



# Analysis through gas chromatography of the products obtained from slow pyrolysis applied to Russian feedstock

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## Abstract

Slow pyrolysis experiments were performed at 500 °C on Russian feedstock (hydrolysis lignin, peat, mixed sewage sludge, and pine and spruce woods, for comparison). The pyrolysis products were analyzed through gas chromatography, and more than 130 components were identified and grouped according to their chemical family. A qualitative analysis of the pyrolysis products showed that the highest amount of molecules (more than 40%) released during the pyrolysis of hydrolysis lignin belongs to the phenol chemical family. They result from the lignin degradation. The peat pyrolysis led to a large amount (more than 50%) of sugars. The molecules detected during the pyrolysis of the mixed sewage sludge are similar to that of the spruce sample and almost the same as that of the pine sample, because the selected sewage sludge is a mixture of municipal and industrial waste from pulp and paper industry. Comparisons between the data obtained for these Russian feedstock and that of the literature concerning quite similar materials exhibit differences which may be the consequence of the feedstock and of the experimental conditions.

**Keywords** Gas chromatography · Russian feedstock · Pyrolysis · Hydrolysis lignin · Peat · Mixed sewage sludge

## Introduction

Biomass may be considered as a promising energy resource that can help to overcome the current dependence on fossil fuels. Biomass can indeed be used to produce high-valued by-products or to generate energy through efficient and appropriate thermal degradations. One of the most developed thermochemical conversion processes is pyrolysis, which is known since ancient times and which is usually performed under low and isothermal temperatures and a non-oxidative atmosphere. The final products of the pyrolysis process are a solid residue, called bio-coal, a condensable organic part and non-condensable gases.

Applying slow pyrolysis to Russian feedstock (hydrolysis lignin, peat, mixed sewage sludge), the products obtained were analyzed through gas chromatography. For comparison, similar analyses were performed on Russian pine and spruce.

Hydrolysis lignin is a by-product of the production of fuels and chemicals through either percolation (Scholler process) or low temperature hydrolysis of wood (Bergius process) [1]. The Scholler process was used from 1920 to 1945. This hydrolysis process was carried out with sulfuric acid on wood chips to produce glucose and fuel [2]. The Bergius process was developed during World War I. It converts brown coal (also called lignite) into crude oil through hydrolysis with hydrochloric acid [3]. These processes were stopped at the end of World War II, because of their lack of profitability. After World War II and until the twenty-first century, acid hydrolysis of wood and agricultural waste was carried out to produce ethanol, fodder yeast and sugars (hexoses and pentoses) in the former USSR [1]. The current stock of hydrolysis lignin in Russia approximately represents 30 million tons and increases by 1.5 million tons each year [1].

Peat may be classified between renewable and non-renewable energy sources. Its recovery period exceeds 200 years.

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However, peat consumption in Russia lags far below its annual natural growth, which allows to consider peat as a renewable energy source. Peat deposits have a significant importance in the mineral resources of Russia. They are widespread almost all over the Russian territory, and they are mainly explored in Northwestern Russia. Peat is recognized as a unique natural potential of organic origin. It is an energy, industrial and agrochemical resource, necessary for both the development of energy and industry. It contains little fractions of sulfur and mercury, it has a high moisture content and a low ash content, and its lower calorific value is close to that of lignin (approximately  $17.8 \text{ MJ kg}^{-1}$ ). Sulfur and mercury have a significant impact on human health, and sulfur also contributes to acid rain by reacting with water and forming sulfuric acid [4]. A low ash content is required to limit waste management after combustion, and a low moisture content is required to maximize the efficiency of combustion [5].

The mixed sewage sludge which is considered in the present study is composed of municipal (80%) and industrial waste (20%), the industrial part coming from paper and pulp industry and being collected after the bleaching paper process. Sewage sludge is an organic–mineral complex, the organic part of which is biomass and adsorbed and partially oxidized pollutants of sewage, as well as nitrogen and phosphorus-containing compounds. The main components of the sewage sludge mineral part are silicon oxide, aluminum oxide, iron oxide and phosphorus, which may be in the form of low-soluble heavy metal phosphates, as well as calcium [6, 7]. The main part of wastewater from cities, pulp and paper plants, petrochemical industry and other industries is treated with biological methods, using activated sludge. Paper industry is a sector which generates large volumes of wastewater and sludge [8, 9].

The selected feedstock are currently not significantly valorized in Russia, even if their available amounts are high. Further valorizations of hydrolysis lignin, peat and sewage sludge could reduce energy resource shortages and environmental problems. Hydrolysis lignin is not being extensively valorized, because only no profitable uses have been found up to now. Its high moisture content, the presence of residual acid, the complexity of its composition and its extreme heterogeneity make it difficult to use as a fuel. Peat has a high moisture content. Moreover, the gases released during peat combustion are greenhouse gases, as in the case of fossil fuels. The main way to treat sewage sludge in Russia is its mechanical dehydration and storage in sludge reservoirs, where waste decontamination and biodegradation take place for a long time. This method does not meet modern environmental and technical requirements and leads to long-term and often irreversible removal of significant land resources. These processes also present significant risks of groundwater pollution in the zone of influence of waste storage sites. In

many countries, combustion is considered as one of the main routes to dispose this waste further characterized by a high organic content [10–12]. The main advantage of combustion is a significant reduction of the waste mass and volume, which is especially important in the conditions of shortage of available space for landfills and dumps [13]. Many hazardous organic compounds decompose during combustion. The use of the generated heat for power generation and ash and slag residues for the production of some materials can partially offset the cost of waste disposal.

Analytical pyrolysis combined with gas chromatography offers great opportunities to study and describe complex polymers such as hydrocarbons and lignin in biomass. This method allows obtaining detailed information on molecular changes and only requires small amounts of materials [14]. Moreover, it allows determining the proportions of different types of lignin: S (syringyl), G (guaiacyl) and H (*p*-hydroxyphenyl), without intersection with other components [15]. Pyrolysis gas chromatography is widely used to study the pyrolysis process and the components released during the thermal degradation. This method can be used to identify the composition of pyrolysis products using mass spectra libraries [16]. Some authors used pyrolysis gas chromatography–mass spectrometry methods (Py–GC/MS) to describe thermal degradation processes [17–20].

Considering the pyrolysis of wood components, cellulose and hemicellulose decompose to hexoses, pentoses and their derivatives, including furans and light (low molecular weight) oxygen-containing components [21–24]. Lignin decomposes to phenolic components including guaiacol, catechol and other phenols [25, 26]. A pyrolysis mechanism of a  $\beta$ -*O*-4 lignin dimer model (1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-ethanol) was described in [27]. These pyrolysis products react and finally form aromatic hydrocarbons [25]. For example, sugars are transformed into furans and then into aromatic hydrocarbons [28, 29]. Pyrolysis products with low molecular weight such as acids and ketones are exposed to oligomerization, aromatization, hydrogen transfer and oxygen-free reactions, also forming aromatic hydrocarbons [25, 30].

In the present study, the products obtained applying slow pyrolysis to Russian feedstock are analyzed using gas chromatography methods. More molecules are identified than in many papers of the literature, even if the pyrolysis conditions and analyses are quite similar. The properties of the lignocellulosic materials depend on the place and conditions where they grow. The properties of sewage sludge depend on the treatment it received. These elements may explain the differences with these results of the literature.

## Materials and methods

### Russian feedstock characteristics

In the present study, three Russian feedstock (hydrolysis lignin, peat and mixed sewage sludge) and two Russian woody biomass (pine and spruce) are considered.

Hydrolysis lignin was provided by the Bionet Company which produces hydrolysis lignin pellets from the Onega lignin dump, located in the Arkhangelsk region, Northwest Russia.

Peat was extracted from topsoil (up to 1.5 m) near the town of Mezen, Arkhangelsk region, Northwest Russia. The Mezen district belongs to the natural zone of forest tundra. Excess moisture combined with favorable thermal conditions for the growth of mosses causes an intensive process of waterlogging. The Mezen district is characterized by a combination of sparse forests with treeless tundra areas and the prevalence of peaty gley and weakly podzolized soils [31].

The mixed sewage sludge is composed of municipal (80%) and industrial (20%) waste, the industrial part coming from paper industry and being collected after the bleaching paper process. This industrial waste is formed during the primary mechanical treatment of wastewater and wastewater treatment with activated sludge. The mixed sewage sludge was partially dehydrated by decanter centrifuges and transported to the thermal power plant, before being stored in hoppers. The primary sampling of sewage sludge was carried out from the hopper.

Table 1 shows the proximate analyses and combustion properties of the feedstock. The volatile matter (VM) and fixed carbon (FC) contents were obtained by thermogravimetric analysis under nitrogen between 20 and 900 °C with a heating rate of 5 °C min<sup>-1</sup>. Moisture (M) was obtained placing a sample in an oven at 105 °C during 1 h and measuring the difference between the initial and final sample masses. Ash content (Ash) was determined burning the sample at

550 °C under air and weighing the final mass. The higher heating value was determined using a calorimeter IKA C 2000 Basic version 2, and the lower heating value (LHV) was determined from the higher heating value through classical calculations.

The proximate analyses obtained for pine and spruce samples are in good agreement with data from the literature for several woody biomass [32–36]. Biomass samples contain a high percentage of volatile organic compounds. The volatile matter and ash contents of the mixed sewage sludge agree with data from the papers [9, 12], who considered municipal sewage. The moisture percentage of the sewage sludge under consideration in the present study is very low, as it was partially dehydrated (see above). The ash contents of the different Russian feedstock, excluding pine, are higher than that of biomass present in Western Europe, for which values are lower than 1–2%. The proximate analysis of hydrolysis lignin is very close to those of spruce and pine, because it is a by-product of woods through Bergius's process. Many papers devoted to sewage sludge are available leading to different values of the proximate analyses. In the present study, its ash content (12.3%) is quite low when compared to values of the literature ranging from 24 to 55% as dry and ash-free [37, 38]. Because of a low ash content, sewage sludge has a net calorific value (LHV) higher than that found in the literature with data ranging from 10 to 15 MJ kg<sup>-1</sup> [37, 39]. Some paper sewage sludge has a LHV equal to 22.9 MJ kg<sup>-1</sup>, when collected after the clarifier [40]. The lower heating value of peat is slightly lower than that indicated in [41].

The ultimate analyses are presented in Table 2 for the different Russian feedstock. Carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) contents were determined with an EuroVectorEA-3000 analyzer, and oxygen (O) was calculated by difference based on mass balance. The H/C and O/C atomic ratios are computed from these contents.

Hydrolysis lignin contains the highest carbon percentage among the five selected feedstock, while sewage sludge has the lowest carbon percentage. Sewage sludge has also the lowest oxygen percentage, but the highest nitrogen and sulfur percentages. Spruce has the highest oxygen percentage. The hydrogen percentages do not vary so much between the five selected feedstock.

The ultimate analyses of pine and spruce agree with data of the literature [32–36]. The ultimate analysis of peat agrees with values given indicated in [43], for several peats extracted in Canada and Sweden. The ultimate analysis of the sewage sludge agrees with data of the literature concerning several industrial and municipal sewage sludge [12, 39, 44].

According to [42], the values of the H/C and O/C ratios of hydrolysis lignin and peat characterize materials containing mainly lignin. Because peat is the first step of biomass coalification process, its ultimate analysis classifies this

**Table 1** Proximate analysis and lower heating value of the Russian feedstock

Feedstock	VM/% <sup>a</sup>	FC/% <sup>a</sup>	M/% <sup>b</sup>	Ash/% <sup>c</sup>	LHV <sup>a</sup> /MJ kg <sup>-1</sup>
Hydrolysis lignin	65.8	34.2	5.1	4.2	21.6
Peat	68.2	21.0	13.7	2.8	17.8
Mixed sewage sludge	76.7	33.7	5.3	12.3	21.8
Spruce	81.0	18.9	7.2	3.5	20.0
Pine	79.1	20.9	7.4	0.3	20.3

<sup>a</sup>On dry and ash-free mass

<sup>b</sup>On raw mass

<sup>c</sup>On dry mass

**Table 2** Ultimate analysis of the Russian feedstock

Feedstock	C/% <sup>a</sup>	H/% <sup>a</sup>	O/% <sup>a</sup>	N/% <sup>a</sup>	S/% <sup>a</sup>	H/C <sup>b</sup>	O/C <sup>b</sup>
Hydrolysis lignin	59.5	6.5	33.7	0.2	<0.1	1.31	0.42
Peat	52.0	5.8	31.0	1.4	0.1	1.34	0.45
Mixed sewage sludge	46.0	6.3	28.3	1.9	3.6	1.64	0.46
Spruce	52.0	7.6	40.1	0.3	<0.1	1.75	0.58
Pine	47.7	7.0	37.1	0.4	<0.1	1.76	0.58

<sup>a</sup>On dry and ash-free mass<sup>b</sup>Atomic ratio according to [42]**Table 3** Biochemical composition of the Russian feedstock (on dry basis)

Feedstock	Extractives/%	Cellulose/%	Hemi-cellulose/%	Lignin/%
Spruce <sup>a</sup>	n.d <sup>b</sup>	44.3	26.1	28.4
Pine <sup>c</sup>	n.d <sup>b</sup>	45.0	27.7	25.0
Hydrolysis lignin	15.2	15.6	2.3	66.9
Peat <sup>d</sup>	5.4	29.1	51.2	14.3
Mixed sewage sludge <sup>e</sup>	n.d <sup>b</sup>	32.1	7.2	10.9

<sup>a</sup>From literature data [48]<sup>b</sup>n.d: non determined<sup>c</sup>From literature data [32–36]<sup>d</sup>Obtained as means of three Van Soest's protocol applied to the peat sample<sup>e</sup>From literature data [9]

sample as a woody peat with a low rank of coalification to lignite (see [45–47]) and this peat could be considered as degraded wood [46]. Coalification allows atomic H/C ratio to decrease, leading to values ranging from 1.46 to 0.88 for wood peat and coalified peat, respectively, the coalification process depending of the extraction depth [43, 47]. The ultimate analyses for sewage sludge were expected to be close to those of lignocellulosic materials considering its origin.

Table 3 gives the biochemical composition of the Russian feedstock.

As hydrolysis lignin is a by-product of the acid hydrolysis of wood that allows the breakdown of saccharide polymers (hemicellulose and cellulose), lignin is the main polymer in this sample. Hemicellulose is more severely fragmented by acid hydrolysis, because its residual content is lower than cellulose. The composition of hydrolysis lignin highly varies, depending on the composition of the original biomass (wood species, agricultural or agri-food waste, etc.).

The extractive contents are relatively high for hydrolysis lignin and peat. Acid hydrolysis also acts on lignin forming small phenolic entities that are easily extracted by polar solvents such as water and ethanol. Peat contains a huge quantity of extractive and carbohydrate compounds due to

the slow humus coalification, which also generates these compounds during the peat formation in the soil. High level of coalification leads to values of cellulose ranging from 3.3 to 13.5% [45]. In the present case, the cellulose content of 29.1% confirms the low level of coalification of the selected peat. The values of lignocellulosic compounds can highly vary for the same type of tree species, because they depend on the nature of the soil where the tree grew [32–36]. According to Glinska et al., the organic part of paper sewage sludge contents carbohydrates, lipids and proteins. Carbohydrates from paper sewage sludge mainly consists of cellulose [9]. As described by Gao et al., cellulose content in municipal sewage sludge ranges from 7 to 15%, depending on both the stage of the treatment process and the nature of the sludge (primary, secondary, activated or digested sludge) [12]. The cellulose content in the mixed sewage sludge under consideration is equal to 32.1%, as a mixture of industrial and municipal sludge.

### Pyrolysis GC/MS conditions

The sample masses considered for pyrolysis gas chromatography were the following: hydrolysis lignin—134 µg, peat—147 µg, sewage sludge—147 µg, spruce—152 µg and pine—147 µg, respectively.

The samples were thermally degraded under a helium atmosphere using the pyrolyser EGA/PY-3030D (Frontier Lab) with a cryotrap. The pyrolysis products of the samples were analyzed by gas chromatography–mass spectrometry method using GCMS-QP2010Plus device (Shimadzu, Japan).

The pyrolysis conditions were as follows: helium atmosphere, single-shot (single pyrolysis) operation mode, isothermal pyrolysis temperature equal to 500 °C and cryotrap temperature equal to –197 °C.

The chromatography conditions were as follows: capillary column HP-5MS, diameter equal to 0.25 mm, fixed phase thickness equal to 0.25 µm, column length equal to 30 m, sample introduction with a split ratio 1:100, input temperature equal to 280 °C, helium carrier gas, constant pressure gas flow control and flow through the column equal to 1 mL min<sup>-1</sup>. The temperature program started from 30 °C,

and the temperature was maintained constant for 5 min and then increased with a rate of  $5\text{ }^{\circ}\text{C min}^{-1}$  to  $230\text{ }^{\circ}\text{C}$  and with a rate of  $15\text{ }^{\circ}\text{C min}^{-1}$  to  $320\text{ }^{\circ}\text{C}$ . The final temperature was taken equal to  $320\text{ }^{\circ}\text{C}$  and kept constant for 5 min. The temperature of the transfer line with the mass detector was held at  $280\text{ }^{\circ}\text{C}$ , the temperature of the ion source was held at  $230\text{ }^{\circ}\text{C}$ , the ionization energy was 70 eV, the detector voltage was 0.9 kV (according to the automatic configuration), and the mass detector worked in the mass spectra scanning mode (TIC Scan) in the mass range 15–600 Da.

The chromatograms of pyrolysis products of the Russian feedstock under consideration contain a large number of peaks (Fig. 2 in Appendix 1). The main pyrolysis products are analyzed when their peaks have a sufficiently high signal-to-noise ratio for reliable identification. The identification of each pyrolysis product was performed by comparing the obtained chromatographic peak mass spectra with the Wiley-2010 and Nist-2011 mass spectra libraries. An agreement degree with the library spectra higher than 80% was chosen for positive identification. The residence time and mass spectra of pyrolysis products of plant components presented in [49, 50] were also used. The peak area of total ion current was used to estimate the relative content of identified components in the flue gas.

## Results and discussion

The chromatograms were obtained by total ion current using a GC–MS. They are shown in Appendix 1, Fig. 2. The vertical axis represents the full ion current response of the detector, while the horizontal axis represents the time of analysis. The chromatograms allow the identification of many molecules whose identification is given in Appendix 2.

The pyrolysis first proceeds via a dehydration stage with the formation of water. Then devolatilization stages occur associated with the decomposition of sugars and lignin, leading to the emissions of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and volatile organic compounds (VOC). These stages take place in a temperature range of  $220\text{--}350\text{ }^{\circ}\text{C}$ , depending on the biomass [51]. The percentage ratios of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and VOC are presented for each feedstock in Table 4.

Carbon dioxide and water come from the hydrolysis of cellulose and hemicellulose. Because hydrolysis lignin contains low amounts of carbohydrates, water could not be detected and quantified in the experimental conditions of the present study, which involve small sample masses. Water was probably below the quantification limit. As mentioned by several authors, the proportions highly depend on the pyrolysis processes, mainly temperatures and temperature ramps that separate pyrolysis from fast pyrolysis [10, 12].

The main components and peak areas on ion chromatograms corresponding to these components are given in

**Table 4** Groups of identified emitted gases for the Russian feedstock, %

	Hydrolysis lignin	Peat	Mixed sewage sludge	Spruce	Pine
$\text{CO}_2$	10.8	11.4	14.4	8.6	8.3
$\text{H}_2\text{O}$	–	20.3	20.0	11.7	9.5
VOC	89.2	68.3	65.7	79.7	82.1

Appendix 2, which lists the compounds identified by the mass spectrometer. The residence time for each molecule, the proportion of each molecule in the unit area and the name of the chemical family to which the molecule belongs are shown in Appendix 2. Components with short residence time are formic acid, furfural and others. These components are mainly released during the hemicellulose degradation. Acid and furan components come from the thermal degradation of cellulose and hemicellulose [52]. Hydrocarbons are the result of various reactions such as C–C bond breaking and dehydration of carbohydrates and products of their decomposition. The main pyrolysis products are phenols. They result from the lignin degradation—an aromatic component of woody biomass. It is known that when increasing the pyrolysis temperature, the number of formed phenols increases. As experiments were carried out at a sufficiently high temperature ( $500\text{ }^{\circ}\text{C}$ ), a large number of components of the phenol group were found.

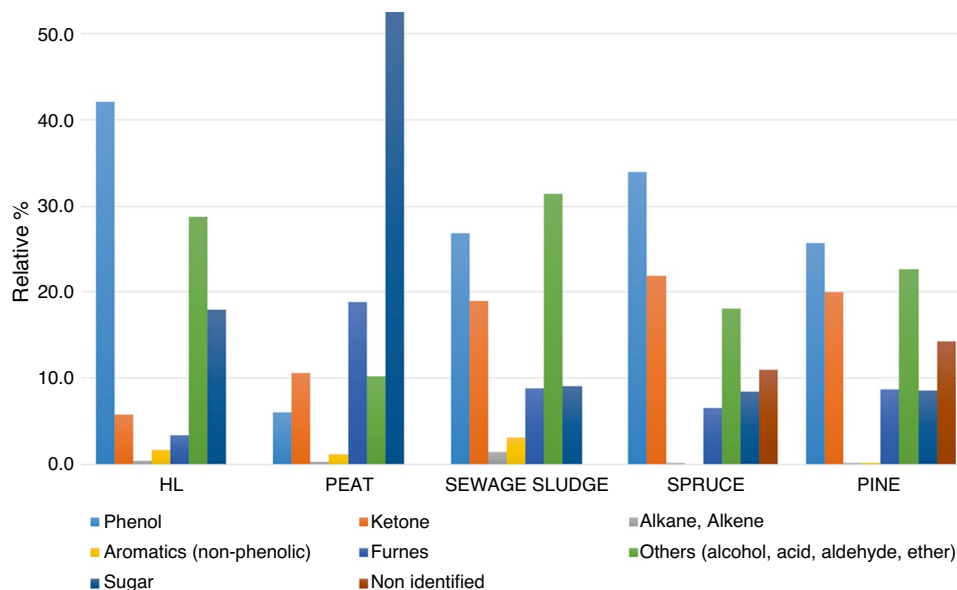
Many papers are available concerning the classification of individual molecules of VOC emitted during different pyrolysis processes of woody biomass under different experimental conditions [52–59]. The volatile organic components were divided according to the chemical families defined in [59]. However, guaiacols being methoxy-substituted phenols, these authors grouped guaiacols and phenols in the same family of phenol. The results of this classification are shown in Fig. 1, which allows estimating the ratio of different chemical families in pyrolysis products for the feedstock under consideration.

High oxygenate molecules dominate in VOC for all feedstock, being both aliphatic and aromatic, due to the break of covalent C–C and C–O bonds of lignocellulosic polymers (lignin, hemicellulose and cellulose). Sugars and phenols are well recognized as tracers of the thermal degradation of hemicellulose, cellulose and lignin, respectively. These results strongly agree with literature data concerning several woody biomass. If these chemical families always constitute the main VOC components, their own proportions depend both on the nature of the sample and on the pyrolysis operating conditions [54, 55, 60–62].

The highest amount of molecules (more than 40%) released during the thermal degradation of hydrolysis lignin belongs to the phenol chemical family. In addition, a



**Fig. 1** Distribution of identified components for each feedstock and gathered by chemical families during pyrolysis performed under the isothermal temperature of 500 °C



significant part of the molecules released during the thermal degradation of hydrolysis lignin are alcohol, acid, aldehyde and ether groups.

The percentage of phenols observed for peat is the lowest (6%) when compared to the other feedstock. Sugars represent a significant part (over 50%) of the products from peat, because peat was extracted from the upper soil layer (up to 1.5 m) and, consequently, is very slightly fossilized. The peat pyrolysis is characterized by the formation of more furans produced during the pyrolysis of the carbohydrate part of the sample (cellulose and hemicellulose). These results agree with previous data concerning the pyrolysis of woody peat samples [60, 61].

The molecules detected during the pyrolysis of the mixed sewage sludge for the groups of phenols, ketones, furans and sugars are close in percentage to that of the spruce sample and almost the same as that of the pine sample. Gao et al. proved that the main VOC emitted during the pyrolysis of several municipal sewage sludge are in decreasing contents: phenols, alcohols, ketones and nitrogen-containing compounds such as pyrroles, pyridines, pyrazines, amines and amides [12]. The proportions indicated in Fig. 1 (see also the last column of Table 4) are similar to those concerning pyrolysis studies cited in this review, except for nitrogen- and sulfur-containing molecules. In the present case, as sewage sludge is a mixture of municipal sludge and paper industry waste, it contains a relative high amount of nitrogen (see Table 2) and few nitrogen-containing compounds were detected: complex pyrazine (2-amino-9-(3,4-dihydroxy-5-hydro), pyrrole (1H indole), nitrile (4-methyl-2-oxopentenenitrile) and complex (oxazolidine, 2,2-diethyl-3-methyl-) (see Appendix 2). As the sulfur content was quite high (3.6%), sulfur-containing molecules were expected, as

indicated by Gao et al. in [12], but none of these compounds were identified in the conditions of the present study.

When compared to other samples, pine and spruce are characterized by a higher number of aldehydes pyrolysis products from carbohydrates (cellulose and hemicellulose), as well as fatty and resin acids.

Alkanes, alkenes and aromatics groups are found in small amounts in pyrolysis products, whatever the feedstock under consideration.

The results obtained for hydrolysis lignin in the present study can be compared to that of the papers by Kim et al. [57] and Windt et al. [54]. Both papers investigated untreated lignin, in contrast to the present paper, where hydrolysis lignin was used. In the paper by Windt et al., pyrolysis experiments were performed at 800 °C with a heating rate of 120 °C s<sup>-1</sup>, while in that by Kim et al. the pyrolysis experiments were performed at 800 °C with a heating rate of 20 °C min<sup>-1</sup>. The pyrolysis conditions also differ: In Windt et al., the pyrolysis was performed under N<sub>2</sub> and N<sub>2</sub>/acetylene mixture, and in Kim et al., the pyrolysis was performed under N<sub>2</sub> and CO<sub>2</sub>. Table 5 presents a comparison of the results of pyrolysis product identification.

In the papers by Windt et al. and by Kim et al., the pyrolysis experiments were performed at a higher temperature (800 °C) than in the present study (500 °C) and smaller numbers of molecules were identified (14–15 against 103). As hydrolysis lignin is the result of acid hydrolysis of lignocellulosic compounds, a slightly different composition of volatile organic compounds can be expected. Despite the absence of phenol function in the hydrolysis lignin, the thermolysis of the ether functions associated with aromatic rings can give C<sub>6</sub>H<sub>5</sub>O radicals and gives by completion phenols

**Table 5** Comparison with the results from the papers by Windt et al. and Kim et al., %

Chemical family	Lignin (Windt et al. [54])	Lignin (Kim et al. [57])	Hydrolysis lignin (this study)
Phenol	53.3	42.8	42.0
Ketone	6.7	21.4	5.7
Alkane, alkene	0	0	0.5
Aromatics (non-phenolic)	0	35.7	1.6
Furans	20.0	0	3.3
Others (alcohol, acid, aldehyde, ether)	13.4	0	28.8
Sugars	6.7	0	18.0
Total compounds Detected	15	14	103

**Table 6** Comparison of the results of pyrolysis product identification with that of the paper by Lee et al., %

Chemical family	Peat (Lee et al. [58])	Peat (present study)
Phenol	15.0	6.1
Ketone	0	10.6
Alkane, alkene	0	0.3
Aromatics (non-phenolic)	10.0	1.3
Furans	15.0	18.9
Others (alcohol, acid, aldehyde, ether)	60.0	10.2
Sugars	0	52.7
Total compounds detected	20	95

and guaiacols. Many sugars from cellulose and hemicellulose still remain in the hydrolysis lignin products.

The results of peat pyrolysis were compared to that of [58], where the pyrolysis was performed under N<sub>2</sub> and CO<sub>2</sub> conditions. Moreover, the temperature of the pyrolysis performed in this paper is much higher (700 °C and 900 °C) than in the present study (500 °C) and the heating rate was low (10 °C min<sup>-1</sup>). Table 6 presents a comparison of the pyrolysis product identification.

The results are significantly different for each family. The reason for such differences may lie in the peat composition. In the paper by Lee et al., peat has a lower carbon content (25.48%) than that (52%) of the peat sample considered in the present study. This means that the peat considered by Lee et al. is more fossilized. The absence of compounds resulting from the degradation of lignocellulosic compounds such as sugars, guaiacols, phenols and aldehydes suggests that the peat considered by Lee et al. initially contains few organic compounds and that carbon mineralization is present in the natural environment from which it was extracted.

Concerning sewage sludge and paper sludge, comparisons with available results from the literature are more complicated due to the differences between the materials. In [63], the authors analyzed the products obtained during

the pyrolysis of digested sewage sludge using Py-GC/MS and Py-FTIR. Six temperatures were considered between 300 and 900 °C. The N fraction of this sewage sludge was found equal to 9.96% much higher than that of the mixed sewage sludge considered in the present study (1.9%, see Table 2). Zuo et al. analyzed in [64] the pyrolysis products of three sewage sludge through TG-MS and Py-GC/MS. Four temperatures were considered among which 500 °C. A hydrothermal carbonization was applied to pulp and paper mill sludge in [65], the authors considering three temperatures among which 550 °C. The results of these papers are summarized in Table 7.

Because of a very high N fraction (9.96%), Zhou et al. observed a very high proportion of nitrogen-containing compounds (56.7%). This high N fraction may be explained by the treatment applied to the raw sewage sludge which could concentrate nitrogenous compounds. Zuo et al. observed a high proportion of aliphatic compounds (alkane, alkene). They did not observe aromatic hydrocarbons. They did not give the details of the oxygenated organic compounds (named AOC with a proportion of 8%). In the present study, there oxygenated organic compounds are only represented by phenols. Zuo et al. also observed a small proportion of steroids and of heterocyclic nitrogenated compounds (named HNC with a proportion of 7%). When analyzing the products from the pyrolysis of pulp and paper mill sludge, Wang et al. observed a high proportion of phenols [65]. They also observed a small proportion of nitrogen-containing compounds (2%). The N fraction of the material was approximately equal to 5%. The mixed sewage sludge considered in the present has proportions of the different chemical families lying between that of the literature.

## Conclusions

In the present study, the products obtained when applying slow pyrolysis to Russian feedstock (hydrolysis lignin, peat and sewage sludge) were investigated by gas chromatography

**Table 7** Comparison of the results of pyrolysis product identification with that of the papers by Zhou et al. on digested sewage sludge, by Zuo et al. on sewage sludge and by Wang et al. on pulp and paper mill sludge, %

Chemical family	SS (Zhou et al. [63])	SS (Zuo et al. [64])	PS (Wang et al. [65])	MSS (this study)
Phenol	0	8	32	6.1
Ketone	0	5*	–	10.6
Alkane, alkene	0	67	–	0.3
Aromatics (non-phenolic)	0	0	6	1.3
Furans	3	5*	4	18.9
Others (alcohol, acid, aldehyde, ether)	38.4	5*	11	10.2
Sugars	0	5*	21	52.7
Total compounds detected	> 110	51	n.d	95

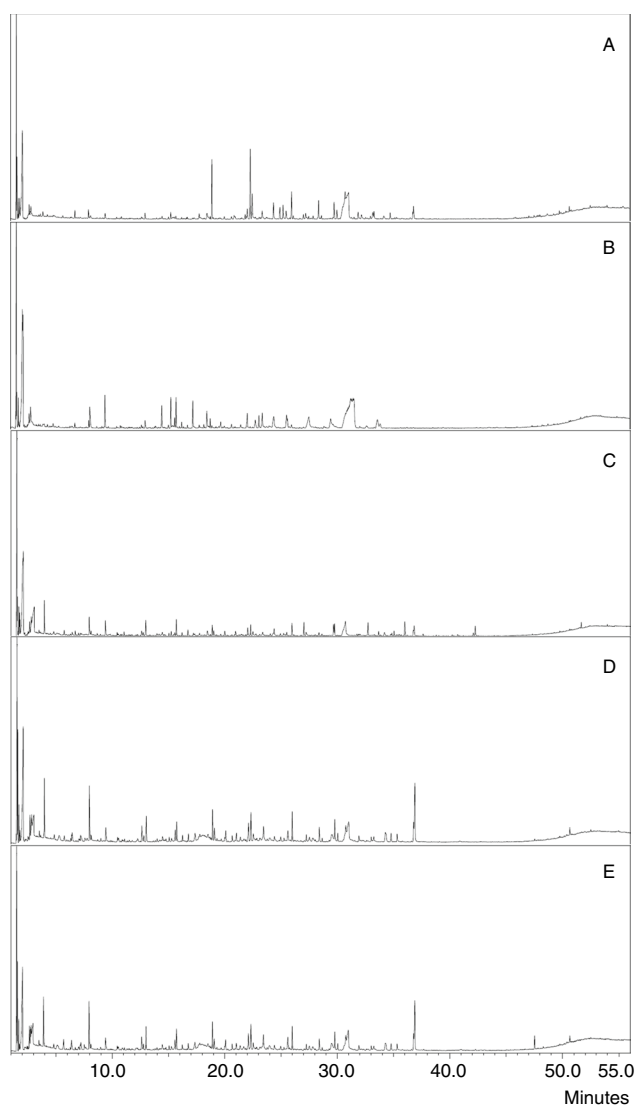
\*The oxygenous compounds observed by Zuo et al. include ketone, furans, sugars and others

methods. The pyrolysis experiments were carried out at a temperature of 500 °C. These conditions provided identification of a large number of components by the mass spectrometer and peak areas on ion chromatograms corresponding to these components. More molecules with a clearly visible peak on the chromatogram were indeed identified in the present study than in many papers of the literature. The gases emitted during the pyrolysis process were first determined as CO<sub>2</sub>, H<sub>2</sub>O and volatile organic components.

The highest amount of molecules (more than 40%) released during the thermal degradation of hydrolysis lignin belongs to the phenol chemical family, which result from the lignin degradation. Sugars represent a significant part (over 50%) of the peat degradation, because peat was very slightly fossilized being extracted from the upper soil layer (up to 1.5 m). The peat pyrolysis is characterized by the formation of more furans produced during the pyrolysis of the carbohydrate part of the sample (cellulose and hemicellulose), which agrees with the literature data. The mixed sewage sludge leads mainly to sugars (more than 52%). The data obtained in the present study globally agree with that of the literature. The differences may be partly explained by the origin of the feedstock or by their treatment conditions or even by the experimental conditions.

## Appendix 1

See Fig. 2.



**Fig. 2** Chromatograms of hydrolysis lignin (A), peat (B), sewage sludge (C), spruce (D) and pine (E) samples obtained from pyrolysis at 500 °C



## Appendix 2

See Table 8.

**Table 8** Components identified after pyrolysis of the lignocellulosic feedstock

Name	Residence time (min)	Area					Chemical family
		Hydrolysis lignin	Peat	Sewage sludge	Spruce	Pine	
Dihydrofuran	2.55	171,868	169,255	245,366			Furane
Acetaldehyde-hydroxy	2.61	425,869					Aldehyde
2,3-Butanedione	2.66		2,238,902	1,451,712			Ketone
Methyl vinyl ketone	2.67	1,213,391					Ketone
3-Buten-2-one	2.68				2,760,455	2,428,806	Ketone
Glycolaldehyde dimer	2.73					2,044,432	Aldehyde
2-Butanone	2.76	458,267			249,332	222,879	Ketone
Furan, 2-methyl-	2.79		3,501,232				Furane
Acetaldehyde, hydroxy-	2.80				2,172,329		Aldehyde
3-Pentanone	2.80					2,812,325	Ketone
Acid acetic	2.81	1,595,924		12,895,310	7,777,803	6,352,003	Acid
Propionic acid anhydride	2.84				2,689,051		Divers
2-Propanone, 1-hydroxy-	3.06			3,466,844	5,637,254	4,997,885	Ketone
1,3-Cyclohexadiene	3.28		103,414				Others
2-Butenal	3.52		141,116	302,950	622,653	552,996	Aldehyde
Benzene	3.64	220,763	156,633				Aromatic
2-Propanone-1hydroxy	3.88	527,541	114,898				Ketone
Formic acid propyl ester	4.28	239,551					Acid
Heptanol	4.28		339,514				Others
Heptane	4.50		112,435	155,235			Others
2-Ethylacrolein	4.64		52,872				Aldehyde
Furan, 2,5 dimethyl	4.78		550,541				Furane
1,4-Dioxin 1,3 dihydro	4.85			407,700	611,447	536,962	Furane
Methacrylic anhydride	5.18					551,241	Ketone
2-Vinylfuran	5.28		124,655				Furane
1,2-Ethanediol	5.29				1,509,699	1,151,429	Others
Glycerin	5.65	305,923		601,467			Others
1,2,3-Propanetriol	5.75				623,636	1,630,212	Others
2,4-Pentadienal	6.28					313,209	Aldehyde
Furan, 2-methyl-	6.32		169,839	138,912	398,232		Furane
4-Hydroxybut-1-en-3-one	6.38				1,339,211	1,884,040	Ketone
2-Butenal 2-methyl	6.40				571,252		Aldehyde
1-Penten-3-one	6.44		262,665				Ketone
(1H)-pyrrole	6.53		168,767				Others
Toluene	6.72	794,038	647,575	598,752		304,026	Aromatic
1-Hydroxy 2-butanone	6.99			310,224		321,625	Ketone
3-Pentanone	7.04				283,657		Ketone
Acetic anhydride	7.04					367,769	Ketone
2-Propanone 1-hydroxy	7.09				384,709		Ketone
2(5h)-furanone	7.19			273,613	595,723	500,481	Ketone
Acid acetic acetyloxy	7.28			260,045	997,720	1,225,262	Acid
Propanal	7.57				613,648	771,351	Aldehyde
2-Oxo-propanoic acid, methyl ester	7.92	943,052	919,113	2,379,033	7,152,861	5,885,735	Acid
(2H)-furan-3-one	8.04	136,049	4,139,077	610,231	783,607	5,885,735	Furane

**Table 8** (continued)

Name	Residence time (min)	Area					Chemical family
		Hydrolysis lignin	Peat	Sewage sludge	Spruce	Pine	
Hexanal	8.12	197,872					Aldehyde
3-Furanmethanol	8.99			172,930	995,499	405,548	Furane
1,6-Heptadien-4-ol	9.12		202,413				Others
Furfural	9.43	692,937	5,611,319	2,208,010	2,048,622	1,863,734	Furane
2-Furanmethanol	10.44		197,213	429,610			Furane
3-Penten-2-one 4-methyl	10.57				493,997	436,046	Ketone
P-xylene	10.75	115,306					Aromatic
2(3H)-Furanone 5-methyl	10.87	219,105	241,685	176,620	332,406	298,809	Furane
1,3-Dioxolane-4-methanol	10.92					295,778	Others
Diazenedicarboxamide	11.01				276,708		Others
2-Propanol acetyloxy	11.09			475,876	358,329	302,014	Others
4-Cyclopentene-1,3-dione	11.51		170,032	172,038	231,923		Ketone
Benzene ethenyl	11.58		162,966				Aromatic
2-Cyclopent-1-one	12.25		89,458	241,825			Ketone
1- Methylacrylic anhydride	12.26				529,345	340,814	Others
Ethanone 1-(2-furanyl)-	12.47		109,607				Ketone
2(5H)-furanone	12.61	190,129		960,468	2,454,183	2,068,231	Furane
Cis-1,2-Cyclohexanediol	12.76			573,503		835,597	Others
2-Cyclohexen-1-ol	12.80		191,714		982,817		Others
1,2-cyclopentanedione	13.03	609,301	1,373,113	2,231,478	3,817,076	3,163,500	Ketone
Cyclohexane 1,2-dimethyl trans	13.88		221,180				Others
2,5-Furandione 3-methyl	13.99				471,188	406,181	Furane
2-Furancarboxaldehyde, 5-methyl-	14.43	230,604	3,930,211				Furane
Hexane 3-bromo	14.78				332,327	297,353	Others
Phenol	15.23	704,972	4,979,157	625,190	440,013	575,852	Phenol
Alpha-acetobutyrolactone	15.59		1,386,968				Ketone
2H-Pyran-2,6(3H)-dione	15.60			468,941	1,664,978	1,600,154	Ketone
Oxazolidine, 2,2-diethyl-3-methyl-	15.73	267,919	4,340,826	2,176,368	2,744,149	2,745,115	Ketone
3-Hydroxy-4-pyrone	16.02	161,534	828,549		747,832	553,887	Ketone
Benzene methyl(1-methylethyl)-	16.63	115,336					Ketone
1,2-Cyclopentanedione 3-methyl	16.72	145,730	396,035	795,128	984,188	797,612	Ketone
4-Methyl-5H-furan-2-one	17.34			440,733		963,714	Furane
Cyclopentanecarboxylic acid 4 pentadecyl	17.36				1,982,154		Ketone
5-Hydroxymethyl-dihydrofuran-2-one	17.66					393,407	Furane
O-cresol	17.76	507,047	352,846	263,378	317,147	481,284	Phenol
Pentanoic acid 4-oxo	17.97					3,493,411	Acid
P-cresol	18.45	885,350	2,640,000	969,710			Phenol
2-Furancarboxylic acid methyl ester	18.64		119,622				Furane
Methyl 2-furoate	18.67				828,679		Ketone
2,3-Dihydro-5-hydroxy-6-methyl-4H-pyran	18.74	254,816	1,298,575	189,513			Ketone
2,5-Dimethyl-4-hydroxy-3(2H)-Furanone	18.778				620,382		Furane
Phenol, 2-methoxy- (Guaiacol)	18.89	6,897,153	301,065	1,433,699	4,132,667	3,246,424	Guaiacol
Cyclopropyl carbinol	19.01	150,604					Ketone
Cyclobutanol	19.07				1,957,334	1,477,669	Others
1,3-Cyclohexanedione 2-Methyl	19.26		164,816	139,917			Ketone
Levogluconone	19.67		930,072				Ketone

**Table 8** (continued)

Name	Residence time (min)	Area					Chemical family
		Hydrolysis lignin	Peat	Sewage sludge	Spruce	Pine	
Maltol	19.69		219,279	183,113	293,959		Ketone
D-Galactose 6-deoxy	19.84		98,245				Sugar
2,4(3H,5H)-Furandione 3-methyl	19.99	272,113	141,544	717,624	1,722,362	1,458,994	Furane
3(2h)-Pyridazinone	19.99					423,436	Ketone
But-1-ene-3-yne 1-ethoxy	20.01			96,678	1,242,647	888,870	Others
Phenol 2,3-dimethyl	20.85		102,297				Phenol
Phenol 2,4-dimethyl	20.86	435,108		151,450	148,325		Phenol
7-Methyl-1,4-dioxaspiro[2.4]heptan-5-One	20.87		153,988				Ketone
6-Methyl-1,4-dioxaspiro[2.4]heptan-5-One	20.98	305,055					Ketone
Oxepane	21.03				1,291,214	1,072,680	Ketone
2(3H)-Furanone dihydro-4-hydroxy-	21.35					941,724	Ketone
Phenol 4-ethyl	21.45		410,267				Phenol
Xanthosine	21.68				904,845		Ketone
Phenol 2-methoxy 3-methyl	21.84	507,760					Guaiacol
2-Methoxy-6-methylphenol	21.87					269,548	Guaiacol
4H-Pyran-4-one 3,5-dihydroxy-2-methyl-	21.96	265,782					Ketone
4-Methyl-2-oxopentanenitrile	22.03	1,378,150	2,722,415	1,136,674	2,908,378	2,313,825	Ketone
Creosol	22.30	8,549,887	110,649	1,444,989	3,996,271		Phenol
2-Methoxy-5-methylphenol	22.31				346,416	3,426,127	Guaiacol
Cathecol	22.46	3,110,022		700,653	1,385,300	1,254,573	Phenol
1,4:3,6-Dianhydro-alpha-d-glucopyranose	22.75		2,357,547	272,379	485,522	437,280	Sugar
2,3-Dihydro-benzofuran	23.07		2,002,718		368,273		Furane
5-Hydroxymethylfurfural	23.36	990,852	3,497,531	597,794	3,167,182	3,193,739	Furane
1,3-Cyclopentanedione 4-hydroxy-2-methyl	23.97					1,319,940	Ketone
1,2-Benzenediol, 3-methyl-	24.36	2,127,560		1,185,076	773,714	886,599	Aromatic
Guaiacol, 4-ethyl-	24.94	1,724,274			727,425		Guaiacol
Phenol 4-ethyl-2-methoxy-	24.96			394,607		602,718	Guaiacol
1,2-Benzenediol, 4-methyl-	25.21	1,814,251		365,248	414,655	308,030	Aromatic
2-Amino-9-(3,4-dihydroxy-5-hydro	25.36		4,970,974	525,544		1,128,016	Others
1H indole	25.37		98,214	169,308			Others
Benzofuran, 2,3-dihydro-2-methyl-	25.61		1,554,393		368,273		Furane
2-Methoxy-4-vinylphenol	25.96	3,288,914	668,666	1,775,105	3,875,236	3,085,632	Guaiacol
3-Methoxy-5-vinylphenol	26.11	313,929		143,890			Guaiacol
Phenol 4-(2-propenyl)-	26.69		101,034				Phenol
1,4-Benzenediol 2,6-dimethyl	27.02	490,712					Phenol
Phenol 2,6-dimethoxy-	27.03		214,244				Phenol
Vanillin	28.37	2,243,877			2,154,804		Phenol
1,2,4-Benzenetriol	27.81				1,213,505		Phenol
1,3-Benzenediol 4-ethyl-	27.88	343,524					Phenol
Benzaldehyde, 4-hydroxy-3-met	28.39			452,619		1,562,621	Aldehyde
Phenol, 2-methoxy-4-(2-propenyl)-	28.62	1,044,995		501,712	435,308	1,251,528	Guaiacol
Phenol, 2-methoxy-4-(1-propenyl)-	29.74	665,304		1,705,048	3,655,998		Guaiacol
Phenol, 2-methoxy-4-propyl-	30.00	1,726,768			1,206,059	1,046,676	Guaiacol
Beta.-d-glucopyranose, 1,6-anhydro-	30.91	16,819,807	79,414,200	7,993,668	13,496,110	12,965,889	Sugar

**Table 8** (continued)

Name	Residence time (min)	Area					Chemical family
		Hydrolysis lignin	Peat	Sewage sludge	Spruce	Pine	
Benzoic acid 4-hydroxy-3-methoxy	31.51	253,995					Guaiacol
Homovanillinyl alcohol	31.88	1,004,427					Aromatic
2-Propanone 1-(4-hydroxy-3-methoxyphenol)	31.90			293,762	1,067,252	866,959	Guaiacol
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	33.29	10,544,577			3,282,195	3,171,239	Guaiacol
Methyl-(2-hydroxy-3-ethoxy-benzyl) ether	34.77	883,938			1,335,744	1,052,156	Aromatic
2-Propenal, 3-(4-hydroxy-3-methoxyphenyl)	36.74	899,558	1,222,357	932,203	3,194,096	2,619,160	Guaiacol
4-((1E)-3-Hydroxy-1-propenyl)-2-methoxyphenol	38.81	1,920,898		234,869	12,834,806	10,173,182	Guaiacol
2,6,6-Trimethylcyclohexane	48.03	406,496					Others
1-Eicosanol	48.69	289,545					Others
Di- <i>n</i> -octyl phthalate	49.76	288,803					Others
3-Methyl stigmasterol	53.99	294,906					Others
Lup-20(29)-ene-3,28-diol 3 beta	55.42	420,605					Others

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