



Influence on off-gassing during storage of Scots pine wood pellets produced from sawdust with different extractive contents

Workson Siwale^{a,d,*}, Stefan Frodeson^a, Jonas Berghel^a, Gunnar Henriksson^b, Michael Finell^c, Mehrdad Arshadi^c, Carina Jonsson^c

^a Environmental and Energy Systems, Department of Engineering and Chemical Science, Karlstad University, SE-651 88, Karlstad, Sweden

^b Division of Wood Chemistry and Pulp Technology, Department of Fiber and Polymer Technology, Royal Institute of Technology, KTH, SE-100 44, Stockholm, Sweden

^c Swedish University of Agricultural Sciences, Department of Forest Biomaterials and Technology, SE-90183, Umeå, Sweden

^d Department of Biomaterials Science and Technology, School of Natural Resources, Copperbelt University, P.O Box 21692, Kitwe, Zambia

ARTICLE INFO

Keywords:

Off-gassing
Carbon monoxide
Carbon dioxide
Methane
Wood extractives
Wood pellets

ABSTRACT

Off-gassing and self-heating are the major challenges when it comes to transportation and storage of wood pellets. The heat generated due to self-heating poses a fire risk while off-gassing of toxic gasses such as carbon monoxide (CO) and some volatile organic compounds (VOCs) is an environmental and human health risk. With the increase in production volumes of wood pellets which has subsequently increased the amounts of wood pellets in transportation and storage, there is need to find lasting solutions to off-gassing and self-heating of wood pellets. The objective of this study was to test the off-gassing abilities of Scots pine wood pellets produced from sawdust with varying amounts of extractives. The aim is to come up with raw material pre-treatment measures so as to produce wood pellets that are not liable to off-gassing. Six (6) types of sawdust raw materials namely; fresh pine sawdust (FPS), stored pine sawdust (SPS), sawdust plus pine rosin (PRS), sawdust plus linseed oil (LOS), sawdust plus tall oil (TOS) and acetone extracted sawdust (AES) were used to produce the pellets. The produced pellets were then subjected to off-gassing tests under controlled conditions using the ECOM J2KN analyser. The concentrations of carbon monoxide, carbon dioxide and methane increased with storage time but slowed down towards the end of the nine days test period. The formation of these gasses were largely dependent on the type of extractives present in the raw material and not the total extractive content. The formation of methane started later than the other gases and coincided with the time when residual oxygen was depleted.

1. Introduction

Biomass is a sustainable alternative energy source that has the potential to substantially replace fossil fuels if well managed. For this reason and the commitment to attain the renewable energy 2020 targets, bioenergy has become the main renewable energy used in the European Union as most member states have increased the use of wood biomass for energy [1]. Residues from agriculture, food industry and forestry/forest industry can be used as feedstock for various bioproducts such as solid, liquid and gaseous biofuels [2,3], platform chemicals and polymers [4, 5]. Alternatively, loose biomass such as sawdust, shavings and other forestry/agriculture residues can directly be combusted or densified into briquettes [6,7] or pellets [8,9] for heat and power generation. Densified biomass such as wood pellets are nowadays preferred because they are a standardized product with known properties and have high transport

and energy storage density, high heating value, low ash content and do not easily undergo microbiological degradation compared with loose biomass [10].

According to the International Energy Agency (IEA), Bioenergy Task 40 report [11], the global annual production of wood pellets has steadily been increasing over the years. It was estimated to be about 7 million tonnes in 2006, increased to 14.3 in 2010 and exceeded 26 million tonnes in 2015. The forestry production and trade statistics on wood pellets production by the Food and Agriculture Organisation (FAO) [12] also indicates that the global wood pellets production increased from about 18 million tonnes in 2012 to about 42 million tonnes in 2020. The major share of the wood pellets produced globally is consumed in Europe and this was about 27.35 million tonnes in 2018 [13] and was expected to increase by 30–40% between the years 2021–2026 [14]. This demand comes from residential and commercial heating, power

* Corresponding author. Environmental and Energy Systems, Department of Engineering and Chemical Science, Karlstad University, SE-651 88, Karlstad, Sweden.
E-mail address: workson.siwale@kau.se (W. Siwale).

plants and combined heat and power (CHP) plants. This increase in demand and production volumes of wood pellets has subsequently increased the amounts of wood pellets in transportation and storage to ensure continued supply.

The storage of woody biomass in general is usually associated with problems such as off-gassing, self-heating, dry matter losses and reduction in fuel quality that can have adverse economic effects [15,16]. Off-gassing and self-heating have been identified as the major challenges to large-scale storage and transportation of wood pellets [17–19]. The heat generated due to self-heating poses a fire risk while off-gassing of toxic gasses such as carbon monoxide and some volatile organic compounds is an environmental and human health hazard [20–23]. Of the commercially available wood pellets on the European market, scots pine wood pellets are more susceptible to self-heating and off-gassing than spruce pellets and pellets made from a mixture of pine and spruce [24].

Literature suggests that the off-gassing of CO, CO₂ and VOCs is as a result of the oxidation of wood extractives [25–27]. However, there is no consensus over exactly which phenomena that explain the heat generation and off gassing – if the mechanism is biological, physical or chemical or a combination. Lignocellulose, which is the main constitution of wood sawdust and other residual biomasses subjected to pelletization, consist of a mixture of cellulose and other polysaccharides (hemicelluloses, pectin), that are covalently cross-linked by lignin, and also some minerals and organic extractives [28]. Extractives are numerous low molecular weight, non-structural organic substances [29]. They include compounds such as fats, fatty acids, fatty alcohols, phenols, terpenes, steroids, resin acids, rosin, waxes and also more hydrophilic compounds such as sugars and lignans [30]. Most extractive compounds are non-polymeric and can be separated from other insoluble cell wall materials by their solubility in either polar or non-polar solvents [31]. Although extractives cover a wide range of individual chemical compounds, their amount is generally small and varies both in nature and concentration. Generally, softwoods have higher extractives content than hardwoods [32]. According to Alen [28], the typical total extractive contents based on wood dry weight for Scots pine (*Pinus sylvestris*) is in the ranges of 2.5%–4.5%. This variation, more especially in phenolic and resin acid content is due to factors like tree age, tree parts and growth conditions [33].

In order to address the off-gassing and self-heating challenges, the ultimate goal of some previous studies has been to develop storage and handling guidelines for wood pellets and biomass in general [34,35]. However, these have limitations because the increase in production volumes entails the use of large silos and storage space. There have also been studies focused on mixing additives to the raw material in order to produce durable pellets [36–38] while, others have been more on quantifying self-heating and off-gassing tendencies [39–41]. Regarding wood pellets with reduced off-gassing, Sedlmayer et al. [42] found that adding an antioxidant acetylsalicylic acid to the raw material reduces the emission rates of CO, CO₂ and VOCs during storage of wood pellets. In another study involving the use of an antioxidants, Arshadi et al. [27] reported that TBHQ (tert-Butylhydroquinone) is an efficient antioxidant at a low concentration (0.5%) in blocking autoxidation of fatty/resin acids in wood pellets. The CO emissions are reduced between 72 and 90% depending on the pellets temperature. In their methods correlation study, Sedlmayer et al. [18] found that there is a strong direct correlation between off-gassing and self-heating of wood pellets. However, the mechanisms responsible and extent of off-gassing and self-heating of wood pellets are yet to be fully understood.

The objective of this study was to investigate the potential role of wood extractives in off gassing by testing the off-gassing abilities of wood pellets produced from Scots pine sawdust with varying amounts of extractives. The extractives were varied by storing, extracting and adding: pine rosin, tall oil and linseed oil to fresh pine sawdust before pelletizing. The aim was to understand some of the mechanisms responsible for off-gassing of wood pellets, as understanding these mechanisms and their effects can inform raw material pre-treatment

measures with the goal of increasing the knowledge on how to produce wood pellets that are not liable to off-gassing and self-heating.

2. Materials and methods

2.1. Raw materials

Freshly produced Scots pine (*Pinus sylvestris*) sawdust was collected in the winter of 2020 from Laxå pellets plant in central Sweden. At delivery, the sawdust had a moisture content (percentage on wet weight basis) of 54%. The sawdust was air-dried in a drying kiln at 40 °C to 8.5% moisture content, sieved through a 3.5 mm mesh wire and kept in sealed plastic bags. The added extractives were tall oil, a residue from pulp mills, pine rosin exudates collected from local forests and linseed oil purchase from a local supermarket in Karlstad.

2.2. Raw material preparation

The pellets were produced from 6 types of sawdust raw materials prepared from the same batch of pine sawdust but with different treatments as follows: fresh pine sawdust (FPS), stored pine sawdust (SPS), sawdust plus pine rosin (PRS), sawdust plus linseed oil (LOS), sawdust plus tall oil (TOS) and acetone extracted sawdust (AES). About 21 kg was prepared for each of the raw material type, the target was to produce about 15 kg of wood pellets for each treatment, required for off-gassing analysis.

The fresh pine sawdust (FPS) was prepared by just conditioning air dried sawdust to about 12% moisture content before pelletization. For stored pine sawdust (SPS), dry fresh pine sawdust was stored under normal room conditions for a period of 9 months and thereafter conditioned to 12%MC in readiness for pelletization. For the three material types with added extractives (PRS, LOS & TOS), 5% (% on dry weight basis) of linseed oil, tall oil and pine rosin were respectively added to dried and conditioned fresh pine sawdust. Each of the respective material mixture was then placed in a SoRoTo 100 L Forced Action Mixer and mixed for 10 min to ensure even distribution of the added extractives.

The acetone extracted pine sawdust (AES) was prepared by extracting air dried fresh pine sawdust in batches of 3 kg with 25 L of acetone over a period of 72 h at room temperature. This method was adopted from Ref. [43] but further modified so as to extract larger amounts of sawdust. The sawdust in 3 kg batches was placed in capped containers and 20 L of acetone was added to each batch (Fig. 1). The mixture was made to stand for 48 h while being stirred at 12 h intervals. After 48 h, 5 L of the solvent was filtered and drained from each batch through the valve at the bottom of the container and fresh 5 L of acetone was added. The mixture was made to stand for 24 h and thereafter, all the solvent was filtered and drained off. The remaining extracted sawdust residue from each batch was then rinsed with 25 L of water to neutralise the remaining acetone. All the filtrates from the extraction process were kept in sealed containers for safe disposal. The extracted sawdust was then air dried and conditioned to 12% MC.

2.3. Determination of extractives and moisture content

Before pelletization, representative samples were collected from each of the six sawdust types for the determination of moisture and extractives content. The oven dry method was used to determine the moisture content while the soxhlet extraction method was used to determine the total amount of acetone-soluble extractives. About 2 g of each milled sawdust type was extracted in a Soxhlet apparatus with 100% acetone as an extraction solvent in duplicate measurements. This was done according to the procedure as outlined in standard method TAPPI T 204 cm-97: solvent extractives of wood and pulp.



Fig. 1. Capped containers used to extract sawdust (a) and extracted pine sawdust (b).

2.4. Pelletization

The pellets were produced in a lab scale pellet press (Model 14–175, Amandus Kahl) with power of 3 KW and 10–50 kg/h production capacity. This production unit is located at the Environmental and Energy Systems section at Karlstad University, Sweden. A flat die with channel diameter of 6 mm and length of 24 mm was used. The die was pre-warmed in an oven at 103 °C and then made to run with trial sawdust until the die temperature increased to the required range of 70 °C to 100 °C. The required die temperature and raw material moisture content were arrived at after conducting a number of pilot pellet productions. Immediately after production and cooling, the pellets were packed and sealed in vacuum-tight plastic bags and thereafter put in the freezer. This was done so as to prevent the pellets from undergoing any reactions before being subjected to off-gassing tests.

2.5. Off-gassing measurement

Sealed plexiglass containers ($H = 420$ mm, $\phi = 240$ mm, internal volume = 19 dm³) were used for measuring of off-gassing. The experiment was conducted at 23 °C and the containers were filled with the pellet samples to about 70% of their volume capacity (Fig. 2). Gas emissions (CO, CO₂, and CH₄) and oxygen levels were measured using a multi-instrument based on electrochemical and infrared (IR) sensors (ECOM J2KN Pro-IN gas analyser, Palgo AB, Sweden). Measurements were taken by introducing the analyser probe into the container's sampling port, which was positioned on the top of the container. The sampling port includes an air lock to avoid losses of gas due to the insertion of the probe. The probe was allowed to equilibrate inside the container for one to 2 min after being inserted before the reading was taken. After the measurement, the probe was removed from the container and a volume of fresh air equivalent to the volume of gas

extracted by the analyser was admitted (according to the analyser display, an average of 1.96 L min⁻¹). Off-gassing emissions were measured over a period of nine (9) days and two measurements; each from a separate container were done for each of the 6 different pellet types. Off-gassing data collected on the second and subsequent sampling occasions were adjusted to reflect the quantity of gas that was removed from the container and replaced with fresh air. The measured values for CO, CO₂ and CH₄ were converted to $\mu\text{l/l}$ using the head space void volume and sampling time and further adjusted to ppm. The measured O₂ concentrations were not converted and are given as volume fraction percentage.

2.6. Linear regression analysis

The linear regression analysis was conducted using the gas concentrations in the plexiglass containers at the end of the nine days test period and the total amount of extractives in each of the six different types of sawdust used. This was done in order to determine whether total extractive content had an effect on off-gassing. The analysis was done using IBM SPSS Statistics Version 26 software.

3. Results

3.1. Concentration of off-gasses and residual O₂

The off-gasses of wood pellets produced from Scots pine sawdust with different amounts of extractives were analysed. The results for the concentrations of CO, CO₂, CH₄ and residual O₂ for all the six (6) different types of wood pellets are presented in Fig. 3 – 6. The graphs plot the daily gas concentrations in ppm for (CO, CO₂ and CH₄) and % (v/v) for O₂ against storage time in hours, for each of the 6 types of wood pellets. The concentrations are arithmetic mean values calculated from



Fig. 2. Wood pellets in 19 L plexiglass cylinders and ECOM J2KN Pro-IN gas analyser used for measuring the concentrations of CO, CO₂, CH₄ and residual O₂.

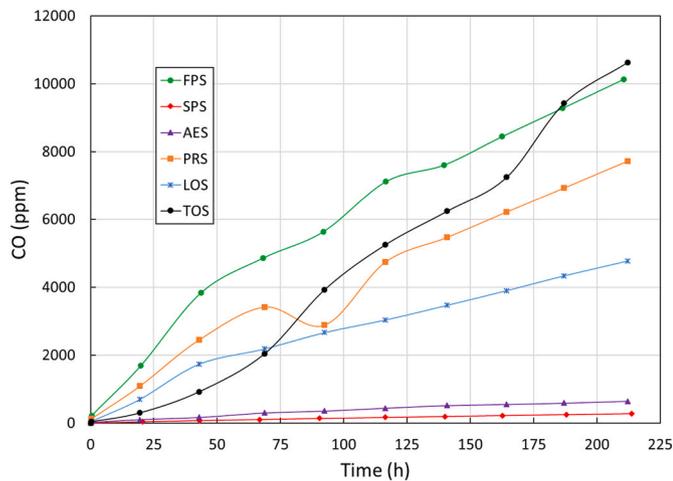


Fig. 3. Concentration of carbon monoxide (CO) in the gas flasks over a nine days test period for each of the six wood pellet type. FPS- fresh pine sawdust (with high natural extractive content), SPS – stored pine sawdust (with lower natural extractive content), AES – acetone extracted fresh pine sawdust (with most of the extractive removed), PRS – fresh pine sawdust with added rosin acids, LOS – fresh pine sawdust with added linseed oil, TOS - fresh pine sawdust with added tall oil fatty acids.

the duplicate gas determinations as described in section 2.5.

The highest mean concentrations of CO were recorded from pellets with added tall oil and fresh pine pellets at 10630 ppm and 10132 ppm respectively, while acetone extracted pellets (644 ppm) and stored pine pellets (272 ppm) recorded the lowest (Fig. 3). There was no CO₂ formed in stored pine pellets while fresh pine pellets had the highest concentration of CO₂ at 8850 ppm and the lowest was from acetone extracted pellets at 1155 ppm (Fig. 4). Fresh pine pellets recorded the highest mean concentration of CH₄ (22832 ppm) and the lowest values were from acetone extracted and stored pine pellets at 163 ppm and 333 ppm respectively. Compared with pellets produced from fresh pine sawdust (FPS), the mean concentrations of CH₄ for pellets with added extractives reduced to 14714 ppm for pellets with added linseed oil, 14554 ppm for pellets with added rosin and 5323 ppm for pellets with added tall oil (Fig. 5). The residual O₂ was consumed in all the pellet types except for

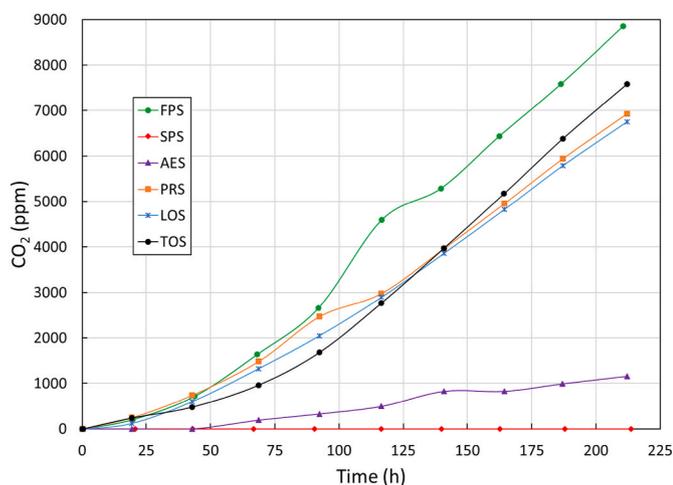


Fig. 4. Concentration of carbon dioxide (CO₂) in the gas flasks over a nine days test period for each of the six wood pellet type. FPS- fresh pine sawdust (with high natural extractive content), SPS – stored pine sawdust (with lower natural extractive content), AES – acetone extracted fresh pine sawdust (with most of the extractive removed), PRS – fresh pine sawdust with added rosin acids, LOS – fresh pine sawdust with added linseed oil, TOS - fresh pine sawdust with added tall oil fatty acids.

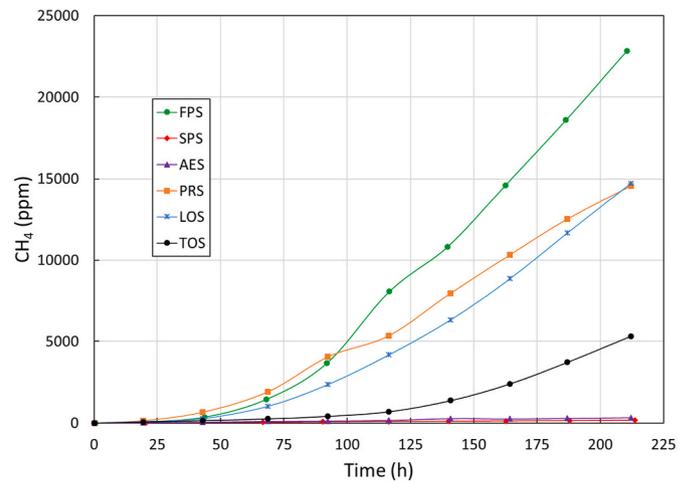


Fig. 5. Concentration of Methane (CH₄) in the gas flasks over a nine days test period for each of the six wood pellet type. FPS- fresh pine sawdust (with high natural extractive content), SPS – stored pine sawdust (with lower natural extractive content), AES – acetone extracted fresh pine sawdust (with most of the extractive removed), PRS – fresh pine sawdust with added rosin acids, LOS – fresh pine sawdust with added linseed oil, TOS - fresh pine sawdust with added tall oil fatty acids.

stored pine and acetone extracted pellets (Fig. 6).

3.2. Effect of total amount of extractives on off-gassing

The results from the determination of moisture and extractive contents are presented in Table 1 while Fig. 7 shows the results for the linear regression analysis between the off-gasses (CO, CO₂ and CH₄) and the total extractive contents of the raw materials. Due to the water content of the tall oil, the moisture content for the TFS material increased to 14.39%. The moisture content for AES was increased to 17.25% as the extracted sawdust proved difficult to pelletize at 12% MC. The coefficients of determination (R²) for all the three off-gasses were above zero but below 0.5. Carbon dioxide had the strongest correlation at R² = 0.4085 while methane had the weakest at R² = 0.1489. A linear correlation is significant when the value of R² is between 0.5 and 1. Since all

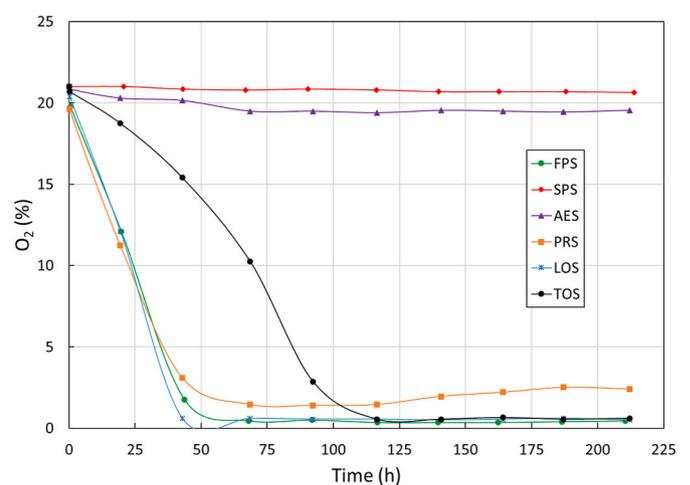


Fig. 6. Residual oxygen (O₂) in the gas flasks over a nine days test period for each of the six wood pellet type. FPS- fresh pine sawdust (with high natural extractive content), SPS – stored pine sawdust (with lower natural extractive content), AES – acetone extracted fresh pine sawdust (with most of the extractive removed), PRS – fresh pine sawdust with added rosin acids, LOS – fresh pine sawdust with added linseed oil, TOS - fresh pine sawdust with added tall oil fatty acids.

Table 1

Moisture and extractive contents of each of the six raw material types used to produce the pellets that were subjected to off-gassing test.

Material Code	Material Description	Moisture Content (ww) (%)	Extractives Content (dw) (%)
FPS	Fresh Pine Sawdust	12.37	5.13
SPS	Stored Pine Sawdust	12.02	4.74
AES	Acetone Extracted Pine Sawdust (fresh)	17.25	1.21
PRS	Pine Sawdust plus Pine Rosin (fresh)	11.41	11.01
LOS	Pine Sawdust plus Linseed Oil (fresh)	11.30	12.39
TOS	Pine Sawdust plus Tall Oil (fresh)	14.39	11.05

the calculated R^2 were below 0.5, the linear correlations between the off-gasses; CO, CO₂ and CH₄ and the total extractive content of the raw materials were not significant.

4. Discussion

The off-gassing emission of gasses such as carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄) and volatile organic compounds (VOC) for different types of wood pellets have been studied before [20, 22,23,27,42]. In this study, three off-gasses; carbon monoxide, carbon dioxide and methane and residual oxygen were detected and measured. The pattern of gas emissions showed generally a similar pattern for formation of carbon monoxide, carbon dioxide and methane. After the nine days test period, the concentrations of CO and CO₂ seemed to have reached their peak while that of CH₄ was still increasing but at a slower rate. This is an indication that off-gassing of wood pellets is faster in freshly produced pellets and slows down as the pellet age increases. The concentrations of CO and CH₄ increased with increasing storage time in all the six pellet types. The same trend was observed for CO₂ in all the pellet types except in stored pine pellets which had no CO₂ formed. There was a residence time of about 50hrs before the formation of CH₄ began while the formation of CO and CO₂ began almost immediately.

Fresh pine pellets generated high concentrations of all the three gases, whereas stored and acetone extracted pellets had very low gas concentrations. None of the pellets with added extractives generated increased gas emissions compared to fresh pine pellets (Figs. 3–5).

Oxygen consumptions were also detected (Fig. 6), and also here, all the added extractives and fresh pine samples showed similar pattern, with a readily oxygen consumption (although the sample with added tall oil had a slower consumption), whereas the stored pine and acetone extracted samples showed a much slower oxygen consumption. The consumption of O₂ and formation of high concentrations of CO and CO₂ in fresh pine pellets and pellets with added extractives (LOS, TOS and PRS) is an indication that some oxidative reactions were taking place. Despite having enough residual O₂, there was low formation of CO and CO₂ in acetone extracted and stored pine pellets. The concentrations of CH₄ increased as the levels of residual O₂ went down for fresh pine pellets and pellets with added extractives and very low concentrations of CH₄ were formed in stored pine and acetone extracted pellets.

The results in this study indicate that stored pine samples lost the ability of fresh pine samples to form carbon monoxide, carbon dioxide, methane and to consume oxygen. A similar effect was obtained when the extractives were removed by acetone extraction. From this it can be tempting to draw the conclusion that the gas emissions are directly connected to the quantity of extractives in the material. However, it is probably not that easy because adding more extractives to fresh pine sawdust did not increase the effect and the linear regression results (Fig. 7) showed that there was no significant linear correlation between the off-gassing of CO, CO₂ and CH₄ and the total extractive contents of the raw materials.

Although ageing (long term storage) of sawdust lowered the extractive content, 92.4% of the extractives still remained in stored pine sawdust (Table 1). One possible explanation to the reduced gas emissions for stored pine pellets is that it is the “right kind” of extractives that are removed during ageing, and that the remaining kind of extractives cannot generate the gas emissions. It is known, that triglyceride content decrease during ageing, whereas other groups of extractives could be relatively constant [44]. However, addition of three different kind of extractives to the wood including triglycerides (linseed oil) and fatty acids (tall oil), did not increase the emissions, but rather lowered them somewhat. This could be explained in a number of ways, one is that the system was simply “saturated” with the substances causing emissions because of the limited available oxygen; the second is that the gas formation is dependent on special sites in the wood. The second hypothesis seems attractive, since it gives a plausible explanation as to why the gas emissions are somewhat lower for the samples with added extractives. But the question is the nature of these sites. Alternatively, it could be

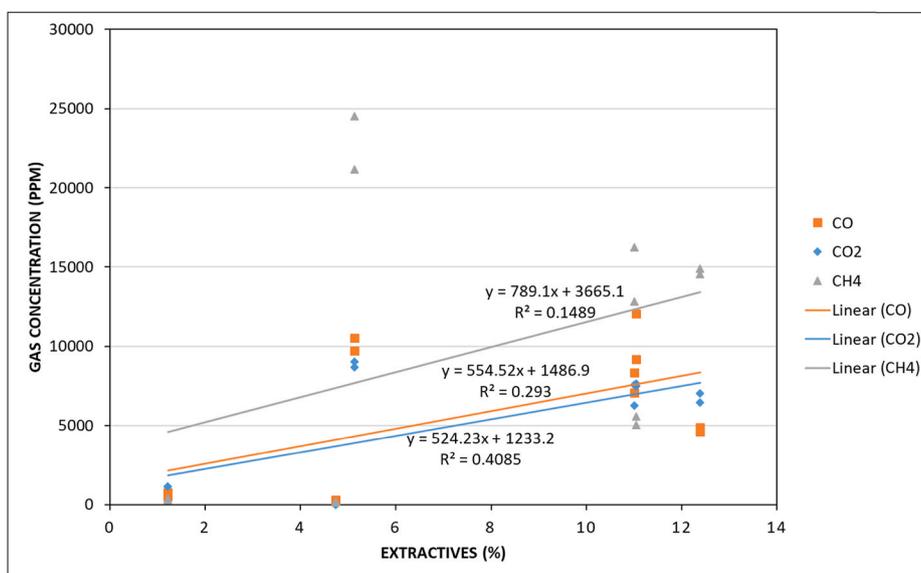


Fig. 7. Linear relations and coefficients of determination between the final gas concentrations of CO, CO₂ and CH₄ in the off-gassing cylinder and the total amount of extractives in the sawdust raw material.

that the added lipophilic extractives (linseed oil, tall oil and pine rosin) have no effect on off-gassing but other wood lipophilic and hydrophilic extractives. The extractive content of Scots pine include hydrophilics such as pinosylvin and its derivatives, lignans and sugars and lipophilics, mainly resin acids [30,33]. Therefore, the reduced gas emissions for acetone extracted pellets may have been due to the reduction in the composition of mainly hydrophilic and some lipophilic extractives resulting from extraction with acetone.

An interesting phenomenon is that methane emission did not start until the oxygen was depleted, indicating that the methane formation is dependent on anaerobic conditions, whereas production of carbon oxides can occur both under aerobic and anaerobic conditions. The explanation for this is unclear, and it shall be noted that to our knowledge, there are no abiotic mechanisms known that generate methane from organics similar to extractives. On the other hand, there are biotic explanations for methane formation [45,46], and living cells, microorganisms and/or parenchyma cells, could indeed be identical with the “gas forming sites” discussed above. Thus, the results in this study are more in line with biotic explanation for the gas emissions, than with abiotic explanations. However, more substantial data is needed.

5. Conclusion

The concentrations of CO, CO₂ and CH₄ were significantly reduced for stored pine and acetone extracted pellets compared to fresh pine pellets and those with added extractives. This clearly shows that producing wood pellets from extractive free sawdust can reduce the off-gassing ability of the pellet. The less emissions of these gasses can reduce the toxic atmosphere in the surroundings during storage and transportation of wood pellets. The gas emissions appears to be dependent on the type of extractives in the raw material and not the total extractive content, as addition of “additional” extractives did neither here give any stronger effect, but rather the opposite. The other notable effect was that methane formation started later than carbon monoxide and carbon dioxide and coincided with the time when residual oxygen was depleted.

Author contributions

Conceptualization, S.F., J.B., G.H., M.F. and W.S.; methodology, W.S., S.F., J.B., G.H., M.F., M.A. and C.J.; raw material collection and pelletization, W.S., S.F. and J.B.; gas measurements, M.F. and C.J.; data analysis and writing - original draft, W.S.; writing - review and editing, S.F., J.B., G.H., M.F., M.A. and C.J.; supervision, J.B., S.F., G.H. and M.F.; funding acquisition, S.F. and M.F. All authors have read and agreed to this version of the manuscript.

Funding

This work was part of the project on secure and well-characterised raw materials and products through innovative adaption of pellets manufacturing processes (SVINPELS, project no 47997-1) at Karlstad University and the Swedish University of Agricultural Studies funded by the Swedish Energy Agency. It is also part of the PhD work for the first author at Karlstad University.

Acknowledgments

The authors want to thank Lars Pettersson at Environmental and Energy Systems, Karlstad University and Laxå pellets AB for providing the sawdust.

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