

# Masterarbeit

## Experimental investigations and design of a new apparatus for measurement of emissions from stored pellets

ausgeführt zum Zwecke der Erlangung des akademischen Grades eines  
Diplom - Ingenieurs

unter der Leitung von

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

E166 - Inst. f. Verfahrenstechnik, Umwelttechnik und Techn. Biowissenschaften

und

Dipl.-Ing. Waltraud Emhofer

Bioenergy 2020+

A - 3250 Wieselburg

eingereicht an der Technischen Universität Wien  
Fakultät für Maschinenwesen und Betriebswirtschaft

von

Verena Trinkel

0626756

9125 Kühnsdorf, Nord 5

Wien, am 01.10.2012

## Acknowledgments

First of all I would like to thank the company bioenergy2020+ for giving me the opportunity to write this thesis at their location in Wieselburg. I would also like to give my thanks to Dipl.- Ing. Waltraud Emhofer who supervised this work.

I'd like to thank Prof. Hermann Hofbauer who supported this work as my supervisor.

I am very grateful for my parents, Gerda and Johann, who supported my studies in Vienna and who always hand out me helpful advices whenever needed. I also would like to thank my sister, Tina, for her support and our discussions.

# Contents

<b>1</b>	<b>Introduction</b>	<b>5</b>
<b>2</b>	<b>Scope of the work</b>	<b>7</b>
<b>3</b>	<b>Theoretical background</b>	<b>7</b>
3.1	Definition . . . . .	7
3.2	Emissions from pellets during storage . . . . .	9
3.2.1	Toxicity of emissions . . . . .	9
3.2.1.1	Carbon monoxide . . . . .	10
3.2.1.2	Volatile organic compounds . . . . .	10
3.2.2	Mechanisms for the release of emissions during storage . . . . .	11
3.2.2.1	Auto-oxidation . . . . .	12
3.2.2.2	Biomass decomposition . . . . .	14
3.2.3	Influences on the emission during storage . . . . .	14
3.2.3.1	Condition of raw material . . . . .	15
3.2.3.2	Duration of storage . . . . .	15
3.2.3.3	Storage temperature . . . . .	16
3.2.3.4	Headspace volume . . . . .	17
3.2.3.5	Moisture content of pellets . . . . .	18
3.2.3.6	Wood species . . . . .	19
<b>4</b>	<b>Experiment for the auto-oxidation of fatty acids as a reason for emission from pellets</b>	<b>20</b>
4.1	Used equipment and material . . . . .	20
4.2	Test procedure . . . . .	21
<b>5</b>	<b>Pretest</b>	<b>23</b>
5.1	Used equipment . . . . .	23
5.2	Raw material . . . . .	24

5.3	Test procedure . . . . .	25
5.4	Processing of data . . . . .	26
5.5	Discussion of storage test setup . . . . .	28
<b>6</b>	<b>Laboratory reactor</b>	<b>29</b>
6.1	Requirements . . . . .	30
6.2	Measurement technology . . . . .	33
6.2.1	Gas analysis . . . . .	34
6.2.2	Sensors . . . . .	40
6.2.3	Data logging system . . . . .	42
6.3	Gas-mixing-station . . . . .	42
<b>7</b>	<b>Results and discussion</b>	<b>43</b>
7.1	Results and discussion of the experiment for auto-oxidation of fatty acids .	43
7.2	Results and discussion of pretests . . . . .	44
7.2.1	Comparison of shavings . . . . .	44
7.2.2	Comparison of shavings and pellets . . . . .	49
7.3	Results and discussion of the new designed laboratory reactor . . . . .	53
<b>8</b>	<b>Conclusion and outlook</b>	<b>54</b>

## List of Figures

1	Number of newly installed pellet boilers in Austria < 100kW per year [3] . . . . .	5
2	Production capacity (Produktionskapazität), production (Produktion) and consumption (Verbrauch) of pellets in Austria [3] . . . . .	6
3	Specification of wood pellets for non-industrial use [1] . . . . .	8
4	Classification of organic pollutants [17] . . . . .	11
5	General scheme of the chemical wood components [19] . . . . .	12
6	Principle path of fatty acids auto-oxidation [20] . . . . .	13
7	Carbon dioxide (CO <sub>2</sub> ) concentrations as a function of storage time at different storage temperatures using British Columbia wood pellets [12] . . . . .	16
8	Carbon monoxide (CO) concentrations as a function of storage time at different storage temperatures using British Columbia wood pellets [12] . . . . .	17
9	Emission factor of CO <sub>2</sub> over time at different temperatures and relative humidity (closed symbols: no water present; open symbols: water present at the bottom) [22] . . . . .	18
10	Emission factor of CH <sub>4</sub> over time at different temperatures and relative humidity (closed symbols: no water present; open symbols: water present at the bottom) [22] . . . . .	19
11	Filling material . . . . .	22
12	Used measuring adapter . . . . .	23
13	Principle of measurement with the measuring adapter . . . . .	23
14	Run of CO during experiment number 1 . . . . .	27
15	Drawing of the designed laboratory reactor with following utilities:1 - measurement points for temperatures, 2 - inlet of reactor, 3 - outlet of reactor, 4 - measurement port for GC, 5 - measurement point for humidity, 6 - measurement point for pressure, 7 - filter layer for GC, 8 - plug, 9 - sparger plate . . . . .	33
16	Schematic of data handling system . . . . .	34

17	Schematic of GC system (Trägergas = carrier gas, Druckregelung = pressure regulation, Strömungsregler = current controller, Injektionsspritze = syringe, Probe = sample, Injektorheizung = injector heating, Säulenofen = column oven, Kapillartrennsäule = column, Säulenausgang, exit of column, Detektor = detector, Datenverarbeitung = data processing) [35] . . .	35
18	Types of columns [35] . . . . .	36
19	Types of stationary phases [35] . . . . .	37
20	Cross section of a thermal conductivity detector [34] . . . . .	38
21	Wheatstone bridge circuit (Trägergas = carrier gas, Trägergas plus Analyte = carrier gas plus analyte [35] . . . . .	38
22	Flame ionization detector [35] (Zündspule = ignition coil, Sammelelektrode (Kathode) = collector electrode (cathode), Flammendüse (Anode) = flame jet (anode), Luft = air, Wasserstoff = hydrogen, Ausgang der GC - Säule = exit of the GC column, Trägergas plus Moleküle mit C-C- und C-H-Bindungen = carrier gas with C-C- and C-H-bonds . . . . .	39
23	Scheme of the gas-mixing-station . . . . .	42
24	Run of CO and VOC of auto-oxidation of linoleic acid . . . . .	43
25	CO emission rates [ $mg_{CO}/kg_{owd}/day$ ] from miscanthus shavings and ash tree shavings over storage time . . . . .	45
26	VOC emission rates [ $mg_{VOC}/kg_{owd}/day$ ] from miscanthus shavings and ash tree shavings over storage time . . . . .	45
27	CO emission rates [ $mg_{CO}/kg_{owd}/day$ ] from larch shavings and spruce shavings over storage time . . . . .	46
28	VOC emission rates [ $mg_{VOC}/kg_{owd}/day$ ] from larch shavings and spruce shavings over storage time . . . . .	47
29	CO emission rates from miscanthus-, ash tree-, larch- and spruce shavings over storage time . . . . .	48
30	VOC emission rates from miscanthus-, ash tree-, larch- and spruce shavings over storage time . . . . .	48
31	CO emission rates in [ $mg_{CO}/kg_{owd}/day$ ] from miscanthus pellets and miscanthus shavings over storage time . . . . .	49

32	VOC emission rates [ $mg_{VOC}/kg_{owd}/day$ ] from miscanthus pellets and miscanthus shavings over storage time . . . . .	50
33	CO emission rates [ $mg_{CO}/kg_{owd}/day$ ] from different kinds of pellets and shavings over storage time . . . . .	51
34	VOC emission rates [ $mg_{VOC}/kg_{owd}/day$ ] from different kinds of pellets and shavings over storage time . . . . .	52
35	Scheme of the new designed laboratory setup . . . . .	53

## List of Tables

1	"Concentration - effect - relationship" for impairment of health due to exposition of VOC [18] . . . . .	11
2	Characteristics FID . . . . .	21
3	Characteristics NGA . . . . .	21
4	Used raw materials in storage tests . . . . .	24
5	Water content and density of used material . . . . .	25
6	Fatty acid content of pellets and shavings . . . . .	52



# Abbreviations, formula symbols, chemical formulas, units

## Abbreviations

<i>VOC</i>	volatile organic compounds
<i>TVOC</i>	total volatile organic compounds
<i>VVOC</i>	very volatile organic compounds
<i>SVOC</i>	semivolatile organic compounds
<i>POM</i>	particular organic matter
<i>PC</i>	personal computer
<i>GC</i>	gas chromatography
<i>FID</i>	flame ionization detector
<i>TCD</i>	thermal conductivity detector
<i>NPD</i>	nitrogen-phosphorus detector
<i>FPD</i>	flame photometric detector
<i>ECD</i>	electron capture detector
<i>owd</i>	ovendry weight
<i>VZ</i>	reference cell
<i>MZ</i>	measurement cell
<i>WCOT</i>	wall-coated open-tubular column
<i>PLOT</i>	porous-layer open-tubular column
<i>SCOT</i>	support-coated open-tubular column
<i>RTD</i>	resistive temperature device
<i>PELD</i>	polyethylene low density
<i>MFC</i>	mass flow controller
<i>NDIR</i>	nondispersive infrared sensor
<i>PTFE</i>	Polytetrafluorethylene

## Formular symbols

<i>V</i>	volume	$m^3$
<i>m</i>	mass	$kg$
$\rho$	density	$\frac{kg}{m^3}$
<i>C</i>	concentration	%

$M$	molar mass	$\frac{g}{mol}$
$WC$	water content	%
$U$	voltage	$V$
$T$	temperature	$^{\circ}C$
$P$	pressure	$bar$
$RH$	relative humidity	%

## Chemical symbols and formulas

$CO$	carbon monoxide
$CO_2$	carbon dioxide
$O_2$	oxygen (molecular)
$CH_4$	methane
$N_2$	nitrogen (molecular)
$N_2O$	nitrogen oxide

## Units

$^{\circ}C$	degree Celsius
$ppm$	parts per million
$ppmv$	parts per million volume
$g$	gram
$kg$	kilogram
$m^3$	cubic meter
$J$	joule
$Wh$	watt hour (3,600 $J$ )
$wt\%$	weight percent
$A$	ampere
$\Omega$	ohm
$d$	day
$l$	liter
$mol$	mol
$F$	farad
$V$	volt
$bar$	bar

## Indices

<i>ar</i>	as received
<i>odw</i>	oven dry weight
<i>CO</i>	carbon monoxide
<i>VOC</i>	volatile organic compounds

## Kurzfassung

Pellets haben auf Grund der gleichbleibenden Brennstoffqualität Vorteile wie beispielsweise eine hohe Energiedichte oder den einfachen Transport. Daher zählen heute Pellets zu einem attraktiven Brennstoff für Industrie als auch für private Haushalte. Die Anzahl der jährlich neu installierten Pelletsöfen steigt daher in Österreich von Jahr zu Jahr.

Während der Lagerung von Pellets werden gesundheitsschädliche Emissionen freigesetzt. Durch diese Emissionen kam es in der Vergangenheit bereits zu einigen Unfällen, bei denen sogar Menschen starben. Aus der Literatur sind aktuell nur wenige Informationen zum Auftreten und zur Zusammensetzung der Emissionen von Pellets während der Lagerung verfügbar. Darüber hinaus sind die Freisetzungsreaktionen an der Oberfläche von Pellets sowie die Faktoren, die diese Reaktionen begünstigen, nur teilweise bekannt.

Das Ziel dieser Diplomarbeit war es, einen Laborreaktor zu konstruieren, um den chemischen Freisetzungsmechanismus, der für die Entstehung der Emissionen von Pellets während der Lagerung verantwortlich ist, zu untersuchen. Der Reaktor wurde auf Basis einer Literaturstudie sowie mit Hilfe von praktischen Experimenten ausgelegt. Anhand der Literaturrecherche wurden Einflussfaktoren, die die Menge an Emissionen beeinflussen, definiert: Die Holzart, die für die Pelletsproduktion verwendet wird, die Beschaffenheit des verwendeten Materials, die Lagerdauer, die Lagertemperatur, der Wassergehalt der Pellets, und der zur Verfügung stehende Sauerstoffgehalt im Lagerraum. Ein Experiment zur Untersuchung der Auto-oxidation von Fettsäuren als Ursache für die Emission von Pellets wurde durchgeführt.

Die praktischen Versuche wurden mit verschiedenen Holzarten an einen bereits bestehenden Laboraufbau durchgeführt. Dieser Aufbau bestand aus Laborglasflaschen, die als Lagerungsbehälter dienten. Zur Emissionsmessung wurden ein Infrarot-Gasanalysator sowie ein Flammenionendetektor verwendet. Auf Basis dieser Experimente wurden folgende Defizite dieses Aufbaus definiert: der Mangel an Temperatur- und Druckmessstellen, die fehlende Möglichkeit den Reaktor zu kühlen und zu heizen als auch, dass das verwendete Messequipment stark verbesserungswürdig war. Durch die Kombination der Ergebnisse aus der Literaturrecherche und den praktischen Versuchen, wurde der Laborreaktor konstruiert. Dieser Laboraufbau bietet die Möglichkeit, die Temperatur, den Druck sowie die relative Feuchte im Reaktor zu messen. Die Emissionsmessung wurde mittels eines Gaschromatographen, der speziell für diese Anwendung ausgelegt ist, realisiert. Der Reaktor muss zur Probenahme nicht mehr geöffnet werden und bietet nun auch die Möglichkeit die Lagertemperatur zu variieren. Mit Hilfe einer für diese Anwen-

zung ausgelegten Gasmischstation kann eine definierte Atmosphäre im Reaktor eingestellt werden. Darüber hinaus kann das Gas auch befeuchtet werden.

Zusätzlich zur Konstruktion des Laborreaktors wurden die Ergebnisse der Experimente diskutiert und mit bereits bei Bioenergy 2020+ durchgeführten Versuchen verglichen.

## Abstract

Wood pellets have a consistent fuel quality which provides many advantages such as the ease of transport and a high energy density. Thus, pellets have become a suitable fuel in private households and industry. The number of newly installed furnaces in Austria is steadily increasing every year.

During the storage of the pellets, poisonous emissions are released. These emissions caused severe accidents in the past, and even resulted in the deaths of people. From the literature, only limited information on the occurrence and the composition of pellets emissions is available. However, the releasing mechanisms of the emissions as well as their promoting factors are not well understood.

The aim of this diploma thesis was to design a laboratory reactor to investigate the chemical mechanisms, which cause the emissions from pellets during storage. The laboratory reactor was constructed on the basis of a literature research and practical experiments. From the literature research, the following factors influencing the type and amount of emissions were defined: the species of wood used for pellet production, the conditions of the raw material, the duration of storage, the storage temperature of pellets, the moisture content of pellets and the available oxygen in the storage room. An experiment for the auto-oxidation of fatty acids as mechanism for the appearance of emission from pellets was performed and discussed. The practical experiments were performed with different raw materials with an existing experimental setup. This setup consisted of laboratory glass bottles, an infrared gas analyzer and a flame ionization detector. The glass bottles were used to store the raw materials and the emission measurement were performed with the infrared gas analyzer and a flame ionization detector. From these experiments, a number of shortcomings were discovered: the lack of temperature and pressure measurement, the lack of the possibility to heat and cool the reactor, improper measurement equipment for the emission measurement was used. By combining both, the literature study and the practical experiments, a laboratory reactor was designed. This reactor provides the possibility to measure the temperature, the pressure as well as the possibility to analyze the emissions with a gas chromatograph, which was especially designed for the chemical properties of the emissions expected. Furthermore, the laboratory reactor does not need to be opened to start the emission measurements. Another improvement is that it is possible to heat and to cool the reactor, which will allow to test the effect of storage temperature on the amount of emissions and on the emission rates. A specially designed gas mixing station guarantees the production of a defined atmosphere. The option to

moister the gas will allow to test the influence of humidity on the emissions from pellets during storage.

In addition the design of the laboratory reactor, the results from the experiments with the laboratory glass bottles as storage were discussed and compared with former experiments carried out at Bioenergy 2020+.

# 1 Introduction

Pellets have a consistent fuel quality, which includes low moisture content, high energy density and homogeneous size and shape. The high requirements for the quality of pellets provide advantages such as the ease of transportation and the possibility to design fully automatic biomass furnaces. Pellets, therefore, provide a similar comfort to common oil and gas heating systems. Thus, pellets have become a suitable fuel for different fields of applications, ranging from stoves and central heating systems up to large-scale plants. [1]

The number of newly installed pellet boilers per year in Austria has been growing in the last 15 years from around 400 in 1997 to more than 10 000 in 2011 (see figure 1). The decrease in sales number in the year 2007 is related to a price peak of pellets in 2006. In the year 2008 the amount of new installed furnaces rises according to the increasing oil and gas prices. [2]

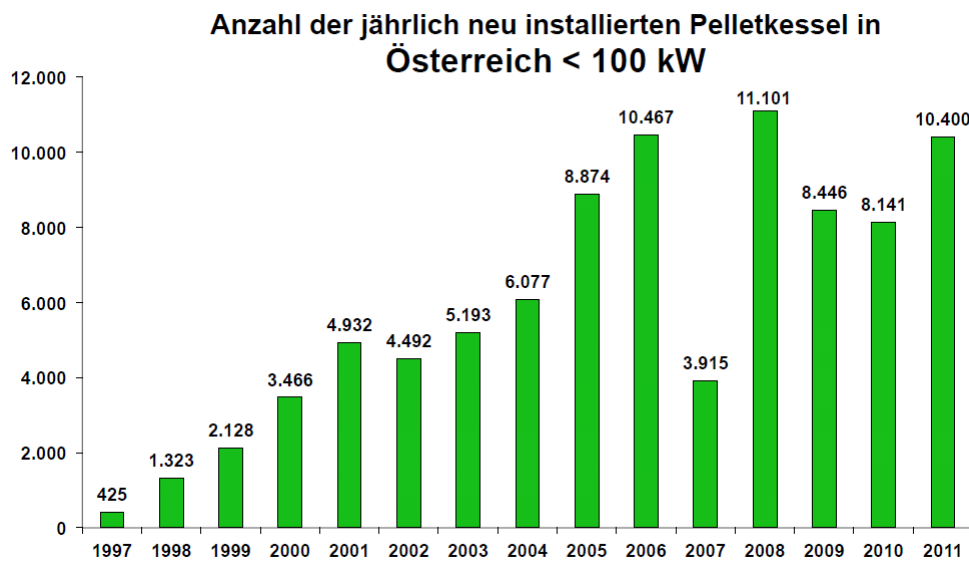


Figure 1: Number of newly installed pellet boilers in Austria < 100kW per year [3]

Similarly, the annual production capacity as well as the production and consumption of pellets has been increasing steadily (see figure 2).



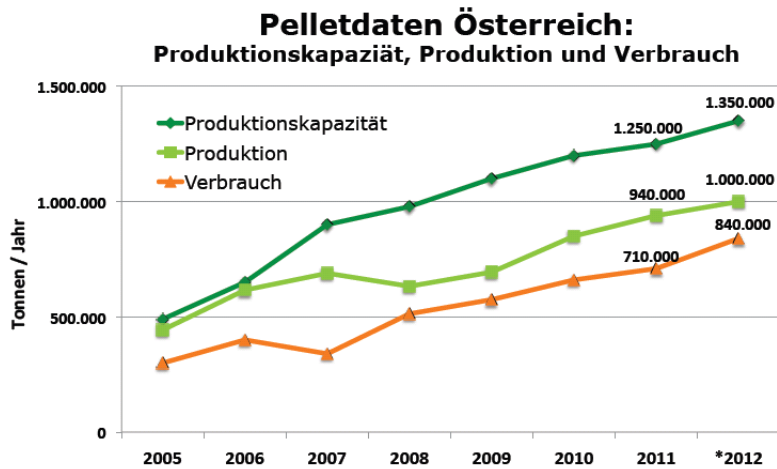


Figure 2: Production capacity (Produktionskapazität), production (Produktion) and consumption (Verbrauch) of pellets in Austria [3]

Safety and health concerns have a high priority during the pellet production, handling and storage. In pellets, as in any other types of biomass, decomposition processes take place. During these processes carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) as well as hydrocarbons are emitted. This off-gassing phenomenon has to be taken serious during transportation, handling and storage. [1]

The off-gassing phenomenon has been investigated for the first time after some accidents, which occurred on board pellet storage vessels during the unloading process. Melin et. al. (2008) reported accidents on two pellets transport ships in the years 2002 and 2006. [4]

Svedberg (2008) reported a further accident in the Port of Helsingborg. This accident occurred during the discharging of wood pellets from a vessel and led to the death of one seaman, one seriously injured stevedore and several slightly injured rescue workers. [5]

More recently, in January 2010, a man died in an indoor pellets storage from carbon monoxide poisoning [6] and in 2011 a young woman in Switzerland died due to carbon monoxide poisoning in a pellets storage. Whether the source of carbon monoxide was off-gassing reactions from pellets or if its source was a backburning incident is unclear. [7]

In order to avoid such incidents, in the future, there is an urgent need to investigate the off-gassing phenomenon of pellets:

The reaction kinetics and the predictability of the total amount of the emissions have to be investigated.

## 2 Scope of the work

The aim of this work was to design a laboratory reactor for the investigation of the release mechanisms of emissions during the storage of pellets.

A literature research was carried out to identify which mechanisms cause the release of the emissions, and which factors influence the amount of emissions. Additionally, an experiment to investigate the auto-oxidation of fatty acids as mechanism for the emissions from pellets during storage was performed and discussed in relation to the literature study.

Practical experiments were performed with different raw materials with an existing experimental setup. This setup consisted of laboratory glass bottles, a infrared gas analyzer and a flame ionization detector. The results from these experiments were discussed and compared with former experiments carried out in the framework of Bioenergy 2020+. Shortcomings of the experimental setup with the laboratory glass bottles were analyzed in order to improve this measurement setup. By combining both, the literature study and the practical experiments, a laboratory reactor for accurate and precise determination of the emissions from pellets was designed.

## 3 Theoretical background

In this chapter pellets as a fuel will be described. Moreover the main emissions from wood pellets, their toxicity as well as the mechanisms and the conditions which promote the off-gassing phenomenon will be described.

### 3.1 Definition

According to the EN14588 standard, a pellet is a pressed biofuel from pulverized biomass. A pellet can be produced with or without additives. In general, they have a cylindrical form with a typical length from 3, 15 to 40mm. An additive is defined as a material, which improves the quality of the fuel, reduces emissions or makes the production more efficient. [8]

In EN 14961-2 the fuel properties for wood pellets and the classes are described. The most significant characteristics are the moisture content, the dimension of the pellet and their ash content. Depending to their properties the wood pellets are grouped into different classes. Property classes A1 and A2 include wood pellets, which are made from

virgin wood and chemically untreated wood residues. Fuels with slightly higher ash and nitrogen content belong to A2. Property class B describes chemically treated industrial wood by-products, residues and used wood are also allowed. Standards for non-woody pellets are listed in part 6 of the EN 14961. [1], [9] The properties of the classes A1, A2 and B are listed in figure 3:

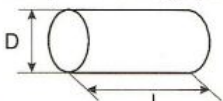
Property class (analysis method)	Unit	A1	A2	B
Origin and source		1.1.3 Stemwood 1.2.1 Chemically untreated wood residues	1.1.1 Whole trees without roots 1.1.3 Stemwood 1.1.4 Logging residues 1.1.6 Bark 1.2.1 Chemically untreated wood residues	1.1 Forest, plantation and other virgin wood 1.2 By-products and residues from wood processing industry 1.3 Used wood
Diameter, D <sup>a</sup> and Length, L <sup>b</sup> 	mm	D06 ± 1.0 3.15 ≤ L ≤ 40  D08 ± 1.0 3.15 ≤ L ≤ 40	D06 ± 1.0 3.15 ≤ L ≤ 40  D08 ± 1.0 3.15 ≤ L ≤ 40	D06 ± 1.0 3.15 ≤ L ≤ 40  D08 ± 1.0 3.15 ≤ L ≤ 40
Moisture, M (EN 14774-1 and -2)	wt. % <sub>ar</sub>	M10 ≤ 10	M10 ≤ 10	M10 ≤ 10
Ash, A (EN 14775)	wt. % (d.b.)	A0.7 ≤ 0.7	A1.5 ≤ 1.5	A3.5 ≤ 3.5
Mechanical durability, DU (EN 15210-1)	wt. % <sub>ar</sub>	DU97.5 ≥ 97.5	DU97.5 ≥ 97.5	DU96.5 ≥ 96.5
Fines at factory gate in bulk transport (at the time of loading) and in small (up to 20 kg) and large sacks (at time of packing or when delivering to end user), F (EN 15149-1)	wt. % <sub>ar</sub>	F1.0 ≤ 1.0	F1.0 ≤ 1.0	F1.0 ≤ 1.0
Additives	wt. % (d.b.)	≤ 2 Type <sup>c</sup> and amount to be stated	≤ 2 Type <sup>c</sup> and amount to be stated	≤ 2 Type <sup>c</sup> and amount to be stated
Net calorific value, Q (EN 14918)	MJ/kg <sub>ar</sub> or kWh/kg <sub>ar</sub>	16.5 ≤ Q ≤ 19.0 or 4.6 ≤ Q ≤ 5.3	16.3 ≤ Q ≤ 19.0 or 4.5 ≤ Q ≤ 5.3	16.0 ≤ Q ≤ 19.0 or 4.4 ≤ Q ≤ 5.3
Bulk density, BD (EN 15103)	kg/m <sup>3</sup>	BD600 ≥ 600	BD600 ≥ 600	BD600 ≥ 600
Nitrogen, N (prEN 15104)	wt. % (d.b.)	N0.3 ≤ 0.3	N0.5 ≤ 0.5	N1.0 ≤ 1.0
Sulphur, S (prEN 15289)	wt. % (d.b.)	S0.03 ≤ 0.03	S0.03 ≤ 0.03	S0.04 ≤ 0.04
Chlorine, Cl (prEN 15289)	wt. % (d.b.)	Cl 0.02 ≤ 0.02	Cl 0.02 ≤ 0.02	Cl 0.03 ≤ 0.03
Arsenic, As (prEN 15297)	mg/kg (d.b.)	≤ 1	≤ 1	≤ 1
Cadmium, Cd (prEN 15297)	mg/kg (d.b.)	≤ 0.5	≤ 0.5	≤ 0.5
Chromium, Cr (prEN 15297)	mg/kg (d.b.)	≤ 10	≤ 10	≤ 10
Copper, Cu (prEN 15297)	mg/kg (d.b.)	≤ 10	≤ 10	≤ 10
Lead, Pb (prEN 15297)	mg/kg (d.b.)	≤ 10	≤ 10	≤ 10
Mercury, Hg (prEN 15297)	mg/kg (d.b.)	≤ 0.1	≤ 0.1	≤ 0.1
Nickel, Ni (prEN 15297)	mg/kg (d.b.)	≤ 10	≤ 10	≤ 10
Zinc, Zn (prEN 15297)	mg/kg (d.b.)	≤ 100	≤ 100	≤ 100
Ash melting behaviour, DT <sup>d</sup> (prEN 15370)	°C	should be stated	should be stated	should be stated

Figure 3: Specification of wood pellets for non-industrial use [1]

## 3.2 Emissions from pellets during storage

During storage, pellets emit mainly the following gases [1]:

- Carbon monoxide
- Carbon dioxide
- Methane
- Aldehydes and ketones including hexanal and pentanal in addition to acetone and methanol

These components were detected in several studies:

Svedberg et. al. (2004) performed measurements of the emissions from wood pellets. The pellets were stored in warehouses, in domestic storage rooms or during the laboratory tests in galvanized steel canisters. The results of these measurements showed that the dominant organic compounds were aldehydes, acetone and methanol. Beside that, carbon monoxide was found. The main aldehyde was found to be hexanal. [10]

Arshadi et. al. (2009) investigated the emission of volatile aldehydes and ketones from wood pellets. During the storage of pellets, the following aldehydes/ketones were detected: methanal, ethanal, acrolein, 2-propanone, propanal, butanal, benzaldehyde, pentanal, toloulaldehyde, hexanal, octanal, and nonanal. Beside the aldehydes/ketones, fatty/resin acids were identified. The fatty/resin acids were first extracted in a soxhlet apparatus with a mixture of petroleum ether and acetone and afterwards analyzed by GC-MS. The main resin acids were found to be dehydroabietic acid and 7-oxo-dehydroabietic acid. [11]

Kuang et. al. (2008) investigated also the off-gas phenomena during the storage of pellets: the main components were CO, CO<sub>2</sub>, and CH<sub>4</sub>. [12]

### 3.2.1 Toxicity of emissions

As already mentioned in chapter 1 accidents in connection with off-gassing from pellets have happened. Therefore, the toxicity of the emissions from pellets will be briefly described below.

### 3.2.1.1 Carbon monoxide

Carbon monoxide is an odorless, tasteless and colorless gas. [13] The human health is affected by CO because it blocks the transmission of  $O_2$  in blood. Carbon monoxide is bound to hemoglobin to form carboxyhemoglobin (COHb). Compared to  $O_2$  the affinity of CO to bond to hemoglobin is more than 200 times bigger. [14]

When humans are exposed to a concentration of  $200\text{ppm}$  for 2 to 3 hours, a slight headache will occur. A concentration of  $400\text{ppm}$  causes headache in the forehead after 1 to 2 hours spreading quickly over the whole head. If the concentration reaches  $800\text{ppm}$ , dizziness and sickness after 45 minutes is the consequence and after an exposure of 2 hours consciousness will be. A concentration of  $1600\text{ppm}$  for 2 hours will lead to death. [15]

Currently, there are no regulations defining the maximal carbon monoxide concentration in pellet storage rooms. Only the need for the use of special cover plates to ensure a gas exchange between the storage room and the environment is regulated in the standard ÖNorm M 7137. [3]

In the directive, VDI 2053, the CO concentration at the workplace is limited to  $60\text{ppm}$  during a 15 minute period. In regulations for car parks, the concentration level is set to  $100\text{ppm}$  as an average half-hourly value. It is recommended, that this value should be reduced to a level of  $60\text{ppm}$  as an average quarter-hourly value. [16]

### 3.2.1.2 Volatile organic compounds

At small concentrations (up to  $25\text{ mg}/\text{m}^3$ ) VOC can cause sensory effects. Sensory effects include sensory irritation, dryness, weak inflammatory irritations of eyes, nose, airways and skin. Higher concentrations of volatile organic compounds will lead to serious health effects such as headache and neurotoxic effects.

The mixture of volatile organic compounds is often expressed as total volatile organic compounds (TVOC), which include very volatile organic compounds (VVOC), volatile organic compounds (VOC), semivolatile organic compounds (SVOC) and organic compounds associated with particular matter or particular organic matter (POM) (see figure 4). [17]

Category	Description	Abbreviation	Boiling-point range*	Sampling media typically used in field studies
1	Very volatile (gaseous) organic compounds	VVOC	<0 to 50–100	Batch sampling; adsorption on charcoal
2	Volatile organic compounds	VOC	50–100 to 240–260	Adsorption on Tenax, graphitized carbon black or charcoal
3	Semivolatile organic compounds	SVOC	240–260 to 380–400	Adsorption on polyurethane foam or XAD-2
4	Organic compounds associated with particulate matter or particulate organic matter	POM	>380	Collection on filters

\* Polar compounds appear at the higher end of the range

Figure 4: Classification of organic pollutants [17]

In table 1 possible effects on human health are listed. Below a concentration of  $0,20 \text{ mg}/\text{m}^3$  there is no impact on the human well-being. With increasing concentration impairments of human well-being occur. Concentrations above  $25 \text{ mg}/\text{m}^3$  cause headache and can lead to neurotoxic effects.

Table 1: "Concentration - effect - relationship" for impairment of health due to exposition of VOC [18]

TVOC-concentration [ $\text{mg}/\text{m}^3$ ]	Effect
<0,20	No impact on the human well-being
0,20 - 3,0	Irritation or impairment well-being possible, if interaction with other exposition parameters is given
3,0 - 25	Exposition shows effect on human well-being; possibility of headache if interaction with other exposition parameters is given
>25	Headache; other neurotoxic effects possible

### 3.2.2 Mechanisms for the release of emissions during storage

In the literature two main mechanisms are described to be responsible for the formation of emissions from pellets:

- Auto-oxidation
- Decomposition

These mechanisms will be described in detail in the following chapters.

### 3.2.2.1 Auto-oxidation

In this chapter first the chemical components of wood will be indicated. Next the auto-oxidation process as mechanism for the release of emission from pellets will be discussed.

#### Chemical components of wood

Wood consists of macromolecular substances and low-molecular-weight substances. The macromolecular substances are the main cell wall components such as cellulose, polyoses (hemicelluloses) and lignin, which are present in all woods. The proportions and chemical composition of lignin and hemicelluloses is different in softwood and hard wood, while cellulose is a uniform component in all woods. The low-molecular-weight substances are extractives and mineral substances, which are generally more related to special wood species in kind and amount. (see figure 5)

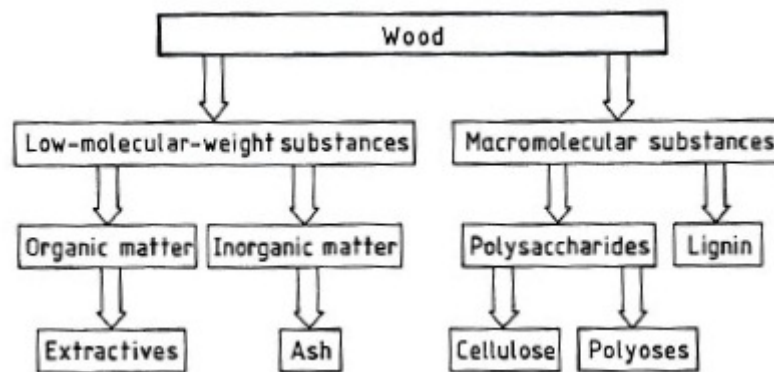


Figure 5: General scheme of the chemical wood components [19]

**Cellulose:** It is the major wood component and makes up approximately one half of both softwoods and hardwoods. It is a linear high-molecular-weight polymer built up exclusively of  $\beta$ -D-glucose. It is the main structural component of the plant cell walls.

**Polyoses (hemicelluloses):** They are in close association with cellulose in the cell wall. The main constituents of polyoses are five neutral sugars: hexoses glucose, mannose, galactose and pentoses xylose and arabinose. The molecular chains are much shorter than in cellulose, have side groups and are branched in some cases.

**Lignin:** The molecules of lignin are built up quite differently from those of polysaccharides. They consist of an aromatic system composed of phenylpropane units. There are structural differences between softwood and hardwood lignin. Moreover, there is more lignin in softwoods than in hardwoods.

Organic matter: The main groups of extractives are: Aromatic compounds (for example tanning compounds, stilbenes, lignans, flavonoids), terpenes, aliphatic acids (saturated and unsaturated higher fatty acids), alcohols.

Inorganic matter: In woods from temperate zones the elements potassium, calcium and magnesium are predominantly. [19]

### Auto-oxidation process

The auto-oxidation process may start after sawing, as damage to cells causes lipids to hydrolyze to free lipid acids, which are more easily oxidized. Free radicals can be produced by light photons and by metals. Another option is the spontaneous reaction. Such a reaction have materials with a readily abstractable hydrogen. After the oxidation process has started, the reaction is self-catalyzed and will continue until all radicals have been neutralized. [20]

Hexanal and other alkanals are probably formed by oxidative degradation of natural lipids in wood. Hexanal, as a major volatile component, is formed from linoleic acid or its esters by radical-induced oxidation by oxygen. Such reactions can be catalyzed through a so called auto-oxidation process. Carbon monoxide may also be formed through the auto-oxidative degradation of fats. [10]

A principle pathway for the auto-oxidation reaction is shown in figure 6.

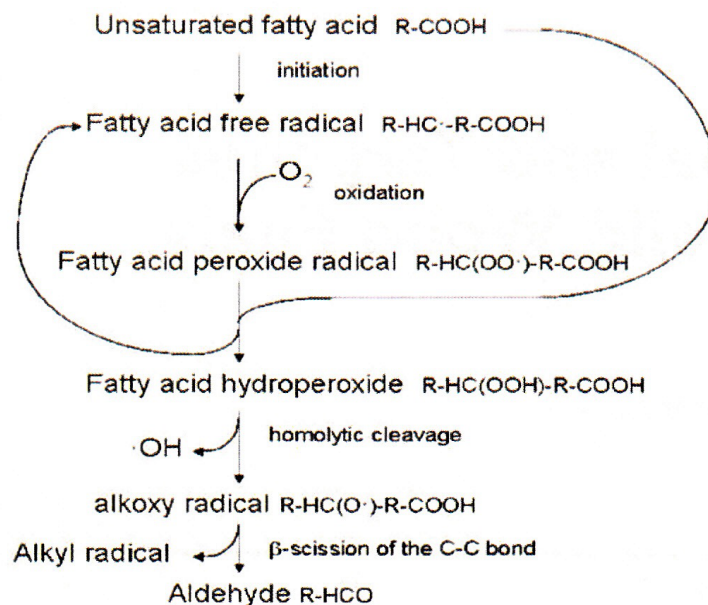


Figure 6: Principle path of fatty acids auto-oxidation [20]



Emhofer and Pointner (2009) argue that auto-oxidation as the mechanism for the release of emissions is most likely. In closed storage system decreasing oxygen concentrations can be observed, as the chemical reaction consumes oxygen. Furthermore, the emission rate increases with increasing storage temperatures (see also 3.2.3.3). The chemical reactions are favored at higher temperatures. Beside that the fatty acid content of pellets decreases during storage as are the emission rates for CO and VOC. This is consistent with the hypothesis that chemical reactions are consuming the reactants while forming the products, in this case the emissions. [21]

Also, Kuang et. al. (2009) described that the chemical process via auto-oxidative degradation of fats and fatty acids may be the dominant mechanism for the off-gassing phenomenon. This statement was again based on the fact that the emission rate increases steadily with increasing temperature. [22]

### **3.2.2.2 Biomass decomposition**

The decomposition of biomass during storage was described in several articles as a reason for the formation of emission.

Meijer and Gast (2004) described a biological decomposition process up to a temperature of 75°C . At temperatures above 75°C a chemical oxidation process occurred. According to Meijer and Gast, only CO<sub>2</sub> is formed during the process of biological decomposition. CO will be formed at higher temperatures as a result of chemical oxidation. [23]

Kuang et. al. (2009) discussed the possibility that the decomposition of biomass may be relevant for the emissions: The biological process may peak at a certain temperature, and above this certain temperatures decreases when bacteria and fungi perish. [22]

Lehtikangas (2000) discovered a microbiological growth on the surface of pellets after storing them for three months. These pellets had a relatively high moisture content of about 21% before storage, which is probably the reason for the microbiological contamination. [24] However nowadays the moisture content of pellets is limited to a maximum of 10wt% according to the standard EN 14961-2. [9]

Because of this regulation the biomass decomposition process can be considered as a non decisive mechanism for the emissions from pellets during storage.

### **3.2.3 Influences on the emission during storage**

The rate of off-gassing is a function of the temperature, the properties of the raw material, pretreatment of the raw material and the pelletising equipment used. [1]

Therefore, the pretreatment of the raw material, the duration of storage, the storage temperature and the used wood species influence the amount of emission produced.

### 3.2.3.1 Condition of raw material

The moisture content of the raw material is amongst other things an important impact factor for the process of densification. Therefore, an optimal moisture content has to be achieved according to the pelletising technology and the applied raw material. [1] The drying process takes place at temperatures between 100°C and 120°C to obtain a moisture content of 10 to 12%. During the drying process, monoterpenes and other volatile compounds are released. [25]

The release of VOC is rapid early in the drying process. The amount of the VOC emissions will increase rapidly at the beginning and then level out. The drying temperature effects the release rate and the total amount of VOC emitted from sawdust. [26]

Granström (2010) reported that the process of drying and pelletizing hastens the hexanal formation. During the drying and pelletizing processes the extractives of the wood have been exposed to oxygen and high temperatures and are likely to contain fatty acid hydroperoxides as well as unsaturated fatty acids. The hexanal formation may be due to an accumulation of semi-stable fatty acids hydroperoxides during the propagation stage of auto-oxidation. [20]

When optimizing the drying temperature in the pellet production it might be possible to reduce the amount of volatile organic compounds. Whether there is any impact on the formation of CO was not a content of the study from Arshadi and Gref (2005). [25]

### 3.2.3.2 Duration of storage

During storage of sawdust, the amount of fatty acids and resin acids decline, which implies that the longer the storage periods of pellets are the less amounts of emissions will be released. [25]

Ganström (2010) investigated the emissions of volatile organic compounds during the storage of undried sawdust, dried sawdust, and wood pellets. As material scots pine was chosen. The pellets which were used in Ganströms (2010) study were made from scots pine sawdust five days after the drying process. Hexanal was detected after only a few days of storage. The hexanal content reached the maximum 25 days after drying (20 days after pelleting) at 26 *mg/kg(owd)*. When the maximum was reached, the hexanal decreased to less than 1 *mg/kg(owd)* after three month of storage. Because of the result

that after three month hardly any hexanal emissions were measured, it was postulated that for the domestic exposure from pellet storage would mostly be a problem the storage of pellets in which the used raw material is 2 to 3 month old. [20]

### 3.2.3.3 Storage temperature

The influence of the storage temperature was investigated by Kuang et. al. (2008, 2009) [12], [22] and by Tumuluru et. al. (2010) [27]. Pellets were stored at different temperatures and the concentration of emissions during storing were measured. When the pellets were stored around room temperature, the emissions increased linear with the time. Above 40°C the emissions increased exponentially. [22] A comparison of the maximum concentration of CO<sub>2</sub>, CO, CH<sub>4</sub> showed that the concentrations of these gases were always higher at a storage temperature above room temperature. The increase of the amount of the emissions depending on the storage temperature can be seen in figure 7 and 8.

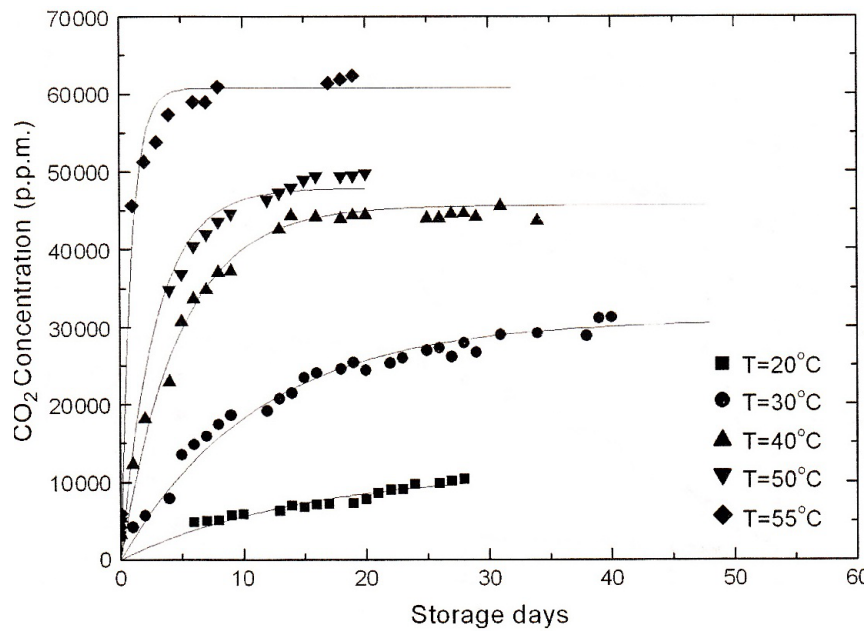


Figure 7: Carbon dioxide (CO<sub>2</sub>) concentrations as a function of storage time at different storage temperatures using British Columbia wood pellets [12]

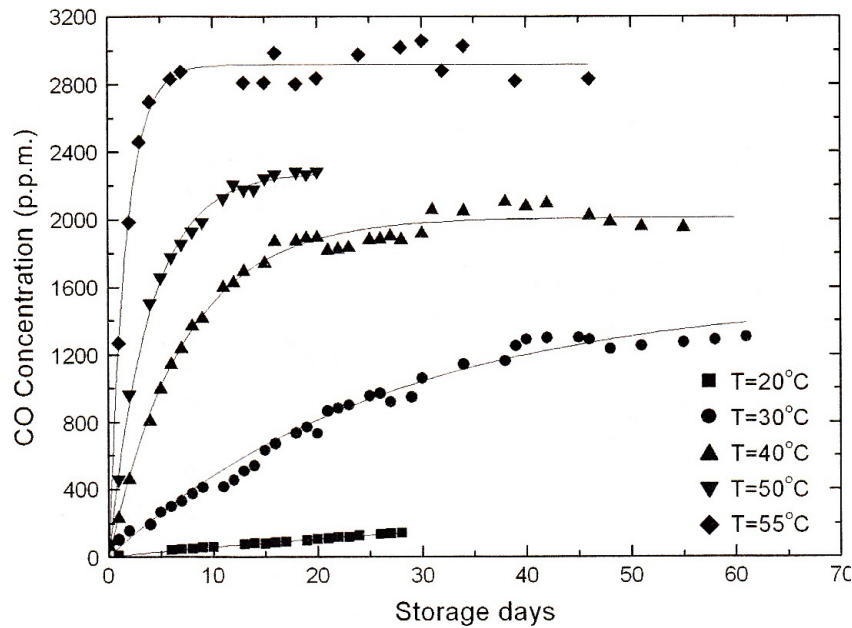


Figure 8: Carbon monoxide (CO) concentrations as a function of storage time at different storage temperatures using British Columbia wood pellets [12]

British Columbia wood pellets, for example, were stored at 20°C and at 40°C in 45l containers. The maximum  $CO_2$  concentration in the containers with a storage temperature of 40°C reached 45651ppm. In contrast, in containers, which were stored at 20°C a maximum concentration of 11576ppm  $CO_2$  were measured. [12]

Also Tumuluru et. al. (2010) investigated the correlation between the amounts of emissions and the storage temperature. The storage studies were carried out at room temperature and at elevated temperatures of 30, 40 and 50°C. After a storage period of 9 days, the concentrations of CO and  $CO_2$  from pellets, which were produced in British Columbia, stored at room temperature reached levels of about 2000ppmv respectively 5000ppmv. These concentrations increased sharply at a storage temperature above room temperature. The maximum concentrations were measured at 50°C. The CO concentration reached 17000ppmv, the  $CO_2$  concentration 70000ppmv and the  $CH_4$  concentration 3000ppmv. [27]

### 3.2.3.4 Headspace volume

The headspace volume is defined as the volume above the packed bed of pellets in the reactor. Thus this volume is comparable with the available oxygen.

Kuang et. al. (2009) [28] investigated the effects of headspace of off-gas emissions from wood pellets in storage. The authors showed that if the headspace volume decreased

the maximal concentrations of CO, CO<sub>2</sub> and CH<sub>4</sub> decreased. Additionally, the lower the headspace volume, the lower was the oxygen concentration after a storage time of 25 days. [22], [28]

### 3.2.3.5 Moisture content of pellets

Kuang et. al. (2009) suggested that the moisture content is an important factor influencing the off-gas emissions from wood pellets in storage. A high moisture content may cause higher emissions of gases such as CO<sub>2</sub>, CO and CH<sub>4</sub> during storage. [22]

In figures 9 and 10, the emission factors for CO<sub>2</sub> and CH<sub>4</sub> over time are shown. Open symbols show the trend of the emission factor for pellets with a higher moisture content in the experimental storage container. To raise the relative humidity in the container a 500ml dish was filled with water and placed at the bottom. The pellets were stored on a screen installed above the dish.

The maximum emission factors for CO<sub>2</sub>, CO and CH<sub>4</sub> were higher at higher relative humidity. The difference in the amount of emissions between low and high relative humidity were more significant for CO<sub>2</sub> and CH<sub>4</sub> than for CO, respectively. [22]

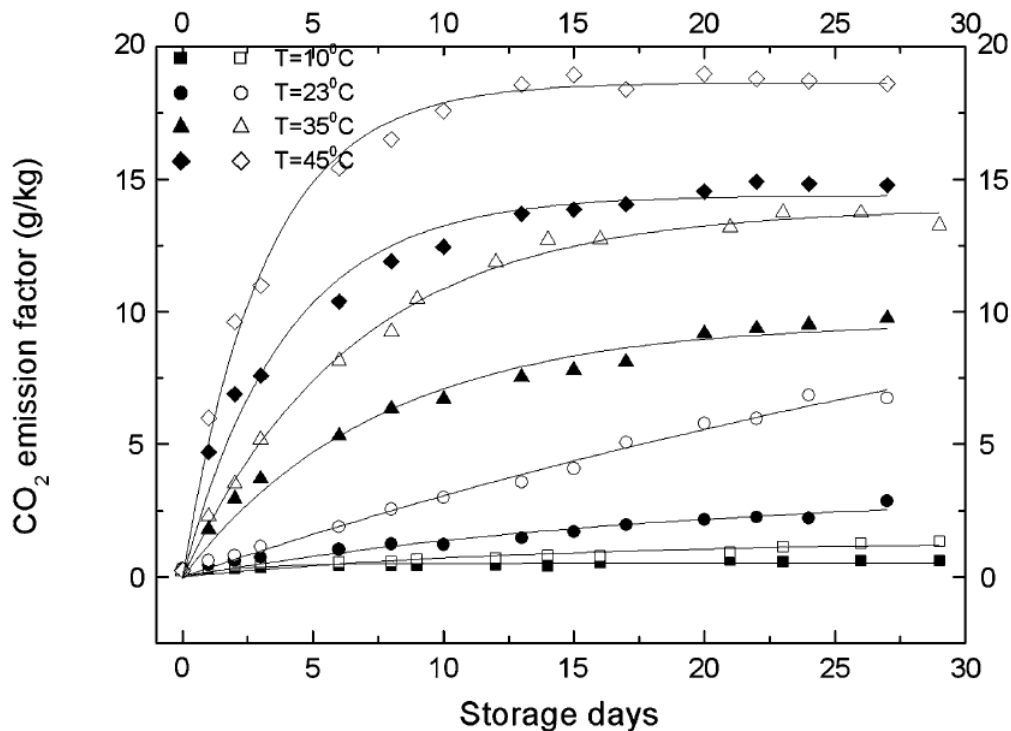


Figure 9: Emission factor of CO<sub>2</sub> over time at different temperatures and relative humidity (closed symbols: no water present; open symbols: water present at the bottom) [22]

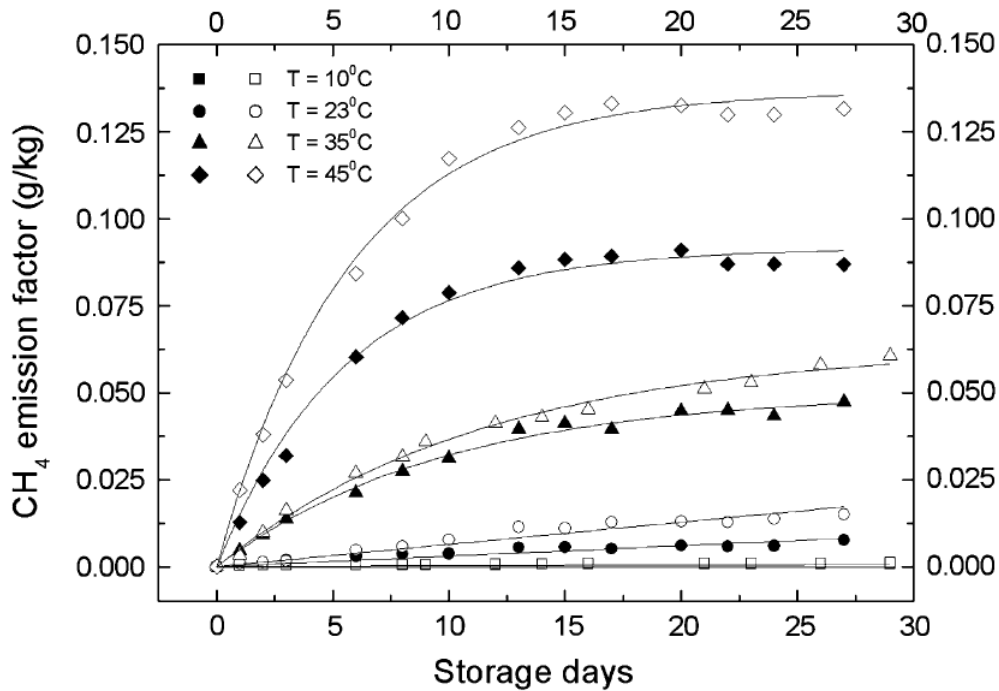


Figure 10: Emission factor of  $\text{CH}_4$  over time at different temperatures and relative humidity (closed symbols: no water present; open symbols: water present at the bottom) [22]

### 3.2.3.6 Wood species

Wood properties are effecting the off-gassing emissions. Kuang et. al. (2008) studied the emissions from five different materials: switchgrass, BC (British Columbia) wood pellets, fines of BC wood pellets, European wood pellets and European torrefied woodchips. The materials were stored over a time period of 27 to 56 days at 20 and 40°C. The concentrations of  $\text{CO}_2$ , CO and  $\text{CH}_4$  were measured. The amount of emissions from all materials mentioned above increased as the storage temperature increased. Moreover the pelletized material emitted more CO,  $\text{CO}_2$  and  $\text{CH}_4$ . [12]

Emhofer and Pointner [21] investigated the influence of used wood species on the emissions in their experiments. Their results clearly showed that the emissions are depending on the type of wood, that was used for the pellet production. [21]

## 4 Experiment for the auto-oxidation of fatty acids as a reason for emission from pellets

As already described in chapter 3.2.2.1, auto-oxidation of fatty acids may lead to emissions from pellets.

Svedberg et. al. (2008) described an experiment where they explored the hypothesis that oxidative degradation of fatty acids occurs and identified the gaseous emissions. The predominant unsaturated fatty acids in wood is linoleic acid. For their study they needed a large quantity of the fatty acid. Thus, Svedberg et. al. (2008) used for the experiments linseed oil. [5] This type of oil was used because its major constituents are triglyceride esters, including palmitic acid (6-7%), stearic acid (3-6%), oleic acid (14-24%), linolenic acid (48-60%) and linoleic acid (14-19%). [29] The linseed oil was stored in a sealed 1 l plastic bottle. The samples were taken from the headspace of the bottle with an airtight syringe and analyzed with fourier transform infrared spectroscopy (FTIR). As a result CO as well as VOC was found, which support the hypothesis that degradation of fatty acids occurs and may explain the formation of gaseous compounds identified in the atmosphere above wood pellets. [5]

Juita et. al. (2011, 2012) also investigated the compounds in the vapor space of linseed oil. As a result, the following VOC were identified: aldehydes, ketones, carboxylic acids, alcohols, and furans. They also reported that these compounds arise in oxidation of linolenic and linoleic chains. [30] They also identified CO as an oxidation product. [29]

Thus, an experiment was carried out, to proof the possibility if the emissions from wood pellets are a reasons of auto-oxidation of fatty acids.

### 4.1 Used equipment and material

The following equipment were used in these experiments:

- Laboratory glass bottles with a volume of 2l
- Measurement adapter
- Flame ionization detector (FID), specified in table 2

Table 2: Characteristics FID

Measured variable	Measuring principle	Measuring range	Measurement precision
VOC	FID	2 - 10 000 <i>ppm</i>	<4 % of reading

- Gasanalyzer Emerson NGA 2000, specified in table 3

Table 3: Characteristics NGA

Measured variable	Measuring principle	Measuring range	Measurement precision
CO	NDIR	0 - 5000 <i>ppm</i>	< 1% from

- Two test gases with a defined concentration of 850 *ppm* CO and 10%  $O_2$  from Linde Gas
- Filling material: polyethylene low density (PE LD) tube

The following raw material was used:

- 5g Linoleic acid, purity > 99% (CAS: 60 - 33 -3) from Sigma Aldrich

## 4.2 Test procedure

In this chapter the preparations for the measurement as well as the emission measurement itself will be described.

### Measurement preparation

The PE-LD tube was cut into pieces with a length of approximately 2,5cm (see figure 11). This pieces were used as filling material, which should provide a larger reaction surface for the fatty acid.



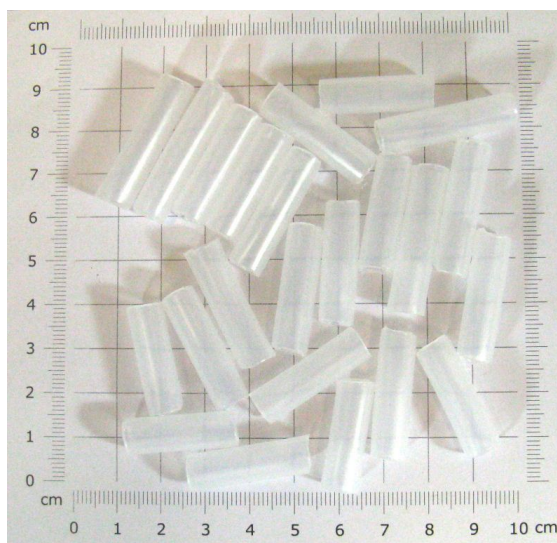


Figure 11: Filling material

Part of the filling material was filled in a glass bottle and the linoleic acid was sprayed onto it. Then the bottle was shaken to distribute the linoleic acid on the filling material. Afterwards some more filling material was given into the bottle and the procedure with the linoleic acid was repeated a second time. Reference measurements were performed with another bottle which contained the filling material only. The bottles were air tight closed and stored at a constant temperature of 21,5 °C for four days.

Before the emission measurement was started, the measurement data were proofed with two test gases, which had a defined concentration of 850 *ppm* CO respectively 10 %  $O_2$ . This procedure was done because instead of the measurement pump of the NGA the pump of the FID was used. This caused that the pressure in the measuring cell of the NGA was not that high than during the calibration, at which the pressure is usually 1 *bar*.

### **Emission measurement**

For the emission measurement the bottle was opened and connected via a special designed measuring adapter and a silicon tube with the gas analyzer (NGA), which enables the measuring of CO in a range of *ppm*. The gas sample was fed from the NGA to the FID to analyze the total amount of volatile organic compounds.

The exchange of the screw cap of the bottle and the measuring adapter must be quickly performed to insure that the gas exchange of the atmosphere in the bottle with the environment is as small as possible.

The measuring adapter was designed in that way that fresh air was fed at the bottom

into the bottle and the assay was taken at the top. This principle is shown in figure 13. Figure 12 shows the measuring adapter.

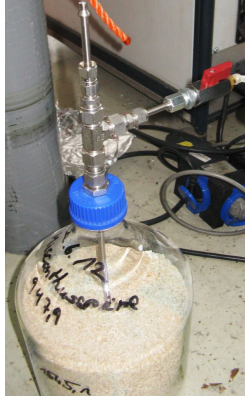


Figure 12: Used measuring adapter

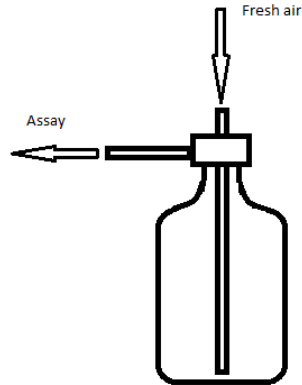


Figure 13: Principle of measurement with the measuring adapter

The resolution of the data logging was one value per second. The measuring data was stored in a "csv"-file and further processed with "Excel".

## 5 Pretest

In this chapter storage experiments will be described. During storage tests the emissions of carbon monoxide and the total volatile organic compounds from different raw materials were measured.

For these observations several materials were used: miscanthus spans, miscanthus pellets, ash shavings, larch shavings and spruce shavings.

Moreover, this experimental work was carried out to evaluate an already existing laboratory setup and to evaluate the improvement opportunities for the design of the new laboratory reactor.

### 5.1 Used equipment

For the storage experiments with glass bottles the following equipment were used:

- Laboratory glass bottles with a volume of 5l respectively 2l

- Measurement adapter
- FID
- Gasanalyzer Emerson, NGA 2000
- Test gases with a defined concentration of 850 *ppm* CO respectively 10% O<sub>2</sub>

The properties of the used measurement devices were already described in chapter 4.1.

## 5.2 Raw material

For the experiments, several types of pellets and shavings were chosen. The following table (see table 4) shows the types of raw material used, the amount of bottles which were used, the used mass as well as the starting date of storage:

Table 4: Used raw materials in storage tests

Material	Bottle Volume [l]	Amount of bottles	Experiment number	Mass [kg]
Miscanthus shavings	5	3	1	0,9882
			2	0,9949
			3	0,9479
Ash tree shavings	5	3	4	0,8950
			5	0,9009
			6	0,9257
Miscanthus pellets	5	2	7	2,0995
			8	2,0973
	2	1	9	0,8316
Larch shavings	5	3	10	0,8004
			11	0,7861
			12	0,8149

Spruce shavings	5	3	13	0,2796
			14	0,3314
			15	0,3130

### 5.3 Test procedure

The raw materials were filled into laboratory glass bottles. The bottles were air tight closed and stored in an air-conditioned room at 21,5 °C for four weeks.

At the beginning of the experiment the moisture content was analyzed. According to the standard ÖNORM EN 14 774 - 2 [31], 100g of each material were dried in a laboratory drying oven at 105 ±2 °C till constant weight.

The density of the raw materials, which is needed for the calculation for the emission rates from the different raw materials, was taken from literature (see table 5). It has to be noticed, that the bulk density varies depending on the moisture content as described in El Bassam and Huisman [32]. Thus, the values taken from the literature are only approximate values. To use more exact bulk densities for the calculation, which will be described in chapter 5.4, the densities had to be determined through experiments.

Table 5: Water content and density of used material

Material	Moisture content [%] <sup>1</sup>	Bulk density [ $\frac{kg}{m^3}$ ]
Miscanthus shavings	9,71	300 <sup>2</sup>
Ash tree shavings	12,53	700 <sup>3</sup>
Miscanthus pellets	5,84	1266 <sup>4</sup>
Larch shavings	13,80	600 <sup>3</sup>
Spruce shavings	8,62	460 <sup>3</sup>

<sup>1</sup>The moisture content was measured when the bottles were filled and after the experimental time of four weeks. For the calculation the averaged value was used.

<sup>2</sup>Bulk density used from: The bulk density varies depending on the moisture content of the material. Thus the bulk density ranges from 300 to 500  $\frac{kg}{m^3}$ . The moisture content depends on the harvest date. The moisture content of the green plant, cropped in September is 50 - 60%. During winter the moisture content decreases and reaches levels of 25 - 40% in early spring. [32] The used miscanthus shavings have a very low moisture content of about 11,69% at the beginning of the experiment

<sup>3</sup>Bulk density used from: [33]

<sup>4</sup>Bulk density used from: Experiments which were carried out at Bioenergy2020+

After a storage time of three days the first measurement took place.

The procedure was the same as already described in chapter 4.2

The duration of an measurement was approximately *15min*.

When the measurement was finished the bottle was purged with compressed air and air tight closed and stored for another three days. Then the measurement was repeated. The measurements took place over a period of four weeks.

After this time the moisture content was analyzed once more according to the ÖNORM EN 14 774 - 2 as described before. This was done because the purges of the bottles with compressed air caused a decrease of the water content of the used material. For the calculation the averaged moisture content was used.

## 5.4 Processing of data

Every measurement took place for about *15 min*, as described before. From the obtained measurement data a three minutes interval was chosen.

An example shows figure 14. This graph was received during the first measurement of experiment number 1. The measurement data from the interval which is marked in figure 14 were averaged and corrected. The correction was necessary because in the experiment the pump of the FID was used instead of the pump from the NGA gas analyzer. This causes a lower pressure in the measuring cell of the NGA than necessary as already described in chapter 4.2. The correction factor was determined through the measuring of the test gas with a defined concentration of *850 ppmCO*. The measured value was lower than *850 ppm*. Thus, the correction factor was defined as: "defined concentration of the test gas/ measurement value of test gas". The averaged and corrected value was further used to determine the amount of CO per kilogram dry fuel per day.

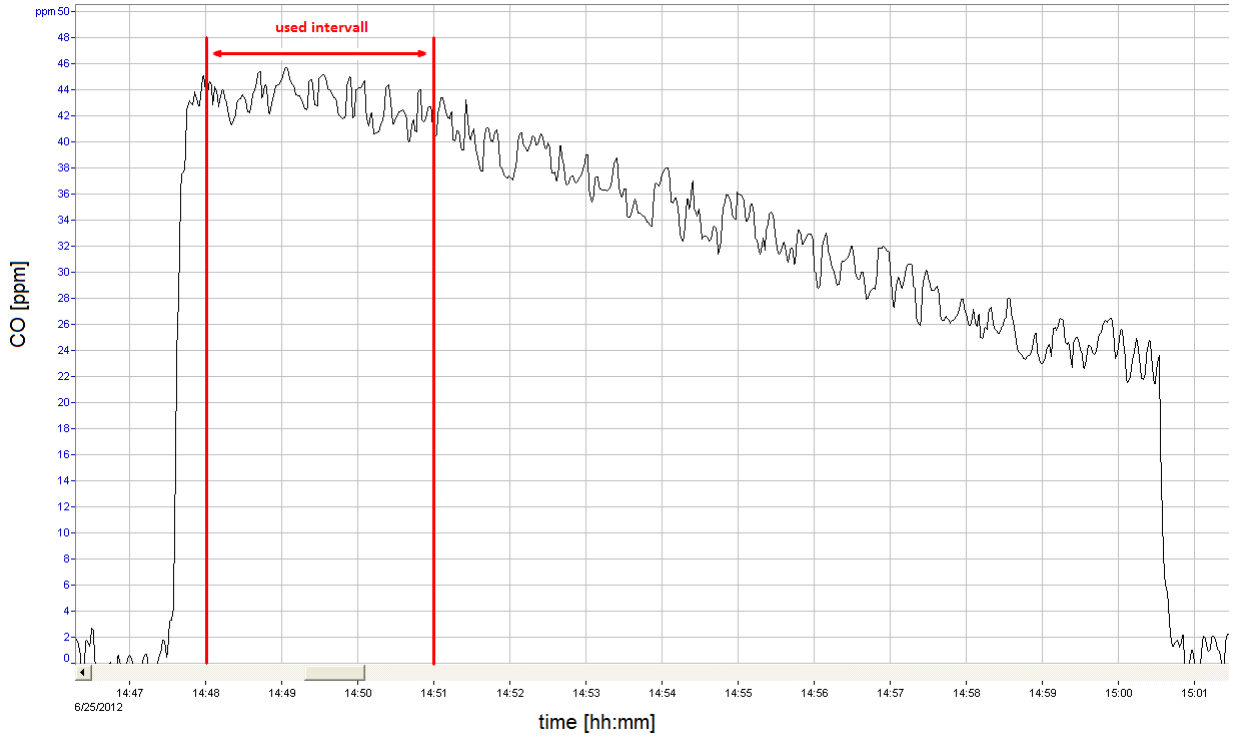


Figure 14: Run of CO during experiment number 1

An example of the calculation for CO is given below.

First of all, the pellet respectively the shaving volume in the laboratory bottle was calculated. Therefore, the bulk density from table 5 was used.

$$V_{Pellet/Shaving} = \frac{m_{Pellet/Shaving}[kg]}{\rho_{Bulk} \left[ \frac{kg}{m^3} \right]} = \frac{0,9885[kg]}{300 \left[ \frac{kg}{m^3} \right]} = 0,00329[m^3] \quad (1)$$

Next the volume of air within the bottle is received through calculation 2:

$$V_{Air} = V_{Bottle} - V_{Pellet/Shaving} = 0,005[m^3] - 0,00329[m^3] = 0,00171[m^3] \quad (2)$$

With  $V_{Air}$  and the average concentration value of CO the volume of CO in the bottle was calculated. In this example the average concentration value of CO is 48 ppm.

$$\begin{aligned}
V_{CO} &= C[ppm] \cdot V_{Air}[m^3] = 48[ppm] \cdot 0,00171[m^3] = \\
&= 48,37[ppm] \cdot 10^{-6} \cdot (0,00171 \cdot 10^6)[ml] = 0,08271[ml]
\end{aligned} \tag{3}$$

With the volume of CO the amount of gas in the bottle in  $mg$  was reckoned with the ideal gas volume ( $V_{idealGas} = 22,414 \frac{l}{mol}$ ) and the molar mass of CO ( $M_{CO} = 28 \frac{g}{mol}$ ):

$$\begin{aligned}
m_{CO} &= \frac{V_{CO}[ml]}{V_{idealGas} \left[ \frac{l}{mol} \right]} \cdot M_{CO} \left[ \frac{g}{mol} \right] = \frac{0,08271[ml]}{(22,414 * 10^3) \left[ \frac{ml}{mol} \right]} \cdot (28 \cdot 10^3) \left[ \frac{mg}{mol} \right] = \\
&= 0,10333[mg]
\end{aligned} \tag{4}$$

Then the mass of CO was divided by the storage time and by the used amount of fuel:

$$\frac{m_{CO}[mg]}{t[d] \cdot m_{Pellet/Shaving}[kg]} = \frac{0,10333[mg]}{3,23[d] \cdot 0,9882[kg]} = 0,0324 \frac{[mg]CO}{[kg]fuel \cdot [d]} \tag{5}$$

Finally, the water content was eliminated:

$$\begin{aligned}
0,0324 \frac{[mg]CO}{[kg]fuel \cdot [d]} \cdot \frac{100}{100 - WC[\%]} &= 0,0324 \frac{[mg]CO}{[kg]fuel \cdot [d]} \cdot \frac{100}{100 - 9,71[\%]} = \\
&= 0,0359 \frac{[mg]CO}{[kg]fuel_{odw} \cdot [d]}
\end{aligned} \tag{6}$$

The calculation for VOC per kilogram dry fuel per day was done in the same way. In this case the molar mass from propane was used.

## 5.5 Discussion of storage test setup

During the storage experiments with the laboratory glass bottles some disadvantages of the used laboratory setup were noticed:

- With the already known experimental setup it was necessary to open the bottle to fix the measuring adapter to start the measurement. This exchange should be done as quickly as possible as already described in chapter 5.3. However, there might be an influence on the result because of the mixing of the gas in the bottles with air. The new setup must allow the measurement of the emissions without the need of opening the storage vessel.
- It is not possible to heat or to cool the laboratory glass bottles. Thus, the new experimental design must allow to heat respectively to cool the reactor.
- It was not possible to measure the temperatures in the bottles. Therefore, the experimental setup must enable the measurement of the temperatures in the middle of the pellets bed as well as near the reactor wall to check if there is a change in the bed temperature. Moreover, the temperature measurement is necessary because the new laboratory reactor should provide the possibility of cooling and heating, as mentioned before. The measurement data must be saved via a data logging system.
- Also the pressure in the bottles could not be measured. In an improved measurement design, also the pressure measurement values must be saved with the help of a data logging system. With this data it will be possible to recognize if the off-gassing reactions have an influence on the pressure in the vessel.
- The gas analysis must be improved. In the old setup the infrared gas analyzer as well as the FID usually need volume flow rates of about  $25 \frac{l}{h}$  respectively  $1 \frac{l}{min}$ . Because of the relatively small gas volume in the bottles and the need that the new reactor should have similar size the new measurement equipment should work with a small probe volume flow rate.

## 6 Laboratory reactor

To obtain more reliable and reproduceable measurement data from storage tests a new laboratory reactor was designed. The construction is based on the literature research (chapter 3) and the pretests (chapter 5). In the following several requirements were defined. Moreover the size of the reactor as well as the chosen measurement technology is described.



## 6.1 Requirements

For the reactor design the following requirements were defined:

- Two work modes: The reactor must work as a closed system or as flow reactor. This two work modes are required to investigate the influence of availability of oxygen during the storage time. As already described in chapter 3.2.3.4 the oxygen concentration in storages have an influence on the concentration of the emissions. If the reactor works as a closed system, there is a defined amount of oxygen in the reactor available. The oxygen concentration will decrease during the time of storage. The second mode, flow reactor, ensures that the oxygen level is constant during the experiment.
- Temperature in the reactor: It must be possible to heat, to cool and to keep the reactor at a constant temperature. These requirements are of interest because the storage temperature has also an effect on the amount of emissions. As described in chapter 3.2.3.3 the higher the temperature the higher the emissions. Therefore, it is of interest to heat the reactor. The possibility to cool the reactor allows to investigate if the emissions getting less at lower temperatures.
- Temperature measurement: The temperature must be measurable in the mid of the packed bed as well as near the reactor jacket. Furthermore, the temperatures at the bottom and at the top of the pellets bed are of interest. These measurement points are needed to monitor the bed temperature if the reactor is heated, cooled or insulated.
- Material: As material for the reactor stainless steel was chosen. This material does not effect side reactions. Moreover the reactor can easily be heated and cooled.
- Amount of pellets: The reactor design must allow to use a variable amount of pellets. Therefore, it is possible to vary the height of the sparger plate on which the pellets are stored (see figure 15). So the used mass of wood pellets can be freely chosen and it is possible to proof if there is an influence on the emissions if more material is used or not.

Furthermore, the emissions of pellets during storage are also depending on the type of raw material (see chapter 3.2.3.6). Beside the emissions of industrial produced pellets, which are commonly used in domestic heating systems, also emission from pellets produced out of alternative raw materials like for example miscanthus or

wheat straw can be investigated. Non industrial pellets are often available only in small amounts.

Thus the ability of variation of the used amount of pellets is a necessary requirement.

- Atmosphere in the reactor: The atmosphere in the reactor must be adjustable. If the reactor is working as a flow reactor the gas which is normally passing through the reactor is technical air but can easily varied as well. In the closed system the atmosphere can vary. As gases technical air, nitrogen and oxygen or a desired mixture ratio of nitrogen and oxygen will be used. The variation of the atmosphere allows to investigate the influences on for example oxygen concentration on the amount of emission or if there are less emissions if the atmosphere in the reactor is 100% nitrogen.
- Size of reactor: For the provision of the reactor volume the following arguments are decisive:
  - From former investigations the emission rates are approximately known ( see [21]). Thus the reactor volume was chosen in a similar size due to the former laboratory settings.
  - It must be possible to measure also the emission of small amounts and different kinds of pellets. Former experiments showed that the emission rate depends on the type of raw material used for the pelletizing process. (see chapter 3.2.3.6) Moreover also non industrial pellets should be investigated, which are often not available in large amounts.
- Humidity: The humidity of the atmosphere in the reactor must be adjustable. If the humidity of the atmosphere changes also the moisture content of the stored pellets will change. This setting option helps to investigate if a change of the moisture content of pellets influences the emissions during storage as described in chapter 3.2.3.5
- Emission measurement: The following emissions have to be measurable:
  - CO in a range of: 0 - 10 000*ppm*
  - CO<sub>2</sub> in a range of: 0- 5%
  - O<sub>2</sub> in a range of: 10 -30 %
  - Total amount of VOC in a range of: 0 - 5000*ppm*

For the emission measurement a gas chromatograph (GC) will be used.

- Pressure and humidity measurement: Pressure and humidity should be measurable at the top of the reactor. The humidity content must be measurable because the influence of moisture content of pellets on the emissions will be examined. The measurement of pressure in the reactor is of interest because it is not well known if there is an underpressure in the system as a result of the reactions which lead to the emissions.
- Data logging system: Temperatures, humidity and pressure measurement data must be logged for further processing. Data from GC will also be logged due to the GC data handling program.

In the following figure (see figure 15) a scheme of the laboratory reactor is shown. There the measurement points for the temperatures, humidity and pressure are marked. Also the connection to the gas chromatography as well as the inlet and outlet of the reactor are depicted.



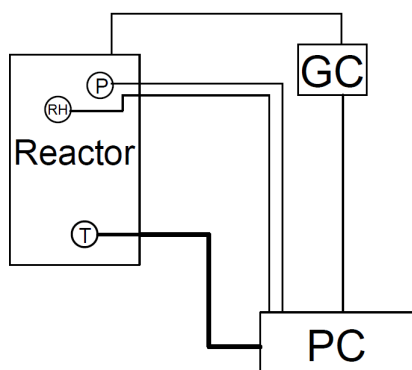


Figure 16: Schematic of data handling system

The chosen measurement technologies will be characterized shortly.

### 6.2.1 Gas analysis

For analyzing the emissions from pellets during the storage a gas chromatograph was chosen. A gas chromatograph needs only small sample volumes. This is important to keep the reactor size in a laboratory range. Moreover the measurement precision is high.

Characteristics of the chosen gas chromatograph:

- Carrier gas: Helium
- Detectors: FID, TCD

In the following an overview of gas chromatography system will be given. Furthermore, the properties of the chosen equipment will be described in more detail.

#### Functionality of a gas chromatograph

Gas chromatography is a separation process, which basic operating principle involves volatilization of the sample in a heated inlet or injector, followed by separation of the mixture in a special column. [34]

In the following figure (see figure 17) a schematic of a typical GC is shown. Main components are the carrier gas supply, regulation for pressure and flow, heated injection system, the separation column with the oven, the detection system as well as the evaluation unit. [35]

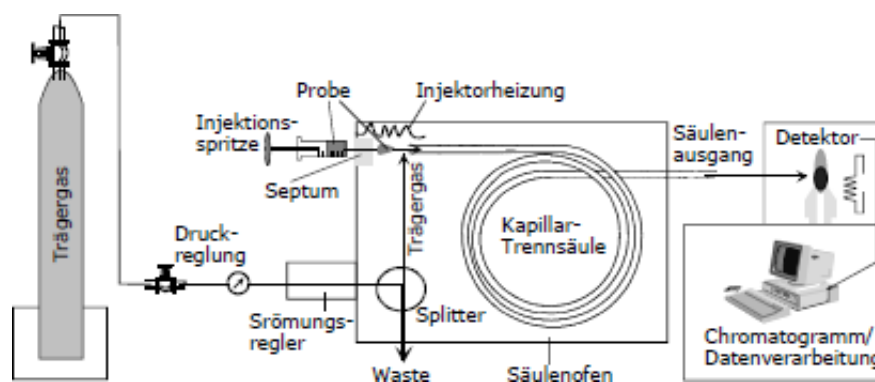


Figure 17: Schematic of GC system (Trägergas = carrier gas, Druckregelung = pressure regulation, Strömungsregler = current controller, Injektions-spritze = syringe, Probe = sample, Injektorheizung = injector heating, Säulenofen = column oven, Kapillartrennsäule = column, Säulenausgang, exit of column, Detektor = detector, Datenverarbeitung = data processing) [35]

### Carrier gas

As carrier gases (the mobile phase) argon, helium, nitrogen, carbon dioxide or hydrogen are used. To remove traces of water a molecular sieve is used. For repeatable measurements it is important that the flow of the carrier gas is constant. The measurement of the flow rate can be arranged at the beginning of the column with a rotameter or at the end of the column via a bubble meter. [35] The carrier gas must be inert and of a very high purity. [34]

### Injection systems

For GC sample introduction process various types of inlets can be used. The injection system depends on the sample, which can be liquid or gaseous. The emissions from pellets during storage are gaseous, therefore, only the inlets for gaseous samples will be described briefly.

The gas can be introduced by injecting the sample through a gas-tight syringe into the injector. The gas sample could also be introduced into the carrier gas stream through a gas sampling valve. Or the gas sample may be adsorbed into a trapping material and then released by heating the trapping material and transferred into the gas chromatograph. [34]

- Gas-tight syringes

The sample size ranges from  $100\mu\text{l}$  to  $2\text{ml}$ .

- Gas sampling valves

Gas sampling valves are installed on the top of the GC, usually in their own separately controlled heating oven.

## Column

The separation occurs within a heated hollow tube (the column) that contains a stationary phase. The components of the injected sample are carried onto the column by the carrier gas. The stationary phase retards the components selectively. [34] The columns are made out of stainless steel or glass. The inner surface of the column is coated with the stationary phase. [35]

There are three different types of columns:

- Wall-coated open-tubular column (WCOT): The inner surface of the columns is coated with liquid polymer as a stationary phase. (see figure 18/a)
- Porous-layer open-tubular column (PLOT): In this columns the stationary phase is a solid polymer. (see figure 18/b)
- Support-coated open-tubular column (SCOT): The stationary phase are particles that are coated with a liquid phase. (see figure 18/c) [34]

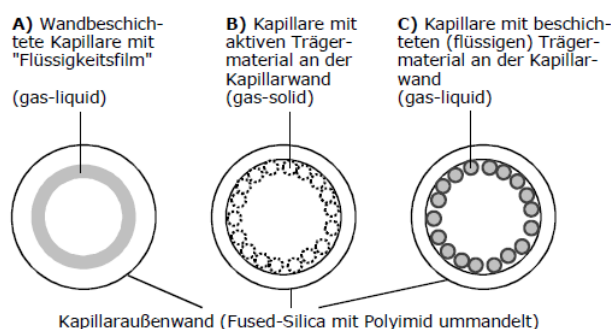


Figure 18: Types of columns [35]

As a stationary phase polar and nonpolar polymers could be used. The stationary phase is chosen due to the following principle: "like dissolves like". This means that polar phases are selective for polar compounds like organic acids, alcohols, and amines. Nonpolar stationary phases are used for example for the separation of halogenated and saturated hydrocarbons. [35]

In figure 19 the structure (Struktur) of some stationary phases which are typically used, their name (Name) and polarity (Polarität: unpolar = nonpolar, polar = polar), and the temperature range (Temperaturbereich) are specified.

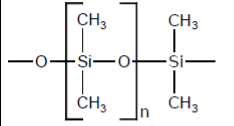
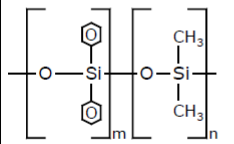
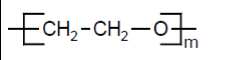
Struktur	Name/ Polarität	Temperaturbereich
	Polydimethylsiloxan unpolar	60–320°C
	Poly-diphenyldimethylsiloxan unpolar bis mittelpolar	60–320°C
	Polyethylen-glycol (PEG) polar	40–250°C

Figure 19: Types of stationary phases [35]

## Detectors

Today several detectors are available, which are described briefly.

- Thermal conductivity detector (TCD)

A TCD is a universal detector and can detect all compounds that can pass the GC column. This detector is commonly used for permanent gases. In figure 20 a typical TCD is shown. It consists of a cell with two channels. The eluate from the column flows through one channel (MZ). The other channel is connected to pure carrier gas as a reference (VZ). [34]

As carrier gases mainly helium or hydrogen are used because their electrical conductivity is approximately 5 to 10 times higher in comparison with other carrier gases. [35] Within the cell there is a Wheatstone bridge circuit (see figure 21), which contains 4 resistors or filaments.



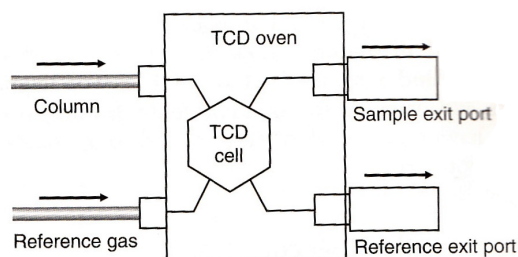


Figure 20: Cross section of a thermal conductivity detector [34]

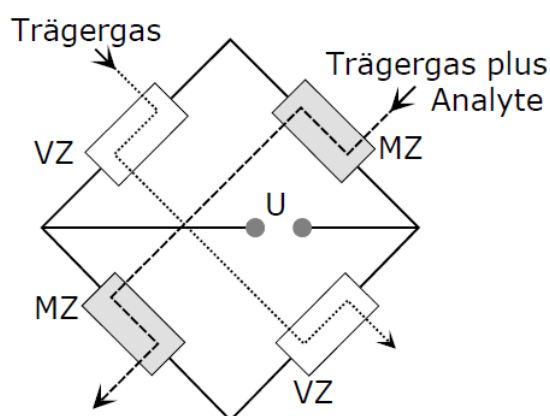


Figure 21: Wheatstone bridge circuit (Trärgas = carrier gas, Trärgas plus Analyte = carrier gas plus analyte [35])

Gas from the column passes through two filaments, the carrier gas through the others. If in all sections would be carrier gas the resistance of each filament is the same thus there is no signal. If the gas from the column is different to the carrier gas the resistance of the filaments, through which passed the sample, will change and a signal will be produced. [34]

- Flame ionization detector (FID)

It is the most commonly used GC detector. The advantages of the FID are a low detection limit, robustness and a wide range of linearity. [35] This detector responds to compounds with a carbon-hydrogen bond. For the detection the FID requires hydrogen and air support gases with a typical air:hydrogen ratio of 10:1. These gases are mixed and burned above a flame jet. [34]

If only hydrogen is burned only radicals and no ions are formed. This results in a very low basic ionization current of about  $3pA$ . [35] If there are also analytes

burned ions are produced. The electrons which are formed in the flame causes a current flow in the gap between the jet tip (anode) and the electrode (cathode), which is amplified and used as signal. [34]

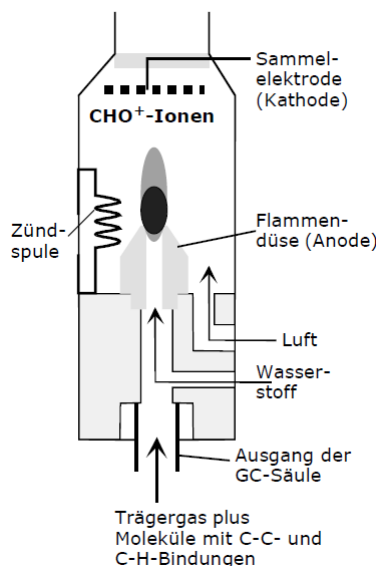


Figure 22: Flame ionization detector [35] (Zündspule = ignition coil, Sammelelektrode (Kathode) = collector electrode (cathode), Flammendüse (Anode) = flame jet (anode), Luft = air, Wasserstoff = hydrogen, Ausgang der GC - Säule = exit of the GC column, Trägergas plus Moleküle mit C-C- und C-H-Bindungen = carrier gas with C-C- and C-H-bonds

- Nitrogen-phosphorus detector (NPD)

The detector responds to compounds in a sample that contains nitrogen and/or phosphorus. As support gases air and hydrogen are required. These gases surround the heated rubidium sulfate bed. The current in the plasma of vaporized rubidium ions increases if nitrogen and phosphorus compounds are present. The reaction with phosphorus compounds is slower than with nitrogen compounds. [34]

- Flame photometric detector (FPD)

This detector is primarily used for detection of volatile organic and inorganic molecules containing sulfur and phosphorus. The analyte is burned in a hydrogen/air flame and chemiluminescent products are formed. With optical filters to select wavelengths specific to the element of interest and a photomultiplier tube the compounds containing sulfur and phosphorus can be selectively detected. [34]

- Electron capture detector (ECD)

This detector is used for halogenated compounds as well as for many other molecules such as  $N_2O$ , nitro-organics, diketones, and diacetal. The ECD contains a radioactive foil, which is used to ionize nitrogen or argon/methane carrier gas. The electrons from the ionization migrate to the anode and produce a current. If the GC eluate contains a compound that can capture electrons, the current is reduced. [34]

The TCD and the FID are suggested as detectors. The TCD is the only detector which can detect the permanent gases. The FID is the best suitable detector for analyzing hydrocarbons.

### 6.2.2 Sensors

To obtain the required data, three types of sensors are required:

- Platinum thermometer

For the temperature measurement a platinum resistance thermometer, PT 100, is used. This sensor was chosen because it is very accurate and repeatable, extremely stable over the time (less than 0,1 °C per year drift), and its resistance linearity. [36]

The operating range of the PT 100 is from -75°C to +350°C. The uncertainty tolerance class is Class B according to the standard DIN EN 60751. [37] The tolerance formula for Class B is [38]:

$$\pm (0,3 + 0,005|t|)[^\circ\text{C}] \quad (7)$$

As measuring configuration a four-wire configuration was chosen. This configuration is used if the utmost in accuracy is required. [39]

Measurement principle:

Resistive temperature devices RTD, such as for example PT 100, consist of an electrical resistor that changes resistance with temperature. The used electrical resistors are materials with a positive temperature coefficient. Commonly used materials are for example nickel, tungsten and platinum. [36] The value of resistance for a PT100 is 100Ω at 0°C. With increasing temperature the resistant increases. [40] To achieve a 100Ω resistance it is necessary to wind a long, thin wire around a ceramic core. RTDs can be mounted in various material. Most commonly they are

mounted in a closed-end stainless steel tube. The tube is packed with vibration damping or heat transfer material such as ceramic powder. [36]

- Pressure transmitter

The operating range of the pressure transmitter is from 0 to 1,6 *bar*. As measurement device a piezo-resistive element is used. [41]

Measurement principle:

Piezo-resistive pressure sensors contain a sensing element made up of a silicon chip. This chip contains a circular silicon diaphragm and four piezoresistors. The resistors refer to the change in resistance caused by strain when pressure is applied to the diaphragm. Due to the amount of pressure applied to the diaphragm the resistor values change. The change in pressure is converted into a change in resistance. The four resistors are connected in a "Wheatstone Bridge". [42]

- Humidity

The selected sensor is a combination of a humidity sensor and a temperature sensor. The working range of humidity sensor is from 0 % to 100% relative humidity. Moreover the temperature is measured with a PT1000 (class A, DIN EN 60751) in range of -40 to +120 °C. For the humidity measurement the accuracy is  $\pm 1,3$  % relative humidity (RH), for the temperature  $\pm 0,2$  °C. [43]

Measurement principle:

With the chosen humidity sensor it is possible to measure the relative humidity (RH), which is described as the ratio of the moisture content of air compared to the saturated moisture level at the same temperature or pressure. [44]

For the laboratory setup, a capacitive sensor is used. This sensor type is operating accurately down to 0% RH. Furthermore, it has a low temperature effect. Thus this type is often used over wide temperature ranges without temperature compensation. In a capacitive RH sensor, change in dielectric constant is almost directly proportional to relative humidity. For 1% RH change, the typical change in capacitance is 0,2 - 0,5 *pF*. These sensors are able to fully recover from condensations. Moreover, they resist chemical vapors. [44]

### 6.2.3 Data logging system

To continuously monitor the temperature, the pressure and the humidity, a data logging system from Delfin is used. The used system provides 24 analog inputs, 6 analog outputs, 2 digital outputs and 28 bit digital input/outputs.

## 6.3 Gas-mixing-station

To enable a defined atmosphere in the reactor, a gas-mixing-station was designed. This facility provides the possibility to regulate the composition of the gas which is fed into the reactor. It is possible to use technical air for the reactor atmosphere or a variable mixture of  $N_2$  and  $O_2$ . Moreover, it is possible to vary the humidity of the used gas. Every mass flow controller (MFC) can be switched on and off with a magnetic valve.

A scheme of this facility is shown in the following figure:

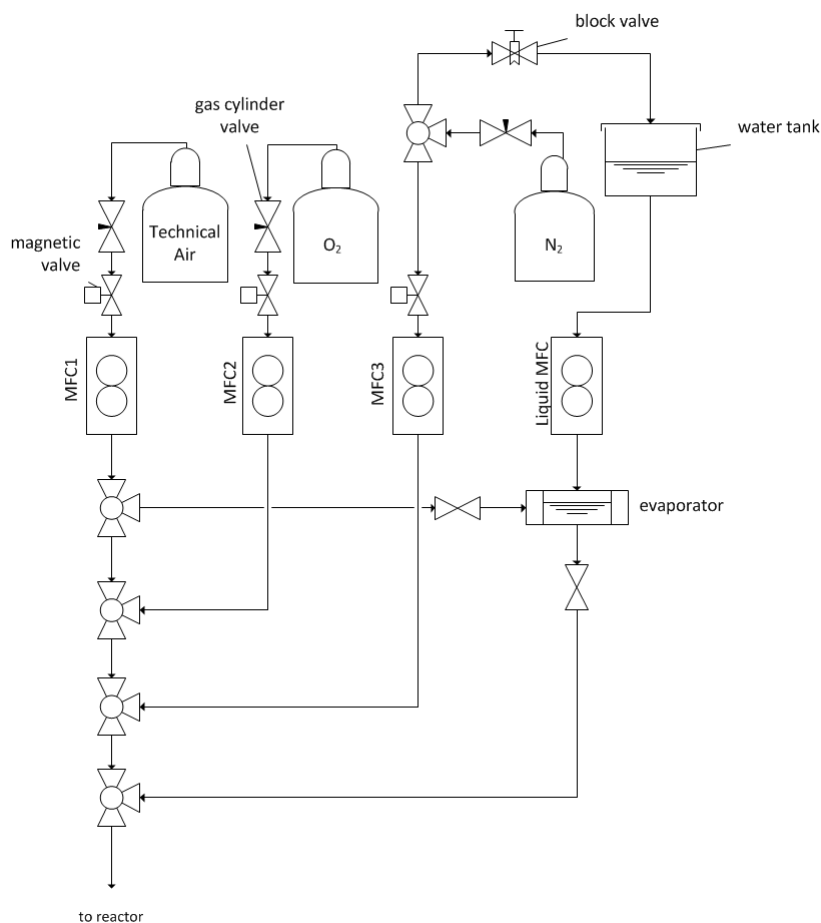


Figure 23: Scheme of the gas-mixing-station

## 7 Results and discussion

In this chapter the results of all experiments will be described and discussed.

### 7.1 Results and discussion of the experiment for auto-oxidation of fatty acids

The following figure shows the measurement data of the experiment with the linoleic acid, which is described in chapter 4. It can be seen (see figure 24) that already 5g of this unsaturated fatty acid leads to emissions of VOC and CO due to auto-oxidation. The maximum of CO was about 195ppm, the one of VOC was close to 900ppm.

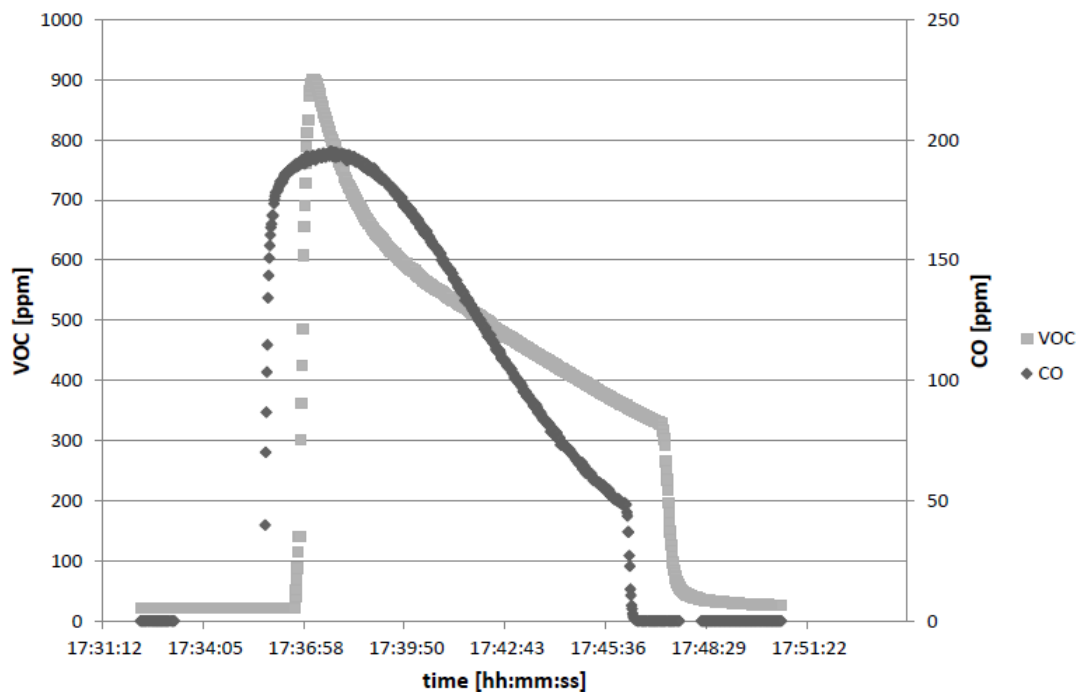


Figure 24: Run of CO and VOC of auto-oxidation of linoleic acid

This result shows that auto-oxidation is most likely the mechanism which leads to emissions from pellets.

It is still unknown if the emissions from fatty acids are decreasing during storage. This question could be answered by an experiment with four bottles. These bottles should be filled with filling material and the linoleic acid distributed in the glass bottles. After four days of storage the measurement of the emissions from the fatty acid should start. Every

day, one bottle should be measured. If the hypothesis that emission rates are decreasing is correct, the CO emission rate will be constant after a while.

Furthermore, it is recommended to perform the same experiments with other types of fatty acids contained in wood.

## 7.2 Results and discussion of pretests

In the following chapter the results of the experiments from the pretests (5) are described and discussed.

The diagrams were constructed in that way that the results of the raw materials which were analyzed during the same experimental time are plotted in one diagram. Additionally to that the results from all shavings which were used are depicted in one diagram. In each figure at the x-axis the time in days and at the y-axis the emissions (CO respectively VOC) in  $mg$  per  $kg_{odw}$  per day are plotted. The measurement procedure is described in chapter 5.3.

### 7.2.1 Comparison of shavings

In the following the results of the emission measurement of shavings are illustrated and discussed.

#### Miscanthus shavings - ash tree shavings

The experiment with miscanthus shavings and ash tree shavings showed a clear trend. During 30 days the amount of CO in  $[ppm/kg_{odw}/day]$  decreased (see figure 25). The CO emission rates from ash tree shavings are higher than the emission rates from miscanthus shavings. This shows that the emissions are depending on the the type of raw material as described in chapter 3.2.3.6.

Figure 26 depicts the VOC emission rates from miscanthus shavings and ash tree shavings over 30 days. The VOC emission rates decreased with time, which was described previously in chapter 3.2.3.2. Similar to the CO emission rates, the VOC emission rates from ash tree shavings were higher than the emission rates from miscanthus shavings. Furthermore, the diagram shows that the VOC emissions from ash tree shavings decreased more rapidly.

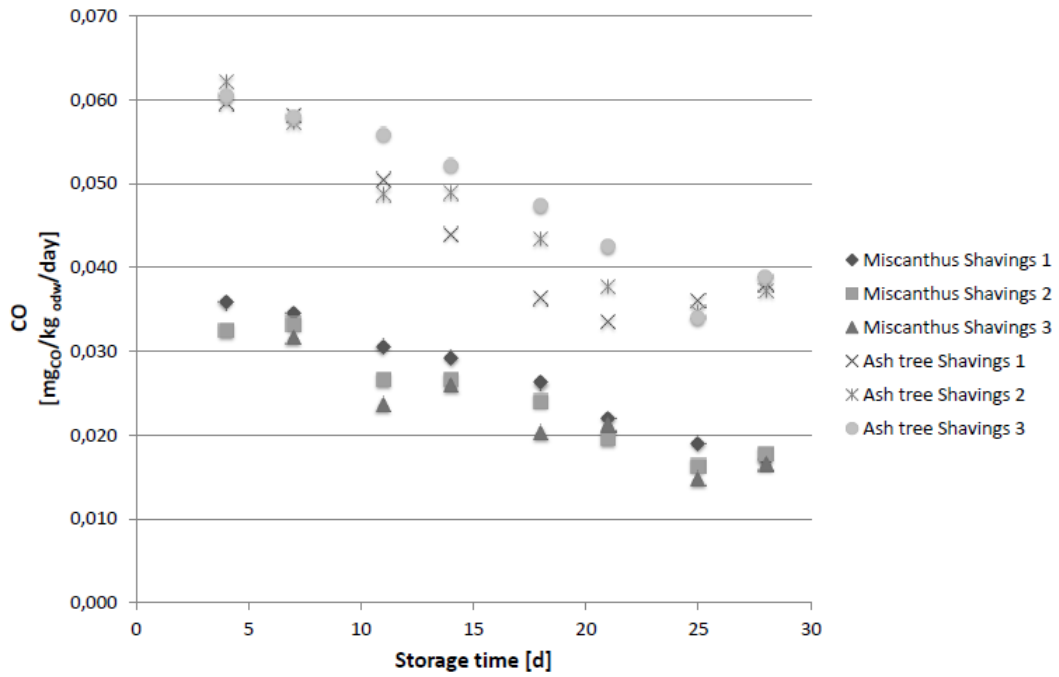


Figure 25: CO emission rates [ $mg_{CO}/kg_{owd}/day$ ] from miscanthus shavings and ash tree shavings over storage time

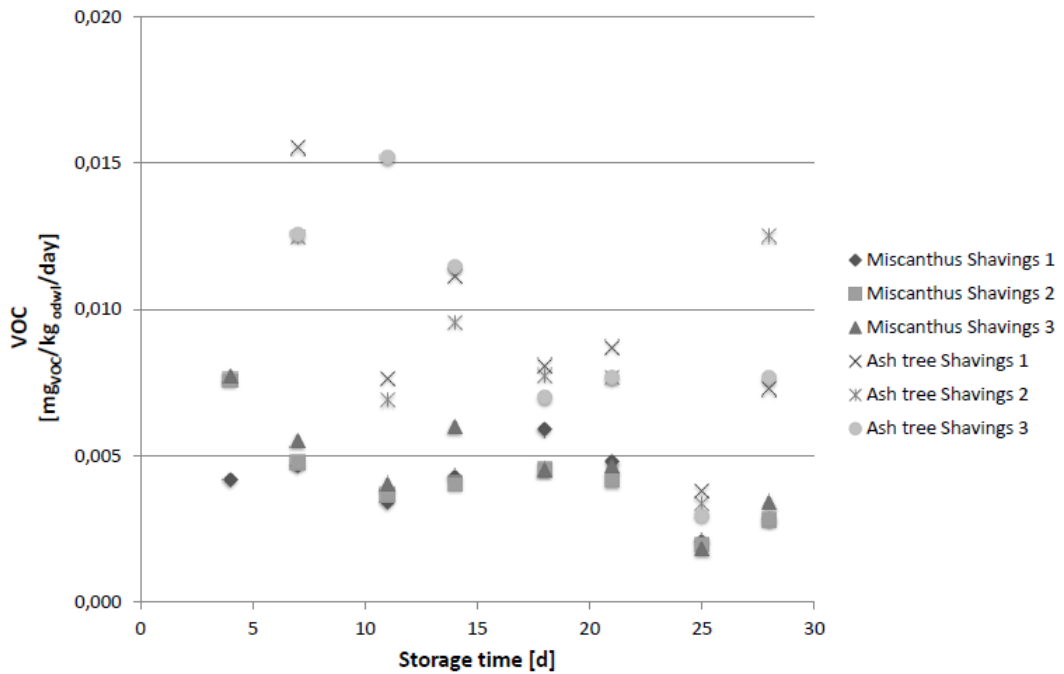


Figure 26: VOC emission rates [ $mg_{VOC}/kg_{owd}/day$ ] from miscanthus shavings and ash tree shavings over storage time



### Larch shavings - spruce shavings

Figure 27 shows the results from the experiments with larch shavings and spruce shavings. The CO emission rates from the spruce shavings were decreasing while the CO emission rates from the larch shaving were slightly increasing. This result is of interest because the experimental conditions, such as storage temperature and storage time, were the same for both kinds of shavings.

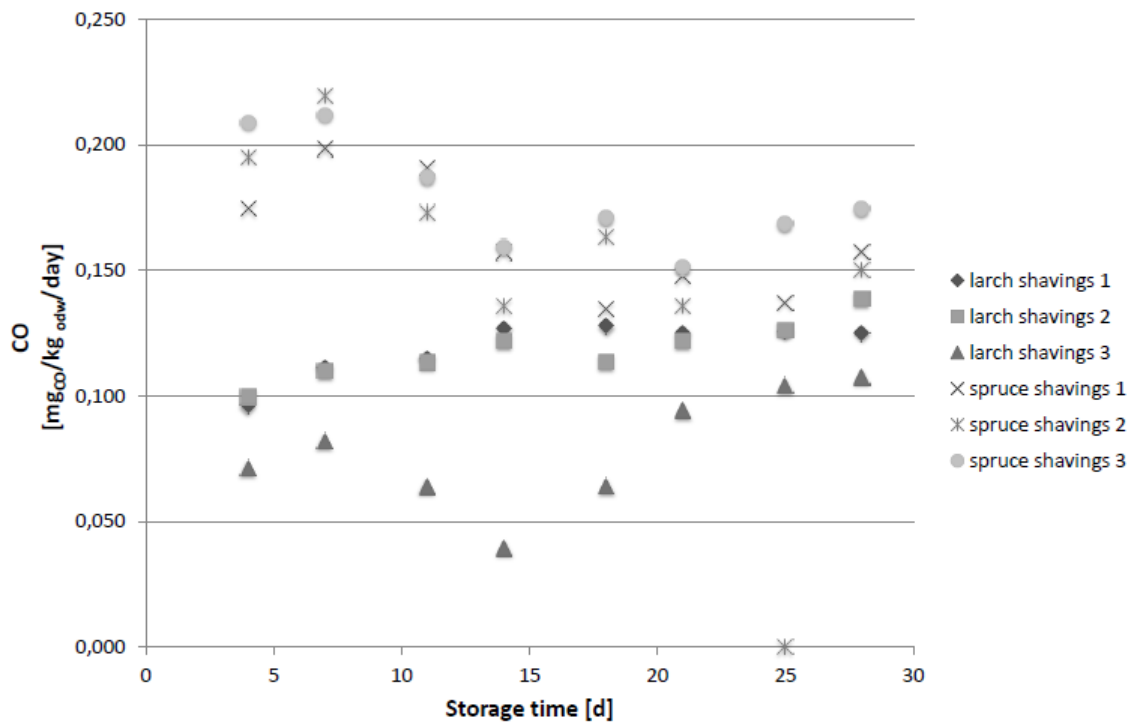


Figure 27: CO emission rates [ $mg_{CO}/kg_{owd}/day$ ] from larch shavings and spruce shavings over storage time

The VOC emission rates from larch shavings (see figure 28) decreased for approximately 14 days, of 30 days, but then increased contrary to expectations. However, it is interesting that the values for both kinds of shavings first decreased and then increased. The reason for that might be a change of the experimental conditions which have not been noticed. Thus, this experiment should be repeated with the new designed laboratory setup .

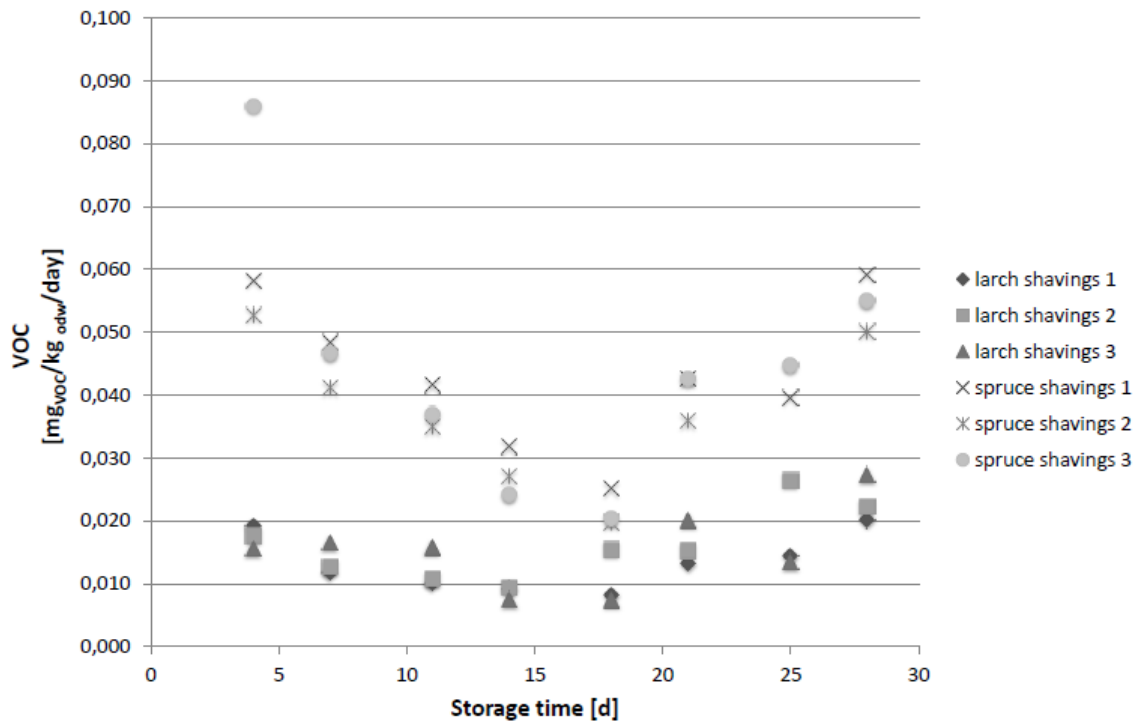


Figure 28: VOC emission rates [ $mg_{VOC}/kg_{owd}/day$ ] from larch shavings and spruce shavings over storage time

### Miscanthus -, ash tree -, larch - and spruce shavings

In figure 29 and 30, CO and VOC emission rates from all used materials are plotted.

CO as well as VOC emission rates in  $ppm/kg_{dryfuel}/day$  are different depending on the kind of raw material (see figure 29 and 30). The CO and VOC emission rates over the storage time are the highest for spruce shavings, followed by larch shavings and ash tree shavings. Miscanthus shavings show the lowest CO and VOC emission rates.

Especially the differences of emissions from miscanthus shavings compared to the emission from spruce shavings are of interest. If the mechanism for formation of the emission is auto-oxidation, as suggested in chapter 3.2.2.1, then the reason for the difference in the amount of emission rates result from different amount of fatty acids. The amount of fatty acids in spruce is about  $0,78wt\%$  (based on oven dry wight). [19] The fatty acid content of miscanthus (winter dry plant) is about  $0,03wt\%$  [45]. (The fatty acid content is stated in mass percent based on oven dry wight of the wood species)

However, there is no explanation for the increase of VOC emissions from spruce- and larch shavings after some time.

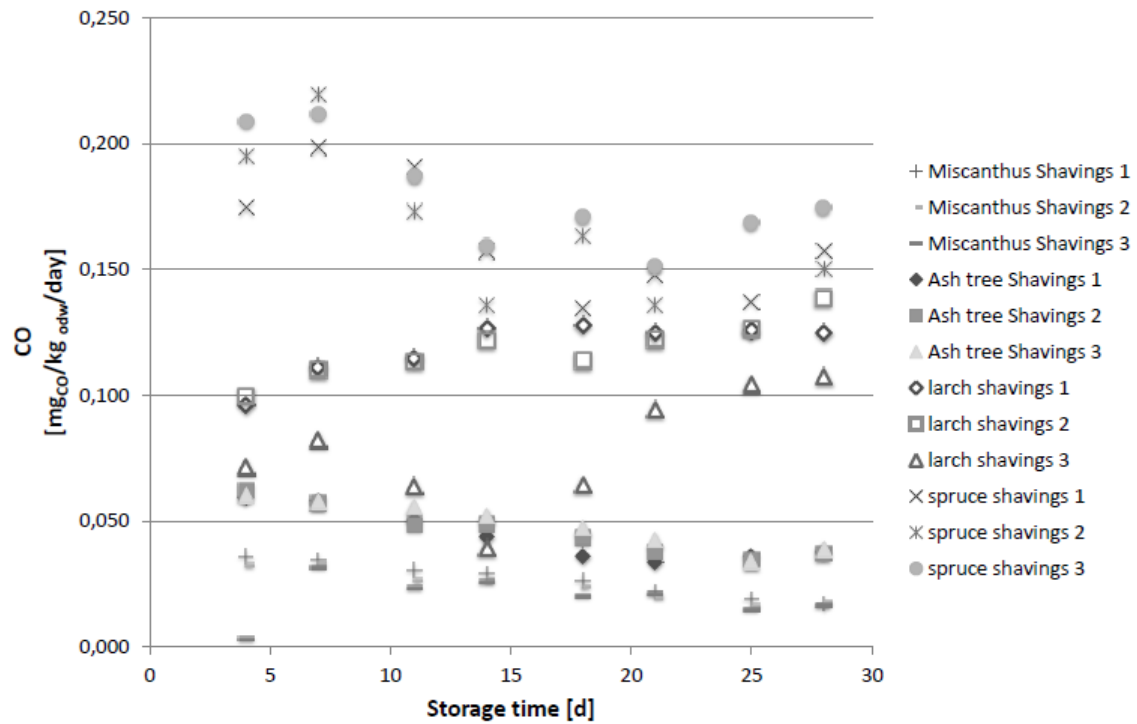


Figure 29: CO emission rates from miscanthus-, ash tree-, larch- and spruce shavings over storage time

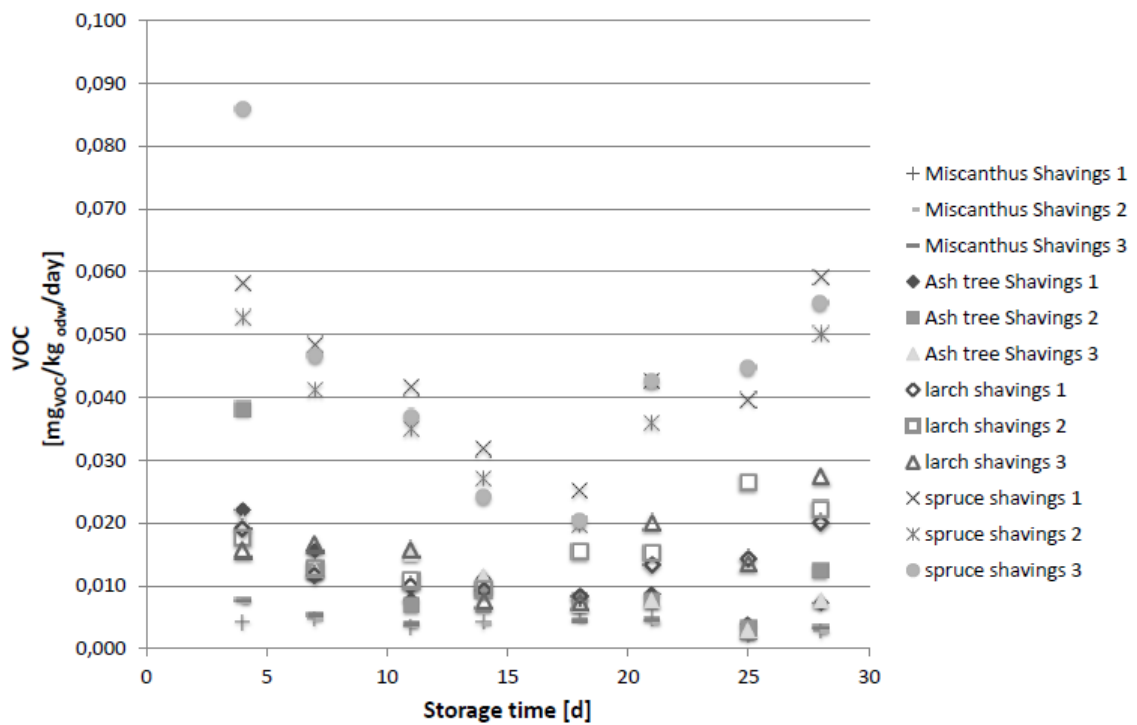


Figure 30: VOC emission rates from miscanthus-, ash tree-, larch- and spruce shavings over storage time

## 7.2.2 Comparison of shavings and pellets

Below the results from the experiment which miscanthus pellets and shaving will be discussed. Furthermore, they will be compared with former performed measurements.

### Miscanthus shavings - miscanthus pellets

In figure 31 the results from the emission measurements from miscanthus shavings and miscanthus pellets are shown. There is a decrease of CO emission rates from pellets as well from shavings as described in detail in chapter 3.2.3.2. The trend in figure 31 is similar to that in figure 25.

The CO emission rates from miscanthus shavings are lower compared to those from miscanthus pellets.

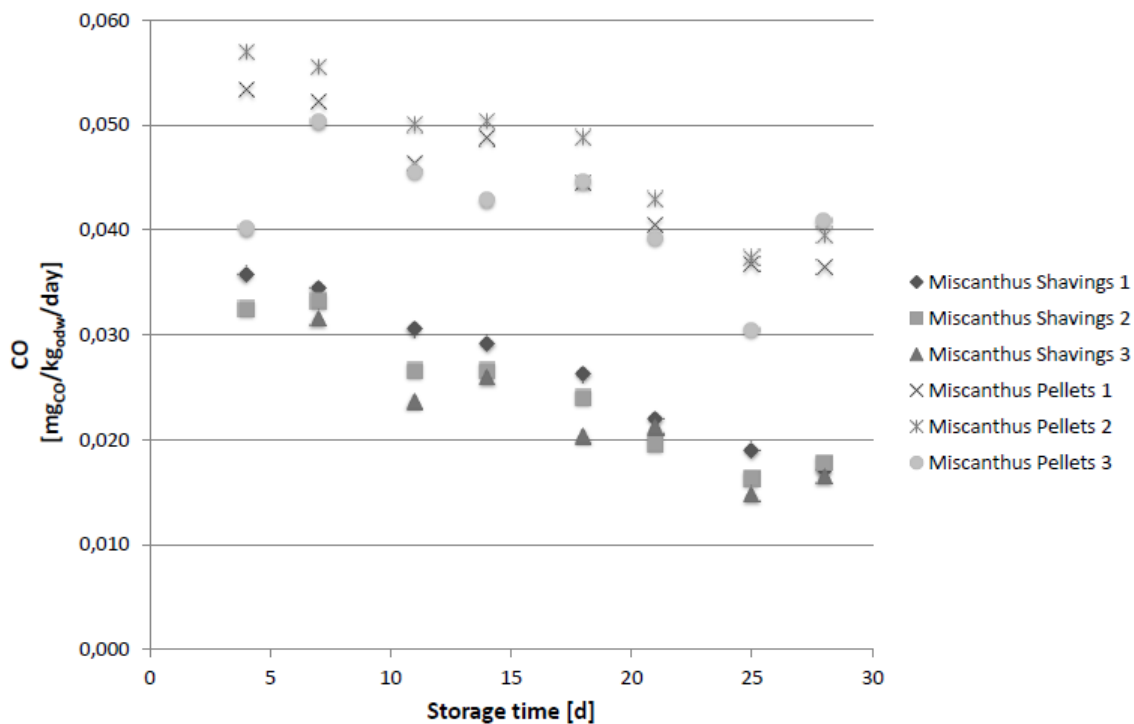


Figure 31: CO emission rates in  $[mg_{CO}/kg_{owd}/day]$  from miscanthus pellets and miscanthus shavings over storage time

Figure 32 shows the VOC emission rates from miscanthus pellets and miscanthus shavings over the experimental time. Except from some outliers, a slight trend is visible. The VOC emission rates were decreasing with the time. Only the measurement points from the miscanthus pellets have values above  $0,007 mg/kg_{owd}/d$  although the conditions

were the same as for miscanthus shavings. The reason for this deviation is unknown at present.

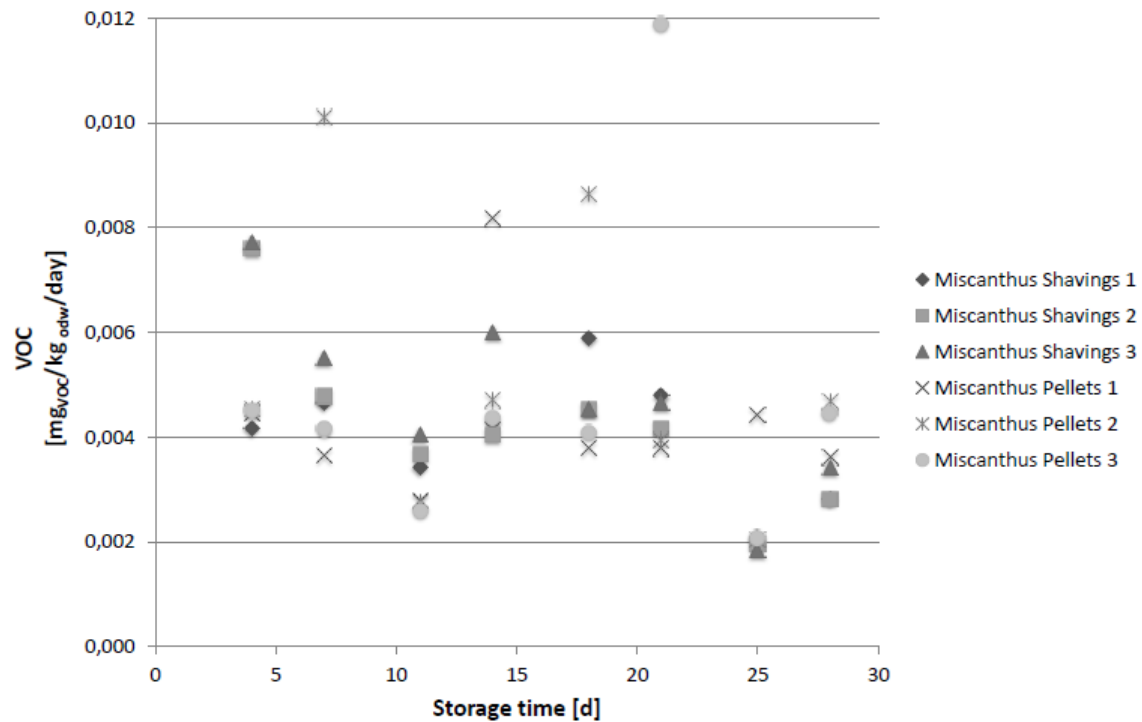


Figure 32: VOC emission rates [ $mg_{VOC}/kg_{owd}/day$ ] from miscanthus pellets and miscanthus shavings over storage time

In the next two diagrams (figure 33, figure 34) the emission rates of CO and VOC from pine -, larch- and spruce- pellets and shavings over the storage time are shown. The emission rates resulted from former experiments carried out at Bioenergy 2020+. In these experiments the same experimental setup was used as described in chapter 5, but the experimental time was only one week instead of four weeks. However, the trend that CO as well as the VOC emission rates are decreasing is visible. The CO and VOC emission rates are not only depending on the wood species but also the emission rates from shavings and pellets of the same wood species are different. The CO emission rates from the pellets are clearly higher than the emission rates from the shavings from the same wood species. This trend is not visible for the VOC emission rates.

These results confirm the result obtained in the storage tests with miscanthus shavings and miscanthus pellets (see figure 31 and figure 32). Also Kuang et. al.(2008) observed that pelletized materials emit more gases than non-pelletized material. As a reason

they mentioned, that perhaps the heat treatment during the manufacturing process of pellets opens the porous structure of wood and thereby increases the surface area of the material. [12] Thus, there must be an influence on the amount of emission resulting from the pelletizing process.

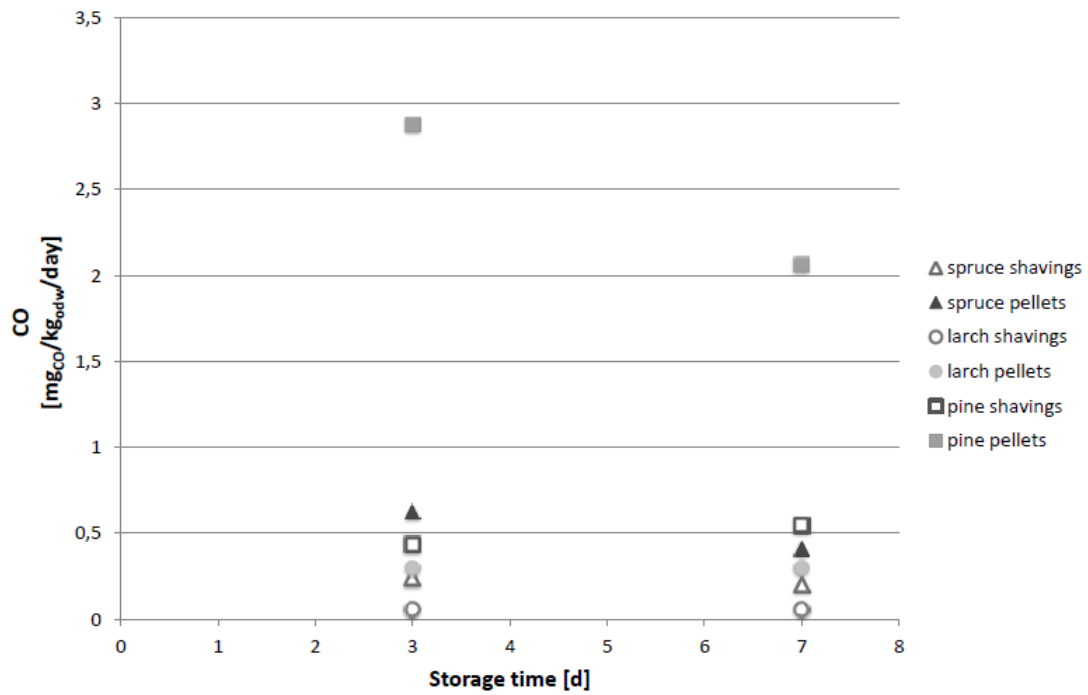


Figure 33: CO emission rates  $[mg_{CO}/kg_{owd}/day]$  from different kinds of pellets and shavings over storage time

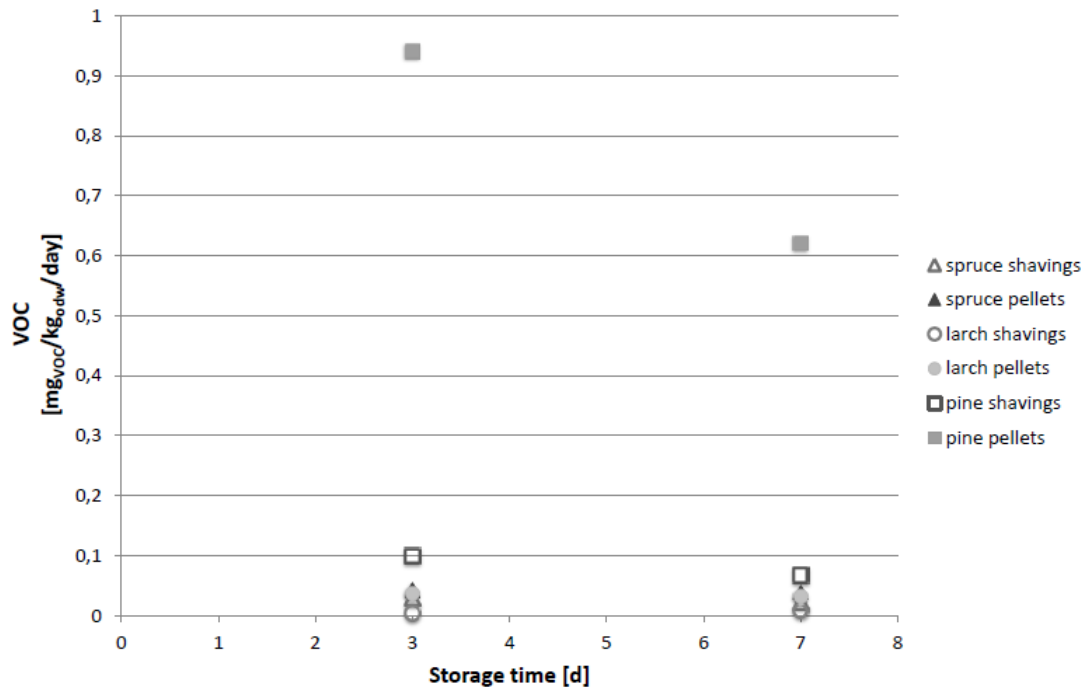


Figure 34: VOC emission rates [ $mg_{VOC}/kg_{owd}/day$ ] from different kinds of pellets and shavings over storage time

In the experiments also the fatty acid content was analyzed. In table 6 the fatty acid content and the maximal CO emission rate of the used materials are listed. The table entries were sorted from the material with the least CO emission rate to the material with the highest CO emission rate.

Table 6: Fatty acid content of pellets and shavings

Wood species	Maximal CO emission rate [ $mg_{CO}/kg_{odw}/day$ ]	Fatty acid content [wt%]
larch shavings	0,056	0,161
spruce shavings	0,240	0,088
larch pellets	0,297	0,073
pine shavings	0,434	0,131
spruce pellets	0,629	0,040
pine pellets	2,878	0,081

The shavings of all wood species have higher fatty acid contents than the pellets from these wood species. But although the shavings have higher fatty acid contents, the CO

emission rates are lower than the CO emission rates from the pellets. Moreover, there is no correlation between the CO emission rates and the fatty acid contents.

### 7.3 Results and discussion of the new designed laboratory reactor

The reactor and the necessary measurement setup was designed to meet the defined experimental requirements based on the results of the literature research and the pretest. The most suitable measurement devices were chosen. For the temperature measurement PT 100 sensors, for the pressure measurement a sensor with a piezo-resistive element and for the humidity measurement a capacitive sensor will be used. The emission measurements will be carried out with a gas chromatograph as already described in chapter 6.2.

Unfortunately the gas chromatograph had a very long time of delivery, which was not foreseeable at the beginning of the work. Thus, it was not possible to carry out measurements with the new designed laboratory reactor within in this master thesis.

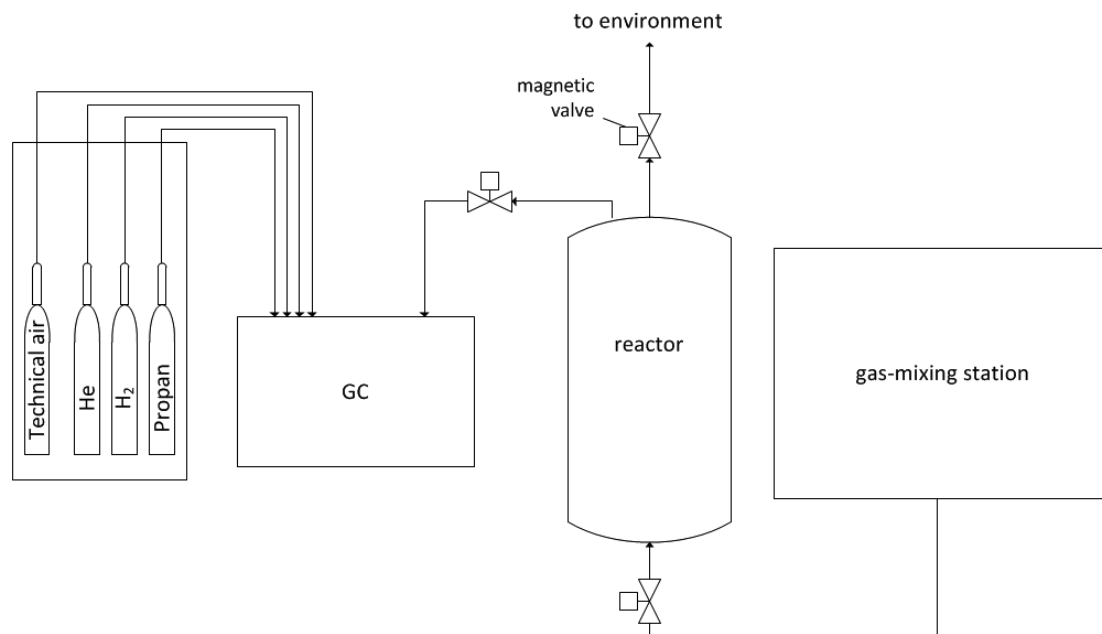


Figure 35: Scheme of the new designed laboratory setup

However, figure 35 shows a scheme of the new laboratory design. This setup will be assembled in an air-conditioned laboratory room. Thus, during the storage and the emission measurements the temperature will be constant at 21,5 °C. All gases, which are needed for the operation of the gas chromatograph, are stored in a gas cylinder cabinet. The gas cylinders are connected via stainless steel tubes with the GC. For the connection



between the reactor and the GC also a stainless steel tube is used. All other connections are realized with PTFE tubes. Magnetic valves at the inlet and outlet of the reactor are needed to close the reactor if it is used as a closed system and for the gas sampling. If the reactor is working as a closed system, it will be purged with technical air for about 30 *min* with a pressure of 1 *bar*. After this time both magnetic valves will be closed simultaneously to ensure that the pressure during storage is 1 *bar*. For the gas sampling to the GC at least atmospheric pressure in the reactor is needed. It can be expected that the reactions, which lead to the emissions during storage, will lead to the reduction of the storage pressure. Therefore, it will be necessary to pump additional nitrogen into the reactor before a GC measurement takes place to increase the pressure to atmospheric level. The magnetic valve at the inlet of the reactor will open till the pressure sensor detects 1,013 *bar*. Then the magnetic valve at the inlet of the reactor will close and the magnetic valve to the gas chromatograph will open. However, the actual gas sampling method will have to be specified once the gas chromatograph is delivered.

## 8 Conclusion and outlook

A laboratory reactor was designed based on (1) the literature research and on (2) experimental tests.

From literature search the following factors that influences the design of the reactor were found:

- Wood species which is used for pellet production
- Condition of the raw material
- Duration of storage of pellets
- Storage temperature of pellets
- Moisture content of pellets
- Available oxygen during storage

On the basis of the literature research also the release mechanisms, auto-oxidation and biomass decomposition, for the emission from pellets were discussed. According to the auto-oxidation as release mechanism an experiment with a fatty acid was carried out. The results showed that CO and VOC emission are products of the auto-oxidation reactions.

The storage experiments were performed with different raw materials with an existing experimental setup. This setup consisted of laboratory glass bottles, an infrared gas analyzer and a flame ionization detector. The glass bottles were used to store the raw materials, and the emission measurement were performed with the infrared gas analyzer and a flame ionization detector. The following shortcomings of this experimental setup were found:

- For the emission measurements, the infrared gas analyzer and the flame ionization detector required a very high sample volume. The sample volume, however, was limited to the volume of the glass bottles.
- It was not possible to heat or cool the laboratory glass bottles. Therefore, the influence the storage temperature on the amount of emission from the pellets could not be measured.
- It was not possible to measure the pressure inside the glass bottles. Therefore, any changes in pressure during the storage period could not be measured. If, for example, there would be an underpressure inside the bottles, the concentration of emissions inside the bottles would decrease when the bottles were opened in order to fix the measurement adapter. This in turn would have a highly negative impact on the measurement values.

Additional to the analysis of the shortcomings of the used measurement setup, the results from the measurements of the different raw materials were discussed. The measurement results from the experiments with the glass bottle setup showed that the emission rates from CO and VOC are decreasing over the time for all wood species. The high value of the emission rates depended on the wood species. Moreover, it was discovered that the CO emission rates from pellets are higher than the CO emission rates from shavings from the same wood species. This trend was not visible for the VOC emission rates. Furthermore, the pelletizing process must have an influence on the amount of CO emissions. However, there was no correlation found between the fatty acid content of pellets and of shavings of the different wood species and the CO emission rate. Therefore, further investigations are needed where not only the total amount of fatty acids are considered but also the amount of specific fatty acids are concerned.

Based on findings of the literature study and the practical experiments, the laboratory reactor was designed. For the temperature measurement inside the reactor, PT 100 sensors were chosen. These kinds of temperature sensors provide a very good linearity

and accuracy in the required measurement range. To investigate whether the emission reactions lead to an underpressure inside the reactor, a capacitive pressure sensor is used. For the emission measurement, a gas chromatograph was chosen because it is working with very small sample volumes in the  $\mu\text{l}$  range. Furthermore, the newly designed laboratory reactor does not need to be opened to start the emission measurements. Another improvement is that it is possible to heat and to cool the reactor, which will allow to test the effect of storage temperature on the amount of emissions and on the emission rate. A specially designed gas mixing station guarantees the production of a defined atmosphere. The option to moister the gas will allow to test the influence of humidity on the emission from pellets during the storage.

With the new designed laboratory reactor experiments will be carried out, in which the influencing factors will be discovered. Moreover, pellets from different wood species will be used to define which wood species release more or less emissions. Additional to that, the experiments for the auto-oxidation of fatty acids will be pursued to investigate if the CO and VOC emission rates are decreasing or increasing over the time.

## References

- [1] I. Obernberger and G. Thek. *The Pellet Handbook; The production and thermal utilisation of biomass pellets*. earthscan, London; Washington DC, 2010.
- [2] Umweltbundesamt. *Klimaschutzbericht 2010*. Wien, 2010.
- [3] proPellets Austria. Netzwerk zur Förderung und Verbreitung von Pelletsheizungen. <http://www.propellets.at>. Accessed: 21-May-2012, 12:00.
- [4] S. Melin, U. Svedberg, and J. Samuelsson. *Emissions from Woodpellets During Ocean Transportation*. Pellet Association of Canada, 2008.
- [5] U. Svedberg, J. Samuelsson, and S. Melin. Hazardous Off-Gassing of Carbon Monoxide and Oxygen Depletion during Ocean Transportation of Wood Pellets. *Annals of Occupational Hygiene*, 52:259 – 266, 2008.
- [6] TGA Fachplaner. TGA Newsletter. <http://www.tga-fachplaner.de/TGA-Newsletter-2010-2/Warnung-vor-Kohlenmonoxid-im-Pelletlager,QU1EPTI3Mjgx0CZNSUQ9MzAwMDI.html>. Accessed: 21-May-2012, 12:30.
- [7] Schweizer Holzzeitung. Kohlenmonoxid im Pelletslager - junge Frau gestorben. <http://www.holz-portal.ch/kohlenmonoxid-im-pellets-lager-junge-frau-gestorben/150/89/35903>. Accessed: 22-May-2012, 16:00.
- [8] EN 14588:2010. *Feste Biobrennstoffe -Terminologie, Definitionen und Beschreibungen*. 2010.
- [9] EN 14961-2:2011. *Feste Biobrennstoffe - Brennstoffspezifikationen und -klassen - Teil 2: Holzpellets für nichtindustrielle Verwendung*. 2011.
- [10] U. Svedberg, H. Högberg, J. Högberg, and B. Galle. Emission of Hexanal and Carbon Monoxide from Storage of Wood Pellets, a Potential Occupational and Domestic Health Hazard. *Annals of Occupational Hygiene*, 48:339 – 349, 2004.
- [11] M. Arshadi, P. Geladi, R. Gref, and P. Fjällström. Emission of Volatile Aldehydes and Ketones from Wood Pellets under Controlled Conditions. *Annals of Occupational Hygiene*, 53:797 – 805, 2009.

- [12] X. Kuang, J. Tumuluru, X. Bi, S. Sokhansanj, C. Lim, and S. Melin. Characterization and Kinetics Study of Off-Gas Emissions from Stored Wood Pellets. *Annals of Occupational Hygiene*, 52:675–683, 2008.
- [13] J. Salvato, N. Nemerow, and F. Agardy. *Environmental Engineering*. 5 edition, 2003.
- [14] Committee on carbon monoxide episodes in meteorological and tropographical areas National Research Council. *The Ongoing Challenge of Managing Carbon Monoxide Pollution in Fairbanks, Alaska*. National Academy Press, Washington, 2002.
- [15] Schornsteinfegerinnung Koblenz. Toxische Wirkung von Kohlenmonoxid. [http://www.schornsteinfeger-innung-koblenz.de/bilder\\_rlp/files/co2.pdf](http://www.schornsteinfeger-innung-koblenz.de/bilder_rlp/files/co2.pdf). Accessed: 04-June-2012, 08:00.
- [16] VDI2053. *VDI Richtlinie 2053 - Raumluftechnische Anlagen für Garagen*. 2004.
- [17] L. Molhave. Total Volatile Organic Compounds (TVOC) in Indoor Air Quality Investigations. *Indoor Air*, 7:225 – 240, 1997.
- [18] B. Seifert. Richtwerte für die Innenraumluf, Die Beurteilung der Innenraumlufqualität mit Hilfe der Summe der flüchtigen organischen Verbindungen (TVOC-Wert). *Bundesgesundheitsblatt - Gesundheitsforschung - Gesundheitsschutz*, 42:270 – 278, 1999.
- [19] D. Fengel and G. Wegener. *Wood: Chemistry, Ultrastructure, Reactions*. Verlag Kessel, Remagen, 2003.
- [20] K. Granström. Emissions of Hexanal and Terpenes during Storage of Solid Wood Fuels. *Forest Products Journal*, 60:27–32, 2010.
- [21] W. Emhofer and C. Pointner. Lagertechnik und Sicherheit bei der Pelletslagerung - Endbericht zu den Ergebnissen aus den AP 2, 4, 5 und 6. Technical report, bioenergy2020+, 2009.
- [22] X. Kuang, J. Tumuluru, X. Bi, C. Lim, S. Sokhansanj, and S. Melin. Rate and Peak Concentrations of Off-Gas Emissions in Stored Wood Pellets - Sensitivities to Temperature, Relative Humidity, and Headspace Volume. *Annals of Occupational Hygiene*, 53:789–769, 2009.
- [23] R. Meijer and C. Gast. Spontaneous combustion of biomass: Experimental study into guidelines to avoid and control this phenomenon. *2nd World Biomass Conference*, 2004.

- [24] P. Lehtikangas. Storage effects on pelletised sawdust, logging residues and bark. *Biomass & Bioenergy*, 19:287 – 293, 2000.
- [25] M. Arshadi and R. Gref. Emission of volatile organic compounds from softwood pellets during storage. *Forest Products Journal*, 55:132 – 135, 2005.
- [26] M. Ståhl, K. Granström, and R. Renström. Industrial processes for biomass drying and their effects on the quality properties of wood pellets. *Biomass & Bioenergy*, 27:621 – 628, 2004.
- [27] J. Tumuluru, X. Kuang, S. Sokhansanj, C. Lim, T. Bi, and S. Melin. Development of a laboratory studies on the off-gassing of wood pellets. *Canadian Biosystems Engineering*, 52:8.1–8.9, 2010.
- [28] X. Kuang, J. Tumuluru, S. Sokhansanj, C. Lim, X. Bi, and S. Melin. Effects of Headspace and Oxygen Level on Off-gas Emissions from Wood Pellets in Storage. *Annals of Occupational Hygiene*, 53:807–813, 2009.
- [29] Juita, B. Dlugogorski, E. Kennedy, and J. Mackie. Oxidation Reactions and Spontaneous Ignition of Linseed Oil. *Proc. Combust. Inst.*, 33:2625 – 2632, 2011.
- [30] Juita, B. Dlugogorski, E. Kennedy, and J. Mackie. Identification and Quantitation of Volatile Organic Compounds from Oxidation of Linseed Oil. *Ind. Eng. Chem. Res.*, 51:5645 – 5652, 2012.
- [31] DIN EN14772 2:2010. *Feste Biobrennstoffe - Bestimmung des Wassergehaltes - Ofentrocknung - Teil 2: Gesamtgehalt an Wasser - Vereinfachtes Verfahren*. 2010.
- [32] N. El Bassam and W. Huisman. Harvesting and Storage of Miscanthus. In *Jonnes M. B. and Walsh M.: Miscanthus: For Energy and Fibre*, chapter 6, pages 86 – 108. James and James (Science Publishers) Ltd, 2001.
- [33] DIN68364:2003. *Kennwerte von Holz; Rohdichte, Elastizitätsmodul und Festigkeiten*. 2003.
- [34] D. Sparkman, Z. Penton, and F. Kitson. *Gas Chromatography and Mass Spectrometry: A Practical Guide*. Academic Press, Oxford, 2011.
- [35] M. H. Gey. *Instrumentelle Analytik und Bioanalytik: Biosubstanzen, Trennmethode, Strukturanalytik, Applikationen*. Springer-Verlag, Berlin, Heidelberg, 2008.

- [36] J. Fontes. Temperature Sensors. In *Wilson J.S.: Sensor technology handbook*, chapter 20, pages 531 – 561. Elsevier, 2005.
- [37] TC Direct. für Temperatur -Sensoren, -Messung und -Regelung. <http://www.tcdirect.de>. Accessed: 04-September-2012, 16:00.
- [38] DIN EN 60751:2009. *Industrielle Platin-Widerstandsthermometer und Platin-Temperatursensoren*. 2009.
- [39] C. Dames. Resistance Temperature Detectors. In *Encyclopedia of Microfluidics and Nanofluidics*, chapter 18, pages 1782 – 1790. Springer-Verlag, 2008.
- [40] E. Hering and G. Schönfelder. *Sensoren in Wissenschaft und Technik; Funktionsweise und Einsatzgebiete*. Vieweg+Teubner Verlag, Wiesbaden, 2012.
- [41] Jumo. Druckmessumformer. <http://www.jumo.at/produkte/druck/druckmessumformer/404366/jumo-dtrans-p>. Accessed: 04-September-2012, 15:00.
- [42] G. Harman. Pressure Sensors. In *Wilson J.S.: Sensor technology handbook*, chapter 16, pages 411 – 465. Elsevier, 2005.
- [43] E+E Elektronik. Feuchtemessumformer für Industrieanwendungen. <http://www.epluse.com/de/produkte/feuchtemesstechnik/feuchtemessumformer-fuer-industrieanwendungen/ee23/>. Accessed: 10-September-2012, 11:00.
- [44] J. Fontes. Humidity Sensors. In *Wilson J.S.: Sensor technology handbook*, chapter 12, pages 271 – 284. Elsevier, 2005.
- [45] W. Lange. Die Extraktstoffe von Riesengras (*Miscanthus sinensis* Anderss.). *Holz-forschung*, 46:277 – 282, 1992.