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Impact of supercritical extraction on solid fuel wood pellet properties and off-gassing during storage

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Biofuel pellets derived from wood raw material are an important carbon neutral source of energy. Their storage and bulk transportation can lead to serious hazards as a result of off-gassing (CO, CO_2, CH_4 combined with serious oxygen (O_2) depletion). Herein, supercritical carbon dioxide extraction ($scCO_2$) has been demonstrated as an efficient tool in significantly reducing these emissions from wood pellets. 84% of the lipids and resin acids have been removed from the sawdust prior to pelletisation. Crucially, this work reports the first off-gassing measurements associated with lipid autoxidation in wood pellets post $scCO_2$ extraction of the sawdust. These off-gassing processes were considerably reduced for $scCO_2$-extracted sawdust pellets, when compared to pellets prepared from virgin untreated sawdust (reference pellets). Significant reductions in the levels of CO, CO_2 and CH_4 (85, 85, and 94% respectively) were observed. A slight reduction in O_2 concentration (20% to 19.3%) was observed for the $scCO_2$-pellets, while an 8% decrease (reduction in O_2 concentration from 20% to 12%) was observed for the reference. The results support a connection between amount of lipids/resin acids and the intermediate products of autoxidation (i.e. 71% reduction in aldehydes) and the off-gassing of CO, CO_2 and CH_4. Finally, there was low impact on the production, durability, calorific values and density of $scCO_2$ pellets compared to the reference pellets. This work demonstrated that $scCO_2$ extraction is effective as a pre-treatment technology for wood based pelletised fuels, considerably reducing the risks associated with off-gassing and oxygen depletion, while also highlighting potential chemicals and biofuels which could be generated from extracts.

Introduction

Several countries are basing their future energy source plans on the use of bioenergy-derived sources, with the goal of decreasing fossil CO_2 emissions. Denmark, for example, has a challenging plan for 2050 where they plan to rely solely on renewable energy from biomass and combinations of wind, wave, and solar power.[1] Biomass is one of the most important alternative energy options available to meet increasingly strict emissions targets. Both solid and liquid biofuels are forms of biomass that have become widely used in Europe and other parts of the world. Normally, such energy products (biomass pellets) are generated by compressing residual sawdust from the wood production industry at high temperature and pressure. The annual production and consumption of wood pellets in Europe in 2013 was about 12 and 18 million tonnes, respectively.[2]

Spontaneous emissions of CO, CO_2 and CH_4 during storage are known as "off-gassing".[3, 4] The safety hazard of wood pellets during storage and transportation is well known.[5, 6] Several accidents have occurred in Europe because of this phenomenon combined with poor ventilation procedures causing irreversible harm or even death in both industrial and household settings.[4, 7, 8] Off-gassing has also been associated with self-heating and fire incidents in the pellet industry.[9, 10]

It has been suggested that autoxidation of fatty acids play a key role on the emissions of VOC (such as aldehydes and ketones).[9] The removal of such compounds from the sawdust prior to pelletising will provide a potential method for decreasing or stopping the off-gassing while providing a valuable feedstock for the chemical and energy industry as part of a biorefinery.[11-13] Previous studies have shown that the extractives may act as lubricants and result in decreasing energy consumption during pellets production; however, they also have a negative impact on pellets strength (durability).[14-16] Lipids and other extractive content in the sawdust may also influence other important pellet properties such as density and gross heat. It is important that mechanical wear during handling of wood pellets is kept to a minimum in order to preserve their integrity and avoid the presence of fines or dust that increases transport losses, humidity uptake and risk of dust explosions in storage and handling. Pellet density is important for combustion and transportation; the higher the density, the more efficient these processes are. However, there is an optimum density which if surpassed leads to incomplete combustion.[17]

Previous work has demonstrated the potential of using supercritical CO_2 ($scCO_2$) as a suitable green extraction solvent for the extraction of lipids and other extractives.[10, 12] Supercritical fluids have relatively low viscosities and high diffusivities making them ideal extraction solvents. [18, 19 18, 19 18, 19 18, 19 18, 19 18, 19 18, 19 18, 19 18, 19] Furthermore, $scCO_2$ extraction is scalable, the CO_2 is easily recycled and the extracts can be separated by a simple depressurisation process leaving no solvent residues.[12, 20]

Herein, $scCO_2$ extraction of the sawdust prior to pelletisation is demonstrated as an effective method of reducing the serious off-gassing problems associated with fuel pellets. Off-gassing measurements of unwanted CO, CO_2, CH_4 and volatile aldehydes of $scCO_2$ pellets were compared to pellets prepared from virgin untreated sawdust (reference pellets). Furthermore, the effects of $scCO_2$ extraction on the physical properties of the pellets according to established standards were investigated.

Materials and methods

Raw material

For the optimisation study; fresh pine sawdust (*Pinus sylvestris L.*) was obtained from a sawmill (SCA Timber AB in Holmsund, northeastern Sweden, latitude 64 °N). For the semi-pilot study and off gassing measurments; fresh pine sawdust (*Pinus sylvestris L.*) was obtained from a saw-mill (Martinsons Såg AB, Hällnäs, northern Sweden, latitude 64 °N). The sawdust raw materials were dried to 7% at 30-35 °C and grinded to 1 mm at the Biofuel Technology Centre (BTC) at the Swedish University of Agricultural Sciences (SLU) in Umeå. The material was shipped to York, UK and kept in cold storage (10 °C) until extracted.

Supercritical carbon dioxide extractions

The $scCO_2$ extractions were conducted using a supercritical extractor (SFE-500, Thar technologies, USA). Supercritical fluid grade carbon dioxide (99.99%, dip-tube liquefied CO_2 cylinder obtained from BOC) was used in the extractions. The CO_2 supplied from a cylinder as a liquid and was maintained in this state through cooling unit (-2 °C) to avoid cavitation in the high pressure pump.

Optimisation experiment extractions; 100 g of sawdust was placed into the 500 ml extraction vessel. The reaction vessel was heated to the required temperature and 5 minutes were allowed for it to equilibrate. An internal pump was used in order to obtain the required pressure (see Table 1). The system was run in dynamic mode, in which the carbon dioxide which contained the extractives was allowed to flow into the collection vessel. A flow rate of 40 g min^{-1} of liquid CO_2 was applied and the extraction was carried out for 4 hours. On completion the system was depressurised over a period of 60 minutes. The extractives were collected by rinsing the collection vessel twice with approximately 100 ml of dichloromethane. The solvent was removed *in vacuo*. The crude extract was weighed and the % yield was calculated. Eight extractions were carried out at various pressures (150, 250 and 350 bar) and temperatures (35, 45 and 55 °C).

Semi-pilot scale extractions: These were conducted using a supercritical extractor (SFE 2 * 5L extractor system, Thar technologies, USA). Supercritical fluid grade carbon dioxide (99.99%, dip-tube liquefied CO_2 cylinder obtained from BOC) was used in the extractions. The CO_2 supplied from a cylinder as a liquid and was maintained in this state through cooling unit (-2 °C) to avoid cavitation in the high pressure pump. 1.8 kg of sawdust was loaded into a 5 L extraction vessel and connected to the extraction system. The required temperature and pressure were applied. The reaction vessel was heated to 55 °C and 5 minutes were allowed for it to equilibrate. Two internal pumps were used in order to obtain the required pressure (350 bar). The system was run in dynamic mode, in which the CO_2 containing the lipids was allowed to flow into three collectors. A flow rate of 300 g min^{-1} of liquid CO_2 was applied and the extraction was carried out for 6 hours. The extractives were collected as for the optimization experiments. A total of 11 kg of sawdust was extracted.

Experimental design and statistical analysis

$scCO_2$ extractions of the sawdust were optimised using a two-level factorial design (Table 1). Evaluation was made by determination of the weight for the extracts (% yield) in the different experiments and GCMS analysis of the remaining FRAs in the extracted sawdust using multiple linear regression (MLR).[21]

Pilot scale pellet production

Reference (non-extracted) sawdust (25 kg) and $scCO_2$-extracted sawdust (11 kg) was shipped to Leipzig and pelletised at the Deutsches Biomasseforschungszentrum (DBFZ). After conditioning of the raw material to a water content of 12-16%, pelletising was performed in a pilot-scale pellet press (15 kW, capacity 110 kg/h, Münch Edelstahl GmbH) using a ring die (press channel specifics: ϕ = 6 mm, L = 30 mm).

Determination of fatty acids (lipids) and resin acids content in sawdust, pellets and extractives fractions.

For determination of fatty acids (lipid content) and resin acids, 3 g of each sample were extracted in a Soxhlet apparatus (Universal Extraction System B-811, Büchi Labortechnik AG, Flawil, Switzerland) with a mixture (90/10 % v/v) of petroleum ether (Merck, bp 40 to 60 °C) and acetone (AnalaR Normapur, VWR Chemicals, 100%) for 1 hour. Thereafter, the solvent was evaporated and 1.0 mg of heptadecanoic acid (Sigma, ≥98%) in hexane (Scharlau analytical grade, 96%, p.a.) (1.0 mg/mL) was added as an internal standard. For saponification, 10 mL of an ethanolic (90%) 0.4 M KOH solution was added and the solution was heated to 70 °C for 4 hours. The solution, now containing the potassium salts of fatty and resin acids, was acidified with 1.5 M HCl. The saponification residues were extracted with petroleum ether (2 times, 25 mL). One mL of the combined extract was transferred to a 14-mL bottle and the solvent was evaporated by

N_2. To the dried sample, exactly 80 µl of Bis-(trimethylsilyl)-trifluoro-acetamide (BSTFA) (Fluka, ≥99%)) and 40 µl of trimethylchlorosilane (TMCS) (Fluka, ≥99%)) were added, and the sample, with a cap, was kept at 70 °C for 45 minutes. Excess BSTFA and TMCS were evaporated by N_2 at room temperature (23 ºC) and the sample was dissolved in 1 mL of dichloromethane (Sigma Aldrich, ≥ 99,9%). The method was based on earlier reports.[21-23] Thereafter the samples were analysed by gas chromatography mass spectrometry (GC-MS), using a Shimadzu GC-2010 instrument with a 30 x 0.25 mm, 0.25 µm film HP-5MS capillary column coated with cross-linked 5 % phenyl methyl siloxane. The column was programmed as follows: Start temperature 100 °C, increase 10 °C min^{-1} to 220 °C, 1 °C min^{-1} to 235 °C and finally 10 °C min^{-1} to 260 °C, held for 5.5 min. Aliquots of 1 µl the silylated samples were injected. The peaks were identified by comparing to reference spectra (NIST MS spectra data base 0.5). Concentrations given are expressed as equivalents of IS (i.e. setting the sensitivity in the analysis of the individual compounds to the same as for heptadecanoic acid). Extractive fractions were analysed using the same procedure (except for the Soxhlet extraction).

Off-gassing measurements

Thermogravimetric analysis coupled with Infrared spectroscopy (TG-IR)

Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (TG-FTIR) was performed using a Netzsch STA 409 at a heating rate of 10 °C·min^{-1}, with typically 30 mg sample under flowing N_2 at 100 mL·min^{-1}, coupled with a Bruker EQUINOX-55 instrument equipped with a liquid N_2 cooled MCT detector.

Measuring off-gassing under laboratory conditions

For off-gassing measurements, two sealed plexiglass containers (H=420 mm, ϕ =240 mm, internal volume= 19 dm^3) were used. The containers were filled with the pellet samples to 70 % of their volume capacity. The experiment was done at 23 °C. Gas emissions (CO, CO_2, and CH_4) and oxygen levels were measured (ppmv) 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 just above the upper surface of the wood pellet layer. 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 two minutes 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). Off-gassing emissions were measured over a period of 48 hours for each sample. 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.

Emission measurements of volatile aldehydes

A laboratory setup modified from Samuelsson *et al.*,[24] was used for heating pellet samples and capturing expelled volatile aldehydes (and ketones). This setup (Figure 1) has three lanes that make it possible to run three different samples in the same experiment. Three randomly taken 10 g aliquots from the 11 kg of $scCO_2$-extracted pellets were placed in the oven at 60 °C inside 500 mL sample cells (glass washing bottles) (Figure 1). Air was pumped through the system at 600 mL/min using an air sampling pump (TSI SidePak™ Model 730 Sampling Pump). The air was passing through an airflow meter, water trap (that absorbs moisture from the surrounding air) and 2 m copper tubing inside the oven (in order to preheat the air to the oven temperature). Before the sample cells the flow was split into three parallel lines.

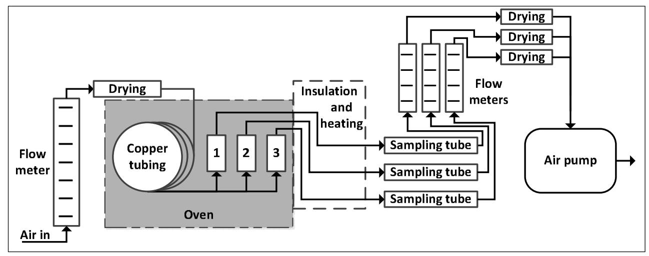

Figure 1. **Aldehyde off gassing/sampling set-up. (1-3; sample cells).**

After passing the flow through mantled heated Teflon hoses (at 45 ºC to avoid condensation), volatile aldehydes and ketones expelled from the pellets were captured in sampling cartridges (LpDNPH, Sigma-Aldrich, MO USA) being converted into their hydrazone derivatives when reacting with 2,4-dinitrophenyl-hydrazine in the cartridges. After the cartridges, the airflow (controlled to 200 mL/min for each sampling line by air flow regulators) was passed through water traps with magnesium perchlorate (LECO, Sweden) in order to protect the sampling pump. Emissions were monitored during 48 hours and samples collected during the time periods 0-1, 1-2, 2-3, 3-5, 5-8, 8-12, 12-24 and 24-48 hours respectively in order to follow the emissions over time and not overload the samplers.

Analysis of aldehydes

The sampling cartridges were eluted with 5 mL acetonitrile (SigmaAldrich Chromasolv gradient grade for HPLC, ≥99.9%,, p.a.) and analysed by High Performance Liquid Chromatography (Shimadzu HPLC Prominence LC-20AD, Kyoto, Japan), using a reverse phase column (RESTEK Ultra C18 150mm x 4.6 mm i.d., 5µm particle size, Restek Corp. PA USA) thermostated at 30°C. Solvents with a total flow rate of 1 mL min^{-1} were A (water) and B (acetonitrile) using a gradient: 35% B from 0 to 25 min, linear increase to 70 % at 70 min, immediate increase to 100% and kept until 75 min. Ten µl of each sample were injected HPLC using the autoinjector. The ultraviolet detector recorded signals at 360 nm. A reference standard mixture (Restek Aldehyde-Ketone DNPH TO-11A 31808; formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, butyraldehyde, benz-aldehyde, iso-valeraldehyde, valeraldehyde, o-, m-, p-tolualdehyde, hexanal and 2,5-dimethylbenzaldehyde, (SUPELCO, 99.5-99.9% purity) was used to build the calibration curves for relevant aldehydes at five levels. The standard deviation of the mean ($RSD\%_{mean}$) for the sum of aldehydes is below 4% (n=3). For individual aldehydes (having low emission levels, <3 ug/g) the $RSD\%_{mean}$ are below 20% and at higher emission levels below 3%. Identity of the sample components were verified by HPLC-MS using a Micromass Quattro micro LC (Waters, MA USA) with an Agilent 1200 system (Agilent Technologies, CA USA). Operating conditions: Neg. APCI, scan 125 - 600 *m/z* with a scan duration of 0.5 s and inter scan delay 0.1 s. Voltages: Corona 6.0 µA, Cone 13 V, Extractor 3 V, RF lens 1.7 V. Temperatures: Source temperature 130 ºC, APCI probe temperature 550 ºC.

Physical quality parameters

In recent reviews relevant standards are discussed.[25, 26]

Energy content

For determination of the gross calorific value (MJ/kg DM) of the pilot test pellets and the reference (three replicates each), an oxygen bomb calorimeter was used (1271Calorimeter, Parr Instrument Company, IL USA).[27]

Density

Density of the pellets ($scCO_2$-extracted sample and reference (three replicates each) were determined by dividing the mass of individual pellets by their measured volume (n=20, RSD < 10%), bulk density was determined according to the standard.[28]

Durability

Durability tests on the pellets from the pilot plant experiment were run (single experiments) according to the standard.[29]

Results and discussion

Supercritical extractions

Optimisation of $scCO_2$ extraction conditions

In the previous work carried out by Arshadi et al.[10], optimisation of supercritical extraction of sawdust was carried out, however a limited pressure range was investigated (80 – 250 bar). Therefore, a lab-scale optimisation study was carried out, whereby the pressure limit was increased to 350 bar.

The factorial experimental design used is a 2^2 (run 1-4) with three centre points and run 4 replicated (Table 1). The response for FRAs in Table 1 showed some extreme values and therefore logarithmic transformation was used. This gave an R^2 of 0.94. The extraction was found to be pressure dependent and conditions of 55ºC and 350 bar maximised the amount of FRAs extracted. Therefore, these conditions were selected for the semi-pilot plant experiments.

Table 1. Laboratory scale $scCO_2$ extraction. Optimisation experiments. Fatty and resin acids (FRAs) remaining in the sawdust.

Exp.	T (ºC)	P (bar)	FRAs (µg g^{-1})
1	35	150	462
2	55	150	1126
3	35	350	219
4	55	350	172
5	45	250	287
6	45	250	276
7	45	250	298
8	55	350	189

Semi-pilot $scCO_2$ extractions

The total amount of extractives in the semi-pilot scale experiment gave a recovery 2.6% of the raw material weight. However, on an industrial scale, it is important to further optimise the conditions in order to gain maximum value from the extraction pre-treatment, especially when taking into consideration expected variation in raw material properties as well as extractive levels and composition. As pointed out in previous studies, adding a co-solvent like ethanol can add to the extraction efficiency.[10]

Extractives in semi pilot plant experiment

The sawdust used was analysed for residual fatty acids (lipids) and resin acids using GC-MS as described in the experimental section. Table 2 highlights the analysis results of the reference and extracted sawdust. The total proportion of lipids and resin extracted by $scCO_2$ extraction was high (84%), with the efficiency for resin acids being 93% and for lipids 58%. However, for industrial applications, additional target and raw material focused optimisations are expected to improve that further, giving higher yields especially for the unsaturated lipids, e.g. by increasing the polarity of the extraction media.[10] The lipids and resin acids accounted for 46% of the total extract weight. In table 3 the fatty and resin acid composition of the extract are shown. The extract also contains a range of other compounds including sterols and the presence of these other components is reflected in the difference between total extractives weight and the GC-MS analysis.

Table 2 Semi-pilot plant scCO_2 extraction. Composition of fatty acids (lipids) and resin acids in sawdust. (Average of 3 replicate analyses, RSD% given as RSD% of the mean.)

Compounds	**Reference sawdust µg g^{-1} (RSD%)**	**scCO_2 extracted sawdust µg g^{-1} (RSD%)**	**Extraction efficiency (%)**
Saturated fatty acids	520 (2)	84 (3)	84
Unsaturated fatty acids	1968 (3)	959 (3)	51
Total fatty acid	2488 (2)	1043 (3)	58
Total lipids	2737 (2)	1148 (3)	58
Total resin acids	7206 (3)	520 (4)	93
Total	9694 (3)	1594 (3)	84

Table 3. Semi-pilot plant scCO_2 extraction. Composition of fatty acids (lipids) and resin acids in scCO_2-extract. Levels of compounds given as µg per gram of sawdust. (Average of 4 replicate analyses, RSD% given as RSD% of the mean. RA=resin acid).

Fatty and resin acid			**µg g^{-1} fatty and resin acids** (RSD%)
IUPAC name	**Common name**	**Lipid number**	
Octanoic acid	Caprylic acid	C8:0	24 (3.2)
Nonanoic acid	Pelargonic acid	C9:0	28 (2.5)
Hexadecanoic acid	Palmitic acid	C16:0	151 (1.3)
Heptadecanoic acid (isomer)	Margaric acid isomer	C17:0	90 (2.8)
(9Z,12Z,15Z)-9,12,15-Octadecatrienoic acid	Linolenic acid	C18:3	150 (2.5)
(9Z,12Z)-9,12-Octadecadienoic acid	Linoleic acid	C18:2	909 (1.9)
(9Z)-Octadec-9-enoic acid	Oleic acid	C18:1	2325 (2.3)
Octadecanoic acid	Stearic acid	C18:0	201 (3.2)
(1R,4aR,4bS,7S,10aR)-1,4a,7-Trimethyl-7-vinyl-3,4,4b,5,6,9,10,10a-octahydro-2H-phenan-threne-1-carboxylic acid	Pimaric acid	RA	1042 (3.1)
	Pimaric acid isomer	RA	155 (2.7)
(1R,4aR,4bS,7R,10aR)-7-Ethenyl-1,4a,7-trimethyl-3,4,4b,5,6,9,10,10a-octa-hydro-2H-phenanthrene-1-carboxylic acid	Isopimaric acid	RA	474 (2.5)
Abieta-7,13-dien-18-oic acid	Abietic acid	RA	920 (6.8)
Abieta-8,11,13-trien-18-oic acid	Dehydroabietic acid	RA	2353 (2.6)
	Abietic acid (isomer)	RA	2449 (3.4)
7-Oxodehydroabietic acid	Oxodehydroabietic acid	RA	348 (5.7)
Saturated fatty acids			**496**
Unsaturated fatty acids			**3384**
Total fatty acid			**3880**
Total lipids			**4268**
Total resin acids			**7741**
Total			**11621**

Off-gassing from wood pellets

The pellets samples before and after scCO_2 extraction were subjected to TG-IR as a simple and effective method to determine the major gases given off during oxidation such as methane (CH_4) carbon monoxide (CO) and carbon dioxide (CO_2). Results indicated that methane was completely oxidised and was not present in the products of oxidation for both samples. Importantly, scCO_2 extraction had a significant reduction on the level of CO formed as there was a much higher amount of CO in the reference pellet sample when compared to the scCO_2-extracted pellet as shown in Figure 2. This phenomenon was observed at low temperature from 220 ^oC up to 380 ^oC. The TG-IR data provided sufficient evidence to warrant a more detailed and large-scale investigation to be carried out on the off-gassing products. of the two samples (reference pellets vs scCO_2-extracted pellets).

A large-scale investigation was carried out whereby off-gassing measurements were carried out on 11 kg of reference and scCO_2-extracted pellets during 30 days of storage. This work reports the first off-gassing data (Figure 3) associated with lipid autoxidation in wood pellets post scCO_2 extraction. Crucially, the results are in agreement with the TG-IR data which indicates that this method could be effective to estimate the suitability of biomass for storage. Figure 3 depicts a CO release during the storage of $13x10^3$ ppmv (30 days), which results in a 8% decrease in O_2 concentration (from 20% to 12%) for the reference pellets prior to extraction. For the scCO_2 extracted pellets however, the level of CO after storage was less than $2x10^3$ ppmv, i.e. approximately 85% lower than the level detected for the reference batch. This is a significant reduction in the levels of CO generated. The lower activity in the extracted pellets reflects positively in a high O_2 level, which slightly decreased from 20% to 19.3% as compared to the O_2 level recorded using the reference made from the same original fresh pine sawdust. The emissions of CO_2 and CH_4 show the same trend, with reductions of 85% and 94% respectively. These off-gassing results are extremely encouraging and highlight the significant potential of $scCO_2$ extraction.

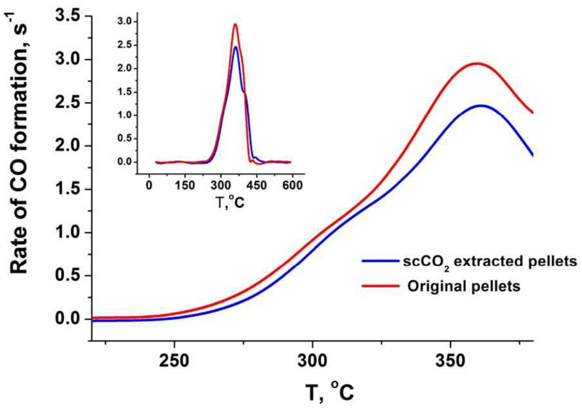

Figure 2. TG-IR analysis of oxidation of a) $scCO_2$-extracted pellets b) reference pellets.

Aldehydes emissions from wood pellets

There are considerably lower emissions of aldehydes and ketones from the pellets made from $scCO_2$-extracted sawdust, with total aldehydes/ketones 51 µg/g (n=6) as compared to the reference pellets that emit 174 µg/g (n=3) in total over the 48 hrs sampling period (after 48 hours the emissions were complete). This is in accordance with the lower levels of lipids/resin acids remaining in the batch after supercritical fluid extraction.

Figure 4 shows the amount of individual aldehydes and ketones emitted from both the $scCO_2$-extracted and the reference (non-extracted) pellets. Emissions of the individual aldehydes from the $scCO_2$-extracted pellets are much lower (26-87 %) as compared to the reference pellets, with exception of the low level emissions of but-2-enal that were unaffected. This reduction in emissions of aldehydes strongly supports the role of fatty acid autoxidation as a source of off-gassing.[30]

The data from the large-scale investigation is consistent with the results obtained by TG-IR data. As such, this demonstrates that TG-IR could be a quick, simple and effective method for screening off-gassing of CO from pellets.

Physical quality of the pellets for energy applications

Pellets produced from the $scCO_2$ extracted sawdust have similar gross heat value as compared to those produced with untreated raw material. The density and also the bulk density of $scCO_2$-extracted pellets were somewhat higher (around 10%) as compared to the reference pellets and it is expected that this would have a positive effect on the transport costs of this energy feedstock. The increased density of the $scCO_2$ pellets is a result of a decreased lubricating effect typically generated by extractives in the dye of the pellet press. Also, the reduction of extractives was reported to reduce the hydrogen bonding in the remaining material and thus the pellet strength is slightly reduced.[15]

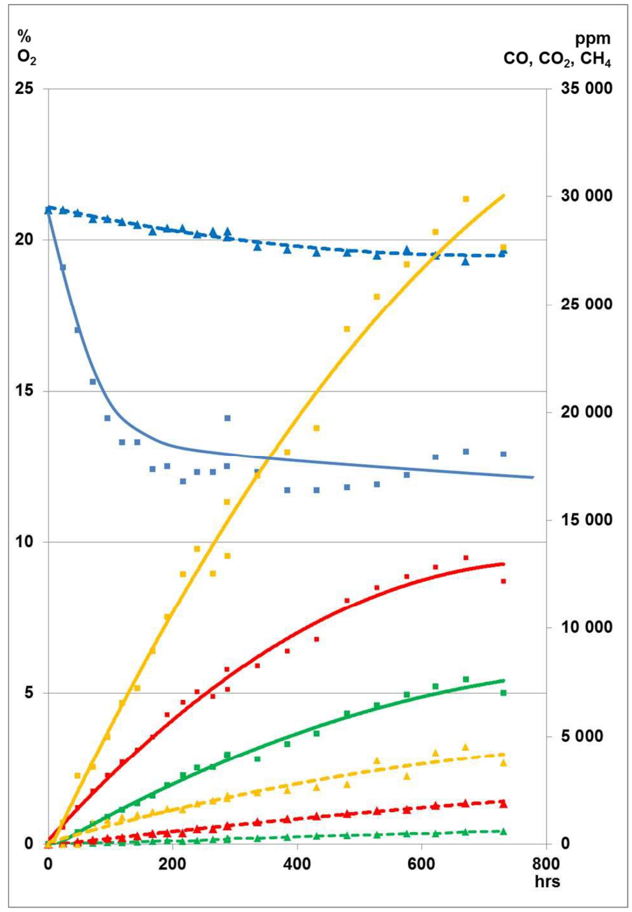

Figure 3. Concentration of CO, CO_2, CH_4 and O_2 measured during off-gassing experiment. $scCO_2$-extracted and non-extracted pellets (Reference), 30 days storage in 19 L test cylinder at 23 ºC. Dotted line: - - - ▲ - - - $scCO_2$ extracted pellets. Solid line: —— ■ —— Reference pellets. ■ ▲= O_2, ■ ▲=CO_2, ■ ▲=CO, ■ ▲=CH_4.

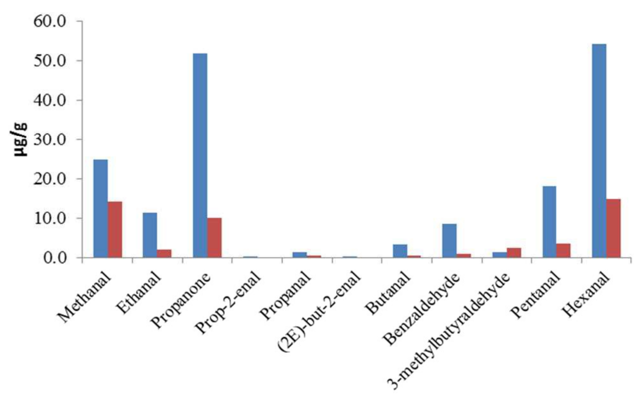

Figure 4. Emissions of aldehydes and ketones during simulated storage of pellets. 48 hrs and 60 ºC. (Blue=Reference pellets, Red=Pellets from $scCO_2$ extracted sawdust. For method standard deviation, see Experimental section.)

The durability of the pellets shows a slight decrease as compared to the reference. However, the amount of material available (11 kg) did not allow for any optimisation of the pelletising process, which should have a potential to increase the durability. The slightly lower gross heat value for extracted material is caused by the removal of the extractives (2.6%) with a high gross heat value. The results are listed in Table 4 and crucially highlight that $scCO_2$ extraction has no appreciable effect on pellet quality.

Table 4. Pellet properties. (Number of replicates and RSD% according to Experimental).

Sawdust samples	T (°C)	P (bar)	Density (g cm^{-3})	Bulk density (Kg/m^3)	Gross heat (MJ/Kg DM)	Durability* (%)
Extracted	55	350	1.2	666	20.19	89.6
Reference	---	---	1.1	591	20.44	95.4
Extract	---	---	---	---	32.59	---

Economic assessment, green metrics and use of extractives as primary feedstock in biorefinery

An economic assessment was conducted to assess the viability of the process (see supplementary information). The assessment conducted was based on a model by Turton *et al.*, which looks into estimating the cost of manufacture (COM) of chemicals (see supplementary information).[31] This methodology has been used extensively in literature and has been proven to be adequate for estimating the costs associated with supercritical extraction of essential oils, waxes and other components from biomass.[32-36] The COM was calculated in terms of five main costs; fixed capital investment (FCI), cost of operational labour (C_{OL}), cost of raw materials (C_{RM}), cost of utilities (C_{UT}) and cost of waste treatment (C_{WT}) using the following equation:

$$COM = 0.280FCI + 2.73C_{OL} + 1.23(C_{RM} + C_{WT} + C_{UT})$$

The COM is based on a small commercial supercritical extraction facility (used for the extraction of natural pigments, spices, nutraceuticals, essential oils etc.) with an annual capacity of around 2000 t/year. A full detailed breakdown of the costs and calculations may be viewed in the Supplementary information. The COM for the supercritical extraction process was estimated to be around €642 per tonne of sawdust. It was observed that the density of the biomass has a great effect on the COM. If extractions were carried out on pelletised sawdust, the COM (based on the density of the pellets in this study) would reduce significantly to €382 per tonne. Furthermore, a one-at-a-time sensitivity analysis was conducted (see Supplementary information) in order to determine which cost parameter (out of the five mentioned) had the greatest effect on the COM. It was found that the fixed capital investment (i.e. the initial cost of the supercritical extraction unit) followed closely by the utility costs (i.e. the electrical power required for the CO_2 pumps and refrigeration) have the greatest effect on the COM while the cost of raw materials (C_{RM}) had the smallest effect. It is estimated that the selling price of sawdust pellets is: a) Sold as a bulk it is in the region of €225 per tonne of 8 mm pellets while it is €235 per tonne of 6 mm pellets, b) Sold as small bags (15 kg) it is €282 per tonne of pellets. The calculated COM for the supercritical extraction is therefore higher. However, a number of assumptions have been carried out in this study. First of all, the costs assume no value for the extracts that have been obtained. In reality this will be a valuable waste stream that will be sold to generate revenue. Secondly, as stated previously, the study only takes into account a small pilot scale supercritical extraction facility (around 2000 t per year) due to the limited data available regarding the costs of supercritical extraction units. Studies have shown that though the initial FCI would be higher, scaling up to a 10,000 t/year plant or higher could significant reduce the COM by over half that stated here (due to a much larger throughput coupled with an automated handling of material which would lead to reduction in labour costs).[37] Furthermore, other factors can be taken into consideration such as building the supercritical facility at the milling site so as to avoid costs associated with the transport of the sawdust.

Table 5 Green Metrics calculated for the supercritical extraction of sawdust.

Metric	Semi-pilot plant scale	Pilot plant scale (2000 t/year)
E-factor	0.53	0.5
Extraction mass efficiency	97.4%	97.9%
Process Mass Intensity	1.53	1.5
Renewables Intensity	1.53	1.5
% Renewables	100%	100%
Space time yield	58.44 kg m^{-3} h^{-1}	6.54 kg m^{-3} h^{-1}

Some green metrics were calculated based on the semi-pilot supercritical extraction carried out in this study. It should be pointed out that the extract (FRAs) obtained from the extraction process was considered to be a waste when in reality it is an added-value product (and not a waste). Therefore, the E-factor will be lower than that shown in Table 5. The same applies to the extraction mass efficiency and process mass intensity. The majority of the waste generated is the CO_2 utilised in the extraction process which is relatively non-toxic. The space time yield improves significantly on moving from a lab-scale semi-pilot system to a 2000 t/year pilot plant due to a reduction in the extraction time.

As stated previously, the extract obtained from the supercritical extraction of sawdust is not a waste. Therefore, in addition to the significant reduction in off-gassing products, $scCO_2$ extraction of pellets leads to the generation of considerable amounts of added-value products which when thinking holistically could be integrated into a wood-pellet green biorefinery. $scCO_2$ extraction has already been shown to be a cost effective technique in a maize stover biorefinery.[12,36] Considering that 12 million tonnes of pellets were produced in 2013 in Europe using the conditions found in the present study, a potential of approximately 312,000 tonnes of extract could be available per year to produce valuable chemicals or liquid fuels.

Chemicals such as the long-chain fatty acids (e.g. C_{18} saturated and unsaturated fatty acids) can be utilised as primary feedstocks for lubricant production and polymer applications.[38] Other applications include use in soaps, detergents, polishes and cleaning compounds.[39] Polyunsaturated fatty acids are well-known nutraceuticals, lowering serum cholesterol in humans.[40]

There is great potential to use the large abundance of resin acids in the extractives as bioactive compounds in pharmacological and phyto-epidemiological applications. These are known to have antimicrobial activity. Dehydroabietic acid and isopimaric acid have antibacterial and antifungal properties.[41-43] Abietic acid has been shown to display anti-inflammatory and anti-thrombotic activities.[44] The use of abietic acid derivatives in drug-delivery applications has also been investigated.[45] Furthermore, rosin, which is primarily composed of abietic acid and pimaric acid, is used in a wide variety of applications including printing inks, varnishes, paints, chewing gum and cosmetics.[46]

Finally, there is potential to utilise the extractives as a feedstock for biodiesel production. Tall oil, which is high in fatty acid and resin acid content and very similar in composition to the extractives obtained in this study, has found to be an ideal feedstock for the production of bio-diesel.[47,48] In Sweden 2% (100,000 cubic meters tall oil diesel per year) of the total diesel consumption is covered by domestic production using tall oil from the pulp and paper and conversion applying a hydration process.[49] However, biodiesel applications do not utilise the full potential of these resources to produce specialty chemical and other higher value-added products.

Therefore, $scCO_2$ extraction of wood pellets prior to storage and bulk transport provides an efficient and effective method to significantly reduce the harmful off-gassing products associated with pellets as well as provide a feedstock of platform molecules for biorefinery applications.

Conclusions

In this study it has been demonstrated that supercritical CO_2 extraction of sawdust intended for the production of wood fuel pellets is a feasible and very promising method for improving the pellet quality in terms of storage stability by minimising the off-gassing phenomena associated with incidents of carbon monoxide poisoning and self-heating/fire.

Optimised extraction conditions based on the amount of fatty acids and resin acids remaining in the sawdust following supercritical extraction was 350 bar and 55 ^{o}C and thus extract the greatest proportions of these compounds. These conditions were therefore selected and applied in the semi-pilot scale experiment, for which total yield of extractives of 2.6% of the total raw material weight was observed.

Pellets produced from the $scCO_2$-extracted sawdust in pilot scale were demonstrated to have comparable calorific value and density as compared to pellets produced from the reference sawdust. Durability, being production parameter dependent, was found to be a bit low but optimisation/adjustment of the pelletising process has a potential to improve the durability.

It was also demonstrated that fatty acids (lipids) and resin acids play a central role in the off-gassing and oxygen depletion process. Emissions of their autoxidation products, aldehydes, are reduced considerably in the pellets made of extracted material.

Consequently, the expected increase in the use of bioenergy will benefit from implementing this $scCO_2$ extraction approach, thereby reducing the serious risks associated with off-gassing (especially CO and CH_4) and oxygen depletion associated with the storage and transport of fuel pellets will also be minimised.

Furthermore, $scCO_2$ extraction of the sawdust has the potential to produce an added-value feedstock for the green chemical and energy industry.

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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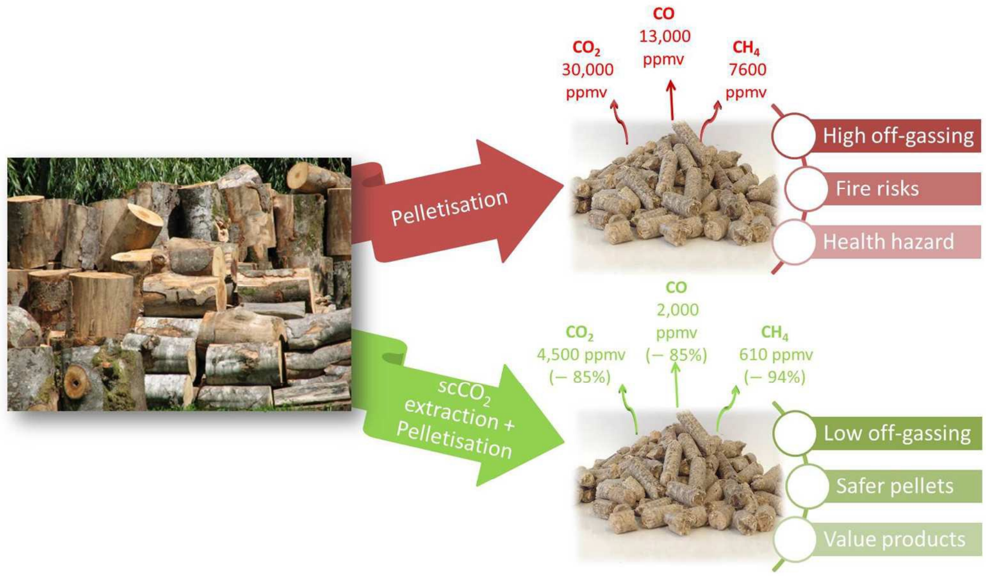

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