Biological Oxidation of Organic Constituents in Tar-Sand Combustion-Process Water

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Summary

A study was performed to characterize a sample of reverse-forward, tar-sand combustion process water, and to conduct an initial evaluation of activated sludge treatment of the process water. No pretreatment of the wastewater was considered necessary prior to biological oxidation other than addition of ca. 0.006*M* caustic/L influent to maintain reactor pH in the desired range of 7.0–7.5. The process water was treated successfully by biological oxidation, achieving an 88% reduction of both COD and soluble organic carbon and a 97% reduction of BOD. The disposition of about 150 organic compounds was evaluated and it was shown that a variety of carboxylic acids and aromatic compounds were removed by treatment. Quinolines and certain higher molecular weight carboxylic acids were not removed as effectively as other compounds. These preliminary results should assist in the design of future investigations with tar-sand process water for purposes of optimizing process treatment and improving sample characterization.

INTRODUCTION

Conversion of fossil-derived resources into alternate fuels generates process wastewaters that may contain a variety of inorganic and organic contaminants. Some of these process wastewaters have a unique composition, for which little or no previous experience exists that would allow one to judge the efficacy of conventional wastewater treatment unit operations. The purpose of this investigation was to characterize a tar-sand process water and to conduct a screening test to assess the potential for wastewater treatment by biological oxidation. The wastewater was the aqueous product recovered with the oil from the *in situ* reverse-forward combustion of a tar-sand deposit. The study is the first known to identify the nature of dissolved organic material before and after biological oxidation; the investigation also presents the first known reported results on biological treatment of tar-sand process wastewater.

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SOURCE OF WATER

An *in situ* reverse-forward combustion (RFC) experiment was conducted in the Uinta Basin of northeastern Utah.[1,2] In such an experiment, a pattern of production wells, surrounded by air injection wells is formed. In the first phase, a combustion front is formed at the production well and is forced to move toward the air injection wells under controlled conditions to prepare the deposit for maximum recovery. In the subsequent forward combustion phase, the burn front moves toward the production well (away from the air injection wells) while the hot combustion gases heat the oil ahead of the flame front and force the oil to flow toward the production wells for recovery. The water collected with the product in the RFC experiment was derived primarily from steam injected with the air, and from groundwater condensing after it was vaporized by the combustion. The water studied in this project was collected from an RFC experiment conducted near Vernal, UT, in 1977–1978 by the Laramie Energy Technology Center (LETC).[3] The water was separated from the oil product, refrigerated, and stored as an unfiltered sample. Later, some of the sample whose control number was marked by LETC as 77-(TARSANDS-2C)-OOW-OO-U, was distributed in five 55-gal drums for analysis and treatment. The inorganic quality of the composite tar-sand process water was analyzed according to *Standard Methods*[4] and is reported in Table I.[5] Other characteristics of the water are reported in Table II. The relatively low pH and relatively high chemical oxygen demand (COD) and soluble organic carbon (SOC) can be noted.

TABLE I
Inorganic Chemistry Analysis of Process Water from Tar-Sand Combustion

Parameter	Average concentration (mg/L)	Parameter	Average concentration (mg/L)
Sodium	2.2	zinc	0.027
Potassium	2.0	nickel	0.010
Magnesium	6.6	arsenic	<0.001
Calcium	24.0	selenium	0.003
Chloride	15.0	mercury	0.00015
Fluoride	2.7	aluminum	0.45
Sulfur	58.0	lithium	0.002
Cadmium	<0.001	cobalt	0.004
Chromium	0.003	molybdenum	0.001
Lead	<0.001	vanadium	<0.001
Copper	0.031	barium	0.017
Iron	60.0	silver	<0.001
Manganese	0.54	boron	<0.1

Source for the data is ref. 5.

TABLE II
Average Concentrations of Selected Parameters in Water Samples[a]

Parameter	Average of five samples	Range
pH	3.9	3.9-4.0
NH_3-nitrogen	49	49-50
Alkalinity (as $CaCO_3$)	107	94-114
COD	2350	2340-2370
TOC	1700	1400-1900
Phenolics (4AAP)	19	17-20

[a]Values are in mg/L, except for pH.

EXPERIMENTAL

Water Treatment

The biological organisms used to seed a complete-mix activated sludge reactor were obtained from a mixture of other activated-sludge treatment systems treating waters derived from coal gasification,[6] oil shale,[7] and coking[8] processes. The organisms were acclimatized to the RFC tar-sand water after the pH of the water was adjusted with sodium hydroxide from 3.9 to 4.5. The water was nutrient enriched with 100 mg/L of sodium phosphate, equivalent to 31 mg/L as phosphorus.

When the pH was increased to provide suitable conditions for the organisms in the activated-sludge reactor, a noticeable "wispy" flocculant material formed and eventually settled within one day if left undisturbed. The flocculant material would settle to form a hazy layer at the bottom of a flask; it would not compress or thicken and could be resuspended easily by a gentle swirl of the flask. Because of the time required for settling, this form of induced coagulation and flocculation was not considered an effective option for prebiological treatment and the material was not removed before biological oxidation. The contribution of the flocculant material to the organic-carbon content can be estimated by comparing total organic carbon (TOC) in the raw process water to soluble organic carbon (SOC) in the activated-sludge influent. These values, 1700 and 726 mg/L, respectively, indicate that the suspended material accounted for about 57% of the organic carbon in the sample.

The biological organisms were acclimated to the tar-sand water before data were collected during steady-state conditions. An acclimation period of ca. 100 days provided ample time to establish steady and representative conditions for concentrations of activated-sludge reactor mixed-liquor volatile suspended solids, and reactor effluent COD, NH_3-N, and pH.

The activated-sludge reactor had a mixed liquor volume of 6 L and was designed with an internal clarifier to allow settling of solids within the system.

Oxygen was provided to the reactor by pumping air through a sparger located near the bottom of the reactor tank. The air supply and a paddle mixer provided the required conditions for a completely mixed, stirred reactor. The reactor liquor was maintained at room temperature, which varied within the 22–25°C range; dissolved oxygen was maintained at greater than 3 mg/L. Mixed liquor pH was maintained at 7.0–7.5 by adjusting influent water pH to a value of 4.5.

Mean cell residence time (θ_c) was maintained at 40 days. This was controlled by wasting from the reactor an aliquot of mixed liquor, filtering, and returning the filtrate to the reactor. This allowed independent control of θ_c and hydraulic detention time (θ_H). The volume of sludge to be wasted was computed to account for the concentration of volatile suspended solids in the reactor effluent. The biological reactor was operated under conditions of extended aeration at a moderate rate of substrate removal. Operating parameters for the biological reactor are summarized in Table III.

These data represent average values for a period of ca. 44 days, or more than seven hydraulic detention periods following the acclimation period. The treatment parameters of the biological oxidation process are reported in Table IV and are an average of a set of values representative of a stable reactor process.

The influent process water was a light-brown/straw-yellow color that was reduced in color from ca. 750–70 platinum–cobalt units. The water had a "wintergreen" odor that persisted during activated-sludge treatment and was unlike the "pungent" or "musty" odors experienced in conventional activated-sludge treatment.

Operational problems such as frothing or formation of pinpoint flocs were not encountered, and sludge settling was good as indicated by the low concentration of suspended solids in the effluent. The results of treating the tar-sand process water by activated sludge indicated that removal efficiencies of 88% for COD and SOC, and 97% for BOD, can be achieved during steady-state operation.

Nitrification of the ammonia to nitrate is evident and this explains, in part, the reduction in concentrations of ammonia and alkalinity. The possibility

TABLE III
Operating Conditions in the Process Water Activated-Sludge Reactor

Parameter	Value
Mean cell residence time	40 days
Hydraulic detention time	6 days
Mixed-liquor suspended solids	2594 mg/L
Mixed-liquor volatile suspended solids	2000 mg/L
Food/Microorganism ratio (COD basis)	0.16
BOD removal rate	0.13 $days^{-1}$
COD removal rate	0.14 $days^{-1}$

TABLE IV
Process Water Characteristics[a]

Parameter	Influent	Reactor effluent
Total dissolved solids	333	722[b]
Suspended solids	68	34
Volatile suspended solids	12	30
Chemical oxygen demand (COD)	1910	226
Biochemical oxygen demand (BOD_5)	1660	57
Soluble organic carbon (SOC)	726	90
Phenolics (4AAP)	14.4	<0.2
Organic nitrogen	2.1	1.9
Ammonia (NH_3-N)	48.8	3.6
Nitrate (NO_3-N)	0.5	9.8[b]
Thiocyanate (SCN)	1.1	0.5
Alkalinity (as $CaCO_3$)	206	61.1
Conductivity (μmho/cm)	640	964[b]
Color (Pt-Co units)	750	70
pH[c]	4.5	7.0-7.4

[a]Average values are in mg/L, except where noted.

[b]The increases in TDS and in conductivity result from the addition of NaOH to raise influent pH. The increase in nitrate is due to biological oxidation of ammonia.

[c]Influent pH is reported as appropriate values after pH adjustment. Effluent pH is reported as the range recorded during operation.

that the air sparger may strip ammonia from the mixed liquor is of relative insignificance because the proportion of ammonia at equilibrium with ammonium is relatively small at pH 7. It is believed that most of the ammonia is removed from the system owing to metabolization and sludge wasting.

The choice of a six-day θ_H was made primarily on the basis of the research objective, which was to test the feasibility of using activated-sludge treatment with the tar-sand combustion process water. It is recognized that a θ_H of six days is a longer period than might be economically suitable in a commercial or large-scale facility. The reactor operated at a BOD removal rate of about 0.13 $days^{-1}$, a COD removal rate of 0.14 $days^{-1}$, and a food to microorganism (F/M) ratio of 0.16. These relatively low rates, together with the performance data shown in Table IV, suggest that hydraulic detention time may be reduced to a few days or less.

A base titration curve for a sample of raw RFC process water is shown in Figure 1. The curve shows that the buffering capacity of the process water is greatest in the range from its original pH of 3.9 to a pH of ca. 5.6. The maximum buffering capacity, as calculated from this curve, is ca. 0.006M/L. Adjustment of the process water to a pH of ca. 4.5 permitted the activated-sludge system to maintain the pH of its mixed liquor at 7.0-7.5. As indicated in Figure 1, the amount of base required to provide this pH adjustment is about

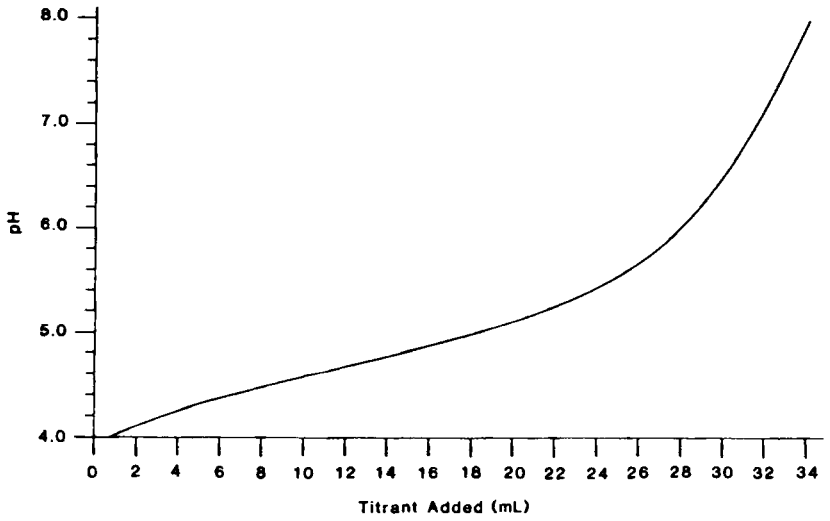


Fig. 1. Base titration curve for a sample of raw process water (100 mL at 0.6*N* with NaOH as titrant).

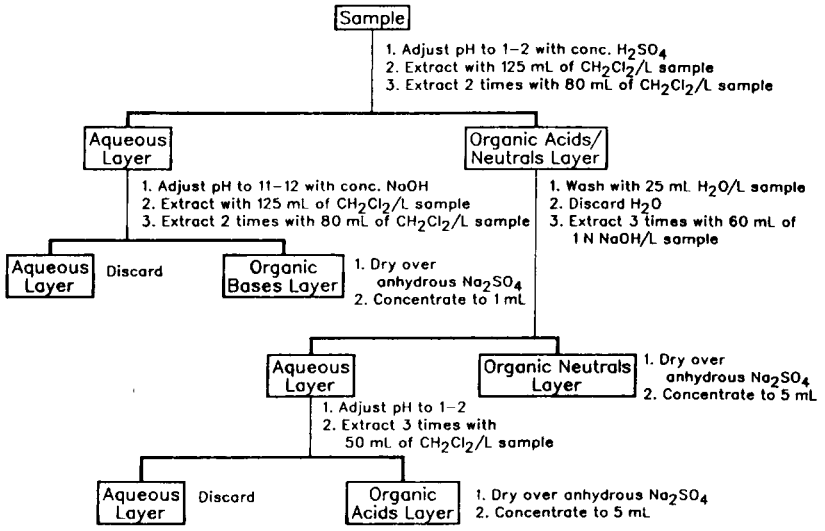
0.24 g NaOH/L influent process water. This NaOH dose is chemically equivalent to about 0.17 g lime (CaO)/L influent.

Organic Constituent Analysis

The raw and biologically treated water samples were partitioned into acid, base, and neutral fractions by methylene chloride solvent extraction (Fig. 2), and these fractions were analyzed by gas chromatography/mass spectrometry (GCMS). The GCMS analysis was performed on aqueous-phase samples that had been filtered through "Mead Flo" glass fiber filters.

In order to study the organic constituents extracted from the aqueous phase of the process water samples, capillary column GCMS was used to identify the organic constituents, and capillary column GC was used to quantify the major components. Quantification was based on a set of standard compounds that were representative of those found in the sample extracts.

The gas chromatograph used was a Hewlett-Packard (HP) model 5840 fitted with cryogenic cooling with liquid carbon dioxide, extra peak storage for integrated areas of up to 500 peaks, and a second generation HP capillary column injection port (model 18835B), which is a modification of the Grob-type splitless injection system. An automatic sampler (HP model 7661) was used and the amount injected was 1 or 3μL (depending on concentration). The capillary column was an HP 50-m fused silica Carbowax 20M with a quoted maximum operating temperature of 220°C. The oven temperature was programmed at 2°C/min from 20 to 200°C with a 2-min hold at 20°C and an 18-min hold at 220°C. The injection port temperature was 225°C and the flame ionization



Note: A 500 mL Kuderna Danish apparatus was used to concentrate the acid, base, and neutral fractions. Final volumes were obtained under a stream of nitrogen.

Fig. 2. Diagram of methylene chloride extraction.

detector temperature was 250°C. Operating conditions for the GC portion of the GC/MS were the same as those used in the GC-only runs.

The data system used was an HP model 5930 equipped with an HP model 5933A computer with a 16K, 16-bit word, core memory, a model 7900A dual disk drive with two 2.5-Mbyte disks (one fixed and one removable), and a Tektronix model 4012 graphic display terminal. Peripheral equipment included a Tektronix model 4631 hard-copy unit. Data collection was done with a standard software package provided by Hewlett-Packard and known as the AQUIRE program; analysis was done with Hewlett-Packard's SPEED program. The mass range scanned was 35–350 AMU, and two analog-to-digital (A/D) measurements were made for each datum point (each 0.1 AMU); cycle time was approximately 2 s.

Standards used in determining response factors and reproducibility of the HP model 5840 gas chromatograph were obtained from Aldrich Chemical Company (Milwaukee, WI), Eastman Kodak Company (Rochester, NY), and Fischer Scientific Company (Fair Lawn, NJ).

Each of the fractions was analyzed on the GC using a split ratio of ca. 20 with an injection volume of 1 μL.[9] Each GC chromatogram was then studied in order to guide the subsequent analysis.

1) When the chromatogram was satisfactory, the fraction was used without dilution or concentration;

2) If it showed overload, the fraction required dilution. An estimate of the dilution required was made and the fraction was rerun at that dilution.

3) If the chromatogram was slightly weak, indicating that an additional small amount of the fraction was required to produce a satisfactory chromatogram. The fraction was then rerun with 3-μL injection and a split ratio of approximately 20.

4) If it was very weak, indicating that considerably more of the fraction would be required to produce an acceptable run. The GC injector was changed to a Grob-type splitless injector and a 1-μL sample was injected.

5) Showed the 1-μL splitless injection to be slightly weak; the fraction was run at 3 μL splitless; if found to be very weak, the fraction was concentrated and run at 3 μL splitless.

The GC was used for quantification of the identified peaks and for establishing the quantity, dilution, or concentration of samples. The GC was also used for selecting the injection method required for both quantification of peaks by GC and identification of peaks by GCMS.

Organic compounds were identified by studying the fragmentation patterns of the mass spectra and the associated retention time and/or by studying the spectra or data in the ASTM *Index of Mass Spectral Data*[10]; Stenhagen, Abrahamson, and McLaffety's *Registry of Mass Spectral Data*[11]; and Heller and Milne's *EPA/NIH Mass Spectral Data Base.*[12] The identified organic compounds were quantified using the integrated areas (area counts) of the HP model 5840 GC and the response factors of representative compounds developed in standard runs with split and splitless injection and with 1- and 3-μL injection.

As in any GCMS or GC-only analysis of complex mixtures, there are numerous potential sources of error. First, there is the problem of discrimination in the extraction process or in the recovery step. Liquid-liquid extraction into acid, base, and neutral fractions is not completely efficient. Also, extraction efficiency varies for different compounds; thus, a single value cannot be factored to correct the extraction efficiency for all compounds. Generally, in a liquid-liquid extraction CH_2Cl_2, typically nonpolar compounds are extracted almost quantitatively whereas strongly polar compounds may remain in the aqueous phase along with such relatively nonpolar compounds as alcohols, ketones, and mercaptans, which are only partly extracted.

A second source of error in GCMS analysis involves the estimation of response factors for the compounds found in these mixtures. In a previous report,[13] a study was conducted using several compounds to establish response factors and reproducibility from run to run. From these results, it can be seen that reproducibility is excellent and is probably within 10%. However, the response factors vary considerably with the specific compound. The area counts per nanogram for a 1-μL injection, splitless, vary from 452 for pyridine to 1190 for dicyclohexyl. For groups of compounds, the range of area counts per nanogram is more narrow: 452 to 526 for four pyridines, 616 to 812 for four anilines. Thus, the range is not as wide for specific types of compounds and, with the appropriate response factors, errors for individual compounds might be expected to be about ±20%.

With splitless injection, ca. 98 ± 2% of the injected sample goes into the column when the injection port is leak-free. With split injection, the split ratio can vary from compound to compound. This split ratio can be determined by dividing the average count per nanogram for splitless injection by that for split injection. The split ratio varied from 19.1 to 24.4 for a series of 14 neutral compounds, and except for two compounds having split ratios of 14.3 and 12.9, it varied from 17.7 to 19.6 for 11 basic compounds. The amount injected, 1μL, appeared to have no discernible effect on the split ratio or on the area counts per nanogram. Thus it appears that, although there are variations in the response factors for compounds and in the split ratios, the variations within a group are relatively small. The response factors used in this study (Table V) were derived using several commercially available standards for each group of compounds.[13] No attempt was made to determine the recovery of different standards after liquid-liquid extraction or to do standard additions to the wastewater to determine recovery.

A third source of error in the analysis occurs when a material is not chromatographable; that is, it will not pass through the column under the temperature programming conditions used. To resolve this situation, liquid chromatography or other methods must be used. Of all the sources of error in the quantitative analysis, perhaps the most serious is the preliminary workup before injection into the GC.

There were several problems encountered in the identification of the compounds present in the process water extract. The mixtures were extremely complex and, despite the high resolution and efficiency of the fused silica capillary columns, not all peaks were resolved. Deconvolution software with the HP data system cannot handle a large number of spectra. Thus, deconvolution must be done visually; this is not only time consuming but is also subject to error. Com-

TABLE V
Response Factors Used in Calculating Mixture Concentration

Type of compound	Area count per nanogram	Compound	Area count per nanogram
Neutral		*Carboxylic acid*	
Alkanes	830	C_3	16.7
Cyclohexanes	880	C_4	24.8
Cyclic compounds	1040	C_5	35.0
Polar compounds	720	C_6	47.0
		C_7	51.4
Basic		C_8	55.0
Pyridines	480	C_9	52.6
Anilines	690	C_{10}	52.6
Miscellaneous	590	C_{11}	52.0
Miscellaneous polar compounds	500	C_{12}	54.5

pounds were identified from MS data and with authentic standards of known GC retention times whenever possible. For many compounds, tentative identification was provided when only MS data were available. Because quantification relies on the behavior of a select set of compounds, further work is required to confirm the concentration of all the compounds identified.

RESULTS

As shown in Table VI, the tar-sand combustion process water was found to consist of approximately equal proportions of acid, base, and neutral fraction organic constituents, with the neutral fraction being predominant. The acid and neutral fractions were removed by biological oxidation at efficiencies of 94% and 99%, respectively, whereas the base fraction was reduced by 76%.

The major peaks of the chromatogram represent more than 150 identified compounds whose disposition was studied as compound classes. These compounds contribute the major portion of the extractable/chromatographable (EC) material that amounts to 76.5 mg/L in the influent sample and 6.4 mg/L in the treated (effluent) sample.

Table VII and Figure 3 summarize the organic constituents found in each of the three fractions of the raw process water and activated-sludge effluent. The phenols and cresols in the acid fraction represent 67% of the total mass of material identified in the influent, whereas the carboxylic acids, which range

TABLE VI
Concentrations of Total Extractable/Chromatographable and Identified Organic Constituents in Process Water

Source and fraction	Extractable/chromatographable organic material: Amount recovered Concentration (μg/L)	Relative proportion (%)	Amount identified Concentration (μg/L)
Influent			
Acid	22,482	29	17,494
Base	20,453	27	12,284
Neutral	33,611	44	14,447
Total	76,546		44,225
		Treatment reduction	
Effluent			
Acid	1226	94	778
Base	4854	76	1367
Neutral	337	99	0
Total	6417		2145

TABLE VII
Summary of Organic Constituents in Process Water and Their Reduction by Treatment with Activated Sludge

Fraction and constituent	Influent		Effluent		
	Amount (μg/L)	Percent of Total	Amount (μg/L)	Percent of total (%)	Percent reduction (%)
Acid fraction					
C_1-C_3 carboxylic acids	54	0.3	—[a]	—	100
C_4-C_6 carboxylic acids	3718	21.3	13.7	17.6	96.3
C_7-C_{11} carboxylic acids	1943	11.1	339	43.6	82.6
Phenols/cresols	11,294	64.6	270	34.7	97.6
Benzoic acid	232	1.3	12	1.5	94.8
Toluic acid	253	1.4	20	2.6	92.1
Total	17,494	100	778	100	95.6
Base fraction					
Pyridine-C_2 pyridines	1817	14.8	10	0.7	99.5
C_3-C_4 pyridines	1718	14.0	68	5.0	96.0
C_5-C_7 pyridines	3028	24.6	275	20.1	90.9
Quinoline-C_2 quinolines	2967	24.2	332	24.3	75.7
C_3-C_4 quinolines	2726	22.2	679	49.6	75.1
Acridine	28	0.2	4	0.3	87.5
Total	12,284	100	1368	100	88.9
Neutral fraction					
Methyl cyclohexenyl ketone	657	4.5	—	—	—
Methyl methylcyclohexenyl ketone	10,198	70.6	—	—	—
Methyl tolyl ketone	632	4.4	—	—	—
Acetophenone	591	4.1	—	—	—
Lactones	1621	11.2	—	—	—
Indanones	748	5.2	—	—	—
Total	14,447	100	—	—	—

[a]Refers to amounts that were not detected.

in size from one to eleven carbons, contributed to approximately 33% of acid fraction EC compounds. Benzoic and toluic acids were also found and contributed a minor portion of the total mass identified in the acid fraction of the process water. As indicated in Table VII, the higher carboxylic acids tend to be slightly more resistant to biological oxidation. Low-molecular-weight carboxylic acids are biodegradable and are also relatively volatile at low pH values. However, since the biological reactor was maintained at pH 7.0–7.5, removal of low-molecular-weight carboxylic acids was probably a result of biological degradation rather than air stripping. Benzoic and toluic acid com-

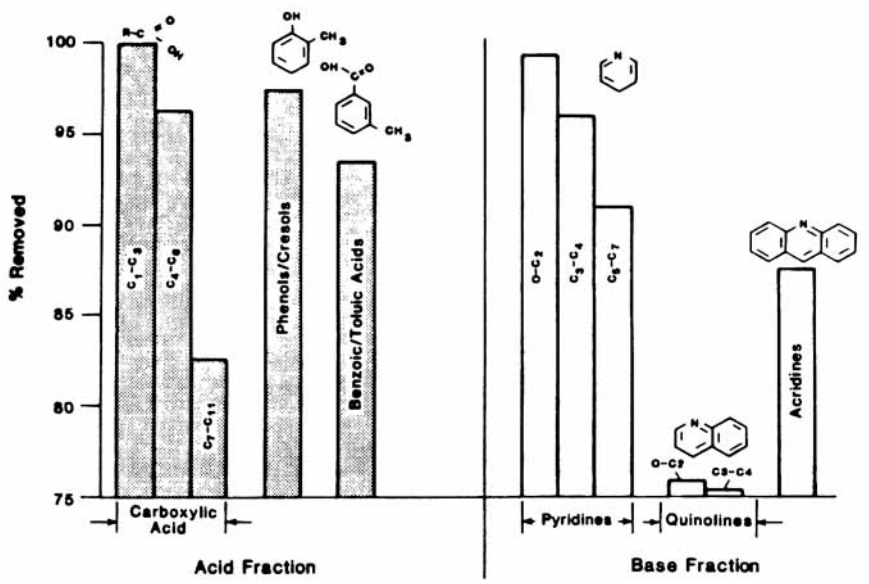


Fig. 3. Removal of organic constituents from process water by treatment with activated sludge.

pounds and phenols and cresols were removed at greater than 90% efficiency. Carboxylic acids greater in size than 12 carbons were not detected in the sample. This is unusual because aqueous samples from petroleum products range in size beyond C_{12} and there is often a preponderance of C_{16} and C_{18} acids in fossil-derived samples. The pH of the raw process water was 3.9; this may have contributed to insolubility of higher molecular weight carboxylic acids in the water. That these compounds were present in the sample but lost during methylene chloride extraction is unlikely because commercial standards of carboxylic acids as large as C_{18} were detected under similar analytical conditions in this study.

The organic compounds in the base fraction of the process water consisted primarily of single-ring nitrogen heterocyclics, i.e., pyridine and its alkyl derivatives up to C_7. A smaller proportion of the identified compounds comprised the fused heterocyclic nitrogen compounds, i.e., quinoline and its alkyl derivatives up to C_2. An extremely small proportion of the process water's base fraction was identified as acridine, a three-ringed nitrogen heterocycle.

The base fraction was apparently the least responsive of the three to biological degradation, with the quinoline group being the most refractory. These compounds were removed at the 75% level, while the pyridines were reduced in the 96-to-100% range. Although acridine appears to have been removed at the 90% level, it is believed that it is as likely that the molecule, because of its relatively large size and low concentration, escaped detection.

CONCLUSIONS

This study provides an initial evaluation of the organic constituents of reverse-forward combustion process water and their specific removal efficiencies by activated-sludge treatment. The study showed that process water from tar-sand combustion contains organic material consisting of a variety of carboxylic acids and aromatic compounds that can be removed by activated-sludge treatment. Of the compound groups tentatively identified, only the quinolines and certain higher molecular weight carboxylic acids appear to be somewhat refractory to this treatment. Activated-sludge treatment resulted in good mixed liquor solids-settling characteristics. Color reduction and nitrification of the influent ammonia were apparent, and high removal efficiencies were reported for BOD, COD, and SOC. It is concluded that biological oxidation is an effective method of removing the dissolved organic material from the process water at high efficiency levels. Approximately 0.015*M* caustic/L influent was necessary in order to maintain pH of the mixed liquor in the desired range of 7.0–7.5. Because of the relatively low F/M ratio, and because no operational problems were encountered at a six-day θ_H, we anticipate that the θ_H could be reduced to a few days or less without significant losses in removal efficiency. Other tests would be required to confirm this speculation. Additional work is necessary to understand how the activated sludge process operating conditions effect removal of organic contaminants in the process water, especially heterocyclic nitrogen compounds. Additional work is also needed to evaluate alternate analytical strategies in order to characterize a greater fraction of the organic contaminants in the process water.

Various methods are presented in the literature which attempt to address the difficult problems of recovering complex mixtures of organics in water. It can be seen in comparing the SOC concentration of the samples listed in Table IV with the total concentration of the EC material from the same samples (see Table VI) that recovery/detection efficiency of the organic carbon material was low. Although the method that was used represents an appropriate approach for the particular goals of this study, other methods which are adjuncts to capillary column GCMS may be used in studies directed toward a more comprehensive understanding of process waters whose organic properties are complex and highly varied. One alternative converts polar compounds to derivatives that can pass through capillary columns. Another is to use direct GCMS analysis of the water sample. This method is useful for identifying major components that are not extractable. A third alternative would use reverse-phase high performance liquid chromatography (HPLC) to identify the compounds that do not pass through a GC column. The use of HPLCMS, in itself, would not be useful because the mixtures are complex and the resolution of the typical HPLC columns is relatively low. However, with reverse phase HPLC/high-resolution MS/low-resolution MS, the second MS acts as an additional resolving device to allow analysis.

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