

CHARACTERIZATION OF PYROLYSIS OILS OBTAINED FROM NON-CONVENTIONAL SOURCES

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INTRODUCTION

The effluents of pulp bleaching are the main problem of wastewater disposal faced by the pulp industry because of their non-biodegradability. Today the demand for quality discharges requires better methods than conventional biological processes. The changes recently proposed to the federal regulations for controlling discharges from pulp and paper industry operations in Canada have required many operations to install secondary biological effluent treatment process. Such treatment often produce sludges that must be removed from the system and disposed of routinely, usually daily or weekly. At present, Ontario and Québec have the strictest solids disposal regulations in Canada, with leachate criteria that approximate the U.S. Environmental Protection Agency (EPA) toxicity characteristic leaching procedure (TCLP) standard [1]. Most pulp and paper mills in the U.S. have some form of biological treatment, the majority having their own treatment plants, but some are tied into publicly owned treatment plants. Of those which have their own treatment plants, two thirds have aerated stabilization basins and one third have activated sludge [2].

Industrial wastewater secondary treatment using activated sludge techniques has gained increased acceptance in the paper industry. The advantages of activated sludge treatment over conventional aerated lagoons are less real estate requirement, less odour emissions, lower capital cost and higher sludge treatment efficiency [3]. One of the main disadvantages is the production of a large amount of sludge which is difficult to dewater and costly to dispose of. The Canadian pulp and paper industry produces about 2,200 t/d of sludge from wastewater treatment operations. Most of this sludge is produced in wood room or primary clarifiers treating total mill effluents. Approximately 54% of this total is incinerated, with most of the balance being landfilled [4]. Long term environmental uncertainties associated with landfilling, as well as increasing costs and a drive to greater energy efficiency, make it preferable to use the sludge.

When old cars and trucks are sent to scrap yards for shredding to recover ferrous and non-ferrous metals, large quantities of non-metallic waste, referred to as autofluff, are generated. Autofluff is a lightweight mixture of plastics, textile, glass, rubber, foam, paper and rust. Also, this material is contaminated with oils, lubricants and other fluids used in automobiles. The trend to substitute lightweight materials for iron and steel reduces the proportion of recycled metals and increases the amount of waste produced [5-8]. The economics of the shredding industry relates to the recovery and resale of the ferrous metal which is used to produce high quality steel. Over the years, the use of ferrous metals in automobiles has declined whereas that of plastics and non-ferrous metals has increased. There is a clear economic and environmental advantage to salvaging cars, since metals can be utilized that would otherwise end up as trash. In 1992, in Canada, one million cars and trucks were sent to scrap yards, while in the U.S., 11 million vehicles were taken off the road [7]. Autofluff production is estimated at 1,800,000 and 2,860,000 t/a, respectively for Canada and the U.S., most of which ends up in landfill sites.

Of the various disposal alternatives, conversion of these materials by pyrolysis or other proven technology to possible value-added products would reduce the use of costly landfill sites for disposal and utilize this potentially valuable resource. The Wastewater Technology Centre (WTC) of Environment Canada has been developing one such technology since 1982. The thermoconversion process involves low temperature treatment of materials such as sludge from the pulp and paper industry or autofluff, to produce liquid and solid fuel products. A key technical feature of this conversion is the formation of a byproduct oil referred to as pulp and paper sludge derived oil (PPSDO) or autofluff oil. The thermal conversion process has been extensively described elsewhere [9-11].

In 1992, Enersludge Inc., WTC and CANMET's Energy Research Laboratory (ERL) of Natural Resources Canada undertook a joint R&D program. ERL investigated pyrolysis oils obtained from autofluff and pulp and paper mill sludges. Analytical results are presented as well as a comparison of these oils with those obtained from tires and municipal sewage sludge.

EXPERIMENTAL

A set of samples was received for each pyrolysis experiment (PPSDO and autofluff oils). The first samples received included compounds with boiling points up to 150°C (-150°C) whereas the second samples contained compounds boiling above 150°C (+150°C). The +150°C samples

were further distilled to yield three additional fractions each. Fractionation was performed using automated ASTM D-1160 short path distillation apparatus. Fraction cuts were selected to reflect conventional cut points from the petroleum industry:

- ▶ 150°C-350°C - typical cut point for middle distillates
- ▶ 350°C-525°C - typical cut point for heavy gas oils
- ▶ +525°C - usual distillate-residue cut point

Physical and chemical analyses were performed according to appropriate ASTM methods.

The ^1H , DEPT ^{13}C and ^{13}C data were acquired on a VARIAN XL300 operated at 300 MHz in the ^1H mode and 75 MHz in the ^{13}C mode. The pulse sequence in DEPT experiments transfers the polarization of the hydrogen to the carbon nucleus to selectively increase its signal. The polarization transfer effect is dependent on the number of hydrogens bonded to a given carbon nucleus. This technique is used to distinguish between primary, secondary, tertiary and quaternary carbon atoms. The NMR spectra are presented in Fig. 1.

Infrared spectra were obtained using a PC-driven BOMEM MB100 Fourier transform infrared (FTIR) spectrometer fitted with a standard sample mounting device. The IR spectra from liquids were collected using a liquid cell fitted with a 13-mm diam circular window. The liquid cell windows are made of KBr and are separated by 0.02 mm. The spectra of the 350°C-525°C colloidal fractions were collected using the smearing technique on conventional 13-mm circular KBr discs. The IR spectra are presented in Fig. 2.

GC/MS work was performed on a Hewlett Packard 5890 GC coupled to a medium resolution mass spectrometer (MS). Chromatographic separation of the sample was done using a Hewlett Packard HP-1 30 m long methyl-silicon bonded fused silica capillary column of medium resolution fitted on the GC. This column is used for separating molecular components in a mixture based on their boiling point. The samples were injected in the GC at 35°C then heated to 200°C at 5°C/min. The temperature was maintained for 10 min at the end of the temperature profile. The chromatographed compounds were identified through a MS data library search.

RESULTS AND DISCUSSION

The +150°C liquids resembled light molasses, similar to a vacuum tower gas oil from a petroleum refinery. The -150°C materials were brown liquids. All samples had an odour characteristic of burnt organic matter. The lower boiling products had the strongest odour. The -150°C oils and the 150°C-350°C fractions were characterized by IR, ^1H & ^{13}C NMR and GC/MS.

Table 1 summarizes the fractionation results for the PPSDO and autoluff samples. For comparison, literature data for a tire oil are also included. With an initial boiling point (IBP) of 155°C, the fractionation of the +150°C autoluff sample yielded 90 wt % of distillate composed of 37 wt % in the middle distillate range and 53 wt % in the heavy gas oil range. This range is similar to that of a typical petroleum sample. The PPSDO +150°C sample had an IBP of 102°C and 76 wt % distillate of which 49 wt % was in the middle distillate range and 27 wt % in the heavy gas oil range. Fractionation of the autoluff sample produced more distillate of a heavier nature than the PPSDO. When compared to tire oil, these oils had higher IBPs because they were condensed at a set temperature whereas the tire oil was not. Therefore we cannot compare the distillate yields further.

During fractionation of the PPSDO +150°C sample, the maximum distillate temperature was 501°C due to the limitation of the pot temperature (400°C) from the automatic apparatus used for the distillation. The material loss was 6.0 wt % due to distillate that was trapped in the column and in the condenser. The trapped distillate was so waxy that heating the condenser to a maximum temperature of 80°C in order to recover some distillate was unsuccessful.

The samples were also analyzed using a series of tests commonly used for fuel analysis. Table 2 shows the results as well as literature data for sludge derived oil (SDO), tire oil, No.2 diesel fuel and No.6 fuel oil. The heat of combustion values for the sludge derived materials namely, PPSDO and SDO, are significantly lower, and their densities at 15°C are higher than the corresponding values for the autoluff oil, tire oil and the two fuels.

Table 2 also gives elemental analysis of the samples. Clearly, PPSDO and SDO produced oils having a lower carbon content. However, their H/C ratios are still comparable to the other data mainly due to their lower hydrogen content. Heteroatom levels, particularly N and O, are very high when compared with the other oils. Pour points of these pyrolysis oils fall in the fuel oil range and are much higher than diesel oils.

Figure 1 shows the proton-decoupled ^{13}C NMR spectra of two autoluff and two PPSDO oil fractions. The spectrum of the -150°C autoluff fraction exhibited a signal at 45 ppm associated with the $-\text{CH}_2\text{O}-$ group, an assignment confirmed by ^{13}C DEPT NMR (not shown). This

functional group is absent in the -150°C PPSDO fraction. The spectrum of the -150°C PPSDO fraction shows a signal at 182 ppm assigned to -COOH carbons. No carbonyl signal was observed in the C=O region of the -150°C autofluff fraction spectrum.

A comparison of the NMR spectra of the high boiling point fractions in Fig. 1 revealed significant differences. The spectrum of the PPSDO fraction shows many signals in the 170-180 ppm region due to various -COO(R,H) carbons. No signal was observed in the -COO- region of the autofluff fraction spectrum. Signals in the 150-160 ppm range on both spectra are due to the oxygen-bonded aromatic carbon in phenols. Signals in the 110-115 ppm region on the autofluff spectrum were assigned to terminal =CH₂'s in olefinic structures by ¹³C DEPT NMR.

Figure 2 shows the infrared spectra of selected autofluff and PPSDO fractions. The PPSDO spectra display absorptions in the 3200-3600 cm⁻¹ region which are more intense than in the autofluff fractions. This intensity also is accompanied by stronger and more complex carbonyl vibration band patterns in the PPSDO's than in the autofluff spectra. This indicates and confirms the presence of carboxylic acids suggested by NMR. Another difference between these two types of oils can be observed in the autofluff fraction spectra which display weak but well resolved olefinic and aromatic =C-H stretching and bending mode bands. This suggests the presence of significantly higher amounts of aromatic and olefinic compounds in the autofluff oil fractions.

Table 3 lists GC/MS derived compound type distributions in the low and high temperature PPSDO and autofluff oil fractions. Table 3 indicates that:

- 1) PPSDO fractions contained carboxylic acids;
- 2) autofluff fractions are more aromatic and olefinic than PPSDO fractions;
- 3) low temperature fractions are more aromatic than high temperature fractions;
- 4) high temperature fractions contain more alcohols than low temperature fractions;
- 5) high temperature PPSDO fraction contains a significant amount of nitriles.

CONCLUSIONS

Our study has shown that pyrolysis oils and their derived fractions are very complex mixtures of compounds including significant proportions of aromatics and olefins as well as nitriles, alcohols and ketones. In addition, carboxylic acids were found in PPSDO. Pyrolysis oil's heat of combustion and density values fall within the normal fuel oil range.

The high content of olefins and aromatics of these oils and their high H/C ratios would suggest possibilities as feedstocks for low cost, large volume surfactant utilization. The surfactants could be produced by sulphonation or sulphation reactions. A large-scale use would be for enhanced oil recovery for both conventional and heavy oil/bituminous sands and for cleaning heavy bunker oil pipelines. Also for PPSDO, polymerization in asphalt could be performed to improve asphalt cement quality for adhesion to aggregates due to its high nitrogen content.

The low sulphur content and the high heating value of the autofluff sample suggest it could be utilized as a liquid fuel, possibly by blending it with fuels of petroleum origin in order to lower the sulphur level. While the autofluff oil cannot be considered as a diesel fuel, it could be considered as a blending agent for use with a No.6 fuel oil. The autofluff characteristics resemble those of the No.6 fuel oil more than those of diesel.

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Table 1 - D-1160 fractionation results of pyrolysis oil samples.

Fraction	PPSDO	Autofluff	Tire oil ¹
IBP (°C)	102	155	37
IBP-350°C (wt %)	49	37	56
350°C-525°C ² (wt %)	27	53	37
Total (IBP-525°C) (wt %)	76	90	93
Residue (+525°C) (wt %)	18	8	7
Loss (wt %)	6 ³	2	n/a ⁴
Water (wt %)	trace	0	n/a

Table 2 - Physical and chemical analysis data of pyrolysis oil samples and petroleum fuels.

Analysis	PPSDO	Autofluff	SDO ⁵	Tire oil ²	No.2 Diesel	No.6 Fuel oil ⁶
Calorific value (MJ/kg)	32.1	41.8	35.3	43	44.9	42.3
(1000 btu/lb)	13.8	18.0	15.2	18.5	19.3	18.2
Density @ 15°C (kg/m ³)	1073.2	931.1	<1002	n/a	864.1	980
Elemental analysis (%)						
Carbon	68.1	83.3	72.4	85.9	86.9	85.7
Hydrogen	8.99	11.4	9.88	10.6	12.4	10.5
Nitrogen	8.82	1.50	6.35	1.4	n/a	2.0
Oxygen	12.6	3.2	10.8	1.2	n/a	n/a
Sulphur	0.39	0.5	1.11	0.9	0.44	0.5-3.5
H/C ratio	1.6	1.6	1.6	1.5	1.7	1.5
Pour point (°C)	6	>24 ⁷	0	-6	-40	0

¹ Data from reference [12]

² End-point for distillation of PPSDO: 501°C and for tire oil: 469°C

³ Large loss due to distillate trapped in column and condenser

⁴ n/a: not available

⁵ Data from reference [13]

⁶ Data from references [14-15]

⁷ Film formed on top preventing pouring of sample. Thus the pour point was reported as >24°C.

Table 3 - Compound type distribution in selected pyrolysis oil fractions by GC/MS.

Compound type	-150°C		102-350°C		150-350°C	
	PPSDO	AUTOFLUFF	PPSDO	AUTOFLUFF	PPSDO	AUTOFLUFF
Alcohols	8.8	10.8	14.7	12.6		
Aldehydes		3.7	0.5	1.3		
Amines	2.4		3.2	0.9		
Amides	3.1		2.7	1.1		
Aromatics	10.2	48.7	5.2	18.2		
Carboxylic acids	27.8		6.0			
Epoxides					0.6	
Esters		0.5	0.2	0.4		
Ethers	0.8		1.2	0.5		
Heterocyclics	5.7		7.1	2.3		
Ketones	2.8	6.8	4.4	5.1		
Nitriles	1.6	5.0	17.4	2.2		
Nitro			0.1			
Olefins	11.7	14.9	6.6	24.0		
Paraffins	14.6	9.7	8.9	29.5		
Total	89.5	100.1	78.2	98.7		

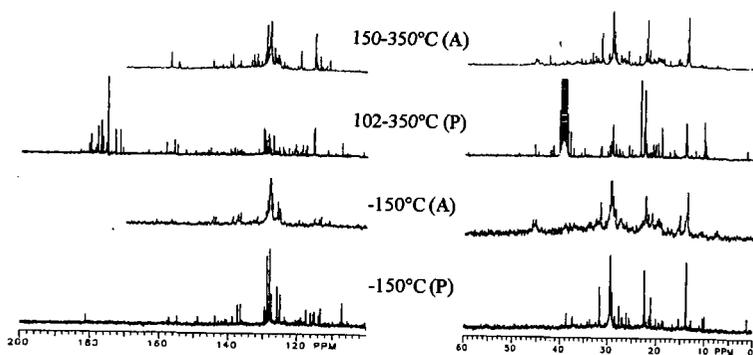


Fig. 1 - ^{13}C NMR regions (0-60 and 100-200 ppm) of selected autofluff (A) & PPSDO (P) fractions.

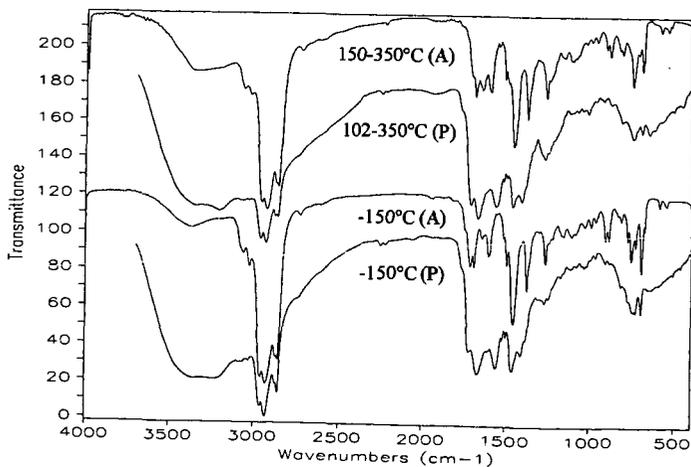


Fig. 2 - IR spectra of selected autofluff (A) & PPSDO (P) fractions