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La Société Canadienne de Génie Agroalimentaire et de Bioingénierie
La société canadienne de génie agroalimentaire, de la bioingénierie et de l'environnement

Paper No. CSBE15-064

Correlation between off-gas concentration and the change of net calorific value during storage

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Written for presentation at the
CSBE/SCGAB 2015 Annual Conference
Delta Edmonton South Hotel, Edmonton, Alberta
5-8 July 2015

ABSTRACT The wood pellet export from Canada to Europe has been increasing steadily in recent years (roughly 1.9 million tonnes in 2013). Due to the distances involved, wood pellets remain in transit and storage for months before their final consumption. The net calorific value (NCV) determines the price of wood pellet purchased in Europe. There have been concerns about the changes of NCV over time. In our recent study, we have showed that NCV increased by 1-2% in wet mass basis over closed storage. In this study, the correlation between the off-gasses concentrations and the NCV are presented. The significant correlation of these two variables implied that there may be adsorption of high energy content off-gasses such as methane and hydrogen onto the bulk of wood pellets during storage, which may result in increase of NCV.

Keywords: net calorific values, off-gas, wood pellets, bioenergy

INTRODUCTION Biomass materials, especially woody biomass, are accepted as relible renewable energy sources around the world. However, the low bulk density and low flowability of raw wood has hindered the wide adoption of this renewable fuel (Tumuluru et al. 2010). Since the 1970s, densification of wood particles to produce wood pellets has emerged as one of the most economically viable way to improve the transportation and handling characteristics of woody biomass (Bartok 2003). Wood pellet is a type of solid biofuel made from compacted sawdust. They are small cylinders of densified wood particles, with a standard diameter of 6 mm and length of 10 to 30 mm (ISO 17225-2 2013). Wood pellets can be used as feedstock in bio-refinery, such as biodiesel and bioethanol production (Kumar et al. 2012) and as a fuel to coal supplement or replacement in heat and/or power generation plants. The general comparison among firewood, coal and wood pellets is given in Table 1 in the context of the United States. As indicated from this table, woody biomass is superior compared to coal in terms of its low ash content and low ignition temperature. Wood pellets have added properties of having lower moisture content, high uniformity and high bulk density compared to firewood.

Mendel et al. (2012), in the book “Wood for Bioenergy” dedicated a chapter for wood pellet as it is one of the most promising biofuels currently traded in the global market. There are two grades of pellets: premium pellets with ash content less than 1 percent and standard pellets with ash content more than 3 percent ash content. Mendel et al. estimated that premium pellets represents 95% of global pellet production in year 2011. The estimate is not surprising as pellets are mainly sold for residential uses and premium pellets are preferred for residential uses in stoves and furnace due to its lower ash content.

As the shift away from fossil fuel, wood pellet is becoming an important global energy commodity to replace coal or heating oil. The consistency and uniformity of pellets allow the automation of the feed mechanism in a pellet stoves (Tumuluru et al. 2010). At the same time, wood pellets are widely used in cogeneration plants where coal and wood pellets are mixed to produce electricity and heat (Wahlund et al. 2002). Due to the ease to switch to wood pellets in existing power plants, wood pellet is crucial as part of the energy portfolio to meet the target of the Renewable Energy Action Plans or carbon mitigation programs in the European Union countries, China, Japan and South Korea (Flach et al 2013).

Table 1: Comparison between firewood, coal and wood pellets (Bartok 2003)

Parameters	Firewood	Coal	Wood Pellets
Availability	Once available in rural areas, now reliable wood supply has to be arranged.	Anthracite (Hard coal) is available in most part of USA.	Widely produced in 40-pound bags and sold through stove dealers, feed stores, and nurseries.
Cost	Its cost is highly related to number of times it is handled and the trucking distance.	Lower cost than wood due to wide availability and large production volume.	More expansive than other fuels due to the equipment and energy needed to manufacture them.
Emissions	High fly ash/particulate and creosote emission.	Higher ash content, hence more fly ash/particulate and soot than wood.	Lower moisture content, hence, lower creosote formation.
Level of Convenience	It takes time to prepare wood log, removing ash and soot from boilers and chimney.	Coal requires more frequent removal of ash than wood.	Pellets can be directly placed into pellet stoves without any extra preparation steps. They produce very small amount of ash if premium pellets are used.
Combustion Properties	It is relatively easy to ignite (at 290 °C) compared to coal.	Harder to ignite (at °500 C) than wood.	Easier to ignite than wood because it is manufactured from wood particles.

Calorific value is the expected amount of energy generated per unit weight of fuel. As wood pellet is mainly used in energy generation, the calorific value aka energy content of wood pellets dictates the amount of energy generated given a certain amount of wood pellets. It is known that coal, natural gas, petroleum, and wood pellets contain hydrogen as one of the constituents. Water (H_2O) is formed as a product of combustion when the hydrogen reacts with oxygen in the air. This water may remain in the vapour state or it may be condensed to the liquid state, giving off a substantial difference of energy. Two types of calorific value are defined to take into account this heat of combustion: the gross calorific value (GCV) corresponds to the water in the combustion products being in the liquid phase and the net calorific value (NCV) corresponds to the water product in vapour phase. The equation below shows the NCV (w.b.) as a function of measured GCV (w.b.), hydrogen X_H, oxygen X_O and nitrogen X_N contents (d.b.) and moisture content (w.b.) M.

$$\mathrm{NCV} = \mathrm{GCV} - [212 \times X_H + 0.8 \times (X_O + X_N)] \times \frac{100 - M}{100} - 24.5M \qquad (1)$$

In the wood pellet industry, NCV on “as-received” or wet basis is selected in the international standard ISO 17225-2 as the standard type of calorific value for wood pellets. In the EN-plus Certification Standard where ISO 17225-2 is based upon, it is stated that the minimum NCV on as-received basis of wood pellets shall be no less than 16.5 GJ/MT for residential uses (EN-plus A1), no less than 16.3 GJ/MT for institutional uses (EN-plus A2) and no less than 16.0 GJ/MT for industrial uses (EN B). To satisfy the EU's Renewable energy directive, in Netherlands, based on NCV of 17.8 GJ/MT or 4.9 MWh/MT wood pellets, 2.8 million metric tonnes (MT) of wood pellets are needed to meet its 10% target of 500 million GJ biomass co-firing (Flach et al. 2013).

In our study, NCV in wet basis was chosen to show graphically the combined effect of bio-chemical changes and the changes in moisture content in wood pellets during closed storage. Closed storage is defined as in-jar storage where no ventilation occurs. This setup is to simulate the storage condition in a pellet cargo ship where no ventilation is allowed in the sealed cargo hold to prevent increase in the moisture content of wood pellets.

Off-gassing measurement was performed in parallel to the measurement of calorific value. The concentration of off-gasses represents the bio-chemical reactions that occurs on the wood pellets during the storage experiment. Correlation coefficients between concentrations of four off-gasses: carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), and hydrogen (H_2), as well as oxygen (O_2) are calculated to draw insights on the bio-chemical reaction occurs during closed storage that resulted in the changes in NCV.

METHODOLOGY

Experimental design The experimental design involves a full factorial design of two factors, which are pellet types (two categories), and storage temperature (three levels). The two categories of pellet types are white wood pellet and mixed wood pellets, which will be described in next paragraph. The three temperature levels are 25°C, 35°C and 45°C. These temperature levels are selected because they represent the storage temperatures during the ocean transportation from British Columbia, through the tropical region of Panama Canal to Europe. In the tropical regions, the average day temperatures are up 33°C (INEC Panama 2014). There, the storage temperature in a cargo hold can reach up to 50 °C during a sunny day due to heat accumulation.

The two types of pellets are received from Pinnacle Renewable Energy (PRE) Inc, the largest pellet producers in Canada; they are 10% bark pellets (“white pellets”) and 40% bark pellets (“mixed pellets”). The white pellets and mixed wood pellets used in the experiment were manufactured at the PRE Inc. pellet plants in Williams Lake and Burns Lake, BC. Two types of pellets, which are representative of the majority of pellet exported by PRE Inc., were selected to observe their differences in pellet properties during storage. In this study, we focus on two pellet properties: net calorific value and off-gas concentration. The pellets were four days old after production when sampled and shipped to the University of British Columbia (UBC) campus in Vancouver, BC.

The mason jars are filled with roughly one-kilogram wood pellets, which were subjected to three temperature conditions. One set was placed on a table in the laboratory (25±2°C throughout the test period). The other two sets were placed in two ovens with temperature set at 35 and 45^{o}C, respectively.

The three samples of wood pellets were withdrawn weekly in the first month, and bi-weekly for the next two month for calorific value measurement. Ten mason jars were used in this study for each pellet type. Figure 1 pictures an example of closed storage.

Figure **Erreur ! Il n'y a pas de texte répondant à ce style dans ce document.**1: An example of closed storage. The label indicates the temperature level, pellet type and the jar number. In this case, it is 35°C, white pellet (denoted as "A"), jar number 10.

Offgassing method The off-gassing tests for both samples were conducted at three nominal temperatures of 25°C, 35°C and 45°C. Room temperature provided the 25°C storage environment. Two identical temperature controlled chambers were used to provide 35°C and 45°C storage environments. For each temperature, two empty containers were used for temperature measurement. The temperature inside the containers was measured with thermocouples and data were 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.

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 analysed by GC/FID (Flame Ionization Detector) and GC/TCD (Thermal Conductivity Detector) methods for the composition of the sampled gases (CO, CO_2, CH_4, N_2, O_2 and H_2). 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, CO_2 and CH_4 and the TCD was used for N_2, O_2 and H_2, 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 (CO_2), methane (CH_4), oxygen (O_2), nitrogen (N_2), hydrogen (H_2) and helium (He). 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.

Sampling events continued for 12 weeks of storage. As the trend of off-gassing profiles were known (Kuang et al. 2008, Yazdanpanah et al, 2013 and 2014), less frequent sampling intervals were chosen to avoid depletion of the gas inside the containers.

Emission factor, f_i (in off-gas species per kilogram of pellets), for gas species i is calculated using equation 2 as given in Kuang et al. (2009).

$$f_i = \frac{P(C_i V_g) M_{wt}}{RTM_p} \frac{C_{n0}}{C_{nt}} \quad (2)$$

Where C_{n0} is the initial concentration of N_2, C_{nt} is the measured concentration of N_2 at time t, M_p is the total mass of wood pellets in container calculated by N_2 balance method, and M_{wt} is the molecular weight of the gas species. V_g is the gas volume in the container volume (V) and pellets volume (V_p). P is gas pressure. The volume occupied by pellets (V_p) was calculated based on weight of pellets divided by the average density of a single pellet. The density of a single pellet is calculated as the average values of the weight of single pellets divided by the volume of single pellets. Volume is calculated from measuring diameter and length of the cylindrical pellet.

RESULTS AND DISCUSSION As shown in Figure 2, NCV of wood pellets appears to increase after 3 months or 12 weeks of closed storage. In white pellets, there are no apparent difference between the NCV of pellets stored at different storage temperatures. In fact, their moisture contents stayed relatively constant in the range of 2.6% to 2.8% (w.b.) throughout the storage period. That was not the case for mixed pellets. Their final moisture contents were 5.9±0.1% for 25°C, 4.6±0.3% for 35°C and 4.5±0.3% for 45°C. The effect of moisture content on calorific value is clear in mixed pellets where pellets stored at 25°C showed lower final NCVs and higher final NCVs were observed for pellets stored at 35°C and 45°C. Nevertheless, the NCVs of mixed pellets were higher than its initial value.

Figures A-1 to A-4 showed the off-gas concentration of carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and hydrogen (H_2) for white pellets and mixed pellets. The trend of oxygen (O_2) depletion is also shown in Figure A-5. The trends of the increase in CO, CO_2, CH_4 and H_2 were very similar to the increasing trend of net calorific value of the wood pellets (NCV). The concentrations of these off-gasses increased on the first 20 days of the storage and plateaued roughly after 20 days. This trend corresponds to a similar increase in NCV over the first 20 days. The NCVs of CH_4 and H_2 is 50 MJ/kg and 120 MJ/kg (Biomass Energy Data Book, 2011). This strongly suggests the adsorption of these high calorific gases onto the wood pellet inner structure, which may increase the overall NCV of wood pellet. Another observation was that the concentrations of CO, CH_4 and H_2 appear to be independent of storage temperature.

The concentration of CO_2, on another hand, is strongly dependent on the storage temperature, where highest CO_2 concentration was observed at lower storage temperature.

Tables A-1 and A-2 shows the final volumetric concentrations and emission factors of off-gases. The emission factors of off-gasses are comparable to previous studies (Kuang et al. 2008 and 2009).

In a previous study (Lee et al. 2015), we stipulated that the auto-oxidation reactions, which occurred on the wood pellets, have produced in high energy compounds, such as methane and hydrogen gases. In the attempts to rationalize the increase in calorific value over storage, the correlation coefficients between concentrations of off-gasses and the NCVs are calculated. Table 2 shows the results of the correlation analysis.

At 25°C (white pellets), the correlation between NCV and the concentrations of off-gasses are statistically significant, with Pearson correlation coefficient of equal or more than 0.9. At 35°C (white pellets), the correlation coefficients decreased to about 0.7-0.8; the correlation coefficients further decreased to the range of 0.5 and 0.6 at 45°C (white pellets). For mixed pellets, the correlation coefficients of NCV and the concentrations of off-gasses are in the range of 0.6 to 0.8. The lower correlation coefficients are likely due to the fluctuations in the NCV data.

The authors aware that correlation does not imply causation. However, it may be stipulated that the reactions that produces the off-gasses resulted in the increase in calorific values. The results from this correlation analysis implied that there may be adsorption of methane and hydrogen onto the wood pellets which may result in an increase in calorific value.

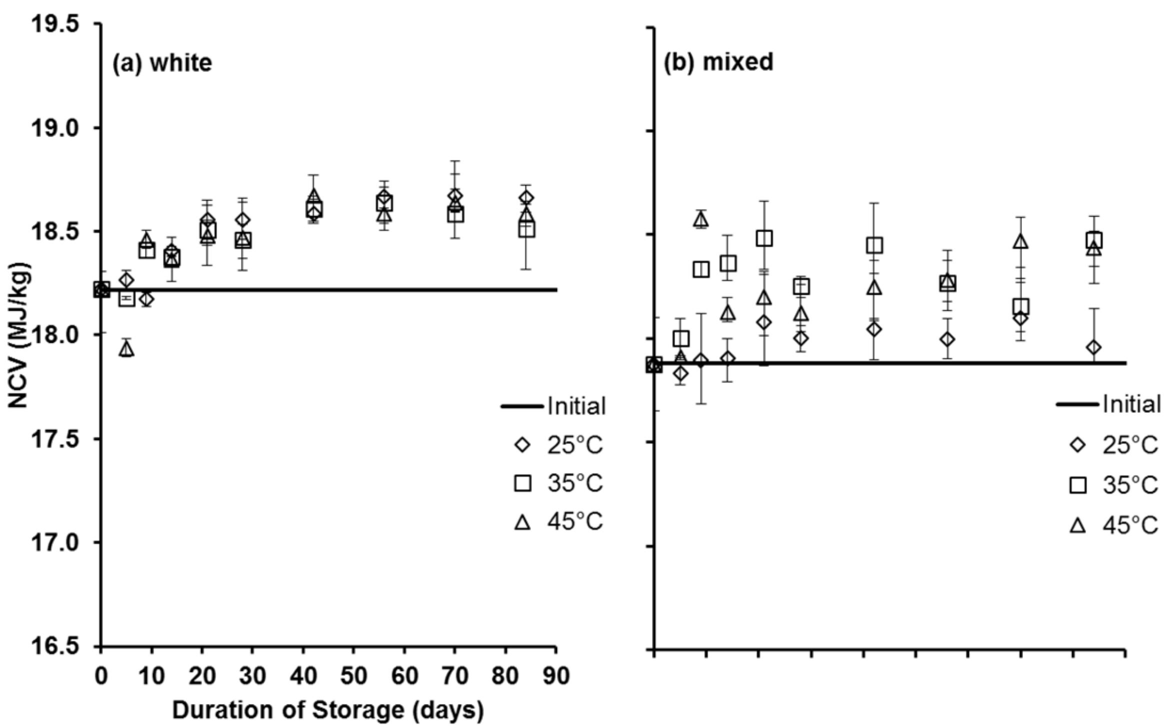

Figure 2: Graphical depiction of the change of NCV at wet basis over closed storage for (a) white pellets and (b) mixed pellets. The error bars give the minimum and maximum values of NCV. The figures is a modified version of Lee et al. (2015).

Table 2: Pearson correlation coefficient (R values) between NCV (w.b.) and (d.b.) and the concentration of off-gasses (CO2, CO, CH4, O2, and H2).

White 25°C	NCV (w.b.)	NCV (d.b.)
CO2	0.92	0.93
CO	0.90	0.91
CH4	0.95	0.96
O2	-0.95	-0.96
H2	0.93	0.92

Mixed 25°C	NCV (w.b.)	NCV (d.b.)
CO2	0.75	0.59
CO	0.74	0.55
CH4	0.7	0.62
O2	-0.77	-0.59
H2	0.7	0.6

White 35°C	NCV (w.b.)	NCV (d.b.)
CO2	0.86	0.82
CO	0.70	0.64
CH4	0.90	0.86
O2	-0.78	-0.75
H2	0.92	0.89

Mixed 35°C	NCV (w.b.)	NCV (d.b.)
CO2	0.77	0.63
CO	0.81	0.69
CH4	0.79	0.69
O2	-0.71	-0.62
H2	0.73	0.61

White 45°C	NCV (w.b.)	NCV (d.b.)
CO2	0.71	0.60
CO	0.51	0.48
CH4	0.62	0.59
O2	-0.62	-0.54
H2	0.77	0.68

Mixed 45°C	NCV (w.b.)	NCV (d.b.)
CO2	0.71	0.63
CO	0.57	0.43
CH4	0.75	0.65
O2	-0.61	-0.37
H2	0.71	0.71

CONCLUSION From this laboratory scale experiment, we may conclude that the calorific value of wood pellets is likely to increase if they are stored under a closed environment with minimal ventilation. Correlation between off-gas concentration and calorific value is clear. To establish their relationship, further experiments on adsorption of off-gasses have to be performed.

NOMENCLATURE

d.b. = dry mass basis

MT = Metric tonne

w.b. = wet mass basis

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APPENDIX A: Additional graphical information

Table A-1: Final volumetric concentrations and emission factors for CO_2, CO, CH_4 and H_2 at different temperatures for white pellets.

White pellets	Volumetric concentration (%v/v)			Emission Factors (g/kg)		
Gas species	25°C	35°C	45°C	25°C	35°C	45°C
CO2	0.952	2.102	4.280	2.083	4.420	8.764
CO	1.270	1.231	1.419	1.768	1.647	1.849
CH4	0.032	0.029	0.027	0.025	0.022	0.020
H2	0.739	0.760	0.642	0.588	0.581	0.478

Table A-2: Final volumetric concentrations and emission factors for CO_2, CO, CH_4 and H_2 at different temperatures for mixed pellets.

Mixed pellets	Volumetric concentration (%v/v)			Emission Factors (g/kg)		
Gas species	25°C	35°C	45°C	25°C	35°C	45°C
CO2	1.424	2.490	4.905	3.681	6.253	12.017
CO	1.151	1.330	1.316	1.894	2.124	2.051
CH4	0.027	0.026	0.029	0.025	0.024	0.025
H2	0.710	0.710	0.653	0.667	0.648	0.582

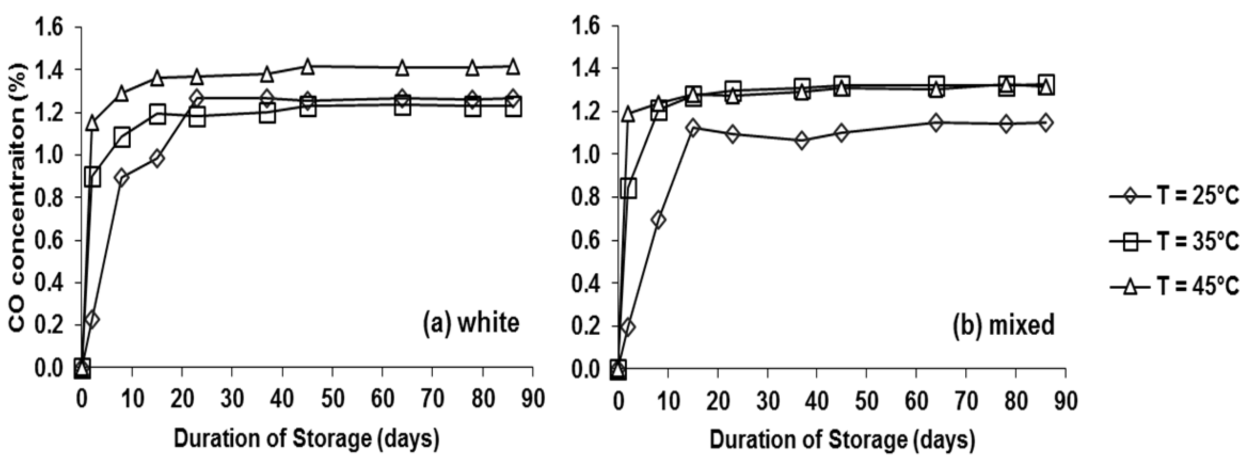

Figure A-1: CO concentration (%v/v) at three temperature levels (25, 35 and 45 °C) for (a) white pellets and (b) mixed pellets.

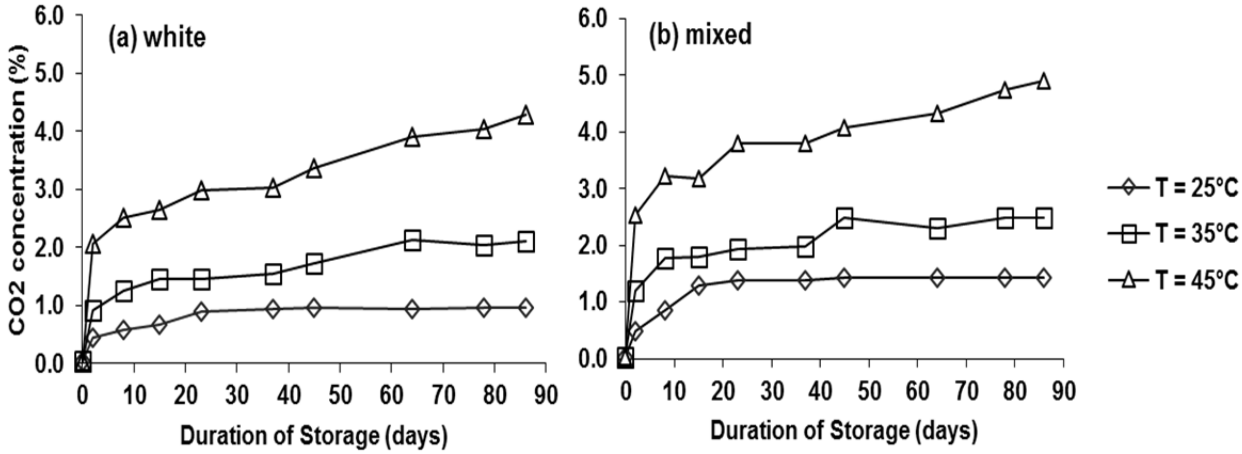

Figure A-2: CO_2 concentration (%v/v) at three temperature levels (25, 35 and 45 °C) for (a) white pellets and (b) mixed pellets.

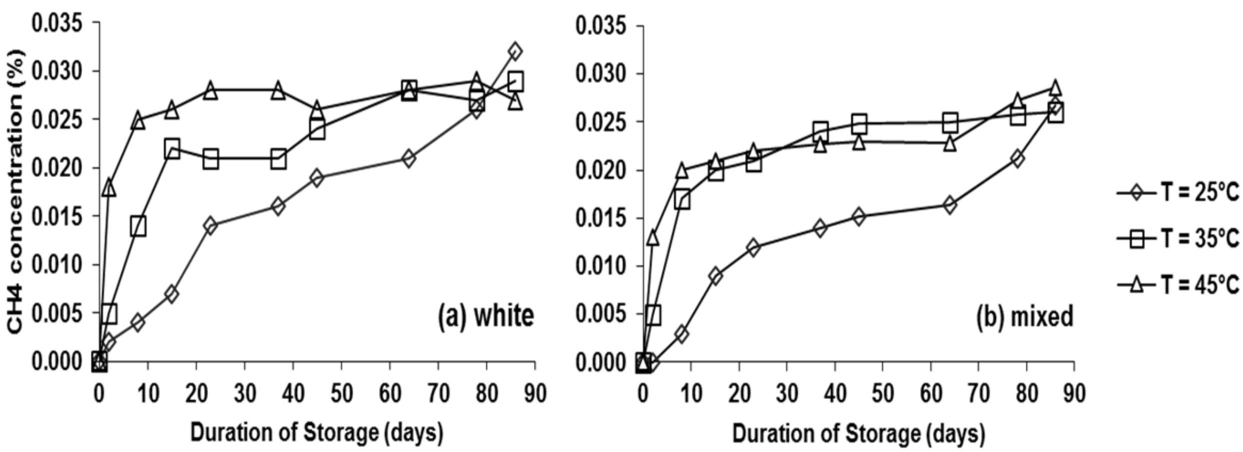

Figure A-3: CH_4 concentration (%v/v) at three temperature levels (25, 35 and 45 °C) for (a) white pellets and (b) mixed pellets.

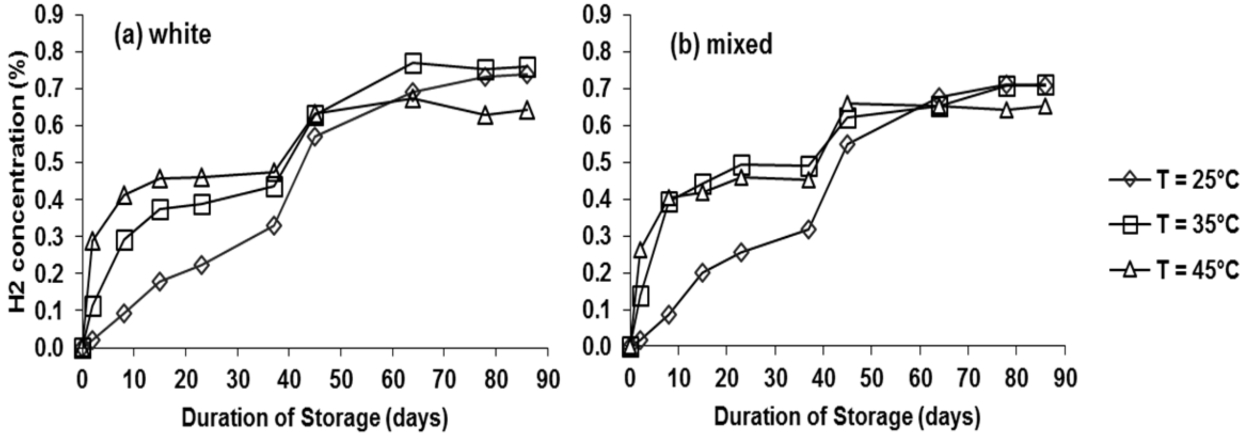

Figure A-4: H_2 concentration (%v/v) at three temperature levels (25, 35 and 45 °C) for (a) white pellets and (b) mixed pellets.

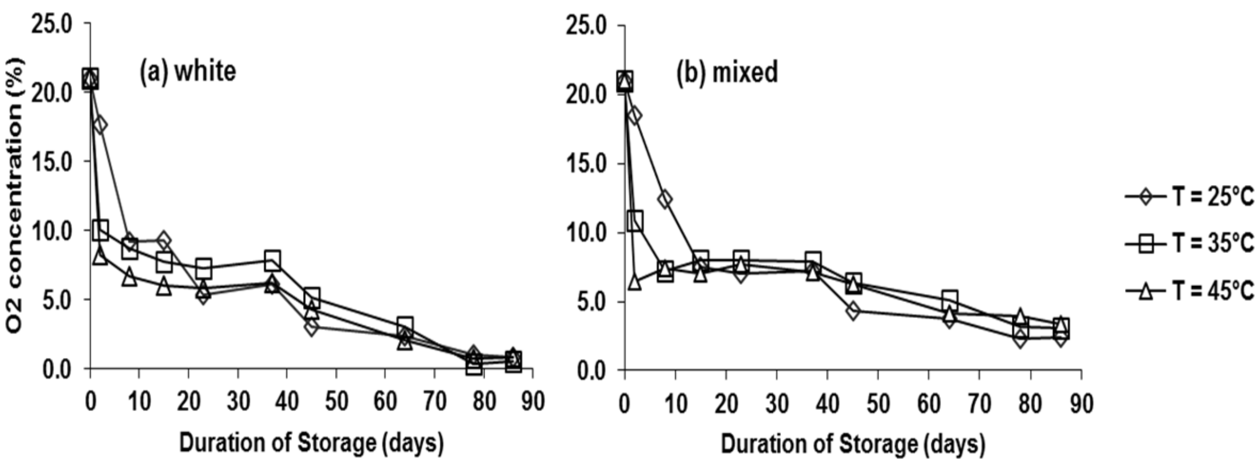

Figure A-5: Oxygen depletion (%v/v) at three temperature levels (25, 35 and 45 °C) for (a) white pellets and (b) mixed pellets.