Article

Understanding Off-Gassing of Biofuel Wood Pellets Using Pellets Produced from Pure Microcrystalline Cellulose with Different Additive Oils

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Abstract: Fuel wood pellets have the tendency of undergoing self-heating and off-gassing during storage and transportation. Self-heating can lead to spontaneous combustion and cause fires while toxic gasses such as carbon monoxide and some volatile organic compounds released due to off-gassing are a human health and environmental hazard. Previous research suggests that the self-heating and off-gassing of wood pellets are as a result of the oxidation of wood extractives. The aim of this study was to identify the extractives, i.e., fatty and resin acids that are responsible for the emissions of carbon monoxide, carbon dioxide and methane from wood pellets by testing the off-gassing tendencies of pellets produced from synthetic microcrystalline cellulose and different additive oils. The additive oils were intentionally selected to represent different types of wood extractives (mainly fatty and resin acids) and they included: tall oil, pine rosin, linseed oil and coconut oil. The highest mean concentrations of carbon monoxide, carbon dioxide and methane were recorded from cellulose pellets with added linseed oil. The concentrations of carbon monoxide and methane for the other four pellet types were negligible and there was no carbon dioxide emission. Pellets with added linseed oil had high off-gas emissions due to the high content of unsaturated fatty acids compared to other pellet types.

Keywords: off-gassing; cellulose pellets; additive oils; fatty and resin acids; solid biofuels; wood pellets; self-heating

1. Introduction

The need to replace fossil based energy, chemicals and material products with renewable and sustainable sources has accelerated the development of various bioenergy products including; solid, liquid and gaseous fuels, platform chemicals and polymers [1–4]. One such bioenergy product which has gained wide usage in Europe and other parts of the world is fuel wood pellets [5,6]. Europe is the largest consumer of fuel wood pellets, its demand in 2018 was 27.35 million tonnes and was expected to increase by 30–40% between the years 2021 to 2026 [7].This demand comes from both small-scale household use in small furnaces as well as commercial combined heat and power (CHP) plants.

Wood pellets are a solid biomass fuel of choice for heat and power generation because, unlike loose residual solid biomasses, wood pellets are a standardized product with known properties and quality. Their desirable properties include: high transport and energy storage density, high heating value, low ash content and they are not easily degraded by microbiological activities [8,9]. However, wood pellets have the tendency of

undergoing self-heating and off-gassing during storage, and this poses a challenge to their long-term storage and long-distance transportation. Self-heating can lead to spontaneous combustion and cause fires [10–13] while toxic gasses such as carbon monoxide and some volatile organic compounds released due to off-gassing [14–17] are a human health and environmental hazard.

Woody biomasses, i.e., wood sawdust and other forestry industrial residues that are subjected to pelletization, are polymeric composites consisting of primarily cellulose, hemicelluloses and lignin (about 90–95%) and low amounts (5–10%) of a large variety of low molecular mass non-structural components, extractives. Depending on their chemical character, extractives can be classified into terpenes and terpenoids, fats and waxes, phenolic compounds and carbohydrates [18]. The differences in terms of composition and chemical structures of the three primary components; cellulose, hemicelluloses and lignin are smaller among different biomass categories compared with the great diversity in extractive composition [19–21]. Therefore, although extractives are low in concentration, they chemically characterize lignocellulosic biomasses. Singularly, cellulose is the major chemical component in woody biomass occupying 40–50% of the total dry weight. It is also the most thermally and chemically stable of all the wood chemical components. This is because of its highly crystalline structure which is made up of linear long chain microfibrils consisting of β-D-glucopyranose monomers linked by glycosidic bonds [22]. Wood extractives on the other hand are the most vulnerable to chemical and thermal degradations due to their low molecular weight and chemical diversity.

It has been reported in literature that the self-heating and off-gassing of wood pellets and other biomass materials is due to oxidation of the extractives [23,24]. However, self-heating is also known to occur in store piled carbonaceous materials such as coal that do not contain extractives in a traditional sense [25,26] and in stored agricultural crops like maize, wheat and soybeans with very low amounts of extractives [27]. Self-heating has also been reported to occur in cellulosic materials like cotton when impregnated with drying oils such as linseed oil [28]. Studies have shown that there is a direct relationship between off-gassing and self-heating of wood pellets. In the methods correlation analysis [29], there was significant correlations between self-heating determined by isothermal calorimetry and off-gassing by the offline and glass flask methods with the correlations of determination (R^2) of 0.84 and 0.83 respectively. This showed that self-heating and off-gassing occur at the same time or are influenced by the same factors. Therefore, considering this direct relationship between self-heating and off-gassing and the occurrence of self-heating in materials other than the wood pellets, there is a likelihood that the heat generation and gas emissions in wood pellets may be due to reactions of other wood chemical components and not just the extractives. In this regard, studying the off-gassing and/or self-heating tendencies of pellets made from isolated wood chemical components can help in understanding the reaction mechanisms and identify the chemical components involved in the self-heating and off-gassing of wood pellets.

In the study of the off-gassing tendencies of fuel wood pellets produced from Scots pine sawdust with different amounts of extractives, Siwale et al. [30], concluded that the off-gassing of carbon monoxide and carbon dioxide was mainly dependent on the type of extractives present in the raw material and not the total amount. Increasing the amount of extractive in the raw material by 5% did not result in increased off-gassing of the wood pellets. Attard et al. [31] further showed that using fat-free sawdust reduced the pellets' off-gassing by 80% compare to ordinary wood pellets. Other studies have also reported the oxidation of wood extractives (mainly fatty and resin acids) to be the possible cause of self-heating and off-gassing of wood pellet [32–34]. However, there are still some questions about the mechanisms behind the heat and gas generation during storage of fuel wood pellets.

In the literature, not so many studies have focussed on the effect of different types of extractives on self-heating and off-gassing of wood pellets, and no study has been reported to have used pellets made from isolated wood chemical components. The use of pure

chemical substances such as cellulose can eliminate the effect of other wood chemical components, i.e., hemicelluloses and lignin. The objective of this study was to test the off-gassing tendencies of pellets produced from synthetic microcrystalline cellulose with different types of representative additive oils. The aim was to identify some of the specific types of extractives, i.e., fatty and resin acids responsible for the off-gassing of fuel wood pellets. Identifying the specific extractives involved and fully understanding the reaction mechanisms can be applied to raw material pre-treatment measures with the view of producing wood pellets that are not liable to off-gassing and self-heating.

2. Materials and Methods

2.1. Raw Materials

The materials used in this study were synthetic pure cellulose powder and four different additive oils. The additive oils were intentionally selected to represent different types of wood extractives (mainly fatty and resin acids) and they included: tall oil; a residue product of Kraft pulping, pine rosin, linseed and coconut oils.

2.1.1. Cellulose

The cellulose used was pharmaceutical grade pure microcrystalline cellulose (MCC) powder (bp/mcc/avicel PH 101/PH 102) purchased from Xi'an Geekee Biotech Co., Ltd. in Xi'an, China. Microcrystalline cellulose is a purified, partially depolymerized cellulose powder synthesized by the acid-hydrolysis of an alpha cellulose (I_β-allomorph) precursor [35]. Its intended use is mainly in the food industry as an anti-caking, thickener, texturizer, emulsifier and bulking agent; in cosmetic as a filler; and in pharmaceutical as a binder. Industrially, MCC is manufactured from wood as well as non-wood lignocellulosics. It has relatively low chemical reactivity and excellent compactibility at low pressures [36], making it amenable to compression processes such as pelletization.

2.1.2. Coconut Oil

Coconut oil is a colourless to pale brownish yellow plant oil derived from kernels, meat, and milk of coconut plant and fruits. Generally, coconut oil is composed of about 90% saturated fatty acids and 10% unsaturated fatty acids [37]. For the purpose of this study, Kung Markatta's virgin coconut oil was used. The oil is cold pressed from the coconuts and its consistency is solid at room temperature but becomes liquid when heated. The product was purchased from a local supermarket in Karlstad, Sweden.

2.1.3. Pine Rosin

Rosins are non-volatile exudates of resins obtained from resinous tree species, primarily pines [38]. Chemically, rosin is a mixture of mainly resin acids with a little amount of diterpenoid alcohols and aldehydes. The resin acid content are mostly abietic type (abietic, levopimaric, palustric, neoabietic and dehydroabietic acids) and less pimaric type (pimaric, sandaracopimaric and isopimaric acids) [39]. Depending on how it is collected, rosin is classified as either gum or wood rosin. In this study, we used solid exudates of gum rosin obtained from the local pine forests.

2.1.4. Linseed Oil

Linseed oil is a colourless to yellowish oil obtained from seeds of the flax plant (*Linum usitatissimum*). It is produced by pressing and/or solvent extraction of the linseed. The oil consists mainly of the esters of glycerol and five fatty acids of which three are unsaturated C18 oleic, linolenic and linoleic while two are saturated C16 palmitic and C18 stearic acids [28,40]. About 90% of the total fatty acids are unsaturated with only 10% being saturated [41]. In this study, we used ready-made Biltema branded linseed oil sourced locally in Karlstad, Sweden.

2.1.5. Tall Oil

Tall oil is a by-product of the kraft pulping process of softwoods. It is obtained as one of the major fractions from the distillation of crude tall oil; a viscous and sticky dark brown liquid which is a co-product of the Kraft pulping process [42]. In terms of composition, tall oil is a mixture of several components which include resin acids and other terpenoids (38–53 wt.%), fatty acids and triglyceride oils (38–53 wt.%), unsaponified (neutral) compounds (6.5–20 wt.%), water (0.5–3 wt.%) and ash (0.1–1 wt.%) [43].

2.2. Preparation of Raw Materials

The pellets were produced from cellulose with additive mixtures as follows: 100% synthetic pure cellulose (SPC), cellulose plus 10% coconut oil (COC), cellulose plus 10% pine rosin (PRC), cellulose plus 10% linseed oil (LOC) and cellulose plus 10% tall oil (TOC). About 20 kg was prepared for each of the materials, the target was to produce about 15 kg of pellets required for off-gassing analysis for each material.

The synthetic pure cellulose (SPC) was prepared by just conditioning cellulose powder to about 5% moisture content, from an initial moisture content of about 1.6%. The 5% moisture content was arrived at after carrying out a number of trial productions to ascertain the pelletability of synthetic pure cellulose powder. The material was conditioned by adding the calculated amount of water needed to attain the required moisture content to cellulose powder. The material was thereafter mixed using a SoRoTo 100 L Forced Action Mixer for 10 min, sealed in plastic bags and kept for 48 h to ensure uniform moisture distribution throughout the batch of material. For the four materials with added oils (COC, PRC, LOC & TOC), 10% (percentage on dry weight basis) of melted coconut oil, milled solid pine rosin and liquid linseed and tall oils were added to their respective weighed (about 20 kg each) batches of dry synthetic pure cellulose powder and the mixture was conditioned to 5% moisture content. To ensure even distribution of the additive oils, each of the respective material mixtures was also mixed using a SoRoTo 100 L Forced Action Mixer for 10 min.

2.3. Pellets Production Process

A lab scale pellet press (Model 14–175, Amandus Kahl) belonging to the Environmental and Energy Systems at Karlstad University, Sweden was used to produce the pellets. The press has a power rating of 3 KW and production capacity of 10–50 Kg/h. It is a flat die system, and, in this case, the die had 6 mm diameter holes and 15 mm press length, giving the L/D ratio of 2.5. Before the actual production began, the die was pre-warmed by placing it in an oven at 103 °C for 24 h and then made to run with trial pure cellulose powder material until the die temperature increased and became consistent in the required range of 70 °C to 100 °C. All the five types of pellets were produced on the same day and continuously one after the other. Immediately after production, the pellets were cooled, packed and sealed in vacuum-tight plastic bags and thereafter put in the freezer in order to prevent them from undergoing any changes before the off-gassing measurements were conducted.

2.4. Measurement of Off-Gases

Plexiglass containers were used for storing the pellets for off-gassing measurements. The containers had the dimensions of height = 400 mm, diameter = 240 mm and internal volume of 18.1 dm^3. For off-gassing determinations, each of the containers was filled with the pellets measuring about 7 kg, corresponding to about 70% of the volume capacity of the container. A multi-instrument based on electrochemical and infrared (IR) sensors (ECOM J2KN Pro-IN gas analyser, Palgo AB, Sweden was used to measure the gas emissions of CO, CO_2, and CH_4 and residual oxygen. The measurements were taken by introducing the analyser probe into the container through the sampling port positioned on the top of the container. The sampling port has an air lock valve to avoid gas losses during insertion of the probe. The probe was allowed to equilibrate inside the container for one to two minutes after being inserted before the reading was taken. When taking out the probe from the

container after the measurement, there was a time period of about 2 s before the valve was closed that allowed a volume of fresh air into the container. This was equivalent to the volume of gas extracted by the analyser and was on average 1.96 L min^{-1} according to the analyser display. The off-gases were measured over a period of thirteen days and two measurements; each from a separate container were conducted for each of the 5 different materials at every measuring time point.

2.5. Isolation of Fatty and Resin Acids and GC-MS Analysis

The additive oils (linseed, coconut, tall oil and rosin) were analysed for fatty and resin acids content. About 50 mg of each of the additive oils was weighed and dissolved in 10 mL of Dichloromethane (CH_2Cl_2) and then 1.0 mL of it was transferred to a 14 mL screw cap bottle and 1.0 mL of heptadecanoic acid with concentration of 20 ug/mL was added to it as an internal standard. The solvent was evaporated by N_2 gas and then 80 μL of Bis-(trimethylsilyl)-trifluoro-acetamide (BSTFA) and 40 μL of trimethylchlorosilane (TMCS) were added to the dried sample. The closed screw cap bottle containing the sample and added chemicals was kept at 70 °C for 45 min. Thereafter, excess BSTFA and TMCS were evaporated by N_2 gas and the dry sample was dissolved in 1.0 mL of CH_2Cl_2 and transferred to the vial for GC-MS analyses. The method was adopted from [17] but modified to suit the additive oil samples.

A Hewlett Packard (HP6890-5973) GC/MS instrument at Swedish University of Agricultural Sciences was used to analyse the dissolved samples for fatty and resin acids identification and quantification. The instrument has an auto-sampler operating in the electron impact mode (EI 70 eV) and is equipped with a 30 m by 0.25 mm HP-5ms capillary column coated with cross-linked (5%-phenyl)-methylpolysiloxane. The column temperature was programmed as follows: 40 °C isothermal for 0 min, 190 °C at 12 °C/minute, and then 290 °C at 5 °C/minute and held for 2 min. Helium was the carrier gas at a constant flow rate of 1 mL/minute. Full scan EI mass spectra (*m*/*z* 35–500) were recorded after injecting 1 μL of the samples and the peaks were identified by the NIST Mass Spectral Search Program (version 2.0). An internal standard heptadecanoic acid of known concentration was used for quantitative analysis of the fatty and resin acids. The relative concentrations of identified compounds were determined by comparing the peak areas in each chromatogram with that of the internal standard.

2.6. Pellet Physical Properties

Two pellet physical properties namely; moisture content and bulk density were determined. The moisture content was determined by drying pellet samples of at least 300 g in an oven at 105 ± 2 °C to a constant weight. For bulk density, a standardised cylindrical container with a specified volume of about 5 l was filled with pellets and the bulk density was measured and calculated after two impact falls from a 15 cm height. The methods are specified and detailed in respective European (EN) standard methods of determination for solid biofuels: EN 14774-1:2009: moisture content—oven dry method and EN 15103:2010: bulk density for pellets.

3. Results

3.1. Pellet Characteristics

Moisture content and bulk density; the pellet physical properties, which are critical when determining the off-gassing concentrations were measured (Table 1). Both the moisture content and bulk density were relatively in the same range for all the five pellet types. There was not so much reduction in the moisture content between the raw material and the pellets due to the low moisture content of the raw material. The pellets were cream white in colour, had a smooth surface and were generally smaller and shorter than ordinary fuel wood pellets.

Table 1. Moisture content (MC) and bulk density for the five different types of pure cellulose pellet.

Properties Materials	Bulk Density (kg/m³)		Raw Material MC (%)		Pellet MC (%)	
	Mean	SD	Mean	SD	Mean	SD
100% pure cellulose pellets	711	2.5	5.0	0.99	4.2	0.08
Pellets containing 10% coconut oil	767	2.1	4.3	1.12	3.6	0.06
Pellets containing 10% pine rosin	802	1.0	4.3	0.67	3.6	0.05
Pellets containing 10% tall oil	749	2.1	4.6	0.86	4.2	0.08
Pellets containing 10% linseed oil	757	2.2	4.7	0.77	4.0	0.07

3.2. Off-Gassing and Fatty/Resin Acids

The off-gas emissions of pellets produced from synthetic microcrystalline cellulose with different types of additive oils were analysed. The additive oils were also analysed for fatty and resin acids content. The identified fatty and resin acids in each of the additive oils are presented in Table 2 while Figures 1–4 presents the gas concentrations of carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and residual oxygen for all the materials during 13 days of storage. The graphs show the cumulative gas concentrations in ppm for (CO, CO_2 and CH_4) and % (*v/v*) for O_2 against storage time in hours, for each of the 5 types of materials. The gas concentration values are arithmetic means calculated from the two gas measurements conducted for each type of material at every measuring time point.

Table 2. Fatty and resin acids identified in the four additive oils by GC-MS. They are presented as a percentage of the total fatty and resin acids content for each of the additive oils.

No.	Compounds		Percentage Composition (%)			
	IUPAC Name	Common Name	Linseed	Tall Oil	Rosin	Coconut
1	Dodecanoic acid	Lauric acid	-	-	-	45.3
2	Tetradecanoic acid	Myristic acid	-	-	-	24.2
3	Hexadecanoic acid	Palmitic acid	7.6	3.4	-	30.6
4	9,12,15 linolenic acid	Linolenic acid	73.9	35.5	-	-
5	9,12 octadecanoic acid	Linoleic acid	7.6	0.8	-	-
6	Octadecanoic acid	Stearic acid	10.9	37.1	-	-
7	9-octadecanoic acid	Oleic acid	-	9.8	-	-
8		Pimaric acid	-	2.1	0.3	-
9	Resin acids	Isopimaric acid	-	6.0	2.0	-
10		Abietic acid	-	5.3	60.2	-
11		Dehydroabietic acid	-	-	37.4	-
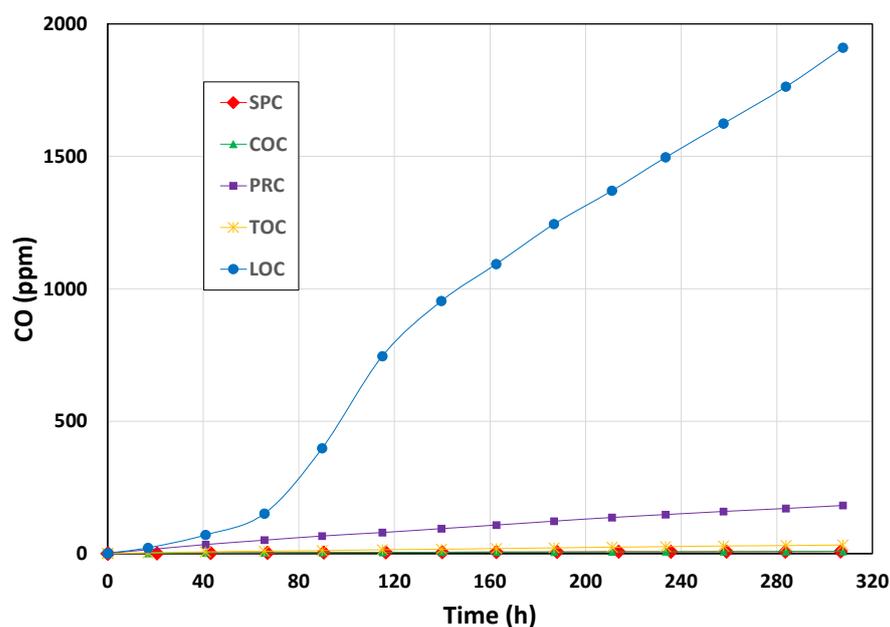
Figure 1. Cumulative carbon monoxide (CO) mean concentrations in the containers over the thirteen days

test period for each of the five materials. Pellets made from: SPC—100% synthetic pure cellulose, COC—cellulose plus 10% coconut oil, PRC—cellulose plus 10% pine rosin, LOC—cellulose plus 10% linseed oil, TOC—cellulose plus 10% tall oil.
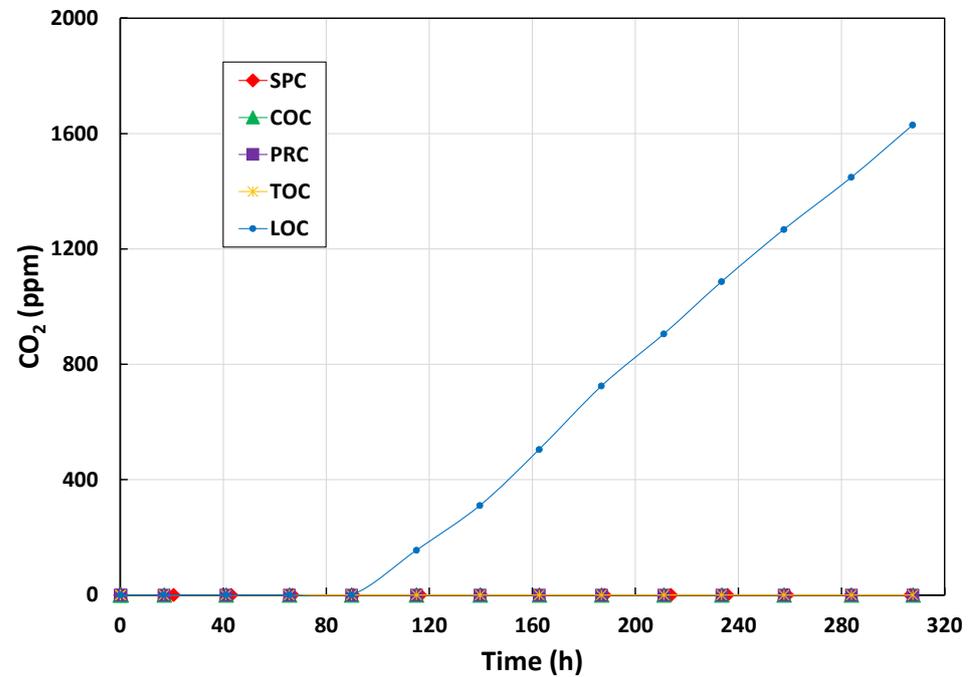
Figure 2. Cumulative carbon dioxide (CO_2) mean concentrations in the containers over the thirteen-day test period for each of the five materials. Pellets made from: SPC—100% synthetic pure cellulose, COC—cellulose plus 10% coconut oil, PRC—cellulose plus 10% pine rosin, LOC—cellulose plus 10% linseed oil, TOC—cellulose plus 10% tall oil.
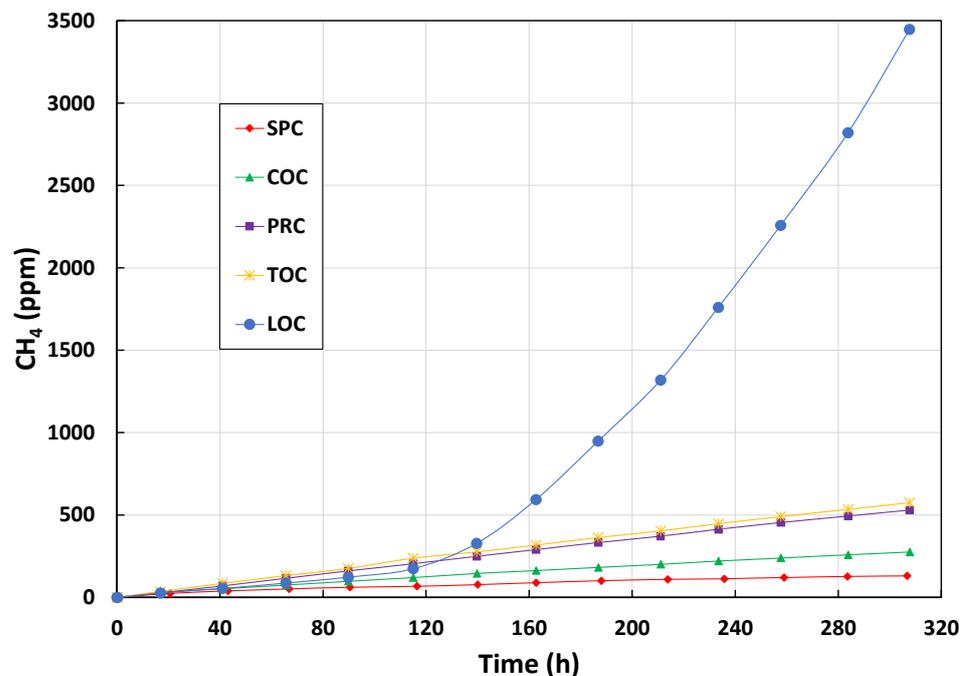
Figure 3. Cumulative mean concentrations of methane (CH4) in the containers over the thirteen-day test period for each of the five materials. Pellets made from: SPC—100% synthetic pure cellulose, COC—cellulose plus 10% coconut oil, PRC—cellulose plus 10% pine rosin, LOC—cellulose plus 10% linseed oil, TOC—cellulose plus 10% tall oil.
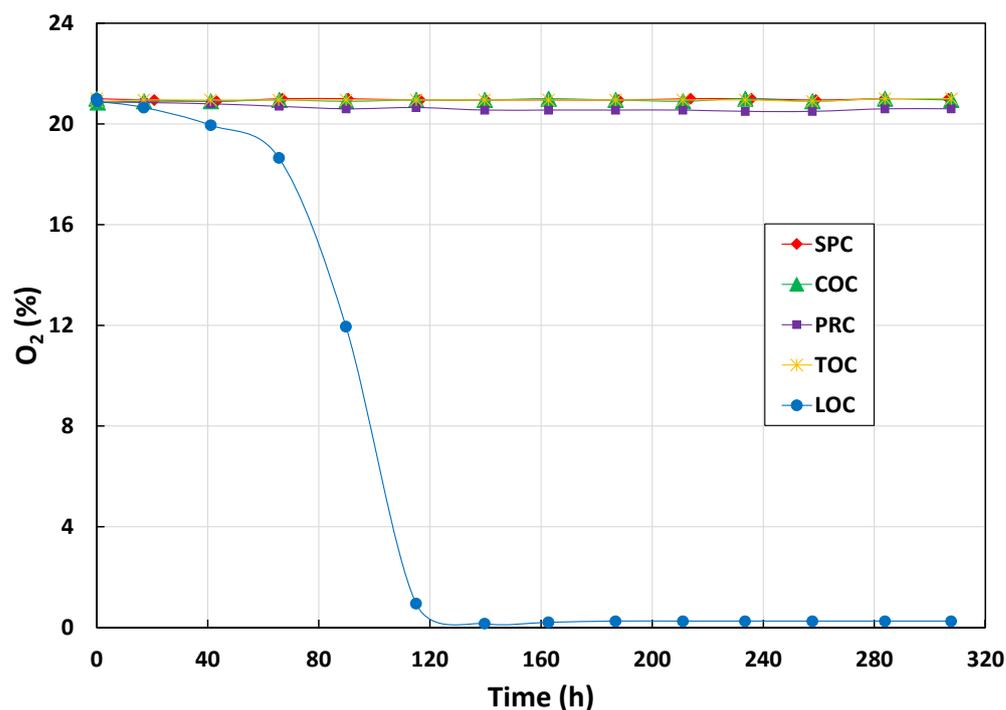
Figure 4. Residual oxygen (O_2) in the containers over the thirteen-day test period for each of the five materials. Pellets made from: SPC—100% synthetic pure cellulose, COC—cellulose plus 10% coconut oil, PRC—cellulose plus 10% pine rosin, LOC—cellulose plus 10% linseed oil, TOC—cellulose plus 10% tall oil.

4. Discussion

Fuel wood pellets and other woody biomasses have been known to emit different kinds of gasses during storage [13,23,24]. This study focused on the emission of carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4) during storage of pellets produced from pure microcrystalline cellulose with different types of additive oils. By using pure cellulose, we avoided the possible reactions and involvement of other wood chemical compounds, e.g., hemicelluloses and lignin in the off-gassing process. Hemicelluloses in particular are known to be chemically and thermally unstable and their saccharide-related molecules start to undergo various oxidations at relatively low temperatures [44]. Pelletization, being a thermal process, may degrade some hemicelluloses and in the process form compounds which can influence off-gassing.

The results showed some notable differences in gas emissions between the pellets with added linseed oil and the other four pellet types. The highest mean concentrations of all the off-gasses; CO, CO_2 and CH_4 were recorded from pellets with added linseed oil (LOC) at 1910 ppm, 1629 ppm and 3446 ppm respectively (Figures 1–3). There was no CO_2 generated throughout the entire storage period for the other four pellet types. The pellets with added pine rosin (PRC) and tall oil (TOC) generated substantial amounts of carbon monoxide at 182 ppm and 33 ppm respectively while the concentrations of carbon monoxide for both synthetic pure cellulose (SPC) pellets and the pellets with added coconut oil (COC) were below 10 ppm (Figures 1 and 2). Methane was detected in all the five pellet types (Figure 3). However, its presence in synthetic pure cellulose (SPC) pellets cannot be attributed to off-gassing but to atmospheric methane [45]. This is because the concentration (130 ppm) was very low to have been initiated by external sources. Except for pellets with added linseed oil, which had complete consumption of residual O_2 (Figure 4), the level of residual oxygen remained relatively close to 21% for the other pellet types.

The variations in the emissions of carbon monoxide, carbon dioxide and methane from pellets with additive oils can be attributed to the differences in the composition of fatty and resin acids of the added oils. Pellets with added linseed oil had high gas emissions

due to their high unsaturated fatty acids content. Previous works by Arshadi et al. [32] and Attard et al. [31] also found unsaturated fatty acids to have high impact on off-gassing. The additive oils (linseed, coconut, rosin and tall oil) contained various types and proportions of fatty and resin acids. Linseed oil had a high content of unsaturated fatty acids (73.9% linolenic and 7.6% linoleic) and low saturated fatty acids while coconut oil, tall oil and rosin had more saturated fatty and resin acids (Table 2). With the exception of coconut oil which had 100% saturated fatty acids (45.3% lauric, 24.2% myristic and 30.6% palmitic), the identified fatty and resin acids together with their respective proportions in the other three additive oils conform with what has been reported in literature [39,41,43]. Despite containing a total of about 45% unsaturated linolenic and oleic acids, pellets with added tall oil had low gas emissions. This is an indication that reducing the amount of unsaturated fatty acids can substantially reduce the off-gassing of carbon oxides and methane.

According to the available literature [32–34], the off-gassing of wood pellets has been attributed to the oxidation of wood extractives. Therefore, considering that the concentration of residual oxygen was decreasing as the concentration of carbon oxides increased in the pellets with added linseed oil, it can be concluded that the formation of carbon oxides was due to α-oxidation of the unsaturated fatty acids (linolenic and linoleic), which are a major component of linseed oil. In the α-oxidation process, the fatty acids are decomposed by the oxidative removal of one carbon atom from a fatty acid to yield CO_2 and a fatty acid shortened by one carbon atom. There was little to no emission of the carbon oxides in other pellets with added oils because their main composition; saturated fatty acids for coconut and tall oil and resin acids for rosin, are highly stable [22]. In saturated organic compounds, all the carbon-to-carbon bonds are single (C−C) bonds while unsaturated compounds have at least one of the carbon-to-carbon bonds that is either a double (C=C) or triple (C≡C) bond. This makes saturated compounds more chemically stable than unsaturated compounds. In woody biomass, both the saturated and unsaturated extractive compounds are components of the aliphatic terpenes and terpenoids and fats and waxes [18]. They include compounds such as fatty acids and resin acids, steroids, triglycerides, sterly esters, sterols and alkanes. Although these extractives can be found both in hardwoods and softwood, they are most predominant in softwoods [19,46], and this can be the reason as to why softwood fuel pellets are more susceptible to off-gassing and self-heating than hardwood pellets [47].

A significant amount of methane was only formed in pellets with added linseed oil, the same pellets that had high carbon dioxide and carbon monoxide concentrations and complete residual oxygen consumption. The concentration of methane started to sharply increase after about 120 h of storage time (Figure 3). This coincided with the time when the residual oxygen was depleted, an indication that methane formation thrived in anaerobic conditions. A similar trend was observed with Scots pine wood pellets by Siwale et al. [30]. While it is difficult to explain the chemical reaction mechanisms responsible for the formation of methane in conditions under which the pellets were stored, the results of this study indicate that its formation is linked to the formation of the carbon oxides and reduction of residual oxygen.

5. Conclusions

The objective of this study was to determine the effect of additive oils on off-gassing of cellulose pellets, with the aim of identifying some of the wood extractives (mainly fatty and resin acids) responsible for off gassing of fuel wood pellets. Pellets with added linseed oil had higher emissions of CO and CO_2 than the other pellet types. When specifically compared to the control material (pure cellulose pellets with no additives), the mean cumulative concentration of CO at the end of the test period substantially increased from 8 ppm to 1910 ppm while CO_2 went up from zero to 1629 ppm. This was due to the higher content of unsaturated fatty acids (73.9% linolenic and 7.6% linoleic) in linseed oil than in the other additive oils. There was not so much increase in gas concentrations from the control material to the three other types of pellets with added tall oil, rosin and coconut oil.

From these results, it can therefore be concluded that one of the main causes of off-gassing of carbon oxides during storage of fuel wood pellets is the oxidation of unsaturated fatty acids and other triglyceride oils that are chemically unstable. These are the major component of the lipophilic extractives found mostly in softwoods. Despite having 100% resin acids and the possibility of oxidation of abietic acid to dehydroabietic acid, pellets with added rosin had very low gas emissions, indicating that resin acids content have little influence on off-gassing of wood pellets. The emission of methane during storage of wood pellets increases with the reduction of oxygen levels in the storage facility. However, the mechanism behind methane formation is still unknown.

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