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CHARACTERIZATION OF EFFLUENT FRACTIONS FROM CLO_2 AND CL_2 BLEACHING OF UNBLEACHED AND O_2 BLEACHED SOFTWOOD KRAFT PULPS

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CHARACTERIZATION OF EFFLUENT FRACTIONS FROM ClO_2 AND Cl_2 BLEACHING OF UNBLEACHED AND O_2 BLEACHED SOFTWOOD KRAFT PULPS

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ABSTRACT

Effluents from OC(EO), OD(EO), and D(EO) laboratory bleaching of softwood kraft pulp were characterized by fractionation and analysis of the fractions. Adsorbable organic halide (AOX) and total organic carbon (TOC) were determined for the effluents and effluent fractions from each stage, with the exception of the oxygen stage. Each fraction was characterized in terms of its size, and in terms of its ratio of chlorine to carbon - an environmentally significant parameter. The fractionation consisted of ether extraction followed by separation of the extract into acidic, phenolic, and neutral subfractions.

Replacement of chlorine with chlorine dioxide after oxygen bleaching sharply reduced the AOX, TOC, and chlorine to carbon ratio (expressed as the number of chlorine atoms per 100 carbon atoms, Cl/C_{100}) of the whole effluents. Larger AOX and TOC reductions were seen in the ether soluble fraction and in the phenolic subfraction of the ether soluble material. Since both Cl/C_{100} and the size of the ether soluble fractions may be expected to correlate with the potential of an effluent for negative environmental effects, these observations show that replacement of chlorine by chlorine dioxide may be more beneficial than the resulting reductions in whole effluent AOX would suggest.

Oxygen delignification prior to a 100% chlorine dioxide stage reduced whole effluent AOX and TOC in rough proportion to the amount of lignin removed in the oxygen stage, but did not affect the overall Cl/C_{100}. The reductions in AOX and TOC in the environmentally significant ether soluble neutral and phenolic fractions were slightly larger. There was also a significant reduction in Cl/C_{100} in these fractions. Oxygen delignification, like chlorine dioxide substitution, may therefore be more beneficial than the overall AOX reduction would suggest.

INTRODUCTION

During the past decade, the possibility that pulp bleaching effluents may harm the environment has become a major issue with environmentalists and the general public alike. Total chlorinated organic material (measured as AOX) is currently of considerable interest. In fact, environmental pressures have led to either proposed or implemented AOX limits in several European countries and Canadian provinces (1, 2). Similar limits are likely in the U. S.

AOX regulation, together with the consumer's desire to buy "environmentally friendly" products, has led pulp mills to implement AOX reduction strategies. The AOX in pulp bleaching effluents may be decreased by one or more of the following process changes: improved brownstock washing (3-5), extended kraft delignification (6-8), O_2 delignification (3, 6, 9, 10), substitution of chlorine dioxide for chlorine (6, 9, 11-16), and oxidative caustic extraction (11, 17-19).

Although process changes can reduce the AOX, their effect on the environment remains uncertain since AOX reduction does not necessarily imply environmental impact reduction (20, 21). Because much of the effluent AOX is believed to be innocuous and only a small fraction potentially harmful, reducing the overall AOX may or may not reduce its environmental effects. The small, potentially harmful fraction is of low molecular weight and consists of hundreds or perhaps thousands of compounds, including certain environmentally troublesome ones. Such compounds or groups of them have been isolated and identified in pulp bleaching effluents. These include chlorophenolics (12, 16, 22-28), chlorinated dioxins (12, 25, 29), chlorinated neutral compounds (28, 30, 31), chlorinated carboxylic acids (28, 32) and chloroform (23, 33).

The complexity of pulp bleaching effluents complicates the task of developing a bleaching process that eliminates the potential for harmful effects on the environment. In an ideal world, a full chemical characterization would be done on effluents from a variety of process alternatives, and data on the environmental effects of each component would be available. It would then be a simple task to choose the alternative that results in minimum environmental effect. Effluents are, however, sufficiently complex to defy full chemical characterization. For example, the toxicity of effluents can only be partially accounted for by identified components (24).

A practical alternative to the impossible ideal of complete analysis, is fractionation of the effluents from candidate bleaching processes and characterization of the fractions in terms that will allow prediction of environmental effects. Such an approach was adopted in the present study. Fractionation was conducted on the basis of ether solubility, volatility and acidity, and the fractions were characterized in terms of their relative amounts and chlorine to carbon ratios. Ether solubility implies low molecular weight (34, 35) and low molecular weight material may be correlated with acute and chronic toxicity (21, 36). The ether extract contains most of the effluent's mutagenicity (30, 37, 38) and toxicity (34). For example, Dence and co-workers (34) found that 92% of the C stage toxicity and 75% of the E stage toxicity resides in the corresponding ether extracts. Furthermore, the toxicities of the extracts were concentrated in the phenolic and neutral subfractions. The amounts of these subfractions therefore assume corresponding significance. The chlorine to carbon ratio may be used as a predictor of toxicity (24, 39) and lipophilicity (40).

EXPERIMENTAL APPROACH

Pulp Bleaching

Three different pulp bleaching sequences were considered in this work: OC(EO), OD(EO), and D(EO). The unbleached pulp was a mill produced kraft with a kappa number of 26.0 before the oxygen stage. The oxygen bleached pulp (kappa 14.1) was collected after the oxygen stage at the same mill. Kappa numbers after bleaching are given in Table I. Only the first two stages of pulp bleaching were done, since they effect the majority of the delignification, and therefore produce most of the effluent load. The D and C stages (referred to collectively as D/C stages throughout this report) were done in a batch reactor at 2% consistency, at 45°C, for 30 minutes, and with a kappa factor of 0.25; the (EO) stages were done in a high shear mixer at 10% consistency, at 70°C, and for 70 minutes.

Effluent Fractionation and Characterization

For the reasons mentioned above, effluent characterization was based on ether extraction. The ether extractable material was further separated into an acidic fraction, a phenolic fraction, and a neutral fraction. This type of procedure has been used in previous studies of mutagenicity (38, 41) and toxicity (34), and analyses of chlorophenols (26, 39), chlorinated neutral compounds (31, 42), and chlorinated carboxylic acids (32).

The TOC-normalized AOX, expressed as organically bound chlorine atoms per hundred carbon atoms (Cl/C_{100}), was determined for each effluent and effluent fraction. To measure Cl/C_{100} on the ether extract and extract fractions, the ether was first completely removed, then AOX and TOC measured on each fraction. The removal of ether was accomplished by evaporation of the sample to dryness or very near to dryness. During this process, other volatiles were also removed. To obtain information on the volatile fraction, a sample of the whole effluent was similarly evaporated and the carbon and chlorine losses determined.

Figure 1 depicts the effluent fractionation scheme, and Table II lists the names or codes of all effluent fractions and provides an explanation of each. The bleaching effluents were extracted exhaustively with ether in continuous liquid-liquid extractors. Two successive extractions were performed, resulting in three fractions: a non-extractable fraction, and two ether extractable fractions. The first ether fraction is material readily extracted and the second is removed slowly over an extended period. The first was further fractionated into acids, phenolics, and neutrals. Each fraction was then evaporated, as represented in Figure 1 by the dashed horizontal lines, to yield the final samples.

Data Analysis

All bleaching sequences were performed in duplicate, and the individual stage effluents from each replication were fractionated and analyzed separately. This resulted in two completely independent sets of data for each sequence. The D/C and (EO) stage data for all fractions are given in Tables III-X. The total TOC and AOX (given in Table III) represents TOC and AOX mass balances around the fractionation scheme and were determined as the sums of the AOX and TOC determinations of the neutrals, the phenolics, the acids, the polar fraction, the hydrophilic fraction, and the volatiles.

In this report emphasis will be placed on the whole effluents and on the ether soluble fraction, the phenolics, and the neutrals, since evidence in the literature indicates these fractions may be more environmentally important than the others. The Cl/C_{100} and the percentage of total TOC are also emphasized, since all needed information can be gained from these two results. The Cl/C_{100} gives an estimate of the relative environmental behavior of the material, and the percentage of the total TOC gives a measure of the total amount of material. The percentage of total TOC is used in order to normalize the TOC data for different levels of removed material.

Analyses of variance (AOV) were done on the data from each fraction, to assess the significance of differences between sequences and between stages. Since data with high Cl/C_{100} clearly had a greater variance than the low Cl/C_{100} data, all Cl/C_{100} data were log transformed to stabilize variance. When AOV showed a significant effect between bleaching sequences, least significant differences were determined using Duncan's multiple range test (43).

RESULTS AND DISCUSSION

Whole Effluents

Data for the whole effluents are presented in Table III. The whole effluents contain 3.8-17 kg/t TOC and 0.1-2.8 kg/t AOX, depending on the stage and sequence.

Figure 2 compares the three partial bleaching sequences with respect to mean TOC production. TOC provides a measure of the total organic load produced by each sequence. As expected, based on the higher pulp kappa number entering the sequence, the D(EO) sequence produces the greatest quantity of TOC. In the case of the oxygen based sequences about half of the organic material has already been removed in the oxygen stage prior to delignification with chlorine based chemicals. This material is recycled to the mill's recovery system and is therefore without environmental significance in the wastewater stream.

A comparison of the oxygen based sequences shows that chlorine produces more TOC than chlorine dioxide in both the D/C and (EO) stages. This is in part due to the more effective delignification done by chlorine, but the difference is too great to be due to this effect alone. The data suggest that the OD(EO) sequence gives a higher carbohydrate yield. This is discussed further below.

Figure 3 presents a similar comparison of mean Cl/C_{100}. In both stages the material released by chlorine bleaching is much more extensively chlorinated than that released by chlorine dioxide bleaching. This is expected since chlorine reacts by both oxidation and substitution while chlorine dioxide only reacts by oxidation (44, 45). The ClO_2 bleaching produces some chlorinated organics as well, as a result of the formation and reaction of HOCl and Cl_2 during the process (46-48).

Insertion of an O_2 stage before ClO_2 has little effect on the extent of chlorination of effluent compounds, although some decrease is seen in the case of the (EO) stage effluents. This may be a result of the action of O_2 delignification. Oxygen in alkaline solution oxidizes free phenolic structures (44, 49), thus reducing the number of sites that are readily substituted by chlorine. Another possible explanation is that material from the OD(EO) sequence is more readily dechlorinated in the caustic extraction stage than that material from the D(EO) sequence.

Ether Soluble Fraction

Table IV presents detailed data for the ether soluble fraction. This fraction contains 0.3-1.4 kg/t TOC, representing 4-13% of the total TOC and 0.01-0.79 kg/t AOX, representing 7-35% of the total AOX. A change from chlorine to chlorine dioxide bleaching reduces both TOC and AOX in this fraction to a greater extent than occurs in the whole effluent.

Figure 4 presents the mean ether soluble TOC as a percentage of total TOC for each bleaching sequence. For both the D/C and (EO) stages, chlorine results in a higher ether soluble TOC content than chlorine dioxide. The D(EO) sequence has a smaller percentage of total TOC in this fraction than OD(EO). Because of the increased lignin removal however, the absolute amounts of removed AOX and TOC in this fraction are greater for D(EO).

Figure 5 similarly compares the sequences with regard to Cl/C_{100}. For both the D/C and (EO) stages, this fraction contains increased chlorine per unit carbon compared to the whole effluents. This further supports the contention that the ether soluble fraction is of environmental interest. The ether soluble fraction is also chlorinated to a much greater extent when chlorine is used rather than chlorine dioxide. In fact the increased degree of chlorine substitution on the organic material in the case of chlorine results in a more hydrophobic effluent and is the likely cause of the increased ether soluble TOC that is also seen when chlorine is used. Use of chlorine dioxide provides two environmental benefits over chlorine use, in the case of the ether soluble material: a large reduction in the amount of organically bound chlorine per unit carbon, and a reduced amount of material within the fraction. There is no significant Cl/C_{100} effect seen between the OD(EO) and D(EO) sequences.

Phenolic Fraction

Detailed results of analysis of the phenolic fraction are shown in Table V. The phenolic fraction contains 0.02-0.12 kg/t TOC or 0.5-1.5% of the total TOC, and 0.002-0.09 kg/t AOX or 0.8-4.1% of the total AOX. Both TOC and AOX are again reduced to a greater extent in this fraction than in the whole effluent, when the change is made from chlorine to chlorine dioxide bleaching.

Figure 6 compares the phenolic TOC as a percentage of total TOC for the three sequences. Chlorine bleaching results in an increased content of phenolic TOC relative to chlorine dioxide for both the D/C and (EO) stages. The reduced amount of phenolic material with ClO_2 bleaching is in accordance with other studies in which the amount of measured chlorophenolics decreased as ClO_2 substitution increased (22, 24, 28, 50).

Figure 7 compares the phenolic fraction Cl/C_{100} for the three bleaching sequences and for both stages. Chlorine produces a much more extensively chlorinated phenolic fraction than does chlorine dioxide. The two benefits from the use of chlorine dioxide rather than chlorine are again seen here: decreased phenolic AOX per unit carbon, as well as a decreased amount of material in the phenolic fraction.

No significant differences were seen between the OD(EO) and D(EO) sequences by the normal AOV. However if only the OD(EO) and D(EO) data are included in the analysis, a significantly greater Cl/C_{100} is seen for D(EO) bleaching compared to OD(EO).

Neutral Fraction

Complete data on the neutral fraction are shown in Table VI. The fraction contains 0.05-0.14 kg/t TOC (0.4-1.2% of the total TOC) and 0.001-0.006 kg/t AOX (0.3-1.4% of the total AOX).

Figure 8 compares the bleaching sequences with regard to neutral fraction TOC as a percentage of the total TOC. There are no statistically significant differences between any of the bleaching sequences, due to scatter in the replicate data.

Figure 9 compares the neutral fraction Cl/C_{100} for the sequences. Again chlorine produces a more highly chlorinated material than does chlorine dioxide, for both D/C and (EO) stages. The D(EO) sequence also produces a more highly chlorinated material than the OD(EO) sequence. This is another indication that oxygen delignification leaves a residual lignin that is less susceptible to chlorine substitution reactions than unoxidized lignin.

Acid Fraction

Table VII presents the detailed results for the acid fraction of the ether soluble material. About 0.2-1.1 kg/t TOC, representing 3-10% of the total TOC and 0.01-0.46 kg/t AOX, representing 6-20% of the total AOX, is contained within this fraction.

Figures 10 and 11 show the acid fraction TOC as a percent of the total, and the acid fraction Cl/C_{100}. Replacement of chlorine with chlorine dioxide results in a decreased percentage of total TOC in the (EO) stage fraction and reduces the Cl/C_{100} for both stages. Oxygen bleaching prior to chlorine dioxide treatment results in a decreased Cl/C_{100} for the (EO) stage fraction, but an increased percentage of TOC in the fraction for both stages. The absolute amounts of TOC and AOX in the acid fraction are again greater for D(EO) bleaching, however.

Polar Fraction

Complete data for the polar fraction, or difficultly ether extractable material, are shown in Table VIII. The fraction contains 0.2-1.1 kg/t TOC or 3-11% of total TOC, and 0.003-0.09 kg/t AOX or 2-20% of the total AOX.

Figures 12 and 13 show the mean polar fraction data for both percent of total TOC and Cl/C_{100}. A change from chlorine to chlorine dioxide use results in a decreased (EO) stage Cl/C_{100} for the fraction. The presence of oxygen bleaching before ClO_2 treatment results in an increased D/C stage Cl/C_{100} but a decrease in the percentage of the total TOC within the D/C stage polar fraction. A decreased (EO) stage Cl/C_{100} is also seen when O_2 bleaching precedes ClO_2 treatment.

Hydrophilic Fraction

Table IX presents the entire data set for the hydrophilic fraction or the non-extractable material. The hydrophilic fraction contains 3.4-13.4 kg/t TOC (68-86% of the total TOC) and 0.07-1.4 kg/t AOX (49-85% of the total AOX).

Figures 14 and 15 show the hydrophilic TOC as a percent of the total TOC, and the hydrophilic fraction Cl/C_{100} for the bleaching sequences. The Cl/C_{100} values for this fraction are similar to those found for "high molecular weight" effluent material in other studies (28, 49, 51, 52). Although there may appear to be differences between the sequences in Figure 14, the percentage of total TOC does not differ significantly. This again is due to scatter in the replicate data. The use of chlorine dioxide in place of chlorine causes a reduced Cl/C_{100} for both stages, and the presence of oxygen bleaching before chlorine dioxide treatment reduces the Cl/C_{100} for both stages as well.

Volatile Fraction

The data set for the volatile fraction is shown in Table X. About 0.3-1.1 kg/t TOC or 4-16% of the total TOC, and 0.005-0.3 kg/t or 1.5-18% of the total AOX is volatile material. Figures 16 and 17 show the mean data for the percent of total TOC and Cl/C_{100}. There are no statistically significant differences, due to scatter in the replicate data.

Yield Implications of Whole Effluent TOC

A summary of the TOC removed in both the D/C and (EO) stages, the CE kappa numbers, the kappa change brought about by the bleaching sequence, and the ratio of TOC to the change in kappa number is shown for each bleaching sequence in Table I. Analysis of variance on the ratio of TOC to kappa change showed that the effluents from pulp chlorination contained significantly more TOC per unit of kappa number reduction than either chlorine dioxide case. The increased amount of TOC in the effluent per unit of kappa loss implies greater carbohydrate loss, or reduced pulp yield with 100% chlorine as compared to 100% chlorine dioxide. In a review of pulp yield data at different levels of ClO_2 substitution, increased yield was seen in 40°C stages at increased ClO_2 substitution, while no such yield increases were seen at lower temperatures (53). This work, in which D/C stages were done at 45°C, is consistent with those results.

Another possible explanation for the decreased TOC per unit kappa number decrease seen with chlorine dioxide bleaching, is formation of carbonate species during bleaching. Such species are evolved as CO_2, and not measured as TOC.

EXPERIMENTAL METHODS

Pulp Bleaching

Two pulp samples were used in these experiments: a 26.0 kappa unbleached southern softwood and a 14.1 kappa O_2 delignified southern softwood. Both pulps were produced at the same mill. The unbleached pulp was collected just before the O_2 stage, and the O_2 delignified pulp was collected just after the O_2 stage. Each pulp was well washed before bleaching.

D/C Stages.

All D/C stages were done in a 20L batch reactor, designed to rapidly add bleaching chemicals. Bleaching was done at 2% consistency, at 45°C, for 30 minutes, and at a kappa factor of 0.25. The mixer was run at 350 rpm. Initial pH in all cases was adjusted to 2 by the addition of sulfuric acid solution.

(EO) Stages.

All (EO) stages were done in a Quantum Technologies high shear mixer at 10% consistency, at 70°C, and for 70 minutes. The NaOH charge was 0.55 X TAC, the O_2 charge was 0.5% on pulp, and 4.1% of the total D/C stage filtrate was included as carryover. The slurry was mixed at 15 Hertz for 3 seconds, every 5 minutes.

Effluent Preparation

The D/C stage effluent was collected by filtration of the 2% slurry; the (EO) stage effluent was similarly collected after the 10% slurry was diluted to 2%. This was done to maintain a similar TOC content in all effluents for ether extraction. Effluent samples were filtered to remove any fibers, quenched with excess Na_2SO_3, and acidified to a pH of less than 2. Ether extractions were always started within 2 days of effluent collection.

Ether Extraction of Effluents

Ether extraction was done on 4L of effluent using continuous liquid-liquid extractors. Extraction was carried out with 500 ml of diethyl ether. The first ether phase was collected after 48 hours of extraction and was replaced with 500 ml of fresh ether. Extraction was continued for 336 total hours. The extraction was then stopped and the second ether phase and the non-extractable materials were collected.

Ether Extract Fractionation

The first ether phase was diluted to 500 ml, 100 ml of the sample collected, and the remaining ether placed in a separatory funnel for fractionation. The ether was extracted 3 times with 25 ml of 0.5 M $NaHCO_3$, and the extracts collected and acidified. The ether was next extracted 3 times with 25 ml of 0.5 M NaOH, and these extracts also collected and acidified. The $NaHCO_3$ soluble material is the acidic fraction, the NaOH soluble material is the phenolic fraction, and the remaining ether soluble material is the neutral fraction.

Sample Preparation

Ether was removed from all samples by evaporation to dryness, or near to dryness. The samples were then dissolved in water, acidified, and diluted to a known volume. To ensure reasonable sample recovery and to be certain the ether was removed, TOC and AOX mass balances were done around the fractionation scheme.

TOC Analysis

Measurement of TOC was done on a Beckman model 915-B Tocamaster analyzer. The instrument was calibrated using standard solutions of potassium hydrogen phthalate. Samples were prepared for TOC analysis by acidifying them, and sparging for 5 minutes with nitrogen to drive off any interfering carbonate species.

AOX Analysis

Measurement of AOX was done on a Dohrman model DX-20 organic halide analyzer. Sample preparation was done by a slight modification of method SCAN-W 9:89 (54). In this case samples were shaken for 4 hours rather one, to more completely adsorb the polar fractions.

SUMMARY AND CONCLUSIONS

Figures 18 and 19 summarize the total D/C + (EO) stage TOC and AOX for the bleaching sequences. The size of each graph is proportional to the TOC or AOX (in kg/t) produced in the corresponding bleaching sequence. Figure 18 shows that D(EO) bleaching produces the most effluent TOC, as expected based on the higher kappa number of the pulp. The OC(EO) sequence produces more effluent TOC than OD(EO) because of both the greater delignification effectiveness of chlorine and possible increased carbohydrate loss. As shown in Figure 19, the OD(EO) sequence results in only a small fraction of the total AOX produced by the OC(EO) sequence. The AOX in the effluent fractions is also smaller by a corresponding amount. As expected, the D(EO) sequence produces about twice the AOX as the OD(EO) sequence.

Certain significant conclusions regarding the nature of bleaching effluents produced by both chlorine and chlorine dioxide bleaching can be based on this research. For the whole effluents, chlorine bleaching gives a higher Cl/C_{100} than ClO_2 bleaching of the same pulp. The same trend is seen for effluent fractions which are environmentally significant. In the case of the ether soluble fraction and the phenolic fraction, not only is the Cl/C_{100} greater for Cl_2 bleaching, but a greater percentage of the total TOC partitions into the ether soluble and phenolic fractions as well. The phenolic and neutral fractions for both the D/C and (EO) stages have lower Cl/C_{100} values when oxygen bleaching precedes chlorine dioxide treatment.

The results of this research provide some new evidence in support of the use of chlorine dioxide and O_2 delignification as a means of environmental improvement. By using ClO_2 in place of Cl_2, not only is the amount of chlorine substitution on organic compounds greatly reduced, but the percentage of material within certain environmentally important fractions is also reduced. Oxygen bleaching, in addition to the expected benefit of reducing in half the total effluent load, provides a decreased level of chlorine substitution of organic compounds in the phenolic and neutral fractions of both D/C and (EO) stage effluents. Therefore, both chlorine dioxide substitution and oxygen bleaching may be more environmentally beneficial than the overall AOX reduction suggests.

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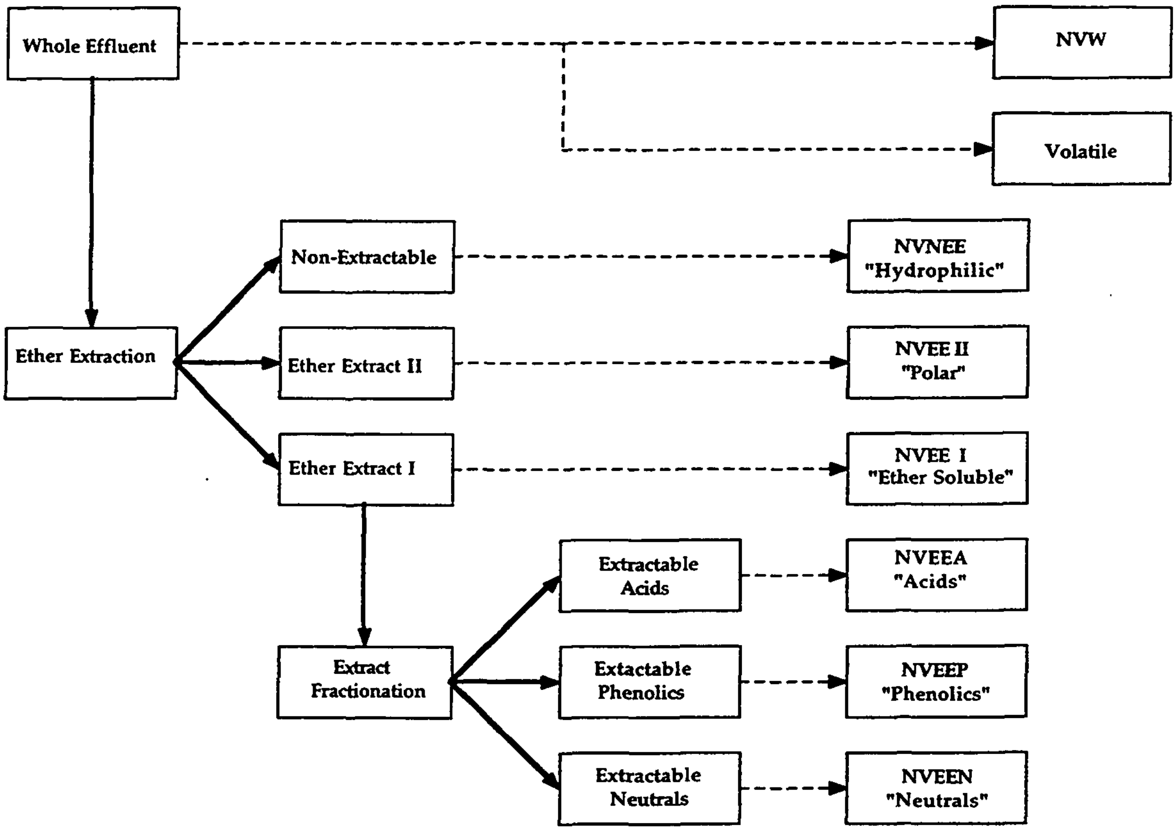
Figure 1. Effluent Fractionation.



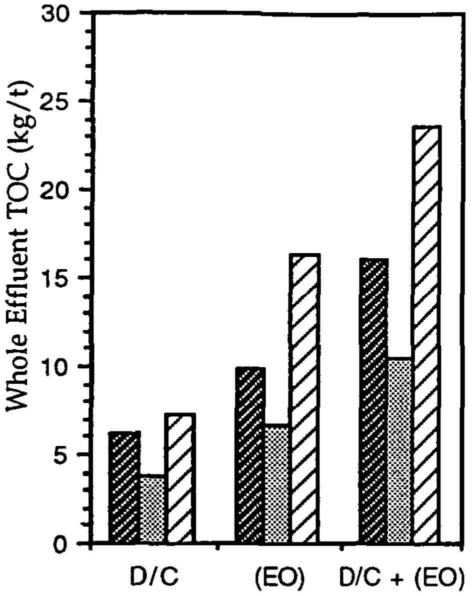


Figure 2. Whole Effluent TOC.

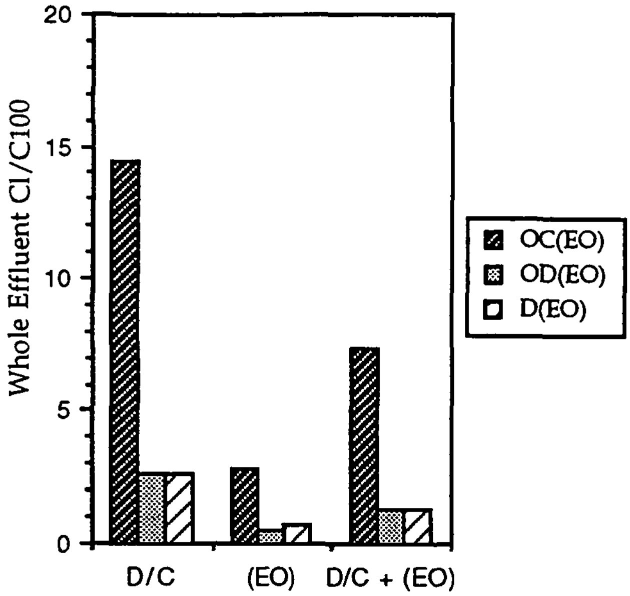


Figure 3. Whole Effluent Cl/C100.

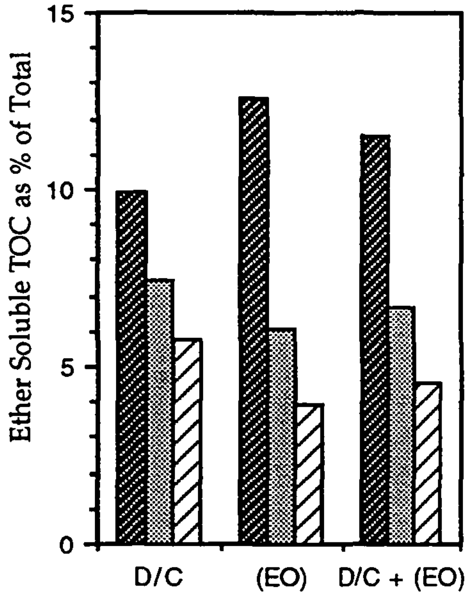


Figure 4. Ether Soluble TOC as % of Total.

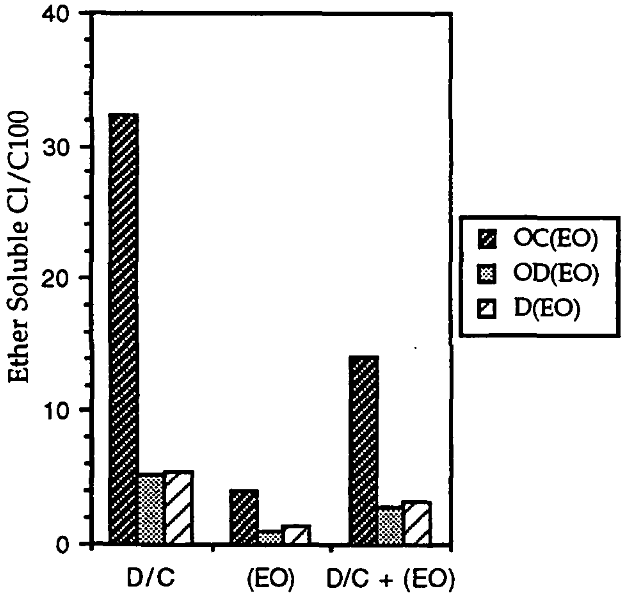


Figure 5. Ether Soluble Cl/C100.

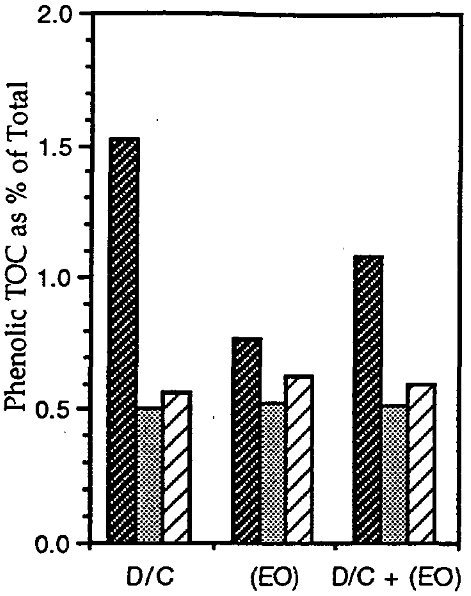


Figure 6. Phenolic TOC as % of Total.

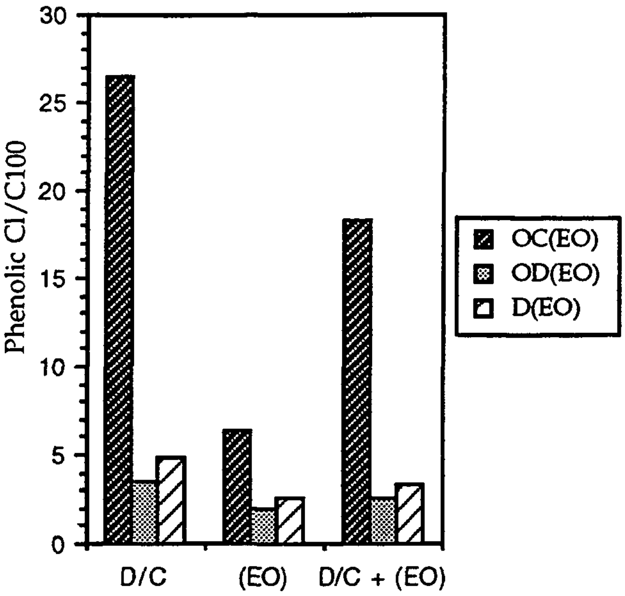


Figure 7. Phenolic Cl/C100.

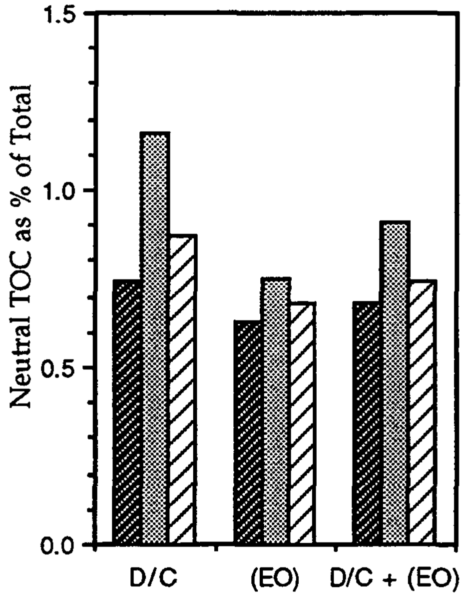


Figure 8. Neutral TOC as % of Total.

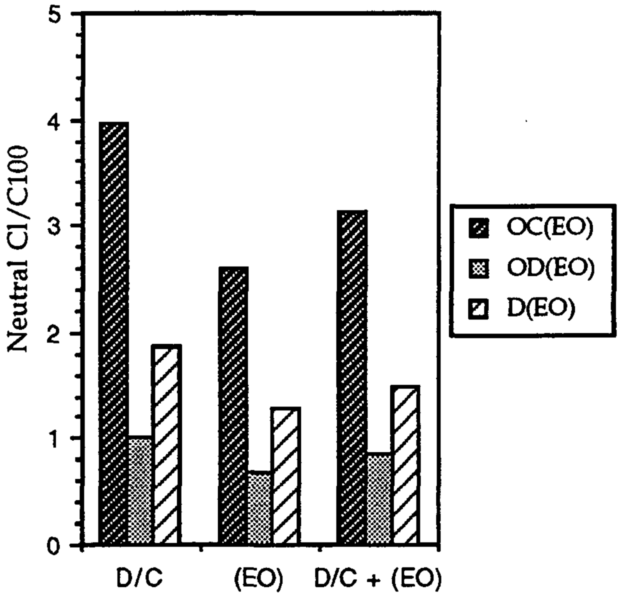


Figure 9. Neutral Cl/C100.

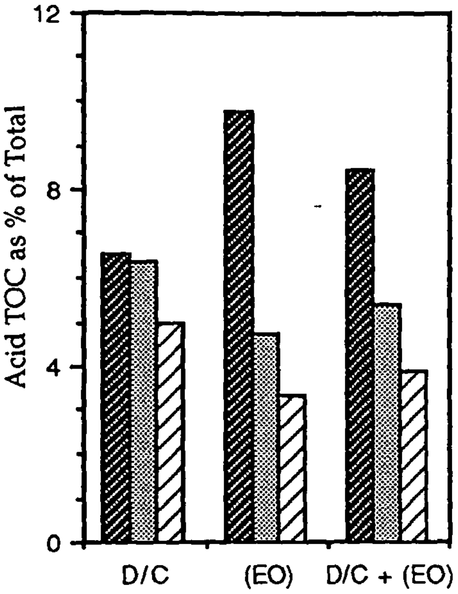


Figure 10. Acid TOC as % of Total.

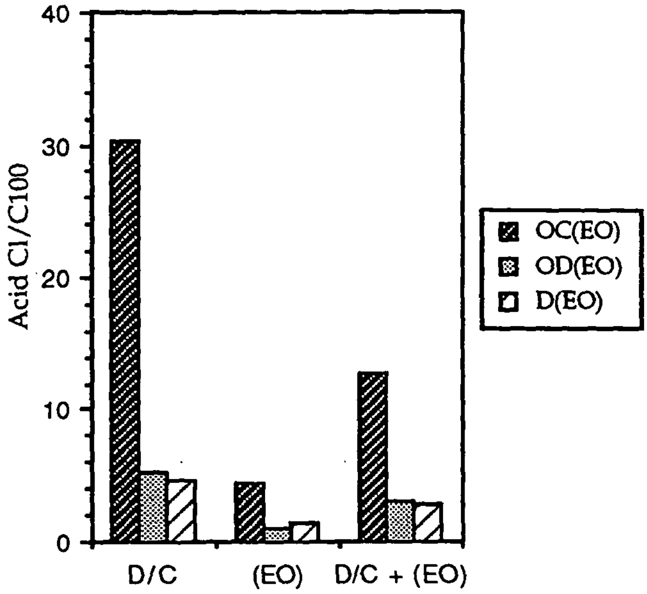


Figure 11. Acid Cl/C100.

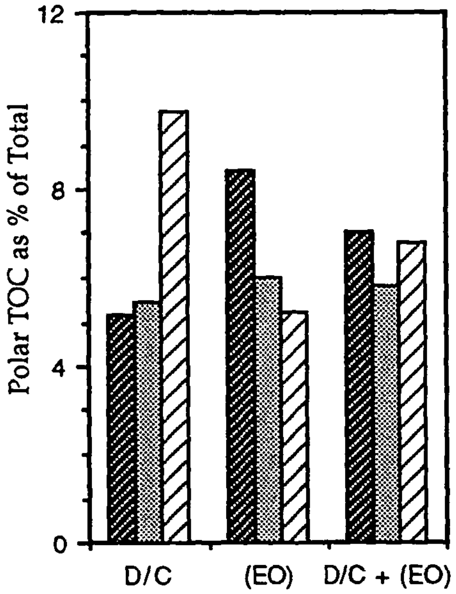


Figure 12. Polar TOC as % of Total.

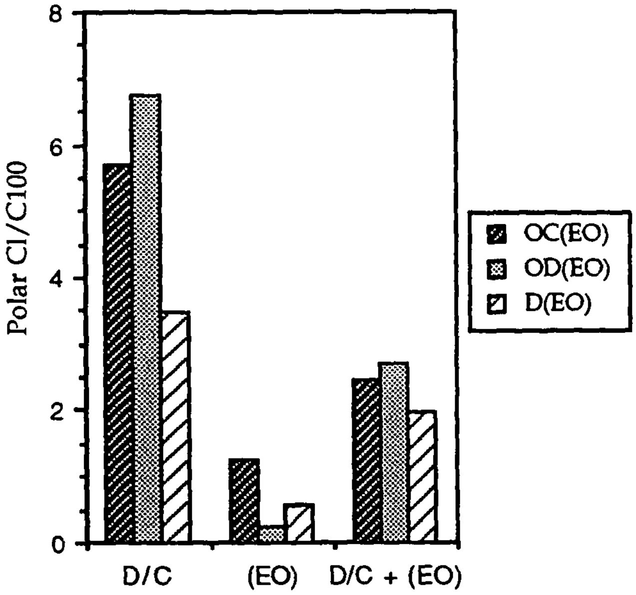


Figure 13. Polar Cl/C100.

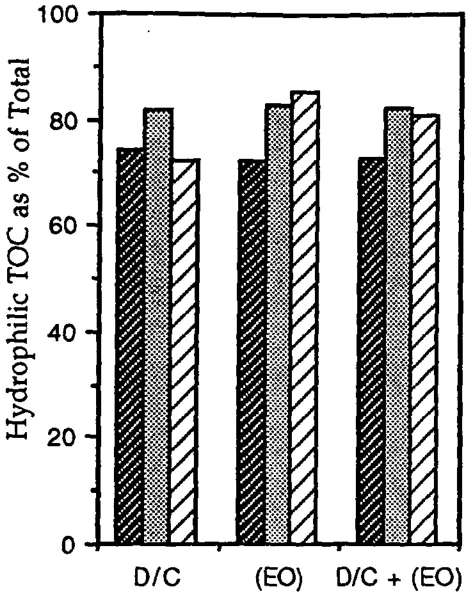


Figure 14. Hydrophilic TOC as % of Total.

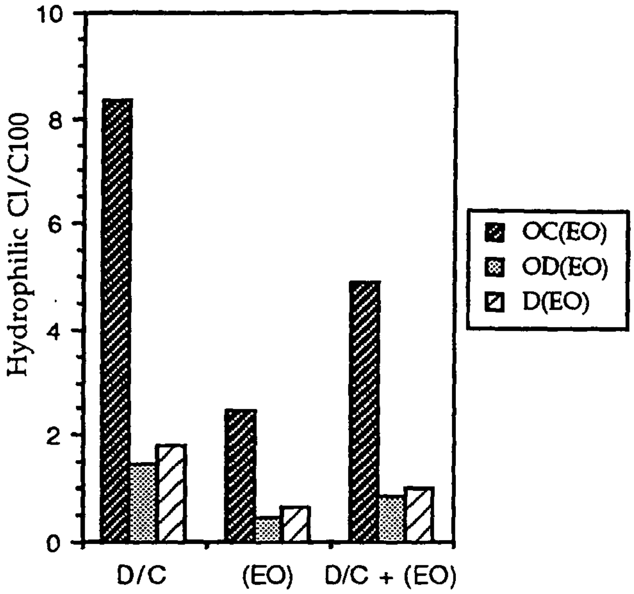


Figure 15. Hydrophilic Cl/C100.

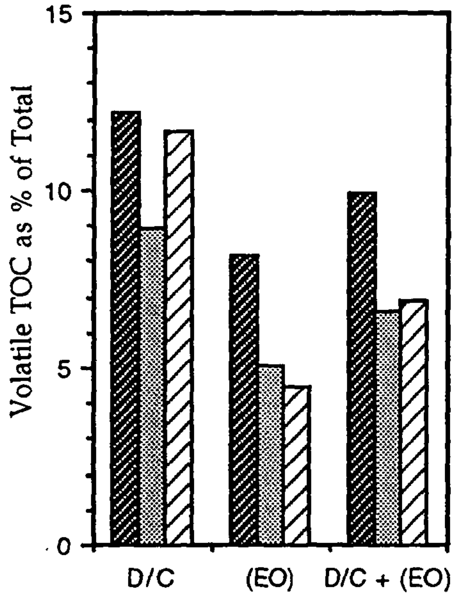


Figure 16. Volatile TOC as % of Total.

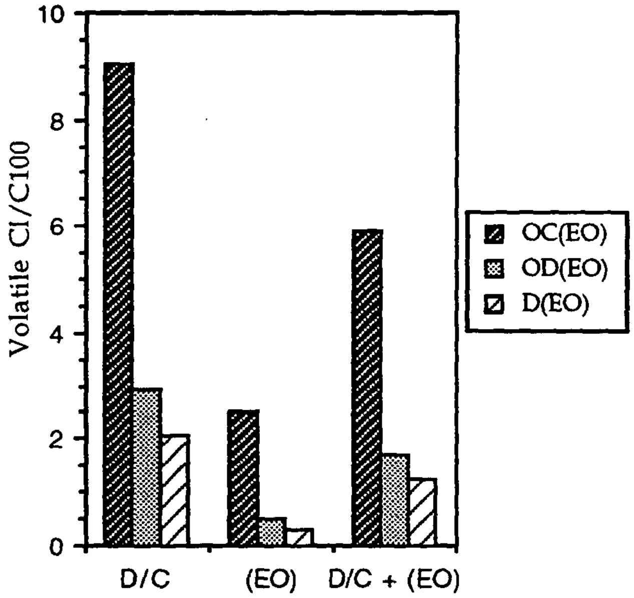


Figure 17. Volatile Cl/C100.

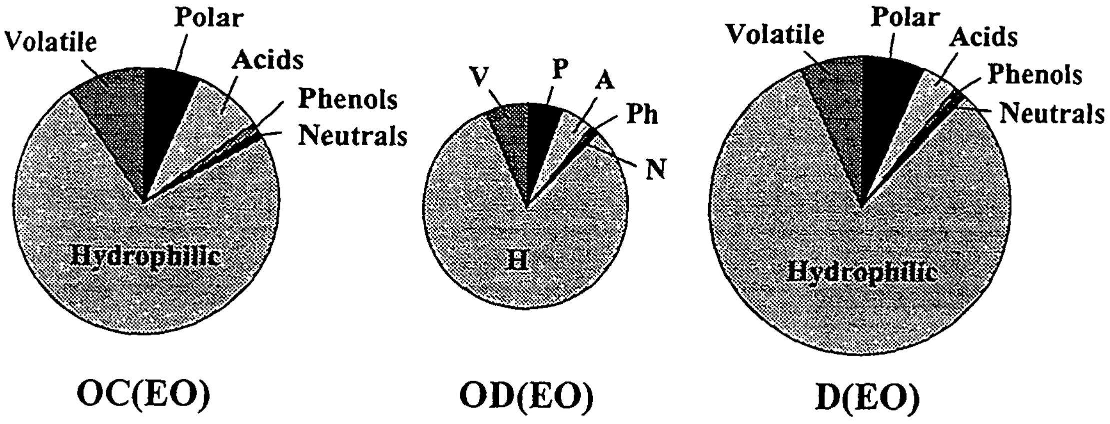


Figure 18. TOC Summary Graphs.

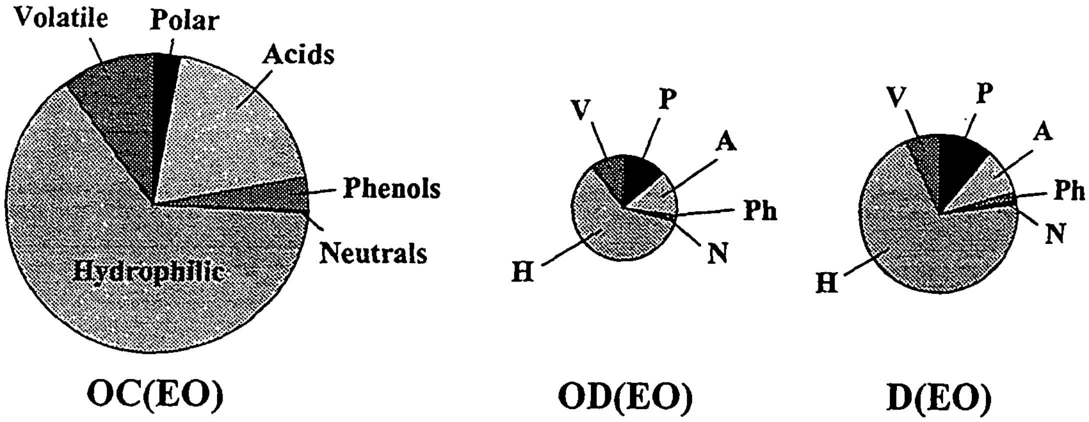


Figure 19. AOX Summary Graphs.

Table I. D/C + (EO) TOC and CE Kappa Number Data.

Sequence	**D/C + (EO) TOC (kg/t)**	**CE kappa**	**Δ kappa**	**TOC/Δ kappa**
OC(EO)	16.6	2.10	12.0	1.38
OC(EO)	15.5	1.74	12.4	1.26
OD(EO)	10.6	4.23	9.87	1.08
OD(EO)	10.4	4.44	9.66	1.08
D(EO)	24.4	5.27	20.7	1.18
D(EO)	22.9	4.83	21.2	1.08

Table II. Effluent Fraction Codes and Descriptions of Fractions.

Fraction Code	Description
NVW	Non-volatile, whole.
NVNEE	Non-volatile, non-ether extractable ("Hydrophilic").
NVEE II	Non-volatile, difficultly ether extractable ("Polar").
NVEE I	Non-volatile, readily ether extractable ("Ether Soluble").
NVEEA	Non-volatile, ether extractable acidic compounds ("Acids").
NVEEP	Non-volatile, ether extractable phenolic compounds ("Phenolics").
NVEEN	Non-volatile, ether extractable neutral compounds ("Neutrals").

Table III. Whole Effluent.

D/C Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	6.15	6.36	3.85	3.80	7.33	7.23
Total TOC, kg/t	7.03	8.17	4.43	4.29	7.87	8.02
AOX, kg/t	2.75	2.56	0.299	0.294	0.552	0.594
Total AOX, kg/t	2.26	2.13	0.297	0.264	0.447	0.551
Cl/C_{100}	15.1	13.6	2.63	2.61	2.54	2.78

(EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	9.37	10.2	6.79	6.60	17.1	15.7
Total TOC, kg/t	9.83	11.6	6.70	6.52	15.6	14.9
AOX, kg/t	0.793	0.858	0.101	0.102	0.341	0.309
Total AOX, kg/t	0.738	0.887	0.0938	0.0930	0.324	0.306
Cl/C_{100}	2.86	2.86	0.50	0.52	0.68	0.67

D/C + (EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	15.5	16.6	10.6	10.4	24.4	22.9
Total TOC, kg/t	16.9	19.8	11.1	10.8	23.5	22.9
AOX, kg/t	3.54	3.42	0.400	0.396	0.893	0.903
Total AOX, kg/t	3.00	3.02	0.391	0.357	0.771	0.857
Cl/C_{100}	7.71	6.98	1.27	1.29	1.24	1.33

Table IV. Ether Soluble Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.681	0.832	0.383	0.267	0.501	0.418
% of Total TOC	9.69	10.2	8.65	6.22	6.37	5.21
AOX, kg/t	0.790	0.632	0.0547	0.0439	0.0751	0.0725
% of Total AOX	35.0	29.7	18.4	16.6	16.8	13.2
Cl/C_{100}	39.2	25.6	4.83	5.56	5.05	5.88

(EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	1.32	1.36	0.406	0.399	0.663	0.542
% of Total TOC	13.4	11.7	6.06	6.12	4.25	3.64
AOX, kg/t	0.173	0.154	0.0127	0.0125	0.0273	0.0220
% of Total AOX	23.4	17.4	13.5	13.4	8.43	7.19
Cl/C_{100}	4.44	3.83	1.06	1.06	1.39	1.37

D/C + (EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	2.00	2.19	0.789	0.666	1.16	0.960
% of Total TOC	11.9	11.1	7.09	6.16	4.94	4.19
AOX, kg/t	0.963	0.786	0.0674	0.0564	0.102	0.0945
% of Total AOX	32.1	26.0	17.2	15.8	13.2	11.0
Cl/C_{100}	16.3	12.1	2.89	2.86	2.97	3.33

Table V. Phenolic Fraction.

D/C Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	0.108	0.123	0.0239	0.0198	0.0462	0.0434
% of Total TOC	1.54	1.51	0.54	0.46	0.59	0.54
AOX, kg/t	0.0935	0.0869	0.00255	0.00201	0.00683	0.00602
% of Total AOX	4.14	4.08	0.86	0.76	1.53	1.09
Cl/C_{100}	29.2	23.8	3.60	3.45	5.00	4.69

(EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	0.0884	0.0725	0.0364	0.0341	0.0820	0.107
% of Total TOC	0.90	0.63	0.54	0.52	0.53	0.72
AOX, kg/t	0.0221	0.00924	0.00243	0.00180	0.00697	0.00730
% of Total AOX	2.99	1.04	2.59	1.94	2.15	2.39
Cl/C_{100}	8.47	4.31	2.26	1.79	2.87	2.31

D/C + (EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	0.196	0.196	0.0603	0.0539	0.128	0.150
% of Total TOC	1.16	0.99	0.54	0.50	0.55	0.65
AOX, kg/t	0.116	0.0961	0.00498	0.00381	0.0138	0.0133
% of Total AOX	3.87	3.18	1.27	1.07	1.79	1.55
Cl/C_{100}	20.0	16.6	2.79	2.39	3.64	3.00

Table VI. Neutral Fraction.

D/C Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	0.0393	0.0750	0.0551	0.0457	0.0784	0.0583
% of Total TOC	0.56	0.92	1.24	1.07	1.00	0.73
AOX, kg/t	0.00591	0.00629	0.00153	0.00148	0.00342	0.00387
% of Total AOX	0.26	0.30	0.52	0.56	0.77	0.70
Cl/C_{100}	5.08	2.83	0.94	1.09	1.48	2.24

(EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	0.0671	0.0676	0.0511	0.0480	0.0685	0.137
% of Total TOC	0.68	0.58	0.76	0.74	0.44	0.92
AOX, kg/t	0.00520	0.00513	0.00129	0.000701	0.00275	0.00495
% of Total AOX	0.71	0.58	1.38	0.75	0.85	1.62
Cl/C_{100}	2.62	2.56	0.85	0.49	1.36	1.22

D/C + (EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	0.106	0.143	0.106	0.0937	0.147	0.195
% of Total TOC	0.63	0.72	0.95	0.87	0.63	0.85
AOX, kg/t	0.0111	0.0114	0.00282	0.00218	0.00617	0.00882
% of Total AOX	0.37	0.38	0.72	0.61	0.80	1.03
Cl/C_{100}	3.54	2.69	0.90	0.79	1.42	1.53

Table VII. Acid Fraction.

D/C Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	0.450	0.548	0.316	0.242	0.432	0.361
% of Total TOC	6.40	6.71	7.13	5.64	5.49	4.50
AOX, kg/t	0.456	0.430	0.0511	0.0369	0.0561	0.0535
% of Total AOX	20.2	20.2	17.2	14.0	12.6	9.71
Cl/C_{100}	34.2	26.5	5.46	5.15	4.39	5.00

(EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	1.02	1.05	0.304	0.321	0.526	0.491
% of Total TOC	10.4	9.05	4.54	4.92	3.37	3.30
AOX, kg/t	0.140	0.135	0.00856	0.00827	0.0192	0.0214
% of Total AOX	19.0	15.2	9.13	8.89	5.93	6.99
Cl/C_{100}	4.67	4.37	0.95	0.87	1.24	1.47

D/C + (EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	1.47	1.60	0.620	0.563	0.958	0.852
% of Total TOC	8.72	8.09	5.57	5.21	4.08	3.72
AOX, kg/t	0.596	0.565	0.0597	0.0452	0.0753	0.0749
% of Total AOX	19.9	18.7	15.3	12.7	9.77	8.74
Cl/C_{100}	13.7	11.9	3.25	2.71	2.66	2.97

Table VIII. Polar Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.533	0.220	0.226	0.248	0.829	0.719
% of Total TOC	7.58	2.69	5.10	5.78	10.5	8.97
AOX, kg/t	0.0632	0.0479	0.0445	0.0502	0.0882	0.0705
% of Total AOX	2.80	2.25	15.0	19.0	19.7	12.8
Cl/C_{100}	4.00	7.35	6.67	6.85	3.60	3.31

(EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	1.05	0.711	0.399	0.395	0.858	0.739
% of Total TOC	10.7	6.13	5.96	6.06	5.50	4.96
AOX, kg/t	0.0288	0.0325	0.00333	0.00280	0.0124	0.0136
% of Total AOX	3.90	3.66	3.55	3.01	3.83	4.44
Cl/C_{100}	0.93	1.55	0.28	0.24	0.49	0.62

D/C + (EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	1.58	0.931	0.625	0.643	1.69	1.46
% of Total TOC	9.39	4.71	5.62	5.95	7.19	6.36
AOX, kg/t	0.0920	0.0804	0.0478	0.0530	0.101	0.0841
% of Total AOX	3.07	2.66	12.2	14.8	13.1	9.81
Cl/C_{100}	1.97	2.92	2.59	2.79	2.02	1.95

Table IX. Hydrophilic Fraction.

D/C Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	4.80	6.50	3.43	3.69	5.41	6.05
% of Total TOC	68.3	79.6	77.4	86.0	68.7	75.4
AOX, kg/t	1.34	1.37	0.144	0.160	0.278	0.333
% of Total AOX	59.3	64.3	48.5	60.6	62.2	60.4
Cl/C_{100}	9.52	7.09	1.42	1.47	1.74	1.86

(EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	6.67	8.88	5.50	5.45	13.4	12.7
% of Total TOC	67.9	76.6	82.1	83.6	85.9	85.2
AOX, kg/t	0.531	0.594	0.0728	0.0745	0.276	0.252
% of Total AOX	72.0	67.0	77.6	80.1	85.2	82.4
Cl/C_{100}	2.69	2.26	0.45	0.46	0.69	0.67

D/C + (EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	11.5	15.4	8.93	9.14	18.8	18.8
% of Total TOC	68.0	77.8	80.2	84.6	80.1	81.8
AOX, kg/t	1.87	1.96	0.217	0.235	0.554	0.585
% of Total AOX	62.3	64.9	55.5	65.8	71.9	68.3
Cl/C_{100}	5.51	4.31	0.82	0.87	1.00	1.05

Table X. Volatile Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	1.11	0.700	0.380	0.396	1.07	0.785
% of Total TOC	15.8	8.57	8.58	9.23	13.6	9.79
AOX, kg/t	0.301	0.186	0.0533	0.0136	0.0141	0.0846
% of Total AOX	13.3	8.73	17.9	5.15	3.15	15.4
Cl/C_{100}	9.17	8.93	4.74	1.16	0.45	3.65

(EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.935	0.797	0.405	0.271	0.653	0.706
% of Total TOC	9.51	6.87	6.04	4.16	4.19	4.74
AOX, kg/t	0.0108	0.110	0.00539	0.00490	0.00661	0.00637
% of Total AOX	1.46	12.4	5.75	5.27	2.04	2.08
Cl/C_{100}	0.39	4.65	0.45	0.61	0.34	0.30

D/C + (EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	2.05	1.50	0.785	0.667	1.72	1.49
% of Total TOC	12.2	7.59	7.05	6.17	7.33	6.50
AOX, kg/t	0.312	0.296	0.0587	0.0185	0.0207	0.0910
% of Total AOX	10.4	9.80	15.0	5.18	2.68	10.6
Cl/C_{100}	5.14	6.67	2.53	0.94	0.41	2.06