Fuels and chemicals from sewage sludge

1. The solvent extraction and composition of a lipid from a raw sewage sludge

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With the objective of producing a low-nitrogen and low-sulphur-containing substrate for pyrolysis to liquids, the lipid fraction of a dried raw Atlanta sludge was extracted with both chloroform and toluene. Although the solvents proved equally good for extraction of lipids, toluene is preferred because the pyrolysis of any residual chloroform in the extractive could present environmental problems. In Soxhlet extraction warm solvent removed about 12 wt% lipid whereas extraction by contact with boiling solvent gave 17–18 wt% lipid. Soxhlet extraction of the sludge resulted in 99.5% rejection of nitrogen and 94% rejection of sulphur. Boiling extraction rejected 99% nitrogen and 84% sulphur. The Soxhlet extract contained 10–13% oxygen whereas boiling extraction gave a lipid containing 14–16% oxygen. On a moisture-free basis, the recovered lipid, 91%, from the separation of the toluene extract was comprised of 65% free fatty acids, 7% glyceride fatty acids and 28% unsaponifiable material. The unsaponifiable matter had a distribution of alkanes ranging from C9 to C16, n-nonane and n-pentadecane being the major hydrocarbons present. The free fatty acid esters and the glyceride fatty acid esters had a distribution of fatty acids ranging from C12 to C18. Palmitic, stearic and oleic acids appeared to be the major fatty acids present. These results are significant for the catalytic thermal liquefaction of sewage sludge lipids for the production of fuel and chemical feedstocks.

(Keywords: extraction; sewage sludge; pyrolysis)

Sewage sludge is an inevitable by-product of wastewater treatment. In recent years, the cost of sewage sludge disposal has become increasingly expensive. A recent study confirmed that sludge treatment costs are in the order of 50% of the total wastewater treatment costs[1]. These costs can range from CAN $350–1050 per metric tonne of dry sludge at plants using incineration. Although significant cost savings can be achieved by optimizing existing systems, alternative new technologies may offer the greatest potential for cost reduction through improved energy recovery. One of these technologies is the thermal liquefaction of sewage sludge to yield fuel and chemical feedstocks.

The conversion of sewage sludge to fuel products has been known for more than 50 years[2]. Recently Bayer and Kutubuddin[3,4] showed that synthetic crude oil could be produced from a sewage sludge by heating it at 300–350°C in an oxygen-free environment for about 30 min. Based on these results, the Wastewater Technology Centre of Environment Canada developed technology for the thermal liquefaction of sewage sludge[5]. The liquefaction takes place in a rotary reactor at temperatures of 350–450°C.

Our investigations[6] showed that the oil is derived from both the protein and lipids in the sewage sludge. However, the oil derived from the protein is high in nitrogen and sulphur and is therefore a nuisance in two ways. First it precludes the use of the oil as a fuel. In addition the polar nature of the nitrogen- and sulphur-containing groups makes the separation of the oil from pyrolytic water very difficult. The lipids are potentially the major precursor of the useful oil; hence it would be advantageous to selectively extract the lipid fraction prior to pyrolysis and thereby lower the nitrogen and sulphur in the oil. The purpose of this paper is to report on two findings: (1) the development of two simple and convenient methods for extracting the lipid fraction from a raw sewage sludge and (2) the determination of the composition of a typical toluene-extracted lipid from the same sewage sludge.

EXPERIMENTAL

Atlanta dry raw sludge was supplied by the Wastewater Technology Centre of Environment Canada (Burlington, Ontario, L7R 4A6). Analytical grade chloroform and toluene were obtained from BDH Inc., Toronto, Ontario, Canada. Extraction thimbles (43 mm × 123 mm) were purchased from E-D Scientific Specialities, Mt Holly Springs, PA, USA. Hydrochloric acid and sodium hydroxide were purchased from Fisher Scientific, Nepean, Ontario, Canada. Analytical standards were supplied by Polyscience Corporation, Niles, IL, USA. Elemental and ash analyses were performed by B.C. Research Corporation, Vancouver, BC, as part of the Bioenergy Development Programme administered by Energy, Mines and Resources and Canmet, Ottawa. I.r. spectra were recorded on a Perkin-Elmer 1310 infrared spectrometer.

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^{13}C nuclear magnetic resonance (n.m.r.) spectra were obtained on a Gemini Varian 200 MHz spectrometer. Deuterated chloroform was used as solvent during analysis. Gas chromatographic analyses were performed on a Hewlett Packard 5880A series gas chromatograph equipped with a flame ionization detector and a 10% stabilized diethylene glycol succinate (DEGS) column (0.9 m × 3.1 mm o.d., 100/120 mesh). The operating parameters were as follows: detector temperature 225°C; injector temperature 225°C; temperature programme, 3 min at 50°C; heated at a rate of 5°C min^{-1} to 110°C; then at a rate of 2°C min^{-1} to 200°C. The carrier gas (He) flow rate was 30 ml min^{-1}.

Soxhlet extraction method

For each run, dried sludge (50 g) in a thimble was placed in a Soxhlet extraction unit and extracted with solvent (300 ml). The time for each siphoning cycle was about 11 min. Various extraction times were used for both solvents. After each extraction, the extracts were concentrated using a rotary evaporator and dried to constant mass in a vacuum desiccator. The extracted sludge was allowed to air-dry for 2 days. It was then placed in an oven at 75°C for 16 h to remove trace amounts of solvents from the residue. The masses of the extractive and the residue were recorded for each run.

Boiling extraction method

For each run, dried sludge (100 g) was placed in a 1 l Erlenmeyer flask equipped with a magnetic stirrer and a condenser. Solvent (600 ml) was added to the flask and refluxed. Various extraction times were used. At the end of each extraction, the resulting slurry was immediately filtered using a Buchner funnel, Whatman filter paper (no. 1) and water aspirator. The filtrates were concentrated using a rotary evaporator and dried to constant mass in a vacuum desiccator. The rest of the procedure was similar to the Soxhlet extraction method. All the extractives were semi-solid. Samples of the original dried sludge, the extracted sludge and the extractives were then analysed for C, H, O, N, S and ash.

RESULTS

The moisture contents of the original dried sludge and the extracted sludge were determined by the Karl–Fisher titration method and were found to be 2% and 1.5%, respectively. This method could not be used for extractives because of the chemical reaction with the Karl Fisher reagent. The moisture content of the chloroform and toluene extractives were determined by oven drying to constant weight and were found to be 4% and 5%, respectively.

Figure 1 shows the amount of lipid fraction extracted versus extraction time for both solvents. *Tables 1* and *2* show the percentage distribution of each element in the extractives, the extracted sludge and the original sludge. *Tables 3* and *4* are the mass balances for all chloroform and toluene samples.

The chemical separation of lipids into various components is outlined in *Figure 2*. Five toluene-extracted lipid samples were chemically separated into grease and free fatty acid fractions. The percentage distribution of these two fractions determined in the samples are presented in *Table 5*. The grease fractions were saponified to obtain unsaponifiables and the glyceride fatty acids.

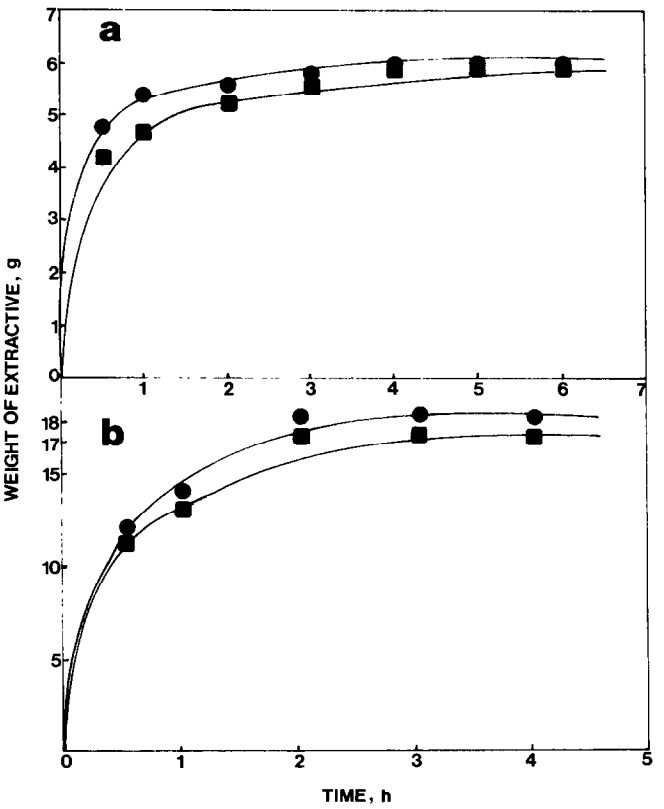

Figure 1 Amount of lipid fraction extracted versus extraction time: (a) Soxhlet extraction method, (b) boiling extraction method. ●, Chloroform extractives; ■, toluene extractives

Table 1 Elemental analyses[a] (wt%) of extractives, extracted sludges and original sludges (Soxhlet extraction method)

Components	C (%)	H (%)	O (%)	N (%)	S (%)	Ash (%)
Chloroform extractives	73.95	11.06	12.79	0.45	0.30	0.29
Extracted sludge	36.53	5.37	26.79	6.72	0.68	21.92
Toluene extractives	76.34	11.58	9.88	0.35	0.42	0.50
Extracted sludge	37.63	5.53	26.37	6.64	0.68	22.15
Original sludge	40.56	6.12	25.82	6.16	0.68	20.00

[a] Values reported here are average values of percentages from three samples

Table 2 Elemental analyses[a] (wt%) of extractives, extracted sludges and original sludges (boiling extraction method)

Components	C (%)	H (%)	O (%)	N (%)	S (%)	Ash (%)
Chloroform extractives	70.53	10.07	15.71	0.32	0.69	0.67
Extracted sludge	36.60	5.73	25.65	6.96	0.76	23.60
Toluene extractives	72.17	10.67	14.15	0.35	0.85	0.60
Extracted sludge	37.01	5.09	24.90	6.98	0.75	22.45
Original sludge	39.52	5.98	26.12	6.02	0.70	20.50

[a] Values reported here are average values of percentages from three samples

Table 3 Mass balances[a] for chloroform and toluene samples (Soxhlet extraction method)

Components	C (g)	H (g)	O (g)	N (g)	S (g)	Ash (g)	Total (g)
Chloroform extractives	4.44	0.66	0.77	0.03	0.02	0.02	5.94
Extracted sludge	16.07	2.35	11.79	2.96	0.30	9.64	43.03
Total	20.51	3.01	12.56	2.99	0.32	9.66	49.05
Toluene extractives	4.50	0.68	0.58	0.02	0.02	0.03	5.83
Extracted sludge	16.59	2.44	11.63	2.93	0.30	9.77	43.66
Total	21.09	3.12	12.21	2.95	0.32	9.80	49.49
Original sludge	20.28	3.06	12.91	3.08	0.34	10.00	49.67

[a] Values reported here are based on a 50 g sample

Table 4 Mass balances[a] for chloroform and toluene samples (boiling extraction method)

Components	C (g)	H (g)	O (g)	N (g)	S (g)	Ash (g)	Total (g)
Chloroform extractives	12.69	1.81	2.83	0.06	0.12	0.12	17.63
Extracted sludge	30.01	4.69	21.03	5.71	0.62	19.35	81.41
Total	42.70	6.50	23.86	5.77	0.74	19.47	99.04
Toluene extractives	12.27	1.81	2.41	0.06	0.14	0.10	16.79
Extracted sludge	30.72	4.22	20.67	5.79	0.62	18.63	80.65
Total	42.99	6.03	23.08	5.85	0.76	18.73	97.44
Original sludge	39.52	5.98	26.12	6.02	0.70	20.50	98.84

[a] Values reported here are based on a 100 g sample

The percentage distribution of these two fractions in different samples is shown in *Table 6*.

The i.r. spectra of the extracted lipids along with its different components obtained from the chemical separation are given in *Figure 3*. Proton-decoupled ^{13}C n.m.r. spectrum of the extractives is shown in *Figure 4*.

All the fatty acids, including glyceride fatty acids, were esterified with methanol and sulphuric acid and subjected

Table 5 Organic components of toluene-extracted lipids from sewage sludge

Sample no.	Original mass (g)	Grease (g)	Total free fatty acids (g)	Recovered lipid (g)	Recovered lipid (%)	Grease (%)[a]	Free Fatty acids (%)[a]
1	2.12	0.69	1.28	1.97	93	35	65
2	2.14	0.71	1.22	1.93	90	37	63
3	2.14	0.70	1.25	1.95	91	36	64
4	2.01	0.61	1.18	1.79	89	34	66
5	2.03	0.62	1.25	1.87	92	33	67

[a] Percentage value adjusted from recovery of lipids

Table 6 Constituents of the grease fraction

Sample no.	Original grease mass (g)	Unsaponifiables (g)	Unsaponifiables (%)[a]	Glyceride fatty acids (g)	Glyceride fatty acids (%)[a]	Recovered grease (g)	Recovered grease (%)
1	2.01	1.50	77	0.45	23	1.95	97
2	1.99	1.61	82	0.36	18	1.97	99
3	2.05	1.54	78	0.44	22	1.98	96

[a] Percentage value adjusted from recovery of grease

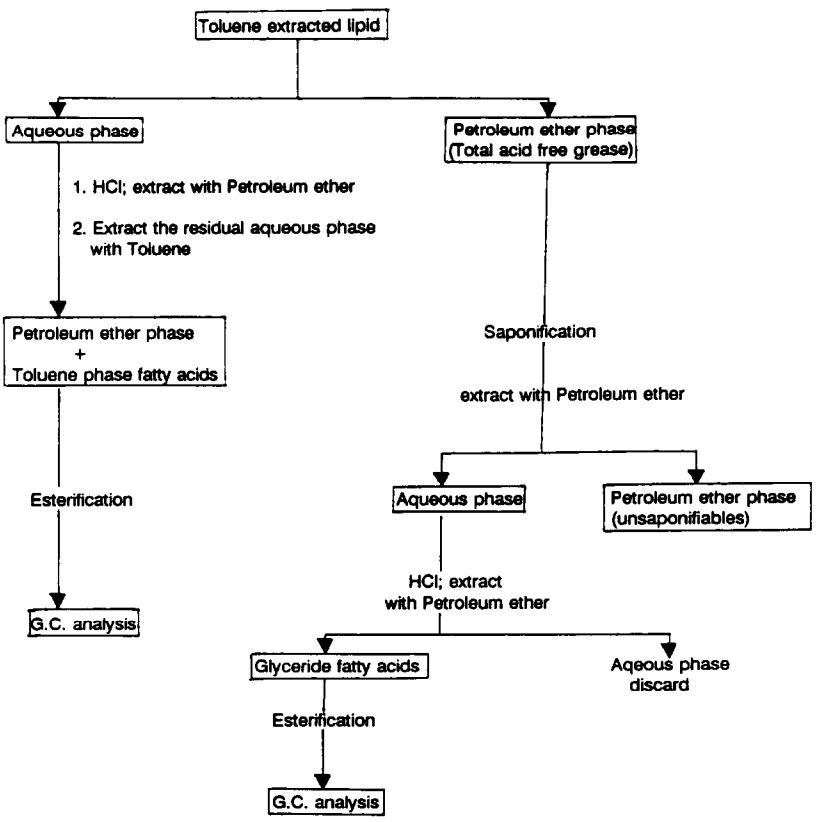

Figure 2 Scheme for chemical separation of lipids into various components

to gas chromatographic analyses for their identification and determination of relative composition in the mixture. Pure fatty acids were also esterified with methanol and sulphuric acid and were used as standards. The gas chromatographic retention times for the standard hydrocarbons and standard methyl esters of fatty acids are

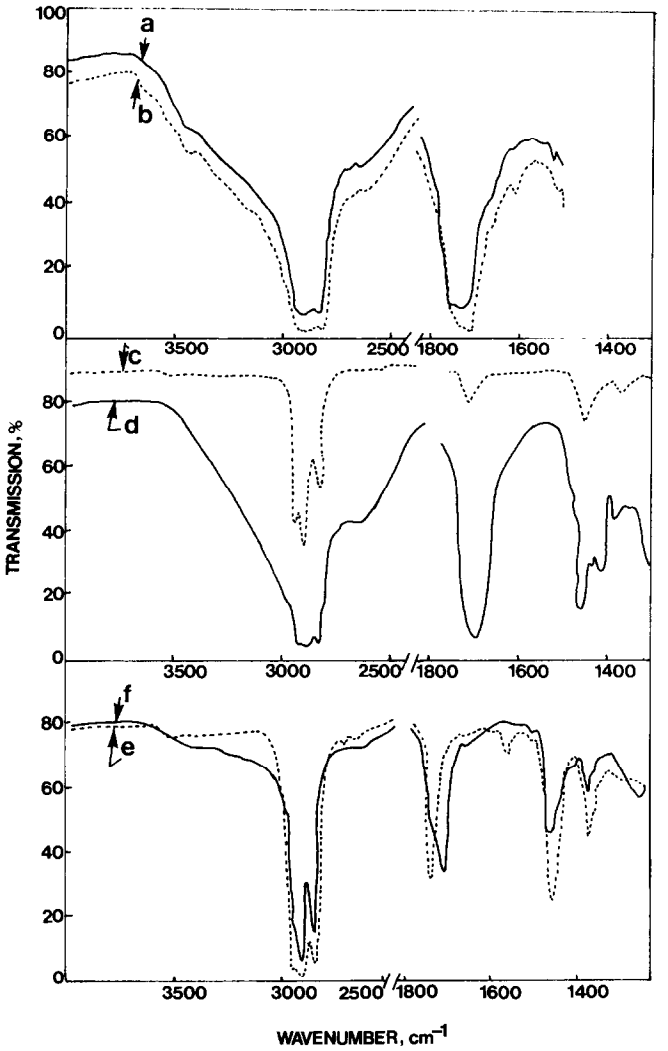

Figure 3 I.r. spectra of sewage sludge lipids (extractives) and its different components obtained from chemical separation. (a) Chloroform extractives, (b) toluene extractives, (c) grease, (d) free fatty acids, (e) unsaponifiables, (f) glyceride fatty acids

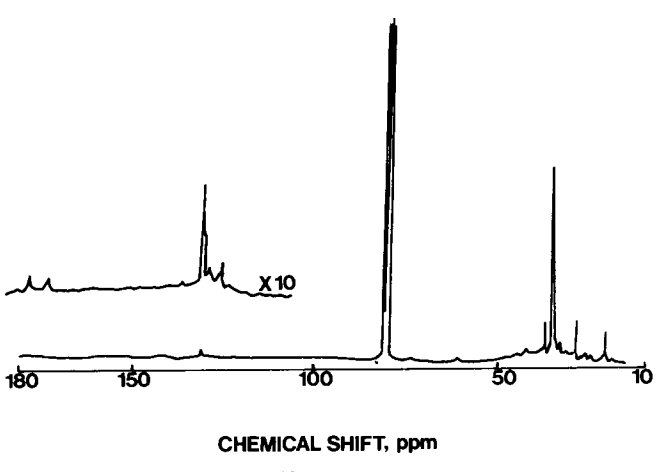

Figure 4 Proton-decoupled ^{13}C n.m.r. spectrum of the extractives

Table 7 Gas chromatographic retention times for the standard hydrocarbons and standard methyl esters of fatty acids

Standards	Retention time (min)
n-Hexane	0.14
n-Heptane	0.18
n-Octane	0.28
n-Nonane	0.48
n-Decane	0.96
n-Undecane	2.18
n-Dodecane	5.00
n-Tridecane	9.17
n-Tetradecane	14.31
n-Pentadecane	19.73
n-Hexadecane	24.71
Methyl laurate	27.49
Methyl myristate	37.06
Methyl palmitate	46.24
Methyl stearate	54.70
Methyl oleate	55.72
Methyl linoleate	58.19

Table 8 Composition of the unsaponifiable matter (percentage of the total unsaponifiable matter)

Hydrocarbons	Distribution (wt%)
n-Hexane	–
n-Heptane	–
n-Octane	–
n-Nonane	5.7
n-Decane	2.8
n-Undecane	0.7
n-Dodecane	4.8
n-Tridecane	3.5
n-Tetradecane	1.2
n-Pentadecane	5.3
n-Hexadecane	2.4
Total per cent	26.4

– Not detectable

Table 9 Composition of the free fatty acids and glyceride fatty acids (percentage of the total free fatty acids and glyceride fatty acids fraction)

Fatty acids (as esters)	Free fatty acids fraction	Glyceride fatty acids fraction
Saturated		
Methyl laurate	0.6	0.7
Methyl myristate	0.5	2.0
Methyl palmitate	44.6	21.1
Methyl stearate	40.7	28.7
Unsaturated		
Methyl oleate	5.1	4.6
Methyl linoleate	0.6	3.0
Total per cent	92.1	60.1

shown in *Table 7*. The percentage distributions of various components determined in the samples are listed in *Tables 8* and *9*. The gas chromatograms of the unsaponifiables and all esterified fatty acids are depicted in *Figures 5* and *6*.

DISCUSSION

Solvent extraction of lipid from a raw sewage sludge

Protein in the original dried sludge is a nuisance because its pyrolysis gives rise to high amounts of nitrogen and sulphur in the oils. Separating the lipid fraction prior to pyrolysis would thus lower the nitrogen

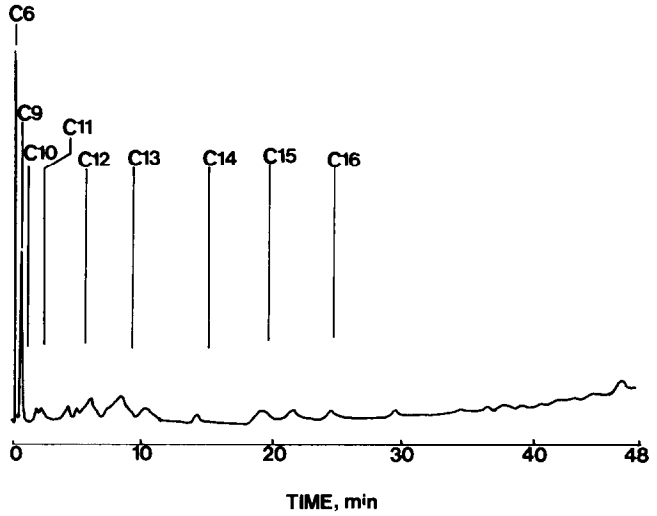

Figure 5 Gas chromatogram of the unsaponifiable materials

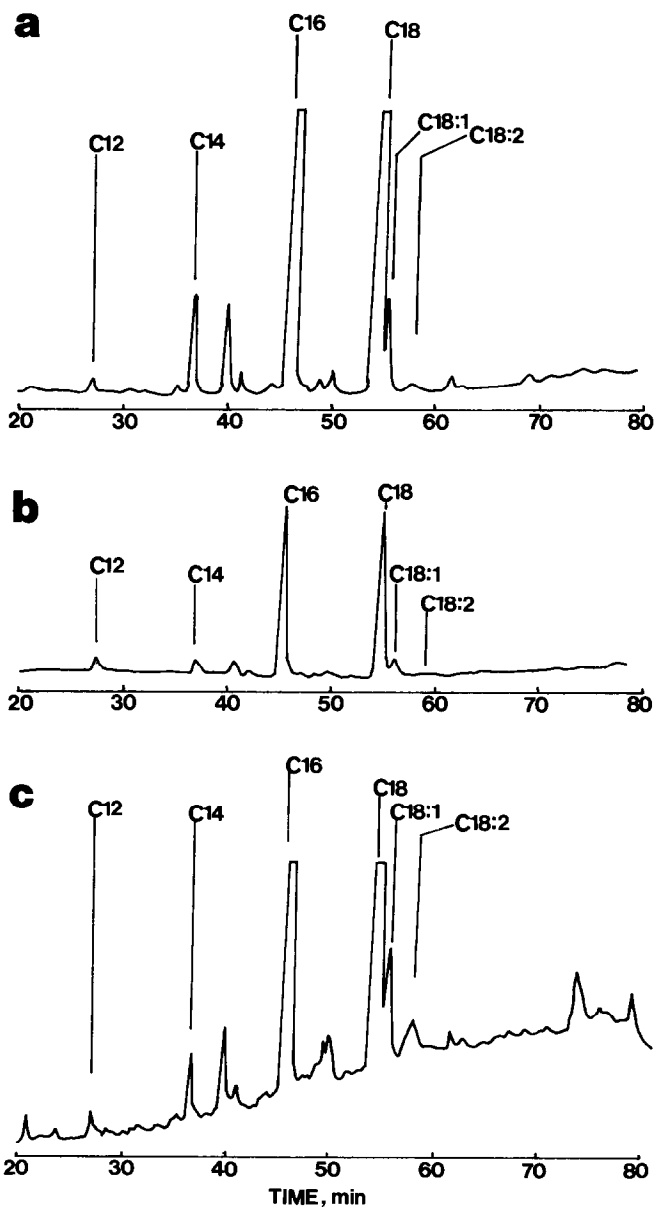

Figure 6 Gas chromatograms of the methyl esters of: (a) petroleum ether phase fatty acids, (b) toluene phase fatty acids, (c) glyceride fatty acids

and sulphur content in the oils. Bligh and Dyer[7] reported a methanol/chloroform/water method for the extraction of lipids from biological materials. Higgins *et al.*[8] also developed a methanol/toluene method for the extraction of lipids from sewage sludge. To avoid the two or three solvent system, we opted for a single solvent extraction method. Chloroform and toluene were chosen from a wide range of potential solvents on the basis of solvent polarity, volatility, non-miscibility with water, boiling point, cost and environmental consideration. Chloroform was selected because of its good solvent properties towards lipids and its low boiling point (62°C). This would allow complete removal and ease of recovery of chloroform before pyrolysis. However, all the chloroform must be removed before the lipid is pyrolysed. The presence of residual chloroform in extractives could result in the formation of toxic substances such as dioxins and other chlorinated organics during subsequent pyrolysis and incineration. A non-chlorinated solvent, toluene, was also selected because of its excellent solvent properties although its boiling point (110°C) is higher than chloroform. This may not be a disadvantage because unlike chloroform, toluene would not have to be removed completely from the extractives prior to the pyrolysis step.

Two extraction methods were investigated. Soxhlet extraction was chosen since it is a simple and convenient method. Extraction takes place with warm solvent and the solvent and sludge are largely separated at the end of the extraction. A boiling extraction method was chosen because it was thought that it would extract the lipid in less time. It can be clearly seen from *Figure 1a* that for each solvent, Soxhlet extraction for 4 h was required to remove 98% of the lipid extractable by this method. After 4 h no more lipid could be extracted from the sludge. At this optimum extraction time, the amount of chloroform extractive was 6 g (12 wt%) and the amount of toluene extractive was 5.9 g (11.8 wt%). As indicated in *Figure 1b*, the boiling extraction method extracted more material and resulted in 17–18 wt% lipid in only 2 h. From these results it is clear that both solvents are equally good for extracting lipids but toluene has to be the preferred solvent based on three important reasons: (1) it is less hazardous, (2) it is cheaper than chloroform and (3) unlike chloroform, it would not have to be removed completely from the extractives prior to pyrolysis. It is also clear that the boiling extraction method removes more material. Whether the boiling extraction method is better or not depends on the degree of nitrogen and sulphur rejection.

Mass (*Tables 3* and *4*) and elemental analyses (*Tables 1* and *2*) were made in order to determine the degree of nitrogen and sulphur separation after solvent extraction. As can be seen from *Tables 3* and *4*, the amount of nitrogen and sulphur in the extractives was very low compared to the original dried sludge. Soxhlet extraction of the sludge resulted in 99.5% rejection of nitrogen and 94% rejection of sulphur whereas boiling extraction rejected 99% nitrogen and 84% sulphur. It is also evident from these results that the Soxhlet extract contained 10–13% oxygen whereas boiling extraction gave a lipid containing 14–16% oxygen.

Figures 3a and *b* represent the i.r. spectra of the chloroform- and toluene-extracted lipids from sewage sludge. The strong peak at 1715 cm^{-1} indicates the presence of a carboxylic carbonyl group. The exceedingly

broad band reaching from 2500–3500 cm^{-1} is hydrogen-bonded O–H stretching. Another carbonyl peak at 1738 cm^{-1} indicates the presence of an ester group. Since all the i.r. spectra of the extractives were almost identical, it was decided to run only one ^{13}C n.m.r. spectrum (see *Figure 4*) for the extractive. The usual straight chain carbon atoms appear as a set of signals (14–32 ppm). Broad signals at 179.7 and 172.9 ppm are assigned to carboxylic acid and ester carbonyls, respectively. The broadening is probably due to the slightly different magnetic environments of the carbonyl groups in the different components. A signal at approximately 60 ppm is attributed to the glycerol carbons in the triglyceride esters. The unsaturated carbon atoms in the ester chains can clearly be seen around 130 ppm. Results from i.r. and ^{13}C n.m.r. clearly indicate the presence of long chain carboxylic acids, esters and hydrocarbons in the extractives.

Both solvent extraction methods are very effective for the selective extraction of lipids from raw sewage sludge. However boiling extraction appeared to be better given that more material was obtained. The toluene extractive from the boiling method contained 0.8% sulphur compared to 0.34% in the Soxhlet extractive, whereas the nitrogen contents (0.35%) in both extractives were very similar. Although a 0.8% sulphur content is slightly higher than that for the sewage sludge it should be noted that the extract contains almost all useful pyrolysis substrate whereas 84% of the sulphur from the sludge is rejected. The most desirable feature of the methods is therefore their ability to reject nitrogen and sulphur and concentrate useful pyrolysis substrate. Another advantage is the possibility and ease of solvent recovery after extraction since both the solvents are relatively volatile.

Characterization of toluene-extracted lipid from sewage sludge

From *Table 5*, it is quite obvious that the free fatty acids constitute the major part, by weight, of the lipid. On average, it was determined that the recovered material, 91%, consisted of 35% grease and 65% free fatty acids. This free fatty acid percentage is calculated based on the total free fatty acids obtained in the recovered lipid (i.e. combination of free fatty acids from petroleum ether extract plus the toluene extract). As can be seen from the flow chart in *Figure 2*, two free fatty acid fractions were obtained. The first was a petroleum ether phase fraction and the second was a toluene-extracted fraction. The petroleum ether phase contained the majority of the free fatty acids. Toluene was used to extract the residual acids from the aqueous solution. Despite this, some mechanical losses occurred as well as losses due to the formation of an emulsion during extraction.

Since the acid-free grease fraction contained esters of fatty acids which existed primarily as triglycerides, a saponification method was employed to determine the types of fatty acids that were present. From an initial 2 g grease sample, on average, 79% unsaponifiable matter was generated along with 21% glyceride fatty acid (*Table 6*). In terms of the total lipids recovered, the unsaponifiables accounted for 28% and the glyceride fatty acids accounted for approximately 7%. *Figures 3c* and *d* show the i.r. spectra of the two fractions of the lipid extractive obtained from chemical separation. As can be seen, the grease fraction has C–H stretching (2850–2950 cm^{-1}) and an ester carbonyl peak (1738 cm^{-1}) whereas the free fatty acid fraction, as expected, has a carboxyl carbonyl peak (1715 cm^{-1}) and O–H stretching (2500–3500 cm^{-1}). *Figures 3e* and *f* demonstrate the i.r. spectra for the two fractions that were obtained from the saponification of the grease fraction. A carboxyl carbonyl peak (1710 cm^{-1}) and O–H stretching (2500–3500 cm^{-1}) were attributed to the carboxylic acid functionality of the glyceride fatty acid. The unsaponifiable fraction shows a carbonyl peak at 1735 cm^{-1} along with C–H stretching (2850–2950 cm^{-1}). This carbonyl peak could not be identified. However, it is definitely not an ester carbonyl because it would not survive the saponification. A similar carbonyl peak in the unsaponifiable fraction has been reported by Higgins *et al.*[8].

Figure 5 shows the gas chromatogram of the unsaponifiable matter. Analytical alkane standards ranging from C6 to C16 were used as markers and their retention times (*Table 7*) are shown in *Figures 5* and *6*. From a comparison of the sample peaks and those in the standards, it is obvious that the unsaponifiable matter of the grease fraction contains many short and long chain hydrocarbons. *Table 8* shows the percentage distribution of the peaks of the unsaponifiable matter that correspond to the alkane standards. The percentage distribution of alkanes was calculated by subtracting the area of the n-hexane peak from the total area of the sample since n-hexane was used as solvent. Then the area of the desired peak was divided by the adjusted total area. From *Table 8*, it appears that n-nonane and n-pentadecane are the major hydrocarbons present in the unsaponifiable matter with contents of 5.3 and 5.7%, respectively. Only 26% of the total composition has been accounted for.

Figures 6a–c show gas chromatograms for all the esterified fatty acids including glyceride fatty acids. Interestingly, *Figures 6a* and *b* are almost identical. These two are the gas chromatograms of the esterified petroleum ether phase fatty acids and toluene-extracted fatty acids. From *Figure 6a*, it was calculated that the sample consisted of 45% palmitic acid and 41% stearic acid (see *Table 9*). Of the two unsaturated fatty acids examined, oleic acid predominated. The distributions of oleic acid and linoleic acid were 5.1 and 0.6%, respectively. It is clear from *Figure 6c* that stearic and palmitic acids constituted the major part of the glyceride fatty acids. The distribution of these two fatty acids were 29 and 21%, respectively (*Table 9*). About 40% of the sample is unknown. The percentage of the unsaturated fatty acids was greater in the glyceride fatty acids fraction than in the free fatty acids fraction. These findings are consistent with those of Higgins *et al.*[8]. Based on the recovered lipid, the contents of palmitic, stearic and oleic acids, as free acids, were 29, 26 and 3%, respectively. These values are in accordance with those of Higgins *et al.*[8], with the exception of the value for oleic acid which is lower.

It is clear that pyrolysis of sewage sludge lipids involves pyrolysis of carboxylic acids, glycerides and hydrocarbons. We have carried out model compound studies of catalytic pyrolysis of the first two groups as well as pyrolysis of the lipid itself. These results will be reported later.

CONCLUSIONS

Both Soxhlet and boiling extraction methods selectively

remove lipids from raw sewage sludge. As anticipated, both methods produced lipids with low nitrogen and sulphur content. The boiling extraction method is preferred if a higher sulphur content in the extract is acceptable. Toluene appeared to be the preferred solvent based on cost, the ability to extract lipids and environmental considerations.

The free fatty acids constituted the largest part, by weight, of the total lipid extracted from sewage sludge. Palmitic and stearic acids appeared to be the major components of the free fatty acids. Oleic and linoleic acids were present in significant quantity. Unsaponifiables were mostly hydrocarbons ranging from C9 to C16. The glyceride fatty acids fraction was found to contain palmitic, stearic, oleic and linoleic acids. The percentage of unsaturated fatty acids was greater in the glyceride fatty acids fraction than in the total free fatty acids.

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