Vacuum pyrolysis of bark residues and primary sludges

Hooshang Pakdel, Geneviève Couture, and Christian Roy

ABSTRACT: Black spruce bark residues and primary sludges derived from the operation of the Daishowa pulp and paper plant in Quebec City, PQ, were processed by vacuum pyrolysis in a laboratory-scale batch reactor. The pyrolysis oil, water, charcoal, and gas were recovered and analyzed. The bark residues yielded 30.6% oil and 34.1% charcoal, and the primary sludges gave 40.1% oil and 30.1% charcoal on a feedstock air-dry basis. The oil phases recovered from the two pyrolysis experiments were fractionated into eight fractions; they were analyzed by gas chromatography/mass spectrometry. Both pyrolysis oil samples had a high content of phenolic compounds. These oils contained various fine chemicals that have possible commercial potential. Aliphatic and aromatic hydrocarbons, as well as long- and short-chain carboxylic acids, are also present in both pyrolysis oils.

KEYWORDS: Analysis, bark, biomass, oil, phenols, pyrolysis, residues, sludge, vacuum, wood waste.

The forest industry generates large quantities of wastes. For example, the pulp and paper industry in the province of Quebec produces approximately 1.6 million tons of wastes annually. It is estimated that about 81.4% of the pulp sludges are currently landfilled and 14.2% are incinerated, while the balance is converted to compost. Only 0.8% of bark residues are recycled; the rest are landfilled or combusted *(1)*. Similarly, most of the lignin is burned as a cheap fuel, and only a small proportion is recycled.

Before the era of petrochemicals, various chemicals were produced from biomass by techniques such as extraction, fermentation, and carbonization. The price of oil is low now, but its real value is high, since it is a limited resource. Biomass represents a potential resource for meeting many of our chemical needs in the petrochemical industry. New technologies have created products and processes that are competitive with oil-based synthetics and contribute to a sustainable environment *(2–5)*. For instance, phenolic compounds derived from biomass have commercial value and can be used as phenol replacement in phenol/formaldehyde resin production *(3)*. Moreover, a vast majority of clinically useful drugs are derived from prototype natural products. The search for efficaciously identifying and extracting source materials is a high-priority research and development activity *(6)*. Because lignin and bark are available in large quantities from pulp mills, it would appear that procedures based on their conversion from pulping liquors would have commercial value *(7, 8)*.

Biomass can be converted into different types of fuels and chemical feedstocks by a variety of thermochemical processes including pyrolysis, which transforms wood to charcoal and a liquid fuel (also called pyrolytic oil). Depending on the pyrolysis process and biomass constituents, the oil composition changes considerably and usually reflects the reactor environment *(9)*. Nevertheless, thermochemical processes can be designed with desirable characteristics. Although older pyrolysis techniques have a low efficiency, the pyroligneous liquors derived from such processes sometimes have com-

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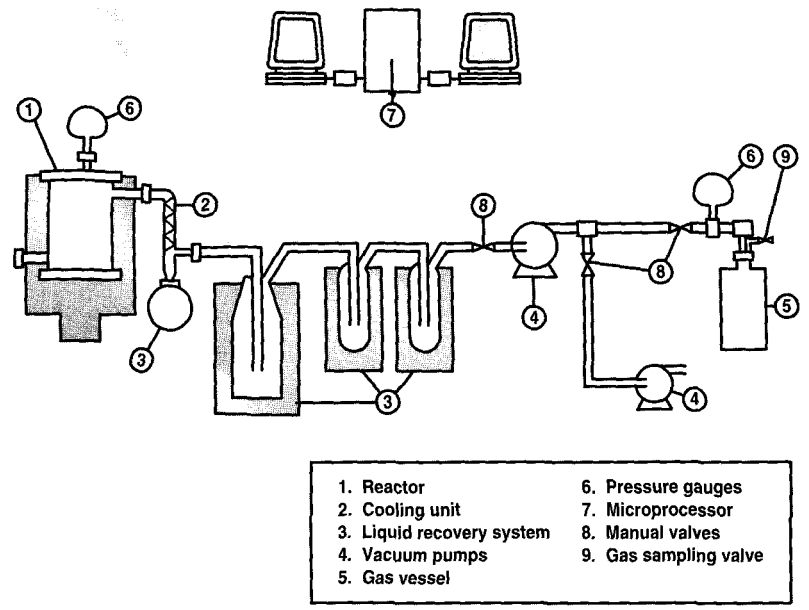
mercial value. For example, the ATOCHEM plant located in Premery, France, is a wood carbonization technology plant that produces 20,000 tons/year of charcoal. The pyroligneous liquors derived from the process are subjected to several distillation steps for producing various fine chemicals such as methylcyclopentenolone and hydroxymethylpyrone *(10)*. In Brazil, the growing demand for acetic acid, ethyl acetate, and methanol has led the wood carbonization industry (producing 11 million tons/year of wood charcoal) to investigate the possible recovery of wood tar volatile products *(11, 12)*. They have calculated that the return on investment for a 40-tons/day charcoal plant would increase from 6% to 29% if acetic acid and methanol could be recovered and sold as by-products along with charcoal *(11)*.

Vacuum pyrolysis, on the other hand, is a new thermochemical conversion technology. It involves rapid cracking of the complex polymeric structures of lignocellulosic materials and produces high yields of a complex primary oil rich in oxygen, along with a good-quality wood charcoal byproduct. There are two general routes for further development of the complex liquid mixtures: the pyrolysis liquid products must either be fractionated into simple mixtures of components with similar chemical and/or physical properties, or the pyrolysis products must be refined into more useful chemicals and/or chemical intermediates. However, knowing the composition of the pyrolysis products is a prerequisite to using them as chemical feedstocks.

The specific objective of this work was to assess the potential of the vacuum pyrolysis technology as a new recycling process to transform pulp and paper residues to useful products, such as oil and charcoal. Bark residues and primary sludges from Daishowa Inc. in Quebec City were the selected feedstocks for the laboratory-scale pyrolysis reactor.

1. Schematic of the batch vacuum pyrolysis system



I. Primary sludges and bark residues analyses

	Primary sludge #B086	*Bark residue #B087*
Moisture, %	3.78	4.17
Proximate analysis (dry basis), %:		
Ash	8.83	2.29
Fixed carbon	14.72	21.69
Volatile matter	76.45	76.02
Total	100.00	100.00
Elemental analysis, %		
C	50.35	54.15
H	6.02	6.25
N	0.49	0.36
S	0.81	0.07
O (by difference)	42.33	39.17
Total	100.00	100.00
Gross calorific value, MJ/kg	18	20

Composting, incineration, and landfilling are three methods currently used by the Daishowa plant to dispose its waste materials.

Experimental

Bark residues and primary sludges

Bark and primary sludge samples were provided by Daishowa Inc., a

II. Fractionation of primary sludges and bark residues pyrolysis oils

Fraction	Eluant[a]	Yield, %[b] Primary sludges	Yield, %[b] Bark
1	Petroleum ether (P.E.)	4.2	2.0
2	25% dichloromethane in P.E.	2.0	1.8
3	50% dichloromethane in P.E.	4.4	4.5
4	75% dichloromethane in P.E.	5.1	4.6
5	Dichloromethane	40.3	8.3
6	Ethyl acetate	14.4	43.1
7	Methanol	26.8	26.5
8	10% formic acid in methanol	8.9	8.0
Total		106.1	98.8

[a]150 mL by fraction
[b]Anhydrous oil basis

III. Yields on vacuum pyrolysis of primary sludges and bark residues

	Primary sludges, wt.%	Bark residues, wt.%
Oils	40.05	30.62
Solid residues/ charcoal	30.06	34.06
Pyrolytic water	14.40	16.71
Moisture	3.78	4.17
Gas	11.71	14.44
Total	100.00	100.00

IV. Oil phase analysis

Chemical analysis	Primary sludges	Bark residues
Moisture, %	3.04	3.37
Elemental composition, wt.%		
C	64.78	69.31
H	7.63	8.07
N	0.41	0.66
S	0.08	0.10
O (by difference)	27.10	21.86
Total	100.00	100.00
Gross calorific value, MJ/kg	25.1	30.9

Quebec City pulp and paper plant that uses thermomechanical and recycled pulps; the process includes a debarking operation. The bark originated from processed wood that was mainly (90%) black spruce; other species included jack pine, balsam fir, aspen poplar, and a small proportion of hardwoods, such as maple and birch. The bark residues also contained inorganic matter such as sand, stones, metal, and plastic-like organic substances. Primary sludges provided by the plant originated from the lignocellulosic wastes rejected from the entire plant operation, after the debarking stage.

The initial moisture content of the two industrial residues was 66% and 60% for the primary sludges and the bark, respectively. The two samples were air-dried at room temperature for one week, and their residual moisture content was 3.8% and 4.2%, respectively. The elemental and proximate analyses of the two samples are summarized in **Table I.**

Pyrolysis

Pyrolysis experiments were performed with approximately 1000 g of feedstock in a 10-L bench-scale reactor (see **Fig. 1**). The temperature of the reactor was raised at 2°C per min to a maximum of 486°C for both tests under a total pressure lower than 3.3 kPa for the sludges and 5.3 kPa for the bark residues.

Fractionation

Approximately 15 g of prewashed and activated silica gel (70-230 mesh, Aldrich) was packed in a 300-mm-long x 15-mm-ID glass column. About 500 mg of oil sample were preadsorbed on 1 g of silica gel and then transferred onto the column. The column was eluted sequentially with various solvents, as described in **Table II.**

GC/MS Analyses

We used an HP-5890 gas chromatograph (GC) with split injection mode at 290°C; it was equipped with a 30-m x 0.25-mm-ID capillary column coated with DB 1701 (J and W) featuring a 0.32-μm film thickness and helium carrier gas with a flow rate of about 1 mL/min. The GC initial oven temperature was 40°C for 2 min; it was then programmed to increase at 5°C/min to 270°C. The end of the column was introduced directly into the ion source of an HP-5970 series qua-

drupole mass selective detector. Typical mass spectrometric (MS) operating conditions were as follows: the transfer line was 270°C, and the ion source was 280°C with a 70-eV ionization potential. Data acquisition was done with HP-UX Chemstation software and an NBS library database. The mass range (m/z = 30 – 600 daltons) was scanned every two seconds.

Results and discussion

Pyrolysis oil

The pyrolysis products were composed of a liquid phase (oil, feedstock moisture, and pyrolytic water), a solid phase (charcoal), and a noncondensable gas phase. Both liquid and solid phases were weighed after each test, and the noncondensable gases were analyzed by gas chromatography. The yields are reported in **Table III,** and the mass balances reached 99.8% and 100.6% for the two tests. This unbalance was attributed to the gas phase, and the yield of gas was corrected accordingly in Table III. The pyrolysis liquid was composed of an oil phase with about 3% moisture and an aqueous phase containing water-soluble organic matter. No analyses were performed on the aqueous phase, but both phases were separated by decantation. The oil yield was remarkably high, especially for the primary sludge. In both cases, the solid residues consisted of carbonaceous substances mixed with inorganic materials. The oil phases from the two pyrolysis experiments were analyzed for residual water content (by Karl Fischer), gross calorific value, and elemental composition. Results are presented in **Table IV.** The aqueous phases contained about 50% by weight of the total organic matters.

The pyrolysis oil phase from the bark sample showed a higher calorific value compared to the one recovered from the primary sludge, which is associated with its higher carbon and hydrogen contents. The

V. GC/MS analysis of primary sludge pyrolysis oil

Fraction	*Compound*
1	Homologous series of *n*-alkanes (C_9 to C_{30})*; *o*-Xylene*; *m+p*-Xylene*; 3,6,6-Trimethylbicyclohept-2-ene; 1,3,5,7-Cyclooctatetraene*; Pinene*; Ethylmethylbenzene; 3-Carene*; Methylethenylbenzene*; Trimethylbenzene (2 isomers); *d*-Limonene*; Phellandrene*; Methylisopropylbenzene; Methylisopropylcyclohexadiene; Propenylbenzene; Butylbenzene; Indene; Ethyldimethylbenzene (3 isomers); Ethenyldimethylbenzene; Methylbenzofuran (2 isomers); Pentylbenzene; Methylindene (2 isomers); Naphthalene*; Dimethylbenzofuran; Hexylbenzene; Methylnaphthalene; Tetrahydrotrimethylnaphthalene; Octahydro-1,9,9-trimethyl-4-methylene-7,3-methanoazulene; Dimethylethyltetrahydronaphthalene; Octahydroisopropyltrimethylphenanthrene; Kaur-16-ene; Ergosten.
2	2-Ethylbenzimidazole; Octahydro-1,9,9-trimethyl-4-methylene-7,3-methanoazulene; Diethyltetramethylbenzene; Methylbiphenyl; Trimethylnaphthalene; Dimethyl-1,1-biphenyl (2 isomers); Fluorene*; 1,1-(1,3-propanediyl)*bis*(benzene), 1-Methyl-2-(2-phenylethenyl)benzene; Dimethylphenanthrene; 1,2-Phenylmethylnaphthalene; Terphenyl; Trimethylphenanthrene; 1-Methyl-7-isopropylphenanthrene; Tetramethylphenanthrene; Homologous series of linear and saturated carboxylic acid methyl esters (C10 to C28)*;
3	Trimethyl-2-cyclopenten-1-one; *o*-Cresol*; Dimethylphenol (3 isomers); Methoxymethylphenol (2 isomers); Dimethoxybenzene; Dimethoxymethylbenzene (2 isomers); Trimethylphenol; Ethylmethylphenol; Eugenol*; Methoxypropylphenol; Isoeugenol; Methoxypropenylphenol.
4	Furfural*; 1-(2-Furanyl)-ethanone; 5-Methylfurfural*; 3-Methylene-2-pentanone; 3-Methylfuranone; Phenol*; 4-Methoxyphenol*; 4-Methylphenol*; Methoxymethylphenol; Dimethylphenol (3 isomers); Ethylphenol; Ethylmethoxyphenol; Ethylmethylphenol; Eugenol*; Methoxypropylphenol; Isoeugenol*; Dihydroinden-5-ol; Vanillin*; 3-Methoxynaphthalenol.
5	2-Cyclopenten-1-one; Furfuryl alcohol*; 2-Methyl-2-cyclopenten-1-one; 1,2-Cyclopentanedione; Furanone*; 3-Methyl-3-penten-2-one; 3-Methyl-1,2-cyclopentanedion; 3-Methylfuranone*; Catechol*; 4-Methylcatechol*; Vanillin*; 1-(4-Hydroxy-3-methoxyphenyl)-2-propanone; Dehydroabietic acid*.
6	2-Methylpropanoic acid; Crotonic acid*; 3-Hydroxy-2-methyl-4-pyrone*; 1,3-Cyclohexanedione; 1-(3-Methoxyphenyl)-ethanone; Resorcinol*; 2-Methyl-1,4-benzenediol; 4,5-Dimethyl-4-hexene-3-one; Hexadecanoic acid*; Heptadecanoic acid*; Resin acids (secodehydroabietic, pimaric, sandaracopimaric, callitrisic, isopimaric, palustric, dehydroabietic, abietic acids)*.
7	Acetic acid*; Hydroxymethylacetate; 2-Methylpropanoic acid; Butanoic acid*; Isocrotonic acid*; Crotonic acid*; 3-Methyl-1,2-cyclopentanedione; 2,3,4-Trimethyl-2-cyclopenten-1-one; 3-Hydroxy-2-methyl-4-pyrone*; Cyclobutanol; Pentanedioic acid monomethyl ester; Dimethylbutanoic acid; Octanoic acid*; 16-Hentriacontanone; Tritriacontanone; C10-C28 carboxylic acids*.

*Confirmed by comparing the GC retention time with standard compound

VI. GC/MS analysis of bark residue pyrolysis oil

Fraction	*Compound*
1	Homologous series of *n*-alkanes and *n*-alkenes (C_{11} to C_{29})*; Methylnaphthalene; Ethylnaphthalene (2 isomers); Dimethylnaphthalene (3 isomers); Trimethylnaphthalene (3 isomers); Octyl and nonylbenzene*; Homologous series of 1-Methylpentylbenzene to 1-Methyldocosylbenzene*; 1-Methyldodecene; Dimethylundecene; Homologous series of Pentylbenzene to Pentadecylbenzene.
2	Dimethylbenzofuran (2 isomers); Ethyl-(1-methylethenyl)benzene; Dimethylindene; Dihydromethylnaphthalene; Tetrahydrodimethylnaphthalene (5 isomers); Methylnaphthalene; Tetrahydrotrimethylnaphthalene; Dimethylnaphthalene; Methylbiphenyl; Dibenzofuran*; Trimethylnaphthalene; Fluorene*; Methyldibenzofuran; 1,1(1,3-Propanediyl)*bis*(benzene); Methylfluorene*; Ethylfluorene; Phenanthrene*; Dimethylfluorene; Methylanthracene; Dimethylphenanthrene; Trimethylphenanthrene; Tetramethylphenanthrene; Dimethylbenz(a)anthracene.
3	Benzaldehyde; Furfurylacetate*; Methylbenzoate; Methoxyphenol; 4-Methylphenol*; Dimethylphenol (3 isomers); Dimethoxybenzene (2 isomers); 2-Methoxymethylphenol; Ethylphenol; Dimethoxymethylbenzene; Methoxyethylphenol; Hydroxyphenyl-1-pentanone; Ethylmethylphenol; Trimethylphenol (2 isomers); Hydroxymethoxyphenylethanone; Methyl-2-isopropylphenol; Methoxypropylphenol; Eugenol*; Isoeugenol*; Homologous series of leaner carboxylic acid methyl esters (C10-C28)*.
4	5-Methylfurfural; Phenol*; 4-Methoxyphenol*; 4-Methylphenol*; Methylphenol (2 isomers); Methoxymethylphenol (2 isomers); Dimethylphenol (3 isomers); Methoxydimethylphenol; Ethylphenol; Ethylmethoxyphenol (2 isomers); Hydroxymethoxyphenylethanone; 2-Isopropylphenol*; Ethenyloxybenzene; Ethylmethylphenol; Diethylphenol; 2-Propylphenol*; 4-Hydroxyindole*; Eugenol*; Methoxypropylphenol; Trimethylphenol; Isoeugenol*; Ethylbenzaldehyde (2 isomers); Dimethylbenzaldehyde; Methylbenzofuran; Benzenedicarboxaldehyde; Ethenylbenzaldehyde; Methoxypropenylphenol; Ethenylbenzaldehyde; Methoxypropenylphenol; Methylbenzenedicarboxaldehyde (2 isomers); Hydroxybenzaldehyde; Dimethylbenzenedicarboxaldehyde; Hydroxymethoxyphenyl-2-propanone; Ethenylbenzofuran; 3-Methylnaphthalenol (2 isomers).
5	2-Pentanol*; Methylpentanol (2 isomers); 3-Penten-2-one; Cyclopentanone; Cyclohexanone; Furfuryl alcohol*; 2-Furanylethanone; 5-Methylfurfural*; Butyrolactone; Furanone*; 3-Methyl-3-penten-2-one; 3-Methylfuranone*; Guaiacol*; 2-Methoxy-4-methylphenol*; Ethylmethoxyphenol; Dihydroindenone; 4-Methoxyphenol*; Catechol*; 2,6-Dimethoxyphenol*; Methylcatechol (2 isomers); Isoeugenol*; Vanillin*; 2,6-Dihdroxy-4-methoxyphenylethanone.
6	Acetic acid*; Acetol*; Furfuryl alcohol*; Furanone*; 1-Methylcyclopenten-2-ol-3-one; Benzoic acid*; Hydroxymethylbutanone; Penten-1-ol; Catechol*; Methylbenzenediol (3 isomers); Vanillin*; Hydroquinone*; Hydroxymethoxyphenylethanone (2 isomers); Hydroxyphenylethanone; Hydroxymethoxyphenylpropanone; Decanoic acid*; Resin acids (secodehydroabietic, pimaric, sandaracopimaric, callitrisic, isopimaric, palustric, dehydroabietic, and abietic acids)*; Hexadecanoic acid*.
7	1,2-Ethandiol*; Crotonic acid*; 3-Hydroxy-2-methyl-4-pyrone*; Pyridine-1-oxide; C10-C28 carboxylic acids*.

* Confirmed by comparing the GC retention time with standard compound

two oil samples were fractionated, and each fraction was analyzed by gas chromatography/mass spectrometry (GC/MS). The bark oil recovery yield was nearly 100% after fractionation. The overestimated yield of 106.1% for the primary sludge-derived oil in Table II was attributed to incomplete removal of both the solvents and the soluble silica gel in the formic acid/methanol fraction.

Tables V and VI show the main chemical composition of Fractions 1-7 for both primary sludge and bark residue pyrolysis oils. All the assignments were based on the library search file capability of the GC/MS. Furthermore, the mass spectra were manually analyzed to eliminate possible computer misinterpretation of the chemical structures. However, library searches do not definitively identify isomeric compounds, as shown in Tables V and VI. A complementary hyphenated technique, such as GC/FTIR (Fourier transform infrared spectroscopy) or simultaneous GC/FTIR/MS, is required for their unambiguous assignments. Those compounds identified by an asterisk in Tables V and VI were confirmed by comparing their GC retention times with standard compounds. Fraction 1 mainly contained linear aliphatic hydrocarbons, and alicyclic hydrocarbons and benzene derivatives were also present. Polycyclic aromatic hydrocarbon derivatives were found in Fraction 2. Fractions 1 and 2 together represented 6.2% and 3.8% of the primary sludges and bark pyrolysis oils, respectively (see Table II). Interestingly, several biomass natural constituents, such as *d*-limonene, ß-pinene, carboxylic acids, and their methyl esters, were found in Fractions 1-2 and 6-7 without modification. The other compounds were produced by thermal degradation of the biomass polymeric structure. Carboxylic acid methyl esters (not reported earlier in the literature) are partially produced under the pyroly-

sis process by the methylation of the carboxylic acids. A detailed and extensive list of carboxylic acid methyl esters has been reported recently in activated sludge and bark residue samples *(13)*. Our finding of polycyclic aromatic hydrocarbons in pyrolysis oils is associated with the recondensation reactions that occur during thermal cracking. However, vacuum application accelerates the removal of vapor products from the reaction chamber and reduces to some extent the recondensation reactions.

Both oils yielded a similar proportion of Fractions 3 and 4, which were mainly characterized by their high content of phenolic-type compounds. Fraction 5 of both oils also has a high phenolic concentration and could be used with Fractions 3 and 4. Similarly, Fraction 6 of the bark pyrolysis oil contained high proportions of phenolic compounds. Their separation and concentration in one or two fractions depend on the fractionation methods used and the column efficiency. A bench-scale unit for separating and recovering phenolic compounds, based on a solvent extraction method, has been described earlier *(14)*. Low-molecular-weight carboxylic acids were also recovered in Fractions 6 and 7. Fractions 7 and 8 in particular were the most polar fractions and were difficult to characterize. Polyalcohols, sugars, dicarboxylic acids, as well as resins and fatty acids, are the main constituents of Fraction 8. We measured 0.5% low-molecular-weight carboxylic acids, 5.5% high-molecular-weight carboxylic acids, and 4.1% resin acids in the sludge-derived pyrolysis oil. The bark-derived oil yielded 0.8% low-molecular-weight carboxylic acids, 7.5% high-molecular-weight carboxylic acids, and 3.1% resin acids. The methods of analyses used have been described elsewhere *(13, 15)*. Canadian woods typically yield 0.5–1% by weight of fatty and resin acids by the pulping process *(16)*, which is significantly lower than the acid yield obtained by vacuum pyrolysis.

VII. Solid residue analysis

	Primary sludges	*Bark residues*
Moisture, %	0.59	0.46
Proximate analysis, wt.%		
Volatile matter	24.54	20.48
Ash	32.64	15.86
Fixed carbon	42.82	63.66
Total	100.00	100.00
Elemental analysis, wt.%		
C	81.78	87.69
H	3.03	3.29
N	0.98	1.02
S	3.49	0.20
O (by difference)	10.72	7.80
Total	100.00	100.00
Gross calorific value, MJ/kg	22.2	28.1

VIII. Pyrolysis gas composition

	Primary sludges, vol.%	*Bark residues, vol.%*
Hydrogen (H_2)	2.36	3.23
Methane (CH_4)	8.95	9.77
Carbon monoxide (CO)	36.16	29.79
Carbon dioxide (CO_2)	47.71	51.19
Ethene (C_2H_4)	0.83	0.78
Ethane (C_2H_6)	0.93	1.33
Propene (C_3H_6)	0.53	0.71
Propane (C_3H_8)	0.62	0.65
Acetaldehyde (CH_3COH)	0.69	0.74
Butene (C_3H_6)	0.21	0.29
Butane (C_4H_{10})	0.14	0.25
Acetone (CH_3COCH_3)	0.42	0.56
Others	0.45	0.72
Total	100.00	100.00
Average molecular wt., g/mol	34.67	35.17
Gross calorific value, MJ/kg	7.8	8.1

Highly polar compounds, such as carboxylic acids, have low responses in gas chromatographic analysis; therefore, their characterization was achieved by derivatization prior to their analysis. Earlier work indicated that vacuum pyrolysis of biomass produces high yields of oil with a relatively low average molecular weight distributed in the range of 100–500 daltons *(15)*. The pyrolysis oil composition is, however, dependent on the reaction condition as well as the initial feedstock. Lignin and bark are the most suitable feedstocks for producing phenolic compounds and high-molecular-weight carboxylic acids by vacuum pyrolysis *(17)*.

The present method of fractionation (Table II) is efficient for a detailed oil analysis but is not a suitable commercial extraction technique *(18)*.

Charcoal

Vacuum pyrolysis of primary sludges and bark residues gave 30 and 34 wt.% charcoal, respectively, on a feedstock air-dry basis. Charcoals from both pyrolysis runs were characterized in terms of gross calorific value, and proximate and elemental analyses. Results are summarized in **Table VII**. The gross calorific value of the bark charcoal is higher than that of the primary sludge charcoal; this can be attributed to its low ash content. However, both solid residues have a high carbon content and relatively high calorific values.

Noncondensable gas

The noncondensable gas phases recovered during both experiments were analyzed by gas chromatography, and the results are presented in **Table VIII**. The high CO_2 content of both gases resulted in a low gross calorific value. The gas can provide a makeup heat source for the pyrolysis process.

Conclusion

Vacuum pyrolysis of primary sludge and bark residues yielded 40% and 31% of pyrolysis oils, 12% and 14% gas, 14% and 17% pyrolytic water, and 30% and 34% charcoal, respectively, on an air-dry feedstock basis. Both pyrolysis oils were rich in phenolic compounds, fatty acids, and benzene derivatives. Some polycyclic aromatic hydrocarbons produced by the recondensation reactions during pyrolysis were also identified in the pyrolysis oils. Typical wood extractives, such as *d*-limonene, ß-pinene, and carboxylic acids, were recovered without modification in the pyrolysis oils. Vacuum pyrolysis produced higher yields of fatty acids than the yields reported for conventional wood pulping processes in the literature.

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CORRECTION

Figure 9(below) was omitted from "Determination of rosin sizing agents in paper by pyrolysis-gas chromatography combined with on-line methylation," by Yasuyuki Ishida, Hajime Ohtani, Takeshi Kato, Shin Tsuge, and Tatsuya Yano published in the March 1994 *Tappi Journal* pages 177-183.

Relationships between addition of rosin into the pulp slurry and rosin retained in paper samples, estimated by Py-GC.