the glass flask were considered for conversion into emission rates. Arithmetic mean values of the rates were calculated and the minimum and maximum values were illustrated in presented figures. The residual $O_2$ concentrations were expressed in volume fraction in %.

### II.3.2.5. Off-gassing determination – pellets tank method

The continuous measurements for off-gassing emissions of wood pellets during storage were performed using the laboratory scale pellets tank. This pellets tank method was developed during the master thesis of Trinkel [57]. Moreover, the detailed procedure of the method was published by Meier [26] [65]. A brief overview of the method and their components are presented in Figure 2. The whole measurement equipment, like gas chromatography (GC) and temperature, pressure and humidity sensors, connected to the reactor was also linked to a computer allowing the monitoring and storage of the received data.

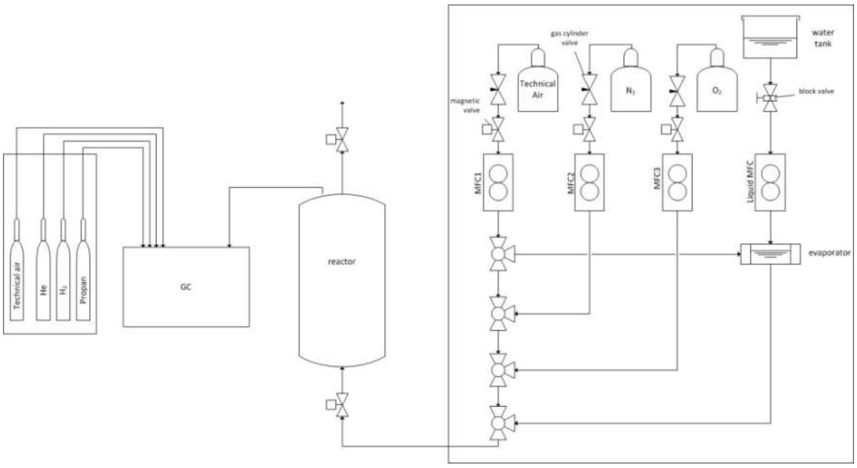


**Figure 2** Design of the pellets tank method.

The formed emissions from pellets during storage were sampled and analysed with the gas chromatograph. The gases were detected using a flame ionisation detector (FID) and a thermal conductivity detector (TCD). Furthermore, the temperature was measured inside the pellets bulk and above the pellets and outside the pellets tank. The relative humidity was monitored above the pellets inside the tank. The used devices and measured parameters are listed in Table 5.

**Table 5:** List of the used devices of the pellets tank method, the measured gases and measurement ranges.

| Device | Parameter | Range |
|---|---|---|
| FID | $CO_2$ | 1 ppm – 10% (V/V) |
| | $CH_4$ | 1 ppm – 10% (V/V) |
| | CO | 1 ppm – 10% (V/V) |
| | $VOC_{tot}$ | 1 ppm – 5% (V/V) |
| TCD | $CO_2$ | 0.01 – 100% (V/V) |
| | $O_2$ | 0.01 – 100% (V/V) |
| | $N_2$ | 0.01 – 100% (V/V) |
| | $CH_4$ | 0.01 – 100% (V/V) |
| | CO | 0.01 – 100% (V/V) |
| temperature sensor | T | -75 – 350 °C |
| humidity sensor | RH | 0 – 100% |

The performing of the measurements as well as the calculation of emission rates and factors were described in detail by Meier *et al.* [26] and Meier [65].

#### II.3.2.6. Analysis of volatile compounds

The formed volatile compounds of biomass pellets were analysed using headspace solid phase micro extraction (HS-SPME) and gas chromatography - mass spectrometry (GC-MS). The detailed description of the used method was published in Pöllinger-Zierler *et al.* [52] [66] [67] [68]. The extraction and enrichment of the volatile compounds from ground pellets batches were performed using a HS-SPME prior to GC-MS (Agilent 7890 GC/MS) analysis. Therefore, volatile compounds were enriched and sampled on a 2 cm fibre (50/30 µm DVB/Carboxen/PDMS). The fibre was exposed into the headspace above the ground pellets. The separation and the identification of the volatile compounds were performed on the GC-MS system. The compounds were identified by comparison of the obtained mass spectra with mass spectra from literature and from mass spectra databases as well as by internal standards.

#### II.3.2.7. Sensory description of pellets - sensory panel

The descriptive sensory analysis of biomass pellets was performed using a human sensory panel consisting of 15 well trained panellists [52] [67] [68]. The panellists were trained with odours expected from the investigated pellets batches. The sensory evaluation was carried out under standardised conditions. For this purpose, 2 g of the ground pellets were filled into blue odour glasses with a volume of 0.11 L and the glasses were covered. The covers were removed immediately before the blind tasting of the odour of each pellets sample.

## II.4. Results and discussion

### II.4.1. Off-gassing characteristics of wood pellets

#### II.4.1.1. Off-gassing and extractive content in raw material and wood pellets

The off-gassing behaviour of sawdust from European larch (*Larix decidua*), Norway spruce (*Picea abies*), Loblolly pine (*Pinus taeda*) and hardwood mixture (*Fagus grandifolia* and *Ulmus americana*) and pellets made from these raw materials were analysed using the glass flask method. The wood pellets batches were produced using a Kahl flat die pellets mill (type 14 - 175) in the technical laboratory of BEST. Moreover, the total extractive content of all sawdust batches and the produced pellets were determined. The investigated pellets batches, their off-gassing emissions and their total amount of extractive content are presented in Table 6 and Figure 3. Some of these results, in particular the extractive contents, have already been published in the Master's thesis by Irene Schmutzer-Roseneder [51].

**Table 6** List of the investigated batches and further information on the raw material. The emission rates, the residual $O_2$ concentration and the total amount of extractive content are given.

| Batch | Raw material | Sample | CO | $CO_2$ | $VOC_{tot}$ | Residual $O_2$ | Extractive content |
|---|---|---|---|---|---|---|---|
| | | | in mg $kg^{-1}$ $pellets_{db}$ $day^{-1}$ | | | in % (V/V) | in % (m/m) |
| RM 1 | spruce | sawdust | 0.42 | 6.49 | 0.05 | 19.8 | 2.6 |
| WP 1 | spruce | pellets | 1.04 | 2.99 | 0.07 | 16.1 | 2.0 |
| RM 2 | pine | sawdust | 0.72 | 7.06 | 0.18 | 19.4 | 3.5 |
| WP 2 | pine | pellets | 4.56 | 8.00 | 1.51 | 0.5 | 3.4 |
| RM 3 | larch | sawdust | 0.10 | 3.11 | 0.01 | 20.3 | 2.5 |
| WP 3 | larch | pellets | 0.04 | 0.47 | 0.00 | 20.1 | 1.8 |
| RM 4 | hardwood | sawdust | 0.12 | 67.20 | 0.03 | 18.4 | 2.5 |
| WP 4 | hardwood | pellets | 0.16 | 1.97 | 0.00 | 20.0 | 1.6 |

The results of sawdust and pellets batches revealed that the determined extractive contents of all sawdust batches were higher than for the pellets produced from them. That reduction could be explained by the thermal and mechanical treatments in the pelletising process. However, almost no reduction was achieved in the pine samples. The lower extractive content in pellets compared to raw material samples was previously described [21]. Furthermore, wood is known to reduce extractives during drying [14] [16] [18] [19] [69]. However, in the present work the reduction of extractives caused by raw material drying can be excluded, as the raw material was not further dried before pelletisation. The determined extractive contents were in the range of 1.6 to 3.5% (m/m). The highest content was determined for the two pine batches. The quantified extractive contents of the investigated batches were comparable to literature values. Extractives with a content of about 3.1 to 4.0% (m/m) are known for pine [9] [70] and between 2 and 2.2% (m/m) for spruce [9].

Comparing the off-gassing emissions, it was evident that more $CO_2$ was formed than CO. Both emissions were higher than the determined amount of $VOC_{tot}$. Regarding CO emissions, the most reactive batches were the pine batches (RM 2 and WP 2). The CO emissions of the pine pellets batch were 6 times higher than for the original raw material. Although the difference in CO emissions between pellets and original raw material is so high, the content of extractives hardly differs. Moreover, the pine pellets batch demonstrated the highest $O_2$ consumption. However, the $CO_2$ rate (67.2 mg $kg^{-1}{}_{db}$ $day^{-1}$) of batch RM 4, the hardwood sawdust, was striking, because it was at least eight times higher than for the remaining pellets batches. Moreover, it was the highest emission rate for $CO_2$ of the entire thesis.

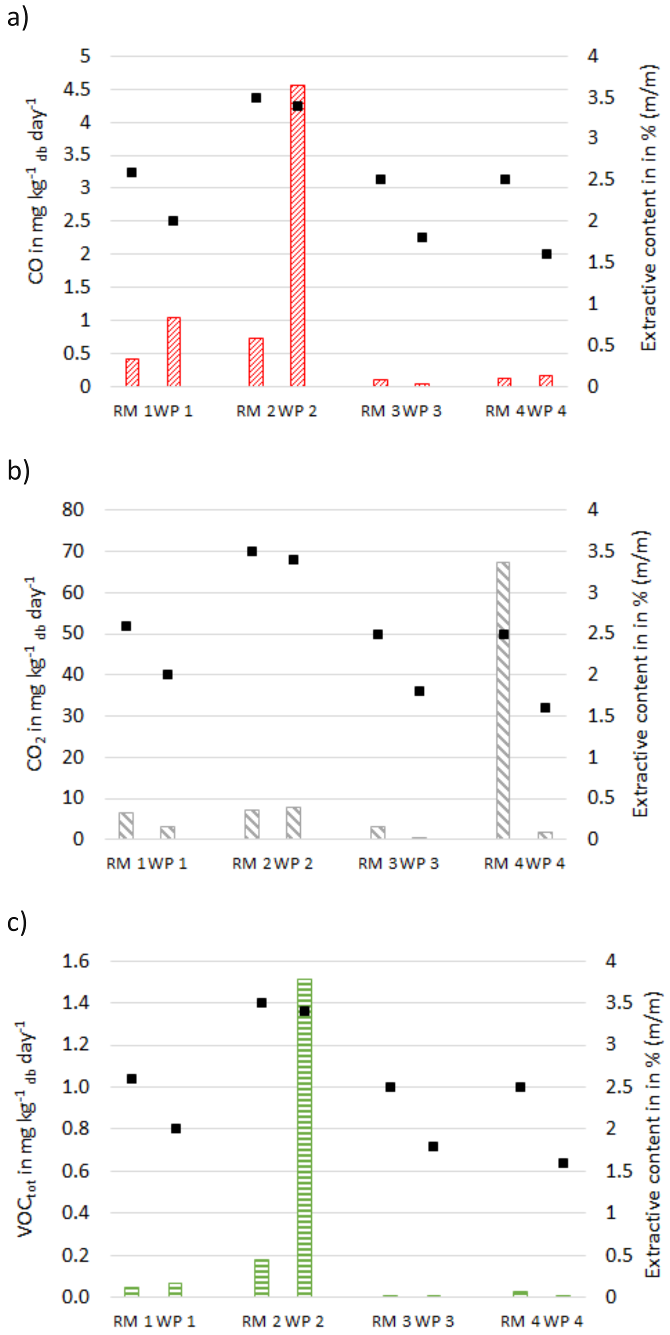


**Figure 3** Illustration of the emission rates in columns for a) CO, b) $CO_2$ and c) $VOC_{tot}$ and the determined extractive content (in black squares) of the investigated raw material and wood pellets batches.

The CO emission rates of the pellets were higher than those of the raw material in 3 out of 4 cases, whereas, for the $CO_2$ rates, the rates of the raw materials were 3 times higher than those of the pellets. For $VOC_{tot}$ emissions, the rates of the pellets were twice higher and twice lower than for the raw materials. The influence of pelletisation indicated different effects on the off-gassing behaviour of wood pellets. No obvious trend could be identified on the basis of the available data. Following explanations can be given for this. It is a small test set up with only one produced pellets batch of each type of raw material. Since wood, and thus also sawdust and pellets, are characterised by a certain inhomogeneity in the composition of their ingredients, the inhomogeneity and the limited number of samples may be reasons for the inconsistent results. Furthermore, pelletising of different raw materials in the same pelletising mill can lead to different process conditions. The raw material may be mechanically processed in different ways. Thus, the pellets are activated differently with regard to their off-gassing potential leading to various off-gassing activities.

#### II.4.1.2. Off-gassing and extractive content of wood pellets

The off-gassing emissions and the content of extractives of five commercially available wood pellets were determined. One bag of wood pellets (each 15 kg) was purchased from 5 different Austrian pellets producer at DIY stores.

Some of presented results, in particular the extractive contents, were published in the Master's thesis by Irene Schmutzer-Roseneder [51]. The investigated commercially available pellets batches and their off-gassing emissions are listed in Table 7.

**Table 7** List of the investigated wood pellets batches. The emission rates, the residual $O_2$ concentration and the total amount of extractive content are given.

| Batch | CO | $CO_2$ | $VOC_{tot}$ | Residual $O_2$ | Extractive content |
|---|---|---|---|---|---|
| | in mg $kg^{-1}$ $pellets_{db}$ $day^{-1}$ | | | in % (V/V) | in % (m/m) |
| WP 5 | 0.09 | 5.23 | 0.01 | 20.2 | 1.7 |
| WP 6 | 0.14 | 0.94 | 0.02 | 19.9 | 1.9 |
| WP 7 | 0.03 | 5.21 | 0.01 | 20.4 | 2.0 |
| WP 8 | 0.33 | 1.21 | 0.04 | 18.8 | 2.1 |
| WP 9 | 0.03 | 5.25 | 0.01 | 20.4 | 2.8 |

The pellets batches WP5 to WP9 were arranged in ascending order according to their extractive content (see Figure 4). The off-gassing emissions for CO, $CO_2$ and $VOC_{tot}$ did not follow this trend. Thus, the joint consideration of off-gassing emissions and extractive content showed no direct correlation. Even though only five wood pellets batches were examined, it can be assumed that the extractive content is not the only factor responsible for the formation of emissions. First of all, it should be mentioned that the production date of the investigated pellets batches was unknown. It was proven that the formation of emissions decreases with increasing pellets age [21] [26] [65]. Moreover, the exact composition of the raw materials was not known. Since the pellets came from the Austrian market, it was assumed that they were spruce or pellets from a mixture of spruce and pine [71] [72]. It was previously shown that pine pellets tend to form more emissions than spruce pellets [21] [27] [73] [74]. In addition, other treatment steps, the pelletising process as well as the intermediate storage could have influenced the later formation of emissions. Even though it is known that the emissions depend on the extractives [53] [75] [76], no link to the total extractive content was indicated. It is possible that individual extractives are responsible for the emission formation. It is therefore likely that there is a relation between individual extractives and the formation of emissions. This was confirmed by a journal publication in 2022, that the formation of gases depends largely on the type of extractives present in the raw material and not on the total amount of extractives [77].

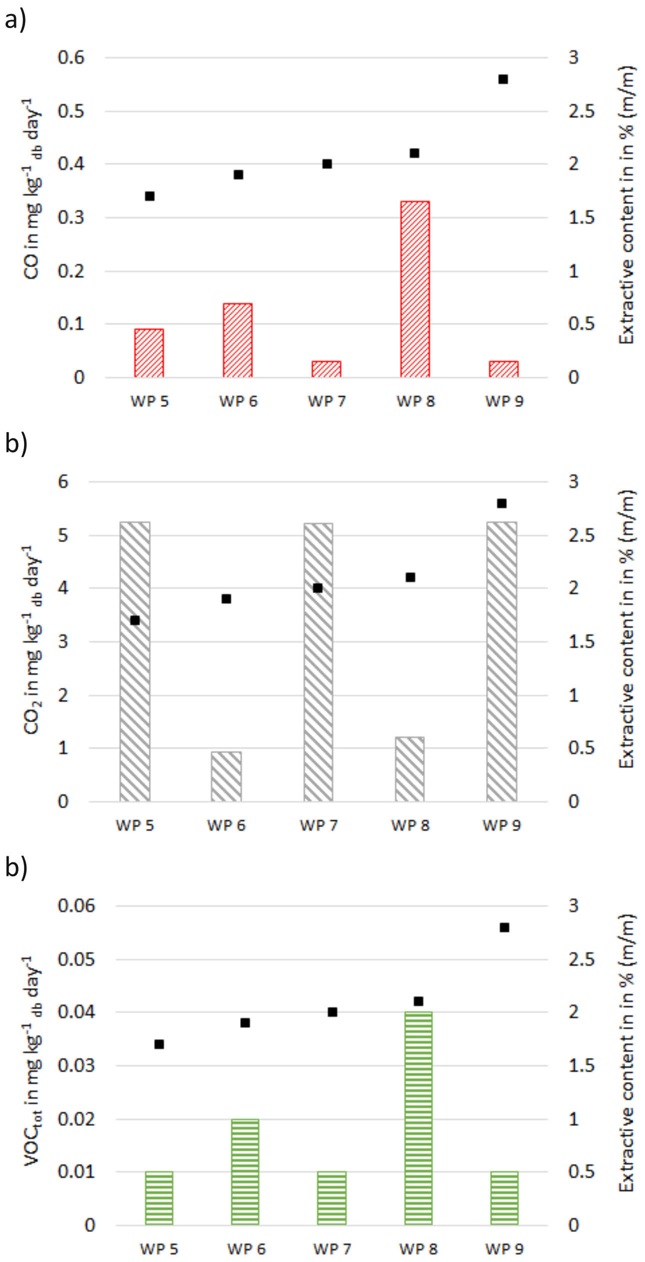


**Figure 4** Illustration of the emission rates in columns for a) CO, b) $CO_2$ and c) $VOC_{tot}$ and the determined extractive content (in black squares) of the commercially available wood pellets batches.

### II.4.1.3. Off-gassing emissions and sensory properties of wood pellets

Two commercially available wood pellets batches class A1 according to ISO 17225-2 [2] were investigated concerning their off-gassing emissions and their sensory properties; more precisely, their formation of aldehydes and acids [52] [67]. The malodorous sample came from an end user who had complained about the odour. This chapter is based on the publication “Identification of malodourous emissions of wood pellets during storage” [52].

The comparison of emissions for CO, $CO_2$ and $VOC_{tot}$ of the reference (WP 10) with the malodourous (WP 11) wood pellets batches shows, for all off-gassing emissions, higher values of sample WP 10 (see Table 8 and Figure 5). The so-called malodourous sample (WP 11) therefore formed less $VOC_{tot}$ overall.

**Table 8** List of the investigated batches and the determined emission rates for CO, $CO_2$ and $VOC_{tot}$ and the residual $O_2$ concentration.

| **Batch** | **Description** | **CO** | **$CO_2$** | **$VOC_{tot}$** | **Residual $O_2$** |
|---|---|---|---|---|---|
| | | **in mg $kg^{-1}$ $pellets_{db}$ $day^{-1}$** | | | **in % (V/V)** |
| WP 10 | reference | 0.29 | 3.49 | 0.30 | 18.2 |
| WP 11 | malodourous | 0.14 | 1.05 | 0.02 | 20.5 |

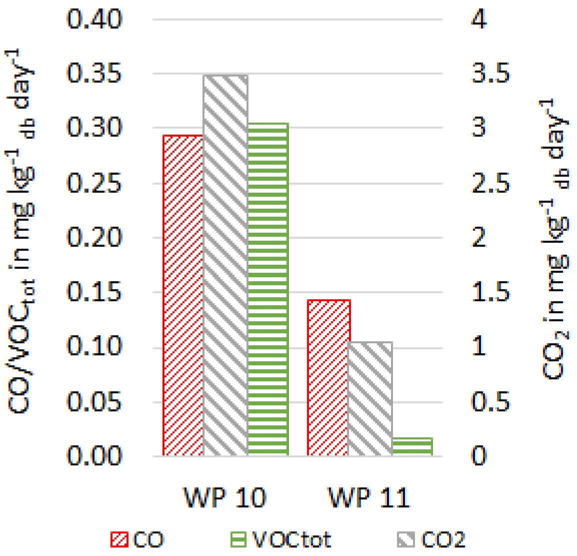


**Figure 5** Illustration of the emission rates for CO, $CO_2$ and $VOC_{tot}$ of the reference (WP 10) and malodourous (WP 11) wood pellets batches.

Furthermore, the individual VOCs of both batches were analysed. Figure 6 depicts the different distribution of volatile compounds. The same volatile compounds were determined in both batches. However, the relative amounts of longer-chain acids and aldehydes were higher for WP 11, the malodourous batch, than for WP 10. These longer-chain compounds were partially responsible for the malodourous smell. Furthermore, the 3-methyl-butanoic acid in the malodourous pellets batch was also higher than in WP 11. This acid has a low odour threshold (0.0018 mg $m^{-3}$). This low odour threshold and the higher amount in batch WP 11 were most likely the causes of the perceived unpleasant odour. Concluding, amounts of VOCs alone are not responsible for the perceived odour of a pellets sample. To enable the assessment of odour, the composition of the volatiles must be known. Based on the results, it could not be concluded that the CO formation for malodourous pellets is higher than for non malodourous pellets. However, it could indeed be that pellets with a noticeable and unpleasant odour also have a high CO reactivity. Due to the amount of data available, no general conclusions can be drawn.

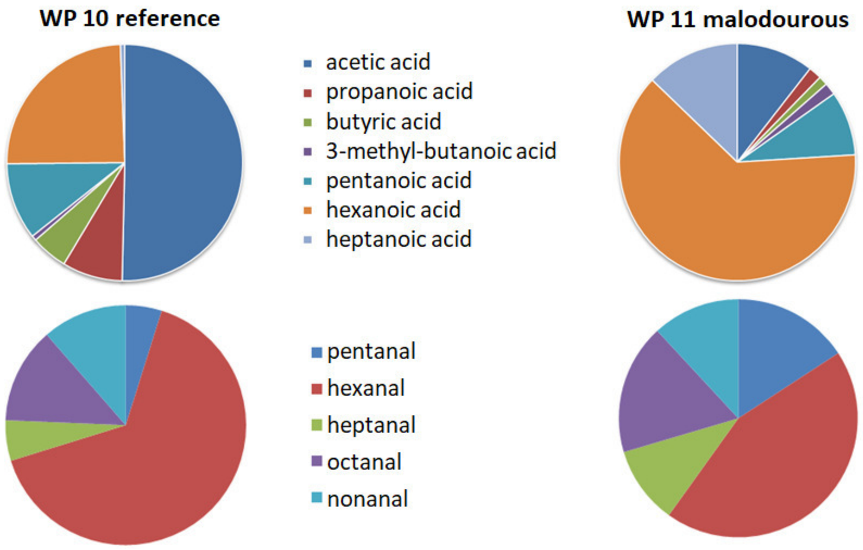


**Figure 6** Illustration of the determined acids and aldehydes of the two pellets batches WP 10 and WP 11 (Source: Pöllinger-Zierler *et al.* 2018 [52]).

### II.4.1.4. Link between off-gassing and self-heating

The presented results are derived from the peer-reviewed journal paper number 1. For this purpose, eleven wood pellets batches made of *Pinus sylvestris* (pine), *Picea abies* (spruce) or blends of them were investigated (see Table 9) applying three self-heating and four off-gassing methods (see Table 10). The procedure of the analyses and off-gassing results are discussed in more detail by Sedlmayer *et al.* 2018 [23].

**Table 9** List of the investigated pellets batches and the corresponding batch number of the referring peer-reviewed journal paper. The composition, the used raw material and the production of the wood pellets are given. The table is adapted according to Sedlmayer *et al.* 2018 [23].

| Batch | Journal batch | Pine/spruce ratio | Production site |
|---|---|---|---|
| WP 12 | 1 | 100/0 | DBFZ[1] |
| WP 13 | 2 | 0/100 | DBFZ[1] |
| WP 14 | 3 | 100/0 | German pellets producer 1 |
| WP 15 | 4 | 20/80 | Swedish pellets producer 1 |
| WP 16 | 5 | 0/100 | German pellets producer 2 |
| WP 17 | 6 | 40/60 | Swedish pellets producer 2 |
| WP 18 | 7 | 60/40 | Swedish pellets producer 3 |
| WP 19 | 8 | 50/50 | Swedish pellets producer 4 |
| WP 20 | 9 | 100/0 | BEST[2] |
| WP 21 | 10 | 100/0 | DBFZ[1] |
| WP 22 | 11 | 20/80 | German pellets producer 3 |

[1] DBFZ stands for Deutsches Biomasseforschungszentrum gemeinnützige GmbH

[2] BEST stands for BEST - Bioenergy and Sustainable Technologies GmbH

**Table 10** List of the applied three self-heating and the four off-gassing methods. The most relevant characteristics of the methods are presented (Source: Sedlmayer *et al.* 2018 [23]).

| Method | Purpose | Measured parameter | Unit | Sample amount | Analysis period | Temperature |
|---|---|---|---|---|---|---|
| isothermal calorimetry | self-heating | Maximum specific heat release rate ($HRR_{max}$) | mW $g^{-1}$ | 4 g | 24 h | 60 °C |
| oxi-press | self-heating | Pressure decline ($\Delta p$) caused by oxygen consumption | kPa | 50 g | 2 h | 40 and 100 °C |
| TGA | self-heating | derivative thermogravimetric ($T_{DTG,\ peak}$) - temperature at maximum mass loss rate | °C | 20 mg | 87 min | 30 up to 900 °C |
| VOC emissions | off-gassing | released aldehydes and ketones concentration | mg $kg^{-1}$ | 10 g | 49 h | 60 °C |
| offline method | off-gassing | CO, $CO_2$, and $CH_4$ headspace concentrations | $cm^3\ m^{-3}$ | 7000 - 9100 g | 48 h | 23 and 60 °C |
| glass flask method | off-gassing | CO, $CO_2$ and $VOC_{tot}$ headspace concentration | mg $kg^{-1}{}_{d.b.}$ $day^{-1}$ | 2400 g | 5 d | 22 °C |
| fatty and resin acids | off-gassing | concentration of fatty and resin acids | mg $kg^{-1}$ | 3 g | 1 h | 40 to 60 °C |

The overall self-heating and off-gassing tendency of the eleven wood pellets batches presented a general tendency towards their common self-heating and off-gassing tendency (Figure 7). Therefore, the arithmetic mean ranking point of each pellets batch derived from all applied methods was used (see Supplementary material in Sedlmayer *et al.* 2018 [15]).

Pellets batch WP 19 was identified as the most reactive pellets batch concerning the overall self-heating and off-gassing tendency. WP 19 was ranked in first place by four out of seven methods: oxi-press, VOC emissions, offline and glass flask method. Furthermore, pellets batches WP 19, WP 17 and WP 15 showed the highest reactivity in four out of seven applied methods. All three batches were blends of spruce and pine.

In contrast, WP 12 was shown to be the least reactive batch. A total of three methods (oxi-press, offline and glass flask method) placed WP 12 in last place. Additionally, four of seven methods classified pellets batches WP 12, WP 13 and WP 16 as pellets with the lowest reactivity in terms of their self-heating and off-gassing tendency.

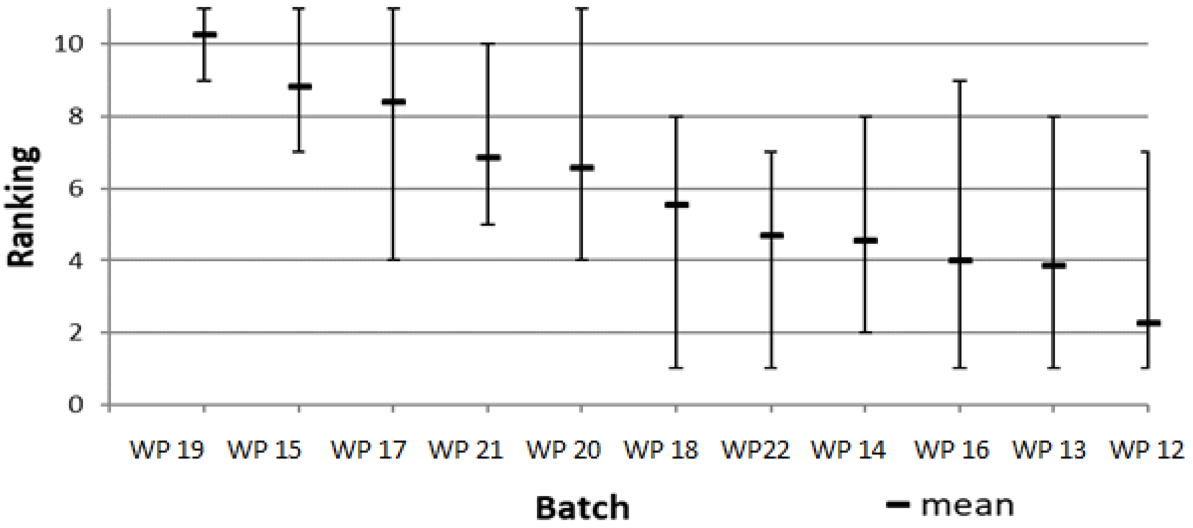


**Figure 7** Illustration of the overall self-heating and off-gassing tendency. The mean ranking points of each pellets batch and the deviation of the evaluation of batches towards their common self-heating and off-gassing tendency derived from all seven methods (three self-heating and four off-gassing methods) are presented. The figure is adapted according to Sedlmayer *et al.* 2018 [23].

Looking at the deviation, it was apparent that WP 19 had the lowest variability. It received ranking points between nine and eleven. By contrast, the largest deviation was observed for WP 16 with individual ranking points from one to nine. This wide deviation indicated that the applied methods evaluated that batch very differently. This is probably due to differences in the applied methods.

In addition, pellets batches with increased self-heating or off-gassing tendency (such as WP 19 and WP 15) were evaluated as highly reactive pellets batches by all off-gassing self-heating methods. Thus, it was shown that reactive pellets were identified as reactive by all methods. Therefore, it can be assumed that by using one of those self-heating and off-gassing methods, reactive pellets would be identified.

The relation between self-heating and off-gassing was investigated using correlation analyses (see Figure 8). The exact procedure can be found in Sedlmayer *et al.* 2018 [15]. The correlation analyses revealed six very significant and three significant correlations. The highest correlation was indicated by comparison of the two off-gassing methods, offline method and glass flask method. This high correlation was very likely due to the similarity of the two methods. Both methods determined the formed emissions in the headspace from stored pellets under sealed conditions.

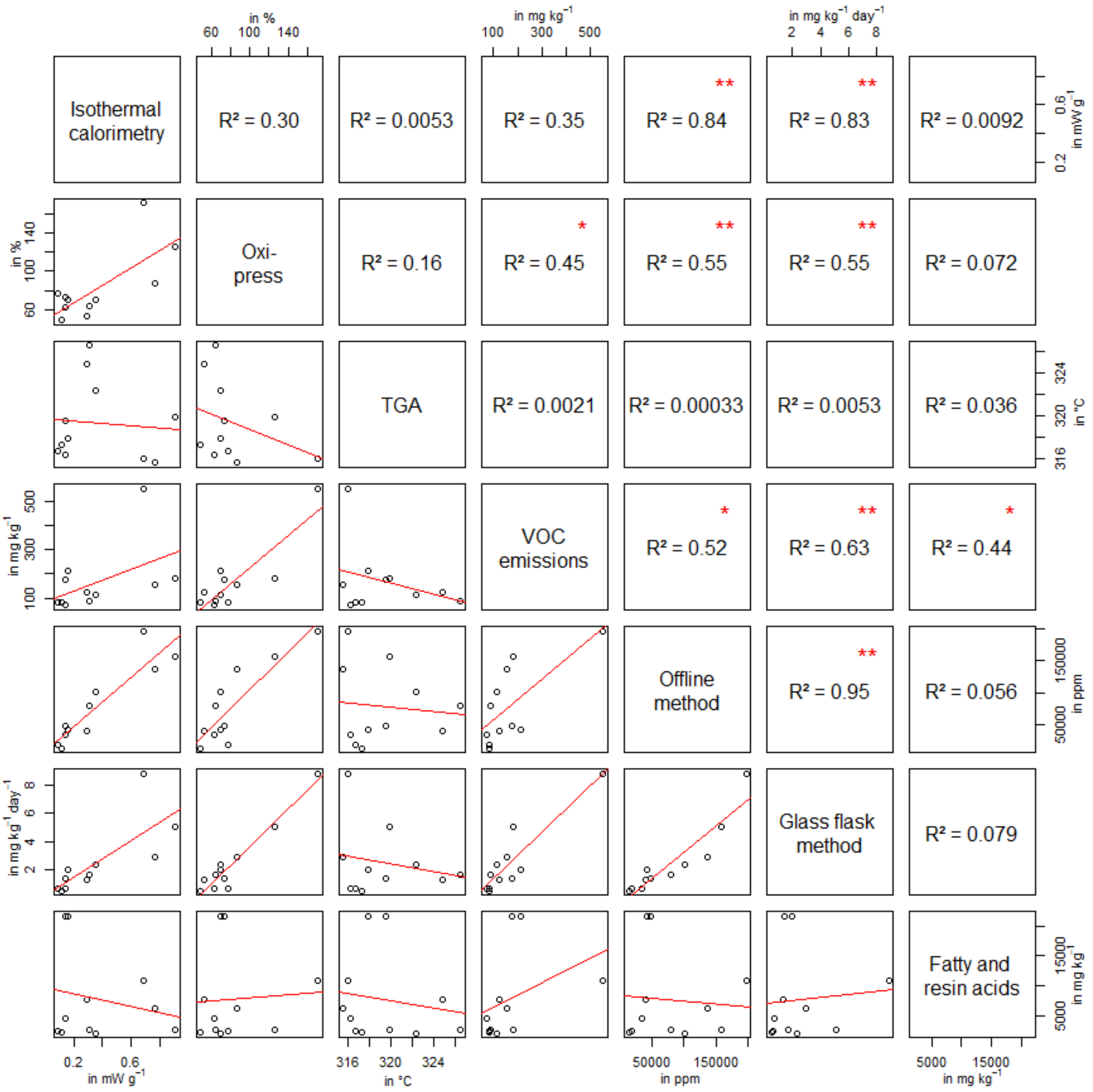


**Figure** 8 Illustration of the relations between the individual methods. The relations are visualised in the scatterplots with additional representation of the linear regressions of the two compared methods. The given values presented the coefficient of determination ($R^2$) (if *p*-thresholds were ≤ 0.05 and 0.01, * and ** indicated it, respectively) (Source: Sedlmayer *et al.* 2018 [23].

The second and third highest correlations were achieved between the results from isothermal calorimetry and offline method and between isothermal calorimetry and glass flask method. In contrast to the correlation between the two off-gassing methods described above, these two correlations were correlations between a self-heating and an off-gassing method. Even though these methods are used to determine different aspects, all three methods assessed the oxidation or degradation of extractives in a wider context. The assessment by these three methods resulted in similar classifications in terms of their self-heating or off-gassing tendency. In addition, results of isothermal calorimetry were validated by the test results of the medium-scale (1 $m^3$) basket heating test and other full-scale tests [43]. Thus, the results from large scale investigations of the same pellets and the good agreement between those three methods strengthened the results. Moreover, the application of these methods for the assessment of self-heating and off-gassing tendency is highly recommended.

Furthermore, the correlation analyses revealed a very significant correlation between the results of VOC emissions and glass flask method. This relation was well explained by the fact that they measured similar parameters. Within VOC emissions the total amount of emitted aldehydes and ketones were measured. With glass flask method the CO, $CO_2$ and total VOC concentrations were assessed. This means that with the glass flask method, as with VOC emissions, the total amount of emitted aldehydes and ketones was included.

Moreover, the comparison of oxi-press with offline method and oxi-press with glass flask method resulted in very high correlations. This relation could also be explained by the analysed parameters. Where the self-heating method Oxi-press measured oxygen depletion, the two off-gassing methods, offline and glass flask method, measured the concentration of released emissions. The release of emissions was caused by the degradation of wood extractives with simultaneous oxygen consumption. The processes for off-gassing formation and oxygen consumption during wood pellets storage are therefore most likely related [27] [29] [78].

The results from Isothermal calorimetry (self-heating method), offline and glass flask method (off-gassing methods) indicated that self-heating and off-gassing behaved similarly or were similarly influenced. Therefore, it was further assumed that off-gassing most likely occurred together with self-heating. It is likely that a self-heating tendency of pellets could be estimated by measuring off-gassing during wood pellets storage.

The assessment of wood pellets from spruce, pine and their blends indicated that TGA and fatty and resin acids can give additional information on self-heating and off-gassing behaviour. However, neither TGA nor fatty and resin acids are recommended to predict self-heating or off-gassing, due to the lack of very significant correlations with the other off-gassing and self-heating methods, but also because they examine considerably different parameters.

## II.4.2. Storage influencing factors on off-gassing emissions from stored wood pellets

### II.4.2.1. Influence of headspace of off-gassing emissions

Kuang *et al.* [56] defined the headspace ratio ($HS_{ratio}$) as the ratio of headspace volume ($V - V_{bulk}$) divided by the container volume (V) (see Equation 1). The bulk volume of the filled pellets ($V_{bulk}$) is calculated by dividing the weight of the pellets ($m_{pellet}$) by the pellets bulk density ($\rho_{bulk}$) (see Equation 2).

$$HS_{ratio} = \frac{V - V_{bulk}}{V}$$

**Equation 1**

$$V_{bulk} = \frac{m_{pellet}}{\rho_{bulk}}$$

**Equation 2**

The headspace ratios of 25, 50 and 75% were investigated in sealed containers by Emhofer [21] and Kuang *et al.* [56] [54]. However, results of the glass flask experiments of the past few years indicated that very reactive pellets sometimes require even higher headspace ratios because the residual $O_2$ concentration was lower than 5%. Thus, it was assumed that the formation of the emissions was inhibited due to the low $O_2$ concentration, making it more difficult to compare the resulting off-gassing emissions.

Thus, the influence of headspace ratio on emission rates was investigated using the glass flask method. The applied method was described in chapter II.3.2.4. The application of the method using sample weight of 2.4 kg revealed a headspace ratio of 39% (V/V) and the use of 0.3 kg pellets resulted in a headspace of 92% (V/V).

The emission rates for CO, $CO_2$ and $VOC_{tot}$ as well as the residual $O_2$ concentration of 7 pellets batches are listed in Table 11. The analysed wood pellets consisted of pine and spruce (ratio of 50/50) and proved to be very reactive with CO emission rates of 1.2 to 2.6 in mg $kg^{-1}$ $pellets_{db}$ $day^{-1}$. In comparison, the examined pellets by Emhofer showed rates of 0.24 to 0.36 mg $kg^{-1}$ $fuel_{db}$ $day^{-1}$ [21]. By increasing the headspace ratio from 39 to 92% all CO emission rates were increased. The same trend was observed for $CO_2$ and $VOC_{tot}$ emission rates. In contrast to the results of Emhofer, the residual $O_2$ concentration of the pellets, increased considerably due to headspace raise.

The influence of headspace on the formation of $CO_2$ is particularly high. By increasing headspace ratio from 39 to 92% the $CO_2$ emission rates were at least doubled and once even tripled. The CO and $VOC_{tot}$ emission rates increased considerably as well. The increase of the headspace ratio led to an increase of the residual oxygen concentration. The lower the residual oxygen concentration at a headspace ratio of 39%, the greater the rise of residual oxygen concentration due to the increased headspace ratio to 92%.

The comparison of the headspace ratios of 39 and 92% and their emission rates considering the residual oxygen concentration, clearly showed that the emission rates were higher at higher headspace ratios. The results indicated that less oxygen was available for the oxidative reaction in the sealed flask when more pellets were filled in the flasks leading to lower emission rates.

**Table 11** List of the investigated pellets batches and the headspace ratio ($HS_{ratio}$) and the resulting emission rates considering the residual $O_2$ concentration.

| Pellets batch | $HS_{ratio}$ in % | pellets weight in kg | CO | $CO_2$ | $VOC_{tot}$ | Residual $O_2$ in % (V/V) |
|---|---|---|---|---|---|---|
| | | | in mg $kg^{-1}$ $pellets_{db}$ $day^{-1}$ | | | |
| WP 23 | 39 | 2.4 | 2.42 | 7.82 | 2.37 | 3.4 |
| | *92* | *0.3* | *4.17* | *23.67* | *4.26* | *18.1* |
| WP 24 | 39 | 2.4 | 2.45 | 6.72 | 1.75 | 1.1 |
| | *92* | *0.3* | *3.60* | *21.33* | *2.78* | *18.3* |
| WP 25 | 39 | 2.4 | 2.41 | 7.45 | 1.77 | 2.6 |
| | *92* | *0.3* | *3.88* | *29.99* | *2.20* | *18.2* |
| WP 26 | 39 | 2.4 | 2.09 | 7.01 | 1.56 | 4.7 |
| | 92 | 0.3 | 2.68 | 14.44 | 2.12 | 17.5 |
| WP 27 | 39 | 2.4 | 2.26 | 9.04 | 1.79 | 4.9 |
| | *92* | *0.3* | *4.19* | *23.47* | *2.75* | *18.2* |
| WP 28 | 39 | 2.4 | 1.15 | 3.84 | 0.27 | 12.5 |
| | *92* | *0.3* | *1.60* | *11.02* | *0.81* | *19.4* |
| WP 29 | 39 | 2.4 | 2.58 | 8.19 | 1.94 | 2.7 |
| | *92* | *0.3* | *2.76* | *16.58* | *1.99* | *18.8* |

When comparing emission rates, it would be advisable to also consider residual oxygen concentration. Therefore, the residual oxygen concentration in the flask at the time of measurement should be given. In this way it can be assessed whether the emissions formed occurred despite, or without a lack of oxygen. Moreover, emission rates would be difficult to compare if they were obtained at very different $O_2$ levels.

According to Kuang *et al.* [56] the peak emission rate factor of $CO_2$, CO and $CH_4$ decreased with decreasing headspace ratio from 75 to 25%. Moreover, the slope of the emission factor curve at the beginning of storage declined as the headspace ratio declined. This was explained by the fact that more wood pellets were in the sealed container and simultaneously less oxygen for oxidation reactions was available in the sealed container.

Furthermore, the influence of different headspace ratio of 25 and 70% on emission rates were investigated. Again, higher CO, $CO_2$ and $VOC_{tot}$ emission rates with higher headspace ratio were determined. Those results showed that despite very high and similar residual oxygen concentration, emissions increased with increasing headspace. For this, no precise explanation could be provided [21].

### II.4.2.2. Influence of available $O_2$ on off-gassing emissions

The following section is based on the peer-reviewed journal paper number 2. The performance and results of these simulated ventilation storage experiments were published in Meier *et al.* [26]. In these experiments the influence of available $O_2$ on CO, $CO_2$, VOC and $CH_4$ off-gassing emissions during storage of commercially available wood pellets (WP 30) were investigated using the pellets tank method. Three experiments with different storage conditions were performed: i) <1% (V/V) $O_2$, >99% (V/V) $N_2$; ii) 20% (V/V) $O_2$, 80% (V/V) $N_2$ and iii) 35% (V/V) $O_2$, 65% (V/V) $N_2$;

The results of these experiments are presented in Figure 9; the detailed discussion can be found in Meier *et al.* [26]. The main findings are outlined below. According to Meier *et al.* [26], the off-gassing formation is presented in emission rates and emission factors. The emission rate is the formed gas emission within 24 hours, from the day before until the respective day. The emission factor is the formed gas emission from the first measurement point until the respective day.

The emission rate of all gases decreased over the three-week storage, regardless of the available $O_2$ concentration. Conclusion: the pellets become less reactive. In contrast, former results from Kuang indicated that under reduced $O_2$ conditions, the concentration of emissions remains constant when stored for several days [54] [56]. The reduction in emissions established by Meier et al. was slower than the decrease in emissions reported by Kuang. This was mainly due to the constant available $O_2$ concentration in the presented simulated ventilation storage.

Moreover, the $O_2$ concentration significantly influenced emission rates. The $CO_2$ and CO emission rates increased with increasing $O_2$ concentration. This was mainly due to the fact that oxidation processes were enhanced at higher $O_2$ concentration. Contrary, the VOC and $CH_4$. emission rates decreased with increased $O_2$ concentration. Because $CH_4$ is not a common oxidation product, this is obvious, even though wood and wood pellets emitted $CH_4$ during storage [12] [29] [54] [56] [78]. However, decrease of VOC emissions despite higher $O_2$ concentration was astonishing. VOC emissions, belongs to intermediate and by products of oxidation processes [79] [80]. The increase of VOC emissions despite lower $O_2$ concentration might be mainly caused by the fact that further degradation processes were inhibited. These in particular would lead to more CO and $CO_2$ emissions. Despite the present results it is entirely feasible that the formation of VOC emissions was enhanced by higher $O_2$ concentration. However, it was assumed that the actually expected VOC increase was overlaid by further reactions of VOCs that led to additional $CO_2$ and CO. Therefore, it is mentioned that the applied experimental setup could not be used for the independent study of these reaction pathways.

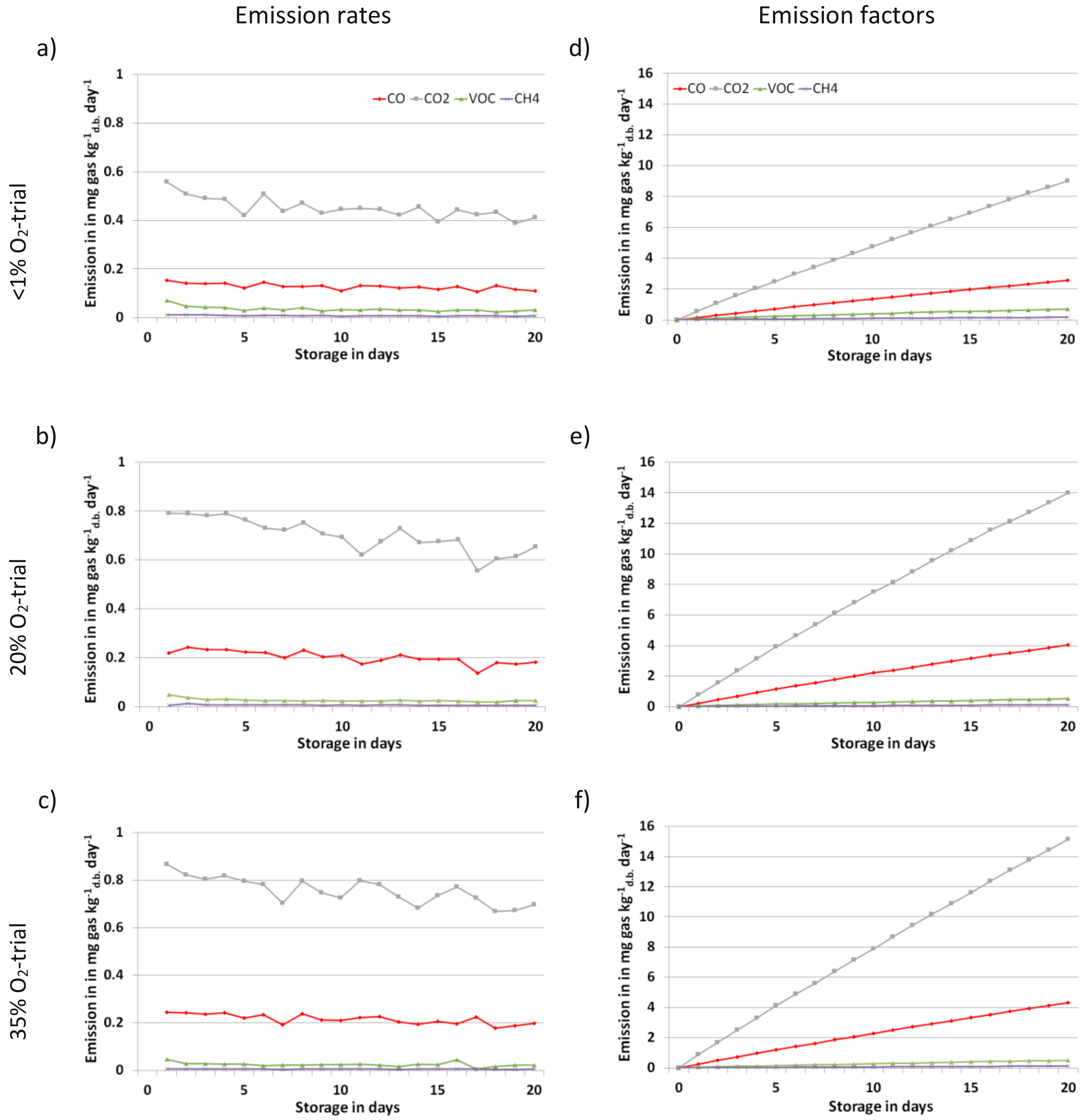


**Figure 9** Illustrations of the emission rate trends of the three experiments a) <1% (V/V) $O_2$, b) 20% (V/V) $O_2$ and c) 35% (V/V) $O_2$ and emission factor trends of d) <1% (V/V) $O_2$, e) 20% (V/V) $O_2$ and f) 35% (V/V) $O_2$. These figures were taken from Meier *et al.* 2016 and were further adapted [26].

In addition, the results of <1% (V/V) indicated lower emission rates compared to higher $O_2$ concentration. It is worth noting, that even with almost no present oxygen, emissions were formed and not suppressed. The emissions formed at <1% (V/V) $O_2$ corresponded to about half to the experiment at 20% (V/V) $O_2$.

The course of emissions under simulated ventilation provided new insights in the context of safety measures applied to pellets storage. The results let assume that pellets stored under ventilated storage conditions compared to pellets stored under sealed storage conditions may have a higher off-gassing activity for a much longer period than previously thought. Ventilation of pellets storages before entry still remains the best practical solution to improve the storage atmosphere and therefore reduce the risk of high CO and low $O_2$ concentrations in pellets storages. It is of great importance that pellets storages are always properly ventilated before entering. Ventilation must also be carried out if the pellets are stored for a long time period.

### II.4.2.3. Influence of relative humidity on off-gassing emissions

The influence of the relative humidity above the pellets bulk on the formation of CO, $CO_2$, VOCs as well as on the consumption of $O_2$ was investigated. For this purpose, two experiments with different relative humidities in the pellets tank (closed system) using saturated salt solutions (see Table 12 ) were performed. Therefore, pellets made from pine sawdust were investigated. The pellets were frozen at -18° C until analysis and were defrosted at 22° C for 16 h. Unlike the procedure described in chapter II.3.2.5, 1 kg wood pellets were put in the pellets tank. The saturated salt solution was then placed on the pellets bulk and the pellets tank was closed.

**Table 12** List of the used salts to set the relative humidity inside the pellets tank, the achieved relative humidity and the average temperature.

| Salt | Chemical formula | Dissolved salt in g 100 $g^{-1}$ $H_2O$ | Expected RH in % | Achieved RH in % | T in °C |
|---|---|---|---|---|---|
| potassium acetate | $CH_3COOK$ | 271 | 22 | 24 | 22.2 |
| sodium chloride | NaCl | 36 | 75 | 62 | 21.9 |

The emission factors and the emission rates of both storage experiments at different relative humidities are presented in Figure 10. The comparison of the emission rates indicated the individual off-gassing behaviour of each measurement point. The comparison of the rates showed the greatest differences for $CO_2$ and VOC. The stored pellets batch tended to emit more $CO_2$ and more VOC at higher humidity. However, the measuring point on day 5 behaved differently in both cases. $CH_4$ emissions also tended to be higher at higher humidity, although the differences were smaller. These observations are consistent with the findings of Kuang *et al*. [54]. In contrast to the $CO_2$, VOC and $CH_4$ emission rates, the CO rates behaved differently. The emission rates for CO were lower at higher humidity.

The emission factors indicated the total amount of formed emissions during the storage test. The $CO_2$ and VOC emission factors were higher at the higher humidity throughout the whole storage period. The CO emission factors behaved the other way around. In any case, it should be noted that the differences in CO emission rates between lower and higher humidity were considerably smaller than in the $CO_2$ and VOC emission rates. This small difference was also seen in Kuang's results at the beginning of the storage experiments [54].

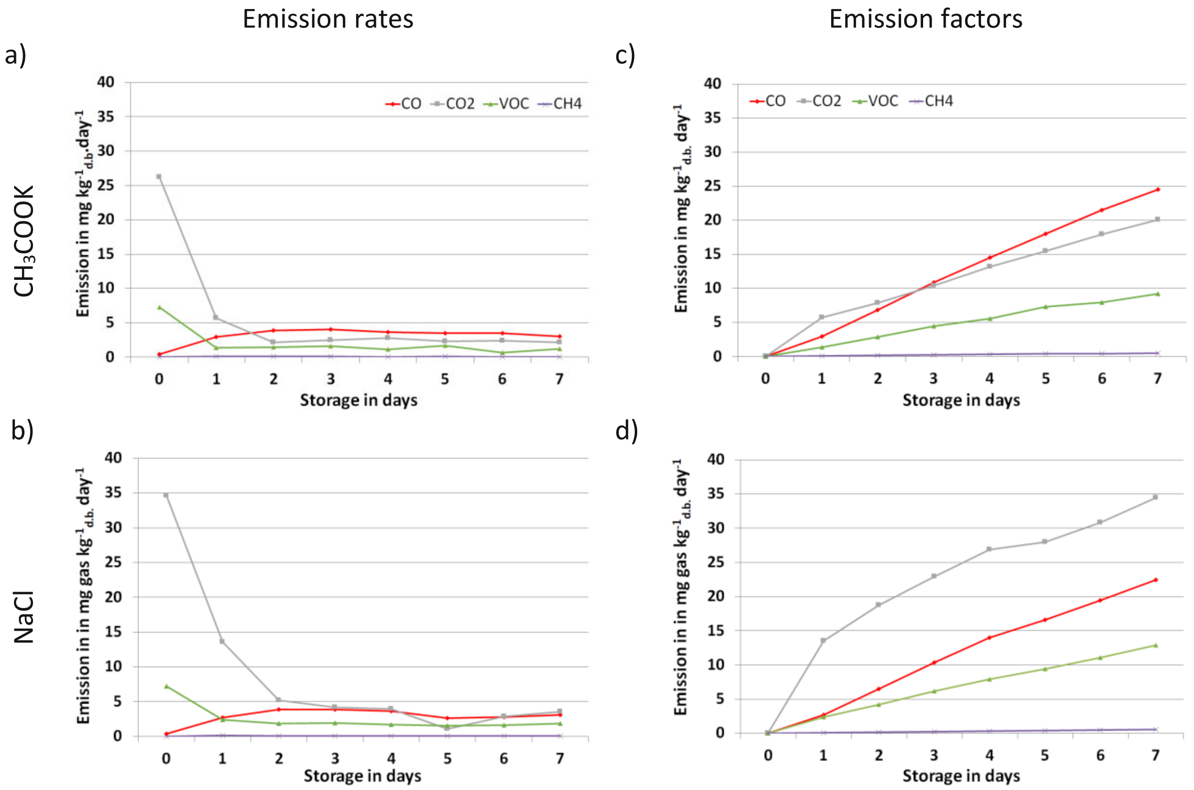


**Figure 10** Illustrations of the emission rate trends of the two relative humidity experiments a) with $CH_3COOK$ and b) with NaCl and emission factor trends of the two relative humidity experiments c) with $CH_3COOK$ and d) with NaCl.

## II.4.3. Off-gassing characteristics of biomass pellets

### II.4.3.1. Various biomass

Besides wood pellets, further biomass pellets were investigated. For this purpose, the glass flask method was used. The investigated pellets batches and their off-gassing emissions are listed in Table 13.

**Table 13** List of the off-gassing emssion rates for CO, $CO_2$ and $VOC_{tot}$ and the residual $O_2$ concentration of the investigated biomass pellets batches.

| Batch | Raw material | CO | $CO_2$ | $VOC_{tot}$ | Residual $O_2$ |
|---|---|---|---|---|---|
| | | in mg $kg^{-1}$ $pellets_{db}$ $day^{-1}$ | | | in % (V/V) |
| BP 1 | straw | 0.08 | 2.89 | 0.01 | 19.1 |
| BP 2 | eucalyptus | 0.04 | 1.12 | 0.02 | 17.8 |
| BP 3 | 50/50 vine pruning/vine pomace | 0.06 | 2.19 | 0.04 | 19.7 |
| BP 4 | torrefied spruce sawdust | 0.42 | 2.36 | 0.01 | 18.6 |
| BP5 | torrefied pine sawdust | 0.23 | 1.25 | 0.00 | 19.2 |

When comparing the emission rates of the biomass pellets from Table 13 with the emission rates of wood pellets from Table 6 and Table 7, the emission rates of the biomass pellets tend to be in the medium to lower range. Especially the values of CO emission rates are low. The highest CO emission rate of 0.42 mg $kg^{-1}$ $pellets_{db}$ $day^{-1}$ was found in BP 4, the pellets made of torrefied spruce sawdust.

Both, Borén *et al.* [60] and Tumuluru *et al.* [81] presented CO emission trends in ppm from torrefied biomass.

Within the five investigated biomass pellets batches the BP 1, the straw pellets batch, formed the highest $CO_2$ emission rate of 2.89 mg $kg^{-1}$ $pellets_{db}$ $day^{-1}$. Furthermore, the highest $VOC_{tot}$ emission rate was calculated for BP 3 with 0.04 mg $kg^{-1}$ $pellets_{db}$ $day^{-1}$. Overall, little off-gassing data is available on different biomass pellets. However, Emhofer published emission rates of various agricultural and torrefied pellets. Off-gassing emissions from ground switchgrass [81], miscanthus shavings and miscanthus [57] pellets. These published emission rates are similar in range compared to the results above. Thus, it could be assumed that non-wood pellets also contain ingredients that degrade through oxidation and form various emissions.

#### II.4.3.2. Sensory evaluation of non-wood and torrefied wood pellets

This section is based on the peer-reviewed journal paper number 3. In total, eight pellets batches from different biomasses were investigated with regard to their sensory properties. Each pellets batch was provided with sensor descriptions by a well-trained sensory panel. Detailed information on the procedure and the investigated pellets batches are published in Pöllinger-Zierler *et al.* [21]. Results of the sensory evaluation are presented in Table 14.

Overall, the attributed sensory descriptors of the pellets corresponded well with the expected odour properties of the used raw material. The pellets were sensory described as follows: The miscanthus and straw pellets batches were attributed to straw or hay like. The straw pellets batch were described as green and herbal. Moreover, the eucalyptus pellets batch was assigned as fresh and minty. The eucalyptus or better known the camphor like notes were also noticed as medicinal by a part of the sensory panel. The odour of the rapeseed pellets batch was perceived as fatty and oily with nutty notes. These sensory notes are expected from a raw material that is rich in fatty acids. The pellets made of dried distillers' grains with soluble were described as roasted, malty and slightly fruity. The pellets made of grapevine were perceived by the panel as fruity and green. The two pellets batches made of torrefied wood were similarly described. Both pellets batches were perceived as smoky, phenolic, and burnt. Moreover, this odour was associated with burning or coking processes. However, the pellets made of torrefied spruce wood pellets received more of these burnt and coked descriptors then the pellets made of torrefied pinewood. Additionally, the torrefied pinewood pellets batch was perceived as resinous and woody [67].

**Table 14** List of the investigated biomass pellets batches and the corresponding batch number of the referring peer-reviewed journal paper. The raw material and source and their obtained sensory description are depicted. The table is adapted according to Pöllinger-Zierler *et al.* 2019 [67].

| Batch | Journal batch | Raw material | Source | Production | Sensory description |
|---|---|---|---|---|---|
| BP 1 | straw | straw | Danish pelletising company | ISPP | greenish, herbage, resinous, aromatic, hay like |
| BP 2 | eucalyptus | eucalyptus | Spanish pelletising company | ISPP | Camphor like, minty, refreshing, medicinal, essential |
| BP 3 | grapevine | 50/50 vine pruning/vine pomace | German research institute | LSPP | dried fruits, green, herbage, sweet |
| BP 4 | torr. spruce wood | torrefied spruce sawdust | Dutch pelletising company 1 | LSPP | smoky, phenolic, woody, aromatic. smoked ham like |
| BP5 | torr. pinewood | torrefied pine sawdust | Dutch pelletising company 2 | LSPP | resinous, burnt notes, dried wood, pungent |
| BP 6 | miscanthus | miscanthus | German research institute | LSPP | dried grain, straw and hay like, “dusty” |
| BP 7 | DDGS | dried distillers’ grains with solubles | German brewery | LSPP | roasted, malty, cereal like, sweetish, mature and ripe fruits |
| BP 8 | rape | extracted rape seed | German oil producing company | LSPP | oily, nutty, rancid, like feed for fattening animals |

The sensory evaluation of the pellets from different biomass provides an estimation of the presumably perceived odour of the pellets during storage. The odour released during storage is considered an important property as the probable emitted malodour has a significant influence on product acceptance by the end user. Even the tasting of small quantities of pellets led to a perceived odour by the panellists. Furthermore, not only the intensity but also the quality of the perceived odour is highly relevant [67].

In other studies wood pellets were also investigated with regard to their odour properties [67] [82]. The panellists tasted the wood pellets and described the pellets odour as following: mushroom sweet, pungent, smelling of urine, rotten fruit, cheesy, fatty, rancid, lemony, cow shed, green, grassy, paint like [82]. Wood pellets are known to emit various VOCs [27] [29] [83] [84]. For instance, hexanal was identified as a major representative of VOCs during the storage of solid wood fuel [28] [29] [85] [86]. Moreover, hexanal is known to emit an unpleasant odour and is responsible for irritant odour [87] [88]. The unpleasant odour is described as green and grassy.

Not only wood pellets but also pellets from other biomass or torrefied wood are associated with a partly unpleasant odour. It should also be mentioned that the smells would be perceived with different intensities by different people. Moreover, it is important that the pellets storage is ventilated to the outside and is tightly connected to the surrounding building. The possible malodours should not be perceived by the end user in order not to worry the end user and reduce product acceptance.

### II.4.3.3. Analysis of VOCs from non-wood and torrefied wood pellets

This section is based on the peer-reviewed journal paper number 3. Again, eight pellets batches from different biomass resources were investigated with regard to their release of individual VOCs. Detailed information on the procedure and the investigated pellets batches are published in Pöllinger-Zierler *et al.* [67].

The VOCs of alternative and torrefied wood pellets were analysed using solid-phase micro extraction (HS-SPME) for the enrichment of VOCs and gas chromatography mass spectrometry (GC-MS) for VOCs identification. Details on the investigated pellets batches are listed in Table 14. In total, 59 volatile compounds from 7 classes (acids, esters, alcohols, aldehydes & ketones, terpenes, heterocyclic compounds and aromatic compounds & phenols) were identified. An overview of all identified substance classes and their relative distribution can be found in Pöllinger-Zierler *et al.* [67]. The five most prevalent VOCs in each pellets batch and the total number of identified VOCs of each batch are shown in Table 15 and Table 16.

**Table 15** List of the 5 most frequent VOCs of the examined biomass pellets batches BP 1 to BP 4.

| Ranking | BP 1 straw | BP 2 eucalyptus | BP 3 grapevine | BP4 torrefied spruce |
|---|---|---|---|---|
| 1 | hexanal | 1,8-Cineol | α-copaene | α-copaene |
| 2 | 2-pentylfuran | o-Cymene | hexanal | 2-furancarboxaldehyde |
| 3 | methyl acetate | limonene | 1-Hexanol | acetic acid |
| 4 | nonanal | hexanal | limonene | propanoic acid |
| 5 | heptanal | α-pinene | acetic acid | 2-methoxyphenol |
| Total VOCs | 25 | 19 | 33 | 24 |

**Table 16** List of the 5 most frequent VOCs of the examined biomass pellets batches BP 5 to BP 8.

| Ranking | BP 5 torrefied pine | BP 6 miscanthus | BP 7 DDGS | BP 8 rapeseed |
|---|---|---|---|---|
| 1 | α-copaene | acetic acid | α-copaene | hexanal |
| 2 | hexanal | hexanal | 2-furancarboxaldehyde | acetic acid |
| 3 | o-cymene | 2-pentylfuran | 2,3-Butanediol | butanoic acid |
| 4 | 2-furancarboxaldehyde | methyl acetate | 2-Phenylethanol | 2-methyl pyrazine |
| 5 | heptanal | 2-furancarboxaldehyde | dihydro-2(3H)-furanone | dihydro-2(3H)-furanone |
| Total VOCs | 27 | 18 | 19 | 22 |

Five out of 59 VOCs were identified in all investigated pellets batches: acetic acid, methyl acetate, hexanal, benzaldehyde, 2-pentylfuran. Hexanal was also detected in connection with the storage of wood pellets [28] [29] [52] [83] [85]. In the eight examined pellets batches, hexanal was identified six times among the 5 most frequent VOCs. It is not surprising that hexanal occurs, as it is a degradation product known to occur in lipids. [89]. In other studies wood pellets were also investigated with regard to their odour properties [67] [82]. Therefore, mainly three groups of chemical substances were identified which were responsible for the malodour of wood pellets during storage: acids, aldehydes and terpenes. A further study examined pellets made from softwood, hardwood, and blended wood pellets and classified four main VOCs, namely: methanol, pentane, pentanal, and hexanal. Pentanal was also determined in five pellets batches in the present study, whereas methanol and pentane were not identified. Moreover, acetic acid, which was determined in all investigated batches, was ranked four times within the top 5. Acetic acid has also been identified as an emission from wood and wood pellets [84] [88]. Another striking feature was that α-copaene appeared four times in the first place. Furthermore, 1,8-cineol was only identified once, in the eucalyptus batch.

Moreover, wood pellets are known to emit various VOCs [27] [29] [83] [84]. For instance, hexanal was identified as a major representative of VOCs during the storage of solid wood fuels [28] [29] [85] [86]. To add to this, hexanal is known to emit unpleasant odour and is responsible for irritant odour [87] [88]. The unpleasant odour is described as green and grassy. Since the perceived odour is dependent on the odour activity value, the perceived smell becomes stronger with increasing hexanal concentration [82].

## II.5. Conclusions

**Off-gassing characteristics of wood pellets**

- Off-gassing emissions and total organic extractive content of sawdust from spruce, pine, larch, and hardwood and wood pellets made from them were determined and compared with each other. The pelletisation of that sawdust decreased the total amount of extractive content. This reduction was mainly due to the thermal and mechanical treatment during the pelletisation process. Based on the present result, no clear trend was found on how emissions are affected by the pelletisation process. It is most likely that CO emissions tend to be increased by the temperature and mechanical treatment during pelletising.
- The joint investigation of the organic extractive content with the off-gassing behaviour of commercially available wood pellets did not show a clear correlation. Even if extractives are basically responsible for the off-gassing behaviour, the emissions cannot be estimated on the basis of the extractive content. This can be explained by the fact that the off-gassing behaviour is influenced by many other factors, such as pelletisation process, storage temperatures, storage time, packaging and delivery of the pellets. Since the investigated pellets batches were intentionally purchased at retail, no information is available on how the pellets were treated prior to off-gassing analyses.

- The analyses of wood pellets regarding their off-gassing and odour behaviour revealed that wood pellets that are perceived with malodour do not necessarily indicate a higher off-gassing reactivity than pellets that are perceived with no malodour. Thus, the decisive factors for the perceived odour of wood pellets are the odour threshold and concentration of the component.
- The link between off-gassing and self-heating was investigated by the parallel investigation of wood pellets with off-gassing and self-heating methods. Results indicated that pellets with a high off-gassing reactivity also have a high self-heating reactivity. Therefore, it is assumed that off-gassing is associated with self-heating. Hence, self-heating tendencies in large scale pellets storages might be estimated by prior off-gassing analyses.

**Storage influencing factors on off-gassing emissions from stored wood pellets**

- Both, the headspace and $O_2$ availability studies revealed that, the more $O_2$ was available during the storage experiment, the higher the emission rates for CO, $CO_2$ and VOC were. This is highly plausible as the reactions responsible for off-gassing are oxidation processes.
- Furthermore, the investigations of the $O_2$ availability indicated that pellets under ventilated storage conditions demonstrate a longer reactivity than already proven in previously closed storage investigations. The oxidation processes are indeed favoured by the recommended ventilation of the pellets storages at the end user. However, it is assumed that the dilution reached through constant ventilation of pellets storages achieves a greater effect.
- The investigation of off-gassing emission at two different relative humidities showed that VOC and $CO_2$ emissions were higher at the higher relative humidity, while CO emissions were higher at the lower relative humidity. The results for CO are not consistent with previously published insights. Therefore, it is suggested to investigate the influence of relative humidity on off-gassing formation again. Moreover, it is worth mentioning that the relative humidity should not be too high during pellets storage, as a high relative humidity is very likely to reduce the physical properties of pellets.

**Off-gassing characteristics of biomass pellets**

- Off-gassing biomass pellets analyses revealed that biomass pellets also form CO, $CO_2$ and VOCs. The amount of formed emissions is roughly in the range of wood pellets. Thus, concluding that when storing large quantities of biomass or biomass pellets, attention should also be paid to increased und thus harmful concentrations of CO.
- The sensory description of biomass pellets indicated very individually perceived odours. As expected, the odour of biomass pellets is dominated by the odour of the inserted biomass

raw material. The assumption is that natural degradation processes raise the resulting VOCs which in turn might increase the odour. Hence, unpleasant odours cannot be excluded during the storage of large amounts of biomass pellets.

- The analyses of the occurring VOCs during the storage of biomass pellets showed that some of the released VOCs are the same and some are different compared to wood pellets. Hexanal, the most prominent VOC regarding the storage of wood pellets, was detected in all investigated biomass pellets batches. Moreover, hexanal is a known degradation product of lipids. Thus, it is supposed that, as with wood pellets, organic ingredients are also degraded in pellets made from other biomass and, therefore, form various VOCs.
- The storage of biomass pellets also entails off-gassing. The extent of this cannot be estimated from the available results. However, even when storing biomass pellets, entering a tightly built storage facility should be avoided. Furthermore, when entering is necessary it is also recommended to ventilate the storage sufficiently before entering.

# III. Effect of pellets production on off-gassing behaviour

## III.1. Introduction

Due to several fatal accidents during wood pellets transportation and storage [13] [90] [91] studies on the investigation of the off-gassing phenomenon were performed. Thereby, CO, $CO_2$, $CH_4$ and various VOCs are identified of so called off-gassing emissions [10] [13] [26] [27] [29] [78] [91]. Simultaneous oxygen depletion occurs during pellets storage leading to an additional danger for humans health [54] [56]. Besides studies on the underlying mechanisms for off-gassing emissions [13] [53] [76] investigations on influencing factors on off-gassing emissions were conducted. Thus, various storage related influencing factors on off-gassing emissions from stored wood pellets were investigated. The temperature and available oxygen in the storage of pellets reveal a considerable influence on the resulting off-gassing emissions. The emissions increased considerably with growing storage temperature [21] [54] [55] [92] [93] and oxygen availability [21] [26] [54].

In addition to storage related parameters, influencing variables based on the pellets material itself were identified. Emhofer [21] revealed that CO emission rates for pine pellets were on average three times higher than for spruce pellets. Furthermore, pine pellets are more reactive than spruce pellets regarding their VOC emissions [21] [27] [73] [74]. Also, the VOC concentrations for softwood pellets are significantly higher than for blended or hardwood pellets [83]. Moreover, the maturity of the used raw material influences the off-gassing emissions from stored wood pellets. The comparison of off-gassing emissions from fresh sawdust with matured shavings reveals that matured shavings form less emissions than fresh sawdust [21]. Investigations have proven that emission rates from stored pellets declined with increasing storage time [21] [22] [26]. Indicating older pellets produced fewer emissions than freshly produced pellets. Already in 2012, Arshadi [75] has indicated a decrease in formed emissions by removing fatty and resin acids from raw material prior to pellets production compared to the wood pellets made from the untreated raw material.

Additionally, production related influential parameters on off-gassing emissions were assumed. The pellets production process itself also indicated an impact on the subsequent off-gassing behaviour. Furthermore, the influence of press conditions on off-gassing properties of wood pellets was demonstrated [21]. Two pellets batches were produced, each from one spruce stem of comparable age under the same process conditions. In addition, another batch of pellets was produced from one of the two logs at half the throughput, increasing the residence time and thermal treatment. The emission rates of the pellets under the same process conditions but comparable raw material differed less than the rates of the pellets batches from the same raw material but different process conditions. Suggesting that the change in pressing conditions caused these higher differences in emission rates. Moreover, Rahman revealed that off-gassing emissions were reduced by continuous ozonisation of the fibres prior to wood pellets production [94]. Thus, it was proposed that with optimal pellets production settings the later formation of aldehydes could be reduced [28].

Previous investigations on off-gassing mechanisms have identified that off-gassing emissions are initiated by autoxidation of unsaturated compounds by oxygen [53]. However, the total degradation mechanisms have not been fully clarified yet. Considering the initiation step for off-gassing emissions, the autoxidation of unsaturated compounds, it can be assumed that is the autoxidation initiation was reduced or eliminated, then CO off-gassing from wood pellets would be substantially minimized. Furthermore, it was shown that extraction of wood components like fatty and resin acids significantly reduced off-gassing emissions [75] [76].

## III.2. Objectives and approach

The objective of this chapter is to prove whether the off-gassing behaviour of pellets can be influenced by intervening in the wood pellets production process. Thus, pelletising trials are performed with the aim of reducing off-gassing emissions. Those investigations are done by modifications in laboratory and industrial wood pellets production processes. Therefore, a total of three approaches are carried out based on the knowledge of the underlying mechanism.

This chapter is based on the peer-reviewed journal paper number 4. In addition, further aspects in pellets production processes are examined and presented in the thesis.

### III.2.1. Addition of additives in pellets production

Firstly, the adding of different additives in wood pellets production is investigated. The application of additives like natural and synthetic antioxidants in food industry is common [95]. The usage of antioxidants for preventing oxidation processes in wood pellets has been investigated [64] [20]. Additives are commonly used in wood pellets production and can be applied in order to improve fuel quality and production process or to reduce emissions. Meeting the requirements of ISO standard 17225-2, the total content of additives must not exceed 2% (m/m) [2].

Thus, within this study, different antioxidative substances in wood pellets production series are investigated. These production experiments are conducted to reduce off-gassing emissions by decreasing the autoxidation of wood extractives. Therefore, the synthetic antioxidant acetyl salicylic acid (ASA) [96] and naturally occurring antioxidants like grape pomace powder (GPP) [97] and hop grains (HG) [98] are used. Moreover, slaked lime and quicklime are applied as further additives in order to investigate the influence on off-gassing emissions due to the saponification of fatty acids [99]. It is assumed that lime binds at the carboxyl group and thus inactivates lipid groups.

- The aim is to produce wood pellets with reduced off-gassing formation by using additives in wood pellets production.

### III.2.2. Blends of raw material in pellets production

Secondly, various wood resources with known antioxidant effects are used [100] [101] [102] [103] for blends in pellets production processes. Some of the ingredients as for example (poly)phenolic compounds may act as antioxidant and thus reduce off-gassing emissions during the subsequent storage [104] [105] [106] [107]. For this purpose, larch (*Larix decidua*), oak (*Quercus robur*), willow (Salix alba) and maritime pine (*Pinus pinaster*) are used. In contrast to the added additives, larger quantities > 2% (m/m) are used for blends.

- The aim is to produce wood pellets with reduced off-gassing formation by blending with different wood raw material in pellets production.

### III.2.3. Ventilation in pellets production

Thirdly, the end of the pellets production process is investigated. Thus, the pellets cooling and ventilation processes are modified. Again, under the assumption that autoxidation is the initial process for off-gassing in wood pellets during storage [53], it might be possible to induce a forced oxidation of wood extractives by the extension of ventilation of the immediately produced pellets after production in order to reduce the subsequent off-gassing emissions. Furthermore, by cooling the ventilation air, the effect of cooling pellets on the off-gassing behaviour is investigated. In addition, the effect of using a different ventilation technology in terms of off-gassing reduction is evaluated.

- The aim is to indicate whether the change in ventilation process in pellets production can reduce the off-gassing formation of wood pellets.

# III.3. Material and methods

## III.3.1. Sample material and pellets production

### III.3.1.1. Wood pellets samples

An overview on the investigated wood pellets batches in this chapter, their batch numbers and sample characteristics are given in Table 17.

**Table 17** List of the investigated wood pellets batches, the used raw material, the production and their characteristics. (LSPP stands for laboratory scale pellets production. ISPP stands for industrial scale pellets production).

| Batch | Raw material | Production | d in mm | Moisture content in % (m/m) | $\rho_{pellets}$ in kg m$^{-3}$ |
|---|---|---|---|---|---|
| WP 32 | 50/50 pine/spruce | LSPP | 6 | 9.1 | 1200$^1$ |
| WP 33 | 50/50 pine/spruce | LSPP | 6 | 8.7 | 1200$^1$ |
| WP 34 | 50/50 pine/spruce | LSPP | 6 | 9.4 | 1200$^1$ |
| WP 35 | 50/50 pine/spruce | LSPP | 6 | 9.5 | 1200$^1$ |
| WP 36 | 50/50 pine/spruce | LSPP | 6 | 8.8 | 1200$^1$ |
| WP 37 | 50/50 pine/spruce | ISPP | 6 | 6.0 | 1200$^1$ |
| WP 38 | 50/50 pine/spruce | ISPP | 6 | 6.2 | 1200$^1$ |
| WP 39 | 50/50 pine/spruce | ISPP | 6 | 6.5 | 1200$^1$ |
| WP 40 | 50/50 pine/spruce | ISPP | 6 | 6.5 | 1200$^1$ |
| WP 41 | 50/50 pine/spruce | ISPP | 6 | 6.4 | 1200$^1$ |
| WP 42 | 50/50 pine/spruce | ISPP | 6 | 6.9 | 1200$^1$ |
| WP 43 | 50/50 pine/spruce | ISPP | 6 | 6.6 | 1253 |
| WP 44 | 50/50 pine/spruce | ISPP | 6 | 7.5 | 1240 |
| WP 45 | 50/50 pine/spruce | ISPP | 6 | 8.0 | 1220 |
| WP 46 | 50/50 pine/spruce | ISPP | 6 | 8.5 | 1180 |
| WP 47$^2$ | 50/50 pine/spruce | LSPP | 6 | 7.9 | 1257 |
| WP 48 | 50/50 pine/spruce | LSPP | 6 | 8.0 | 1236 |
| WP 49$^2$ | 50/50 pine/spruce | LSPP | 6 | 8.1 | 1262 |
| WP 50$^2$ | 50/50 pine/spruce | LSPP | 6 | 8.2 | 1262 |
| WP 51$^2$ | 50/50 pine/spruce | LSPP | 6 | 7.9 | 1277 |
| WP 52 | 50/50 pine/spruce | LSPP | 6 | 8.7 | 1246 |
| WP 53 | 50/50 pine/spruce | LSPP | 6 | 7.5 | 1263 |
| WP 54 | 50/50 pine/spruce | LSPP | 6 | 7.7 | 1251 |
| WP 55 | pine | ISPP | 6 | 3.6 | 1330 |
| WP 56 | pine | ISPP | 6 | 5.0 | 1290 |
| WP 57 | pine | ISPP | 6 | 5.0 | 1250 |
| WP 58 | pine | ISPP | 6 | 3.3 | 1210 |
| WP 59 | pine | ISPP | 6 | 3.5 | 1198 |
| WP 60 | 50/50 pine/spruce | ISPP | 6 | 7.8 | 1223 |
| WP 61 | 50/50 pine/spruce | ISPP | 6 | 8.1 | 1247 |
| WP 62 | 50/50 pine/spruce | ISPP | 6 | 8.1 | 1246 |
| WP 63 | 50/50 pine/spruce | ISPP | 6 | 8.3 | 1247 |

| Batch | Raw material | Production | d<br>in mm | Moisture content<br>in % (m/m) | $\rho_{pellets}$<br>in kg m$^{-3}$ |
|---|---|---|---|---|---|
| WP 65 | 50/50 pine/spruce | ISPP | 6 | 7.5 | 1261 |
| WP 66[2] | 50/50 pine/spruce | LSPP | 6 | 8.7 | 1263 |
| WP 67[2] | 50/50 pine/spruce | LSPP | 6 | 9.5 | 1259 |
| WP 68 | 50/50 pine/spruce | LSPP | 6 | 8.2 | 1254 |
| WP 69 | 50/50 pine/spruce | LSPP | 6 | 7.4 | 1294 |
| WP 70[2] | 50/50 pine/spruce | LSPP | 6 | 7.8 | 1246 |
| WP 71 | 50/50 pine/spruce | LSPP | 6 | 8.5 | 1255 |
| WP 72 | 50/50 pine/spruce | LSPP | 6 | 8.2 | 1245 |
| WP 73 | 50/50 pine/spruce | ISPP | 6 | 8.7 | 1275 |
| WP 74 | 50/50 pine/spruce | ISPP | 6 | 8.3 | 1301 |
| WP 75 | 50/50 pine/spruce | ISPP | 6 | 7.5 | 1300 |
| WP 76 | 50/50 pine/spruce | ISPP | 6 | 7.4 | 1274 |
| WP 77 | 50/50 pine/spruce | ISPP | 6 | 7.0 | 1300 |
| WP 78 | 50/50 pine/spruce | ISPP | 6 | 6.8 | 1205 |
| WP 79 | 50/50 pine/spruce | ISPP | 6 | 5.0 | 1179 |
| WP 80 | 50/50 pine/spruce | ISPP | 6 | 5.5 | 1214 |
| WP 81 | Pine | ISPP | 6 | 3.6 | 1098 |
| WP 82 | Pine | ISPP | 6 | 4.1 | 1123 |
| WP 83 | Pine | ISPP | 6 | 3.3 | 1107 |
| WP 84 | Pine | ISPP | 6 | 3.5 | 1187 |
| WP 85 | Pine | ISPP | 6 | 3.6 | 1160 |
| WP 86 | Pine | ISPP | 6 | 3.3 | 1160 |

[1] assumed value

[2] These samples are already listed in chapter II. Nevertheless, due to readability, new sample numbers have been assigned. WP 23 = WP 47; WP 24 = WP 49; WP 25 = WP 50; WP 26 = WP 51; WP 27 = WP 66; WP 28 = WP 67; WP 29 = WP 70;

#### III.3.1.2. Preliminary tests

In a laboratory scale pelletisation test, pellets batches were produced from pure sawdust of *Picea abies* (Norway spruce) with different amounts of antioxidants. The produced pellets batches were investigated in glass flask experiments. Very low emission rates resulted in those storage experiments. Thus, no obvious differences between the produced batches were determined. The available wood pellets on the European market are mainly made of spruce and mixtures of pine and spruce [72]. Since pellets made of *Pinus Sylvestris* (Scots pine) indicated higher off-gassing emissions [21], pine sawdust was added in further wood pellets production experiments for off-gassing studies.

#### III.3.1.3. Addition of additives in pellets production

This section is based on the peer-reviewed journal paper number 4. Additional data is included for more insights. In total, 7 pelletisation series were performed in two laboratory scale pellets mills and two industrial scale pelletising plants resulting in 34 wood pellets batches.

***Additives***

According to ISO 17225-2, additive addition up to 2% (m/m) is permitted [2]. A widely used additive improving wood pellets production in Austria is starch. Starch is commonly applied in smaller quantities than the allowed 2% (m/m) [108] [109]. In this study starch with a concentration of 0.5, 0.8 and 1% (m/m) and rye flour with a concentration of 0.8% (m/m) was used. Moreover, the synthetic antioxidant acetylsalicylic acid (ASA), natural antioxidants like hop grains (HG) and grape pomace powder (GPP) were added. Likewise, slaked lime and lime were applied.

Acetylsalicylic acid: The synthetic antioxidant acetylsalicylic acid (CAS number: 50-78-2) is also referred to as 2-Acetoxybenzoic acid and commercially available as aspirin. ASA is odourless and available as white powder. With a melting point of 136 °C [110] ASA is suitable for pelletisation because maximum temperatures of about 120° C are common in the pelletisation process [111]. ASA was usually used in powder form in the following pellets production series. However, once dissolved ASA was investigated in pellets production. Therefore, ASA was dissolved in water, whereby the solubility of ASA in water with 3 g $L^{-1}$ [110] was considered.

Grape pomace powder (GPP) is an abundant by-product from the wine industry, which consists of the remaining skin, seeds and stalks [97] [112] [113]. GPP is applied in animal nutrition, pharmaceuticals, cosmetics or food industry to improve stability [97].This popular use of GPP is due to the phenolic and polyphenolic compounds, which have a proven antioxidant effect [97] [112] [113] [114].

Hop grains (HG) or hot trub is a by-product of beer production that is abundant. Moreover, further by-products from brewery are spent grain and spent yeast. All of them have a high content of phenolic compounds revealin antioxidant effects [115]. Hop and HG are known to contain a variety of antioxidant ingredients [98] [115] [116] [117] [118] [119].

Slaked lime: Calcium hydroxide (CAS number: 1305-62-0) or more commonly known as slaked lime, hydrated lime, or calcium hydrate has the chemical formula of $Ca(OH)_2$. Calcium hydroxide is a white to beige powder with a melting point of ≥ 450 °C. It has a water solubility of 1.85 g $L^{-1}$ at 20 °C [120].
Lime: Calcium oxide (CAS number: 1305-78-8) or commonly known as quicklime has the chemical formula CaO. Calcium oxide is a white, odourless, crystalline solid with a melting point of 2850 °C and water solubility of 1.65 g $L^{-1}$ at 20 °C [121].

In addition to the antioxidant substances, slaked lime and quicklime were investigated to achieve saponification of fatty acids. The addition of lime to woody biomass prior to pelletisation might lead to a reduction in autoxidation processes. Calcium hydroxide and calcium oxide are used in very different fields of application. Calcium hydroxide for saponification is used for different oils and fats [122] [123]. Furthermore, $Ca(OH)_2$ is able to inactivate lipoteichoic acid through deacylation of the lipid moiety [124] [125]. Furthermore, calcium oxide is used for transesterification [99] and in the processing of sewage sludge [126].

***Laboratory and industrial scale pellets production (LSPP and ISPP)***

The produced 34 wood pellets batches consisted of pine or blends of pine and spruce. The detailed composition of those pellets is listed in Table 18.

**Table 18** List of the produced pellets batches with additives. The pellets batches were either produced in laboratory scale pellets production (LSPP) or in industrial scale pellets production (ISPP). The Roman numerals stand for the number of series. The used additives and their added amount as well as the raw material composition are given.

| Batch | Paper [1] | Production series | Raw material | Additive 1 | Additive 1 in %(m/m) | Additive 2 | Additive 2 in %(m/m) |
|---|---|---|---|---|---|---|---|
| WP 32 | | LSPPI | 50/50 spruce/pine | - | - | starch | 0.8 |
| WP 33 | | LSPPI | 50/50 spruce/pine | ASA | 0.8 | starch | 0.8 |
| WP 34 | | LSPPII | 50/50 spruce/pine | - | - | rye flour | 0.8 |
| WP 35 | | LSPPII | 50/50 spruce/pine | ASA | 0.8 | rye flour | 0.8 |
| WP 36 | | LSPPII | 50/50 spruce/pine | slaked lime | 0.8 | rye flour | 0.8 |
| WP 37 | A 0 | ISPP I | 50/50 spruce/pine | - | - | starch | 0.5 |
| WP 38 | A 0.3 | ISPP I | 50/50 spruce/pine | ASA | 0.3 | starch | 0.5 |
| WP 39 | A 0.8 | ISPP I | 50/50 spruce/pine | ASA | 0.8 | starch | 0.5 |
| WP 40 | B 0 | ISPP II | 50/50 spruce/pine | - | - | starch | 0.5 |
| WP 41 | B 0.3 | ISPP II | 50/50 spruce/pine | ASA | 0.3 | starch | 0.5 |
| WP 42 | B 0.8 | ISPP II | 50/50 spruce/pine | ASA | 0.8 | starch | 0.5 |
| WP 43 | | ISPP III | 50/50 spruce/pine | - | - | starch | 0.5 |
| WP 44 | | ISPP III | 50/50 spruce/pine | slaked lime | 0.1 | starch | 0.5 |
| WP 45 | | ISPP III | 50/50 spruce/pine | slaked lime | 0.3 | starch | 0.5 |
| WP 46 | | ISPP III | 50/50 spruce/pine | slaked lime | 0.5 | starch | 0.5 |
| WP 47 | D 0 | LSPP III | 50/50 spruce/pine | - | - | starch | 1 |
| WP 48 | | LSPP III | 50/50 spruce/pine | HG | 1.5 | starch | 1 |
| WP 49 | | LSPP III | 50/50 spruce/pine | GPP 1 | 1.5 | starch | 1 |
| WP 50 | D 0.1 | LSPP III | 50/50 spruce/pine | ASA | 0.1 | starch | 1 |
| WP 51 | D 0.5 | LSPP III | 50/50 spruce/pine | ASA | 0.5 | starch | 1 |
| WP 52 | | LSPP III | 50/50 spruce/pine | ASA[2] | 0.3 | starch | 1 |
| WP 53 | | LSPP III | 50/50 spruce/pine | lime | 0.1 | starch | 1 |
| WP 54 | | LSPP III | 50/50 spruce/pine | lime[2] | 2 | starch | 1 |
| WP 55 | | ISPP IV | pine | - | - | - | - |
| WP 56 | | ISPP IV | pine | slaked lime[2] | 0.1 | - | - |
| WP 57 | | ISPP IV | pine | slaked lime[2] | 0.25 | - | - |
| WP 58 | | ISPP IV | pine | slaked lime[2] | 0.5 | - | - |
| WP 59 | | ISPP IV | pine | slaked lime[2] | 0.75 | - | - |
| WP 60 | C 0 | ISPP V | 50/50 spruce/pine | - | - | starch | 0.5 |
| WP 61 | C 0.05 | ISPP V | 50/50 spruce/pine | ASA | 0.05 | starch | 0.5 |
| WP 62 | C 0.1 | ISPP V | 50/50 spruce/pine | ASA | 0.1 | starch | 0.5 |
| WP 63 | C 0.15 | ISPP V | 50/50 spruce/pine | ASA | 0.15 | starch | 0.5 |
| WP 64 | | ISPP V | 50/50 spruce/pine | GPP 2 | 0.5 | starch | 0.5 |
| WP 65 | | ISPP V | 50/50 spruce/pine | GPP 2 | 1.5 | starch | 0.5 |

[1] Nomenclature of pellets batches in the peer-reviewed journal paper number 4.

[2] dissolved; The additive was added in dissolved form.

#### III.3.1.4. Blends of raw material in pellets production

Two pellets production series were conducted, one in the laboratory scale pellets facility and one in the industrial pelletisation plant leading to a total of 12 wood pellets batches.

***Blends:*** Different wood species were used as blending material. Various plants especially some of their ingredients are known to act as antioxidants [100]. Phenolics are important representatives of this group [127]. Moreover, Jablonsky *et al.* identified 235 ingredients of softwood bark and their bioactivity [128]. In order to investigate the potential of blending raw material to reduce off-gassing emissions, wood species with a proven antioxidant effect were used for this work [100] [101] [102] [103]. The used blending wood resources and their amount are shown in Table 19. As the applied blended materials were wood, larger quantities than 2% (m/m) were added, as they are not considered as additives according to ISO 17225-2 standard [2].

Quercus species and their health effect as well as their usage in herbal medicine, consumption as food or beverage and the application in wood constructions are responsible for the popularity of this species. Oak (*Quercus robur*) is probably the most well-known representative among the used wood species and its antioxidative effects are well documented [101] [107] [129] [130]. This effect is mainly based on phenolic ingredients [101] [107] [129], such as flavonoids [129] [130], tannins and its proanthocyanidin content [130].

Moreover, willow (*Salix alba*) is known for its antioxidant properties [103] [106] [131] [132]. Important for the antioxidative effect are phenolic compounds like flavanols and procyanidins [103].

Maritime pine (*Pinus pinaster*), especially its bark, is a very important supplier of antioxidant substances [133]. Maritime pine bark is a commercially available dietary supplement under the brand name pycnogenol [100] [104] [134]. The most common antioxidative substances are flavonoids, procyanidin [104], polyphenols and ferulic acid [135].

Larch (*Larix decidua*) is also said to have an antioxidative effect [102] [105] [136] [137] [138]. Polyphenols are mostly mentioned as antioxidants, whereby taxifolin [105] and larixol [136] are also very dominant.

***Laboratory and industrial scale pellets production***

For wood pellets production a mixture of pine and spruce is used. The twelve pellets batches and their detailed composition are listed in Table 19.

**Table 19** List of produced blended pellets batches and their blending composition. The wood pellets batches were produced of spruce and pine in either a laboratory scale pellets production (LSPP) or industrial scale pellets production (ISPP).

| Batch | Production series | Raw material | Blends | Blends in % (m/m) | Starch in % (m/m) |
|---|---|---|---|---|---|
| WP 66 | LSPP | 50/50 spruce/pine | - | - | 1 |
| WP 67 | LSPP | 50/50 spruce/pine | oak saw dust (*Quercus robur*) | 20 | 1 |
| WP 68 | LSPP | 50/50 spruce/pine | willow wood chips (*Salix alba*) | 20 | 1 |
| WP 69 | LSPP | 50/50 spruce/pine | maritime pine bark (*Pinus pinaster*) | 5 | 1 |
| WP 70 | LSPP | 50/50 spruce/pine | larch saw dust (*Larix decidua*) | 20 | 1 |
| WP 71 | LSPP | 50/50 spruce/pine | oak bark (*Quercus robur*) | 5 | 1 |
| WP 72 | LSPP | 50/50 spruce/pine | willow bark (*Salix alba)* | 5 | 1 |
| WP 73 | ISPP | 50/50 spruce/pine | - | - | - |
| WP 74 | ISPP | 50/50 spruce/pine | oak sawdust without bark (*Quercus robur*) | 10 | - |
| WP 75 | ISPP | 50/50 spruce/pine | oak sawdust without bark (*Quercus robur*) | 20 | - |
| WP 76 | ISPP | 50/50 spruce/pine | larch sawdust (*Larix decidua*) | 20 | - |
| WP 77 | ISPP | 50/50 spruce/pine | larch sawdust (*Larix decidua*) | 40 | - |

#### III.3.1.5. Ventilation in pellets production

Two pellets production series were carried out in two different industrial pelletisation plants under different ventilation conditions achieving 9 pellets batches. The produced pellets batches and their different ventilation measures are listed in Table 20.

**Industrial scale pellets production - Ventilation experiment I (VE I)**

Spruce and pine sawdust (ratio 50:50) were used for pellets production. After pelletisation, pellets were transferred by the conveyor belt into a Kahl counterflow cooler. The residence time of the pellets in the cooling section was determined and defined as average cooling interval of 15 min. Imitating the cooling procedure of the used Kahl counterflow cooler of the industrial pelletisation plant, the obtained volume flow of the supply air of the cooler of the industrial pelletisation plant was calculated. Therefore, a Prandtl pipe was used for determining the velocity. The diameter of the supply air pipe was taken, temperature and relative humidity of the supplied air were measured.

In contrast to the defined sampling procedure in chapter III.3.2, 100 kg pellets were sampled immediately after the press without cooling and placed in the specially erected cooling tower (Figure 11). The used cooling tower was made of wood three-layer boards and had a square dimension of 0.75 * 0.75 m. The cooling tower was equipped with a metal mesh with a width of 3.15 mm. The supplied and exhausted air had a 150 mm pipe diameter, where ambient air was supplied from bottom to top using a fan for air adjustment. The temperature and relative humidity of the supply air were measured. Moreover, a Prandtl tube with live transmission of differential pressure was used.

Therefore, the calculated differential pressure should be achieved by reducing or increasing the fan flow rate. Obtaining the same air volume flow in the imitated ventilation test compared to the settings of the cooling in Kahl counterflow cooler of the industrial pelletisation plant, the fan was manually adjusted.

In this test series, three pellets batches with different cooling intervals were produced, pellets batches with 0 min ventilation, 15 min ventilation and 30 min ventilation, respectively.

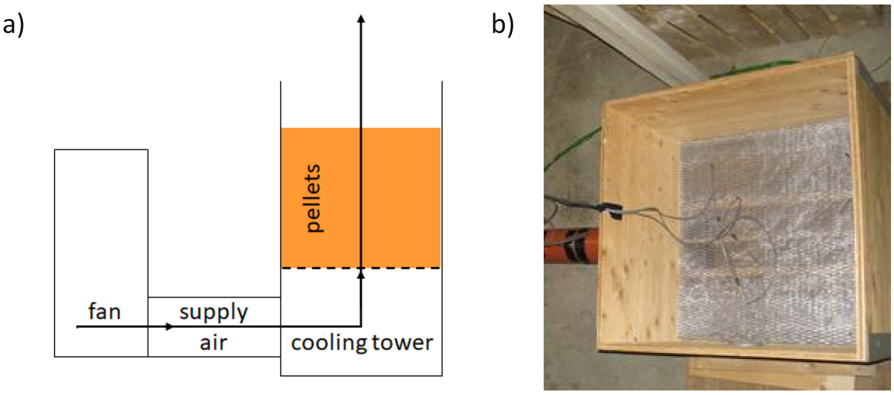
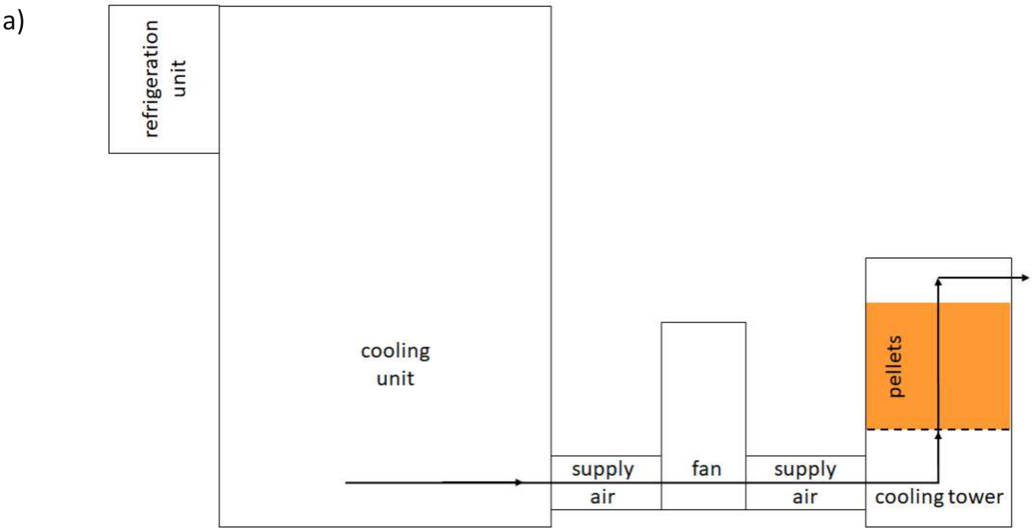


**Figure 11** Setup of ventilation experiment I: a) experimental setup, b) interior of the bottom of the cooling tower (metal mesh with a mesh width of 3.15 mm).

### Industrial scale pellets production - Ventilation experiment II (VE II)

Freshly cut pine sawdust was used as raw material for pelletisation. After pelletising, the pellets are usually cooled by a screw cooler (Rematec GmbH). Two outward turning and counter rotating screws conveyed the hot pellets over a 5.3 m long round hole grate. The cooling air (ambient air) flowed from the top to the bottom of the 25 cm high pellets bed. The residence time of the pellets in the cooling section was 13 min and was defined as average ventilation interval. The second cooling opportunity was the cooling tower already described above. The detailed equipment is illustrated in Figure 12.



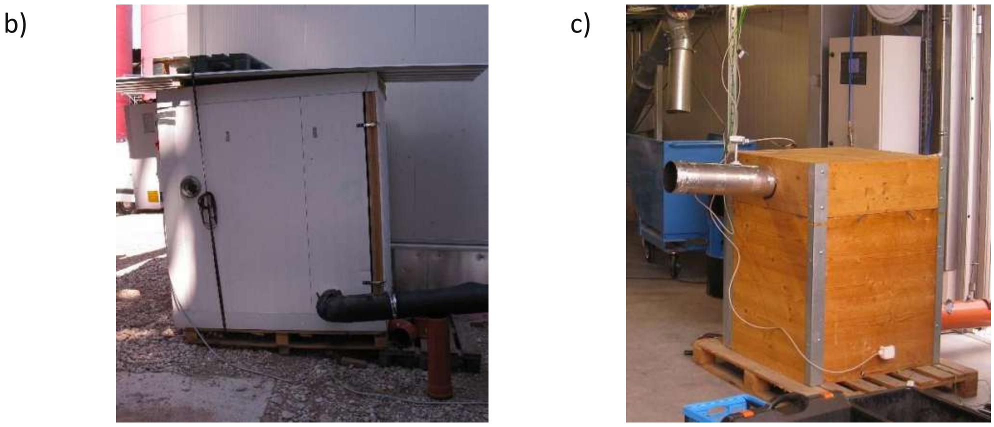


**Figure 12** Setup of the ventilation experiment II: a) scheme of the experimental setup; b) cooling unit with refrigeration unit. c) cooling tower.

The supplied air was either ambient air or cooled (ambient) air. Therefore, the cooled air was ambient air which was cooled down by a temperature difference of 20° C using a cooling unit (Figure 12 a) and a Viessmann refrigeration unit (FS 2500 EVO-113). The temperature and relative humidity of the supplied air were measured. Moreover, a Prandtl tube with live transmission of differential pressure was used. A calculated differential pressure should be achieved by reducing or increasing the air flow rate. Obtaining the same air volume flow in the imitated ventilation test compared to the settings of the cooling in the screw cooler of industrial pelletisation plant, the supply air was adjusted by modifying the air flow rate.

In contrast to the defined sampling procedure in chapter III.3.2, 100 kg pellets were sampled immediately after the press without cooling and placed in the extended cooling tower (Figure 12). The experimental variations were designed by considering the two existing cooling options, cooling tower and screw cooler, respectively. An overview of the ventilation variation is presented in Table 20. The following three parameters were varied.

- **Ventilation temperature:** The ventilation temperature was equal to ambient temperature in industrial pelletisation plant. As a second ventilation temperature, the ambient air was cooled down by a temperature difference of 20 °C with a cooling unit.
- **Ventilation interval:** Two cooling intervals were set. The first cooling interval was the average ventilation interval of 15 min during pellets production. The second chosen ventilation interval was twice as long – 30 min.
- **Cooling technology:** Two technologies were used for cooling the pellets. First, the existing screw cooler of the industrial pelletisation plant was used. This screw cooler is equipped with two outward turning and counter rotating screws. Second, the erected cooling tower was used.

The produced pellets batches and their different ventilation variations are listed in Table 20.

**Table 20** List of the produced pellets batches in the industrial scale pellets production (ISPP) ventilation experiments (VEs) I & II. An overview of their different cooling and ventilation applications is presented.

| Batch | Production series | Raw material | Ventilation technology | Temperature | Interval |
|---|---|---|---|---|---|
| WP 78 | ISPP VEI | 50/50 pine/spruce | tower | ambient | 0 |
| WP 79 | ISPP VEI | 50/50 pine/spruce | tower | ambient | average |
| WP 80 | ISPP VEI | 50/50 pine/spruce | tower | ambient | 2*average |
| WP 81 | ISPP VEII | pine | tower | ambient | average |
| WP 82 | ISPP VEII | pine | tower | ambient | 2*average |
| WP 83 | ISPP VEII | pine | tower | cooled | average |
| WP 84 | ISPP VEII | pine | tower 2 | cooled | 2*average |
| WP 85 | ISPP VEII | pine | screw | ambient | average |
| WP 86 | ISPP VEII | pine | screw | ambient | 2*average |

### III.3.2. Pellets sampling and pre-treatment

Former investigations proved the considerable influence of pellets age (time since production) and storage temperature on off-gassing formation of wood pellets during storage [21] [56]. To enable comparable pellets batches and results, a uniform procedure for accurate pellets sampling was introduced. Moreover, the pre-treatment of pellets batches prior to off-gassing determination was established. Details and the exact procedure for pellets sampling and pre-treatment were published in Sedlmayer *et al.* [64]. The pellets were sampled after the cooling unit during the production. All sampled pellets of each batch were carefully mixed and divided using the established method coning and quartering [139]. 10 kg pellets of each batch were filled in airtight and opaque plastic bags, closed and transferred to the laboratory. After exactly 72 h, all pellets batches were deep-frozen at -18 °C. The pellets batches were removed from the freezer 16 h before off-gassing analyses.

### III.3.3. Off-gassing determination

For off-gassing determination the glass flask method was used [21] [23] [64] which was described in chapter II.3.2.4.

### III.3.4. Determination of core temperature of fresh pellets

Within this chapter the term core temperature is defined as follows. The core temperature is the internal temperature of the pellets that is reached when no heat is supplied or removed from the outside. When measuring the core temperature, an equilibrium temperature is reached when the temperature gradient between the surface temperature and the temperature inside the pellets are equal. Thus, this method was used to determine whether the ventilation variations of the different cooling and post-treatment processes affected the temperature of the produced pellets.

Therefore, the 44 L insulation box (see Figure 13 b) was filled with 25 kg of pellets. (Technical specification of insulation Thermoli® Basta-Box XL: temperature range -20 to 110 °C; keeps material hot or cold for up to 10 hours;) Data loggers (see Figure 13 a)) for temperature and humidity measurements and for CO measurements were positioned in the middle (see MP 1 in Figure 13 c)) and the insulation box was closed (see Table 21). A further data logger for measurements of temperature and humidity was positioned on the outer top of the insulation box (see MP 2 in Figure 13 c)). Subsequently, the insulation boxes were stored at room temperature for approximately 50 h avoiding exposure to sunlight to exclude external heating. The moisture content of the stored pellets was determined according to ISO 17225-2 [2], which was described in chapter II.3.2.1. Afterwards, the data loggers were connected with the computer. The data was evaluated using Easy Log software from Lascar electronics which was accessible on the homepage.

**Table 21** Manufacturer specifications of used data loggers from Lascar electronics.

| Product name | Measured parameter | Range | Uncertainty | Measurement interval |
|---|---|---|---|---|
| Easy Log EL-USB-2 | T | - 35 to + 80 °C | ± 2 °C | every 10 min |
| Easy Log EL-USB-2 | RH | 0 to 100 % RH | ± 6.0 % RH | every 10 min |
| Easy Log EL-USB-CO | CO | 0 to 1000 ppm | ± 6 ppm | every 5 min |

**Figure 13** a) The used data loggers, b) the performance of the core temperature determination and c) scheme of the core temperature determination.

# III.4. Results and discussion

## III.4.1. Addition of additives in pellets production

The basic work on this chapter was published in Paper 4. Additional data was added to demonstrate the impact of additives on the reduction of off-gassing.

### III.4.1.1. Off-gassing reduction by the application of acetylsalicylic acid

The influence of acetylsalicylic acid (ASA) on off-gassing reduction emissions was examined several times resulting in 18 pellets batches which were produced in six pelletisation series. ASA was added in various concentrations from 0.05 to 0.8% (m/m).

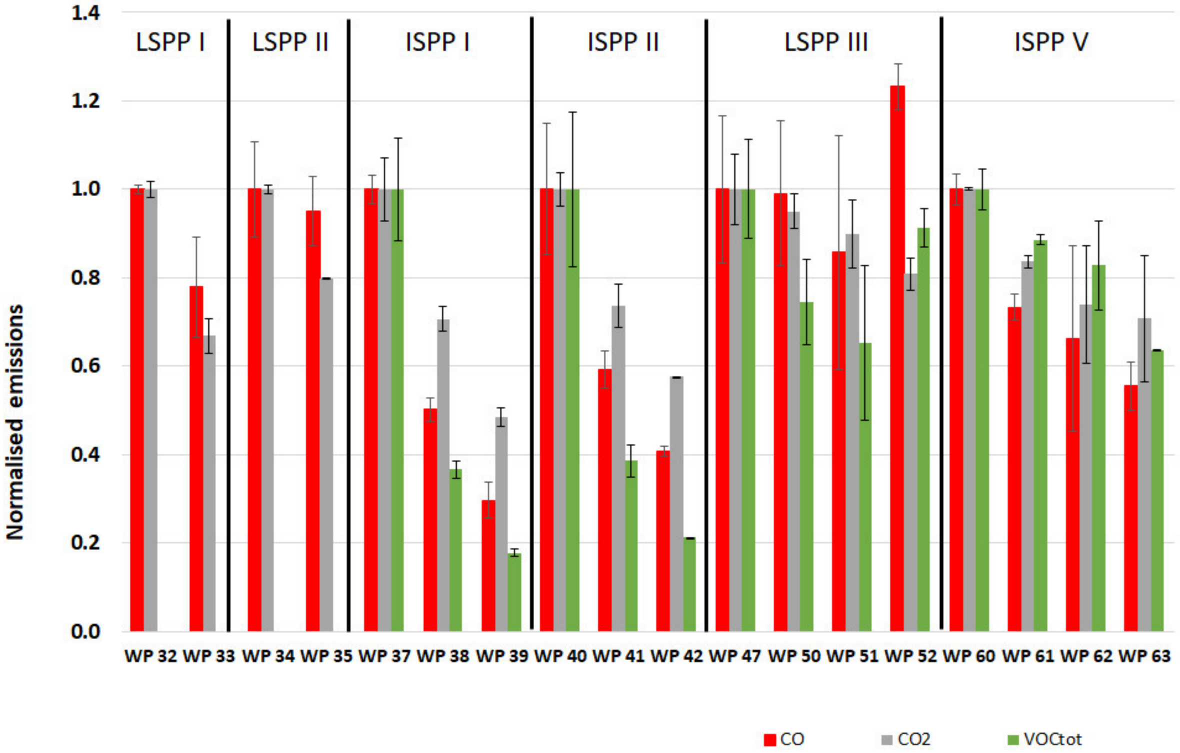


**Figure 14** Illustration of normalised CO, $CO_2$ and $VOC_{tot}$ emission rates of 18 pellets batches produced by six pelletisation series. The influence of addition of ASA in concentration of 0.05 to 0.8 (m/m) on off-gassing emission reduction is investigated. The error bars (n=3) show the minimum and maximum emission rates.

The normalised CO, $CO_2$ and $VOC_{tot}$ emission rates of the 18 pellets batches produced in six pelletisation series are illustrated in Figure 14. The normalised emission rates were used enabling comparable results for all pelletisation series. Therefore, a reference batch was defined within each test series. This reference batch was produced without any added additives and the emission rates were set to 1. The emission rates of the corresponding pellets batches were put in relation to the reference batch. The pellets batches related to each of these normalised rates were located to the right. Moreover, the used additives, their added amounts and the corresponding emission rates of the investigated pellets batches are presented in Table 22.

Considering Figure 14, the missing $VOC_{tot}$ normalised emission rates of the first two series, LSPPI and LSPPII, are striking. This was caused by a measuring device failure.

Viewing all normalised emission rates, it was noticeable that only one normalised emission rate was higher than the normalised rates for the reference pellets batches (>1). This was batch WP 52. CO emissions were increased by more than 20%. In contrast to all other pellets batches, in WP 52 ASA was added in liquid condition. It was likely that the liquid addition in pellets production led to an inhomogeneous distribution. As a result, less raw material was mixed with ASA. Due to this result and because of the simultaneously poorer practical applicability, ASA was not added again in liquid form.

**Table 22** List of the investigated pellets batches. The used additives and the added concentration (c) as well as their off-gassing emssion rates for CO, $CO_2$ and $VOC_{tot}$ and the residual $O_2$ concentration are given. Furthermore, the initial pellets weights in the glass flask experiments are presented.

| Batch | Production series | Additive | c | CO | $CO_2$ | $VOC_{tot}$ | Residual $O_2$ | Pellets weight |
|---|---|---|---|---|---|---|---|---|
| | | | in %(m/m) | in mg $kg^{-1}$ $pellets_{db}$ $day^{-1}$ | | | in % (V/V) | in kg |
| WP 32 | LSPPI | - | - | 3.18 | 7.20 | n.d.[1] | 1.1 | 2.4 |
| WP 33 | LSPPI | ASA | 0.8 | 2.47 | 4.82 | n.d.[1] | 3.1 | 2.4 |
| WP 34 | LSPPII | - | - | 2.84 | 6.26 | n.d.[1] | 1.8 | 2.4 |
| WP 35 | LSPPII | ASA | 0.8 | 2.70 | 5.00 | n.d.[1] | 1.5 | 2.4 |
| WP 37 | ISPP I | - | - | 2.00 | 2.77 | 0.59 | 4.6 | 2.4 |
| WP 38 | ISPP I | ASA | 0.3 | 1.00 | 1.96 | 0.22 | 12.2 | 2.4 |
| WP 39 | ISPP I | ASA | 0.8 | 0.59 | 1.35 | 0.11 | 15.8 | 2.4 |
| WP 40 | ISPP II | - | - | 1.79 | 2.68 | 0.53 | 5.9 | 2.4 |
| WP 41 | ISPP II | ASA | 0.3 | 1.06 | 1.97 | 0.21 | 11.7 | 2.4 |
| WP 42 | ISPP II | ASA | 0.8 | 0.73 | 1.55 | 0.11 | 14.6 | 2.4 |
| WP 47 | LSPP III | - | - | 2.37 | 7.66 | 2.32 | 3.4 | 2.4 |
| WP 50 | LSPP III | ASA | 0.1 | 2.35 | 7.27 | 1.73 | 2.6 | 2.4 |
| WP 51 | LSPP III | ASA | 0.5 | 2.03 | 6.89 | 1.52 | 4.7 | 2.4 |
| WP 52 | LSPP III | ASA[2] | 0.3 | 2.92 | 6.19 | 2.12 | 1.3 | 2.4 |
| WP 60 | ISPP V | - | - | 3.26 | 13.08 | 1.31 | 17.8 | 0.3 |
| WP 61 | ISPP V | ASA | 0.05 | 2.40 | 10.94 | 1.16 | 18.4 | 0.3 |
| WP 62 | ISPP V | ASA | 0.1 | 2.16 | 9.68 | 1.09 | 18.5 | 0.3 |
| WP 63 | ISPP V | ASA | 0.15 | 1.81 | 9.26 | 0.84 | 18.8 | 0.3 |

[1] n.d. indicates not detected

[2] dissolved; The additive was added in dissolved form

Analysing the normalised CO rates, it became apparent that, with the exception of the addition of ASA in liquid form, the CO emissions were always reduced compared to the reference pellets batches. The highest reduction in CO emission by about 70% was achieved by adding 0.8% (m/m) ASA (batch WP 39). The lowest reduction was observed in batch WP 50. In this case, 0.1% (m/m) ASA was added and emissions were almost the same. Thus, the addition of 0.1% ASA showed no considerable effect on the reduction of CO emissions. However, a significant reduction of CO emissions was observed for batch WP 61. ASA was added at a rate of 0.05% (m/m) and about 27% less CO was emitted. Therefore, it was assumed that the lack of reduction of CO with the addition of 0.1% ASA was not due to the too low dosage but to the dosage itself and the mixing with the raw material.

The consideration of the $CO_2$ normalised emission rates revealed that the highest $CO_2$ reduction of 51% was achieved by the highest addition of ASA (WP 39). The lowest reduction was observed in pellets batch WP 50. 0.1% (m/m) ASA was added and the emissions were reduced by 5%. It was noticeable that pellets batch WP 61 with the addition of the lowest ASA concentration of 0.05% (m/m) again reduced more $CO_2$ by 16%.

In terms of $VOC_{tot}$ emissions, the highest total reduction was achieved. The pellets batch WP 39 with an ASA concentration of 0.8% (m/m) led to a reduction of 82%. The lowest reduction of 9% was measured for pellets batch WP 52 with liquid ASA addition of 0.3% (m/m). Excluding that batch, the lowest $VOC_{tot}$ reduction of 11% was achieved in batch WP 61 with the addition of 0.05% (m/m) ASA, which was the lowest ASA concentration.

In summary, the highest reductions for CO, $CO_2$ and $VOC_{tot}$ emissions were achieved by the same pellets batch WP 39. As expected with increasing amounts of added ASA, emissions were continuously reduced. However, even very low ASA concentrations led to considerable emission reductions. As already discussed by Sedlmayer *et al.* [64], the effectiveness of ASA as an antioxidant to reduce off-gassing did not only depend on the applied amount. For best results in off-gassing reduction, the antioxidant should be added homogeneously and should be well distributed and mixed with the raw material. The proper application of the antioxidant, for example dissolved or solid, indicated an influence on reduction potential. A sufficient reaction time between the antioxidant and the raw material could also be crucial to the reduction of emissions. In order to achieve an effective off-gassing reduction, if feasible, preliminary tests should be carried out in advance in the respective pelletisation plant. ASA in general was convincing in terms of its reduction properties and also in terms of its applicability in pellets production.

In literature, other antioxidants such as tert-butylhydroquinone (TBHQ) and propyl gallate (PG) were studied in pellets production processes and their effect on the formation of emissions during the storage of wood pellets. Results indicated that TBHQ, even at low concentration of 0.5% (m/m), is an efficient antioxidant in preventing autoxidation of fatty and resin acids in wood pellets. The pellets batch with added TBHQ emitted less CO by 72% and 90% compared to the reference pellets batch. Through the addition of PG, the CO and $CO_2$ emissions were not reduced. PG only partially prevented autoxidation, implying the addition of a higher amount [76]. Moreover, TBHQ was blended with wood fibres and investigated using isothermal calorimetry. The blending with 5% (m/m) of TBHQ resulted in considerable reduction of self-heating by 62% $HRR_{max}$ compared to fibres without TBHQ [140]. That reduction was lower than those mentioned by Arshadi [76], but show the potential of TBHQ in reducing off-gassing and self-heating.

### III.4.1.2. Off-gassing reduction by the application of natural antioxidants

Two naturally antioxidants, hop grains (HG) and grape pomace powder (GPP), were added in laboratory scale pellets production (LSPP). GPP was also added in industrial scale pellets production (ISPP).

In order to enable comparable results, normalised emission rates are illustrated in Figure 15. Therefore, a reference batch was defined within each test series. This reference batch was produced without any added additives and the emission rates were set to 1. The emission rates of the corresponding pellets batches were put in relation to the reference batch. The used additives, their added amounts and the corresponding emission rates of the investigated pellets batches are presented in Table 23.

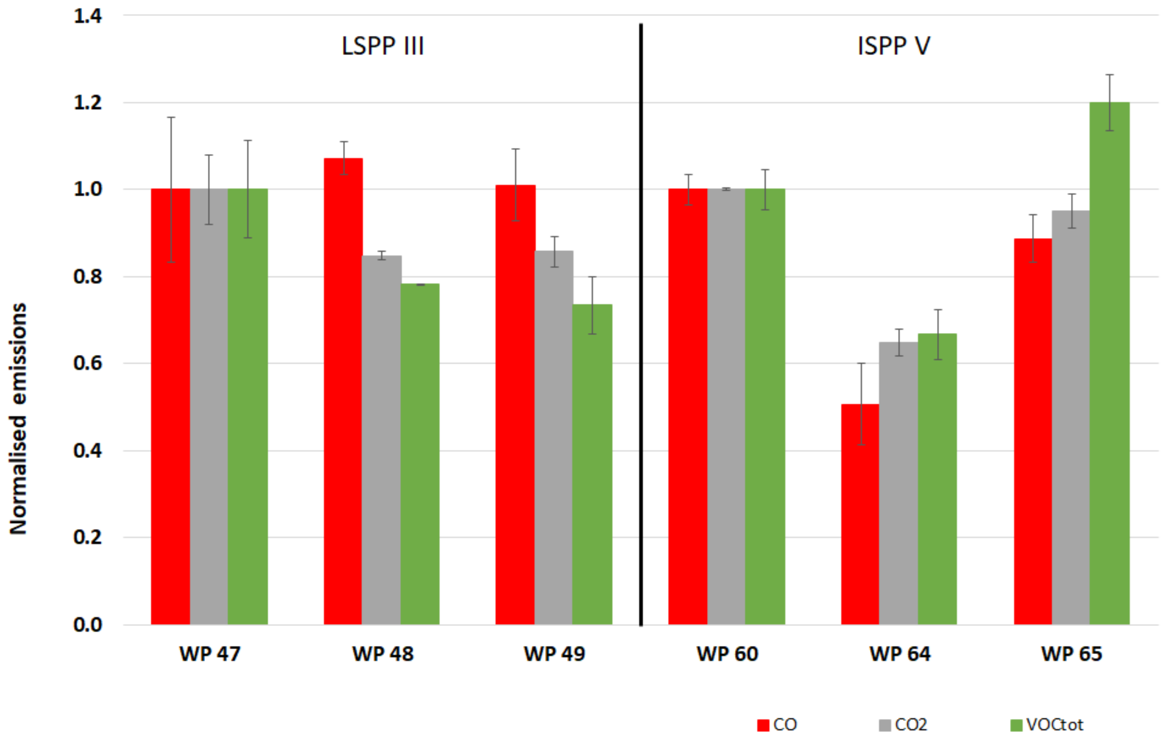


**Figure 15** Illustration of normalised emission rates of wood pellets with natural antioxidants. The error bars (n=3) show the minimum and maximum emission rates.

Firstly, HG and GPP 1 were added at each 1.5% (m/m). The addition of both resulted in higher CO emissions. In contrast, the $CO_2$ emissions were reduced by at least 14% and $VOC_{tot}$ emissions were reduced by more than 20%. However, both added natural antioxidants are known for their antioxidative effects [97] [112] [115] [116]. There may be several reasons for the lack of CO reduction. It could be that by the addition of 1.5% (m/m) HG or GPP 1 not enough antioxidant active substances were inserted. Moreover, an insufficient residence time or deficient mixing with the raw material could also have been the reason. Furthermore, it is possible that the used additives could not sustain the increased temperatures during the pelletising process. Another reason could be that too many ingredients were introduced by the addition of 1.5% (m/m) HG or GPP 1. This means that the addition of the two natural antioxidants introduced further organic ingredients which degraded during storage and led to additional emissions.

**Table 23** List of the investigated pellets batches. The used additives and the added concentration (c) as well as their emission rates for CO, $CO_2$ and $VOC_{tot}$ and the residual $O_2$ concentration are given. Furthermore,the initial pellets weights in the glass flask experiments are presented.

| Batch | Production series | Additive | C | CO | $CO_2$ | $VOC_{tot}$ | Residual $O_2$ | Pellets weight |
|---|---|---|---|---|---|---|---|---|
| | | | in % (m/m) | in mg kg$^{-1}$ pellets$_{db}$ day$^{-1}$ | | | in % (V/V) | in kg |
| WP 47 | LSPP III | - | - | 2.37 | 7.66 | 2.32 | 3.4 | 2.4 |
| WP 48 | LSPP III | HG | 1.5 | 2.54 | 6.49 | 1.82 | 0.3 | 2.4 |
| WP 49 | LSPP III | GPP 1 | 1.5 | 2.40 | 6.56 | 1.71 | 1.1 | 2.4 |
| WP 60 | ISPP V | - | - | 3.26 | 13.08 | 1.31 | 17.8 | 0.3 |
| WP 64 | ISPP V | GPP 2 | 0.5 | 1.65 | 8.48 | 0.88 | 18.9 | 0.3 |
| WP 65 | ISPP V | GPP 2 | 1.5 | 2.90 | 12.43 | 1.58 | 17.9 | 0.3 |

Despite the results from LSPP, GPP was also applied in ISPP. Investigating the influence of GPP on off-gassing reduction two different concentrations 0.5 and 1.5% (m/m) were examined. Thus, it should be investigated whether the application of 1.5% (m/m) GPP 2 inserted are too many ingredients resulting in increased emissions. The results indicated that a lower addition led to a higher reduction in emissions. The addition of 0.5% (m/m) GPP 2 resulted in decreased CO, $CO_2$ and $VOC_{tot}$ emissions. CO emissions were reduced by almost 50%. By contrast, the addition of 1.5% (m/m) GPP 2 reduced CO by 11% and $CO_2$ by 5%, but increased $VOC_{tot}$ emissions by about 20%. The increase in VOC emissions could be explained by the fact that more ingredients were added due to the higher addition of GPP [112] [114]. It was supposed that the degradation of some ingredients of GPP led to an increased occurrence of VOCs.

Comparing the results of the two batches with each 1.5% (m/m) GPP 1&2 of the two pelletisation series, differences became apparent. It was clearly shown that in LSPP series the $VOC_{tot}$ emissions were reduced even with an addition of 1.5% (m/m), unlike in the ISPP series. In contrast, the CO emissions increased in LSPP series, but decreased in the second series. In both series the $CO_2$ emissions were reduced. These different effects could not be explained at the current state of knowledge. Further investigations would be necessary. However, it was assumed that the causes were due to the different GPPs or the pelletising processes (e.g. temperature during the pelletising process). It should also be noted that these were individual trials.

### III.4.1.3. Off-gassing reduction by the application of quicklime and slaked lime

Four pelletisation series resulting in 14 pellets batches were performed investigating the applicability of quicklime and slaked lime in pellets production processes and their reducing off-gassing potential.

The normalised CO, $CO_2$ and $VOC_{tot}$ emission rates of all 14 pellets batches produced in four series are illustrated in Figure 16. The normalised emission rates were used enabling comparable results of all pelletisation series. All reference pellets batches could be identified by the normalised rates (1). Moreover, the used additives, their added amounts and the corresponding emission rates of the investigated pellets batches are presented in Table 24.

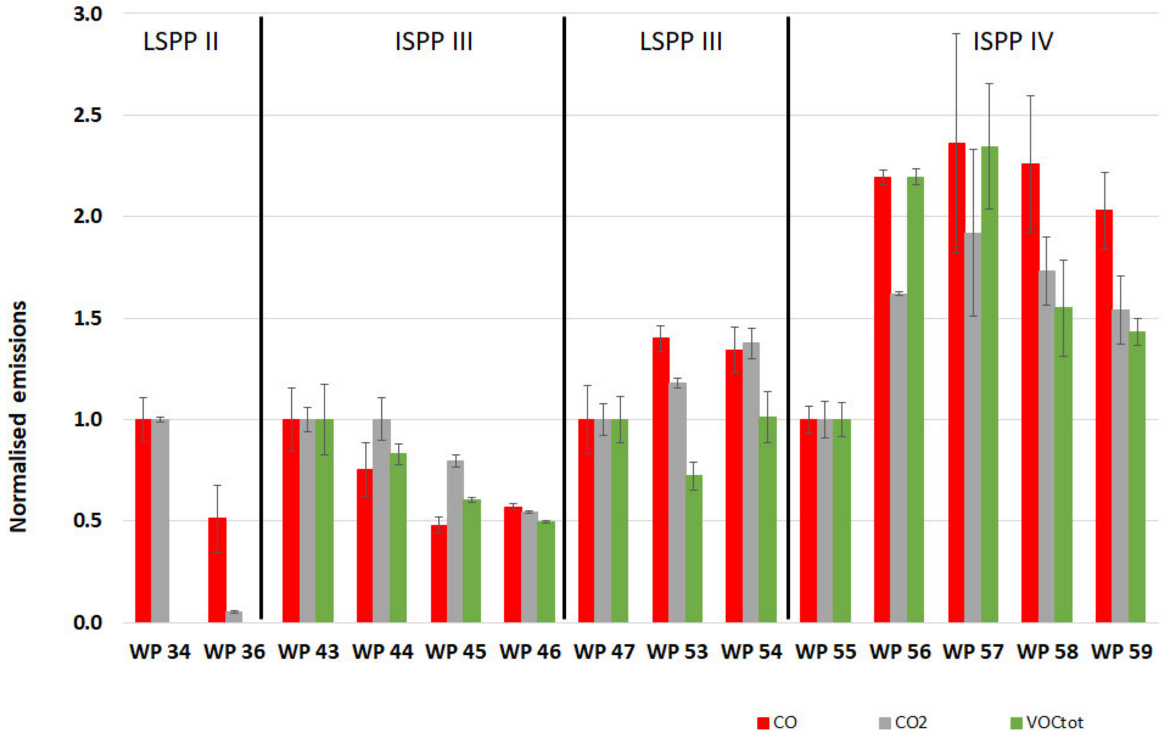


**Figure 16** Illustration of normalised CO, $CO_2$ and $VOC_{tot}$ emission rates of 14 pellets batches produced by four pelletisation series. The influence of addition of lime in concentrations of 0.1 to 2% (m/m) on off-gassing emission reduction is investigated. The error bars (n=3) show the minimum and maximum emission rates.

When looking at Figure 16, the missing $VOC_{tot}$ normalised emission rates of the first pelletisation series are clearly visible. This was caused by a measuring device failure.

In the first two pictured pelletisation series slaked lime was added as a solid. The results of the LSPP II, indicated the high performance of slaked lime on off-gassing reduction. The usage of 0.8% (m/m) led to a decline in CO emissions of 49%. Furthermore, the $CO_2$ emissions were reduced by an outstanding 95%. Macroscopic evaluation showed that the pellets were shinier compared to the pellets without any added slaked lime. This shine made them look glassy. In addition, a higher energy demand was observed during pelletising compared to the reference pellets batch.

Due to the high performance of slaked lime in the LSPP II, slaked lime at lower concentrations of 0.1, 0.3 and 0.5% (m/m) were investigated in industrial scale pellets production (ISPP III). The normalised CO emission rates were always reduced compared to the reference pellets batch. The highest reduction in CO emission by about 52% was achieved by adding 0.3% (m/m) slaked lime (batch WP 45). Even the addition of 0.1% (m/m) led to a CO reduction of 25%.

The consideration of the $CO_2$ normalised emission rates revealed that the highest $CO_2$ reduction of 56% was achieved by the highest addition of slaked lime of 0.5% (m/m). The addition of 0.1% (m/m) slaked lime indicated no influence on $CO_2$ formation.

Assessing $VOC_{tot}$ emissions proved that increasing addition of slaked lime led to decreasing in $VOC_{tot}$ emissions. The highest reduction of 50% was achieved by adding 0.5% (m/m) slaked lime. Even the addition of 0.1% (m/m) led to a reduction of 16% $VOC_{tot}$ emissions.

**Table 24** List of the investigated pellets batches. The used additives and the added concentration (c) as well as their off-gassing emssion rates for CO, $CO_2$ and $VOC_{tot}$ and the residual $O_2$ concentration are given. Furthermore, the initial pellets weight in the glass flask experiments is presented.

| Batch | Production series | Additive | c | CO | $CO_2$ | $VOC_{tot}$ | Residual $O_2$ | Pellets weight |
|---|---|---|---|---|---|---|---|---|
| | | | in %(m/m) | in mg kg$^{-1}$ pellets$_{db}$ day$^{-1}$ | | | in % (V/V) | in kg |
| WP 34 | LSPPII | - | - | 2.84 | 6.26 | n.d.[1] | 1.8 | 2.4 |
| WP 36 | LSPPII | slaked lime | 0.8 | 1.45 | 0.32 | n.d.[1] | 12.6 | 2.4 |
| WP 43 | ISPP III | - | - | 1.74 | 5.84 | 1.17 | 5.9 | 2.4 |
| WP 44 | ISPP III | slaked lime | 0.1 | 1.31 | 5.85 | 0.97 | 10.6 | 2.4 |
| WP 45 | ISPP III | slaked lime | 0.3 | 0.83 | 4.65 | 0.71 | 13.8 | 2.4 |
| WP 46 | ISPP III | slaked lime | 0.5 | 0.99 | 3.17 | 0.58 | 11.9 | 2.4 |
| WP 47 | LSPP III | - | - | 2.37 | 7.66 | 2.32 | 3.4 | 2.4 |
| WP 53 | LSPP III | lime | 0.1 | 3.32 | 9.03 | 1.68 | 0.5 | 2.4 |
| WP 54 | LSPP III | lime[2] | 2 | 3.19 | 10.53 | 2.35 | 0.7 | 2.4 |
| WP 55 | ISPP IV | - | - | 2.98 | 8.04 | 1.28 | 18.3 | 0.3 |
| WP 56 | ISPP IV | slaked lime[2] | 0.1 | 6.53 | 13.03 | 2.81 | 16.2 | 0.3 |
| WP 57 | ISPP IV | slaked lime[2] | 0.25 | 7.03 | 15.44 | 3.00 | 15.9 | 0.3 |
| WP 58 | ISPP IV | slaked lime[2] | 0.5 | 6.74 | 13.93 | 1.98 | 16.6 | 0.3 |
| WP 59 | ISPP IV | slaked lime[2] | 0.75 | 6.05 | 12.37 | 1.83 | 17.0 | 0.3 |

[1] indicates not detected

[2] dissolved; The additive was added in dissolved form.

In a further pelletisation series (LSPP III) lime was added as solid and dissolved material comparing the applicability and their impact on off-gassing emissions. The results indicated the usage of lime, whether solid or dissolved, in the applied laboratory pellets press proved to be inappropriate to reduce off-gassing emissions. All emissions except for one measured $VOC_{tot}$ value increased despite the addition of quicklime as a solid or dissolved.

By modifying slaked lime to dissolved slaked lime and the sprayed application, a better wetting of the raw material and more homogeneous mixing should be achieved. Furthermore, in comparison to slaked lime, dissolved slaked lime should not remove water from the pellets during pelletisation. Therefore, the dissolved slaked lime improved the pelletisation process by acting as a kind of lubricant during pelletisation. However, no improvement was achieved with regard to off-gassing.

In ISPP IV series dissolved slaked lime and its influence on off-gassing reduction potential was investigated. Therefore, slaked lime was added, dissolved in the range from 0.1 to 0.75% (m/m).

Considering the normalised emission rates, it was obvious that all emissions definitely increased by the addition of dissolved slaked lime. The CO emission rates of all pellets batches with added dissolved slaked lime revealed twice as high CO emission rates than the pellets batch without dissolved slaked lime.

A close look at the figure showed that the addition of quicklime or slaked lime as a solid or dissolved material had different effects on the subsequent off-gassing behaviour. When lime was added in dissolved form, no reduction on off-gassing emission could be achieved.

However, results indicated that slaked lime added as solid in wood pellets production can be a possible application for off-gassing reduction. This was demonstrated in LSPP II and ISPP III. The effectiveness of slaked lime relating to off-gassing reduction most likely depends on the good performance of the addition in the production process.

It is essential to mention, that the pressing conditions changed due to the addition of lime. Among other things, a higher energy consumption (according to the pelletiser) was recorded. Furthermore, the pellets were described as glassy. In addition, it should be noted that the addition of slaked lime increases the ash content. Therefore, in order to meet the limits of ISO17225-2, only a very small amount of lime might be added [2].

#### III.4.1.4. Long-term off-gassing reduction by the application of additives

The pellets batches of three pelletisation trials were analysed in long-term experiments investigating the long-term behaviour of ASA and slaked lime on the reduction of off-gassing emissions.

First, the long-term behaviour of ASA was investigated. Therefore, pellets batches of the two pelletisation series ISPP I (Figure 17) and ISPP II (Figure 18) were examined over a time period of 42 days in glass flasks experiments. The following data are taken from publication 4. The left illustrations (a, d and g) show the cumulative amounts of formed gases over 42 days for each pellets batch. The middle illustrations (b, e and h) depict the calculated emission rates of each measuring point of each pellets batch. The right illustrations (c, f and i) demonstrate the normalised emission rates over time and are given as normalised data in reference to batch WP 37 and WP 40, respectively. Overall, the pellets from ISPP I and ISPP II behaved very similarly, which is demonstrated in the graphs.

Considering the cumulative amounts of formed gases shown in Figure 17 and Figure 18 a, d and g, it is shown that the antioxidant ASA reduced the CO, $CO_2$ and $VOC_{tot}$ emissions over the 42 days.

The emission rates shown in the graphs (b, e and h) indicate the course of the rates over the six-week period. The graphs display that the emission rates at the first measurement time did not have the highest rate. The rates always increased at the second measurement time point. However, a reduction of all CO and $CO_2$ emission rates was always achieved in comparison to the batches without ASA. The addition of ASA did not result in a reduction of VOC emissions at the 6th (for ISPP I) or 4th (for ISPP II) measuring point.

The presented off-gassing emissions suggest that the addition of ASA is a good measure to reduce emissions, especially at the beginning of the pellets storage when the emissions are highest. Furthermore, the implementation and application in production showed no difficulties, whereby an additional feeding system was installed to add ASA. Further detailed discussion of the results can be found in the peer-reviewed journal paper number 4.

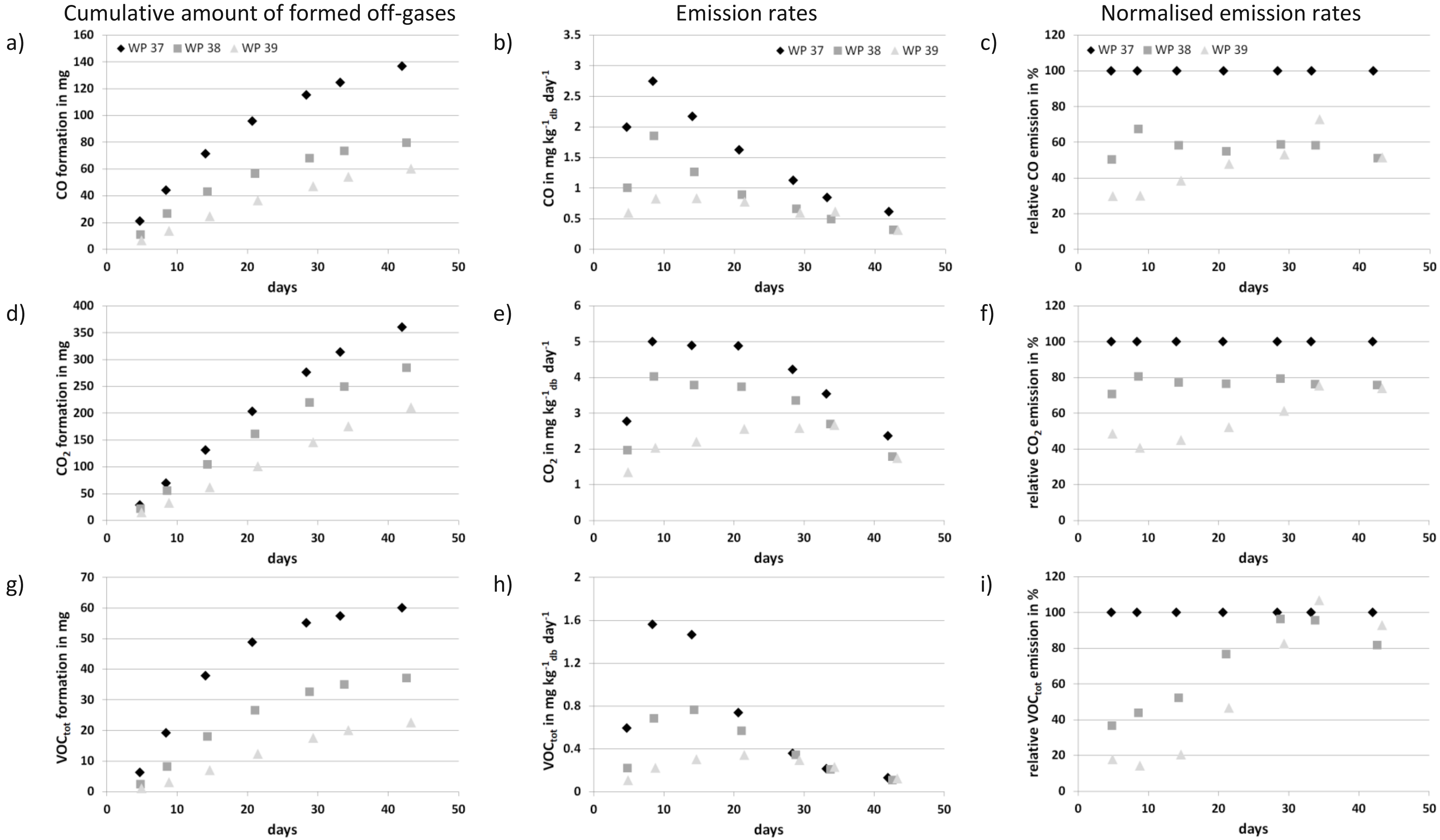


**Figure 17** Illustrations of cumulative CO, CO$_2$ and VOC$_{tot}$ formation, of emission rates and of normalised emission rate of pellets batches WP 37, WP 38 and WP 39 over the course of the six-week storage experiment. Different concentrations of ASA were used in the batches: 0 (WP 37), 0.3 (WP 38) and 0.8 %(m/m) (WP 39). The left figures show the cumulative amount of formed off-gases for pellets batches WP 37, WP 38 and WP 39 of a) CO, d) CO$_2$ and g) VOC$_{tot}$ over the course of the six-week storage experiment. The middle illustrations represent the emission rates of pellets batches WP 37, WP 38 and WP 39 of b) CO, e) CO$_2$ and h) VOC$_{tot}$ over the course of the six-week storage experiment. The right figures show the normalised (data from batch WP 37 as reference) normalised emission rates of c) CO, f) CO$_2$ and i) VOC$_{tot}$ over the course of the six-week storage experiment (source Sedlmayer *et al.* 2020 [64]).

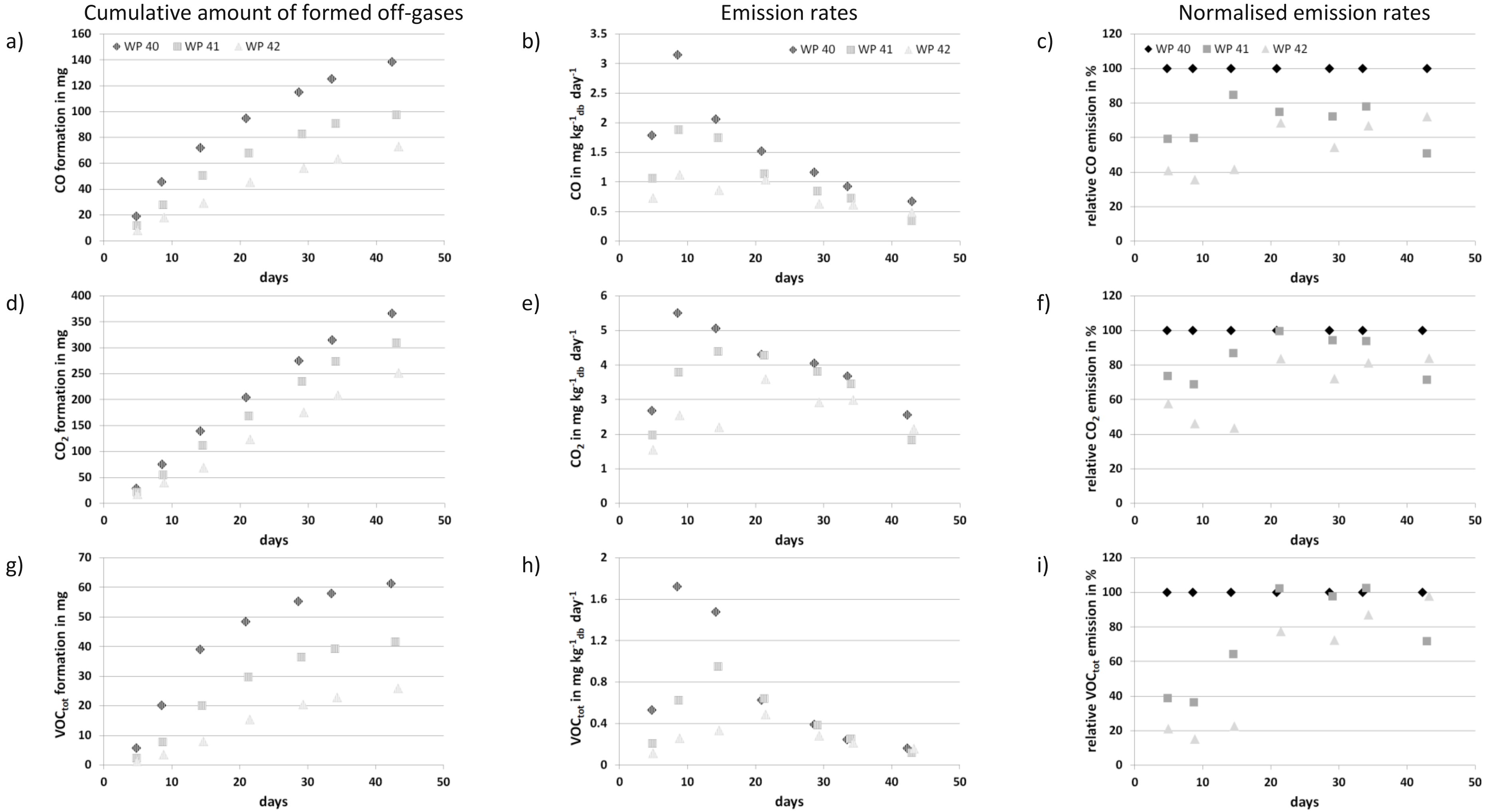


**Figure 18** Illustrations of cumulative CO, $CO_2$ and $VOC_{tot}$ formation, of emission rates and of normalised emission of pellets batches WP 40, WP 41 and WP 42 over the course of the six-week storage experiment. Different concentrations of ASA were used in the batches: 0 (WP 40), 0.3 (WP 41) and 0.8 %(m/m) (WP 42). The left figures show the cumulative amount of formed off-gases for pellets batches WP 40, WP 41 and WP 42 of a) CO, d) $CO_2$ and g) $VOC_{tot}$ over the course of the six-week storage experiment. The middle illustrations represent the emission rates of pellets batches WP 40, WP 41 and WP 42 of b) CO, e) $CO_2$ and h) $VOC_{tot}$ over the course of the six-week storage experiment. The right figures show the normalised (data from batch WP 40 as reference) normalised emission rates of c) CO, f) $CO_2$ and i) $VOC_{tot}$ over the course of the six-week storage experiment.

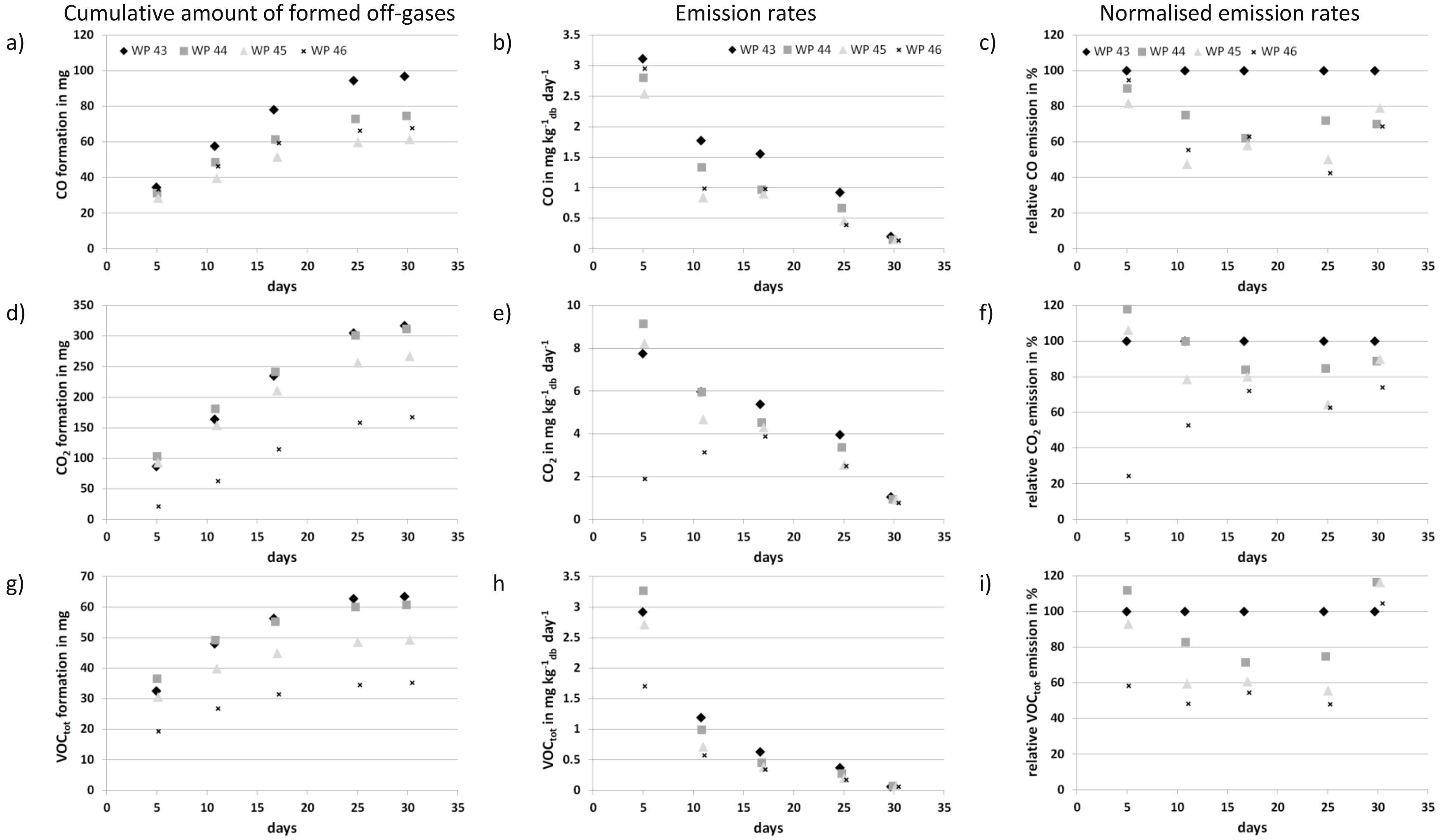


**Figure 19** Illustrations of cumulative CO, $CO_2$ and $VOC_{tot}$ formation, of emission rates and of normalised emission of pellets batches WP 43, WP 44, WP 45 and WP 46 over the course of the 30-day storage experiment. Different concentrations of slaked lime were used in the batches: 0 (WP 43), 0.1 (WP 44), 0.3 (WP 45) and 0.5 %(m/m) (WP 46). The left figures show the cumulative amount of formed off-gases for pellets batches added with slaked lime, batches WP 43, WP 44, WP 45 and WP 46, of a) CO, d) CO2 and g) $VOC_{tot}$ over the course of the 30-day storage experiment. The middle illustrations represent the emission rates of pellets batches of b) CO, e) CO2 and h) $VOC_{tot}$ over the course of the 30-day storage experiment. The right figures show the normalised (data from batch WP 43 as reference) normalised emission rates of c) CO, f) CO2 and i) $VOC_{tot}$ over the course of the 30-day storage experiment.

In addition to the long-term tests of ASA, slaked lime was also studied in long-term tests investigating the long-term behaviour over a storage period of 30 days (Figure 19) on off-gassing emissions of wood pellets.

The cumulative amounts of formed gases (shown in Figure 19 a, d and g) demonstrate that slaked lime reduced the total amount of formed CO over the 30 days. Moreover, the total amount of formed $CO_2$ and $VOC_{tot}$ was also reduced. However, this was not achieved at each measuring point.

The emission rates shown in the graphs (b, e and h) show the course of the rates over the 30 days. The demonstrated emission rates revealed that the emission rates at the first measurement time were the highest rates, with one exception in the case of $CO_2$ emission rates.

The reduction in emissions is more evident by comparison of the normalised emission rates (Figure 19 c, f and i). All CO emission rates were reduced by adding slaked lime. Considering the $CO_2$ emission rates, it was found that at the first measuring point the emissions were only reduced in one batch. At each subsequent measurement point, a reduction was always achieved regardless of the added amount of slaked lime. Furthermore, the $VOC_{tot}$ emissions of one batch were not reduced at the first measurement point. The course also indicated that the $VOC_{tot}$ emission rates were not reduced at the last measuring point. At all intermediate measuring points, a reduction on $VOC_{tot}$ emission rates was achieved by all added slaked lime concentrations. Overall, the addition of different concentrations of slaked lime in industrial pelletisation revealed a decrease in the release of CO, $CO_2$ and $VOC_{tot}$ from the second week of storage onwards for the measurement in the long-term storage, with the exception of $VOC_{tot}$ emissions at the last measurement point. However, the off-gassing level at this point in time is already only a fraction of the original starting level at the beginning of the measurement series.

The presented off-gassing emissions suggest that the addition of slaked lime might be a measure to reduce CO emissions, whereby an additional feeding system during pelletisation has to be installed to add slaked lime. However, the application in production indicated a higher energy consumption. Moreover, the addition of slaked lime inevitably leads to higher ash contents. Therefore, low concentrations of considerably less than 0.5% (m/m) have to be added.

## III.4.2. Blends of raw material in pellets production

### III.4.2.1. Off-gassing emissions by the application of blends

Normalised emission rates of pellets from laboratory scale pellets production (LSPP) with blended wood resources were compared to wood pellets without any further added biomass material from the same test series enabling a better comparability. Moreover, the six used blending wood resources, their added amounts and the corresponding emission rates of the investigated pellets batches are presented in Table 25.

The blending with various wood resources in LSPP led to reduction of off-gassing emissions in 2 out of 6 applications (see Figure 20). The CO emissions were reduced when oak saw dust (20 % m/m) and maritime pine bark (5 % m/m) were added. Simultaneously, the $CO_2$ and $VOC_{tot}$ emissions were minimized. The comparison of the residual $O_2$ concentration within the glass flask indicated that the reactivity of these two batches was lowest, as the residual $O_2$ concentration was highest. Although less maritime pine bark had been blended than oak sawdust, the blending with maritime pine bark was more efficient in terms of off-gassing reduction. A dilution of the determined emission rates can be excluded, since the reduced amount of emissions is higher than the added amount of the blended wood resources.

**Table 25** List of the investigated pellets batches. The blending raw material and the blending concentration (c) in mass fraction as well as their off-gassing emssion rates for CO, $CO_2$ and $VOC_{tot}$ and the residual $O_2$ concentration are given. Furthermore,the initial pellets weights in the glass flask experiments are presented.

| Batch | Production series | Blend | c | CO | $CO_2$ | $VOC_{tot}$ | Residual $O_2$ | Pellets weight |
|---|---|---|---|---|---|---|---|---|
| | | | in %(m/m) | in mg kg$^{-1}$ pellets$_{db}$ day$^{-1}$ | | | in % (V/V) | in kg |
| WP 66 | LSPP | - | - | 2.26 | 0.65 | 2.91 | 4.9 | 2.4 |
| WP 67 | LSPP | oak saw dust | 20 | 1.15 | 0.11 | 1.27 | 12.5 | 2.4 |
| WP 68 | LSPP | willow wood chips | 20 | 2.35 | 0.32 | 2.67 | 2.2 | 2.4 |
| WP 69 | LSPP | maritime pine bark | 5 | 0.70 | 0.17 | 0.87 | 15.7 | 2.4 |
| WP 70 | LSPP | larch saw dust | 20 | 2.58 | 0.47 | 3.06 | 2.7 | 2.4 |
| WP 71 | LSPP | oak bark | 5 | 2.68 | 0.07 | 2.75 | 0.3 | 2.4 |
| WP 72 | LSPP | willow bark | 5 | 2.64 | 0.22 | 2.86 | 0.7 | 2.4 |
| WP 73 | ISPP | - | - | 8.78 | 31.09 | 4.10 | 14.2 | 0.3 |
| WP 74 | ISPP | oak sawdust without bark | 10 | 6.07 | 20.65 | 2.39 | 16.1 | 0.3 |
| WP 75 | ISPP | oak sawdust without bark | 20 | 3.24 | 12.22 | 1.18 | 18.1 | 0.3 |
| WP 76 | ISPP | larch sawdust | 20 | 5.99 | 21.11 | 2.55 | 15.9 | 0.3 |
| WP 77 | ISPP | larch sawdust | 40 | 3.58 | 14.05 | 1.70 | 17.7 | 0.3 |

The higher emission reduction of maritime pine bark may be due to the addition of bark, which may have a higher antioxidant content. However, the addition of 5% (m/m) bark might considerably increase the ash content of the corresponding pellets batch. Blending with oak sawdust is not expected to increase the ash content. Therefore, there should be no issues in meeting the requirements of the ISO 17225-2 for ash content [2].

Even if no reduction in CO emissions was achieved by the other blended wood resources, they all revealed a reduction in $CO_2$ emissions. The highest reduction of 57% was achieved when 20% oak sawdust was blended. The pellets batch with blended larch sawdust (20% (m/m)) gained a reduction of 9%.

$VOC_{tot}$ emissions were also reduced by up to 91% in 4 out of 6 pellets batches, whereas the highest impact was shown by blending with maritime pine bark of 5% (m/m). The blends with larch sawdust of 20% (m/m) and willow bark of 5% (m/m) led to an increase in $VOC_{tot}$ emissions. That increase may be due to added ingredients and their degradation products.

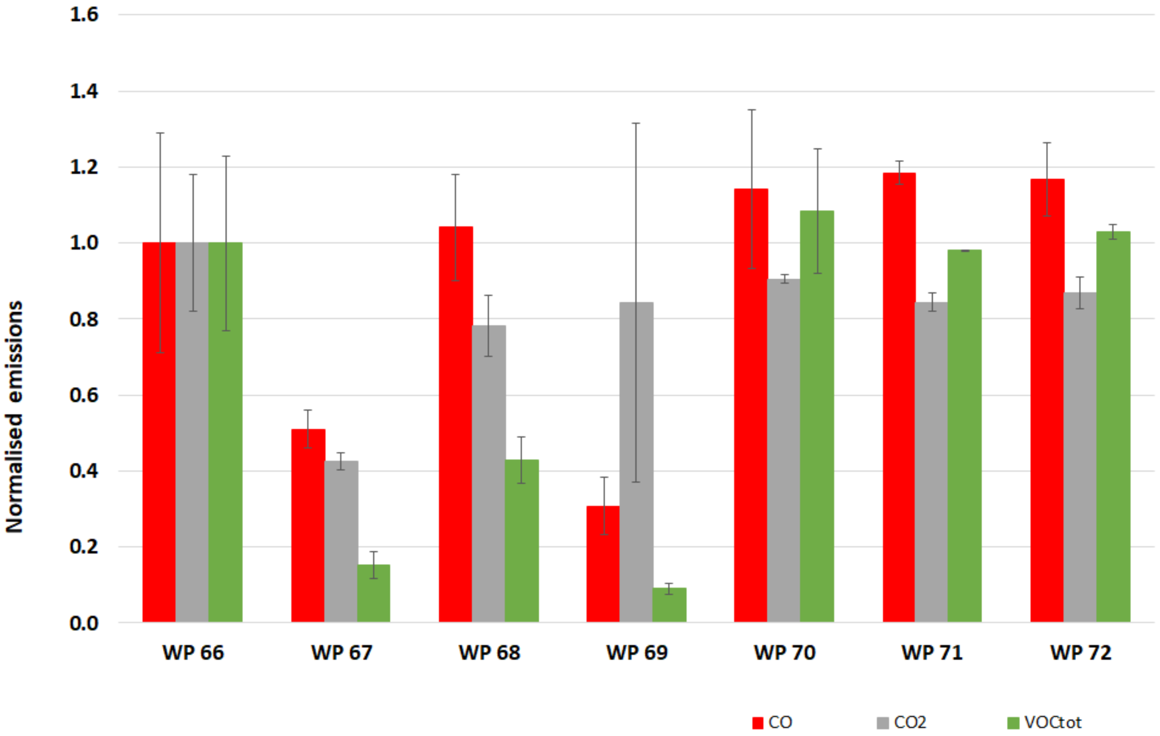


**Figure 20** Illustration of normalised CO, $CO_2$ and $VOC_{tot}$ emission rates of seven blended pellets batches. The error bars (n=3) show the minimum and maximum emission rates.

Contrary to expectations, the addition of 5% (m/m) bark, neither oak nor willow, did not result in a reduction of CO emissions. As the applied raw materials for blending tests were wood, the antioxidant ingredients may vary and therefore no reduction was achieved. There are other possible reasons that may affect the off-gassing reduction. The mixing time between the raw material and the blending material should be sufficiently long. Furthermore, attention should be paid to a homogenous mixing of the raw material with the blending material. The existing temperatures during the wood pellets production process may also have a considerable contribution to the effectiveness of the blending material.

### III.4.2.2. Reduction of off-gassing potential by blending oak and larch

In industrial scale pellets production (ISPP) two different blending materials were investigated, oak sawdust without bark and larch sawdust, each with two concentrations of 10 and 20 % (m/m) and 20 and 40 % (m/m), respectively. The normalised emission rates of pellets with blended wood resources were compared to the reference pellets batch. This is the wood pellets batch without any further added blending material. The emission rates of the reference pellets batch were set at 1. The emission rates of the remaining 4 pellets batches were set in relation to this. The effectiveness of the blending with oak sawdust without bark and larch sawdust is depicted in Figure 21. The two investigated blending wood resources, their added amounts and the corresponding emission rates of the investigated pellets batches are presented in Table 25.

The results (see Figure 21 a-c) demonstrated that the CO, $CO_2$ and also $VOC_{tot}$ emissions of all blended pellets batches were reduced compared to the reference pellets batch. Simultaneously, an increase in residual $O_2$ concentration was observed in all batches compared to the reference (see Table 25).

Thus, the investigation proved that blending with oak or larch resources was suitable for use in CO emission reduction. The most obvious reduction was achieved by blending of 20% (m/m) oak sawdust without bark, where the CO emissions were reduced by 63%. Even the blend of 10% (m/m) led to a reduction of 31%. Blending with larch also proved to be promising in terms of CO reduction. Blends of 20 and 40% (m/m) larch reduced CO emissions by 32 and 59%. Comparing the CO reduction with the blending ratio, oak was about twice as efficient as larch. Likewise, very high reductions in both $CO_2$ and $VOC_{tot}$ emissions were also obtained through the blend with oak and larch. Overall, the highest reduction was achieved by blending 20% (m/m) oak, which reduced the $VOC_{tot}$ by 71%.

An exclusive dilution of off-gassing emissions can be excluded for both added blending materials. CO, $CO_2$ and $VOC_{tot}$ emissions were reduced comparatively more than the blending quantity of oak and larch was. It was considered that this was a real reduction and not only a dilution effect.

The off-gassing results suggested that oak is better suited to decrease CO formation than larch. Since oak sawdust was added without bark, no problems with increased ash content were expected. However, the blending of 20 and 40% (m/m) larch sawdust could increase the ash content to such an extent that the requirements from ISO 17225-2 would not be fulfilled.

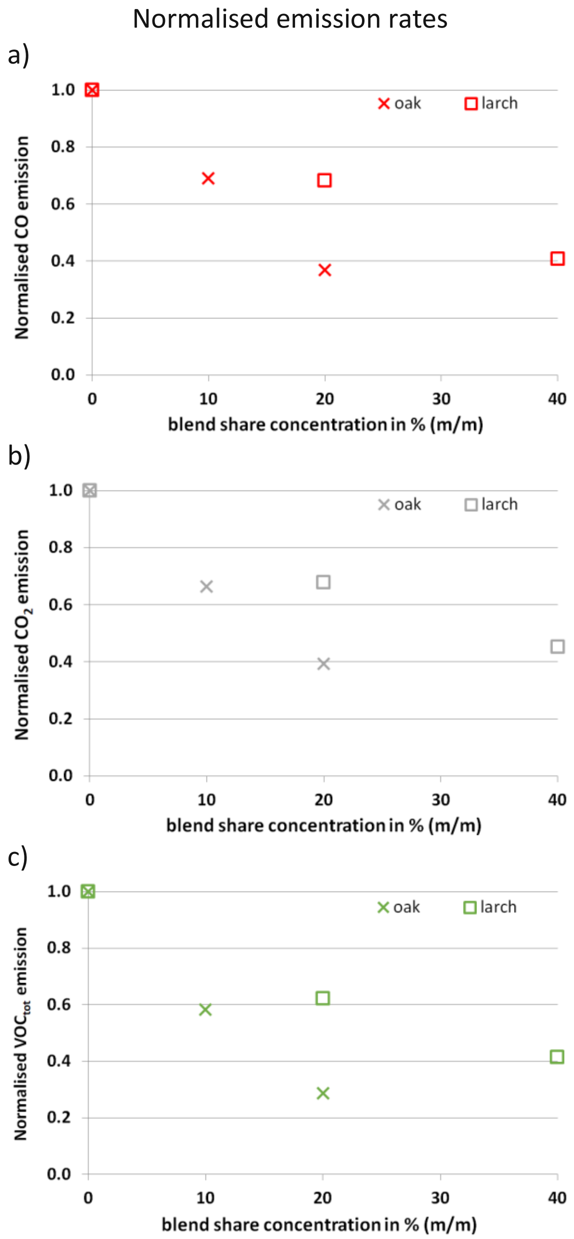


**Figure 21** Illustration of normalised emission rates for a) CO, b) $CO_2$ and c) $VOC_{tot}$ of pellets batches WP 73 to WP 77 blended with oak sawdust and larch sawdust.

In both pelletisation trials oak and larch sawdust was used for blending. The consideration of both pelletising series suggests that oak saw dust is very suitable for reducing off-gassing emissions.

However, the results were different for larch. In both pelletisation series larch sawdust with bark was blended. The difference was striking in the influence on off-gassing emissions by using larch. The results of LSPP revealed an increase in CO and $VOC_{tot}$ emissions (see Table 25). Contrary, in ISPP a considerable reduction of all emissions by blending with larch was achieved. This difference may be due to the raw material itself, the mixing of the blending material with the raw material, the residence time before pelletising and the thermal treatment during production.

## III.4.3. Ventilation in pellets production

### III.4.3.1. Influence of ventilation time on off-gassing

Three pellets batches with varying cooling duration of 0, 15 and 30 minutes were produced in the course of industrial scale pellets production in ventilation experiment I (VE I). The following results are presented with the calculated emission rates. Therefore, the differently applied ventilating approaches were compared to each other within a test series. The error bars in Figure 22 show the minimum and maximum emission rates. The average ventilation time in the used industrial pelletisation plant was determined to be 15 minutes. Considering emission rates for CO in VE I, the CO emission rates decreased with increasing ventilation duration. The same trend was shown for $CO_2$ and $VOC_{tot}$ emission rates. However, the difference in CO emission rates between 0 and 15 min ventilation is higher than the reduction between 15 and 30 min ventilation. The CO emission rates were reduced by 17% with 15 min ventilation and by 26% with 30 min ventilation compared to pellets batch without ventilation. A higher reduction in $CO_2$ emission rates was achieved by ventilation for 15 min by 43% and by ventilation for 30 min by 42% compared to the unventilated batch. Moreover, the $VOC_{tot}$ emission rates were reduced by around 40% through ventilation.

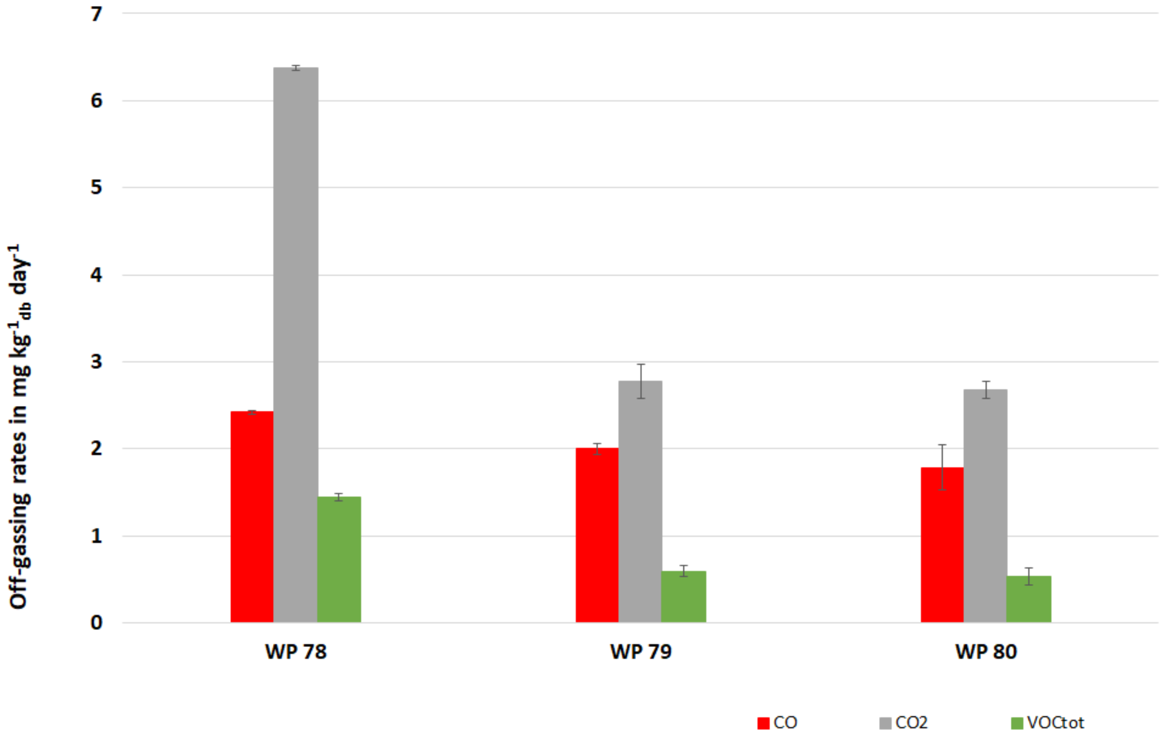


**Figure 22** Illustration of emission rates for CO, $CO_2$ and $VOC_{tot}$ of pellets batches WP 78 to WP 80 applying different ventilation duration. The error bars (n=3) show the minimum and maximum emission rates.

Avoiding condensate during wood pellets storage and maintaining physical characteristics of wood pellets [141] [142], they were transported directly to the cooling section after pelletisation. Thus, wood pellets were not filled into intermediate storage or filled directly into the silo tank lorries without ventilation. The present tests proved the importance of ventilation regarding off-gassing emissions. Considering the results, it could be assumed that the effect of ventilation in relation to the emission reduction was limited.

Besides the off-gassing determination in glass flasks, the core temperature of the manually ventilated pellets batches in insulation boxes was determined. The core temperature of the investigated pellets batches was determined in order to prove the applied ventilation. The applied temperature data logger of WP 79 (15 min cooled) was not working. Thus, no temperature measurements were available. The temperature profile (Figure 23) of pellets batches was illustrated. It was clearly shown that the non-ventilated pellets batch was not cooled. After 20 min the temperature maximum of 87 °C was reached and the core temperature within the insulation box was obtained. Contrary, the maximum temperature of the 30 min ventilated pellets batch was achieved after 22 min with a temperature of 25 °C. The CO maxima were presented to show when and how high the reached CO maxima were in the insulation boxes. The two CO maxima were striking with 1228 ppm after 8 min and 125 ppm after 64 min for the non-ventilated, and for the 30 min ventilated pellets batch. This indicated that the cooling of pellets by ventilation was successful. Ventilation also reduced the rapid formation of CO within the closed insulation box. It was assumed that the ventilated pellets were already reacted by the ventilation, whereas the non-ventilated pellets reacted in the insulation boxes. Furthermore, it is supposed that the lower occurring temperatures in the insulation boxes reduced the reaction rates leading to lower formation of CO emissions.

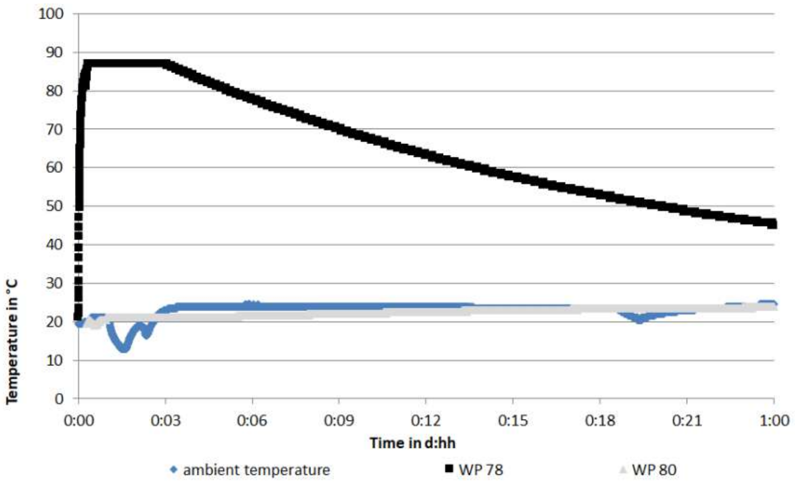


**Figure 23** Illustration of the temperature course of two pellets batches WP 78 and WP 80 within the insulation boxes indicating the core temperature. The ambient temperature (blue course) is given for comparison.

### III.4.3.2. Long-term off-gassing behaviour of ventilated pellets

The long-term behaviour of pellets with varying ventilation intervals regarding their off-gassing behaviour was analysed over a time period of 42 days (Figure 24). Therefore, the three pellets batches were stored in seven consecutive glass flasks experiments as described in chapter III.3.3. The cumulative amounts of formed gases are presented in Figure 24 a) c) and e) on the left. On the right side the changes of the emission rates are illustrated (Figure 24 b), d) and f)) over the 42 days of storage experiments.

Considering the entire measurement points in Figure 24 a) the ventilation did not show a considerable improvement on CO formation. It even appeared that the unventilated pellets batch produced the smallest amount of CO in total, after 42 days of storage. However, the first measurements show that less CO formed when the pellets were ventilated after production. This is additionally indicated by the CO emission rates in Figure 24 b). Considering both ventilated pellets batches, a very similar trend in cumulative CO formation and also in the course of the CO emission rates was revealed.

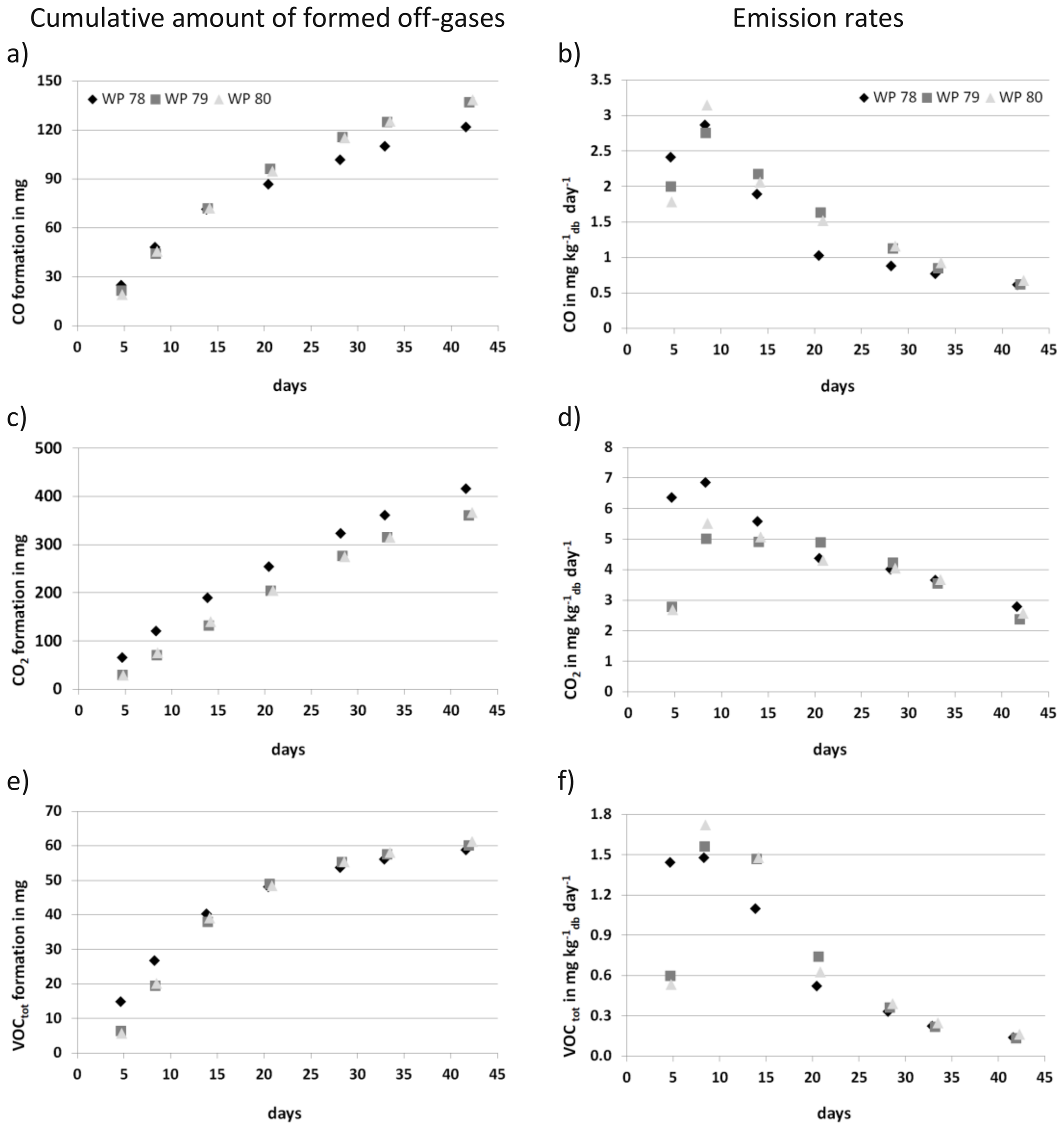


**Figure 24** Illustration of the cumulative amount of formed a) CO, c) $CO_2$ and e) $VOC_{tot}$ of the ventilation pellets batches during the 42 days of storage in glass flask experiments. The right graphs show the emission rates in mg kg$^{-1}$$_{db}$ day$^{-1}$ of b) CO, d) $CO_2$ and f) $VOC_{tot}$ during the 42 days of storage in glass flask experiments.

An explanation for the lower formation of CO of the non-ventilated pellets batch compared to the ventilated batches could be as follows. Probably, the non-ventilated and therefore still hot pellets already formed a higher amount of CO after the pelleting process compared to the ventilated pellets batches prior to the pellets storage in glass flasks experiments. This assumption was confirmed by the measured CO data and the above-mentioned CO maximum in the insulation boxes during the determination of core temperature. If hot fresh produced pellets should indeed be very reactive with regard to the formation of CO, caution is also required when handling hot fresh pellets. This means that attention should be paid to possible CO emissions during cooling or storage in the pelletising plant.

A closer look on the $CO_2$ formation and emission rates (Figure 24 c) and d)) indicated that both ventilated pellets batches behaved very similarly. Furthermore, it was shown that, especially at the beginning of the long-term storage experiment, higher $CO_2$ emission rates were determined by the non-ventilated pellets batch than by the ventilated ones. This trend was very similar for the measured $VOC_{tot}$ values (Figure 24 e) f)). Altogether, the two ventilated pellets batches behaved very similarly in terms of their off-gassing behaviour.

### III.4.3.3. Influence of ventilation time, temperature and technology on off-gassing

Two ventilation technologies for cooling of hot pellets were used for studying the influence of ventilation time, ventilation temperature and ventilation technology on off-gassing emissions. Therefore, six pellets batches were produced and analysed. Table 26 provides the pellets batches and a detailed list of the variations of the industrial scale pellets production ventilation experiment II (VEII). The following results present the calculated emission rates (see Figure 25).

**Table 26** List of the variations of the industrial scale pellets production ventilation experiment II (VEII). In total, six different pellets batches with varying ventilation temperature (ambient or cooled), ventilation time (average or twice as long as average) and ventilation technology (cooling tower or screw cooler) were produced.

| Batch | Temperature | | Time | | Technology | |
|---|---|---|---|---|---|---|
| | ambient | cooled | average | 2*average | cooling tower | screw cooler |
| WP 81 | X | | X | | X | |
| WP 82 | X | | | X | X | |
| WP 83 | | X | X | | X | |
| WP 84 | | X | | X | X | |
| WP 85 | X | | X | | | X |
| WP 86 | X | | | X | | X |

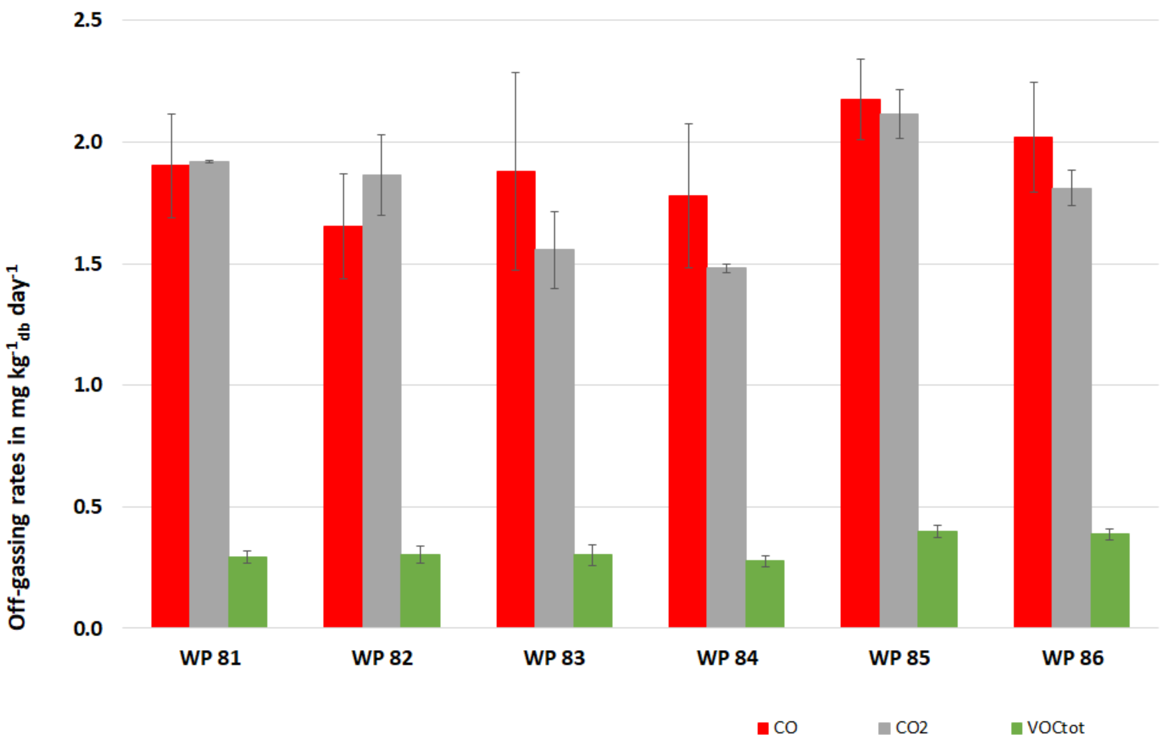


**Figure 25** Illustration of emission rates for CO, $CO_2$ and $VOC_{tot}$ of pellets batches WP 81 to WP 86 applying different cooling variations. The error bars (n=3) show the minimum and maximum emission rates.

### Ventilation time

In total, the parameter ventilation time was investigated three times. Therefore, the following pellets batches were compared with each other i) WP 81 with WP 82; ii) WP 83 with WP 84 and iii) WP 85 with WP 86. Considering the CO emission rates of those three pairs, it was shown that the CO emission rates were reduced by 5 to 13%. This trend was also proven for $CO_2$ emission rates, where the $CO_2$ emission rates were decreased by 3 to 14%. However, the $VOC_{tot}$ emission rates behaved differently. In two out of three pairs of comparison, $VOC_{tot}$ emission rates were reduced by 3 and 8%, whereas $VOC_{tot}$ emission rates were increased once despite doubling of the ventilation time. The comparison of ventilation time indicated an improvement concerning reduction in emission rates by doubling the ventilation time.

The results from core temperature determination showed that in two out of three determinations the maximum temperature was reduced by doubling ventilation time (see Table 27). The CO maximum values of the core temperature determinations of the batches with double ventilation time were higher and were also achieved at a shorter time compared to the CO maximum values of batches with average ventilation time. It seemed that the longer ventilated ones are more reactive in the beginning. This trend was contrary to the results from the glass flask methods analysing the same pellets batches. As discussed in VE I, it was likely, that the twice as long ventilated pellets batches compared to pellets ventilated for an average length of time were more reactive at the beginning regarding the formation of CO. However, during the subsequent storage experiments the longer ventilated pellets produced less CO. A possible explanation for this could be that the longer ventilation and the resulting longer forced oxidation led to further CO formation and the pellets reacted even more in the insulation box. Thus, the later CO formation in pellets storages or during transportation could be reduced.

**Table 27** List of the results in the course of the core temperature determination. The core temperature of the pellets in the insulation boxes and the time duration when this was set are indicated. In addition, the CO maxima in the insulation boxes and the time duration until they were reached are given.

| Batch | Core temperature in °C | Duration in h | CO max in ppm | Duration in h |
|---|---|---|---|---|
| WP 81 | 43 | 1.7 | 542 | 19.1 |
| WP 82 | 39 | 3.1 | 759 | 17.8 |
| WP 83 | 13 | 0.8 | 280 | 7.2 |
| WP 84 | 18 | 1.0 | 457 | 5.8 |
| WP 85 | 51 | 1.8 | 969 | 16.0 |
| WP 86 | 46 | 1.5 | 1103 | 11.5 |

### Ventilation air temperature – cooling

Furthermore, the influence of ventilation temperature for pellets cooling in pellets production on off-gassing emissions was investigated. The results of pellets batches WP 81 and WP 83 were considered together as well as WP 82 and WP 84. The difference between the pairs was the ventilation temperature. For pellets batches WP 81 and WP 82 ambient air was used. For the other two batches WP 83 and WP 84 the ventilation air was cooled down by a temperature difference of 20 °C. When comparing the parameter ventilation temperature, no definite trend was identified. By using cooled air compared to ambient air for ventilation, the CO emission rates were once lower and once higher. The $VOC_{tot}$ emission rates were similar. The cooling of ventilation air was only successful for $CO_2$ emission rates. The $CO_2$ emission rates of pellets ventilated with cooled air were reduced by 19 and 21% compared to the rates of pellets ventilated with ambient air.

The results for determination of core temperature indicated that the cooler the ventilation temperature the cooler the achieved core temperature. In addition to the reduction in core temperature, the CO maxima were also reduced by cooling the ventilation air. The maximum CO value of WP 81 was 542 ppm and 280 ppm for WP 83. The CO maxima values of WP 82 with 759 ppm and WP 84 with 457 ppm behaved similarly. Thus, the ambient air compared to the cooled ait, probably favoured the autoxidation processes leading to higher CO maximum values. A further explanation could be, that the ventilation with cooled air slowed down the processes and resulted in lower CO maximum values.

### Ventilation technology

Moreover, two cooling technologies specifically, the outward turning counter rotating screw with the cooling tower with a flow through from bottom to top were compared with the effect on the subsequent off-gassing behaviour during pellets storage. Considering the CO emission rates of the pellets batches WP 85 and WP 81 as well as WP 86 and WP 82, the CO emission rates of the pellets cooled by the manually installed cooling tower were lower. The reduction in CO emission rates was 13 and 18%. However, this trend was not reproduced when assessing $CO_2$ values. The measured $CO_2$ emission rates were once reduced by 9% and once the $CO_2$ emission rate was increased. Nevertheless, the different use of cooling technologies resulted in the largest difference in $VOC_{tot}$ emission rates. Reductions by 22 and 27% were achieved.

Besides the off-gassing behaviour the achieved core temperature of the pellets batches is listed in Table 27. Comparing the batches WP 85 with WP 81, it was obvious that the achieved core temperature was lower when the pellets batches were cooled by the manually installed cooling tower. The same result was achieved when comparing the core temperature of pellets batches WP 86 with WP 82. This lower core temperature could indicate a better cooling. This could have been achieved by a more homogenous ventilation air distribution within the cooling unit.

Overall, the best ventilation result in terms of CO reduction was achieved in applying the manually insulated cooling tower with double residence time in the cooler and the use of ambient air. Considering $CO_2$ emissions, the best result was observed by using the manually insulated cooling tower with double residence time in the cooler and the use of cooled air. With the same setup, the best result for the reduction in $VOC_{tot}$ was also achieved. In summary, the ventilation time showed the highest influence in terms of off-gassing reduction in the investigated parameter, ventilation time, ventilation air temperature and two used technologies.

# III.5. Conclusions

Various pellets production series were performed in order to investigate the influence of modifications in pellets production on off-gassing emissions. Therefore, different approaches were investigated.

**Usage of additives**

- The highest reduction of CO emissions of more than 70% was obtained with an addition of 0.8% (m/m) acetylsalicylic acid (ASA).
- The addition of 0.5% (m/m) grape pomace powder (GPP), a natural antioxidant, achieved a CO reduction of almost 50%.
- The addition of 0.3% (m/m) lime also resulted in a CO reduction of more than 50%.

The addition of ASA in wood pellets production indicated great potential for off-gassing reduction. However, the addition should be optimized in the respective plant to ensure particularly good results in terms of reducing off-gassing. Furthermore, physical wood pellets characteristics must be evaluated to ensure that they are not affected. The application of ASA proved off-gassing reduction over a longer period. Therefore, such a measure would also reach end users and might increase the safety along the pellets supply chain.

The use of natural antioxidants obtained different results. A higher efficiency related to the off-gassing reduction was observed with a lower addition of natural antioxidants. It has been shown that grape pomace powder (GPP) can considerably reduce off-gassing emission. Further research on the applicability of natural antioxidants is still needed.

The usage of slaked lime will only be effective in off-gassing reduction if it is applied in solid form. Even though slaked lime reduced off-gassing emission, it has been shown that its application is not so obvious. More energy is consumed and a possible higher level of abrasion cannot be excluded. In any case, the addition of slaked lime will increase the ash content. This means that the quantity added should be distinctly less than 0.5% (m/m) in order to fulfil the requirements for graded wood pellets of ISO 17225-2 [2]. It can also not be excluded that other wood pellets characteristics may be affected which, among other things, could also affect combustion properties.

**Blending with antioxidant raw materials**

- Both the blending of 5% (m/m) maritime pine bark and the blending of 20% (m/m) oak sawdust without bark reduced CO emissions by more than 60%.

The addition of wood raw materials such as oak, larch and maritime pine indicated high potential for off-gassing reduction. The applicability would probably have to be tested in each pelletisation plant. If the bark content is too high, additional attention must be paid to the ash content and other wood pellets characteristics. Furthermore, raw material prices and their availability need to be considered for economic reasons.

**Modifications of ventilation in the pellets production process**

- The use of the two ventilation technologies, cooling tower and screw cooler, resulted in different emission rates. The use of the cooling tower led to a moderate CO reduction of up to 18%.
- Doubling the ventilation time and the associated forced oxidation reduced CO emissions by a maximum of 13%.

Both the ventilation time and the ventilation technology demonstrated an influence on the CO emission behaviour. The exchange of the ventilation technology revealed the highest influence in terms of off-gassing reduction from the investigated parameter, ventilation time (forced oxidation), ventilation air temperature (cooling) and the two used technologies. Even if the ventilation time or its extension indicated a positive effect on the subsequent off-gassing behaviour, an extension of ventilation time is often difficult to achieve in pellets production due to the production capacity.

**Off-gassing reduction in pellets production**

Different modifications in the pellets production demonstrated varying degrees of influence on the off-gassing behaviour of wood pellets. Only individual measures were assessed within this study. No assessment was made on the impact of several combined measures. It is still unclear whether an additional improvement could be achieved if several measures were applied which would possibly improve the storage atmosphere and perhaps increase the safety along the pellets supply chain.

# IV. Pellets storage

## IV.1. Introduction

The usage of wood pellets in the industrial and residential sector has multiplied over the last 20 years [1] [8] [7]. This high growth in wood pellets usage has led to an increase in storage of wood pellets. Pellets are stored at the producer, intermediary, power plant or at the end user's own site. Wood pellets are transported from the production site to the next storage location in one or more transportation steps. Therefore, wood pellets are shipped by sea using cargo, by train, silo tanker or truck [1] [143]. In recent years, great efforts have been made to increase storage safety. For this purpose, international standards for storage safety have been established along the pellets supply chain [4] [5].

The very first fatal accident regarding hazards of storing and transporting wood pellets occurred in 2002. One person died in a stairway between two cargo holds which had been filled with wood pellets [13] [144]. In the following years, accidents with fatal outcomes in connection with the storage and transportation of wood pellets were reported again and again [90] [91] [144] [145] [146] [147] [148] [149] [150] [151]. The examination of 26 production sites and 250 measurements clearly showed that the maximum working place concentration for CO of 30 ppm [30] is exceeded many times. Within this comprehensive study, the storage along the production at the retailer and at the end user were studied [143]. A further study monitored 16 non ventilated and 8 ventilated wood pellets storage facilities of different types. CO peaks of freshly stored pellets were all found to be above the workplace concentration value. In addition, it was found that the tighter the storage structure, the higher the CO peaks are inside the storage. In total, in two pellets storage facilities CO concentrations > 1000 ppm were detected [21]. A further study investigated pellets storages and boiler rooms. There, the maximum concentration of 155 ppm CO was detected inside a storage. According to those results, the authors mentioned, no concentrations had been observed that would have caused short-term health effects [152]. Moreover, another study confirmed that CO concentrations are generally low in studied homes [153]. Thus, in literature are quite different statements regarding a possible hazard in the storage of wood pellets at the end user's storage facility.

In addition, to the above-mentioned studies of pellets storage, studies were conducted on the stratification and purging of off-gassing emissions during wood pellets storage [22] [154] [155]. The forced ventilation, the applied purging, decreases the off-gassing concentration in pilot scale experiments [154]. Furthermore, within pilot scale tests a stratification of CO is observed. Moreover, a large decrease in $O_2$ to below 5% in the headspace can be achieved within one week [155]. The stratification of CO and the rapid decrease in $O_2$ raise the question in what way ventilation of pellets storage facilities increases storage safety.

Although some investigations have already been undertaken regarding wood pellets storages, detailed information of the stored pellets with respect to their off-gassing behaviour is missing.

## IV.2. Objectives and approach

The objective of this chapter is to prove whether ventilation or cross-ventilation in wood pellets storage facilities improves the storage atmosphere. Therefore, two approaches are performed: i) monitoring of real wood pellets storages in the field and ii) ventilation trials in pellets storage facilities. This chapter is based on the peer-reviewed journal paper number 5. In addition to these published experiments, further aspects of pellets storage and ventilation measures are investigated.

### IV.2.1. CO monitoring in the field in real wood pellets storages

Firstly, the CO concentrations in real wood pellets storage facilities at end users are measured in order to show the CO course during the storage of wood pellets. Simultaneously, the emission rates of those pellets stored inside the storages are analysed to provide further details on the CO courses.

- The aim is to show that ventilation during wood pellets storage affects the storage atmosphere considering CO concentration.

### IV.2.2. Ventilation of CO in wood pellets storages

Secondly, ventilation of CO in pellets storages is investigated. Therefore, the decline of CO in pellets storages by usage of different ventilation settings are examined. The use of a second ventilation, cross-ventilation, is analysed.

- The aim is to show whether cross-ventilation increases the air exchange. Furthermore, the aim is to indicate the influence of the cross-sectional area of ventilation openings on CO reduction in pellets storages.

# IV.3. Material and methods

## IV.3.1. Wood pellets samples

An overview on the investigated wood pellets batches in this chapter, their batch number and sample characteristics are given in Table 28.

**Table 28** List of the investigated wood pellets batches, the used raw material, the production and their characteristics. (ISPP stands for industrial scale pellets production)

| Batch | Raw material | Production | d in mm | Moisture content in % (m/m) | $\rho_{pellets}$ in kg m$^{-3}$ |
|---|---|---|---|---|---|
| WP 87 | unknown[1] | ISPP | 6 | 7.9 | 1190 |
| WP 88 | 50/50 pine/spruce | ISPP | 6 | 7.7 | 1215 |
| WP 89 | 50/50 pine/spruce | ISPP | 6 | 8.4 | 1185 |
| WP 90 | 50/50 pine/spruce | ISPP | 6 | 9.3 | 1204 |
| WP 91 | unknown[1] | ISPP | 6 | 6.3 | 1245 |
| WP 92 | unknown[1] | ISPP | 6 | 7.9 | 1221 |
| WP 93 | unknown[1] | ISPP | 6 | 8.2 | 1198 |

[1] purchased on the Austrian market; Pellets quality A1 according to ISO 17225

## IV.3.2. Measuring equipment and calculation

### IV.3.2.1. Measuring equipment for CO monitoring in real wood pellets storages

In the course of the field monitoring trials, the real pellets storage facilities were equipped with two data loggers. One logger recorded the CO concentration and the second measured temperature and relative humidity. Figure 26 and Table 29 show detailed information on the applied data loggers.

**Figure 26** Illustration of the applied data loggers: a) EL-USB-CO for CO measurement and b) EL-USB-2 to measure relative humidity and temperature (source: LASCAR electronics).

**Table 29** Manufacturer specifications of used data loggers from Lascar electronics.

| Product name | Measured parameter | Range | Uncertainty | Measurement interval |
|---|---|---|---|---|
| Easy Log EL-USB-2 | T | - 35 to + 80° C | ± 2 °C | every 10 min |
| Easy Log EL-USB-2 | RH | 0 to 100 % RH | ± 6.0 % RH | every 10 min |
| Easy Log EL-USB-CO | CO | 0 to 1000 ppm | ± 6 ppm | every 5 min |

### IV.3.2.2. Equipment for ventilation tests in wood pellets storages

For CO and $O_2$ measurements in the ventilation trials the Ecom J2KNpro or the Varioplus Industrial was used. The detailed information on measured parameters is specified in Table 30.

**Table 30** Information on the gas analyser and the measured parameters and their specifications (Source: Emhofer [21]).

| Gas analyser | Parameter | Measurement Principle | Range | Accuracy |
|---|---|---|---|---|
| Ecom J2KNpro | $O_2$ | electrochemical cell | 0 – 21 % | ≤ 5% |
| | CO | electrochemical cell | 0 – 2500 ppm | ± 3% |
| Varioplus Industrial | CO | nondispersive infrared | 0 – 2000 ppm | ± 10 ppm |

The temperature was measured using thermocouples type K (NiCr-Ni) with an application range of - 40 to 1000 °C (accuracy of ± 1.5 °C). The thermocouples are very robust against external influences and react quickly to temperature changes [156].

Synthetic gases (obtained from Linde AG) were used for the setting of a specific CO concentration. Therefore, synthetic air (20% V/V $O_2$; 80% V/V $N_2$) was mixed with pure CO (≥99.997%). The investigated pellets storage facility was then filled with the mixture until a homogeneous and defined CO concentration was achieved.

#### IV.3.2.3. Calculation of air exchange rate

Air exchange rates were calculated according to ISO 12569 - Thermal performance of buildings and materials - Determination of specific airflow rate in buildings - Tracer gas dilution method [157]. Within the ventilation experiments, the tracer gas was CO. The 2-point concentration decay method was applied. Using this method, the measurement must be completed within several hours and the concentration of the measured gas has to be homogenously distributed in the measured area. The experiments were started when the desired CO concentration in the pellets storage was reached. The air exchange rate was calculated based on the measured concentration of CO in the investigated wood pellets storage tank. Further details on the calculations are found in Emhofer [21] [158].

### IV.3.3. Off-gassing determination

For off-gassing determination the glass flask method was used [12] [15] [16]. This method based on the method of Kuang [13] was described in detail in chapter II 3.2.4.

### IV.3.4. Pellets storage facilities

#### IV.3.4.1. Pellets storage rooms

Four wood pellets storage rooms, which were all located in the basement, were monitored for CO measurements. One storage room (monitoring trial 1) was erected from three-layer panels. The other storage rooms (monitoring trials 2-4) were bricked and plastered and were equipped with an entrance door. The storage rooms had different pellets storage capacities which are listed in Table 31. All storage rooms were equipped with two Storz A couplings for filling with pellets.

### IV.3.4.2. Underground pellets storage tank

Monitoring and ventilation trials were performed with buried plastic underground storage pellets tanks (GEOtank GEO 11/EG 2). The respective pellets tanks (see Figure 27) had a volume 11 m³ and hold up to 6 tonnes of wood pellets. Two Storz A couplings for filling the pellets were located under the lid at the top of the tank.

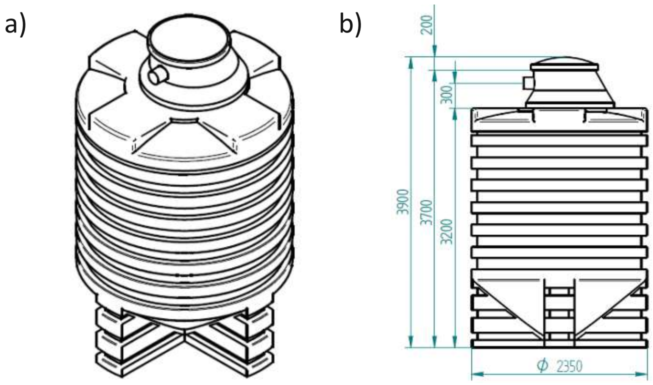


**Figure 27** Illustrations of the GEOtank a) general design and b) dimensions in mm of the used underground storage tank (source: GEOplast Kunststofftechnik GmbH).

### IV.3.4.3. Concrete pellets storage tank

The following descriptions are based on the appended peer-reviewed journal paper number 5. The concrete pellets tank (see Figure 28) was made of reinforced concrete and had a total volume of 10.27 m³. Two Storz A couplings for filling the pellets were located at the top of the tank.

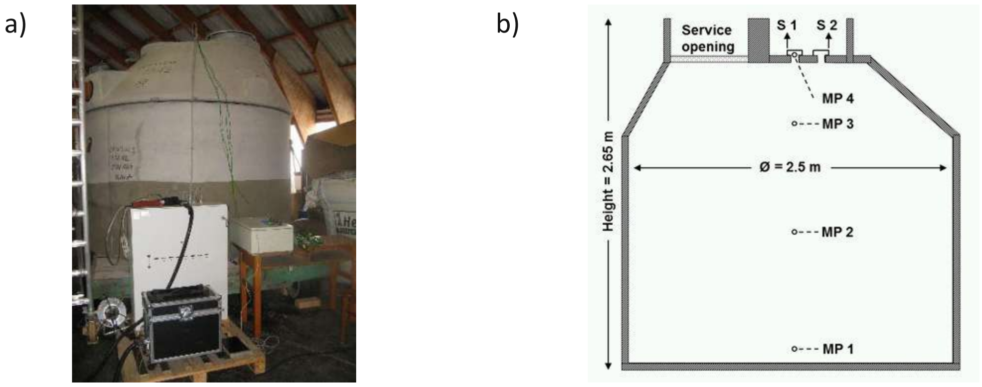


**Figure 28** a) Setup of the concrete storage tank showing the used gas analysing equipment including the switch board for measurement cycles and the measurement data recording; b) Design of the concrete storage tank and the measurements position points (MP1 – MP4); (Source: Emhofer et.al 2015 [21]).

## IV.3.5. CO monitoring in the field in real pellets storages at the end users

The investigated pellets storage facilities were filled with commercially available A1 wood pellets before the start of the monitoring trials. The monitored pellets storage facilities were located at end users and were in operation during the monitoring trials. Thus, during the monitoring trials, the pellets were removed by the pellets removal device according to energy demand. For CO, temperature and relative humidity measurements, data loggers were applied. The time of logger installation in relation to pellets delivery is given in Table 31. Inside the pellets storage rooms, the loggers were installed at Storz A coupling straight in front at a distance of 30 cm. Additionally, a CO data logger was installed in each of the adjacent basement rooms at the entry door to the pellets storage room (monitoring trial 1-4). At the same time 10 kg pellets were taken and deep-frozen at -18° C until the later off-gassing analysis. Additionally, to the installation of the data loggers, the storage rooms were equipped with two ventilation caps B (see Figure 29 c). The ventilation caps had a cross-sectional area (CSA) of 12 cm². The caps were installed at both Storz A couplings which are used for filling with wood pellets by silo truck.

**Table 31** List of the monitoring trials in the field and detailed information about the trials. The storage capacity indicates how many tonnes of pellets the storage holds. The delivered amount represents the amount of delivered pellets in the last delivery (time of delivery). The estimated amount estimates the pellets amount stored at the start of the monitoring trial.

| Monitoring trial | Storage capacity in t | Delivered amount in t | Time of delivery in weeks | Estimated amount in t | Description of the pellets storage facility |
|---|---|---|---|---|---|
| 1 | 15 | 12 | 24 | 3 | storage room constructed from three-layer panels with door (90*200 cm) |
| 2 | 8 | 6 | < 1 | 7 | brick built and plastered basement room with door (85*200 cm) |
| 3 | 10 | 9 | < 1 | 9 | brick built and plastered basement room with door (80*120 cm) |
| 4 | 8 | 6 | < 1 | 8 | brick built and plastered basement room with door (90*200 cm) |
| 5 | 6 | 6 | < 1 | 6 | underground storage tank |
| 6 | 6 | 6 | < 1 | 6 | underground storage tank |
| 7 | 6 | 6 | < 1 | 6 | underground storage tank |

For the monitoring trials with the underground storage tanks the data loggers were placed at the top of the Storz A couplings in the downward direction, 30 cm below the Storz A couplings. At the same time 10 kg pellets were taken and deep-frozen at -18° C until analysis. The tank was equipped with 2 caps supplied by the manufacturer. According to the manufacturer, these caps had a pressure compensation and protected the tank from water entry.

After the attachment of the data loggers, the monitoring trials were started. At the end, the recorded data was transferred to a personal computer where the data was analysed with the supplied software.

## IV.3.6. CO ventilation in pellets storage facilities

### IV.3.6.1. Ventilation of CO in an underground pellets storage tank

The cross ventilation from carbon monoxide depending on cross-sectional area (CSA) were investigated using a plastic underground pellets storage tank. Analysing different ventilation conditions of the GEOtank, different caps for the two Storz A couplings (Storz 1 and 2) were used. Therefore, an insulated chimney (see Figure 29 a)) was installed on Storz 2 within all three ventilation trials. Due to the volume of the stored pellets of 0.5 m³, the air volume above the pellets was reduced to 10.5 m³ air.

**Table 32** List of caps and chimneys and the corresponding cross-sectional areas (CSA).

| Ventilation trial | Storz 1 | CSA Storz 1 in cm² | Storz 2 | CSA Storz 2 in cm² |
|---|---|---|---|---|
| 1 | open (no cap) | 95 | insulated chimney | 133 |
| 2 | ventilation cap A | 22 | insulated chimney | 133 |
| 3 | ventilation cap B | 12 | insulated chimney | 133 |

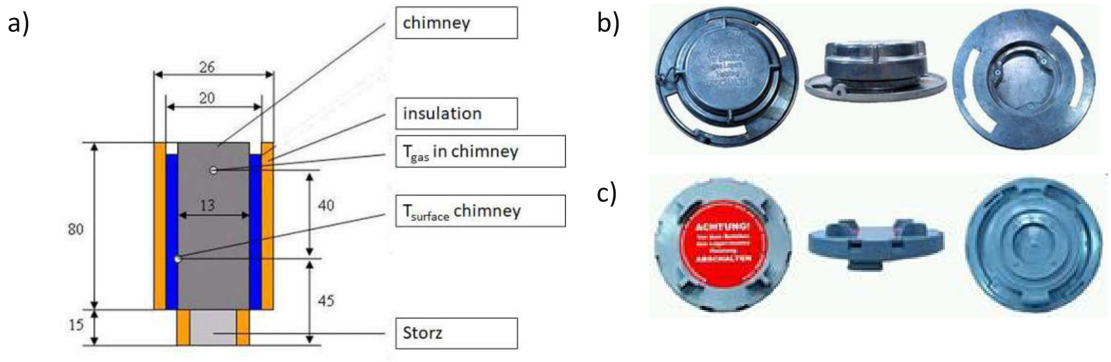


**Figure 29** Schemata of the used a) insulated chimney and figures of the applied ventilated caps b) ventilation cap A c) ventilation cap B (Source: Emhofer [21].

The settings mentioned in Table 32 were prepared for the tree ventilation trials. Two temperatures were recorded during the trials: i) temperature of the surrounding and ii) inside the GEOtank. The atmosphere above the pellets was set to a specific concentration of CO using the mixed gases. The start concentration was measured with gas analyser Rbr-ecom J2KNpro and the experiment was started. Every 10 min the CO concentration was measured. The experiment was continued until a CO difference of about 150 ppm CO was measured inside the GEOtank.

### IV.3.6.2. Ventilation of CO in a concrete pellets storage tank

The following experiments are based on the appended peer-reviewed journal paper number 5. The ventilation of CO was investigated by varying the equipment on both Storz couplings (S1 and S2 in

Figure 28 b)) of a concrete pellets storage tank. The used ventilation equipment and procedure is described in detail by Emhofer *et al.* [158] – the peer-reviewed journal paper number 5.

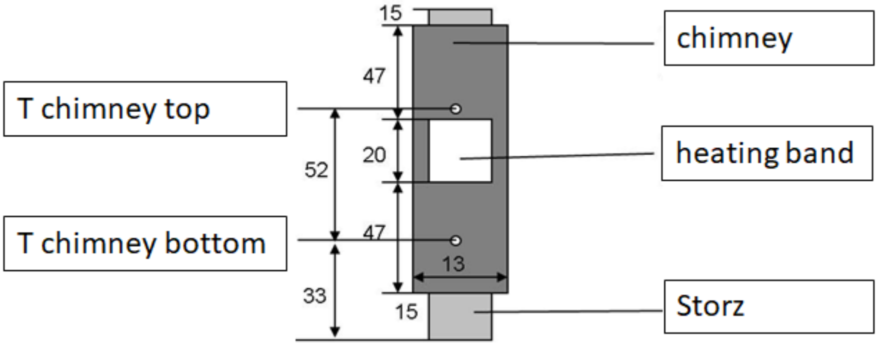


**Figure 30** Schemata of the used heated chimney.

The concrete pellets tank was filled with approximately 800 ppm CO at the beginning of each experiment. The CO concentration was measured at three measurement points (MP1 – MP3 depicted in Figure 28 a)) using the Varioplus Industrial gas analyser. In total 10 ventilation trials were performed (see Table 33).

**Table 33** Description of experimental setup of the trials 1 – 10 (Source: Emhofer *et al.* [158]). For the ventilation trials 1, 2,9, and 10 ventilation cap A (illustrated by Figure 29 b) with a CSA of 22 cm² was applied. For ventilation trials 3 and 4 the heated chimney (Figure 30) was used but the heating band was not used. In the ventilation trials 5 und 6 the heated chimney was installed. For the ventilation trials 7 and 8 the insulated chimney (Figure 29 a) with a mixture of ice and water was used.

| Ventilation trial | Storz 1 Short | Storz 1 explanation | Storz 2 short | Storz 2 explanation |
|---|---|---|---|---|
| 1 | opening | ventilation cap A | closed | closed with blind bolt |
| 2 | opening | ventilation cap A | open | ventilation cap B |
| 3 | chimney | chimney (heated chimney) | closed | closed with blind bolt |
| 4 | chimney | chimney (heated chimney) | open | ventilation cap B |
| 5 | heated | heated chimney | closed | closed with blind bolt |
| 6 | heated | heated chimney | open | ventilation cap B |
| 7 | cooled | ice-cooled chimney | closed | closed with blind bolt |
| 8 | cooled | ice-cooled chimney | open | ventilation cap B |
| 9 | opening | ventilation cap A | closed | closed with blind bolt |
| 10 | opening | ventilation cap A | open | ventilation cap B |

# IV.4. Results and discussion

## IV.4.1. CO monitoring in the field in real pellets storages at the end users

In total seven real wood pellets storages were monitored in the field at the end user. Four different pellets storage rooms were investigated using ventilation caps. Additionally, three monitoring trials in an underground storage tank with caps that provided pressure compensation were performed. In Table 34 the main results of the monitoring trials are listed. The monitoring trials lasted between 30 and 64 days. The storage capacity specified the maximum storage of wood pellets. The filling quantity indicated how many tonnes of pellets were stored at the start of the monitoring measurements. The share of fresh pellets in relation to the total stored quantity was given because fresh pellets are known to be more reactive in terms of off-gassing formation. In addition, the time of pellets delivery was given in relation to the start of monitoring trial.

The CO measurements of the neighbouring cellar room along the monitoring trials confirmed the tight construction of the pellets storage rooms. The CO peak readings were in the range of 0 to 1 ppm (see right column in Table 34). The workplace concentration value gives the limit for the maximum permissible concentration of a hazardous substance in the air at the workplace for a particular substance. This value is set at 30 ppm for CO [159]. The findings implied that for the investigated pellets storage rooms, no danger existed in the adjacent basement rooms.

The monitoring trials demonstrated different CO peaks in a range from 5 to > 1000 ppm (see Table 34). The time at which these CO peaks were measured also varied considerably. These CO peaks were reached after less than 1 hour up to 40 days. The CO values measured after 1 week also varied. The average temperature and relative humidity during the monitoring trials were given. The temperatures in the underground pellets tanks were lower than in the pellets storage rooms in the basement.

The comparison of the CO peaks indicated lower peaks for the ventilated storage rooms (ventilation trials 1-4) than for the only pressure compensated underground storage tanks, as awaited. As expected, the lowest CO peak was measured in monitoring trial 1. The following explanations were feasible. The filling quantity of the storage was around 20%, which led to a corresponding dilution of the formed CO. Moreover, the pellets were delivered 24 weeks before the start of the monitoring trial. Therefore, the stored pellets were less reactive than freshly delivered pellets [21].

**Table 34** Details of the monitoring trials in the field. The storage capacity of each wood pellets storage, its filling quantity, the share of fresh pellets and the passed time since pellets delivery when the monitoring trials started. The monitoring duration and the highest CO concentrations in the adjacent basement room are given. The highest measured CO value and when it was reached are displayed. The measured CO value after one week and the average storage temperature and relative humidity are shown.

| | Monitoring trial | Storage capacity in t | Filling quantity in % | Fresh pellets in % | Time of delivery in weeks | Duration in days | CO peak adjacent room in ppm | CO maximum in ppm | Time of CO maximum in h or days | Temperature in ° C | Relative humidity in % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| storage room | 1 | 15 | 20 | 0 | 24 | 30 | 1 | 5 | < 1 h | n.d.[1] | n.d.[1] |
| | 2 | 8 | 88 | 86 | < 1 | 58 | 1 | 30 | 5 days | 16 | 10 |
| | 3 | 10 | 90 | 100 | < 1 | 56 | 1 | 56 | 7 days | 21 | 33 |
| | 4 | 8 | 100 | 75 | < 1 | 56 | 0 | 155 | 13 days | 15 | 39 |
| underground storage tank | 5 | 6 | 100 | 100 | < 1 | 40 | not installed | 436 | 40 days | 5 | 39 |
| | 6 | 6 | 100 | 100 | < 1 | 34 | not installed | 263 | 5 days | 5 | 45 |
| | 7 | 6 | 100 | 100 | < 1 | 64 | not installed | 1051[2] | < 1 h | 12 | 50 |

[1] n.d. indicates not detected

[2] The CO value exceeded the measuring range of the used logger.

In literature, a monitoring series of 24 ventilated and non-ventilated pellets storages revealed CO peaks in the range from 10 up to more than 2500 ppm. The measured CO peaks within those ventilated pellets storages did not exceed 271 ppm [21]. The present CO values in ventilated storage rooms were less than 156 ppm (see Table 34). However, a further study depicted much lower CO concentrations within twelve pellets storages at the end user with CO concentration of ≤ 58 mg m$^{-3}$. It must be mentioned here that some of those pellets had already been stored for several months prior to the monitoring experiments [143]. This certainly led to the reported low CO values. A further CO monitoring series in and next to wood pellets storages revealed CO peaks in the range of 14 to 155 ppm CO [152].

In addition, to the present monitoring trials, the stored pellets from the monitoring trials were examined with regard to their off-gassing behaviour. Therefore, the pellets batches at the beginning of the monitoring trials were sampled and analysed using the glass flask method. The CO emission rates were intended to provide further information on the monitoring trials (see Table 35).

**Table 35** List of the investigated pellets batches taken before the monitoring trials. The emission rates for CO, $CO_2$ and $VOC_{tot}$ and the residual $O_2$ concentration are presented.

| Batch | Monitoring trial | CO | $CO_2$ | $VOC_{tot}$ | Residual $O_2$ in % (V/V) | Pellets weight in kg |
|---|---|---|---|---|---|---|
| | | in mg kg$^{-1}$ pellets$_{db}$ day$^{-1}$ | | | | |
| WP 87 | 1 | 0.03 | 0.51 | 0.00 | 20.9 | 2.4 |
| WP 88 | 2 | 2.00 | 2.77 | 0.59 | 4.6 | 2.4 |
| WP 89 | 3 | 1.00 | 1.96 | 0.22 | 12.2 | 2.4 |
| WP 90 | 4 | 0.59 | 1.35 | 0.11 | 15.8 | 2.4 |
| WP 91 | 5 | 0.56 | 2.38 | 0.13 | 15.9 | 2.4 |
| WP 92 | 6 | 0.22 | 1.22 | 0.06 | 18.8 | 2.4 |
| WP 93 | 7 | 0.81 | 2.06 | 0.21 | 14.3 | 2.4 |

The pellets batch of monitoring trial 1 showed the considerably lowest emission rates for CO, $CO_2$ and $VOC_{tot}$. As mentioned before, this monitoring trial also revealed the lowest CO peak. Comparing the emission rates and the measured CO peaks of monitoring, trials 2-4 with monitoring trials 5-7 proved a better ventilation of the ventilated storage rooms. This is indicated by the considerably lower CO peaks at partially higher CO emission rates in trials 2-4.

The ventilation of wood pellets storages has been nationally regulated since 2012 for newly installed storages in Austria [160]. Since 2018, the ventilation and further requirements for safe handling and storage of wood pellets in residential and other small-scale applications were internationally specified [4]. According to the results, this is a good measure to reduce the CO concentration in wood pellets storages. But it should be noted that even in the ventilated storage rooms, the prevailing CO concentration may be much too high. This means that utmost caution is required when handling pellets storages and sufficient ventilation is essential before entering. Monitoring tests of the underground storage tanks showed that life-threatening CO concentrations prevailed in some cases. In addition to sufficient ventilation, the use of a CO warning device is urgently recommended when handling an underground pellets storage tank.

As additional information to the field monitoring trials, the CO courses are presented in Figure 31. The CO course of monitoring trial 1 (Figure 31 a)) showed that only a low CO concentration prevailed in that pellets storage room. At the end of the trial, no CO was measured. The CO courses of monitoring trials 2-4 (see Figure 31 b-d) were shown side by side because they were similar storage rooms and equipped with the same ventilation caps. When comparing the 3 monitoring trials, the different courses were obvious. Within monitoring trial 2, the pellets with highest reactivity regarding their CO emission represented the lowest CO peak. The comparatively low CO peak was probably due to the lower filling level and the associated lower share of fresh pellets compared to the total storage capacity. The CO peaks and the corresponding CO emission rates of the pellets from trial 2-4 indicated that dilution of CO was achieved through the inserted ventilation caps. At the same time, the pellets removal and the associated additional air further supported the dilution.

Monitoring trials 5-7 (see Figure 31 e-g) offered the best comparability. All three tanks contained no pellets before filling and were completely filled with fresh pellets. As the CO emission rates increased, elevated CO peaks were also observed. Nevertheless, they had different CO profiles. This was probably due to the different removal of the pellets and the varying CO emission rates. In trials 5 and 7, pellets were still in the tank at the end of the monitoring trials. However, in trial 6 (see Figure 31 f) no pellets were left in the tank. This explained the considerably lower measured CO concentration at the end of the trial.

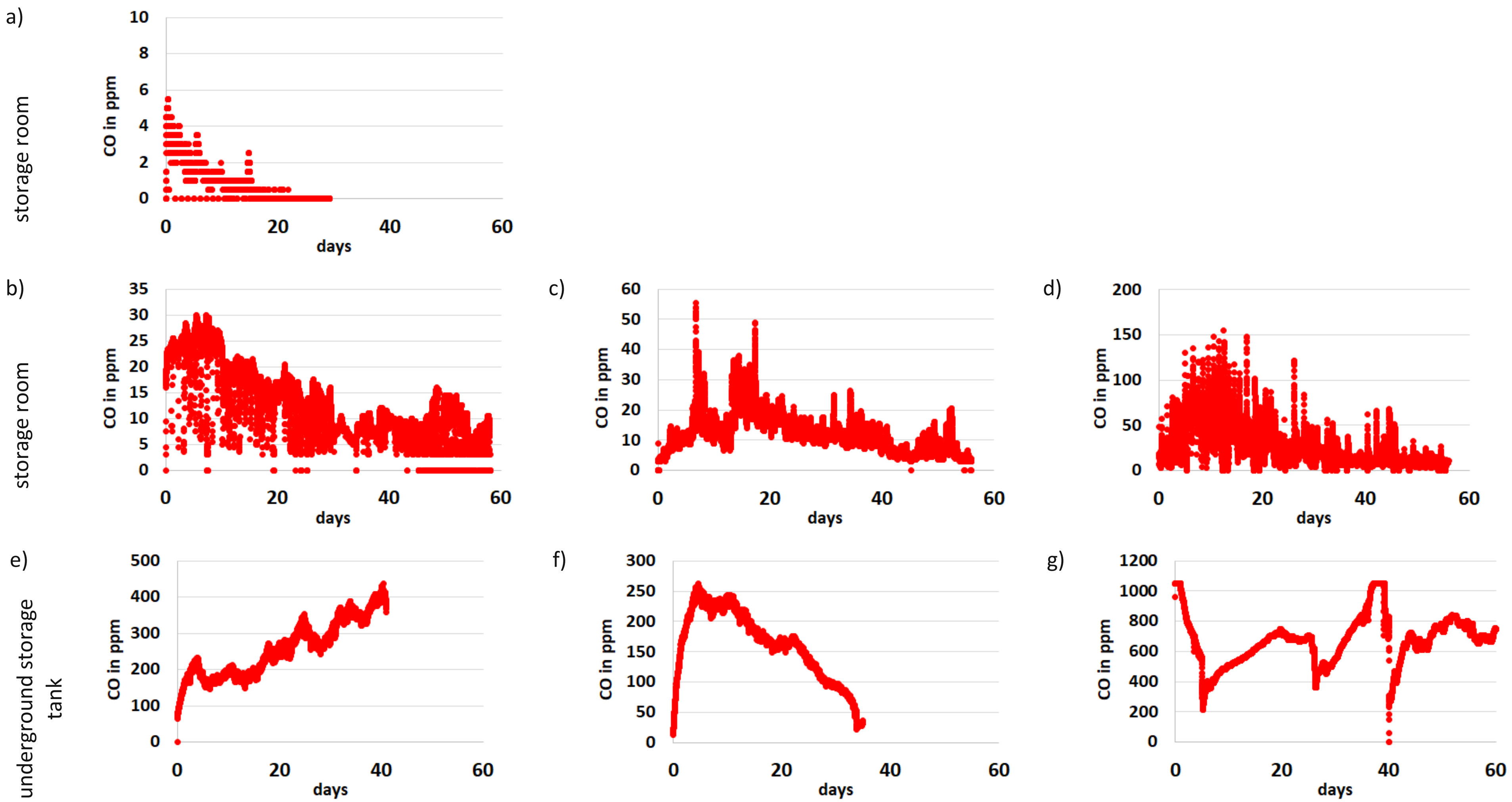


**Figure 31** Diagrams of the CO courses of monitoring trials a) 1, b) 2, c) 3, d) 4, e) 5, f) 6 and g) 7.

## IV.4.2. CO ventilation in pellets storage facilities

### IV.4.2.1. Ventilation of CO in a concrete pellets storage tank

The following results are based on the appended peer-reviewed journal paper number 5. The results are presented as follows in an amended form [158]. The detailed experimental procedure of the ventilation trials as well as the duration, the individual CO start and end concentrations, and air exchange rates are provided in Table 36.

**Table 36** List of the ventilation trials. Test setup using the different attachments on Storz 1 and Storz 2 as well as the CO concentrations, the trial duration and the calculated air exchange rates (AER). AER 1 is calculated over the entire experimental duration whereas AER 2 is calculated over the first hour of the ventilation trial.

| Ventilation trial | Storz 1 | Storz 2 | CO start in ppm | CO end in ppm | Duration in h | AER 1 in $m^3h^{-1}$ | AER 2 in $m^3h^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1 | opening | closed | 807 | 463 | 44.0 | 0.13 | 0.26 |
| 2 | opening | open | 856 | 190 | 9.1 | 1.71 | 0.53 |
| 3 | chimney | closed | 847 | 199 | 38.2 | 0.39 | 0.34 |
| 4 | chimney | open | 806 | 130 | 11.1 | 1.70 | 0.45 |
| 5 | heated | closed | 875 | 175 | 10.2 | 1.64 | 1.16 |
| 6 | heated | open | 850 | 170 | 2.3 | 7.10 | 7.81 |
| 7 | cooled | closed | 866 | 199 | 25.2 | 0.60 | 1.18 |
| 8 | cooled | open | 846 | 167 | 2.2 | 7.89 | 7.31 |
| 9 | opening* | closed | 860 | 318 | 44.0 | 0.23 | 0.28 |
| 10 | opening* | open | 838 | 174 | 5.7 | 2.85 | 0.42 |

* The ventilation trials 1 and 2 were repeated in ventilation trials 9 and 10.

The comparison of the two calculated AERs, AER1 and AER2, did not follow a trend. The AER1s were partially higher and partially lower compared to the AER2s. However, opening the Storz 2 always increased the AERs, regardless of whether the AERS were calculated over the entire period or over the first hour.

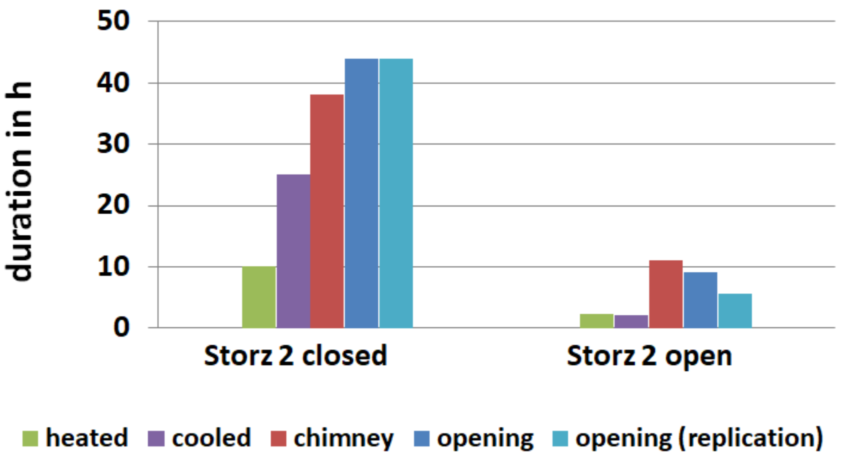


**Figure 32** Representation of the ventilation trial duration using different attachment of caps and chimneys on Storz 1 and Storz 2, respectively. Four different settings were varied on Storz 1: heated chimney, cooled chimney, chimney or without a chimney (opening). Storz 2 was either open or closed.

Figure 32 indicates the accelerated CO decrease by opening the Storz 2. That is, a second ventilation -cross ventilation- demonstrably improved the air exchange. Thus, a considerable shortening of the test duration was achieved. Major improvements in terms of shortening the ventilation trial duration, i.e. shortened CO reduction, through the opening of Storz 2, were obtained in all ventilation trials (Storz 2 open: ventilation trials 2, 4, 6, 8, and 10).

Both ventilation trial series, in which the chimney was heated or cooled (Storz 1) under open or closed Storz 2 showed comparatively lower trial durations. From this, it was indicated that the temperature effect was a major factor contributing to the increase in ventilation. The underlying paper additionally investigated the influence of temperature on the air exchange rates in the pellets storage tank. For further information see the peer-reviewed journal paper number 5.

#### IV.4.2.2. Ventilation of CO in an underground pellets storage tank

Three ventilation trials were performed in order to investigate cross ventilation with the purpose of CO reducing. Table 37 displays the implemented caps and chimneys and the resulting CO reduction, the calculated air exchange rates and the duration of the trials. The duration described the time period it took to reduce the initial CO concentration by about 150 ppm (143, 159 and 168 ppm).

**Table 37** Experimental data and results of the ventilation trials 1-3. The attachments to Storz 1 and 2 specifying their cross-sectional area (CSA) as well as the CO concentrations, the ventilation trial duration and the calculated air exchange rate (AER).

| Ventilation trial | Storz 1 | CSA in cm² | Storz 2 | CSA in cm² | CO start in ppm | CO end in ppm | Duration in h | AER in $m^3h^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | no cap | 95 | chimney | 133 | 338 | 170 | 0.75 | 9.4 |
| 2 | cap A | 22 | chimney | 133 | 352 | 193 | 2.57 | 2.4 |
| 3 | cap B | 12 | chimney | 133 | 505 | 362 | 3.92 | 0.9 |

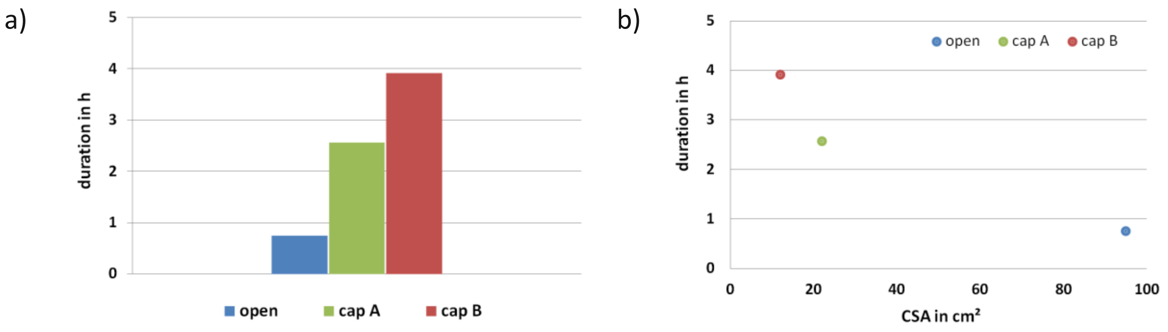


**Figure 33** a) Representation of the ventilation trial duration using different attachment of caps on Storz 1. b) Representation of the test duration decrease as a function of the cross-sectional area (CSA).

Different air exchange rates were determined caused by different ventilation conditions during the trials. The conditions were changed by installing different caps to Storz 1. Maximum ventilation was realized without using any cap (open Storz 1) combined with the insulated chimney (Storz 2). In order to enable comparable results, the reduction of CO was set to about 150 ppm for the calculation of air exchange rates of the three ventilation trials. The left diagram in Figure 33 indicates how long it requires to reduce the CO concentration in the underground storage tank using no cap (open) by 168 ppm, using cap A by 159 ppm and using cab B by 143 ppm. The CO reduction within the underground storage tank depended on the CSA of the applied caps. Figure 33 b indicates that the ventilation trial duration decrease (CO reduction) is accelerated with increasing CSA. With increasing CSA, the duration decreases while the air exchange rate increases.

## IV.5. Conclusions

**Monitoring trials in the field of real wood pellets storage facilities**

The monitoring trials in the field of real wood pellets storages showed a broad range on CO courses and different CO peaks.

The monitoring series indicated that the investigated wood pellets storage rooms were tightly built, because a CO leakage into the adjacent rooms was not observed.

Furthermore, the monitoring trials indicated the influence of fresh pellets on the storage atmosphere. At the beginning of the pellets storage high CO emissions are measured. This is because dilution is not achieved in storages fully filled with wood pellets. Moreover, wood pellets are likely to be more reactive concerning their CO formation at the beginning. Therefore, ventilation to the outside is essential at the beginning of the wood pellets storage reducing the CO in storages.

However, without sufficient ventilation to the outside or sufficient air exchange, very high CO concentrations can be obtained during the entire pellets storage period. The results of the underground storage tanks revealed harmful CO concentrations. Extreme caution is required over a much longer period compared to ventilated storage rooms. The underground storage tanks should not be entered. And if entering is necessary, sufficient ventilation and the use of a CO warning device is highly recommended.

The legally prescribed ventilation caps (for the construction of pellets storage facilities) indicated the reduction of the CO concentration. However, in wood pellets storage rooms which were equipped with ventilation caps, CO concentrations were detected that were many times higher than the workplace concentration value.

**Ventilation and cross ventilation of pellets storage facilities**

The ventilation trials of pellets storage tanks clearly indicated that a second ventilation opening (cross ventilation), enhanced the air exchange between the storage and the environment. Thus, the occurring CO was reduced and cross ventilation proved to be a measure to increase the storage safety.

Furthermore, the investigations demonstrated that the size of cross-sectional area of the ventilation opening immensely influenced the air exchange. The results further indicated that the installation of caps with a cross-sectional area as large as possible is highly recommended.

Setting a temperature difference between inside and outside the pellets tank by the application of temperature treated chimneys (cooled or heated) favoured the air exchange. Therefore, it is assumed that if there is a temperature difference between the storage facility itself and the environment into which the ventilation takes place, the air exchange and the CO reduction are favoured.

**Measures for safe handling of wood pellets storages**

The monitoring and ventilation trials of wood pellets storage facilities confirmed the already provided recommendations to not enter a pellets storage without further precautions. Based on the investigations, the following recommendations are made.

- Entering wood pellets storage facilities should be completely avoided especially when the storage was recently filled with wood pellets.
- If entering of wood pellets storages is nevertheless necessary, sufficient ventilation of the storage should be ensured before entering.
- In doubt, notify another person and carry a CO warning device.
- Cross ventilation of the pellets storage during the entire wood pellets storage period must be provided.
- The usage of ventilation caps with the largest possible cross-sectional area is recommended.

# V. Key findings and outlook

Biomass is omnipresent and is used and stored in a broad variety. As a representative of biomass, wood pellets are used for energy or heat utilisation. Off-gassing emissions are formed during storage, production, and transportation of wood pellets. Therefore, predominant degradation reactions which are initiated by autoxidative reactions, cause the formation of emissions, the depletion of atmospheric oxygen ($O_2$) and the occurring odour during the storage of wood pellets.

## V.1. Key findings

The major finding of characterisation of different wood pellets batches is that wood extractives are responsible for the off-gassing formation. However, it is not the total amount of the extractive content but rather individual extractives.

- Wood pellets made of larch, pine, spruce or hardwood reveal different off-gassing activities. Comparing emission rates of the respective raw materials and the total extractive contents, no considerable dependence is identified. Furthermore, the analyses of wood pellets batches with respect to their off-gassing emissions and total extractive content indicate that the total content of extractives does not provide indicative information about the off-gassing activity. Because it is known that extractives are the cause of off-gassing emissions [47], this confirms the presumption that it is not the total content but rather one or more individual extractives. This assumption has been recently confirmed by a publication of Siwale *et al.* [161].
- The sensory analyses with simultaneous determination of the off-gassing emissions indicate that wood pellets perceived with malodour do not necessarily release higher CO or $VOC_{tot}$ emissions compared to non malodourous wood pellets. Both, pellets with unpleasant and not perceived odour, form various acids and aldehydes, such as acetic acid or hexanal. Therefore, it can be assumed that not the total amount of VOCs is responsible for the development of the odour. Moreover, individual VOCs and their concentration in dependence of their odour thresholds are responsible for the perceived odour.
- The common investigation of self-heating and off-gassing characteristics of wood pellets batches indicates the link between off-gassing and self-heating. This implies that pellets with a high off-gassing reactivity will tend towards self-heating. However, when comparing the total content of fatty and resin acids with the off-gassing or self-heating tendencies, it reveals that the content of fatty and resin acids does not allow any conclusions about the actual

activity in terms of off-gassing or self-heating. Again, it can be deduced that it is rather individual acids that are responsible for the off-gassing activity.

The conditions during the storage of wood pellets prove to have a considerable influence on the formation of off-gassing emission.

- Influencing factors on the emission formation of stored wood pellets, likewise storage temperature, are well known. In the context of this thesis, it was concluded that $O_2$ plays a significant role in off-gassing activity. That additionally supports the assumed mechanism for off-gassing formation, namely oxidative degradation of wood extractives.
- Furthermore, the measured off-gassing behaviour depends strongly on the performance of the applied method for off-gassing determination. In the course of this thesis, a uniform and defined method for the determination of off-gassing and oxygen depletion has been established. This uniform method is required in order to compare results. Furthermore, the specification of the headspace ratio and the presentation of the residual oxygen concentration would improve the comparability and the assessment of off-gassing results. The methods used in the literature for determining the off-gassing behaviour differ, which makes it difficult to compare the results. However, in the meantime, a (more complex) laboratory method for off-gassing and oxygen depletion characteristics has been published as international standard [49].

Biomass pellets, just like wood pellets, demonstrate the potential for the formation of off-gassing emissions during their storage.

- As in the analyses of off-gassing emissions from wood pellets, different biomass pellets form CO, VOCs, and $CO_2$. At the same time, atmospheric oxygen is depleted. This indicates that some contents of biomass are degraded by oxidative processes. In addition, similar aldehydes, e.g. hexanal, as in the case of wood pellets, are detected. Assuming that similar or the same extractives are degraded to hexanal in wood pellets as well as in other biomass pellets.
- However, it should be noted that the investigated biomass pellets emit a broad spectrum of VOC emissions. This leads to the assumption that there is a multitude of different degradation reactions, depending on the individual constituents of each biomass.
- In addition, it should be considered that during the storage of biomass pellets, caution is also required when entering such a biomass storage facility regarding a toxic atmosphere.

Specified modifications in the pellets production process lead to significant CO reduction during the subsequent storage of wood pellets.

- Among the modifications applied in the pelletising process, the best approach in terms of CO emission reduction is the usage of additives. In detail, the most effective applied additive was the acetylsalicylic acid which reduced the CO emissions by up to 70%. The advantage of adding additives is that they can be integrated into the existing pelletising process. However, it has to be considered that an adjustment of the process conditions during pellets production may occur additionally. Furthermore, the economic viability of pellets production is strongly dependent on the additional additive costs. Nevertheless, the usage of additives is a permitted way to increase storage security for the end user by reducing off-gassing activity.
- The blending with antioxidative wood raw materials is a further promising measure in off-gassing reduction. The blending trials reveal reduction in CO emissions by more than 60%. The blending of up to 20% different wood resources might impact the pelletising process in terms of varying process conditions and settings. Furthermore, if raw materials for blending have to be purchased additionally, this can result in major additional costs. Furthermore, the blending of raw materials with a high bark content, for example, can lead to an increased ash content. The ash content is limited by standards. Thus, the proportion of the blending quantity is limited by the increase in ash content.
- The modifications at the end of the pelletising process, the variation of ventilation time, ventilation air temperature and ventilation technology, influence the off-gassing behaviour. Therefore, the highest CO reduction (of 18%) is achieved by changing the technology. The exchange of a ventilation/cooling technology in an industrial pelletising mill would lead to additional investment costs. Moreover, the extension of the ventilation time for cooling the pellets, aiming at a forced oxidation, reduced the CO emissions (by 13%). This implementation is also associated with additional costs in pellets production due to the necessary reduction in throughput.

Ventilation in particular cross ventilation improves the atmosphere in wood pellets storage with regard to the presence of CO.

- When handling wood pellets storages, extreme caution should always be paid on safe handling despite suitable ventilation caps. Moreover, the gained knowledge suggests that ventilation caps with a larger cross-sectional area would further reduce the occurring emissions. Nevertheless, the high reactivity of pellets, especially freshly delivered wood pellets should not be underestimated. Sufficient ventilation before handling wood pellets storages is a mandatory safety measure.

- In contrast to the studies on CO emissions and $O_2$ depletion of wood pellets during storage, there is hardly any information available on the development of odours or possible odour complaints caused by the storage of wood or biomass pellets. Little is also known about the toxicity of individually formed volatile organic compounds (VOCs). However, it can be assumed that the used ventilation caps in wood pellets storage facilities also lead to a decrease in odour and the presence of VOCs.

## V.2. Outlook

The detailed mechanism responsible for the formation of off-gassing emissions during the storage of wood pellets has not been fully clarified yet. For CO formation a multistage process has been assumed. The mechanism starts by the autoxidation of extractives, likewise fatty acids and terpenes, resulting in hydroxyl radicals. In the next step, the radicals react with the hemicellulose and form CO. Moreover, various short- and long-chain aldehydes are formed. However, it is still unknown where the total amount of formed CO comes from, since there is inadequate mass of extractives (unsaturated compounds) in wood [53]. A further study supports the role of fatty acids and other triglyceride oils responsible for off-gassing emissions. At the same time, the influence of resin acids on the formation of off-gassing is estimated to be low [161]. The work in this thesis also confirms the assumption that the cause for off-gassing are oxidative degradation processes of extractives. The detailed mechanisms, more precisely which extractives lead to which emissions through which degradation pathways, have not been clarified. This is a research question that might need to be clarified in the future.

The investigations in relation to the storage-related influencing variables on the off-gassing behaviour clearly illustrate that one or more defined methods for determining the off-gassing behaviour are necessary. In this context, both, the storage-related influencing factors as well as pellets characteristics are to be considered or defined. Requirements for such a method are that a defined amount of pellets is stored in a closed container with a specific volume (which defines the headspace ratio) for a defined period of time. Moreover, the occurring storage temperature, the measurement of gas components is specified (at least CO and $O_2$) and the storage container is protected from direct exposure to sunlight. Furthermore, for the calculation of the emission rate the actual storage duration, the moisture content and the particle density of the investigated pellets batch should be considered. At the moment a simplified method for screening carbon monoxide is under development considering the suggested storage-related influencing factors [50]. Since 2020 a laboratory method for the determination of off-gassing emission and oxygen depletion using closed containers was published as technical specification which also considers the proposed storage-related factors [49]. However, on the one hand the screening method is very simple and may not be informative enough for some use cases and on the other hand the laboratory method is very time consuming and comprehensive. Therefore, a defined method with less effort but high informative value is desirable.

The off-gassing behaviour of wood pellets is considerably affected by modifications in the pellets production process. Both, the applied measures of adding additives as well as blending with raw material perform better in terms of CO reduction than the applied ventilation variations for cooling the pellets. The three measures are all tried out and evaluated individually in laboratory and industrial pelletisation processes. It is possible that the combination of several measures could reduce CO emissions even further.

In addition, based on the finding that it is mainly fatty acids and other triglycerides that cause emissions, more targeted antioxidant additives could be used in order to increase the reduction of CO. In the course of this thesis, it was not further considered if or how one of those three modifications along the pellets production process influence the fuel properties such as ash content or mechanical durability. Furthermore, no combustion tests of these pellets were carried out evaluating any differences compared to conventionally produced wood pellets. Thus, the combustion property of those modified pellets is still an open issue.

The performed storage experiments in real pellets storages reveal that ventilation or cross-ventilation improves the storage atmosphere in terms of occurring CO concentration. Various measures have already been implemented ensuring the safety of end users during storage of wood pellets with regard to high CO concentrations and oxygen depletion. First of all, a warning sign was introduced to indicate the danger. This sign for example requires ventilation before entering such a pellets storage. In addition, existing pellets storage rooms have been upgraded with ventilation caps. Moreover, an international standard for safe handling and storage of wood pellets in residential and other small-scale applications is valid [4]. This standard specifies requirements for the pellets storage facilities improving safety. Besides the CO emissions and the depletion of oxygen, a broad variety of VOCs are formed. In recent years, end users repeatedly complained to pellets producers about the malodour next to wood pellets storages. Odour active VOCs are responsible for this malodour. Whether these odour active compounds also include toxic compounds or not, has not been investigated in relation to the storage of wood pellets yet.

# Appendix

## Abbreviations, acronyms and symbols

| Abbreviation | Description |
|---|---|
| AER | air exchange rate |
| ASA | acetylsalicylic acid |
| BEST | Bioenergy and Sustainable Technologies GmbH |
| BP | biomass pellets |
| c | concentration |
| $CaO$ | calcium oxide |
| CAS number | chemical abstracts service number |
| $Ca(OH)_2$ | calcium hydroxide |
| $CH_3COOK$ | potassium acetate |
| $CH_4$ | methane |
| cm | centimetre |
| $cm^2$ | cubic centimetre |
| $cm^3\ m^{-3}$ | centimetre per cubic metre |
| CO | carbon monoxide |
| COHb | carboxyhaemoglobin |
| $CO_2$ | carbon dioxide |
| CSA | cross-sectional area |
| d | diameter |
| DBFZ | Deutsches Biomasseforschungszentrum gemeinnützige GmbH |
| DDGS | dried distillers' grain with solubles |
| DIY store | do it yourself store |
| FID | flame ionisation detector |
| g | gram |
| GC | gas chromatography |
| GC-MS | gas chromatography - mass spectrometry |
| GPP | grape pomace powder |
| $g\ L^{-1}$ | gram per litre |
| $g\ 100\ g^{-1}$ | gram per 100 grams |
| h | hour |
| HG | hop grains |
| $HS_{ratio}$ | headspace ratio |
| HS-SPME | headspace solid phase micro extraction |
| $h_{pellet}$ | height of the pellets |
| $HRR_{max}$ | maximum specific heat release rate |
| $H_2O$ | water |
| ISO | International Organization for Standardization |
| ISPP | industrial scale pellets production |
| kg | kilogram |
| $kg\ m^{-3}$ | kilogram per cubic metre |
| kPa | kilopascal |
| L | litre |

| Abbreviation | Description |
|---|---|
| m | mass |
| m | metre |
| $m^3$ | cubic metre |
| $m^3\ h^{-1}$ | cubic metre per hour |
| mbar | millibar |
| mg | milligram |
| $mg\ kg^{-1}$ | milligram per kilogram |
| $mg\ kg^{-1}_{d.b.}\ day^{-1}$ | milligram per kilogram dry basis and day |
| $mg\ m^{-3}$ | milligram per cubic metre |
| min | minute |
| mm | millimetre |
| MP | measurement point |
| $m_{pellet}$ | mass of the pellets |
| $mW\ g^{-1}$ | milliwatt per gram |
| NaCl | sodium chloride |
| $Na_2SO_4$ | sodium sulphate |
| NiCr-Ni | nickel chromium - nickel |
| $N_2$ | nitrogen |
| $O_2$ | oxygen |
| PG | propyl gallate |
| ppm | parts per million |
| *p*-threshold | probability threshold |
| RH | relative humidity |
| RM | raw material |
| $R^2$ | Coefficient of determination |
| S1 | storz 1 |
| S2 | storz 2 |
| T | temperature |
| t | ton |
| TBHQ | tert-butylhydroquinone |
| TCD | thermal conductivity detector |
| TGA | thermal gravimetric analysis |
| $T_{DTG,peak}$ | temperature at maximum mass loss rate |
| V | volume |
| $V_{bulk}$ | volume of the pellets bulk |
| VE | ventilation experiment |
| VOC | volatile organic compound |
| $VOC_{tot}$ | total volatile organic compound |
| WP | wood pellets |
| % | percentage |
| % (m/m) | mass percent |
| % (V/V) | volume percent |
| (V/V) | volume by volume |
| °C | degree Celsius |
| µm | micrometre |
| $\rho_{bulk}$ | bulk density of the pellets |
| $\rho_{pellet}$ | particle density of the pellets |
| $\rho_{raw\ material}$ | density of the raw material |

# List of figures

# List of tables

# References

[1] Obernberger I, Thek G. The Pellet Handbook - The production and thermal utilisation of biomass pellets. Obernberger I, Thek G, editors. Earthscan Ltd. London. 2010.

[2] ISO 17225-2 Solid biofuels - Fuel specifications and classes - Part 2: Graded wood pellets. International Organization for Standardization. 2021.

[3] ISO 17225-1 Solid biofuels - Fuel specifications and classes - Part 1: General requirements. International Organization for Standardization. 2021.

[4] ISO 20023 Solid biofuels - Safety of solid biofuel pellets - Safe handling and storage of wood pellets in residential and other small-scale applications. International Organization for Standardization. 2018.

[5] ISO 20024 Solid biofuels - Safe handling and storage of solid biofuel pellets in commercial and industrial applications. International Organization for Standardization. 2020.

[6] Bioenergy Europe. Statistical Report. Bioenergy Europe. Brussels. 2021.

[7] Bioenergy Europe. Statistical Report. Bioenergy Europe. Brussels. 2018.

[8] Bioenergy Europe. Statistical Report - Key Findings. Bioenergy Europe. Brussels. 2019.

[9] Fengel D, Wegener G. Wood - Chemistry Ultrastructure Reactions. Kessel Verlag. Remagen. 2003.

[10] Alakoski E, Jämsén M, Agar D, Tampio E, Wihersaari M. From wood pellets to wood chips, risks of degradation and emissions from the storage of woody biomass - A short review. Renewable Sustainable Energy Reviews. 2016;54:376-383.

[11] Krigstin S, Wetzel S. A review of mechanisms responsible for changes to stored woody biomass fuels. Fuel. 2016;175:75-86.

[12] Kuang X, Shankar TJ, Bi XT, Sokhansanj S, Lim CJ, Melin S. Characterization and Kinetics Study of Off-Gas Emissions from Stored Wood Pellets. The Annals of Occupational Hygiene. 2008;52:675-683.

[13] Svedberg U, Samuelsson J, Melin S. Hazardous Off-Gassing of Carbon Monoxide and Oxygen Depletion during Ocean Transportation of Wood Pellets. The Annals of Occupational Hygiene. 2008;52:259-266.

[14] Otwell L, Hittmeier M, Hooda U, Yan H, Su W, Banerjee S. HAPs Release from Wood Drying. Environmental Science & Technology. 2000;34:2280-2283.

[15] Bridgewater AV, Elliott DC, Fagernäs L, Gifford JS, Mackie KL, Toft AJ. The nature and control of solid, liquid and gaseous emissions from the thermochemical processing of biomass. Biomass and Bioenergy. 1995;9:325-341.

[16] Englund F, Nussbaum RM. Monoterpenes in Scots Pine and Norway Spruce and their Emission during Kiln Drying. Holzforschung. 2000;54:449-456.

[17] Banerjee S, Pendyala K, Buchanan M, Yang R, Abu-Daabes M. Process-based control of HAPs emissions from drying wood flakes. Environmental Science & Technology. 2006;40:2438-2441.

[18] Granström KM. Emissions of sesquiterpenes from spruce sawdust during drying. European Journal of Wood and Wood Products. 2009;67:343-350.

[19] Rupar K, Sanati M. The release of organic compounds during biomass drying depends upon the feedstock and/or altering drying heating medium. Biomass and Bioenergy. 2003;25:615-622.

[20] Paczkowski S, Kraft R, Kharazipour A. Storage-induced emissions from different wood species. Holzforschung. 2013;67:907-912.

[21] Emhofer W. Emission from Wood Pellets during Storage. PhD thesis. Vienna University of Technology. Vienna 2015.

[22] Yazdanpanah F. Evolution and stratification of off-gasses in stored wood pellets. PhD thesis. University of British Columbia. Vancouver. 2013.

[23] Sedlmayer I, Arshadi M, Haslinger W, Hofbauer H, Larsson I, Lönnermark A, Nilsson C, Pollex A, Schmidl C, Stelte W, Wopienka E, Bauer-Emhofer W. Determination of off-gassing and self-heating potential of wood pellets - Method comparison and correlation analysis. Fuel. 2018;234:894-903.

[24] Tumuluru JS, Kuang X, Sokhansanj S, Lim C, Bi T, Mani S, Melin S. Studies on Off-gassing during Storage of Wood Pellets. In: ASABE Annual International Meeting. St. Joseph, Michigan. 2007.

[25] Svedberg U, Petrini C, Johanson G. Oxygen Depletion and Formation of Toxic Gases following Sea Transportation of Logs and Wood Chips. The Annals of Occupational Hygiene. 2009;53:779-787.

[26] Meier F, Sedlmayer I, Emhofer W, Wopienka E, Schmidl C, Haslinger W, Hofbauer H. Influence of Oxygen Availability on off-Gassing Rates of Emissions from Stored Wood Pellets. Energy & Fuels. 2016;30:1006-1012.

[27] Arshadi M, Gref R. Emission of volatile organic compounds from softwood pellets during storage. Forest Products Journal. 2005;55:132-135.

[28] Arshadi M, Geladi P, Gref R, Fjällström P. Emission of Volatile Aldehydes and Ketones from Wood Pellets under Controlled Conditions. The Annals of Occupational Hygiene. 2009;53:797-805.

[29] Svedberg U, Högberg H, Högberg J, Galle B. Emission of Hexanal and Carbon Monoxide from Storage of Wood Pellets, a Potential Occupational and Domestic Health Hazard. The Annals of Occupational Hygiene. 2004;48:339-349.

[30] Wiberg N. Lehrbuch der anorganischen Chemie. de Gruyter. Berlin, Boston. 2008.

[31] Prockop LD, Chichkova RI. Carbon monoxide intoxication: An updated rewiew. Journal of the Neurological Sciences. 2010;262:122-130.

[32] VOHR HW. TOXIKOLOGIE -BAND 2: TOXIKOLOGIE DER STOFFE. WILEY-VCH. WEINHEIM. 2010.

[33] RAUB J, MATHIEU-NOLF M, HAMPSON N, THOM S. CARBON MONOXIDE POISONING - A PUBLIC HEALTH PERSPECTIVE. TOXICOLOGY. 2000;145:1-14.

[34] CHRIS H. CAUSES AND CLINICAL SIGNIFICANCE OF INCREASED CARBOXYHEMOGLOBIN. 2005. [ACCESSED ON DECEMBER 15 2022]. AVAILABLE FROM HTTPS://ACUTECARETESTING.ORG/EN/ARTICLES/CAUSES-AND-CLINICAL-SIGNIFICANCE-OF-INCREASED-CARBOXYHEMOGLOBIN.

[35] WINTER PM, MILLER JN. CARBON MONOXIDE POISONING. JAMA. 1976;236:1502-1504.

[36] PERMENTIER K, VERCAMMEN S, SOETAERT S, SCHELLEMANS C. CARBON DIOXIDE POISONING: A LITERATURE REVIEW OF AN OFTEN FORGOTTEN CAUSE OF INTOXICATION IN THE EMERGENCY DEPARTMENT. THE INTERNATIONAL JOURNAL OF EMERGENCY MEDICINE. 2017;10:14.

[37] UNITED STATES ENVIRONMENTAL PROTECTION AGENCY. AIR EMISSIONS INVENTORIES. UNITED STATES ENVIRONMENTAL PROTECTION AGENCY. 2021. [ACCESSED ON NOVEMBER 12 2022]. AVAILABLE FROM: HTTPS://-WWW.EPA.GOV/AIR-EMISSIONS-INVENTORIES/WHAT-DEFINITION-VOC.

[38] THE COUNCIL OF THE EUROPEAN UNION. COUNCIL DIRECTIVE 1999/13/EC ON THE LIMITATION OF EMISSIONS OF VOLATILE ORGANIC COMPOUNDS DUE TO THE USE OF ORGANIC SOLVENTS IN CERTAIN ACTIVITIES AND INSTALLATIONS. THE COUNCIL OF THE EUROPEAN UNION. 1999. [ACCESSED ON NOVEMBER 12 2022]. AVAILABLE FROM: HTTP://EUR-LEX.EUROPA.EU/LEGAL-CONTENT/EN/TXT/PDF/?URI=CELEX:31999L0013&FROM=EN.

[39] JO JS, KWON YS, LEE JW, PARK BH J S RHO, CHOI WI. ACUTE RESPIRATORY DISTRESS DUE TO METHANE INHALATION. TUBERCULOSIS AND RESPIRATORY DISEASES. 2013;74:120-123.

[40] BOLLINGER N. NIOSH RESPIRATOR SELECTION LOGIC. U. S. DEPARTMENT OF HEALTH AND HUMAN SERVICES. CINCINNATI. 2004.

[41] BLOMQVIST P, PERSSON H, VAN HEES P, HOLMSTEDT G, GÖRANSSON U, WADSÖ L, SANATI M, RUPAR-GADD K. AN EXPERIMENTAL STUDY OF SPONTANEOUS IGNITION IN STORAGES OF WOOD PELLETS. IN: PROCEEDINGS OF FIRE AND MATERIALS. SAN FRANCISCO, CALIFORNIA. 2007.

[42] LÖNNERMARK A, PERSSON H, BLOMQVIST P, LARSSON I, RAHM M, DAHL J, LINDHOLST S, PL. SELF-HEATING AND OFF-GASSING FROM BIOMASS PELLETS DURING STORAGE. IN: WORLD BIOENERGY 2012. JONKOPING, SWEDEN. 2012.

[43] LARSSON I, LÖNNERMARK A, BLOMQVIST P, PERSSON H. MEASUREMENT OF SELF-HEATING POTENTIAL OF BIOMASS PELLETS WITH ISOTHERMAL CALORIMETRY. FIRE AND MATERIALS. 2017;41:1007-1015.

[44] BABRAUSKAS V. IGNITION HANDBOOK. FIRE SCIENCE PUBLISHERS. ISSAQUAH WA. 2003.

[45] KOPPEJAN J, LÖNNERMARK A, PERSSON H, LARSSON I, BLOMQVIST P, ARSHADI M, VALENCIA-REYES E, MELIN S, HOWES P, WHEELER P, BAXTER D, NIKOLAISEN L. HEALTH AND SAFETY ASPECTS OF SOLID BIOMASS STORAGE, TRANSPORTATION AND FEEDING. IEA BIOENERGY. 2013.

[46] BLOMQVIST P, PERSSON B. SPONTANEOUS IGNITION OF BIOFUELS - A LITERATURE SURVEY OF THEORETICAL AND EXPERIMENTAL METHODS. SP TECHNICAL RESEARCH INSTITUTE OF SWEDEN. 2003.

[47] Attard TM, Arshadi M, Nilsson C, Budarin VL, Valencia-Reyes E, Clark JH, Hunt A. Impact of supercritical extraction on solid fuel wood pellet properties and off-gassing during storage. Green Chemistry. 2016;18:2682-2690.

[48] Samuelsson R, Nilsson C, Burvall J. Sampling and GC-MS as a method for analysis of volatile organic compounds (VOC) emitted during oven drying of biomass materials. Biomass and Bioenergy. 2006;30:923-928.

[49] ISO/TS 20048-1 Solid biofuels - Determination of off-gassing and oxygen depletion characteristics - Part 1: Laboratory method for the determination of off-gassing and oxygen depletion using closed containers. International Organization for Standardization. 2020.

[50] ISO/FDIS 20048-2 Solid biofuels - Determination of off-gassing and oxygen depletion characteristics - Part 2: Operational method for screening of carbon monoxide off-gassing. International Organization for Standardization. 2022.

[51] Schmutzer-Roseneder I. Einfluss von Holzart und Rohstoff auf die Entstehung von Emissionen von Holzpellets während der Lagerung. Master thesis. University of Natural Resources and Applied Life Sciences. Vienna. 2012.

[52] Pöllinger-Zierler B, Sedlmayer I, Hofbauer H, Wopienka E, Siegmund B. Identification of malodourous emissions of wood pellets during storage. In: Flavour Science. Graz, Austria. 2018.

[53] Rahman MA, Hopke PK. Mechanistic Pathway of Carbon Monoxide Off-Gassing from Wood Pellets. Energy & Fuels. 2016;30:5809-5815.

[54] Kuang X, Shankar TJ, Bi XT, Lim CJ, Sokhansanj S, Melin S. Rate and Peak Concentrations of Off-Gas Emissions in Stored Wood Pellets - Sensitivities to Temperature, Relative Humidity, and Headspace Volume. The Annals of Occupational Hygiene. 2009;53:789-796.

[55] Tumuluru JS, Sokhansanj S, Lim CJ, Kuang XY, Melin S. Effect of low and high storage temperatures on headspace gas concentrations and physical properties of wood pellets. International Wood Products Journal. 2013;2:207-216.

[56] Kuang X, Shankar TJ, Sokhansanj S, Lim CJ, Bi XT, Melin S. Effects of Headspace and Oxygen Level on Off-gas Emissions from Wood Pellets in Storage. The Annals of Occupational Hygiene. 2009;53:807-813.

[57] Trinkel V. Auslegung einer Kinetikapparatur zur Messung des Ablaufs von Reaktionen an der Oberfläche von Pellets. Master thesis. Vienna University of Technology. Vienna. 2012.

[58] Wang S, Yuan X, Li C, Huang Z, Leng L, Zeng G, Li H. Variation in the physical properties of wood pellets and emission of aldehyde/ketone under different storage conditions. Fuel. 2016;183:314 321.

[59] Granström KM. Sawdust age affect aldehyde emissions in wood pellets. Fuel. 2014;126:219 223.

[60] Borén E, Yazdanpanah F, Lindahl R, Schilling C, Chandra RP, Ghiasi B, Tang Y, Sokhansanj S, Broström M, Larsson SH. Off-Gassing of VOCs and Permanent Gases during Storage of Torrefied and Steam Exploded Wood. Energy & Fuels. 2017;31:10954-10965.

[61] DIN 68364 Properties of wood species - Density, modulus of elasticity and strength. Deutsches Institut für Normung. 2003.

[62] ISO 18134-2 Solid biofuels - Determination of moisture content - Oven dry method - Part 2: Total moisture - Simplified method. International Organization for Standardization. 2017.

[63] ISO 18847 Solid biofuels - Determination of particle density of pellets and briquettes. International Organization for Standardization. 2016.

[64] Sedlmayer I, Bauer-Emhofer W, Haslinger W, Hofbauer H, Schmidl C, Wopienka E. Off-gassing reduction of stored wood pellets by adding acetylsalicylic acid. Fuel Processing Technology. 2020;198:1-7.

[65] Meier F. Pellet off-gassing during storage: The impact of storage conditions and type of source material. Master thesis. University of Natural Resources and Applied Life Sciences. Vienna. 2014.

[66] Pöllinger-Zierler B, Sedlmayer I, Reinisch C, Siegmund B, Wopienka E, Pointner C, Haslinger W. Mikrobielle Kontamination als Ursache für Fehlgerüche bei der Lagerung von Holzpellets. In: World Sustainable Energy Days 2015. Wels, Austria. 2015.

[67] Pöllinger-Zierler B, Sedlmayer I, Reinisch C, Hofbauer H, Schmidl C, Kolb L, Wopienka E, Leitner E, Siegmund B. Interrelation of Volatile Organic Compounds and Sensory Properties of Alternative and Torrefied Wood Pellets. Energy & Fuels. 2019;33:5270-5281.

[68] Pöllinger-Zierler B, Sedlmayer I, Wopienka E, Siegmund B. Malodourous emissions of wood pellets during storage. In: 15th Weurman Flavour Research Symposium. Graz, Austria. 2017.

[69] Granström KM, Månsson B. Volatile organic compounds emitted from hardwood drying as a function of processing parameters. International Journal of Environmental Science and Technology. 2008;5:141-148.

[70] Schäfer M, Roffael E. On the formaldehyde release of wood. Holz als Roh- und Werkstoff. 2000;58:259-264.

[71] Thek G, Obernberger I. Wood pellet production costs under Austrian and in comparison to Swedish framework conditions. Biomass and Bioenergy. 2004;27:671-693.

[72] Wopienka E, Griesmayr S, Friedl G, Haslinger W. Quality check for European wood pellets. In: 9th Industrieforum Pellets. Stuttgart, Germany. 2009.

[73] Hagström K. Occupational exposure during production of wood pellets in Sweden. PhD thesis. Örebro University. Örebro. 2008.

[74] Arshadi M, Nilsson C, Geladi P. Monitoring chemical changes for stored sawdust from pine and spruce using gas chromatography-mass spectrometry and visible-near infrared spectroscopyJournal of Near Infrared Spectroscopy. 2007;15:379-386.

[75] Arshadi M, Hunt AJ, Clark JH. Supercritical fluid extraction (SFE) as an effective tool in reducing auto-oxidation of dried pine sawdust for power generation. RSC Advances. 2012;2:1806-1809.

[76] Arshadi M, Tengel T, Nilsson C. Antioxidants as additives in wood pellets as a mean to reduce off-gassing and risk for self-heating during storage. Fuel Processing Technology. 2018;179:351-358.

[77] Siwale W, Frodeson S, Berghel J, Henriksson G, Finell M, Arshadi M, Jonsson C. Influence on off-gassing during storage of Scots pine wood pellets produced from sawdust with different extractive contents. Biomass and Bioenergy. 2022;156:106325.

[78] Guo W. Self-Heating and Spontaneous Combustion of Wood Pellets during Storage. PhD thesis. University of British Columbia. Vancouver. 2013.

[79] Hancock RA, Leeves NJ. Studies in Autoxidation. Part I. The Volatile By-Products resulting from the Autoxidation of Unsaturated Fatty Acid Methyl Esters. Progress in Organic Coatings. 1989;17:321-336.

[80] Juita, Dlugogorski BZ, Kennedy EM, Mackie JC. Identification and Quantitation of Volatile Organic Compounds from Oxidation of Linseed Oil. Industrial & Engineering Chemistry Research. 2012;51:5645-5652.

[81] Tumuluru JS, Lim CJ, Bi XT, Kuang X, Melin S, Yazdanpanah F, Sokhansanj S. Analysis on Storage Off-Gas Emissions from Woody, Herbaceous, and Torrefied Biomass. Energies. 2015;8:1745-1759.

[82] Sedlmayer I. Study on malodorous emissions from wood pellets. In: 13th Industrieforum Pellets. Berlin, Germany. 2014.

[83] Soto-Garcia L, Ashley WJ, Bregg S, Walier D, LeBouf R, Hopke PK, Rossner A. VOCs Emission from Multiple Wood Pellet Types and Concentrations in Indoor Air. Energy & Fuels. 2015;29:6485-6493.

[84] Costa C, Taiti C, Zanetti M, Proto AR, D'Andrea S, Greco R, Dematte L, Mancuso S, Cavalli R. Assessing VOC Emission by Wood Pellets Using the PTR- ToF-MS Technology. Chemical Engineering Transactions. 2017;58:445-450.

[85] Granström KM. Emissions of Hexanal and Terpenes during Storage of Solid Wood Fuels. Forest Products Journal. 2010;60:27-32.

[86] Hagström K, Axelsson S, Arvidsson H, Bryngelsson IL, Lundholm C, Eriksson K. Exposure to Wood Dust, Resin Acids, and Volatile Organic Compounds During Production of Wood Pellets. Journal of Occupational and Environmental Hygiene. 2008;5:296-304.

[87] Back EL, Allen LH. Pitch Control, Wood Resin and Deresination. Back EL, Allen LH, editors. TAPPI Press. Atlanta. 2000.

[88] Risholm-Sundman M, Lundgren M, Vestin E, Herder P. Emissions of acetic acid and other volatile organic compounds from different species of solid wood. Holz als Roh- und Werkstoff. 1998;56:125-129.

[89] Koelsch C, Downes T, Labuza T. Hexanal Formation via Lipid Oxidation as a Function of Oxygen Concentration: Measurement and Kinetics. Journal of Food Science. 1991;56:816-820.

[90] Gauthier S, Grass H, Lory M, Krämer T, Thali M, Bertsch C. Lethal Carbon Monoxide Poisoning in Wood Pellet Storerooms-Two Cases and a Review of the Literature. The Annals of Occupational Hygiene. 2012;56:755-763.

[91] Melin S, Svedberg U, Samuelsson J. Emissions from Woodpellets During Ocean Transportation (EWDOT) – Research Report. University of British Columbia. Vancouver. 2008.

[92] Tumuluru J, Kuang X, Sokhansanj S, Lim C, Bi T, Melin S. Wood Pellet Properties Produced in British Columbia and Studies on Off-Gas Emissions at Low and High Storage Temperatures. In: ASABE Annual International Meeting. St. Joseph, Michigan. 2009.

[93] Tumuluru J, Kuang X, Sokhansanj S, Lim C, Bi T, Melin S. Effect of Storage Temperature on Off-gassing and Physical Properties of Wood Pellets. In: ASABE Annual International Meeting. St. Joseph, Michigan. 2008.

[94] Rahman MA, Squizzato S, Luscombe-Mills R, Curran P, Hopke PK. Continuous Ozonolysis Process To Produce Non-CO Off-Gassing Wood Pellets. Energy & Fuels. 2017;31:8228-8234.

[95] Brewer MS. Natural Antioxidants: Sources, Compounds, Mechanisms of Action, and Potential Applications. Comprehensive Reviews in Food Science and Food Safety. 2011;10:221-247.

[96] Valero D, Díaz-Mula HM, Zapata PJ, Castillo S, Guillén F, Martínez-Romero D, Serrano M. Postharvest treatments with salicylic acid, acetylsalicylic acid or oxalic acid delayed ripening and enhanced bioactive compounds and antioxidant capacity in Sweet cherry. Journal of Agricultural and Food Chemistry. 2011;59:5483-5489.

[97] Beres C, Costa GNS, Cabezudo I, da Silva-James NK, Teles ASC, Cruz APG, Mellinger-Silva C, Tonon RV, Cabral LMC, Freitas SP. Towards integral utilization of grape pomace from winemaking process: A review. Waste Management. 2017;68:581-594.

[98] Barbosa-Pereira L, Bilbao A, Vilches P, Angulo I, LLuis J, Fite B, Paseiro-Losada P, Cruz JM. Brewery waste as a potential source of phenolic compounds: Optimisation of the extraction process and evaluation of antioxidant and antimicrobial activities. Food Chemistry. 2014;145:191-197.

[99] Correia LM, Saboya RMA, de Sousa Campelo N, Cecilia JA, Rodríguez-Castellón E, Cavalcante Jr CL, Vieira RS. Characterization of calcium oxide catalysts from natural sources and their application in the transesterification of sunflower oil. Bioresource Technology. 2014;151:207-213.

[100] Yazaki Y. Utilization of Flavonoid Compounds from Bark and Wood: A Review. Natural Product Communications. 2015;10:513-520.

[101] Sillero L, Prado, Andrés MAR, Labidi J. Characterisation of bark of six species from mixed Atlantic forest. Industrial Crops and Products. 2019;137:276-284.

[102] Dziedzinski M, Kobus-Cisowska J, Szymanowska D, Stuper-Szablewska K, Baranowska M. Identification of Polyphenols from Coniferous Shoots as Natural Antioxidants and Antimicrobial Compounds. Molecules. 2020;25:3527.

[103] PIATCZAK E, DYBOWSKA M, P?UCIENNIK E, KOSLA K, KOLNIAK-OSTEK J, KALINOWSKA-LIS U. IDENTIFICATION AND ACCUMULATION OF PHENOLIC COMPOUNDS IN THE LEAVES AND BARK OF SALIX ALBA (L.) AND THEIR BIOLOGICAL POTENTIAL. BIOMOLECULES. 2020;10:1391.

[104] PACKER L, RIMBACH G, VIRLGILI F. ANTIOXIDANT ACTIVITY AND BIOLOGIC PROPERTIES OF A PROCYANIDIN-RICH EXTRACT FROM PINE (PINUS MARITIMA) BARK, PYCNOGENOL. FREE RADICAL BIOLOGY AND MEDICINE. 1999;27:704-724.

[105] ZULE J, CUFAR K, TISLER V. HYDROPHILIC EXTRACTIVES IN HEARTWOOD OF EUROPEAN LARCH (LARIX DECIDUA MILL.). DRVNA INDUSTRIJA. 2016;67:363-370.

[106] ZAITER A, BECKER L, PETIT J, ZIMMER D, KARAM MC, BAUDELAIRE É, SCHER J, DICKO A. ANTIOXIDANT AND ANTIACETYLCHOLINESTERASE ACTIVITIES OF DIFFERENT GRANULOMETRIC CLASSES OF SALIX ALBA (L.) BARK POWDERS. POWDER TECHNOLOGY. 2016;301:649-656.

[107] DRÓZDZ P, PYRZYNSKA K. ASSESSMENT OF POLYPHENOL CONTENT AND ANTIOXIDANT ACTIVITY OF OAK BARK EXTRACTS. EUROPEAN JOURNAL OF WOOD AND WOOD PRODUCTS. 2018;76:793-795.

[108] HOLZHOF SCHMIDT GMBH. TECHNISCHES DATENBLATT. 2016. [ACCESSED ON NOVEMBER 24 2019]. AVAILABLE FROM: HTTP://WWW.HOLZHOF-SCHMIDT.AT/PELLETS/.

[109] HEIZINOS-HOLZPELLETS. QUALITÄT DIE ÜBERZEUGT "HEIZINOS-HOLZPELLETS". 2017. [ACCESSED ON NOVEMBER 24 2019]. AVAILABLE FROM: HTTPS://WWW.HEIZINOS.AT/PELLETS-QUALITAET.

[110] SIGMA-ALDRICH. MATERIAL SAFETY DATA SHEET - ACETYLSALICYLIC ACID. 2018.

[111] ARSHADI M, GREF R, GELADI P, DAHLQVIST SA, LESTANDER T. THE INFLUENCE OF RAW MATERIAL CHARACTERISTICS ON THE INDUSTRIAL PELLETIZING PROCESS AND PELLET QUALITY. FUEL PROCESSING TECHNOLOGY. 2008;89:1442-1447.

[112] MONTEIRO GC, MINATEL IO, PIMENTEL JUNIOR A, GOMEZ-GOMEZ HA, DE CAMARGO JPC, DIAMANTE MS, PEREIRA BASÍLIO LS, TECCHIO MA, PEREIRA LIMA GP. BIOACTIVE COMPOUNDS AND ANTIOXIDANT CAPACITY OF GRAPE POMACE FLOURS. LWT - FOOD SCIENCE AND TECHNOLOGY. 2021;135:110053.

[113] SIROHI R, TARAFDAR A, SINGH S, NEGI T, GAUR VK, GNANSOUNOU E, BHARATHIRAJA B. GREEN PROCESSING AND BIOTECHNOLOGICAL POTENTIAL OF GRAPE POMACE: CURRENT TRENDS AND OPPORTUNITIES FOR SUSTAINABLE BIOREFINERY. BIORESOURCE TECHNOLOGY. 2020;314:123771.

[114] NAKOV G, BRANDOLINI A, HIDALGO A, IVANOVA N, STAMATOVSKA V, DIMOV I. EFFECT OF GRAPE POMACE POWDER ADDITION ON CHEMICAL, NUTRITIONAL AND TECHNOLOGICAL PROPERTIES OF CAKES. LWT - FOOD SCIENCE AND TECHNOLOGY. 2020;134:109950.

[115] HRNCIC MK, SPANINGER E, KOSIR IJ, KNEZ Z, BREN U. HOP COMPOUNDS: EXTRACTION TECHNIQUES, CHEMICAL ANALYSES, ANTIOXIDATIVE, ANTIMICROBIAL, AND ANTICARCINOGENIC EFFECTS. NUTRIENTS. 2019;11:257.

[116] SANZ V, TORRES MD, LÓPEZ VILARIÑO JM, DOMÍNGUEZ H. WHAT IS NEW ON THE HOP EXTRACTION? TRENDS IN FOOD SCIENCE AND TECHNOLOGY. 2019;12:12-22.

[117] Holubková A, Mosovská S, Baloghová B, Sturdík E. Hop pellets as an interesting source of antioxidant active compounds. Potravinárstvo : Scientific Journal for Food Industry. 2013;1:53-57.

[118] Ruiz-Ruiz JC, Aldana GdCE, Cruz AIC, Segura-Campos MR. 9 - Antioxidant Activity of Polyphenols Extracted From Hop Used in Craft Beer. Biotechnological Progress and Beverage Consumption. 2020;19:293-310.

[119] Kowalczyk D, Swieca M, Cichocka J, Gawlik-Dziki U. The phenolic content and antioxidant activity of the aqueous and hydroalcoholic extracts of hops and their pellets. Institute of Brewing and Distilling. 2013;119:103-110.

[120] Sigma-Aldrich. Material Safety Data Sheet - Calcium hydroxide. 2020.

[121] Sigma-Aldrich. Material Safety Data Sheet- Calcium oxide. 2020.

[122] Proaño F, Stuart JR, Chongo B, Flores L, Herrera M, Medina Y, Sarduy L. Evaluation of three saponification methods on two types of fat as protection against bovine ruminal degradation. Cuban Journal of Agricultural Science. 2015;49:35-39.

[123] Poulenat G, Sentenac S, Mouloungui Z. Fourier-Transform Infrared Spectra of Fatty Acid Salts - Kinetics of High-Oleic Sunflower Oil Saponification. Journal of Surfactants and Detergents. 2003;6:305-310.

[124] Baik JE, Jang KS, Kang SS, Yun CH, Lee K, Kim BG, Kum KY, Han SH. Calcium Hydroxide Inactivates Lipoteichoic Acid from Enterococcus faecalis through Deacylation of the Lipid Moiety. Journal of Endodontics. 2011;37:191-196.

[125] Safavi KE, Nichols FC. Effect of calcium hydroxide on bacterial lipopolysaccharide. Journal of Endodontics. 1993;19:76-78.

[126] Valderrama C, Granados R, Cortina JL. Stabilisation of dewatered domestic sewage sludge by lime addition as raw material for the cement industry: Understanding process and reactor performance. Chemical Engineering Journal. 2013;232:458-467.

[127] Cheynier V, Comte G, Davies KM, Lattanzio V, Martens S. Plant phenolics: Recent advances on their biosynthesis, genetics, and ecophysiology. Plant Physiology and Biochemistry. 2013;72:1-20.

[128] Jablonsky M, Nosalova J, Sladkova A, Haz A, Kreps F, Valka J, Miertus S, Frecer V, Ondrejovic M, Sima J, Surina I. Valorisation of softwood bark through extraction of utilizable chemicals. A review. Biotechnology Advances. 2017;35:726-750.

[129] Hamad AMA, Ates S, Olgun C, Gür M. Chemical Composition and Antioxidant Properties of Some Industrial Tree Bark Extracts. BioResources. 2019;14:5657-5671.

[130] Skrypnik L, Grigorev N, Michailov D, Antipina M, Danilova M, Pungin A. Comparative study on radical scavenging activity and phenoliccompounds content in water bark extracts of alder (Alnus glutinosa (L.) Gaertn.), oak (Quercus robur L.) and pine (Pinus sylvestris L.). European Journal of Wood and Wood Products. 2019;77:879-890.

[131] Raiciu AD, Popescu M, Manea S, Dima SO. Antioxidant Activity and Phyto-therapeutic Properties of Gemmo-Derivatives Obtained from Rosmarinus officinalis, Vaccinium myrtillus, Salix Alba, Ribes nigrum, and Betula Pubescens. Revista de Chimie. 2016;67:1936-1939.

[132] Sulaiman GM, Hussien NN, Marzoog TR, Awad HA. Phenolic Content, Antioxidant, Antimicrobial and Cytotoxic Activities of Ethanolic Extract of Salix alba. American Journal of Biochemistry and Biotechnology. 2013;9:41-46.

[133] Braga MEM, Santos RMS, Seabra IJ, Facanali R, Marques MOM, de Sousa HC. Fractioned SFE of antioxidants from maritime pine bark. The Journal of Supercritical Fluids. 2008;47:37-48.

[134] Maimoona A, Naeem I, Saddiqe Z, Jameel K. A review on biological, nutraceutical and clinical aspects of French maritime pine bark extract. Journal of Ethnopharmacology. 2011;133:261-277.

[135] Virgili F, Pagana G, Bourne L, Rimbach G, Natella F, Rice-Evans C, Packer L. Ferulic acid excretion as a marker of consumption of a French maritime pine (pinus maritima) bark extract. Free Radical Biology and Medicine 2000;28:1249-1256.

[136] Salem MZM, Zeidler A, Böhm M, Mohamed MEA, Ali HM. GC/MS Analysis of Oil Extractives from Wood and Bark of Pinus sylvestris, Abies alba, Picea abies, and Larix decidua. BioResources. 2015;10:7725-7737.

[137] Sillero L, Prado R, Labidi J. Simultaneous microwave-ultrasound assisted extraction of bioactive compounds from bark. Chemical Engineering and Processing - Process Intensification. 2018;156:108100.

[138] Sillero L, Prado R, Labidi J. Optimization of Different Extraction Methods to Obtaining Bioactive Compounds from Larix Decidua Bark. Chemical Engineering Transactions. 2018;70:1369-1374.

[139] ISO 14780 Solid biofuels - Sample preparation. International Organization for Standardization. 2017/Amd1:2019.

[140] Narron RH, Winowiski T, Gargulak J, Hendrics K. Fiber-first approach to isothermal calorimetry for quantification of self-heating reduction by antioxidants for the wood pelleting industry. Fuel. 2020;274:117788.

[141] Lee JS, Sokhansanj S, Lau AK, Lim SJ. Physical properties of wood pellets exposed to liquid water. Biomass and Bioenergy. 2020;142:105748.

[142] Deng T, Alzahrani AMA, Bradley MS. Influences of environmental humidity on physical properties and attrition of wood pellets. Fuel Processing Technology. 2019;185:126-138.

[143] Auras S, Weiß R, Feihle G, von der Heyden T, Gabriel S. Kohlenmonoxid aus Holzpellets: Ermittlung und Beurteilung von Expositionen in Lagern entlang der Logistikkette. Gefahrstoffe Reinhaltung der Luft. 2017;77:363-370.

[144] Anderson S. Report - Bulk Carrier SAGA SPRAY - VRWW5 - Fatal Accident on 16 November, 2006. Swedish Maritime Safety Inspectorate. Norrköping, Sweden. 2007.

[145] Svedberg U, Knutsson A. Faror och hälsorisker vid förvaring och transport av träpellets, träflis och timmer i slutna utrymmen. Arbets- och miljömedicinska kliniken. Sundsvall, Sweden. 2011.

[146] Tragödie im Pellets-Bunker; 2010. [accessed on January 11 2020]. Available from: www.solinger-tageblatt.de/Tragoedie-im-Pellets-Bunker-48c68170-e8d0-4661-a671-a12e89c2aad9-ds.

[147] Junge Mutter stirbt an Gasvergiftung; 2011. [accessed on November 24 2019]. Available from: http://www.luzernerzeitung.ch/nachrichten/zentralschweiz/lu/luzern/Junge-Mutter-stirbt-an-Gasvergiftung;art92,76019.

[148] Senden - Bei Arbeiten am Pelletbunker des Cabrio-Bades ist ein 27-jähriger Mann lebensgefährlich verletzt worden; 2012. [accessed on November 24 2019]. Available from: http://-www.wn.de/Muensterland/Kreis-Coesfeld/Senden/2012/06/Unfall-im-Pelletbunker-27-Jaehriger-im-Cabrio-Bad-fast-erstickt.

[149] Man omkom i arbetsplatsolycka; 2014. [accessed on November 24 2019]. Available from: http://mvt.se/nyheter/man-omkom-i-arbetsplatsolycka-9562741.aspx.

[150] Sailor dead on board ship in Fredericia; 2014. [accessed on November 24 2019]. Available from: http://maritimedenmark.dk/?Id=17734.

[151] SafeSpace: Suntis, Three Dead in Timber Hold; 2014. [accessed on November 24 2019]. Available from: http://maritimeaccident.org/tags/wood/.

[152] Soto-Garcia L, Huang X, Thimmaiah D, Rossner A, Hopke PK. Exposures to Carbon Monoxide from Off-Gassing of Bulk Stored Wood Pellets. Energy & Fuels. 2015;29:218-226.

[153] Rossner A, Jordan CE, Wake C, Soto-Garcia L. Monitoring of carbon monoxide in residences with bulk wood pellet storage in the Northeast United States. Journal of the Air & Waste Management Association. 2017;67:1066-1079.

[154] Yazdanpanah F, Sokhansanj S, Lim CJ, Lau A, Bi X. Effectiveness of purging on preventing gas emission buildup in wood pellet storage. The Canadian Journal of Chemical Engineering. 2015;93:1024-1032.

[155] Yazdanpanah F, Sokhansanj S, Lim CJ, Lau A, Bi S, Melin S. Stratification of off-gases in stored wood pellets. Biomass and Bioenergy. 2014;71:1-11.

[156] Fontes J. Temperature Sensors In: Wilson JS. Sensor technology handbook. Newnes. Burlington. 2005.

[157] ISO 12569 Thermal performance of buildings and materials - Determination of specific airflow rate in buildings - Tracer gas dilution method. International Organization for Standardization. 2017.

[158] Emhofer W, Lichtenegger K, Haslinger W, Hofbauer H, Schmutzer-Roseneder I, Aigenbauer S, Lienhard M. Ventilation of Carbon Monoxide from a Biomass Pellet Storage Tank - A Study of the Effects of Variation of Temperature and Cross-Ventilation on the Efficiency of Natural Ventilation. The Annals of Occupational Hygiene. 2015;59:79-90.

[159] Rechtsinformationssytem des Bundes. Grenzwerteverordnung 2021. Verordnung des Bundesministers für Arbeit über Grenzwerte für Arbeitsstoffe sowie über krebserzeugende und fortpflanzungsgefährdende (reproduktionstoxische) Arbeitsstoffe. Rechtsinformationssytem des Bundes. 2021. [accessed on Dezember 15 2022]. Available from https://www.ris.bka.gv.at/GeltendeFassung.wxe?Abfrage=Bundesnormen&Gesetzesnummer=20001418.

[160] ÖNORM M7137 Compressed wood in natural state - Woodpellets - Requirements for storage of pellets at the ultimate consumer. Austrian Standards Institute. 2012.

[161] Siwale W, Frodeson S, Finell M, Arshadi M, Jonsson C, Henriksson G, Berghel J. Understanding Off-Gassing of Biofuel Wood Pellets Using Pellets Produced from Pure Microcrystalline Cellulose with Different Additive Oils. Energies. 2022;15:2281.

# Peer-reviewed journal papers

## Paper 1

### DETERMINATION OF OFF-GASSING AND SELF-HEATING POTENTIAL OF WOOD PELLETS – METHOD COMPARISON AND CORRELATION ANALYSIS

## Citation:

Sedlmayer I, Arshadi M, Haslinger W, Hofbauer H, Larsson I, Lönnermark A, Nilsson C, Pollex A, Schmidl C, Stelte W, Wopienka E, Bauer-Emhofer W. Determination of off-gassing and self-heating potential of wood pellets - Method comparison and correlation analysis. Fuel. 2018;234:894–903.

## Paper 2

# INFLUENCE OF OXYGEN AVAILABILITY ON OFF-GASSING EMISSIONS FROM STORED WOOD PELLETS

## Citation:

Meier F, Sedlmayer I, Emhofer W, Wopienka E, Schmidl C, Haslinger W, Hofbauer H. Influence of Oxygen Availability on off-Gassing Rates of Emissions from Stored Wood Pellets. Energy & Fuels. 2016;30:1006–1012.

## Paper 3

# INTERRELATION OF VOLATILE ORGANIC COMPOUNDS AND SENSORY PROPERTIES OF ALTERNATIVE AND TORREFIED WOOD PELLETS

## Citation:

Pöllinger-Zierler B, Sedlmayer I, Reinisch C, Hofbauer H, Schmidl C, Kolb L, Wopienka E, Leitner E, Siegmund B. Interrelation of Volatile Organic Compounds and Sensory Properties of Alternative and Torrefied Wood Pellets. Energy & Fuels. 2019;33:5270–5281.

# Paper 4

## Off-GASSING REDUCTION OF STORED WOOD PELLETS BY ADDING ACETYLSALICYLIC ACID

## Citation:

Sedlmayer I, Bauer-Emhofer W, Haslinger W, Hofbauer H, Schmidl C, Wopienka E. Off-gassing reduction of stored wood pellets by adding acetylsalicylic acid. Fuel Processing Technology. 2020;198:106218.

## Paper 5

# VENTILATION OF CARBON MONOXIDE FROM A BIOMASS PELLET STORAGE TANK – A STUDY OF THE EFFECTS OF VARIATION OF TEMPERATURE AND CROSS-VENSTILATION ON THE EFFICIENCY OF NATURAL VENTILATION

## Citation:

Emhofer E, Lichtenegger K, Haslinger W, Hofbauer H, Schmutzer-Roseneder I, Aigenbauer S, Lienhard M. Ventilation of Carbon Monoxide from a Biomass Pellet Storage Tank – A Study of the Effects of Variation of Temperature and Cross-ventilation on the Efficiency of Natural Ventilation. Annals of Occupational Hygiene. 2015;59:79-90.

# Curriculum Vitae

## DI Irene Sedlmayer M.Sc.

(formerly: Schmutzer-Roseneder)

[redacted]
✉ [redacted]
✉ [redacted]
☎ [redacted]
☎ [redacted]

## Employments

| | | |
|---|---|---|
| since 2015 | | *Researcher at BEST – Bioenergy and Sustainable Technology GmbH (formerly: BIOENERGY 2020+ GmbH) in Gewerbepark Haag 3,* 3250 Wieselburg-Land<br>Working fields: off-gassing from wood pellets; characterisation of solid biomass fuels; thermochemical conversion technologies: biomass combustion - emission measurement, pyrolysis - biochar and application; |
| 2012 - | 2015 | *Junior Researcher at BEST*<br>Working fields: biomass combustion and energetic use of biomass in small-scale; off-gassing from wood pellets; characterisation of solid biomass fuels; |
| 2008 - | 2011 | Laboratory work (sample preparation, measurement and evaluation) at Quantas Analytics GmbH – analytical service laboratory in the field of mycotoxins |

## Education

| | | |
|---|---|---|
| since 2015 | | Doctoral programme in *Technical Sciences* at Institute of Chemical, Environmental and Bioscience Engineering at Vienna University of Technology |
| 2009 - | 2011 | Master programme *Material and Energetic Exploitation of Renewable Raw Materials* at University of Natural Resources and Life Sciences in Vienna;<br>Master programme *Renewable Resources* at Technical University of Munich at TUM - campus Straubing<br>Master thesis - *Einfluss von Holzart und Rohstoff auf die Entstehung von Emissionen von Holzpellets während der Lagerung* |
| 2006 - | 2009 | Bachelor programme *Biotechnische Verfahren* at University of Applied Sciences Wiener Neustadt at campus Tulln<br>Bachelor thesis - *Isolation of a pure culture for aerobic detoxification of deoxynivalenol* |
| 1997 - | 2005 | Grammar School in Wieselburg, Austria |
| 1993 - | 1997 | Elementary School in Wang, Austria |

## Scientific activities

### *Peer-reviewed journal Papers*

Sedlmayer I, Bauer-Emhofer W, Haslinger W, Hofbauer H, Schmidl C, Wopienka E. Off-gassing reduction of stored wood pellets by adding acetylsalicylic acid. Fuel Processing Technology. 2020;198:106218.

Pöllinger-Zierler B, Sedlmayer I, Reinisch C, Hofbauer H, Schmidl C, Kolb L, Wopienka E, Leitner E, Siegmund B. Interrelation of Volatile Organic Compounds and Sensory Properties of Alternative and Torrefied Wood Pellets. Energy & Fuels. 2019;33:5270-5281.

Sedlmayer I, Arshadi M, Haslinger W, Hofbauer H, Larsson I, Lönnermark A, Nilsson C, Pollex A, Schmidl C, Stelte W, Wopienka E, Bauer-Emhofer W. Determination of off-gassing and self-heating potential of wood pellets - Method comparison and correlation analysis. Fuel. 2018;234:894-903.

Klauser F, Schwabl M, Kistler M, Sedlmayer I, Kienzl N, Weissinger A, Schmidl C, Haslinger H, Kasper-Giebl A. Development of a compact technique to measure benzo(a)pyrene emissions from residential wood combustion, and subsequent testing in six modern wood boilers. Biomass & Bioenergy. 2018;111:288-300.

Meier F, Sedlmayer I, Emhofer W, Wopienka E, Schmidl C, Haslinger W, Hofbauer H. Influence of Oxygen Availability on off-Gassing Rates of Emissions from Stored Wood Pellets. Energy & Fuels. 2016;30:1006-1012.

Emhofer E, Lichtenegger K, Haslinger W, Hofbauer H, Schmutzer-Roseneder I, Aigenbauer S, Lienhard M. Ventilation of Carbon Monoxide from a Biomass Pellet Storage Tank – A Study of the Effects of Variation of Temperature and Cross-ventilation on the Efficiency of Natural Ventilation. Annals of Occupational Hygiene. 2015;59:79-90.

### *Oral presentation*

Sedlmayer I. SMELL - Study of malodorous emissions from wood pellets. 13th Industrieforum Pellets. Berlin, Germany. 2014.

Schmutzer-Roseneder I. Emissions from wood pellets during storage referring to the extractive content. WSEDnext. Wels, Austria. 2013.

### *Conference Contributions*

Emhofer W, Sedlmayer I, Wopienka E, Pointner C, Weissinger A, Schmidl C, Haslinger W, Pöllinger-Zierler B, Siegmund B, Leitner E, Pichler W, Götzl R, Weigl M. Production related Optimization of Wood Pellets Storage Properties. 5th Central European Biomass Conference. Graz, Austria. 2017.

Pöllinger-Zierler B, Sedlmayer I, Wopienka E, Siegmund B. Malodourous emissions of wood pellets during storage. 15th Weurman Flavour Research Symposium. Graz, Austria. 2017.

Reichert G, Haslinger W, Kirchhof JM, Schmidl C, Sedlmayer I, Schwabl M, Stressler H, Sturmlechner R, Wöhler M, Hochenauer C. Honeycomb catalysts integrated in firewood stoves - potentials and limitations. 5th Central European Biomass Conference. Graz, Austria. 2017

Meier F, Schwabl M, Sedlmayer I, Kistler M, Schmidl C, Weissinger A, Haslinger W. Benzo(a)pyrene Emission in the Flue Gas from Modern Biomass Boilers. 24th European Biomass Conference and Exhibition. Amsterdam, Netherlands. 2016.

Emhofer W, Lichtenegger K, Haslinger W, Sedlmayer I. Natural ventilation measures for CO off-gassing in small pellet storages. World Sustainable Energy Days next 2015. Wels, Austria. 2015.

Emhofer W, Sedlmayer I, Pöllinger-Zierler B, Pointner C, Wopienka E, Haslinger W. A preliminary study on the influence of the pelletizing process on the off-gassing behaviour of wood pellets. 23rd European Biomass Conference. Vienna, Austria. 2015.

Pöllinger-Zierler B, Sedlmayer I, Reinisch C, Siegmund B, Wopienka E, Pointner E, Haslinger W. Mikrobielle Kontamination als Ursache für Fehlgerüche bei der Lagerung von Holzpellets. World Sustainable Energy Days 2015. Wels, Austria. 2015.

Reichert G, Schmidl C, Schwabl M, Sedlmayer I, Stressler H, Sturmlechner R, Wöhler M, Haslinger W. Emission Reduction of Firewood Stoves by Integrated Honeycomb Catalysts. World Sustainable Energy Days next 2015. Wels, Austria. 2015.

Ehrig R, Kristöfel C, Rauch P, Kolck M, Gugler H, Pointner C, Schmutzer-Roseneder I, Strasser C, Wörgetter M. Economic and ecological comparison of torrefaction-based biomass supply chains in Central Europe, 4th Central European Biomass Conference. Graz, Austria. 2014.

Pointner C, Schmutzer-Roseneder I, Feldmeier S, Kristöfel C, Ehrig R, Schwabl M, Strasser C, Wörgetter M. Torrefied pellets – influence of torrefaction on pellet characteristics and combustion. 4th Central European Biomass Conference. Graz, Austria. 2014.

Feldmeier S, Schmutzer-Roseneder I, Schwabl M, Wopienka E, Haslinger W, AshMelT- Development of a Practical and Reliable Ash Melting Test for Biomass Fuels, in particular Wood Pellets. World Sustainable Energy Days 2013. Wels, Austria. 2013.

Schmutzer-Roseneder I, Emhofer W, Haslinger W. Emissions from wood pellets during storage referring to the extractive content. World Sustainable Energy Days next 2013. Wels, Austria. 2013.

Ehrig R, Gugler H, Kristöfel C, Pointner C, Schmutzer-Roseneder I, Feldmeier S, Kolck M, Rauch P, Strasser C, Schipfer S, Kranzl L, Wörgetter M. Economic Comparison of Torrefaction-Based and Conventional Pellet Production-to-End-Use Chains. 21st European Biomass Conference. Copenhagen, Denmark. 2012.