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Wheat straw and peat for fuel pellets - organic compounds from combustion

Maria Olsson

*Chemical Environmental Science, Department of Chemical and Biological Engineering,
Chalmers University of Technology, SE-412 96 Göteborg, Sweden
maria.olsson@chalmers.se, Phone +46 31 772 30 05, Fax: +46 31 772 29 99*

Abstract

Wood pellets are an environmentally friendly biofuel with no net contribution to global warming. Today, the demand for wood pellets for residential heating is rapidly increasing in Sweden and many other countries. Therefore, alternative raw materials for pellet production, such as wheat straw and peat, are of great interest.

Before these new fuels are widely used, it is important to study the emissions to air during combustion. The smoke contains a large number of compounds which, to varying degrees, can affect health and the environment. Specific organic compounds from five sequential combustion stages; initial smouldering, early flaming, late flaming, after-flame smouldering and final glowing, were determined for incomplete combustion of straw and peat/wood pellets on a laboratory scale and compared to those from softwood pellets.

The emissions from incomplete combustion reflect the chemical composition of the fuel. During initial smouldering of the studied fuels, methoxyphenols from the lignin of the fuels were released at high concentrations. Relatively high concentrations of 1,6-anhydroglucose and furan-related compounds, originating from the polysaccharides of the fuel, were also found during this stage, especially in peat/wood pellet smoke. During flaming burning, wood pellets burned more efficiently and with even lower emissions than the other fuels. After-flame smouldering of the studied pellets, especially straw pellets, released high concentrations of compounds that are hazardous to health and the environment.

Keywords: Burning, volatile hydrocarbons, benzene, polycyclic aromatic hydrocarbon, PAH, lignin, cellulose, hemicelluloses, biomass

1. Introduction

Wood pellets are a biofuel that is much in demand and increasingly replacing oil and firewood for residential heating and hot water production [1]. The current annual Swedish production of softwood pellets is above one million tonnes. Almost half of this amount is used in nearly 100 000 Swedish residences and the rest in larger combustion plants.

Alternative raw materials for pellet production are of great interest in view of the increasing demand for wood pellets. Wheat straw and peat are examples of such new raw materials.

The availability of wheat straw amounted to 44 million tonnes in Europe and 1.7 million tonnes in Sweden in 2000 [2]. Peat covers 3 % of the world's land area, and the production of

peat for energy use was 70 million m^3 (corresponding to approximately 70 TWh) in 2005 [3]. The corresponding figure for Sweden was 25 % of the land area, with an annual regrowth rate of about 20 million m^3 while the amount for energy production was 3.5 million m^3 [3].

Pellet appliances designed to combust a less easily burnt fuel with a higher ash content than wood pellets can be used for peat/wood and straw pellets. There are already pellet burners for straw pellets on the market in Sweden, and it has been proven possible to combust wheat straw pellets in adapted residential boilers with low emissions of carbon monoxide and nitrogen oxides and relatively low emissions of sulphur dioxide [4]. Peat/wood pellets are at present not used for residential heating in Sweden.

It is of great importance to study the emissions of specific organic compounds to air during combustion before pellets of peat/wood and straw can be widely used as residential fuels. The smoke contains many different compounds which can affect health and the environment. In this study, organic compounds in the emissions from incomplete combustion of straw and peat/wood pellets were determined. Compounds in the smoke from softwood pellet combustion were used as a comparison. Softwood pellets are an environmentally favourable fuel with low emissions to air and can therefore be used in densely populated areas [1, 5, 6]. Emissions from incomplete combustion reflect the chemical composition of the fuel and indicate the compounds that can be emitted during, for example, start-ups and temporary disturbances.

2. Experimental

Three different commercial pellets were studied (Table 1, [4, 7-9]). Further information on the softwood pellets used for comparison purposes can be found in a previous study [10].

Table 1: Data on the studied wheat straw, peat/wood and softwood pellets.

Pellet	Wheat straw pellets	Peat/wood pellets	Softwood pellets
Producer	Energi E2 A/S, Denmark	Mebio, Sweden	BrikettEnergi AB, Sweden
Raw material	Wheat straw	35 % peat and 65 % softwood sawdust	Sawdust and shavings, pine and spruce,
Moisture content (% w/w)	4	7	8
Ash content (% w/w)	6 [7]	1.3 [8]	0.5 [9]
Heat value (kWh kg^{-1})	4.0 (15 % moisture) [4]	4.9 (8.5 % moisture) [8]	4.8 (9 % moisture) [9]

Seven pellets (about 5 g) were placed on a steel net covered by a 20 cm high aluminium sheet cone (Fig. 1). The pellets were set aflame from below, using a butane torch. During burning, air was allowed to move freely through the net and cone. All samples were collected at the top of the cone. A gas-tight glass syringe was used for sampling carbon monoxide, carbon dioxide, oxygen and organic compounds (≤ 7C). At the same time, smoke was pumped through a cartridge containing Tenax adsorbent upon which organic compounds (≥ 6C) were collected. The Tenax cartridge was cooled above the surface of liquid nitrogen just before sampling, in order to prevent break-through of volatile organic compounds, e.g. benzene, due
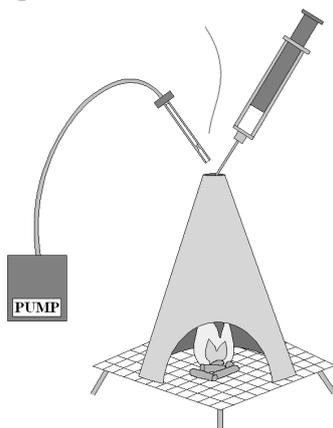
to the relatively high sampling temperatures.

Figure 1: Gas sampling during laboratory combustion using Tenax adsorbent with a pump (left, organic compounds ≥ 6C) and a gas tight syringe (right, carbon dioxide, carbon monoxide, oxygen and organic compounds ≤ 7C).

Gas chromatography in combination with different detection methods was used to analyse the smoke samples. Carbon dioxide was separated on a porous polymer column and carbon monoxide and oxygen on a molecular sieve column and determined by a thermal conductivity detector [10]. Organic compounds (≤ 7C) were separated on an aluminium oxide column and determined by a flame ionisation detector (GC-FID) [10]. The response was determined using propane as a reference gas and set equal (1.0) for all hydrocarbons, and to 0.6 for furan. Organic compounds (≥ 6C) were thermally desorbed in the injector, separated on a medium polar column and determined using a mass spectrometer (GC-MS) [10]. Quantitative determinations were made by integrating the current from selected ions and recalculating it to total ion current using data from the NIST library. No NIST data were available for the syringols $SyCH_3$, $SyCH_2CH_3$, $SyCH=CH_2$ and $SyCH=CHCH_3$. Ion proportions from peaks in previous studies [11] were used for the recalculations. The relative response was set equal for all compounds studied. The analyses of benzene by both GC-MS and GC-FID were used for intercalibration between these two systems.

A thermo-couple was inserted between the pellets in order to measure the temperature. The moisture content of the pellets and the proportions of biomass lost during the flaming and glowing combustion stages were determined by weighing.

3. Results and discussion

Combustion of a few pellets of straw, peat/wood or softwood can be divided into five sequential stages (I-V, Fig. 2). During the first stage, initial smouldering (I), moisture evaporates and volatile compounds are released. During early flaming (II), the temperature is 400-450ºC and a considerable amount of the virgin fuel is still visible. In the late flaming stage (III), there is no virgin fuel left, only charred surfaces. During this stage the temperature increases to 450-500ºC. The early and late flaming stages both last for 1-2 min. When flaming ceases, the short after-flame smouldering stage (IV) is entered without any

major drop in temperature. Following the after-flame smouldering stage, the final glowing stage (V) begins. This continues for up to 20 min, during which the temperature slowly decreases.
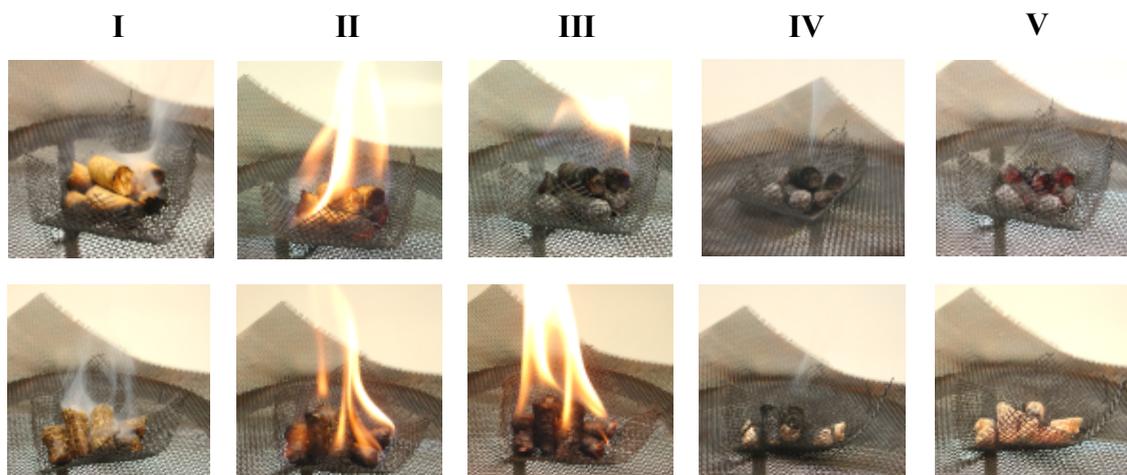
I	II	III	IV	V

Figure 2: Initial smouldering (I), early flaming (II), late flaming (III), after-flame smouldering (IV) and final glowing (V) of wheat straw pellets (top row) and peat/wood pellets (bottom row).

During laboratory combustion of straw, peat/wood and wood pellets, more than 98 % of the combustible part (ashes excluded) of the fuel was burnt (about 85 % during early and late flaming and 15 % during final glowing).

The content of compounds in smoke reflects both the chemical composition of the fuel and the combustion conditions. The chemical composition of the fuel, which differs greatly between wheat straw, peat and softwood, is therefore of major interest (Table 2).

Table 2: Chemical composition of wheat straw [12, 13], peat [14-16] and softwood (average of pine and spruce) [17] (% w/w of dry material).

	Wheat straw	Peat	Softwood
Lignin	20	6-40	28
Cellulose	24	0-20	41
Hemicelluloses	21 [a]	10-25	25 [b]
Starch	3	-	traces
Protein	4	5-25	0.6 [c]
Humic acids	-	3-50	-
Residual components	28 [d]	rest [e]	5 [f]

[a] Mainly xylan (including arabinose, acetyl and uronic acid residues)
[b] Mainly glucomannan (including galactose and acetyl) and xylan (including arabinose and uronic acid residues)
[c] Calculated by multiplying the nitrogen content of the softwood pellets (0.1 % w/w, [9]) by 6.25 [12]
[d] Mainly ash, low-molecular weight carbohydrates and waxes
[e] Mainly pectins, resins, waxes and ash
[f] Mainly extractives, other polysaccharides and ash

Wheat straw is mainly made up of cellulose, hemicelluloses and lignin [12, 13]. Peat is formed from anaerobic decomposition of white moss (*Sphagnum*) and other bog plants. It is a heterogeneous fuel and data presented in Table 2 is average values from different studies on peat [14-16]. Softwood is mainly made up of cellulose, lignin and hemicelluloses [17]. The peat/wood pellets studied were produced from 35 % peat and 65 % softwood sawdust and thus mainly contained cellulose, hemicelluloses and lignin.

In Table 3-5, the concentrations of the compounds studied in smoke from the different combustion stages of wheat straw, peat/wood and softwood pellets are presented. The concentrations of the compounds emitted varied a great deal between the different combustion stages. The analysis of organic compounds ($\leq$ 7C) is illustrated in Fig. 3, a GC-FID chromatogram from early flaming (II, Fig. 2) of wheat straw pellets.
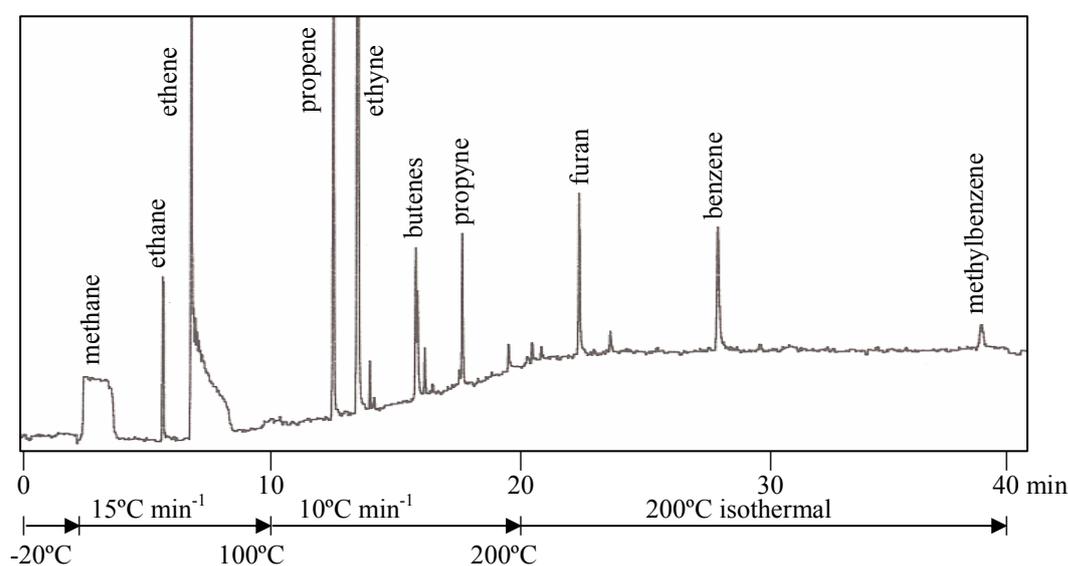
Figure 3: Gas chromatogram showing the separation of organic compounds ($\leq$ 7C) in the emissions from the early flaming (II) of wheat straw pellets.

3.1 Initial smouldering (I)

The pellets were gently ignited (insufficient to set the fuel completely on fire), and smoke samples from initial smouldering were collected when the flames had died down. The total concentrations of organic compounds were high in comparison with the subsequent stages, especially in the case of peat/wood pellets.

Methoxyphenols with antioxidant effect were released at high concentrations during initial smouldering. Ethenylguaiacol ($GuCH=CH_2$), *trans*-propenylguaiacol ($GuCH=CHCH_3$ (*E*)), vanillin (GuCHO) and coniferaldehyde ($GuCH=CHCHO$) were the most common methoxyphenols in the smoke from all of the fuels studied. Dimethoxyphenols, mainly syringol (SyH), were also present in smoke from the combustion of wheat straw and peat/wood pellets. Methoxyphenols are primary pyrolysis products from the lignin of the fuel

Table 3: Concentrations of compounds in smoke from wheat straw pellets during the different combustion stages (conc. = average concentrations, s.d. = standard deviations, mg m^{-3}, Gu=4-hydroxy-3-methoxyphenyl, Sy=4-hydroxy-3,5-dimethoxyphenyl).

	Initial smouldering (I)		Early flaming (II)		Late flaming (III)		After-flame smouldering (IV)		Final glowing (V)	
No. of analyses	5		5		5		6		6	
	conc.	s.d.	conc.	s.d.	conc.	s.d.	conc.	s.d.	conc.	s.d.
Carbon dioxide	6100	1700	120000	20000	110000	20000	28000	4000	21000	2000
Carbon monoxide	630	300	220	140	270	110	3100	400	2200	400
Methane	11	5	5.5	3.2	6.5	2.4	750	470	13	9
Ethane	7.5	3.8	1.2	0.9	1.8	0.6	300	190	0.4	0.5
Ethene	7.5	3.4	13	8	5.5	1.9	100	70	0.4	0.4
Propane	2.8	1.5	0.3	0.4	0.5	0.2	76	54	<0.03	
Propene	5.9	2.9	2.2	1.4	1.2	0.4	98	66	0.04	0.07
Ethyne	1.2	0.5	4.3	2.6	0.9	0.6	2.0	1.6	0.5	0.1
1,3-Butadiene	1.4	0.6	0.04	0.01	0.06	0.04	12	9	<0.03	
Benzene	1.0	0.4	0.8	0.4	0.5	0.1	30	18	1.4	1.0
Methylbenzene	1.5	0.7	0.2	0.2	0.5	0.2	46	30	0.2	0.2
Naphthalene	0.2	0.1	0.3	0.3	0.2	0.1	8	2	0.4	0.2
Furan	5.2	2.4	0.9	0.5	0.2	0.2	6.6	3.1	<0.03	
2,5-Dimethylfuran	1	1	1	1	0.6	0.3	2	1	<0.03	
2-Furaldehyde	50	30	10	10	3	1	0.4	0.3	0.5	0.2
5-Hydroxymethyl-2-furaldehyde	3	1	20	10	2	1	<0.03		<0.03	
Benzofuran	0.5	0.2	0.6	0.2	0.2	0.1	3	2	0.04	0.02
1,6-Anhydroglucose	2	1	20	10	1	1	2	1	0.2	0.1
Phenol	20	10	10	10	7	6	100	100	0.3	0.1
GuH (guaiacol)	30	10	9	5	2	1	7	10	0.2	0.1
GuCH$_3$	7	3	10	10	2	2	4	5	0.1	0.0
GuCH$_2$CH$_3$	10	10	10	10	1	1	5	8	0.08	0.03
GuCH=CH$_2$	200	100	20	10	0.9	0.5	4	5	0.5	0.3
GuCH=CHCH$_3$ (E)	50	30	30	20	1.0	0.5	5	7	0.2	0.1
GuCHO	20	10	100	100	9	5	4	3	1.0	0.4
GuCH=CHCHO	6	3	3	3	0.7	0.3	<0.03		0.3	0.2
SyH (syringol)	100	100	200	200	3	1	20	30	1	1
SyCH$_3$	8	5	20	10	0.7	0.3	5	8	0.1	0.1
SyCH$_2$CH$_3$	10	10	20	10	0.8	0.3	2	3	0.1	0.1
SyCH=CH$_2$	20	10	3	1	<0.03		<0.03		0.05	0.04
SyCH=CHCH$_3$ (E)	8	6	9	5	<0.03		2	2	0.01	0.03
SyCHO	5	3	10	10	2	1	<0.03		0.2	0.1
Sum of organic comp.	600		500		50		2000		20	

[18-20]. Both methoxyphenols with guaiacyl structure (Gu=4-hydroxi-3-methoxyphenyl) and dimethoxyphenols with syringyl structure (Sy=4-hydroxi-3,5-dimethoxyphenyl) were present in smoke from wheat straw pellet combustion. The guaiacyl/syringyl ratio in wheat straw lignin has been found to be slightly over one [21]. Guaiacyl derivatives were predominant in peat/wood smoke. However, dimethoxyphenols were also present, making up about 10 % of the total methoxyphenol concentration. Mosses, such as the peat forming white moss, contains no or minor amounts of lignin, but contains non-lignin polyphenols [22, 23]. Other bog plants incorporated in the moss contain different types of lignin [24] from which the methoxyphenols are considered to originate. Both guaiacyl and syringyl derivatives have previously been studied from pyrolysis of peat [24]. The guaiacyl derivatives were

predominant in softwood pellet smoke, which is similar to results from previous studies [25, 26].

Table 4: Concentrations of compounds in smoke from peat/wood pellets during different combustion stages (conc. = average concentrations, s.d. = standard deviations, mg m^{-3}, Gu=4-hydroxy-3-methoxyphenyl, Sy=4-hydroxy-3,5-dimethoxyphenyl).

	Initial smouldering (I)		Early flaming (II)		Late flaming (III)		After-flame smouldering (IV)		Final glowing (V)	
No. of analyses	5		6		5		6		6	
	conc.	s.d.	conc.	s.d.	conc.	s.d.	conc.	s.d.	conc.	s.d.
Carbon dioxide	4500	800	92000	22000	110000	30000	26000	3000	27000	3000
Carbon monoxide	460	200	130	50	190	70	4500	800	3100	1000
Methane	22	9	4.3	1.4	15	4	680	430	230	240
Ethane	5.4	2.4	0.6	0.3	1.6	0.8	140	80	12	20
Ethene	11	3	6.6	2.4	5.9	1.9	61	34	6.5	8.8
Propane	2.5	1.9	0.1	0.1	0.3	0.3	24	17	0.5	1.1
Propene	7.7	2.9	1.3	0.6	1.3	0.3	33	21	0.9	1.6
Ethyne	2.1	1.3	3.1	1.2	1.9	1.0	3.0	1.6	2.8	1.1
1,3-Butadiene	2.5	0.8	0.04	0.02	0.04	0.02	3.7	2.8	0.02	0.04
Benzene	2.9	0.9	0.4	0.2	0.7	0.1	32	21	13	12
Methylbenzene	3.0	1.3	0.2	0.1	0.3	0.1	20	17	0.9	1.3
Naphthalene	2	1	7	5	0.4	0.2	3	2	1	1
Furan	24	10	0.7	0.4	0.3	0.3	3.2	2.2	0.2	0.2
2,5-Dimethylfuran	6	4	2	2	2	2	0.4	0.3	<0.03	
2-Furaldehyde	600	400	20	10	9	4	1	1	2	2
5-Hydroxymethyl-2-furaldehyde	100	100	200	100	20	10	2	3	2	1
Benzofuran	1	1	0.2	0.1	0.1	0.1	4	3	0.5	0.5
1,6-Anhydroglucose	100	100	90	50	100	100	8	6	2	2
Phenol	100	100	10	3	5	1	200	200	2	2
GuH (guaiacol)	100	100	5	3	2	1	10	20	0.7	0.6
GuCH$_3$	200	100	10	7	2	2	20	30	2	2
GuCH$_2$CH$_3$	200	200	5	4	0.7	0.5	10	20	0.7	0.6
GuCH=CH$_2$	2000	2000	20	10	5	3	7	13	2	1
GuCH=CHCH$_3$ (E)	4000	3000	200	100	5	3	10	30	6	4
GuCHO	400	200	400	200	30	10	10	10	10	10
GuCH=CHCHO	200	100	20	30	8	5	0.3	0.7	2	1
SyH (syringol)	80	70	70	40	3	1	3	4	1	1
SyCH$_3$	30	20	20	10	1	1	2	3	0.3	0.1
SyCH$_2$CH$_3$	20	10	9	5	0.6	0.2	<0.03		0.2	0.1
SyCH=CH$_2$	30	20	0.8	0.4	0.1	0.1	<0.03		0.1	0.1
SyCH=CHCH$_3$ (E)	30	20	10	10	0.2	0.4	<0.03		0.2	0.2
SyCHO	10	10	9	4	3	1	<0.03		0.4	0.2
Sum of organic comp.	9000		1000		200		1000		300	

Methoxyphenols are antioxidants and may therefore partly counteract the negative health effects of hazardous compounds in the smoke [18, 19]. The syringyl derivatives are stronger antioxidants than the corresponding guaiacols [19]. The concentrations of methoxyphenols decreased with increasing combustion efficiency, which is in accordance with results presented in literature [27]. In previous studies, high concentrations of methoxyphenols have been found in smoke from the combustion of firewood in a traditional tiled stove [27] and in alder smoke used for industrial meat curing [11]. Lower concentrations of methoxyphenols

have been determined in smoke from a residential pellet stove [1]. Methoxyphenols have also been studied during pyrolysis of wheat straw lignin [21]. Phenol is formed at somewhat higher combustion temperatures than the methoxyphenols and is a pyrolysis product of both lignin and hemicelluloses [20, 28-30].

Table 5: Concentrations of compounds in smoke from softwood pellets during the different combustion stages (conc. = average concentrations, s.d. = standard deviations, mg m^{-3}, Gu=4-hydroxy-3-methoxyphenyl, Sy=4-hydroxy-3,5-dimethoxyphenyl).

	Initial smouldering (I)		Early flaming (II)		Late flaming (III)		After-flame smouldering (IV)		Final glowing (V)	
No. of analyses	8		7		7		9		11	
	conc.	s.d.	conc.	s.d.	conc.	s.d.	conc.	s.d.	conc.	s.d.
Carbon dioxide	2400	400	110000	10000	87000	15000	22000	2000	22000	2000
Carbon monoxide	140	120	94	32	130	60	3700	400	1300	200
Methane	6.4	2.6	2.7	0.7	11	8	470	100	29	25
Ethane	1.4	0.8	0.3	0.1	1.2	1.0	80	23	1.0	1.3
Ethene	2.8	1.2	3.3	1.2	3.2	1.6	41	11	0.7	0.7
Propane	0.5	0.2	<0.03		0.2	0.2	10	4	0.04	0.07
Propene	1.4	0.7	0.5	0.2	0.7	0.4	16	6	0.09	0.11
Ethyne	0.9	0.6	1.4	0.5	0.8	0.5	2.4	0.3	1.4	0.5
1,3-Butadiene	0.6	0.2	0.1	0.1	0.1	0.1	0.6	0.3	<0.03	
Benzene	0.4	0.2	0.2	0.1	0.3	0.2	13	2	1.9	1.2
Methylbenzene	0.3	0.2	0.04	0.02	0.1	0.1	7.1	1.7	0.1	0.1
Naphthalene	0.2	0.2	0.3	0.1	0.06	0.04	1	1	0.2	0.1
Furan	4.2	2.3	0.3	0.1	0.5	0.5	0.7	0.3	0.04	0.06
2,5-Dimethylfuran	1	1	0.1	0.1	0.09	0.08	0.2	0.1	0.09	0.31
2-Furaldehyde	90	70	10	10	4	2	2	2	0.9	1.3
5-Hydroxymethyl-2-furaldehyde	50	30	20	10	6	3	4	2	2	1
Benzofuran	0.3	0.2	0.09	0.04	0.06	0.02	2	1	0.1	0.1
1,6-Anhydroglucose	30	20	20	10	20	10	5	3	1	1
Phenol	10	10	1	1	1	1	50	40	0.9	1.2
GuH (guaiacol)	60	30	1	1	2	1	8	11	0.8	0.8
GuCH$_3$	100	100	2	1	2	1	20	20	2	2
GuCH$_2$CH$_3$	100	100	0.7	0.2	0.7	0.3	9	11	0.9	1.7
GuCH=CH$_2$	500	400	4	2	3	2	5	4	2	2
GuCH=CHCH$_3$ (E)	1000	1000	9	9	7	8	20	20	9	9
GuCHO	300	200	60	50	20	20	20	10	10	10
GuCH=CHCHO	200	100	30	10	6	3	3	2	1	1
SyH (syringol)	<0.03		<0.03		<0.03		<0.03		<0.03	
SyCH$_3$	<0.03		<0.03		<0.03		<0.03		<0.03	
SyCH$_2$CH$_3$	<0.03		<0.03		<0.03		<0.03		<0.03	
SyCH=CH$_2$	<0.03		<0.03		<0.03		<0.03		<0.03	
SyCH=CHCH$_3$ (E)	<0.03		<0.03		<0.03		<0.03		<0.03	
SyCHO	<0.03		<0.03		<0.03		<0.03		<0.03	
Sum of organic comp.	3000		200		90		800		70	

The highest concentrations of furan and furan-related compounds such as 2,5-dimethylfuran, 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde were found during initial smouldering of all the fuels studied. Furan-related compounds are decomposition products of the polysaccharides of the fuels (mainly cellulose, hemicelluloses and starch) [18, 20, 29-32]. Furan and benzofuran are possibly carcinogenic to humans [33]. The concentrations of furans

decreased with more efficient combustion, which is in accordance with results presented in the literature [18, 20, 30].

In the case of softwood pellets, the concentration of 1,6-anhydroglucose was at its highest during initial smouldering. The anhydrosugar 1,6-anhydroglucose originates from the polysaccharides of the fuels [18, 31, 32, 34-36]. It is assumed to mainly appear condensed on particulate matter in the smoke, as it is polar and has a low volatility [18, 37]. 1,6-Anhydroglucose is not associated with negative environmental or health effects. High concentrations of 1,6-anhydroglucose have previously been found in a similar study of smoke from oat combustion [10].

3.2 Early and late flaming (II-III)

Early flaming samples (II) were collected early in the flaming phase, when a significant amount of the virgin fuel was still visible, whereas late flaming samples (III) were collected when all surfaces were charred. During early and late flaming, the highest combustion efficiencies were measured, calculated as $[CO_2]/([CO_2]+[CO])$. This was consistent with results from the combustion of oats and softwood pellets in previous studies [10, 38]. The highest concentrations of carbon dioxide were found during early flaming. During the early and late flaming stages, the concentration of oxygen in the smoke was 16-17 %.

Among the organic compounds ($\geq$ 6C), syringol (SyH) and vanillin (GuCHO) were dominant in the smoke from early flaming of straw pellets. Vanillin (GuCHO), 5-hydroxymethyl-2-furaldehyde, *trans*-propenylguaiacol (GuCH=CHCH$_3$ (*E*)) and 1,6-anhydroglucose were dominant in the smoke from early flaming of peat/wood pellets, whereas vanillin (GuCHO), coniferaldehyde (GuCH=CHCHO) and 1,6-anhydroglucose were predominant in softwood pellet smoke.

The concentrations of organic compounds were generally very low during the late flaming phase, although somewhat higher for peat/wood pellets. Major compounds emitted were methane, phenol and vanillin (GuCHO) from straw pellets and methane, 1,6-anhydroglucose and vanillin (GuCHO) from peat/wood and softwood pellets. The total concentration of organic compounds measured was half, or less than half, of that from early flaming in all of the pellets studied. This difference was mainly due to lower concentrations of vanillin.

Generally, the emissions from early and late flaming of wheat straw, peat/wood and softwood pellets were low. However, during flaming burning, softwood pellets burned more efficiently and with even lower emissions than straw and peat/wood pellets. This difference is more pronounced for peat/wood pellets, whereas in the case of straw pellets, the difference is smaller.

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3.3 After-flame smouldering (IV)

After-flame smouldering samples were collected in the smoke formed immediately after the flames had died down. The concentrations of organic compounds during after-flame smouldering were high for peat/wood and wood pellets, although lower than for initial smouldering. In the case of straw pellets, the concentrations were higher for after-flame smouldering than for initial smouldering. Predominant organic compounds emitted from all the pellets studied were methane, ethane, ethene, propene, benzene, methylbenzene, naphthalene and phenol.

Of the compounds studied, some have serious effects on health and the environment. Examples are methane (greenhouse gas), alkenes such as ethene and propene (rapidly photo-oxidant forming and genotoxic), alkanes (photo-oxidant forming), benzene (carcinogenic to humans), 1,3-butadiene (probably carcinogenic to humans), and naphthalene, furan and benzofuran (possibly carcinogenic to humans) [33]. When considering health and environmental aspects, after-flame smouldering gave rise to the highest concentrations of hazardous compounds. This was most pronounced in the case of the wheat straw pellets. However, these compounds are only formed during a short time period, which results in low total emissions. These high concentrations during after-flame smouldering were not found in the previous study of oat combustion [10].

Many of the polycyclic aromatic hydrocarbons (PAH) are toxic and carcinogenic. Their formation during the combustion of organic material is strongly influenced by combustion conditions [30, 39]. Polycyclic aromatic hydrocarbons are mainly formed at temperatures between 700 and 900°C, and their total yield increases with temperature and residence time in the furnace during this temperature interval [18, 30, 39]. At higher combustion temperatures, they are thermally decomposed [1, 18]. They are often condensed on particulate matter. The concentration of naphthalene in smoke from the after-flame smouldering (IV) of straw pellets and the early flaming (II) of peat/wood pellets was relatively high. The concentration of phenanthrene was in the same range as naphthalene for the fuels studied.

In a previous study of the combustion of wheat straw pellets, concentrations of about 0.2 mg m^{-3} of polycyclic aromatic hydrocarbons were measured at carbon monoxide concentrations of 700 mg m^{-3} [40]. A study of peat combustion in residential furnaces found that the concentrations of polycyclic aromatic hydrocarbons in the emissions (1.5 mg m^{-3}) were lower than those from firewood combustion and mainly consisted of phenanthrene, naphthalene and acenaphthylene [41]. This result was explained by the specific fuel composition and combustion processes of peat. Another study of combustion in a modified commercial hot water boiler presented the opposite findings, with almost ten times higher emissions of polycyclic aromatic hydrocarbons (2.5 mg m^{-3}), especially of high molecular weight polycyclic aromatic hydrocarbons, from peat than from wood chips [42].

3.4 Final glowing (V)

Final glowing samples were taken after gentle blowing to improve the glowing and remove charred surfaces. The final glowing stage continued for up to 20 min. Concentrations of organic compounds during the final glowing stage of straw and softwood pellets were very low, with methane, ethyne, benzene and vanillin (GuCHO) as the only prominent compounds. The concentrations from final glowing of peat/wood pellets were somewhat higher but were mainly made up of the same compounds. The carbon monoxide concentrations of all pellets were high during this stage, although this was not indicative of high concentrations of other compounds.

An earlier study of final glowing of oats reported almost negligible concentrations of organic compounds [10].

3.5 General discussion

The results from this laboratory study indicate that wheat straw and peat/wood pellets are fuels with relatively low concentrations of the compounds studied in the combustion emissions, almost as low as the concentrations found in smoke from softwood pellets. The concentrations of naphthalene and phenanthrene were, however, somewhat elevated in the case of peat/wood and straw pellets.

A previous laboratory study comparing the emissions of organic compounds from the combustion of oats and softwood pellets showed higher emissions of 1,6-anhydroglucose and furan-related compounds and lower emissions of methoxyphenols from oats than from wheat straw and peat/wood pellets in this study [10].

When comparing the concentrations of non-methane organic compounds ($\leq$ 7C) measured in this study to those measured in a study of barley straw combustion [43], the proportions, relative to the total amount, of ethane, propane, 1,3-butadiene, benzene and methylbenzene were higher, while the proportions of ethene and ethyne were lower. Most organic compounds ($\geq$ 6C) measured in the present study were also reported in a study of pyrolysis of wheat straw [44].

According to previous results, the composition of the emissions from peat combustion is typically very similar to that from other biomass burning [45]. Two different studies of smouldering combustion of peat, with even lower combustion efficiencies than initial smouldering in this study, showed higher emissions of organic compounds ($\leq$ 7C) compared to carbon dioxide [46, 47]. In one of the studies, concentrations of formaldehyde, acetic acid and formic acid were determined to be in the same range as ethene and propene [47].

According to Obernberger and Thek, 2004 [48], the use of straw pellets for residential heating cannot be recommended at present, due to the fact that small-scale pellet furnaces are neither designed nor suitable for this type of fuel. Instead, the use of straw pellets in medium

and large-scale plants has been suggested, due to the greater robustness and more sophisticated combustion technology of these systems [48]. Despite this, residential straw pellet combustion appliances are already on sale, for example in Sweden, Germany, Denmark and Austria.

This study covers incomplete combustion on a laboratory scale. However, in appropriate combustion appliances it is possible to optimize the combustion in order to achieve better energy efficiency and lower emissions. When improving residential combustion appliances for pellets, it is important to consider the large differences in emissions and in the proportion of the different compounds from the various combustion stages. It is important to supplement combustion appliance tests with analyses of specific compounds to ensure that the combustion also works well in a larger scale in residences. One possible way to decrease the total emissions from combustion of wood pellets is to keep combustion at the flaming combustion stages (II, III, Fig. 2), with high efficiency and low emissions, as much as possible and to avoid unnecessary after-flame smouldering (IV). This could be done, for example, by connecting the combustion appliance to a hot-water storage tank instead of intermittently regulating it towards a thermostat. In the case of wheat straw and peat/wood pellets, the combustion appliance must be efficient in order to avoid unnecessary emissions of compounds that are hazardous to health and the environment.

Combustion of wheat straw and peat/wood pellets differs in many ways from the combustion of wood pellets and may therefore lead to problems other than the emission of the organic compounds measured in this study. It is essential to try to identify these problems in order to minimize future hazards. A high ash content compared to wood pellets (Table 1) makes automatic removal of ash from the combustion appliance necessary. Peat has, depending on where it was harvested, a relatively high content of nitrogen (2.3 %) and sulphur (0.8 %) [49], which will lead to emissions of nitrogen oxides and sulphur dioxide during combustion. Due to the high content of chlorine (0.1-0.6 %) and potassium (0.7-0.8 %), combustion of wheat straw leads to a greater risk of sintering and corrosion compared to wood fuels [4, 40, 48, 50]. A high chloride content may also lead to a higher risk of dioxin formation [51]. The emissions of dioxins from the combustion of wheat straw pellets [40, 51] and peat pellets [52] have been studied.

4. Conclusions

Methoxyphenols, which are primary pyrolysis products of the lignin in the fuels, were released at high concentrations from the initial smouldering of the studied pellets, together with 1,6-anhydroglucose and furan-related compounds at lower concentrations.

The results of this laboratory study indicate that wheat straw and peat/wood pellets are fuels with relatively low emissions during combustion. However, wood pellets burned efficiently and with even lower emissions than straw and peat/wood pellets during flaming burning. The

emissions of the polycyclic aromatic hydrocarbons naphthalene and phenanthrene were higher from straw and peat/wood pellets.

Some of the compounds studied in the smoke have serious effects on health and the environment, e.g. greenhouse gases and photo-oxidant forming and carcinogenic compounds. After-flame smouldering of the studied pellets released high concentrations of these hazardous compounds. The after-flame smouldering stage should therefore be avoided if possible.

In residential combustion appliances, it is possible to optimize the burning of pellets, and the emissions are lower than in the present study of incomplete combustion. When developing pellet combustion appliances, it is essential to consider the emissions from the different combustion stages and to perform analyses of specific compounds.

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