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Measurement of Off-Gases in Wood Pellet Storage

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Additional information is available at the end of the chapter

1. Introduction

Gas emissions (CO_2 , CO , CH_4 and volatile organic compounds) from woody biomass storage systems have been studied extensively in recent years. The decomposition is due to biological, chemical oxidative and slow pyrolytic processes depending on the availability of oxygen [1-3]. The major VOCs emitted from stored wood pellets were aldehydes, some of which are known to cause irritation to the respiratory system [4].

Previous measurements have shown that freshly made wood pellets continue to emit flammable gases CO , H_2 , and CH_4 during storage and handling. A large portion of this emission is CO as opposed to emission of volatile organic compounds (VOC) like formic acid, methanol and aldehydes [5, 6]. More volatile organic compounds emit from stored sawdust and wood chips compared to stored wood pellets [7-9]. This is because of the fact that most of the VOCs easily evaporate during heating and drying processes [10, 11] and as wood pellets pass through high temperature during drying and pelletization, decomposition of extractives would result in less VOCs emission. During pelletization, sawdust is dried at temperatures from 100 to 400 °C so the moisture content goes below 10%. Roffael [12], Rupar and Sanati [13] also reported the emission of VOCs during biomass storage. Large amount of monoterpenes and other volatile organic compounds are emitted during drying [10, 11, 14, 15]. High levels of CO were first measured in compartments of a ship in 2002 when an ocean vessel was discharging wood pellets in Rotterdam, The Netherlands. The wood pellets were shipped from Vancouver, British Columbia and the duration of the voyage was 38 days. One person was killed and

several people were severely injured as a result of exposure to high concentration of CO when entering a stairway adjacent to the cargo space [16]. Svedberg identified that the storage of wood pellets led to the emission of high levels of hexanal as a result of the general degradation processes of wood.

In terms of CO₂, CO, and CH₄ emissions, higher emission factors are associated with higher temperatures, whereas increased relative humidity in the enclosed container increased the rate of gas emission and a corresponding depletion of oxygen [17, 18]. Wihersaari [8] concluded that the CO₂ emissions from fresh forest residues were almost three times higher than the dried materials, and suggested that mixing the heaps during the storage period would probably cause increased emissions rates. Emissions of CO, CO₂ and CH₄ are likely due to biodegradation and auto-oxidative reactions of organic constituents naturally present in wood [1].

2. Experimental set-up

2.1. Small scale experiments

The off-gassing tests were conducted at three nominal temperatures of 25 °C, 40 °C and 60 °C. Room temperature provided the 25 °C storage environment. Two identical ovens were used to provide 40 °C and 60 °C storage environments. Twenty four (24) glass containers, 2L each, were divided into three equal groups for testing at the three temperatures. For each set of 8 containers, 6 containers were used for gas sampling and 2 containers were used for temperature measurement. The temperature inside the containers was measured with thermocouples and data was logged onto a PC. The following procedure was followed for each test container. The empty weight of the container without the lid was recorded (M_1). The container was filled to 75% volume with wood pellets (M_2). Finally, the weight of the wood pellets was calculated (M_3). The lid with sampling port was then applied, thereby sealing the container. Filled containers along two empty containers (for each storage temperature) were arranged in upright position. The two empty jars were included to have consistent condition as the filled jars for temperature reading. Temperature was also directly recorded from a thermocouple inside the oven.

2.2. Pilot scale experiments

All measurements of the gases (CO, CO₂ and CH₄) were made in an experimental silo designed and installed at the Clean Energy Research Centre (CERC), the Department of Chemical & Biological Engineering, University of British Columbia [19, 20]. The experimental silo has a volume of 5.65m³ (1.2m diameter, 4.6m height) and is made of mild steel. The silo is designed to represent the storage of substantial quantities of wood pellets. A two level structure was designed and built to support the pilot scale silo. The set-up was further equipped with sensors for temperature, gas pressure and relative humidity measurements. Thermocouples and pressure transducers were installed at various levels along the height of the silo. Two EXP-32 cards were used to log the temperature and pressure data during the experiments. The experimental data of pressure and temperature were logged into a computer running on the

LABTECH software using a data acquisition board (PCI-DAS08, Techmatron Instruments Inc, Canada) consisting of pressure transducers and thermocouples. However the pilot size of the set-up made it challenging to have it equipped with different monitoring systems and make it sealed. Fourteen 12mm diameter gas sampling ports with 3mm ball valves are provided at 2 sides of the pilot silo along the wall at different levels for gas sampling. The positions of the gas sampling ports in the large silo are indicated in Table 1. Six of the gas sampling ports are located on one side of the silo and another 7 on the other side.

Gas sampling ports on side A		Gas sampling ports on side B	
Gas Port Name	Elevation (m)	Gas Port Name	Elevation (m)
G0	4.16	G0	4.16
G2	3.55	G3	3.35
G4	2.94	G5	2.74
G6	2.33	G7	2.13
G8	1.65	G9	1.52
G10	1.21	G11	0.91
G12	0.50	G13	0.30

Table 1. Location of the gas sampling ports on the experimental silo

3. Materials and methods

3.1. Small and pilot scale experiments

In small scale tests, initially and at intervals, approximately 25 mL of gas was drawn from each container by an air-tight GC syringe (25mL SGE Gas-Tight Syringe, Luer-Lock and TOGAS Luer Lock Adapter, Mandel Scientific Company) and analyzed by GC/FID (Flame Ionization Detector) and GC/TCD (Thermal Conductivity Detector) methods for the composition of the sampled gases (CO, CO₂, CH₄, N₂, O₂ and H₂). In pilot scale tests, Gas samples were collected using an airtight syringe (SG-009770-100mL SGE Gas-Tight Syringe, Luer-Lock, Mandel Scientific, Canada). The syringe had a Luer lock device to help in collecting a known quantity of gas sample. The Shimadzu GC needle used with the 100mL SGE syringe was Togas Loop Fill Interface N711 Needle (Model number: 220-90615-00, Mandel Scientific Inc.).The GC has three columns in series: Porapak-N (80/100 mesh, 3 m), Porapak-Q (80/100 mesh, 3 m) and a MS-5A (60/80, 2.25 m). The FID detector was used for CO, CO₂ and CH₄ and the TCD was used for N₂, O₂ and H₂, with Argon as the carrier gas. Argon was the reference gas for the TCD. Compressed air was the reference gas for the FID.

Gas sampling started one day after loading of the containers. Prior to gas concentration measurements, the GC was calibrated with three different standard gases, which contained known concentrations of carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), oxygen (O₂), nitrogen (N₂), hydrogen (H₂) and helium (He) (Table 2). To ensure steady and accurate readings by the GC, 25 mL of a standard gas with known concentration of gases was injected to the GC for calibration before and after gas analysis every day.

Standard gas 1		Standard gas 2		Standard gas 3	
Components	Concentration (%)	Components	Concentration (%)	Components	Concentration (%)
CO	2.5	CO	0.05	CO	0.50
CO ₂	6.0	CO ₂	0.10	CO ₂	0.50
CH ₄	1.5	CH ₄	0.50	CH ₄	0.10
N ₂	3.0	H ₂	0.50	H ₂	1.00
O ₂	10.0	Air	Balance	Air	balance
He	2.0				
Ar	balance				

Table 2. Compositions (volumetric) of standard gases for GC calibration

4. Results and discussion

4.1. Small scale tests

4.1.1. Off-gas concentration at high temperature and high moisture

The moisture content of the reference wood pellets was 4% as received. They were subsequently conditioned to 9, 15, 35 and 50% moisture content respectively by spraying distilled water on the wood pellets in a container during rotary motion. At 15% moisture or higher the integrity and wood pellet shape were compromised.

The off-gassing tests were conducted at three temperatures 25°C, 40°C and 60°C. For the tests at 25°C, the containers were placed on the lab shelf. To provide the higher storage temperatures two identical ovens were used. The Biomass and Bioenergy Research Group (BBRG) at UBC has developed the method of using multiple smaller containers and sampling a very limited amount of gas from each container at lower frequency rather than frequent sampling from a larger container in order to minimize the distortion in gas concentration due to extraction of gas. This method allows a much smaller sample size to be used for testing.

Eight glass containers with wood pellets were put on the lab shelf for 25°C for testing. The 8 containers were named A-4-X, A-4-Y, A-9-X, A-9-Y, A-15-X and A-15-Y [e.g. A-4-X indicates the first replicate of wood pellets sample at ambient temperature (25°C) and 4% moisture content]. The same format was used for labeling the samples at higher temperature. The letter A was replaced by 40 for the tests at 40°C and with 60 for the tests at 60°C. Each set of 8 containers (6 containers for gas sample measurement and 2 for temperature measurement) were placed in 40°C and 60°C ovens. The temperature inside the containers was measured with thermocouple sensor connected to a computer for temperature logging. All containers were checked before conducting the experiments to ensure proper sealing. The exact same labeling and procedure were used for tests at 15, 35 and 50% moisture content.

To create the baseline for gas concentrations, two empty containers were placed in room temperature (25°C), another two in the 40°C oven and another two in the 60°C oven. 100 mL of gas was drawn from each container and analyzed by the GC for gas composition. Figure 1 to Figure 10 show plots of gas concentrations vs. storage time for the three temperatures and 2 moisture concentrations [4 and 50%] for each gas. The concentration of each gas is presented on the same graph for one moisture content and 3 different storage temperatures. The concentrations are given in percent on volumetric scale in ppmv (parts per million volume). A concentration of 0.6% means 6000 ppmv.

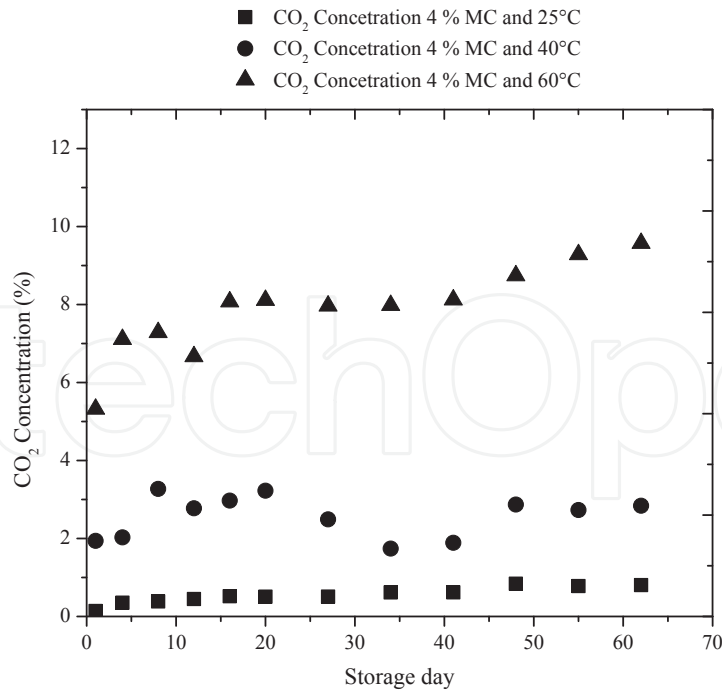


Figure 1. Concentration of CO₂ for wood pellet with 4% moisture content over 62 days at 25°C, 40°C and 60°C.

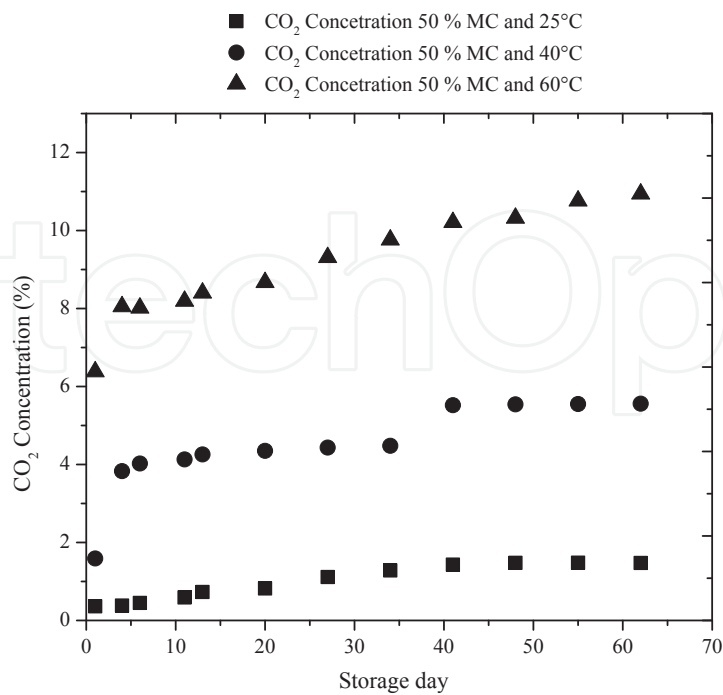


Figure 2. Concentration of CO₂ for wood pellet with 50% moisture content over 62 days at 25°C, 40°C and 60°C

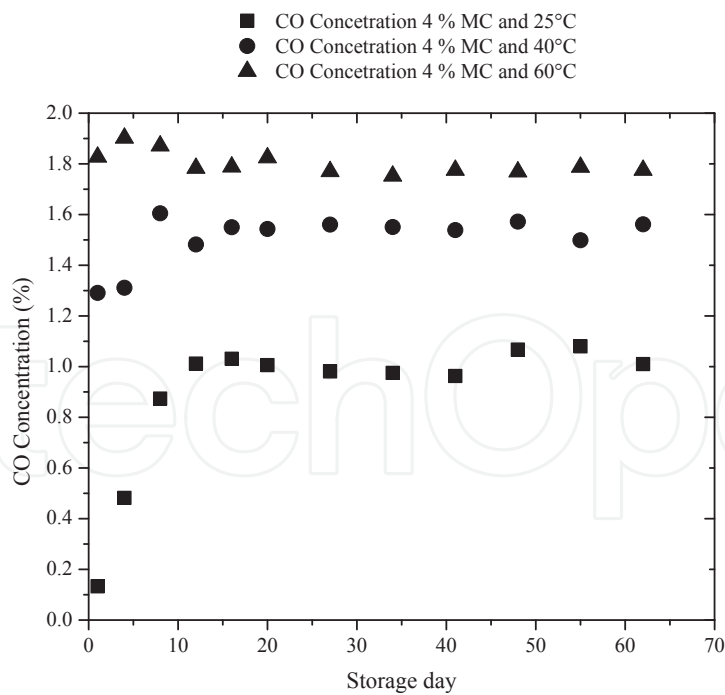


Figure 3. Concentration of CO for wood pellet with 4% moisture content over 62 days at 25°C, 40°C and 60°C

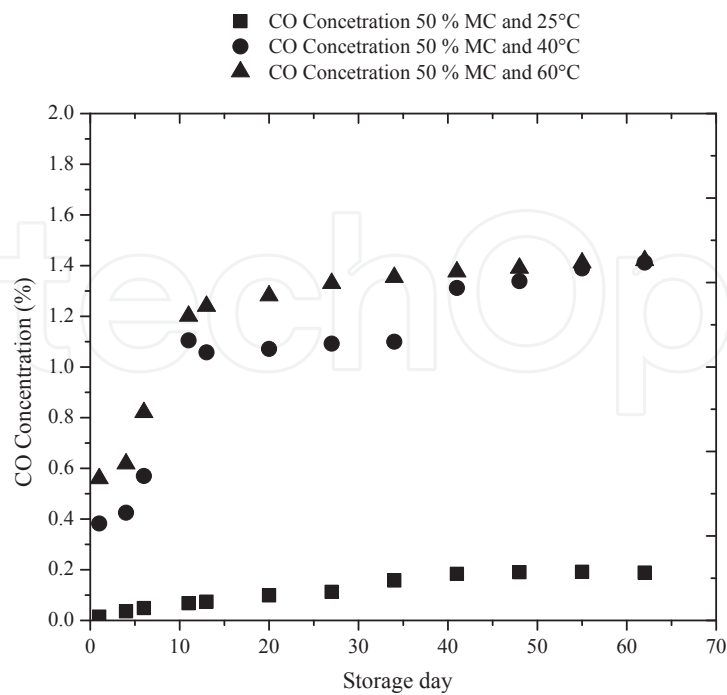


Figure 4. Concentration of CO for wood pellet with 50% moisture content over 62 days at 25°C, 40°C and 60°C

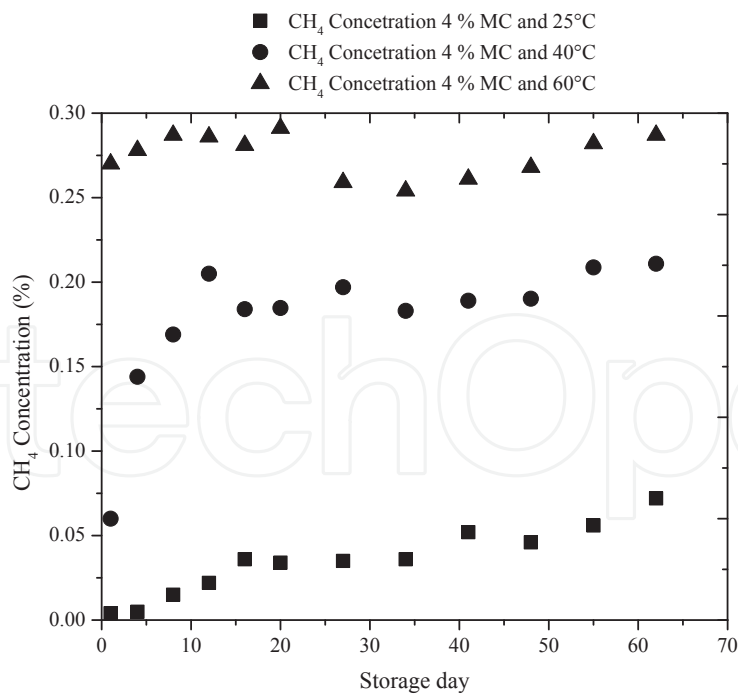


Figure 5. Concentration of CH₄ for emissions from wood pellet with 4% moisture content over 62 days at 25°C, 40°C and 60°C

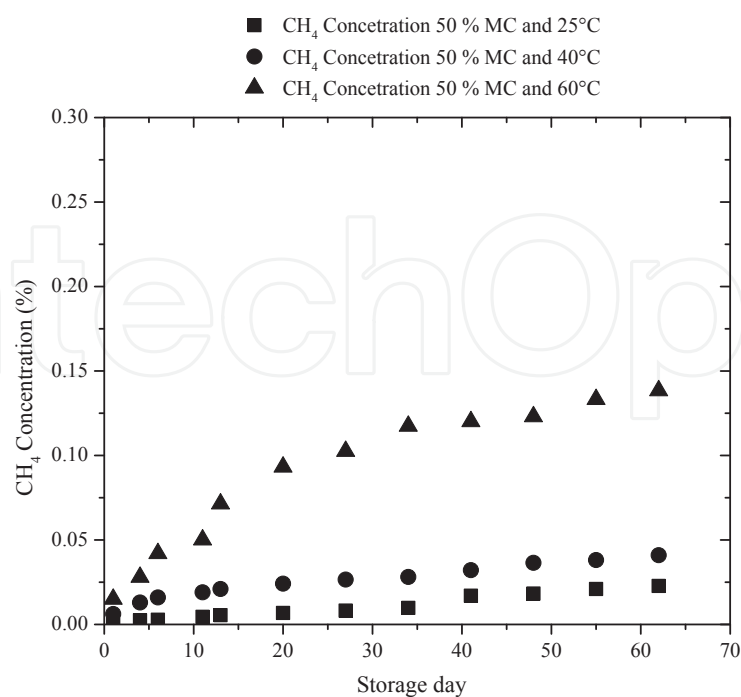


Figure 6. Concentration of CH_4 for emissions from wood pellet with 50% moisture content over 62 days at 25°C, 40°C and 60°C

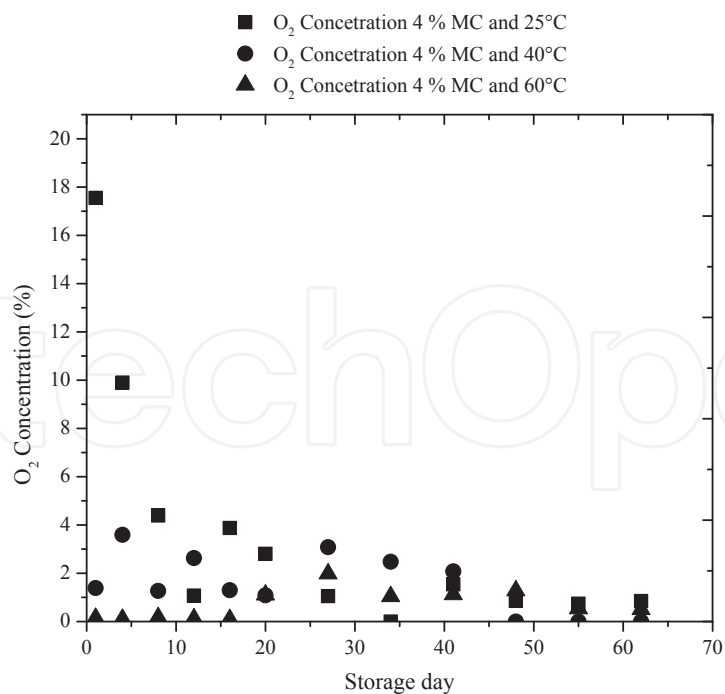


Figure 7. Oxygen depletion for wood pellet with 4% moisture content over 62 days at 25°C, 40°C and 60°C

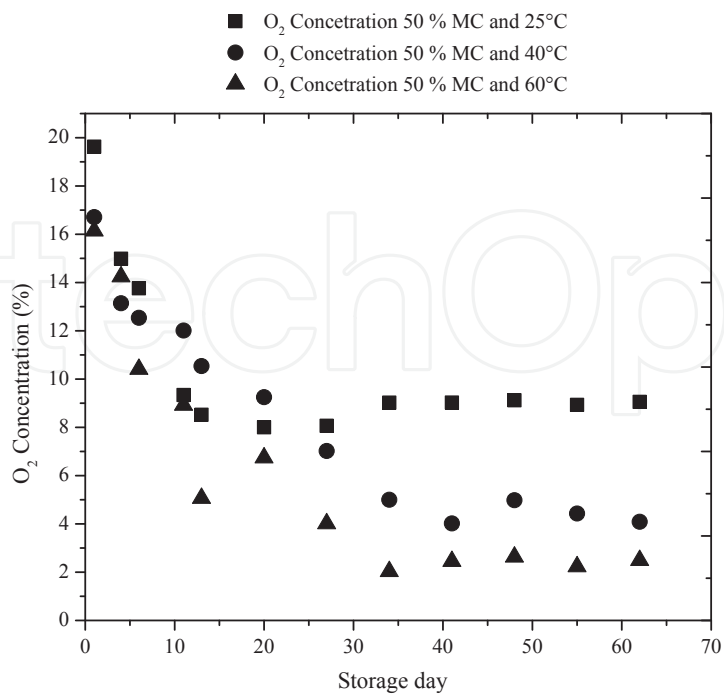


Figure 8. Oxygen depletion for wood pellet with 50% moisture content over 62 days at 25°C, 40°C and 60°C

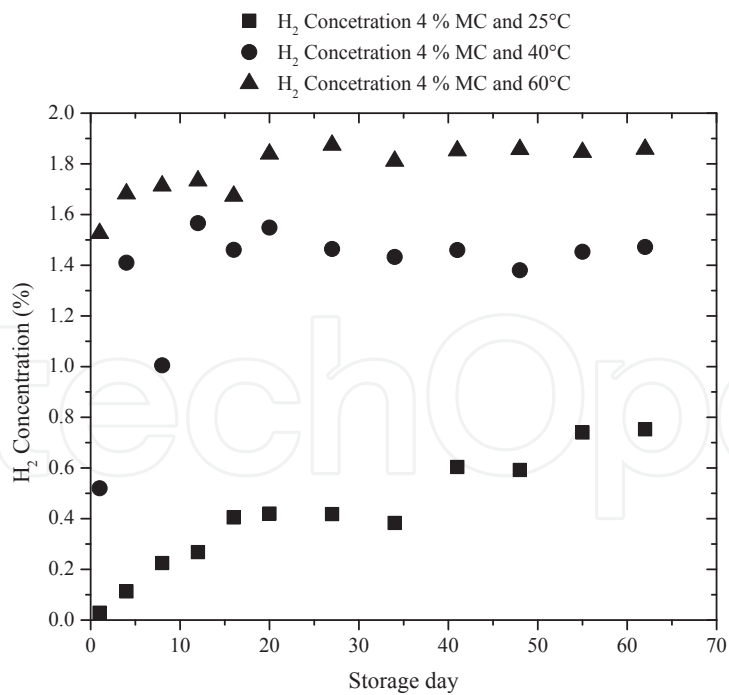


Figure 9. Concentration of hydrogen for emissions from wood pellet with 4% moisture content over 62 days at 25°C, 40°C and 60°C

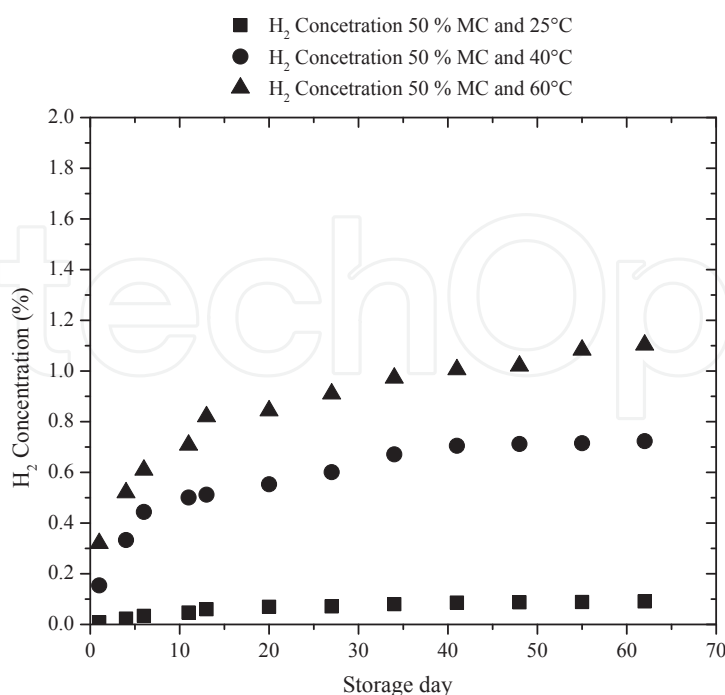


Figure 10. Concentration of hydrogen for emissions from wood pellet with 50% moisture content over 62 days at 25°C, 40°C and 60°C

Plots in Figure 1 to 2 show the concentration of carbon dioxide over time at 25°C, 40°C and 60°C for wood pellets with 4 and 50% moisture content respectively. Figures of carbon dioxide concentration for wood pellets with 9, 15 and 35% moisture content are presented in Appendix A. As expected, the higher the temperature, the higher the concentration of the CO₂ gas. However, for wood pellets with 4, 9 and 15% moisture content at 25°C, the CO₂ concentration increased from ~0.9% to ~1.7% instead showing a relation between time and moisture content. At 25°C when the moisture content increased higher to 35 and 50%, the maximum concentration of CO₂ did not go beyond what was seen for the wood pellets with 15% moisture content. At 40°C and 60°C, the increase was from 2.84% to 5.55% and 9.58% to 10.94% respectively (for wood pellets with 4% to 50%). The maximum concentration of CO₂ was observed at 15% moisture content. Above 15% moisture content, the maximum concentration of CO₂ increased only marginally at 40°C and stayed almost the same at 60°C.

Figure 3 to 4 show CO concentration at 4 and 50% moisture content at 25°C, 40°C and 60°C [Rest of the Figures for CO can be found in Appendix A]. The concentration of CO increased over time for wood pellets with 4 and 9% moisture content as the storage temperature increased. CO concentration did not increase at 25°C, 40°C and 60°C for wood pellets with 15% moisture content. The CO concentrations at room temperature and the six moisture contents the peak concentration of CO was the same for 4% and 9% moisture content and decreased to ~0.8% for wood pellets with 15% moisture content. The concentration decreased even further for wood pellets with 35 and 50% moisture content. At 40°C, for wood pellets with 4 and 9 and 15%, carbon monoxide concentration decreased from 1.5% to 1.4% and 1.1% respectively. For

wood pellets with 35%, the peak concentration stayed at 1.0% and increased slightly when the moisture content of wood pellets increased to 50%. The same CO concentration change was observed at 60°C for wood pellets with 4 and 9 and 15%. When the moisture content increased to 35%, CO peak concentration increased to 1.52% but stayed the same for higher moisture content like 50%.

Similar to carbon dioxide concentration, methane concentration over time increased with storage temperature for all levels of moisture contents except for 35% where the concentration was quite the same at 40°C and 60°C. An increase in temperature from 25°C to 40°C caused the peak concentration of CO to increase from 0.07% to 0.21%. Further increase in temperature to 60°C, resulted in peak concentration of CO to 0.28%. Except for the gas concentration at 25°C, concentration of CO decreased over time as the moisture content increased to 40°C and 60°C respectively.

Plots in Figure 7 to 8 as well as Figure A.10 to A.12 show the concentration of oxygen for wood pellets with six different moisture content at 25°C followed by the concentration at higher temperatures (40°C and 60°C) as a function of time. Depletion of oxygen was least significant for samples at 25°C and moisture content higher than 15%. For wood pellets with 4%, 15%, 35% and 50% moisture content the oxygen content decreased as a function of time. However, for wood pellets with 9% moisture content the oxygen depletion was more rapid during the first few days, at 25°C to 40°C. After 20 days the, oxygen concentration was leveling out at 5-6% at 25°C and reached 0% very quickly at 40°C.

Figure 9 to 10 shows the concentration of hydrogen for wood pellets with 4 and 50% moisture content over time at 25°C followed by the concentration at higher temperatures (40°C and 60°C). The release of hydrogen was minimal for samples with 50% moisture at 25°C. It was concluded that for the same moisture content, the hydrogen concentration increased as the temperature increased. However for wood pellets at the same temperature, the hydrogen concentration decreased as the moisture content increased.

4.1.2. Estimation of flammability of emissions from wood pellets

This research conducted to provide a scientific basis to determine whether or not the concentration of the composite mix of gases emitted from wood pellets could reach flammable concentrations and if so, under what conditions. Table 3 summarizes the results of the calculations using the ISO 10156:2010 Standard [21].

The $\sum_{i=1}^n A_i \left[\frac{100}{T_{Ci}} - 1 \right]$ factor in

Table 4 represents the equivalent concentration of flammable gases as measured.

The $\sum_{k=1}^p B_k K_k$ factor in Table 4 represents the equivalent concentration of the flammable gases in a mixture of nitrogen as calculated, which if mixed with full complement of air (oxygen), may sustain a flame if ignited with an external source. Since the oxygen content is extremely low in an enclosed cargo hold there is even lower risk of fires and explosions in the oxygen

deprived conditions in an enclosed cargo hold than in open atmospheric conditions saturated with oxygen.

Wood pellets exported to Europe have typically between 4 and 6% moisture. The 15% and higher represented wood pellets which have been accidentally exposed to moist conditions for a prolonged period of time. Testing of wood pellets with abnormal moisture content is important to make sure there is good safety margin for long duration shipments such as a 30-34 days voyage from for example British Columbia to Europe. The emission of gases from wood pellets reached a peak (plateau) as summarized in Table 3 within the first 20-30 days. At the same time the oxygen content decreased rapidly to a very low level as the emission of CO₂ increased resulting in a near inert condition in the space. The flammability of the mixed gases was calculated when exposed to air with full complement of oxygen as per the ISO Standard. The research was carried out over a period of 62 days, just to ensure the gas evolution continued to be stable. The same calculations are done for 62 days as well and presented in Table 4.

Gas Species	25°C			40°C			60°C		
	4%	9%	15%	4%	9%	15%	4%	9%	15%
	Moisture	Moisture	Moisture	Moisture	Moisture	Moisture	Moisture	Moisture	Moisture
CO ₂	0.617	1.334	1.110	1.741	3.572	3.620	7.980	8.490	10.290
CO	0.975	1.119	0.678	1.551	1.329	1.120	1.752	1.551	1.120
CH ₄	0.036	0.041	0.019	0.183	0.174	0.096	0.254	0.225	0.120
H ₂	0.383	0.421	0.365	1.460	1.209	0.946	1.811	1.473	1.230
CO/CH ₄ /H ₂ mixture (sum)	1.394	1.581	1.062	3.194	2.712	2.162	3.817	3.248	2.470
Sum	2.011	2.915	2.172	4.935	6.284	5.782	11.797	11.738	12.760
O ₂	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
N ₂	97.989	97.085	97.828	95.065	93.716	94.218	88.203	88.262	87.240
Flammability determination in accordance with ISO 10156 Standard									
$\sum_{i=1}^n A_i \left[\frac{100}{T_{Ci}} - 1 \right]$	12.398	13.907	10.253	35.659	30.013	23.510	43.556	36.311	28.641
$\sum_{k=1}^n B_k K_k$	98.915	99.086	99.493	97.677	99.074	99.648	100.173	100.997	102.675
Flammable	No	No	No	No	No	No	No	No	No

Table 3. Concentration of gases from wood pellets after 34 days of storage

Gas Species	25°C			40°C			60°C		
	4%	9%	15%	4%	9%	15%	4%	9%	15%
	Moisture	Moisture	Moisture	Moisture	Moisture	Moisture	Moisture	Moisture	Moisture
CO ₂	0.805	1.643	1.593	2.840	4.680	4.820	9.571	10.925	11.890
CO	1.010	1.103	0.758	1.561	1.412	1.112	1.775	1.560	1.128
CH ₄	0.072	0.086	0.062	0.211	0.177	0.114	0.287	0.241	0.132
H ₂	0.753	0.680	0.559	1.472	1.251	1.071	1.858	1.482	1.261
CO/CH ₄ /H ₂ mixture (sum)	1.835	1.869	1.379	3.244	2.840	2.297	3.920	3.283	2.521
Sum	2.640	3.512	2.972	6.084	7.520	7.117	13.491	14.208	14.411
O ₂	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
N ₂	97.360	96.488	97.028	93.916	92.480	92.883	86.509	85.792	85.589
Flammability determination in accordance with ISO 10156 Standard									
$\sum_{i=1}^n A_i [\frac{100}{T_{Ci}} - 1]$	19.328	18.740	14.484	36.215	31.229	25.802	44.838	36.702	29.345
$\sum_{k=1}^p B_k K_k$	98.568	98.953	99.418	98.176	99.500	100.113	100.866	102.179	103.424
Flammable	No	No	No	No	No	No	No	No	No

Table 4. Concentration of gases from wood pellets after 62 days of storage

5. Pilot scale tests

5.1. Off-gas concentration in silo head-space

Gas composition analysis was performed for the first 9 weeks after loading the pilot silo. Results (Figure 11 to Figure 13) showed a rapid increase in the concentration of CO₂, CO and CH₄ in the head-space of the silo. Off-gas concentrations in the first 7 days were 1.0-1.6% CO₂, 0.8-1.0% CO and 0.73- 0.85% CH₄. All gas concentrations increased with storage time. Figure 14 shows the increase in the CO/CO₂ ratio with time, which reached a constant value after 50

days of storage. Some scattering of data is seen between days 10 to 15 with a peak CO/CO₂ ratio of about 0.59 on day 10. Minimum oxygen concentration in the bed was also seen on day 10 (Figure 15). It could be explained by slightly (~2%) lower local relative humidity recorded by the cable and higher H₂ and thus the shift of water-gas shift reaction towards reactants. Oxygen concentrations were also measured according to the same gas sampling schedule. As shown in Figure 15 the O₂ level dropped dramatically from 21% to 7-8% after 3 days and reached close to 0% after 1 week and again after 3 weeks of storage. The concentration of carbon dioxide in the head-space increased to about 2.7% (27,000 ppm), and this is higher compared to the CO₂ concentrations in the pellet bed which could be attributed to the exposure of pellet surface to head-space oxygen and thus higher local emission. Lab-scale experiments had been previously performed to determine the effect of oxygen availability on the emission rates of off-gasses. Highest emission of CO₂ was seen in containers with higher percentage of head-space or where oxygen was pumped in regularly. When wood pellets were stored in helium, minimum emission of CO₂ was detected. For carbon monoxide, its concentration increased from the very first days of storage and reached a maximum value of about 1.7% after 9 weeks of storage. This accumulated concentration was well above the threshold [22] limit value (TLV) for human health, and it can cause injuries and immediate death.

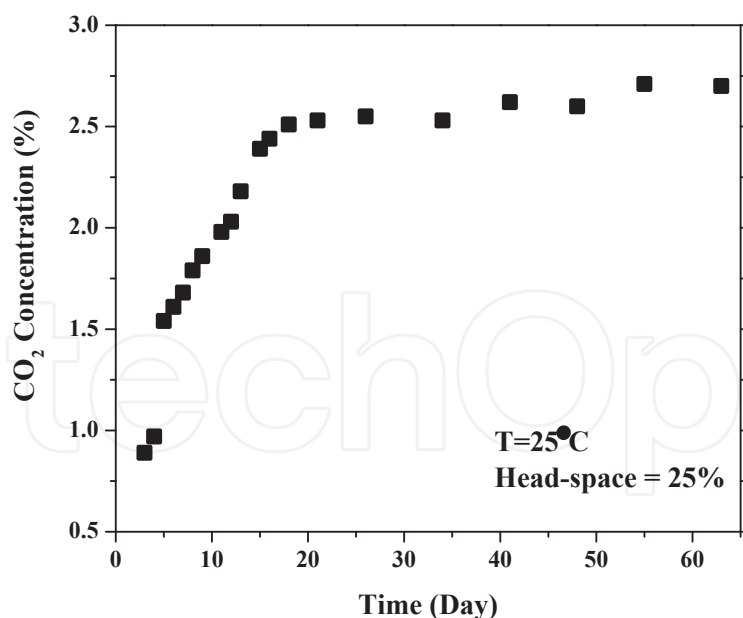


Figure 11. CO₂ concentration in head-space of the silo as a function of storage time for wood pellets. (G0: head-space gas sampling port) [Concentrations are volume percentage]

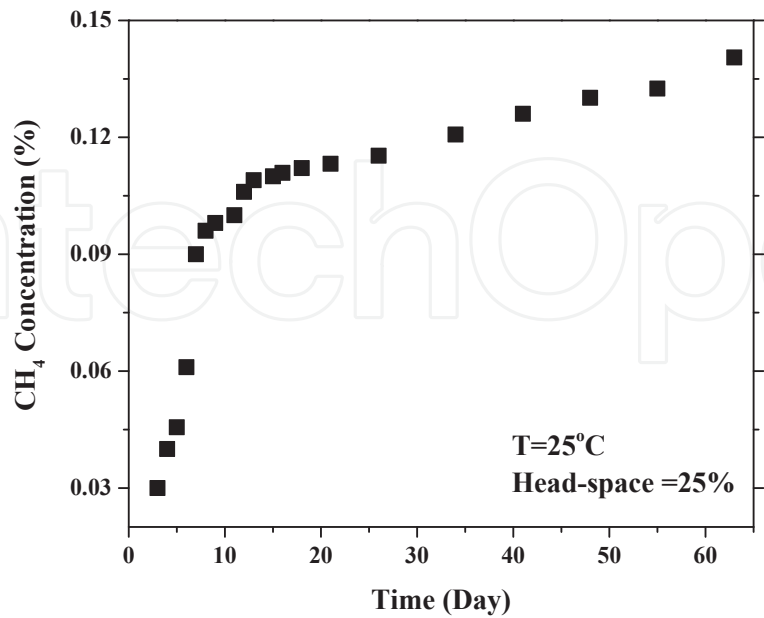


Figure 12. CH₄ concentration in head-space of the silo as a function of storage time for wood pellets. (G0 head-space gas sampling port) [Concentrations are volume percentage]

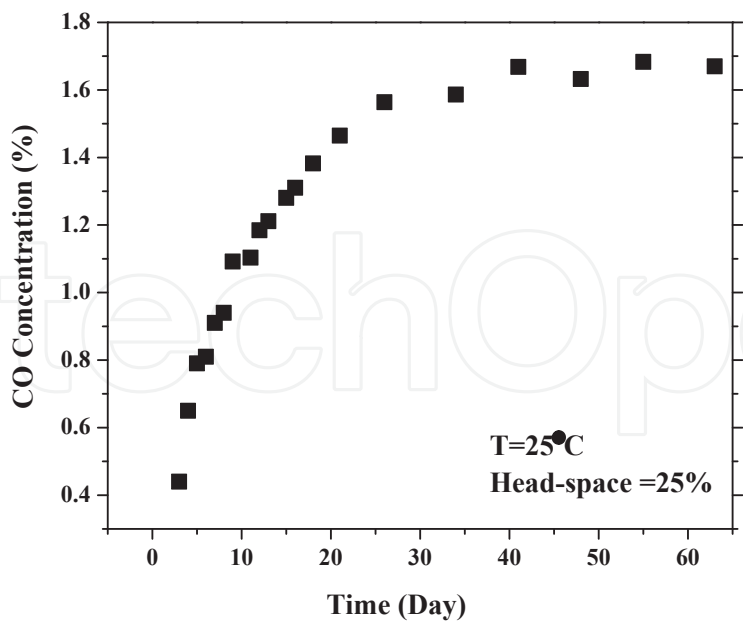


Figure 13. CO concentration in head-space of the silo as a function of storage time for wood pellets. (G0 head-space gas sampling port) [Concentrations are volume percentage]

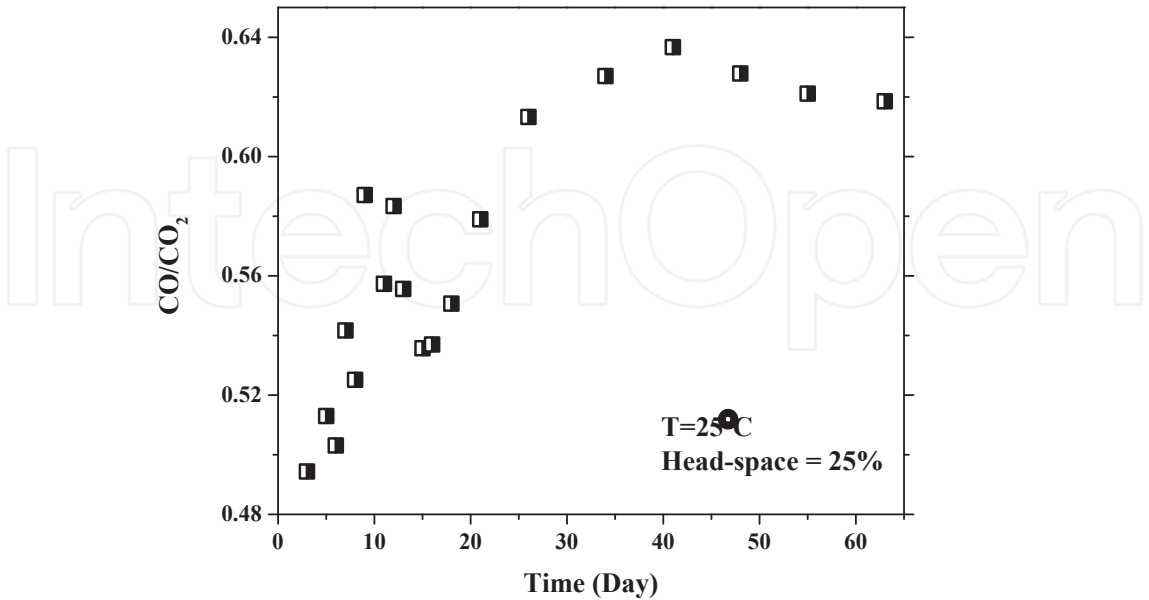


Figure 14. CO/CO₂ ratio in head-space of the silo as a function of storage time for wood pellets. (G0 head-space gas sampling port) [Concentrations are volume percentage]

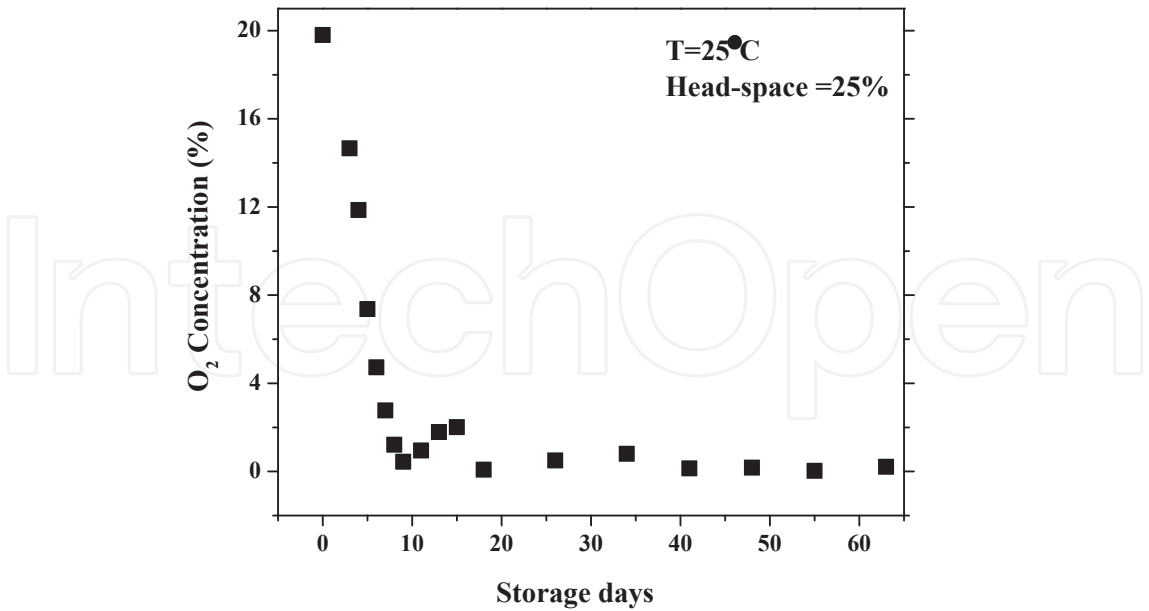


Figure 15. O₂ concentration in head-space of the silo as a function of storage time for wood pellets. (G0 head-space gas sampling port) [Concentrations are volume percentage]

The gas emissions are converted to emission factors using Eqn (1) in order to compare the results with other researchers' work on the same basis:

$$f_i = \frac{P(C_i V_g) M_{wt} C_{N0}}{RT M_p C_{Nt}} \quad (1)$$

where f_i is emission factor of species "i", C_i is the gas concentration, M_{wt} is the molecular weight (g), V_g is the gas volume (m^3), R is universal gas constant (8.314 J/mol K), T is temperature (K), P is the pressure (Pa), M_p is the mass of pellets (kg). Assuming that the amount of N_2 remains constant during off-gassing process, C_{N0}/C_{Nt} is introduced as a correction factor to balance the change in gas volume where C_{Nt} is the concentration of nitrogen measured at any time and C_{N0} is the concentration of nitrogen at the beginning of test. The gas emission results for 25% head-space are compared to those obtained by Kuang et al. [1] for the storage of wood pellets. As shown in Table 5, the peak emission factors of all three gases derived from this study (using a large pilot silo) are higher than their findings (using a small lab-scale reactor); though both sets of values are in the same order of magnitude.

Peak emission factor (g/kg)	This study (Storage volume=5200 L)	Kuang et al. [1] (Storage volume=45 L)
CO	0.0191	0.0124
CO ₂	0.0485	0.0200
CH ₄	0.0009	0.0002

Table 5. Comparison of peak emission factor for CO, CO₂ and CH₄ with previous research

Methane emission is due to the activities of anaerobic microorganisms. For instance, in a typical anaerobic digestion process for biogas production from readily biodegradable feedstock, the methane content can range from 50-70%. In this study, the CH₄ concentration was observed to increase from 0.03% to 0.14% after 9 weeks, while an oxygen deficient environment was created in the silo just a few days after the start of the test. The relatively low CH₄ contents are in line with the results of total bacteria counts, which were less than 5 cfu/g of pellets as compared to orders of magnitude higher microbial counts in a typical anaerobic digester.

5.2. 3D analysis of longitudinal distribution of emitted gases

The measured concentrations of the gases derived from all 13 gas sampling ports over time are plotted in 3D graphs and contours. The contour plots would provide a supplemental view of how the various gases are stratified in the bed. Figure 16 show the 3D and contour plots of the concentration of carbon dioxide in all locations. For the first several days, the gas concentration was quite the same for all locations. After 10 days, CO₂ concentrations were different; yet, after about 40 days, the concentrations became uniform again everywhere in the silo. The contour plot clearly illustrates that the CO₂ concentration was always higher in the head-space

compared to the other areas within the pellet bulk. CO_2 emission is more sensitive to temperature versus CO ; this could explain why higher CO_2 concentration was observed in the silo head-space. While the peak CO_2 concentration of 2.7% was reached just after 2 weeks in the head-space of silo, such a high concentration was not seen in the pellet bulk section until after 45 days. Carbon dioxide concentration was above the threshold limit value for worker safety and this limit was reached sooner in the silo head-space. In terms of worker safety, both the Occupational Safety and Health Administration (OSHA) and the American Conference of Governmental Industrial Hygienists (ACGIH) have set the permissible exposure limit (PEL) and the threshold limit value (TLV), respectively for CO_2 of 5,000 ppm (0.5%) by volume over an 8-hour average exposure.

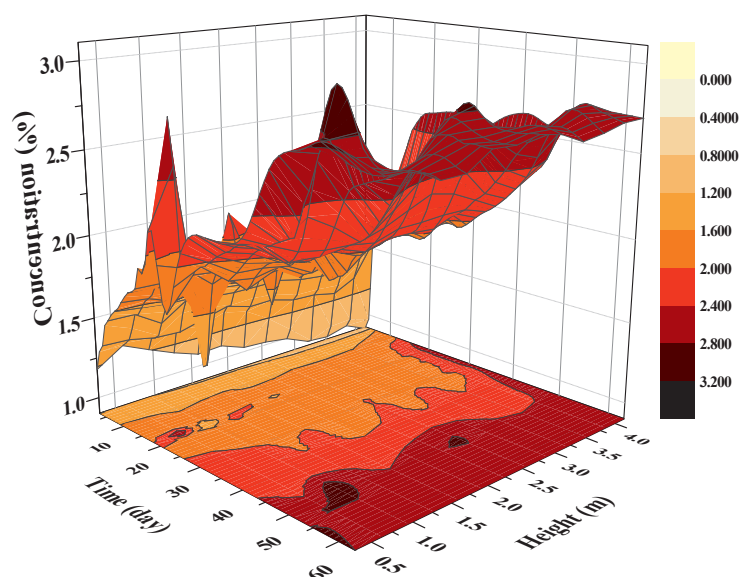


Figure 16. map of CO_2 concentration in the silo at all locations (G0 to G13) during 63 days of storage [Concentrations are volume percentage]

Figure 17 shows the overview of carbon monoxide emission, accumulation and dispersion over 63 days of storage. As distinguished from the concentration profile for carbon dioxide, a higher CO concentration was observed in the head-space of the silo at the beginning of the test, and the CO concentrations were similar in most other locations within the pellet bulk. This difference may be due to the gas dispersion phenomenon. Nevertheless, after 18 days of storage, stratification was observed with the highest concentration of CO at the G5, G6 and G7 locations (2.03-2.54 m from the bottom of the silo). Due to close value of density for air and carbon monoxide, not much gravitational stratification of CO was expected. Although carbon monoxide emissions are attributed to oxidation of unsaturated acids in wood pellets, the exact pathway through which CO is emitted hasn't been identified yet. More distinct stratification of gas was seen in this study for carbon monoxide compared to other off-gases, which could be attributed to the high uptake of CO by pellets during storage.

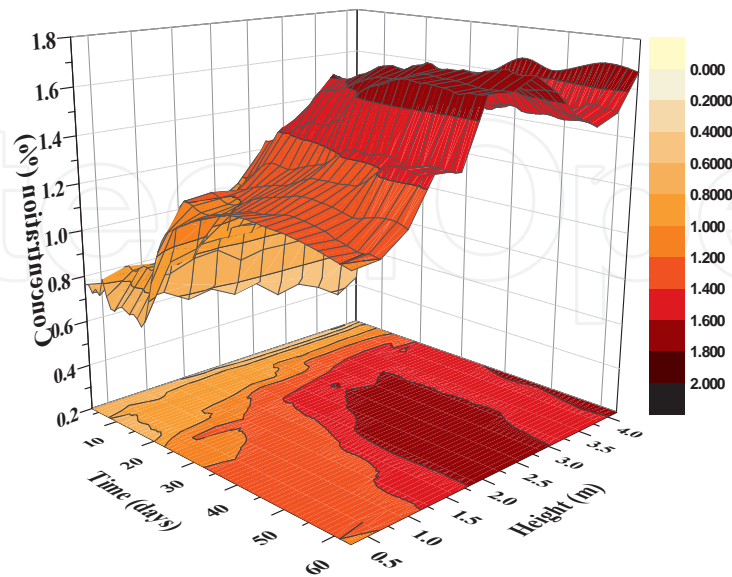


Figure 17. map of CO concentration in the silo at all locations (G0 to G13) during 63 days of storage [Concentrations are volume percentage]

Figure 18 illustrate the distribution of emitted methane (CH_4) during 63 days of sealed storage of wood pellets. After 4 days, the concentration of methane was the highest close to the bottom of the silo. Over time the emitted gas started to stratify; but after 48 days almost the same concentration was observed in all locations, with slightly higher CH_4 concentration at the upper sections of the silo near the interface of wood pellets and head-space. The same stratification was noted until the end of the test. Methane emission has a similar behavior as carbon dioxide; both gases reached higher concentrations more quickly in the head-space than in the other areas within the pellet bed.

Diffusion of gases in air and its effect on oxygen deficiency could also partly account for the created environment. Studies [23, 24] have been conducted to understand how easily the released gases (carbon dioxide, helium and sulfurhexafluoride) would mix with air and whether they would remain fully mixed. The gases were found to diffuse in air more readily than expected and modest gas velocities due to natural convection would fully mix the released gases with fresh air. In the wood pellet storage, gases were emitted over time from the first day till the gas concentrations reached a plateau. Some gas stratification was detected in the early weeks of storage especially for carbon monoxide which is due to chemical and physical adsorption between the material and the gases as well as differences in temperature and relative humidity at various levels in the silo. However after a few weeks, gases started to mix and remained mixed. In this regard, natural convection within the silo can bring about gas mixing.

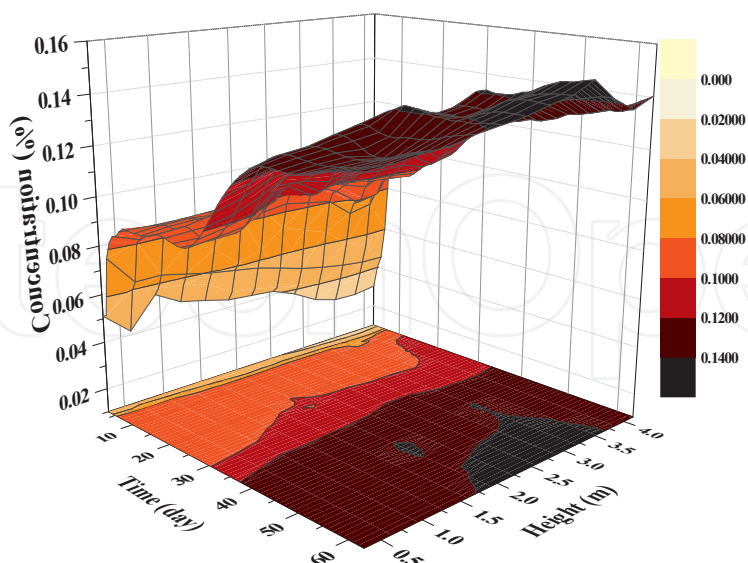


Figure 18. map of CH_4 concentration in the silo at all locations (G0 to G13) during 63 days of storage [Concentrations are volume percentage]

5.3. Oxygen depletion

Figure 19 demonstrates the oxygen depletion in the silo head-space during storage of wood pellet, which is much faster than the oxygen within the bed of wood pellets. Oxygen concentration dropped very quickly in less than 10 days of storage and this can be partially explained by the emission of carbon monoxide. Depletion of oxygen is partly related to CO formation but a greater amount could be due to the radical-induced oxidative degradation of natural lipids, particularly the polyunsaturated linoleic acid [1]. A high energy of desorption required to overcome the bond indicates chemical adsorption of oxygen to the pellets. The auto-oxidation of fatty acids starts with formation of free radicals. In the presence of oxygen, hydroxyperoxide radicals are formed and in interaction with an unsaturated fatty acid produce two hydroxyperoxides and a new free radical. When pellets stored in air, hydroxyperoxides are formed from oxidation of fatty acids. Depending on whether oxygen bond or carbon bond break in them alcoxyl radical, aldehydes, acids, hydrocarbons or ketones will be formed.

In order to examine the role of oxygen availability in the storage space on the rate of off-gassing, a set of experiments was conducted under controlled environment conditions. The same reactors described in small scale tests section were used in these experiments. Pellets were placed in 6 sealed reactors (2L by volume) that were purged with different gases. In two of the reactors pellets were stored in oxygen-free environments. When pellets were stored in an environment dominated by N_2 after purging, CO emission was as high as when pellets were stored under regular conditions. However when the reactors were purged with He (helium), the peak CO emission decreased to 25% of the values when pellets were stored under regular conditions. A hypothesis is that, although oxygen availability can accelerate the emission of

non-condensable gases, the O_2 content of the pellet material could be high enough to induce high amount of CO emission compared to pellets stored in air. Emission of carbon monoxide for pellets stored in CO_2 showed 50% less emission compared to pellets stored in air. Results obtained from stored pellets exposed to different head-space (HD) percentage showed that an increase in head-space is related to the peak emission factor for carbon monoxide and carbon dioxide with the following linear relationships (average values of two replicates each):

$$f_{CO} = 3 \times 10^{-4} [HD\%] + 0.0065$$

$$f_{CO_2} = 1.9 \times 10^{-3} [HD\%] + 0.0041$$

Oxygen concentration was also measured in all 13 locations including the head-space. Ever since the first gas sample was taken on day 2 of storage, the O_2 concentration decreased to 15% in the reactor. As seen in Figure 19, O_2 concentration was depleted rapidly to less than 5% within the first 7 days thus generating an oxygen-deficient atmosphere in a confined space. More oxygen was available within the bed of pellets compared to the head-space as a result of oxygen being trapped within the pellets until 40 days of storage when oxygen was consumed everywhere in the reactor. When oxygen levels fall below 19.5% by volume, air cannot support metabolism for an unlimited period of time. At 17% oxygen, the symptoms might simply be worse as reflected by hyper-ventilation. The oxygen-deficient atmosphere becomes more dangerous when oxygen content is further lowered to 15%; people can quickly progress to dizziness and rapid heartbeat. Finally, oxygen levels below 13% can lead to unconsciousness and eventually to death at around 6% oxygen [25].

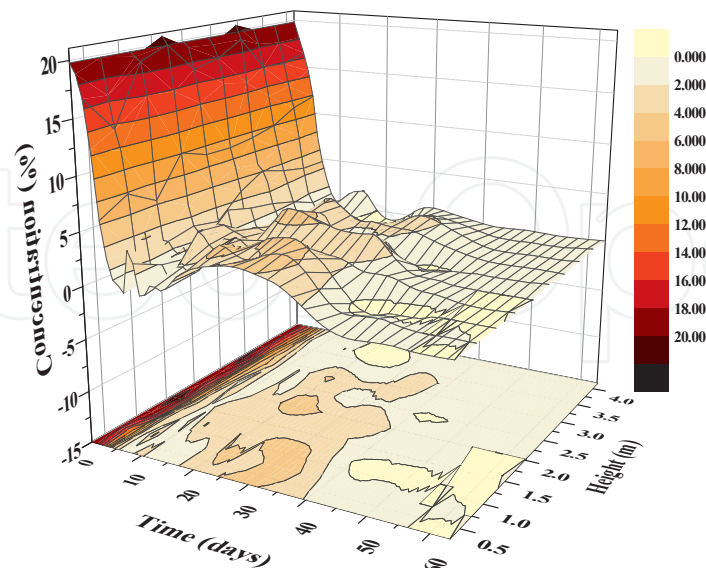


Figure 19. map of O_2 concentration in the silo at all locations (G0 to G13) during 63 days of storage [Concentrations are volume percentage]

5.4. 3D Analysis of radial distribution of emitted gases

Figure 20 shows CO₂ concentrations in the head-space and the bottom of the silo respectively. The gas concentration was measured at the same elevation but at 3 different radial positions (0.0, 0.6 and 1.2 m from the center) in order to investigate any possible radial concentration gradient. The results showed no significant variations in the CO₂ concentrations in different radial positions, due to the uniform radial temperature profile. The same measurements were made for all three gases (CO₂, CO and CH₄); again no significant differences in any of the gas concentrations were observed at different radial positions. However, Figure 20 clearly shows the difference in CO₂ concentrations along the axial locations, with the head-space concentration higher than that at the silo bottom which could be due to lower rate of mixing in the silo compared to the rate of reaction. The same observations were obtained for radial concentrations of carbon monoxide and methane over time.

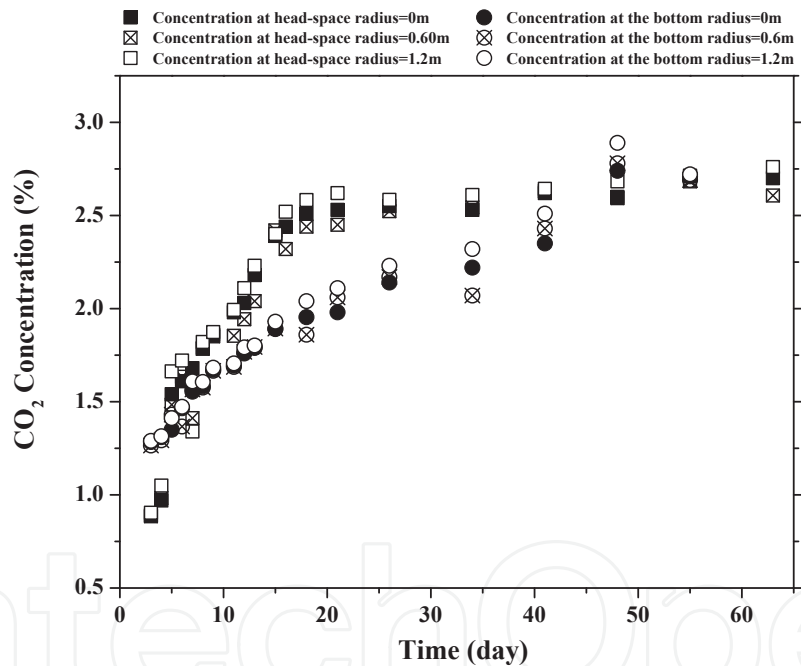


Figure 20. CO₂ concentration in the silo head-space and the bottom of the silo at different radial positions

6. Concluding remarks

The chapter has discussed various measurements of gases and volatiles, resulting data on emission concentrations and emission factors of gases in storages of wood pellets. The potential

for flammability of gases emitted from wood pellets samples with moisture contents ranging from 4 to 50% stored in environment of 25 °C to 60 °C was investigated. The gas emission for CO₂, CO, CH₄ followed exponential profiles and the gas concentration was proportional to storage temperature, as expected. For samples with less than 15% MC at room temperature, CO₂ concentration increased up to ~1.7% which was the highest peak emission compared to even pellets with 35% and 50% MC. At higher temperatures, the maximum CO₂ concentration increased from 2.8% (40 °C, 4% MC) to 5.6% (40 °C, 50% MC) and from 9.6% (60 °C, 4% MC) to 10.9% (60 °C, 50% MC). For pellets with 4 and 15% MC, the concentration of CO increased as the temperature increased from 25 °C to 60 °C. However at a constant temperature of 25 °C, the peak concentration of CO was the same for wood pellets with 4% and 9% moisture contents and lower for pellets with 15%, 35% and 50% MC. Oxygen depletion was observed among all experimental conditions but showed to decrease more rapid for pellets with 9% MC (25 °C and 40 °C) compared to wood pellets with 4%, 15%, 35% and 50% MC. Least depletion of oxygen was observed for samples at 25 °C and 50% MC and accelerated as the temperature increased. In terms of the gas mixture (CO/CH₄/H₂), at higher temperatures (40 °C and 60 °C), the gas concentration decreased as the moisture content increased. Using ISO method for estimating the potential flammability of the gases emitted from the wood pellets, it can be concluded that gas concentrations does not reach flammable concentrations within the 5-week or even the 9-week testing period.

Emission and stratification of off-gasses from storage of wood pellets was also studied in pilot scale. The focus of the study was to investigate the spatial and temporal concentration of off-gases and purging effectiveness. Emission and stratification of off-gases was studied in pilot scale storage for over one year. Non-condensable gases that emitted from storage of material were carbon monoxide, carbon dioxide, methane and hydrogen. To study the stratification of gases, analysis of gas composition was done over time for different axial and radial positions. The emitted gases showed to have higher emission factor compared to work done with white wood pellets in small scale. It could be explained by the fact that off-gassing is a surface phenomenon and thus much active surface is available for reaction when larger amount of wood pellets are stored. Concentration of gases at plateau after 9 weeks of storage was 2.7 % CO₂, 0.14% CH₄ and 1.7% CO in the reactor head-space. After a few days of storage some stratification were observed for carbon monoxide and methane. The clear stratification of carbon monoxide could be due to high uptake of CO by wood pellets over time. The unstable environment in the storage of wood pellets in the first few weeks of storage was due to very rapid consumption of oxygen in the space, reaction of emitted CO and CO₂ with pellets, development of high temperature spots within the bulk due to higher activity of pellets and thus higher local temperatures, and moisture migration within the bed. Oxygen plays an important role in accelerating the emission of carbon monoxide. Results from experiment where material was kept in oxygen-free environment (N₂-rich) confirmed the same lethal concentration of CO possibly through consuming the oxygen within the material.

Appendix A

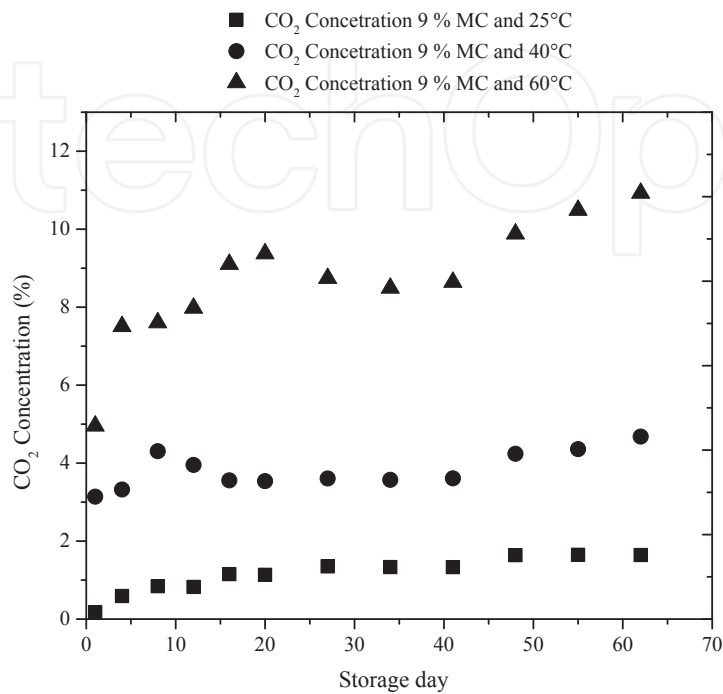


Figure A 1. Concentration of CO₂ for wood pellet with 9% moisture content over 62 days at 25°C, 40°C and 60°C

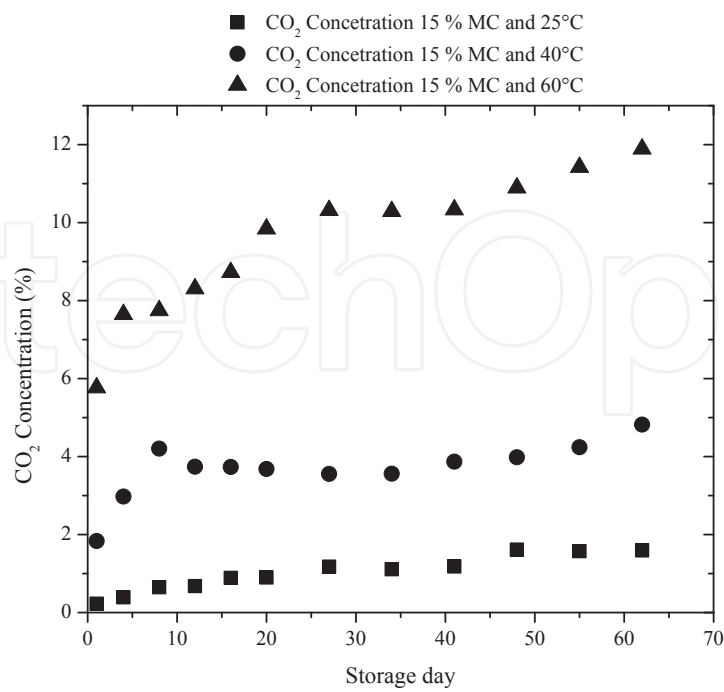


Figure A 2. Concentration of CO₂ for wood pellet with 15% moisture content over 62 days at 25°C, 40°C and 60°C

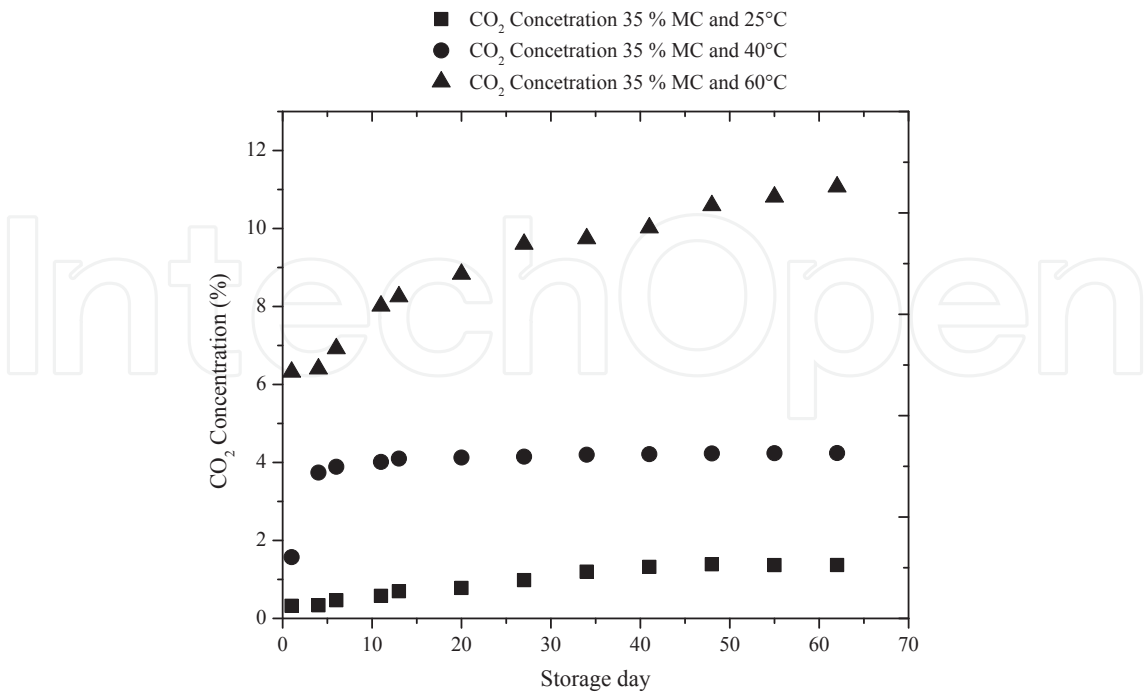


Figure A 3. Concentration of CO₂ for wood pellet with 35% moisture content over 62 days at 25°C, 40°C and 60°C

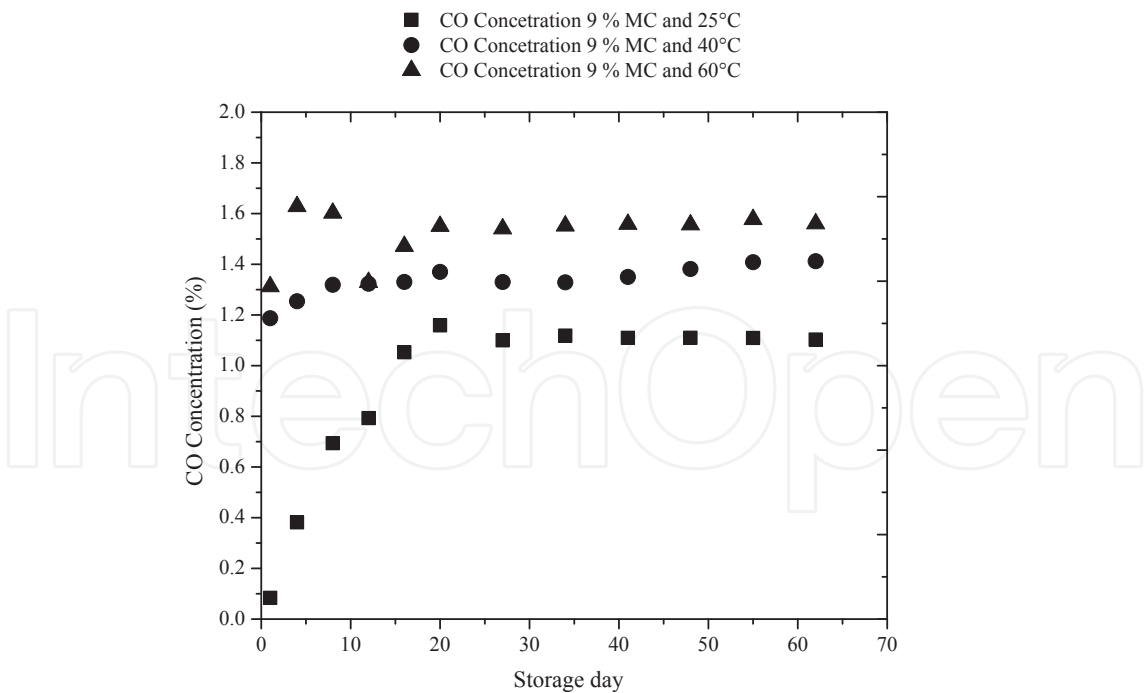


Figure A 4. Concentration of CO for wood pellet with 9% moisture concentration over 62 days at 25°C, 40°C and 60°C

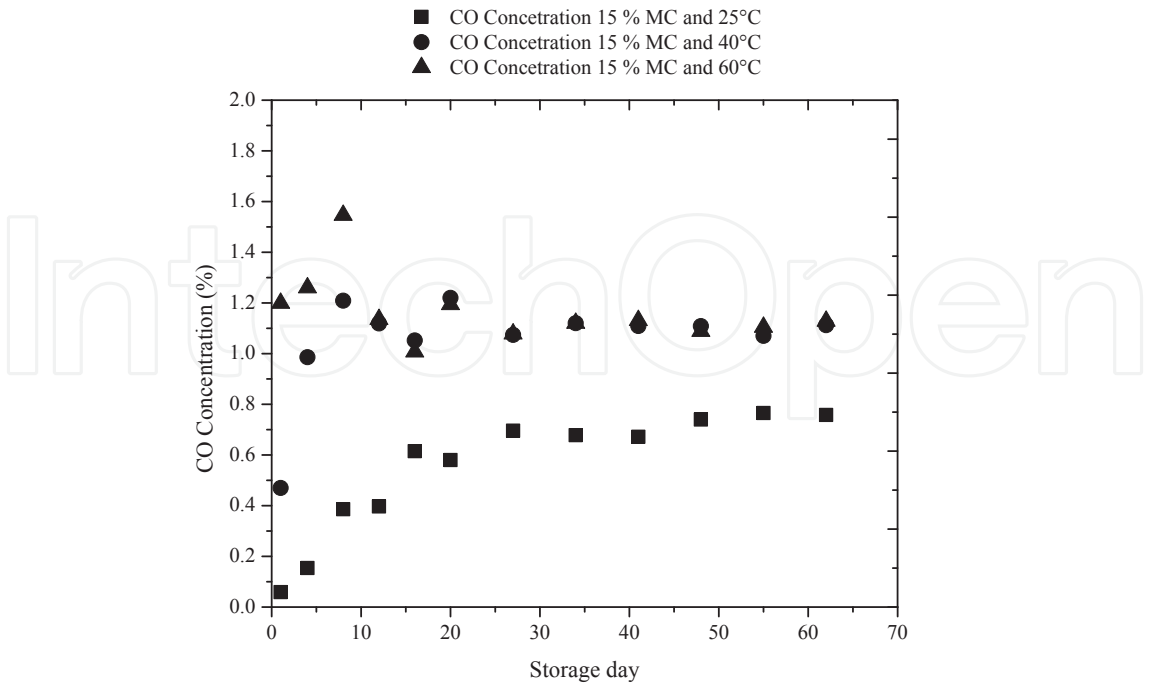


Figure A 5. Concentration of CO for wood pellet with 15% moisture concentration over 62 days at 25°C, 40°C and 60°C

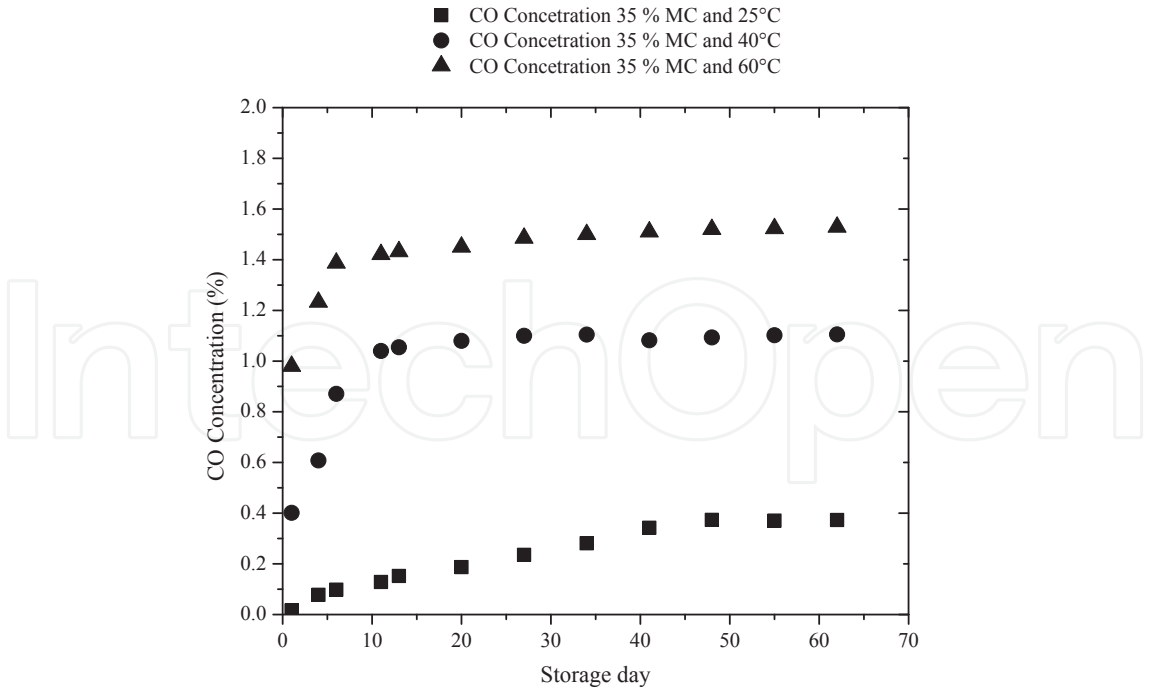


Figure A 6. Concentration of CO for wood pellet with 35% moisture content over 62 days at 25°C, 40°C and 60°C

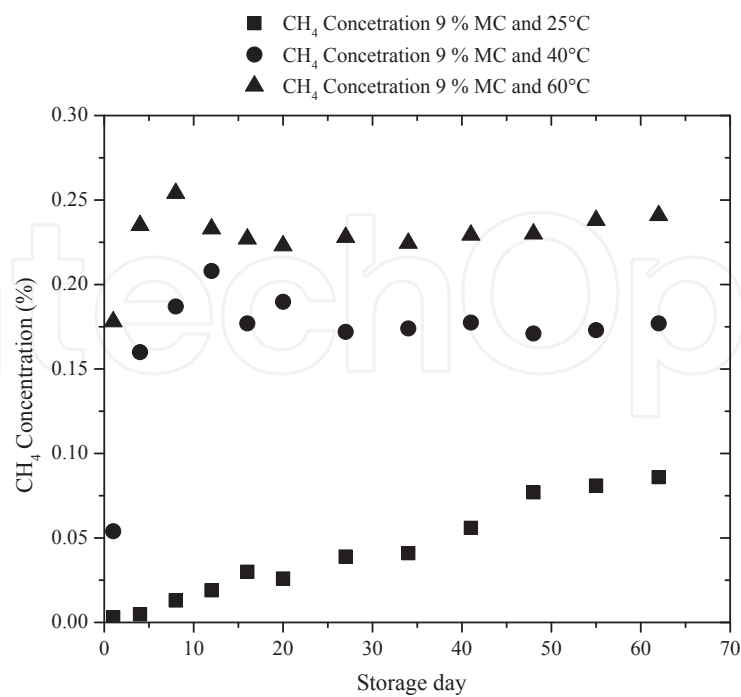


Figure A 7. Concentration of CH₄ for emissions from wood pellet with 9% moisture content over 62 days at 25°C, 40°C and 60°C

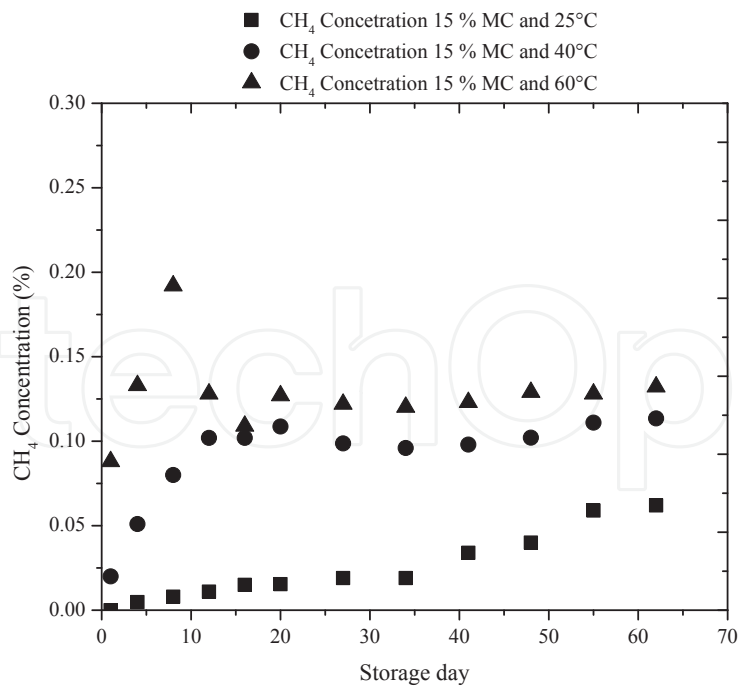


Figure A 8. Concentration of CH₄ for emissions from wood pellet with 15% moisture content over 62 days at 25°C, 40°C and 60°C

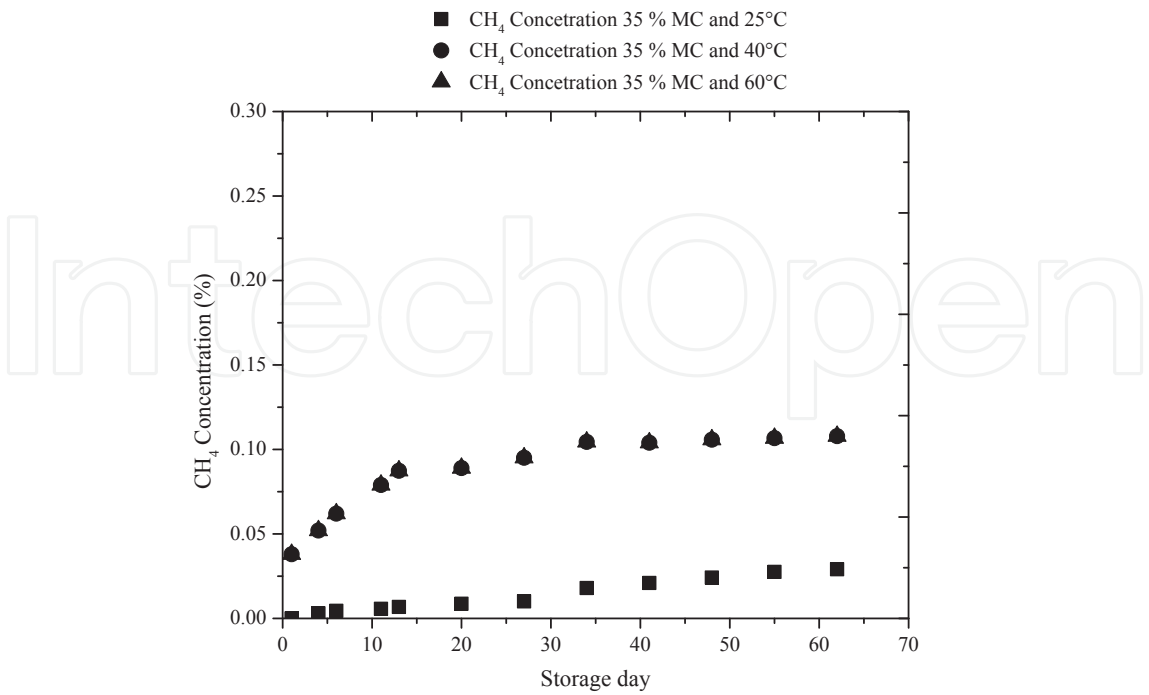


Figure A 9. Concentration of CH₄ for emissions from wood pellet with 35% moisture content over 62 days at 25°C, 40°C and 60°C

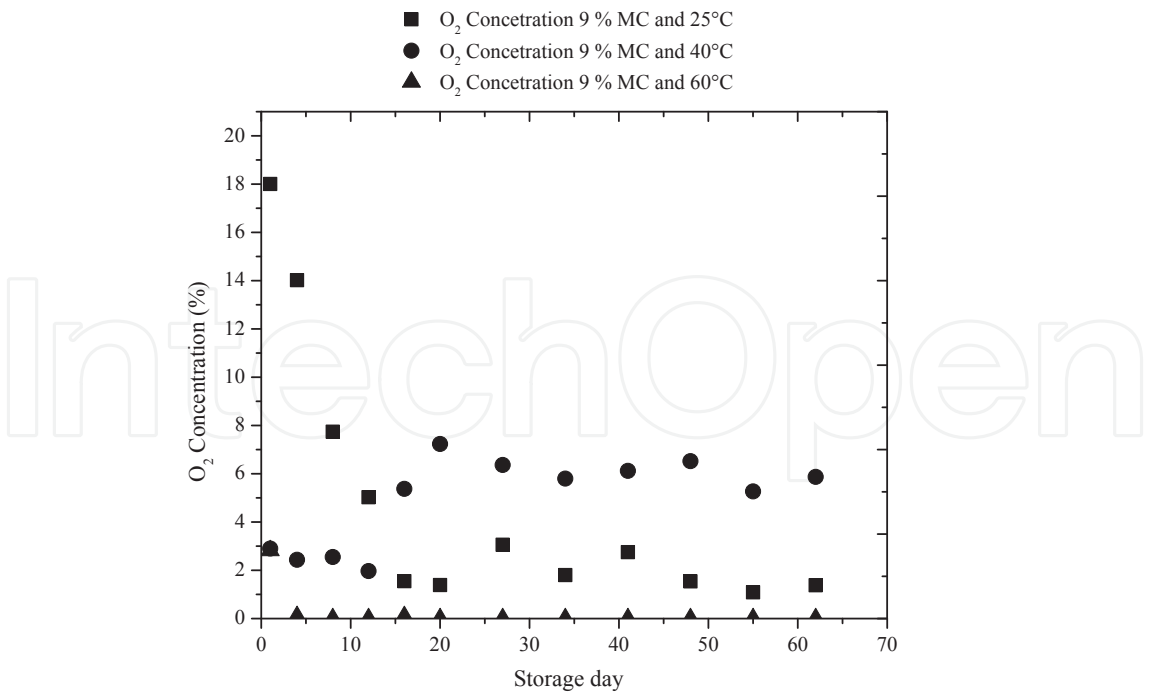


Figure A 10. Oxygen depletion for wood pellet with 9% moisture content over 62 days at 25°C, 40°C and 60°C

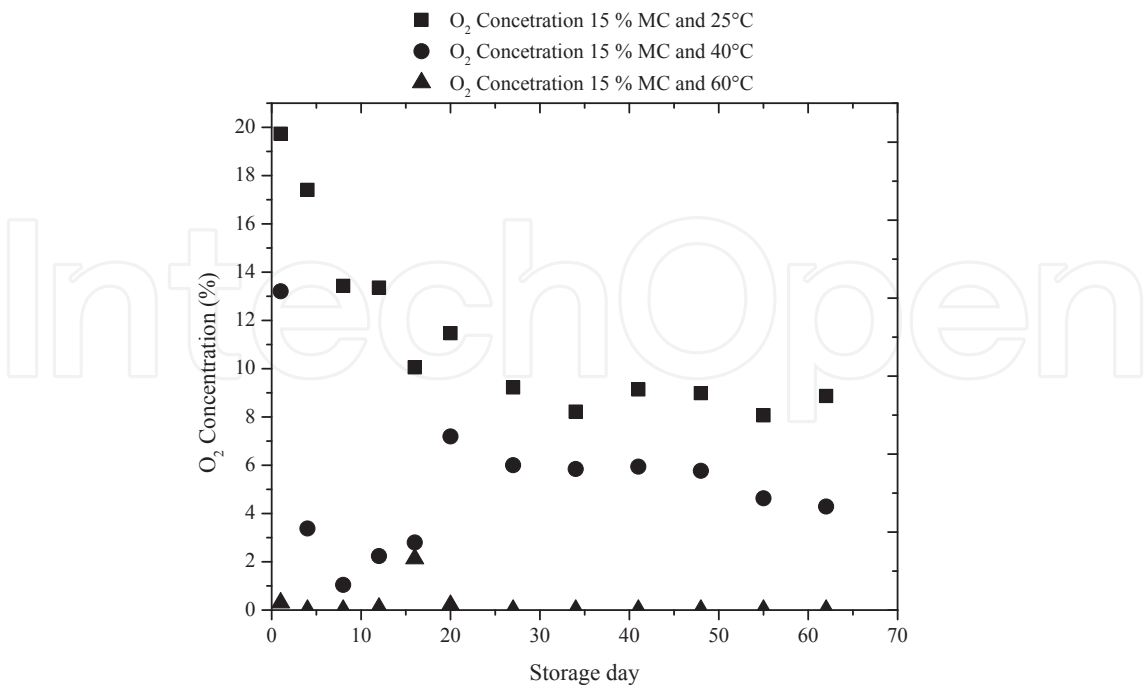


Figure A 11. Oxygen depletion for wood pellet with 15% moisture content over 62 days at 25°C, 40°C and 60°C

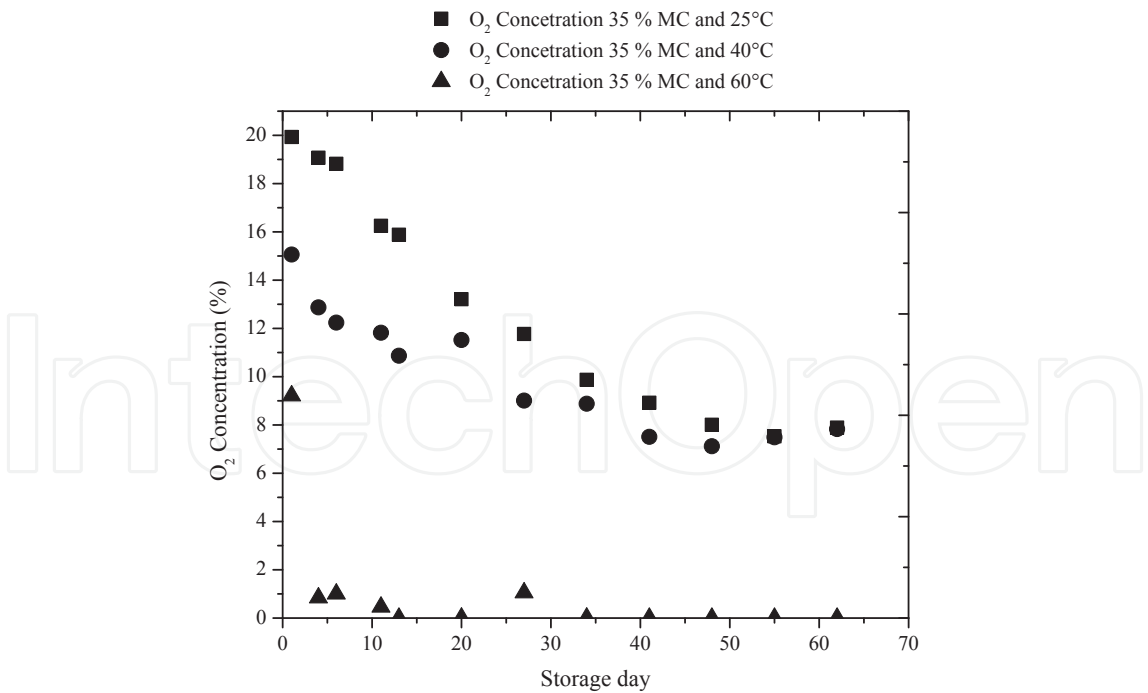


Figure A 12. Oxygen depletion for wood pellet with 35% moisture content over 62 days at 25°C, 40°C and 60°C

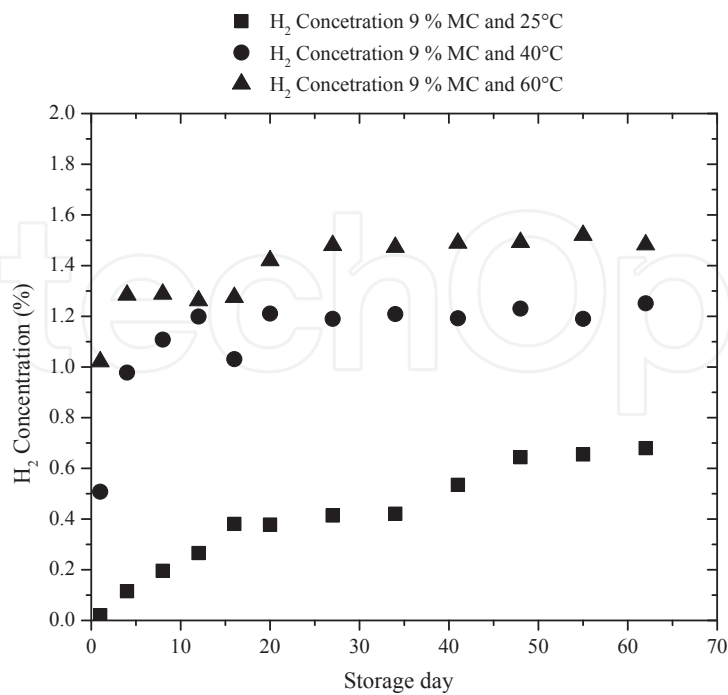


Figure A 13. Concentration of hydrogen for emissions from wood pellet with 9% moisture content over 62 days at 25°C, 40°C and 60°C

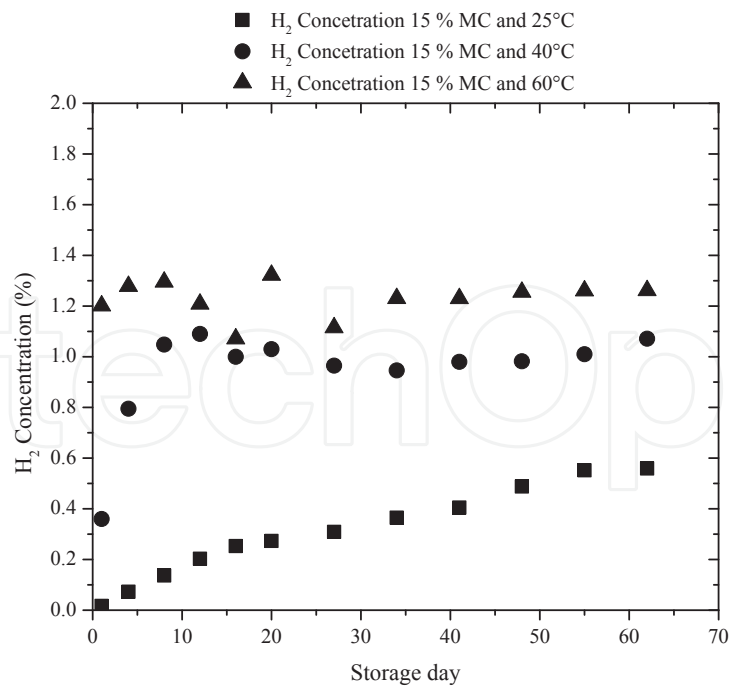


Figure A 14. Concentration of hydrogen for emissions from wood pellet with 15% moisture content over 62 days at 25°C, 40°C and 60°C

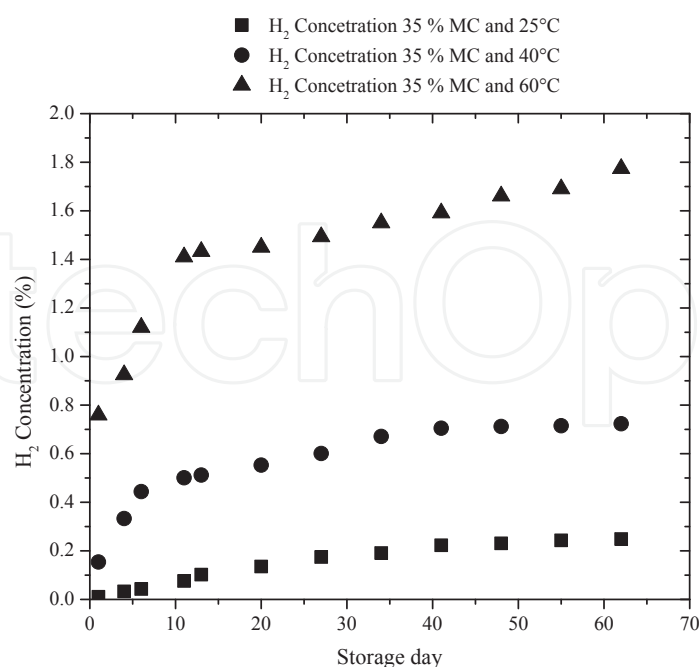


Figure A 15. Concentration of hydrogen for emissions from wood pellet with 35% moisture content over 62 days at 25°C, 40°C and 60°C

Acknowledgements

This research was funded in parts by the Wood pellet Association of Canada, Natural Sciences and Engineering Research Council of Canada and Oak Ridge National Laboratory. Thanks are also extended to Premium Pellet Ltd. and Fibreco Export Inc. and Pinnacle Renewable Energy Group, Inc. for donating wood pellets for this study.

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References

- [1] Kuang X, Shankar TJ, Bi XT, Sokhansanj S, Lim CJ, Melin S. Characterization and kinetics study of off-Gas emissions from stored wood pellets. *Ann Occup Hyg* 2008; 52: 675-683.
- [2] Tumuluru J, Kuang X, Sokhansanj S, Lim CJ, Bi T, Melin S. Development of laboratory studies on the off-gassing of wood pellets. *Canadian Biosystems Engineering* 2010; 52: 8.1,8.9.
- [3] Guo W. Self heating and spontaneous combustion of wood pellets during storage. PhD Dissertation, University of British Columbia 2013.
- [4] Hagström K. Occupational exposure during production of wood pellets in Sweden. Doctoral Dissertation 2008.
- [5] Svedberg URA, Hogberg HE, Hogberg J, Galle B. Emission of hexanal and carbon monoxide from storage of wood pellets, a potential occupational and domestic health hazard. *Ann Occup Hyg* 2004; 48: 339-349.
- [6] Arshadi M, Gref R. Emission of volatile organic compounds from softwood pellets during storage. *For Prod J* 2005; 55: 132-135.
- [7] Risholm-Sundman M, Lundgren M, Vestin E, Herder P. Emissions of acetic acid and other volatile organic compounds from different species of solid wood. *Holz Als Roh-Und Werkstoff* 1998; 56: 125-129.
- [8] Wihersaari M. Evaluation of greenhouse gas emission risks from storage of wood residue. *Biomass & Bioenergy* 2005; 28(5): 444-453.
- [9] Wihersaari M. Greenhouse gas emissions from final harvest fuel chip production in Finland. *Biomass & Bioenergy* 2005; 28: 435-43.
- [10] Manninen A, Pasanen P, Holopainen JK. Comparing the VOC emissions between air-dried and heat-treated Scots pine wood. *Atmos Environ* 2002; 36: 1763-1768.
- [11] Banerjee S. Mechanisms of terpene release during sawdust and flake drying 2001; 55: 413-416.
- [12] Roffael E. Volatile organic compounds and formaldehyde in nature, wood and wood based panels. *Holz Als Roh-und Werkst* 2006; 64: 144-149.
- [13] Rupar K, Sanati M. The release of terpenes during storage of biomass. *Biomass Bio-energ* 2005; 28: 29-34.
- [14] McGraw GW, Hemingway RW, Ingram LL, Canady CS, McGraw WB. Thermal degradation of terpene: camphene, delta-3-carenic, limonene and alfa-terpinene. *Environmental Science & Technology* 1999; 33: 4029-4033.

- [15] Granstrom KM. Emissions of Hexanal and Terpenes during Storage of Solid Wood Fuels. *For Prod J* 2010; 60: 27-32.
- [16] Melin S, Svedberg U, Samuelsson J. Emission from wood pellets during ocean transportation 2008; WPAC Research Report.
- [17] Kuang X, Shankar TJ, Bi XT, Lim CJ, Sokhansanj S, Melin S. Rate and peak concentrations of off-gas emissions in stored wood pellets-sensitivities to temperature, relative humidity and headspace volume. *Ann Occup Hyg* 2009; 53: 789-796.
- [18] Kuang X, Shankar TJ, Sokhansanj S, Lim CJ, Bi XT, Melin S. Effects of headspace and oxygen level on off-gas emissions from wood pellets in storage. *Ann Occup Hyg* 2009; 53: 807-813.
- [19] Yazdanpanah F. Evolution and stratification of off-gasses in stored wood pellets. PhD Dissertation, University of British Columbia 2013.
- [20] Tumuluru JS, Sokhansanj S, Lim CJ, Bi X, Meli S, Swaan J. Design and Instrumentation of a Large Column Container to Study the Off-Gassing, Gas Stratification and Physical Properties of Wood Pellets during Storage. ASABE Annual General Meeting 2009.
- [21] ISO 10156 Standard. Gases and gas mixtures – Determination of fire and oxidizing ability for selection of cylinder valve outlets 2010.
- [22] US. Department of Labor. Occupational Safety and Health Administration (www.osha.gov).
- [23] Carpenter TM, Fox EL. Absence of stratification and rapidity of mixing of carbon dioxide in air samples. *J Biol Chem* 1927; 73:379-381.
- [24] Theilacker JC, White MJ. Diffusion of gases in air and its affect on oxygen deficiency hazard abatement. Transactions of the cryogenic Engineering conference - CEC 2006; 51.
- [25] Koppejan J, Lönnermark A, Persson H, Larsson I, Blomqvist P, Arshadi M, et al. Health and safety aspects of solid biomass storage, transportation and feeding. IEA Bioenergy 2013.

