Environmental Impacts of Thermochemical Biomass Conversion

Final Report

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INTRODUCTION

This report presents information derived by Pacific Northwest Laboratory in support of the DOE Biomass Thermochemical Conversion Program entitled, "Evaluation of Environmental Impacts of Thermochemical Biomass Conversion" conducted over a 27-month period. Thermochemical conversion in this instance is limited to fast pyrolysis, upgrading of fast pyrolysis oils, and gasification. Environmental impacts of all types were considered within the project, but primary emphasis was on discharges to the land, air, and water during and after the conversion processes. The project discussed here is divided into five task areas:

1. Pyrolysis Oil Analysis,
2. Hydrotreating of Pyrolysis Oil,
3. Gas Treatment Systems for Effluent Minimization,
4. Strategic Analysis of Regulatory Requirements, and
5. Support of the IEA Environmental Systems Activity.

The pyrolysis oil task was aimed at understanding the oil contaminants and potential means for their removal. The hydrotreating task was undertaken to better define one potential means for both improving the quality of the oil but also removing contaminants from the oil. Within Task 3, analyses were done to evaluate the results of gasification product treatment systems. Task 4 was a review and collection of regulatory requirements which would be applicable to the subject processes. The IEA support task included input to and participation in the IEA Bioenergy activity which directly relates to the project subject.

Each of these tasks is described in this report along with the results to date. Conclusions and Recommendations from the overall project are given.

Task 1 was concentrated mostly in the first year of this project. Task 2 was initially included in the pyrolysis oil task but was expanded in the second year of the contract. Details of tests conducted for this task are given in Appendix A. Task 3 was delayed, for the most part, to the second year of the project when actual gasifier samples were available from PDU operations. Task 4 includes a review of regulations that has provided an ongoing series of information for process development in the field of biomass thermochemical conversion. The latest report is provided as Appendix B, which is an assessment of regulatory requirements for process effluents. The support to the Task 5 activity has been limited mostly to the second year of the project.

Task 1. PYROLYSIS OIL ANALYSIS

Fast pyrolysis of biomass is being widely studied as a means to produce useful liquid fuels. The potential means of fast pyrolysis have been well-documented [1] and several reactor systems engineered [2], but the demonstration of the use of the liquid product is still in its infancy. Direct utilization of the product as a combustion fuel in a boiler has undergone limited testing [3]. Upgrading of the product to higher quality fuels has also been investigated in the laboratory [4]. Current interest lies in the use of the liquid product as a turbine fuel, a diesel fuel, a source of oxygenates for gasoline, and a co-feed to petroleum refineries.

A major concern in this respect is the small amount of inorganic components (ash-forming materials) remaining in the pyrolysis oil. Particularly troublesome are the alkali metals. Deposition of these components in combustion systems, on upgrading catalysts, or release to the environment is being studied. Analysis to date of the fast pyrolysis oils has provided only a limited view of the inorganic components.

Another item of interest is the form of the water component. The water has been viewed as a major factor in the inconsistent elemental (carbon, hydrogen, nitrogen / CHN) analysis of this type of oil. In addition, dispersed discreet water phases may serve as the site of alkali in the oil. Research in this area was conducted by PNL to provide data on the amount and form of water and alkali in biomass flash pyrolysis oil. This information may be used in determining the suitability of this product for the uses delineated above.

Three types of biomass fast pyrolysis oil were evaluated in this study: one each derived from a hardwood, a softwood, and a herbaceous biomass. The raw oils were analyzed first to provide a comparison with other analyses reported in the literature. Then the oils were separated into different fractions by various methods in order to determine where the inorganic components resided in the oil. Particular attention was paid to the alkali metals (potassium and calcium often represent the largest share of the inorganic component of the pyrolysis oil). At the same time, the form of the moisture in the oil was evaluated. Separation methods included filtration, centrifugation, and phase separation by addition of water. The fractions were analyzed by standard chemical methods, including atomic adsorption (AA), inductively coupled plasma - atomic emission spectroscopy (ICP-AES), CHN micro-elemental analysis, optical microscopy, and Karl Fischer titration.

ANALYTICAL METHODS

The various analytical methods used are described below.

Elemental Analysis

A Perkin-Elmer (P-E) 240B analyzer was used for analysis of carbon, hydrogen, and nitrogen; oxygen was determined by difference. The P-E 240B determines carbon, hydrogen, and nitrogen by detecting and measuring their combustion products (CO_2 , H_2O , and N_2). Combustion occurs in pure oxygen under static conditions, and the products exit from the combustion furnace through the reduction tube (which reduces any NO) and through the series of detectors and traps. The instrumental readout is in

millivolts, which was used to calculate the composition based on reference compounds.

Trace element analysis was performed by either AA, ICP-AES, or ICP-MS. Organic sample preparation for AA involved acid digestion. Initially, sample preparation for the ICP-AES involved an alkali fusion followed by dissolution. The fusion was performed individually with either caustic sodium or potassium. By this procedure, sodium could be measured in the sample fused in potassium or vice versa. In evaluating the results, cross contamination is apparent, as sodium and potassium numbers are higher by 1 or 2 orders of magnitude in all cases; therefore, the ICP-AES numbers for sodium and potassium are not reported. Later analyses used the acid digestion with peroxide method like that used with the AA for sample preparation; however, reproducibility at the low levels of contamination, found in the hot-filtered oil especially, also rendered these results nearly useless. In the end, the method found to be most useful was acid carmelization followed by ashing overnight in a muffle furnace at relatively low temperature, 500°C, and then digestion in aqua regia with microwave heating.

Moisture

Karl Fischer titration was used by means of the Aquatest IV unit developed by Dow Chemical Co. In this instrument, the reagent is electrolytically generated in the presence of water. Using a sensing electrode, the instrument generates enough reagent to react with the water in the sample and calculates the water content based on the use of direct current electricity for electrolysis.

Ash

Ash was determined by combustion in a muffle furnace. Porcelain crucibles were used throughout. The samples were slowly heated over several hours to 500°C to allow evolution of volatiles. They were then ashed at 600°C for 1 hr and again at 700°C for an additional 2 hr, so that all black was burned out of the sample.

Char

Char was recovered on a Whatman #42 paper (particle retention of 2.5 μm). The sample was mixed with methanol and stirred at room temperature. The solution was then filtered, washed with additional methanol, and air dried.

Centrifuge

Samples of 48 g were placed in capped 50-ml polyethylene tubes. A Sorvall RC-2 refrigerated centrifuge, with an SS-34 rotor, which had been calibrated by the manufacturer, was used for the tests. Based on the calibration, the 8600-rpm test was equivalent to 8700G. The centrifuge was kept at 10°C to 20°C by the refrigeration unit.

OIL ANALYSIS

The biomass pyrolysis oil samples evaluated in this study were produced in the vortex fast pyrolysis reactor at NREL. The samples were derived from oak hardwood; southern pine softwood; and a high-growth herbaceous biomass, switchgrass. Samples of three whole oils and also one hot-filtered switchgrass oil were analyzed. All were produced at similar severity of conditions, <1 s at approximately 520°C; however, the hot-filtered oil was

exposed for an additional 5 seconds to temperatures in excess of 400°C in the baghouse. Specific details of the composition of these oils are provided in Table 1. The hot-filtered oil underwent only a limited analysis, but it is clear from the alkali analyses that the hot-filtration process can remove the vast majority of the inorganic contaminants in the pyrolysis oil.

Elemental analysis for potassium, calcium, and sodium was also undertaken on the ash sample recovered from each whole oil (results in Table 2). The results confirm the low levels of alkali metals in the pyrolysis oils. Calculating back to the total alkali metal content shows that the recovered ash represents about half of the alkali metal content found in the raw oil. The ash method (including firing at >600°C) apparently results in some loss of these elements. A similar effect has been reported for whole biomass [5]. The sodium analysis could not be used because estimation of the contamination of the sodium in the ash recovery wash water was not possible.

The oil compositions are similar to those reported in earlier sources; however, only limited data are available in the literature on the inorganic component of pyrolysis oils. Most often it is ignored, apparently because it is a minor component. Data from the literature show that the ash content is low in these oils [6-10], mainly because the biomass feed is low in ash. The inorganics reported are those commonly found in biomass [7,8]. For these samples, the wood oils are cleaner than the herbaceous oil on a basis of char and ash contamination. In fact, the switchgrass oil is the poorest quality fuel by most standards, such as moisture, oxygen content, and sulfur, as well as solids and ash.

Table 1. Description of Biomass Pyrolysis Oils

	<u>OAK</u>	<u>SOUTHERN PINE</u>	<u>SWITCHGRASS</u>	<u>HOT-FILTERED</u>
NREL test # production date	Run #154 6/4/92	Run #150 3/17/92	Run #146B 2/18/92	Run #157 8/5/93
<u>ANALYSIS</u>				
Elemental, raw oil, %				
carbon	46.9	46.0	38.8	42.1
hydrogen	7.5	7.9	8.5	7.4
nitrogen	0.0	0.1	0.0	0.0
oxygen (by difference)	45.6	46.0	52.7	50.6
Moisture	16.3	10.2	16.7	NA
Ash	0.086	0.033	1.041	NA
Char (MeOH insol)	0.74	0.13	4.18	NA
Char-free ash	0.018	0.017	0.395	NA
Trace element, raw oil, ppm				
calcium	160[93]	160[79]	745	[5.1]
silicon	112	93	3130	NA
potassium	55	10	165	[1.5]
iron	86	47	243	NA
aluminum	55	41	237	NA
sodium	2	<0.1	--	[23.9]
sulfur	<60	<50	347	NA
phosphorus	<50	<50	254	NA
magnesium	<55	<45	335	0.4
nickel	<22	<20	52	NA
chromium	<17	<17	47	NA
zinc	28	14	23	NA
lithium	25	7	12	NA
titanium	17	5	14	NA
manganese	15	6	27	NA
barium	<3	<2	13	NA

Trace element analyses by ICP-AES except K, Ca, and Na by AA with ICP results in brackets. The "less than" numbers represent values below the level of detection for the particular sample as prepared, not the limit of the instrumental technique itself.

NA = not analyzed

Table 2. Composition of Pyrolysis Oils Based on Ash Analysis

<u>ANALYSIS</u>	<u>OAK</u>	<u>SOUTHERN PINE</u>	<u>SWITCHGRASS</u>
Trace element, raw oil, ppm			
calcium	78	39	542
potassium	27	4.0	165

Ash is apparently concentrated in the char byproduct of these processes [9,11,12]. The char remaining in the oil contains a higher proportion of the ash. Based on the data in Table 1, the char must contain 10% to 15% ash (calculated by difference). However, the char-free oil (methanol-soluble after an extended period of contact) is still not free of ash. On the other hand, as seen by the analysis of the hot-filtered sample (which is switchgrass-derived), if the char is removed at an early stage of the oil recovery process, then the alkali contamination will be greatly reduced relative to the whole oil sample. Except for sodium, the alkalis are found at much lower levels in the hot-filtered oil than in the non-filtered oil. The high sodium content is believed to be derived from the glass bottle used to store the oil sample.

The whole oil samples were allowed to stand for 2 months after sampling at NREL and receipt at PNL. The age of the oils since production ranged from several months to nearly a year. Once the containers were opened, the three oils had different appearances. The oak oil appeared uniform without any phase separation, while the pine oil had a frothy top brown-black layer of oil that contained many fine particulates. The top layer

represented less than 10% of the oil sample as received and could be separated from the bulk of the oil. This bulk pine oil, which was lighter brown in color and less viscous, was also less viscous than the oak oil. The smaller sample of switchgrass oil also had a foamy top layer, estimated at one-fourth of the total sample. The oil on the whole contained much black particulate material. These differences suggest the nonuniformity problems that can be expected with biomass pyrolysis oil but may be representative only of the particular reactor system used. The analyses reported in Table 1 are for the whole oils from oak and switchgrass (sampled after adequate agitation). The pine oil data are for the bulk oil with the foam skimmed off.

The hot-filtered oil sample had already fractionated into two oil layers upon receipt at PNL (about 2 months after production). The analyses of these two layers, given in Table 3, suggests a separation of a water-rich top layer from a water-deficient heavy bottom layer. There is evidence also of the alkali metals preferentially fractionating to the water-rich layer.

Table 3. Composition of Fractions from Hot-Filtered Oil

<u>ANALYSIS</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>O, by diff.</u>	<u>K</u>	<u>Ca</u>	<u>Mg</u>	<u>Na</u>
Top phase	40.3	8.6	1.1	50.0	2.26	5.53	0.51	55.5
Bottom phase	54.9	7.8	0.6	36.7	<0.5	5.04	0.76	32.3
Whole oil	42.1	7.4	0.0	50.6	1.49	5.08	0.37	23.9

CHN in %, trace element in ppm.

MICROSCOPIC ANALYSIS OF PYROLYSIS OILS

An optical microscope was used to investigate the composition of the pyrolysis oils. As seen in Figure 1, the oils appear to be yellow solutions containing large numbers of char particles. There is no evidence of water droplets in the oil. Numerous clear round objects were observed, which were later determined to be gas bubbles based on their transparency in the electron microscope.

Particle size analysis of the oil samples is given in Table 4. The particles are typically micrometer-sized. Mean particle diameters of $<3\text{ }\mu\text{m}$ were determined with the range of particles extending up to near $50\text{ }\mu\text{m}$. The effect of the centrifugation was quantified based on the particle size distribution. Following centrifugation, the bulk of the larger particles was not present, but the mean particle size was almost unchanged. In other words, the separation of about one third of the mass of the char by centrifugation apparently removed the larger particles without greatly affecting the number average particle size. Although the amount of particulate (char) varies greatly among the three samples, the particle sizes are similar, with the switchgrass fiber being slightly longer than the fibers in the other two oils.

Consistent analytical results for pyrolysis oil is not readily achieved, causing a perception of an inhomogeneity of the oil. The consistency of elemental analyses was evaluated in a round-robin analytical program organized through the IEA [13]. In that study the variability of the analytical results was quantified, and the moisture content was identified as the critical component leading to the inconsistency. However,

A Oak Oil

B Switchgrass Oil

Figure 1. Microscopic Views of Pyrolysis Oils

we find no separate phase of water droplets in the oils. Based on the foam (water/char) formation noticed in two of the oil samples, it may be more complete to consider that the inconsistent distribution of the char (with adhered water) may be the cause of the analytical inconsistency.

Table 4. Particle Size Analysis of Char in Pyrolysis Oil

<u>OIL SAMPLE</u>	<u>FIBER LENGTH</u>	<u>EQUIVALENT DIAMETER</u>	<u>DIAMETER RANGE</u>
Oak, raw	5.5 μm	2.6 μm	0.5-42 μm
Oak, centrifuged	3.6 μm	2.1 μm	0.5-12 μm
Pine, raw	4.5 μm	2.7 μm	0.5-11 μm
Switchgrass, raw	7.9 μm	2.7 μm	0.5-35 μm

THIN-LAYER CHROMATOGRAPHY OF PYROLYSIS OILS

Thin-layer chromatography (TLC) was attempted as a means to do a "quick and easy" separation and recovery of the alkali-containing components in the pyrolysis oil. Alumina plates were used to chromatograph the oils in acetone and acetone/water developing solvent systems. Separation of the oils was achieved, as indicated by movement of different intensity colored spots up the plate. Acid violet (aqueous violuric acid) was not useful for identifying any alkali-containing components on the plates. Upon further consideration, the low concentration of the alkali metals in the pyrolysis oils in combination with the very small sample size contained on the TLC plate probably would not allow detectable quantities of alkali salts to be recovered for the AA. Therefore, this method of separation and recovery was abandoned.

PHASE ANALYSIS AND PARTITIONING OF TRACE COMPONENTS

An important characteristic of biomass pyrolysis oil is that the oil, including a large fraction of water, is stable as a single phase. Separation of an aqueous phase is not ordinarily found for fast pyrolysis systems. In this study, no separable water phase could be found. Analysis of the oil samples, after 2 months standing, showed no separate aqueous phase. Oil samples were withdrawn from the top and bottom of the oak and pine oils in order to measure the moisture content. These samples showed a consistent difference in moisture contents which was greater than the expected experimental variation. The difference suggested water migration to the top of the sample, a not unexpected result considering the higher density (~ 1.2 g/ml) of the bulk oil. Actual separation into two phases occurred only in the hot-

filtered oil, wherein a water-rich layer was found above a water-deficient layer.

Centrifugation of the pine and oak oils was undertaken to attempt to separate the aqueous and solid phases from the oil. Well-shaken, whole oil samples were placed in a centrifuge which was run at an equivalent of 8700G for two 1-hr periods. This test was equivalent to leaving the oils standing for 2 years ($2 \times 8700 \text{ hr} @ 1G$). No separation of an aqueous phase was found. After the centrifuge test, the oil samples were poured from the centrifuge tubes; and char particulate, which had separated by the centrifugation, was scraped from the top sides of the tubes. This char was washed with methanol, and the recovery was determined to be 29% and 36% of the total char for the oak and pine oils, respectively. These particles were recovered at the end of the centrifuge test, and it is not known if they separated early in the test or how much more could be separated by further centrifuging. These results suggest that centrifugation may serve (after some optimization) as a char separation technique but would not be useful for moisture removal.

A second phase separation technique used in this study was the addition of water to precipitate the heavy tar. The separation of the aqueous soluble organics by addition of water is well known. An unknown piece of information is the fate of the inorganic components during such a separation. The extent of water miscibility of the pyrolysis oil is a function of the hydrophilicity of the organic components. Generally, the more oxygenated the oil, the higher the expected water solubility.

In the water addition tests, the water was added to the pyrolysis oil samples in portions with stirring. Table 5 provides a summary of the observations in these tests.

Table 5. Phase Separation of Pyrolysis Oil by Water Addition

<u>SUBSTRATE</u>	<u>MOISTURE</u>	<u>DESCRIPTION</u>
Oak oil (64.45 g)	16.3%	uniform
+ water (6.51 g)	24.0%	tar blobs redispersed
+ water (6.48 g)	30.3%	less easily redispersed
+ water (6.44 g)	35.5%	not readily redispersed
+ water (8.46 g)	40.9%	heavy tar blobs not redispersed
Pine oil (64.90 g)	10.2%	uniform
+ water (6.53 g)	18.4%	stringy tar, not easily redispersed
+ water (6.95 g)	25.6%	stringy tar, not easily redispersed
+ water (6.58 g)	31.5%	settled tar layer not redispersed

The end results were that the oak oil separated after the addition of water to a total amount (including existing dissolved water) just greater than 35%, while the pine oil separated after water addition to the 25% to 30% range. Much of the difference in the amount of dissolved water leading to separation was represented by the difference in the original moisture contents of the oils.

The aqueous and tar phases were analyzed for trace element components. The results of the analyses are given in Table 6. No clean separation into either the aqueous or tar phase occurred for any of the elements. A higher percentage of most of the inorganic elements went into the tar phase while a similar or higher percentage of potassium went into the aqueous phase. One interpretation of these results is that the bulk of the inorganic material resides with the char, which separates in the heavy tar phase. The potassium components, being typically more water soluble, tend to move to the aqueous phase. The sodium separation is not clear because the sodium concentration in the water used for the separation (about 20 ppm) was much greater than in the pyrolysis oil. It is apparent that a water separation will lead to major losses of the oil into the aqueous phase, while only an imperfect separation of the alkali metals will be accomplished. The loss of organic into the aqueous phase ranged from one-half to one-third of the dry tar mass for the two oils tested. Only very pure water could be used in a water separation or else the separated oil could end up more contaminated (as in this case with sodium) than the original oil.

Char recovery by filtration was also tested. Methanol was used as a diluent to facilitate the filtration. Analysis of the insoluble chars showed the inorganic elements to be concentrated in the chars. The analytical results are given in Table 7. Levels of 1 to 2 orders of magnitude higher were found in the chars for the elements analyzed. However, the inorganic content of the chars represented only a portion (one-fifth to one-half, based on ash analysis) of the total inorganic content of the whole oil. Therefore, this level of separation of the char

(>2.5 μ m in methanol wash) would not leave a clean, ash-free oil. As shown in Table 8 there are significant levels of nonfilterable alkali components in the methanol soluble oils.

Table 6. Trace Element Analysis of Pyrolysis Oil Fractions

<u>ANALYSIS</u>	<u>OAK</u> <u>AQUEOUS</u>	<u>OAK</u> <u>TAR</u>	<u>SOUTHERN PINE</u> <u>AQUEOUS</u>	<u>SOUTHERN PINE</u> <u>TAR</u>
Trace element, ppm				
calcium	20(52)	102(88)	132	80
potassium	44	41	17	7.2
sodium(est.)	4.5	52	4.4	66
silicon	66	119		
iron	30	65		
aluminum	15	52		
sulfur	17	<50		
phosphorus	10	<45		
magnesium	14	<35		
nickel	<2	<20		
chromium	<2	<15		
zinc	32	20		
lithium	2.5	12		
titanium	5.7	8		
manganese	11	8		
barium	3.2	3		
copper	<2	<7		

Analyses by ICP-AES except potassium, calcium, and sodium by AA with ICP-AES in parentheses. The "less than" numbers represent values below the level of detection for the particular sample as prepared, not the limit of the instrumental technique itself.

Table 7. Trace Element Analysis of Biomass Pyrolysis Oil Chars

<u>ANALYSIS</u>	<u>OAK CHAR</u>	<u>SOUTHERN PINE CHAR</u>	<u>SWITCHGRASS CHAR</u>
Trace Element, ppm (% of element in raw oil)			
calcium	4580 (21%)	8100 (7%)	4600
potassium	1300 (18%)	667 (9%)	1890
sodium	60 (20%)	372 (> 484%)	4010
silicon		3452 (5%)	
iron		1772 (5%)	
aluminum		1417 (4%)	
sulfur		349 (> 1%)	
phosphorus		550 (> 1%)	
magnesium		903 (> 2%)	
nickel		288 (> 1%)	
chromium		524 (> 4%)	
zinc		258 (2%)	
lithium		110 (2%)	
titanium		130 (3%)	
manganese		353 (8%)	
barium		170 (> 11%)	
copper		39 (NA)	

Analyses of calcium, potassium, and sodium by AA; others by ICP-AES.

Table 8. Analysis of MeOH-Soluble Biomass Pyrolysis Oils

<u>ANALYSIS</u>	<u>OAK OIL</u>	<u>SOUTHERN PINE OIL</u>	<u>SWITCHGRASS OIL</u>
Trace element, ppm (% of element in raw oil)			
calcium	56 (44%)	58 (46%)	40 (6%)
potassium	50 (91%)	34 (62%)	1390 (879%)

An important point to consider in this case is that the oil samples were several months old before they were analyzed. It is possible that ash components were leached from the char while the oils were in storage. Char separation immediately after oil formation, such as represented by the hot-filtered sample, does result in a cleaner oil. Storage of these samples will require consideration of the storage medium. The high sodium level in the hot-filtered sample is suspected to have resulted from storage in conventional glass bottles. Analysis of fresh oil samples is needed for comparison.

Task 2. PYROLYSIS OIL HYDROTREATING

Before fast pyrolysis oils can be used in turbine-based electrical power generation systems, they must be upgraded to burn in an environmentally acceptable manner. Low-severity hydrotreating was investigated as a method to produce turbine-quality fuels from biomass fast pyrolysis oils. Hydrotreating is derived from the refinery process of reacting catalytically hydrogen with petroleum to remove heteroatoms, metals, or unsaturated compounds. The testing conducted in this study was an extension of the earlier work at PNL on production of high-octane gasoline from biomass liquefaction products [14-16]. The existing bench-scale continuous-feed reactor system at PNL was used for these experiments. Difficulties in handling the high viscosity products from these tests led to several plumbing modifications in the reactor.

The procedures used for the study and results of the tests are detailed in Appendix A. From the several tests performed, a range of products were produced. Oxygen contents ranged from a few percent to over 20% compared with the 40-plus% in the feed oils. Operating the reactor in the upflow mode led to fractionation of the products and an inconclusive assessment of the whole product oil properties. In order for the product oil to have a viscosity in the range of turbine fuel the severity of the hydrotreating should be sufficient to reduce the oxygen content to less than 20%. Hourly space velocities will likely be less than 0.5 liters of feedstock per liter of catalyst bed to achieve sufficient treatment. Hydrogen consumption may be as low as 250 liters per liter of oil feed (1400 SCF/bbl). Byproduct

gas will be available to generate much of this requirement. The byproduct hydrocarbon gases can be readily steam-reformed to produce hydrogen. Though no calculations were made for the present case of low-severity hydrotreating, an earlier process assessment of high-severity hydrotreating of biomass fast pyrolysis oil to gasoline showed that by-product gas production was sufficient to produce all the needed hydrogen [17]. Losses of carbon between 5% and 10% of that in the feed will occur in the byproduct water stream.

These test results have helped to focus future process development of low-severity hydrotreating of biomass fast pyrolysis oil. Deoxygenation of >50% will be required to produce turbine-quality fuel. Therefore, liquid hourly space velocities will need to be less than 0.5 with current catalysts. Downflow operations are suggested by the difficulties observed in the upflow operations. Organic contamination of the byproduct water stream will be high and further treatment will require innovative catalytic processes for organic destruction with efficient recovery the organic value.

Task 3. GASIFICATION WASTEWATER SAMPLE ANALYSIS

Water scrubbing of biomass gasification fuel-gas product is being evaluated for producing clean gas products for turbine-based electrical power generation. In particular, the water quench and scrub systems are currently available technologies that are being tested. During this study analysis and treatment of the water scrub effluents are being done to provide information for evaluation of disposal requirements.

EFFLUENT SAMPLES FROM BIOMASS GASIFICATION

Samples for these studies were provided from the tests being done in the Battelle Columbus Operations gasifier under contract to DOE. Two water samples for analysis were received from the BCO Indirectly Heated Biomass Gasifier on April 8, 1994. The samples included two 1-liter bottles of water: one, a "fresh water" sample from the West Jefferson pilot area where BCO operates the gasifier and, two, a scrubber discharge sample from the venturi (first scrubber stage). The samples were collected at BCO on April 4, 1994, during test 8-6. The West Jefferson water is the feed water for the gasifier and the scrubbers.

The feedstock for the gasifier test was sawdust from Sauder Woodworking. No test-specific analysis of the feed was available, but analyses of earlier samples of this same stream were reported as follows:

Carbon	46.5%
Hydrogen	5.5%
Nitrogen	2.5%
Sulfur	0.03%
Oxygen	38.8%
Ash	1.0%

with ash analysis as follows:

CaO	43.1%
Na ₂ O	9.7%
MgO	6.3%
K ₂ O	5.8%
SO ₃	3.7%
P ₂ O ₅	3.2%
Mn ₃ O ₄	2.3%
BaO	1.2%
SrO	0.1%
Undetermined	balance

The two samples were received well-sealed in polyolefin bottles with screw caps. The West Jefferson water was clear and colorless; the scrubber water was brown colored and slightly translucent. Although actual tar droplets were not evident upon receipt of the samples, after storage in a refrigerator, bits of tar were noticeably adhering to the wall of the bottle. Some of these were recovered separately and dissolved in dichloromethane for analysis.

Results of analysis of the two water samples are provided in Table 9. The pH of the scrubber water is increased relative to the feed. The increased pH is due primarily to the dissolved ammonia. In fact, the base effect of the ammonia must be buffered somewhat by the other contaminants (e.g., organic acids) since this concentration of ammonia in the scrubber water (0.03N) should generate a pH of about 10.8. The COD (chemical oxygen demand) of 4500 ppm suggests an organic contamination of about 2000 ppm. The conductivity measurements also provide a reference for the increase of contamination, indicating an increase by nearly an order of magnitude in the amount of conductive materials.

Table 9. Analysis of Gasification Waters

Procedure	Feed Water	Scrubber Water
pH	7.42	9.00
COD, HACH method	48 ppm	4500ppm
Conductivity, mMho/cm	620	2980
NH ₃ , gas sensing electrode	0.1 mg/L	519.9 mg/L
NO ₃ - as "N", HACH method	0.30 mg/L	53.75 mg/L
CN-, ion chrom.	<2ppb	150ppm
Elemental analysis		
Carbon, %	0.0	0.10
Nitrogen, %	0.0	0.0
Sulfur, ppm	27.60	35.69
Calcium, ppm	59.52	13.45
Potassium, ppm	-0-	-0-
Magnesium, ppm	36.22	38.66
Sodium, ppm	24.28	19.16
Iron, ppm	10.01	4.76
Silicon, ppm	13.44	17.88
Phosphorus, ppm	1.10	-0-
Boron, ppm	3.78	2.70
Strontium, ppm	13.89	2.13
Zinc, ppm	1.45	2.46
Aluminum, ppm	0.64	-0-
Zirconium, ppm	0.49	0.69
Titanium, ppm	0.34	0.17
Nickel, ppm	0.62	0.14
Manganese, ppm	0.12	0.03
Copper, ppm	0.15	0.15
Chromium, ppm	0.35	-0-
Cadmium, ppm	0.04	-0-
Barium, ppm	0.17	0.79
Silver, ppm	-0-	-0-
Lead, ppm	-0-	-0-

others @ <0.01ppm = Be, Bi, Ce, Co, Dy, Eu, La, Sn, Te, V, Y.

Hg, Se, As not analyzed.

In addition to ammonia, nitrate, nitrite, and cyanide were analyzed in these samples. Measurable increases are found in all of these components. An important consideration is whether these nitrogenous materials are derived solely from the wood feedstock or whether replacement of the nitrogen carrier gas in the gasifier could result in significant reductions of the levels found in the scrubber water.

Elemental analysis of the water streams was also undertaken. Carbon and nitrogen analysis was performed by a micro-combustion/reduction technique. The results confirm the analyses of the COD and nitrogenous components. The trace element analysis (performed by ICP-AES) appears to be inconsistent in that some elements are increased in the scrubber water but many others are actually at lower concentrations. Of the elements identified earlier in the ash of the feedstock, sulfur, magnesium, and barium are found at higher levels in the scrubber water, while calcium, sodium, manganese and strontium are lower. None of the elements were found in the scrubber water at concentrations >50 ppm. Of the eight hazardous metals identified in RCRA (Resource Conservation and Recovery Act), the five that were analyzed (Ba, Cd, Ag, Cr, Pb) were found to be below allowable limits. However, this sample was recovered with the scrubber running in a once-through mode. In fact, only 8.5 lb/hr of ash were being fed with a scrubber flow of 4080 lb/hr. Future tests incorporating a recycle mode in the scrubber will be more representative of commercial operation, but buildup of the trace element concentrations to higher levels will result. Also, earlier analyses of the BCO tars [18] showed that significant amounts of char and ash were recovered in the tars. Ash loss

into the tar via char should be investigated. Furthermore, the low trace element concentrations should not be relied on for evaluating the effects of trace element contamination of the catalysts in the hot gas conditioning step.

Qualitative analysis of the organic components in the scrubber water was performed by gas chromatography-mass spectrometry. The list of components found is given in Table 10. The percent composition numbers are relative concentrations of the organics as quantified by the total ion current in the mass spectrometer. These numbers are not truly representative of concentration but give some relative information as the more prominent species in the water. Concentrations of the organics are better represented en masse in the COD number.

Table 10. Organic Components in BCO Scrubber Water

<u>Component</u>	<u>Percent of Organics, approximate</u>
phenol	46%
o-, m-, p-cresol	17%
propylene glycol	4%
1-H-indole	4%
2,3-dihydrobenzofuran	4%
pyridine	3%
isoquinoline	2%
propionic acid	2%
acetamide	2%
benzonitrile	2%
dimethylphenol (2)	2%
acetic acid	1%
benzene	trace
naphthalene	trace
methylpyridine (2)	trace
1,4-benzodioxin	trace
methylbenzofuran	trace

Concentrations of specific components would only be important if certain highly toxic materials were identified. Of those found here, the components of concern would be the pyridine, cresols and the benzene. The pyridine is likely over its RCRA limit (5 mg/L), but the cresols are probably under their limit (200 mg/L) individually. More definitive analysis for benzene will be needed to determine if it exceeds its very low limit (0.5 mg/L).

Table 11 lists the organic components identified in the tar phase recovered from the wall of the scrubber water sample bottle. It is assumed that this material is representative of the separate tar phase collected at BCO. Its composition is very much the same as that found in earlier analyses of tar byproducts from the BCO gasifier [7,18]. Since the components are almost all polycyclic aromatic hydrocarbons, it is reasonable to compare the total ion current from the mass spectrometer as a relative measure of concentration of the components in the tar. From these measurements it is apparent that the tar contains primarily the 3- and 4-ring polycyclics. The tar is nearly heteroatom free as would be expected for a tar produced at the temperatures used at BCO (900°C).

These samples indicate that the scrubber water from the BCO Indirectly Fired Biomass Gasifier will be contaminated to a limited degree by nitrogenous and organic byproducts of gasification. The amount of contamination will depend in part on the temperature in the separator as the solubilities of the organic tar components are low at 20°C and apparently drop even lower at 0°C. Sufficient quantification of any tar phase collected separately from the scrubber water is important in

Table 11. Organic Components in BCO Tar

<u>Component</u>	<u>Percent of Tar</u>
phenanthrene/anthracene	16%
fluoranthene/pyrene (4)	13%
acenaphthylene	6%
11H-benzofluorene (2)	6%
fluorene + 16 amu (2)	6%
9H-fluorene	5%
naphthalene	2%
acenaphthene	2%
phenylnaphthalene	2%
methylfluorene (2)	1%
methylphenanthrene (3)	1%
dibenzofuran	1%
methylnaphthalene (2)	1%
biphenyl	1%
methylbiphenyl (2)	trace
dimethylnaphthalene (3)	trace
indole	trace
quinoline	trace
indene	trace
phenol	trace
toluene	trace

seeing the total picture. These samples provide a baseline for further studies in that the tests were performed without hot gas conditioning, i.e., catalytic treatment to complete the gasification process.

EFFLUENT SAMPLES FROM CATALYTICALLY CLEANED GASIFICATION

A second set of water samples from the BCO Indirectly Heated Biomass Gasifier was received at PNL on July 7, 1994. The samples included fourteen 1-liter bottles of water; four were "supply water" samples; five were scrubber discharge samples from the venturi (first scrubber stage); and five were scrubber

discharge samples from the spray tower (second scrubber stage). The samples were collected at BCO during Tests 8-10, -11, -12, -13, and -14. The last four tests were performed with the fluidized catalyst bed for tar cracking. The identity of the catalyst is proprietary.

The feedstock for the gasifier test was hog fuel from Weyerhaeuser with the following analysis given:

Carbon	51.65%
Hydrogen	5.86%
Nitrogen	0.85%
Sulfur	0.03%
Oxygen	38.06%
Ash	3.55%
Chlorine	0.07%

and with ash analysis provided as follows:

SiO ₂	53.25%
CaO	28.88%
Na ₂ O	0.64%
MgO	2.04%
K ₂ O	3.11%
Fe ₂ O ₃	3.38%
Al ₂ O ₃	3.76%
SO ₃	1.65%
P ₂ O ₅	1.00%
Mn ₃ O ₄	0.28%
BaO	0.12%
SrO	0.21%
TiO ₂	0.52%
Undetermined	1.16%

The samples were received well-sealed in polyolefin bottles with screw caps. The supply water samples were clear and colorless; the venturi scrubber and spray tower water samples contained some brown particulate but were clear except for the tan or light yellow color. The 8-14 venturi sample was exceptional in that it contained a significant amount of solids,

both settled and in a floating foam. The water phase was analyzed to get the reported results. An attempt to quantify the solids by filtration and drying showed that the dry filterable solids content was nearly one third of the sample. The solids appeared to be tar-free char and sand-derived solids.

Results of analysis of several of the water samples are provided in Table 12. Only samples from test runs 8-10, 8-12, and 8-14 were analyzed. There is very little difference between these catalyzed and uncatalyzed scrubber samples (8-10 vs. 8-12 & 8-14). However, the 8-10 samples do not appear like the scrubber sample, analyzed earlier, from an uncatalyzed run either. Apparently, the difference in feedstock is significant in the uncatalyzed cases. The effect of the catalyst would be more apparent in measurements of the condensed tar phase and the gas composition and yield. The pH is near neutral in all samples. The low ammonia content affects the pH only slightly. The 8-14 venturi sample (mentioned above) is the exception with a high pH. The COD of 100 to 700 ppm suggests an organic contamination of about 40 to 300 ppm. The conductivity measurements also provide a reference for the increase of contamination, indicating barely any measurable increase in the amount of conductive materials.

Again, in addition to ammonia; nitrate, nitrite, and cyanide were analyzed in these samples. Measurable increases are found in ammonia and cyanide, but the change in nitrate and nitrite is barely noticeable. The two sets of ion chromatograph nitrate data are from two different laboratories and provide reasonable corroboration at these low levels of contamination. The Hach colorimetric method results also confirm the low nitrate/nitrite levels. The increase in ammonia and cyanide in the scrubber

Table 12. Analysis of Second Set of Gasification Waters

Procedure	Supply 8-10	Venturi 8-10	Spray 8-10	Supply 8-12	Venturi 8-12	Spray 8-12	Venturi 8-14	Spray 8-14
pH	7.67	NA	7.48	8.58	7.65	7.61	9.97	7.82
COD, HACH method, ppm	6	710	147	6	360	440	128	119
Conductivity, μ Mho/cm	854	1314	878	550	1198	1060	650*	935
NH ₃ , gas sensing electrode, mg/L	0.1	75.2	7.2	0.3	80.5	48.0	85.7	9.6
Total NO ₃ ⁻ /NO ₂ ⁻ , HACH, mg/L	0.3	4.7	1.8	1.5	3.9	3.9	0.7	0.8
Chloride, ion chrom., ppm	36.7	37.7	36.4	35.6	43.7	32.8	62.8 [#]	35.1
Sulfate, ion chrom., ppm	93.3	150	96.8	21.5	78.1	89.7	104 [#]	119
Nitrite, ion chrom., ppm	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0 [#]	<1.0
Nitrate, ion chrom., ppm	0.46	0.20	<1.0	2.41	<1.0	0.28	0.53 [#]	0.08
CN ⁻ , ion chrom., ppb	<10	11300	1200	<10	33	6300	180 [#]	850
Nitrate, ion chrom., ppm	0.60	0.40	0.30	0.50	0.29	0.26	7.2 [#]	0.43
Elemental Analysis								
Sulfur, ppm	34.81	58.45	37.31	9.05	31.42	37.94	47.15 ⁺	46.22
Calcium, ppm	87.38	70.86	76.64	36.54	60.04	61.90	5.76 ⁺	87.18
Potassium, ppm	-0-	4.2	1.62	1.37	41.7	1.18	127.0 ⁺	0.74
Magnesium, ppm	45.90	48.15	55.26	45.51	33.00	43.13	-0 ⁺	46.95
Sodium, ppm	16	21	18.39	17.60	24	24.28	49 ⁺	17.90
Iron, ppm	-0-	0.86	0.03	-0-	0.38	0.34	3.05 ⁺	0.11
Silicon, ppm	8.27	7.72	7.99	8.45	7.99	7.39	0.61 ⁺	6.05
Phosphorus, ppm	-0-	0.13	-0-	-0-	0.15	0.10	-0 ⁺	-0-
Boron, ppm	1.45	1.54	1.60	1.23	1.90	1.43	2.89 ⁺	1.56
Strontium, ppm	20.39	17.12	16.71	16.70	4.87	12.44	0.55 ⁺	19.01
Zinc, ppm	0.06	-0-	0.05	0.04	0.02	0.04	13.16 ⁺	0.03
Aluminum, ppm	-0-	-0-	-0-	-0-	-0-	-0-	2.3 ⁺	-0-
Tin, ppm	0.15	0.22	0.16	0.12	0.23	0.19	-0 ⁺	0.14
Neodymium, ppm	0.60	0.45	0.54	0.34	0.35	0.43	-0 ⁺	0.59
Manganese, ppm	-0-	0.02	0.05	-0-	0.12	0.01	-0 ⁺	0.02
Copper, ppm	-0-	0.12	0.05	-0-	-0-	0.05	-0 ⁺	0.07
Molybdenum, ppm	-0-	0.01	0.01	-0-	0.03	0.01	-0 ⁺	-0-
Barium, ppm	0.10	0.10	0.10	0.08	0.12	0.10	-0 ⁺	0.08

others @ <0.01ppm = Ag, Be, Cd, Co, Dy, Eu, La, Li, Ti, V, Y, Zr.

others @ <0.1ppm = Bi, Ce, Cr, Ni, Pb, Te.

Hg, Se, As - not analyzed.

*interference from solids?; # filtered sample; + high dilution used, 50:1.

waters versus the supply water is much less than seen in the earlier test. This lesser amount of contamination can be attributed to a feedstock effect since the hog fuel is much lower in nitrogen than the sawdust used earlier. An important consideration is whether these nitrogenous materials are derived solely from the hog fuel feedstock or whether replacement of the nitrogen carrier gas in the gasifier could result in significant reductions of the levels found in the scrubber water. The difference between the results using the two feedstocks suggests that the major effect is from the feedstock not the nitrogen carrier gas.

Elemental analysis of the water streams was also undertaken. The trace element analysis (performed by ICP-AES) again shows little effect from passing through the gasifier; i.e., some elements are increased in the scrubber waters, but many others are actually at lower concentrations. It appears that the controlling factor in the scrubber water contamination by trace elements is the contamination in the feed water and not the biomass feedstock. Of the elements identified earlier in the ash of the feedstock, the high levels of calcium and silicon seem to have no impact on the scrubber water concentrations. The measurable levels of iron, phosphorus, manganese, and potassium seem to be appearing in the scrubber waters, while the magnesium, sodium, strontium, and sulfur are lost in the large amounts in the supply water. Copper and molybdenum also appear in the scrubber waters, although they were not identified in the biomass. Possibly, they are derived from the gasifier construction materials. Only calcium, magnesium, and sulfur were found in the scrubber waters at concentrations in the 50 to 100

ppm range. Of the eight hazardous metals identified in RCRA, the five that were analyzed (Ba, Cd, Ag, Cr, Pb) were found to be below allowable limits. In addition, they were below Safe Drinking Water limits except for lead which has use-specific treatment requirements. However, these samples were recovered with the scrubber systems running in a once-through mode. Conventional commercial operation would be with a recycle of the scrubber waters which could lead to a buildup of the biomass trace elements over time.

TEES® PROCESSING FOR CLEANUP OF SCRUBBER EFFLUENT

In addition to the effluent analyses, a test was undertaken to evaluate the Thermochemical Environmental Energy System, (TEES®)[19], a PNL technology for treatment of organics in water. An initial batch test with the scrubber water sample from the earlier set of samples was done to verify the applicability of the technology. The results of that test suggest that TEES could be used to clean up the organics in the scrubber effluents while producing additional medium-Btu gas product. The test produced a 94% reduction in COD. Larger samples will be required to test in a continuous reactor system to determine kinetics of the process, but this preliminary test result suggests reasonable kinetics would be achieved in the use of the TEES technology with biomass gasification scrubber wastewater.

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Task 4. ASSESSMENT OF REGULATORY REQUIREMENTS

Regulatory requirements and restrictions must be considered during the development stage of any biomass thermochemical conversion facility. A series of semi-annual reports prepared for NREL have provided a listing of potential hazardous process effluent components and reviewed the extent that these materials are regulated. The components considered were those identified in earlier studies of biomass thermochemical conversion effluents [20,21]. The review of regulations was an extensive coverage of all federal regulations including DOE directives. The latest in the series of semi-annual reports is included here as Appendix B.

In general, the statutes and regulations reviewed protect human health and the environment by regulating discharges to the air, groundwater, surface water, and soil. Each regulation contains performance and design standards and criteria that must be met by plant operators. The specific site of a biomass conversion plant will determine the exact level of pollution control required. In addition, the regulations seem to be subject to continual change which almost always leads to tighter control. As a result, when the biomass conversion plant is built, the level of pollution control required will almost certainly be more stringent than it is now.

Task 5. SUPPORT TO THE IEA ENVIRONMENTAL SYSTEMS ACTIVITY

Support to the IEA, Bioenergy, Environmental Systems activity involves two-way communication of ideas and developments between and among the various participants. This communication is accomplished remotely through the mail and the several forms of modern telecommunication and directly by participation in Working Group meetings. The accomplishments of the IEA activity include the completion of several specific studies including literature reviews and experimental research.

As part of the U.S. participation, the gasification effluent analysis effort (Task 3) was incorporated into the activity. Other involvement included reviews of the pyrolyzate and biomass drier effluent analyses conducted in New Zealand, environmental impact modeling performed in the U.K., and biotreatment method development in Norway.

As a participant in the activity, D.C. Elliott (PNL) attended the September 1994 Working Group meeting in Rotorua, New Zealand. A presentation was given on the status of the biomass energy program in the U.S. A second presentation was given on recent results at PNL involving analysis of scrubber waters from the biomass gasification system at BCO. Other types of participation included the discussions and review of other participants input and the preparations for the final report of the 3-year effort within the Environmental Systems activity.

The Working Group meeting also included informative tours of the New Zealand Forest Research Institute's many facilities including the tree breeding nursery, the wastewater application project, the analytical laboratories, the wood drying

laboratories, and the genetic engineering laboratories. In addition, tours of a New Zealand forest harvesting area, a pulp and paper mill, and a lumber and wood products mill were given.

NATIONAL PROGRAM REVIEWS

The following reviews are summaries of the presentations by the several national representatives at the Working Group meeting in Rotorua, New Zealand, in September 1994.

Norway

The biotreatment project at the Agricultural University of Norway is coming to an end this year and a new project is being proposed. Interest in bioenergy in Norway is limited because of the large reserves of petroleum. Private cofunding of 50% is expected as a future research requirement for government funds; however, the proposed continuation of the project will include only 20% cofunding. The Industry and Bioenergy Council is funding the current work, but the new project will be proposed to the Environmental Council. Another major effort in this area is the Bioenergy and the Environment Program to be funded by the Nordic Energy Research Program. This program will include research at Technical Research Centre of Finland (Biotechnology and Food Research), VTT; The Technical University of Denmark (Institute of Environmental Science and Engineering), DTU; and the University of Lund in Sweden. The main activity areas include:

1. Analytical methods related to the utilization of lignocellulosic raw materials for energy production.
2. Pretreatment of lignocellulosic materials.

3. Influence of inhibitors on the fermentation of lignocellulosic hydrolysate.
4. On-line process analysis.
5. Use of anaerobic thermophilic bacteria for fermentation of cellulose or hemicellulose to ethanol.
6. Combined production of ethanol, other products, and energy.
7. Optimization of enzyme components for hydrolysis of different lignocellulosic material.
8. Modeling and simulation.

Apparently, most of the work will be done at Lund with only tasks 5 & 6 at DTU and Task 7 at VTT. Norway's participation would be through some student exchanges with VTT and Lund. Norway seems to be pulling back from the IEA involvement.

United Kingdom

Bioenergy development support comes through ETSU (Energy Technology Support Unit, Department of Trade and Industry). They have been reviewing budgets and find that the IEA investment is good value, although expansion of support to IEA is unlikely. In the U.K. there is a new 5-yr Strategy for Renewables. The Bioenergy Program portion is all thermochemical conversion with a balance of gasification and pyrolysis to liquids. The Waste Program portion includes both landfill gas research and waste combustion but no gasification or pyrolysis. The NFFO (non-fossil fuel obligation) has provided support to renewable energy commercialization through subsidies of produced electricity supported from taxes on fossil fuels. An Agreement of Cooperation for Bioenergy Research between the U.K. (Department of Trade and Industry) and the U.S. (DOE) was recently announced.

European Union

The Europeans continue to strongly support bioenergy development through several of the Directorates General of the European Commission. DG-XII (R&D) and DG-VI (Agricultural policy) commonly support the AIR Program which includes 2 million ECU (European currency units, 2 million ECU = 2.4 million U.S. dollars) for five projects. DG-XII also supports the JOULE Program which includes another 2 to 3 million ECU per year of research funding for bioenergy projects. DG-XVII (Demonstrations) is funding the THERMIE Program funded at 10 million ECU per year. DG-I (International) coordinates collaboration outside EU including an active agreement with Australia and an expected agreement with Canada. The EU program includes a range of bioenergy research with a major emphasis on pyrolysis to liquids. It supports the 200 kg/hr fast pyrolysis plant of Union Fenosa in Spain, operating since August 1993, and the 15 ton/day fast pyrolysis plant of ENEL in Italy, expected on line in mid-1995. The research also includes a wide range of supporting and developmental research in pyrolysis, as well as combustion tests in engines, turbines, and boilers. A major new effort is the expected announcement of three biomass-based IGCC plants to be built.

New Zealand

The Rio Agreement on carbon dioxide emission limitations is being implemented in New Zealand with a strong program of increased forestry planting and movement toward biomass fuels. Although biomass is not viewed as an economical power source, forestry and lumber wastes, particularly bark, are viewed as energy resources. The biomass energy research has been at a very

low level in recent years in New Zealand, basically maintaining contact with developments in other countries. The new Research Strategy for the Public Good Science Fund includes a reinvigorated biomass energy program. For the first 2 years, emphasis will be on evaluating new biomass technology for the New Zealand situation. After that, new technology development programs will be initiated. Bioenergy is classified as a Non-Traditional Renewable Resource, along with wind and solar energy. Funding for research on this group of resources is scheduled to increase from 51,000 NZ\$ in 1993 to 1,135,000 NZ\$ in 1997 (33,000-726,000 US\$).

ENVIRONMENTAL SYSTEMS ACTIVITY FINAL REPORT

The report will include all the work performed within the activity (by direct contract), as well as related efforts in the participating countries. The report will be edited and printed in New Zealand for distribution through the normal IEA channels. A great deal of work will be covered in the report, although much of the emphasis has shifted away from the actual analysis and treatment of process effluents because the effluents are not available.

CONCLUSIONS

The conclusions, based on the results in the five task areas, are presented by task area below.

PYROLYSIS OIL ANALYSIS

The product oil from fast pyrolysis in the NREL vortex reactor is of relatively consistent composition despite the use of different biomass feedstocks. The carbon, hydrogen, nitrogen, oxygen, and moisture contents are similar for all feedstocks tested, because the amounts of these components in the feedstocks are relatively constant. However, the char content and ash content vary widely as a result of the difference in ash content of the feedstock.

Hot-filtration provides a product low in alkali metals but can lead to product phase separation. After cooling and condensation of the oil, much of the char content can be readily separated from the oil by either filtration (after solvent dilution) or centrifugation. However, much fine particulate char ($<2.5\mu\text{m}$) remains in the oil and is likely the site of much of the remaining ash in the oil.

The water in the oil is dissolved in the oil and is not present as a highly dispersed separate phase. No water phase could be detected by optical microscopy or electron microscopy. No water phase was separable by high-speed centrifugation. Some of the water is likely physically associated with the char particles. Water can fractionate from the oil by means of spontaneous separation of the product into a water-rich phase and water-deficient phase in some cases.

Water wash does not appear to be a reasonable way to separate the alkali content from the pyrolysis oil. Some alkali partitions into the aqueous phase but much remains with the tar phase (likely as part of the char particulates). A water separation of the tar leads to massive losses of organic into the aqueous stream.

GASIFICATION EFFLUENT ANALYSIS

Analysis of the scrubber waters from the BCO gasifier shows evidence of the effective cleaning of the product gas by removal of phenolic and aromatic tars, nitrogenous components, and trace metals in the quench spray tower and venturi scrubber.

Hot catalytic treatment of the gas product leads to lower levels of contamination in the scrubber wastewater streams.

Nitrogenous contaminants in the scrubber waters appear to be feedstock derived as opposed to being produced from the nitrogen carrier gas. The contaminants include nitrate and nitrite, ammonia, and cyanide.

LOW-SEVERITY HYDROTREATING

Intermediate-quality products can be produced by low-severity hydrotreating of biomass fast pyrolysis oils. Lower temperatures and faster throughputs can be used to reduce the severity of the processing. The viscosity of the products (at equivalent water content) increases with the oxygen content of the dry oil. Deoxygenation greater than 60% will be required to produce oils of sufficiently low viscosity to be useful as turbine fuel.

The low-severity hydrotreating product oils are readily fractionated into high-volatility and low-volatility fractions. The low-volatility fraction also has a high viscosity. Production of these materials in an upflow reactor is difficult to control and operate.

REGULATORY MONITORING

A large number of the chemical components identified in the potential products and effluents from biomass thermochemical conversion processes are found on the various lists of toxic and hazardous chemicals identified by the various environmental regulations in place in the U.S. As a result, the products and effluents may be regulated if produced in the form currently envisioned. Numerous federal regulations and state interpretations thereof will impact on biomass thermochemical conversion.

IEA ENVIRONMENTAL SYSTEMS ACTIVITY SUPPORT

The IEA Working Group has had a project scope which was consistent with the scope of this project. The emphasis within the group has been in assessment of the environmental impacts of thermochemical conversion processes. Interaction on the international scale provides a means of leveraging the federal dollar investment with the research being performed in other participating countries. Significant information was obtained on biomass drying effluents, biomass ash composition and properties, and modeling and assessment of environmental impacts.

The initial plan for the activity included an ambitious program of analyses and treatment studies of process effluents. Much of this work was not completed due to lack of timely or

available samples of process effluents. Future plans for the activity seem to emphasize computer modeling as a means of evaluating environmental impacts of the processes.

RECOMMENDATIONS

The following activities are recommended based on this study:

- Continue the analytical effort using fresh product oils to compare with the older products tested already. Analysis of the hot-filtration products can be used to evaluate the technology. Apply additional analytical effort to identifying the alkali metal components in the oil.
- Continue the support to the biomass gasification program by analyzing and assessing the condensate streams from the operating systems.
- Continue hydrotreating process development to determine the potential for production of clean turbine fuel and petroleum refinery compatible oils. Evaluate the effect of space velocity and processing temperature on product properties in a downflow reactor configuration. Evaluate existing catalyst formulations for biomass pyrolysis oil hydrotreating and determine catalyst stabilities and lifetimes. Consider selective hydrotreating catalysts for mild reduction of oxygenated functional groups. Determine the extent of contamination remaining in the product liquids.
- Continue review of environmental regulations as they pertain to biomass thermochemical conversion and maintain an updated regulations review document.

- Continue the international interaction and information exchange by participation in the IEA, Bioenergy, Environmental Systems Working Group. The objective of the Environmental Systems activity is to investigate and evaluate systems that permit thermal and bio-conversion processes to meet environmental requirements. Although analysis of process effluents is critical for process developers to undertake in order to fully define their processes and assess processing impacts, there seems to be a decided lack of inclination toward such analyses; perhaps for fear of discovering a negative impact (author's speculation). This "head in the sand" attitude should not be tolerated within the U.S. DOE research program. Active participation in the IEA Environmental Systems activity should be supported, as well as mandating cooperation from the researchers in the DOE program to provide samples and data for the evaluation of the IEA Working Group. This type of analysis will only serve to support process development either by setting aside concerns of others through answers to questions or by identifying research requirements to allow implementation of the new technologies.

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APPENDIX A

LOW SEVERITY HYDROTREATING OF FAST PYROLYSIS OIL TO PRODUCE CLEAN
TURBINE FUELS

**LOW SEVERITY HYDROTREATING OF FAST PYROLYSIS OIL
TO PRODUCE CLEAN TURBINE FUEL**

TOPICAL REPORT

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INTRODUCTION AND BACKGROUND

Studies on upgrading biomass fast pyrolysis oils by hydrotreating are being conducted at PNL. The ultimate goal is the production of clean turbine fuels. Upgrading biomass pyrolysis oils to hydrocarbon fuels requires oxygen removal and molecular weight reduction. Catalytic processing with hydrogen (hydrotreating) can be used to accomplish both of these requirements. Hydrotreating for upgrading biomass oils differs from processing petroleum or coal liquids because of the importance of deoxygenation. This topic has received only limited attention in the literature.^{1,2,3,4,5,6} Early batch reactor tests at PNL with model compounds showed that sulfided cobalt molybdenum catalysts were the best choice for deoxygenation. Sulfided nickel molybdenum catalysts were more effective for ring saturation and reforming.³

This report describes the work over the past two years to optimize the process for turbine fuel production from fast pyrolysis oil. A fixed-bed reactor operated in an upflow mode is being used for the hydrotreating tests at PNL.⁶ Earlier operations in the conventional downflow mode (trickle-bed) plugged the outlet line and the bottom of the reactor with a coke-like material. Severe coking in a trickle-bed reactor has also been observed with other heavy, unstable oils such as tar sands bitumen⁷ and flash pyrolysis coal tar.⁸ In both cases the oil was successfully processed in some form of upflow reactor, either a fixed-bed or a fluidized-bed.

A two-phase flow pattern exists in the fixed-bed upflow reactor. Gas and volatile (primarily hydrocarbon) products move through the reactor quite rapidly. Unconverted (oxygenated) non-volatile oil does not leave the reactor until it reaches the top of the reactor and overflows into the product line.

EARLIER STUDIES AT PNL

In our first attempt to hydrotreat a pyrolysis oil⁹ at 350°C and 2000 psig with a CoMo catalyst, a reactor blockage occurred within several hours after startup. When the reactor was opened the catalyst bed was coked solid. Further testing⁹ disclosed that with pyrolysis oils the temperature in the reactor must be kept below 280°C to prevent massive coke formation. At this low temperature very little hydrogen is consumed in the reactor, but a large amount of CO₂ is generated. In the presence of a CoMo or Ni catalyst, a heavy oil is produced from the pyrolysis oils. This pretreated oil can be further hydrotreated at higher temperatures to produce light hydrocarbon fuels. Although very little hydrogen is consumed in the first step, a hydrogenation catalyst is required.

As shown by these earlier results, two separate reaction steps are required to upgrade biomass pyrolysis oils to hydrocarbon fuels. In a nonisothermal mode, the reactor can be operated with the inlet (bottom) at 250°C to 280°C and the outlet (top) at 370°C to 400°C. With this progressively hotter temperature regime it is possible to hydrotreat the pyrolysis oil in a single reactor vessel and produce gasoline range hydrocarbons.

Based on earlier two-stage and nonisothermal operations, material balance calculations were used to estimate the yield and quality of the oil that could be produced at steady-state at a liquid hourly space velocity (LHSV) of approximately 0.15 L of feed per liter of catalyst bed per hour. At steady-state about 0.50 to 0.55 L of oil would be produced per liter of pyrolyzate feed. The oil would contain 2% to 3% oxygen and would have a H/C mole ratio of 1.5 and a density of 0.90 to 0.92. About 50 to 60 vol% of the oil would be in the gasoline boiling range. Of the remainder, about 30% is distillable gas oil (diesel, #2 fuel oil) and the rest is undistillable residual oil¹⁰. The current research program is aimed at extending this understanding of biomass pyrolysis oil hydrotreating into the range of turbine fuel production at less severe processing conditions.

The results of the earlier tests for the U.S. Department of Energy and the Canadian Ministry of Energy, Mines, and Resources¹¹ can be used to obtain a prediction of results under less severe processing conditions. As shown in Figure 1, an extrapolation of data to higher space velocity processing can be used to predict the oxygen content of hydrotreated biomass fast pyrolysis oils and the hydrogen requirement to produce such oils. Using these data, we can predict that a space velocity of 0.4 would produce a product with an oxygen content of approximately 15%. Such an oil should require less hydrogen consumption, possibly as little as 200 L/L of oil feed (0.015g/g), and would be produced in higher yield because there would be less gas formation. These results are based on continued use of the high temperature regime (up to 400°C) and 14MPa of pressure in the reactor. Lower temperatures and pressures could also be used to

achieve less severe hydrotreating of the oil. Optimization of this conceptual low-severity hydrotreating process was undertaken in this research effort.

Figure 1. Processing Rate Effect on Product Oxygen Content and Hydrogen Consumption

PYROLYSIS OIL HYDROTREATING IN FY 1993

A schematic of the reactor system used in 1993 is shown in Figure 2. The reactor is 7.5 cm I.D. by 25 cm and holds 700 to 900 ml of catalyst. During 1993, the system was restarted from cold oil storage after 4 years of inactivity. The data acquisition software (LabTech Notebook) was updated from Version 4.13 to Version 7.0. Data acquisition files were re-created from existing files. All equipment was put into functioning order. The reactor was loaded with a sulfided, $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst (Katalco NT506 1/16"E).

Figure 2. Schematic of Continuous-Flow, Bench-Scale Hydrotreater
- Initial Configuration

A single test run to demonstrate the operability of the equipment using Georgia Tech Research Institute entrained-flow pyrolysis oil was terminated early by a pressure seal failure. The test was restarted and additional processing accomplished at higher flow rates before the test was terminated by plugging in the product line. The operational results from this test are given in Table 1.

Table 1. Upgrading of Pyrolysis Oil, 1993 Results

PROCESSING CONDITIONS

Temperature, top/bottom, °C	330/280	390/260	412/269	386/254
Pressure, psig	2050	2030	2030	2010
LHSV, vol oil/vol cat/h	0.21	0.15	0.30	0.34

YIELDS

Total oil, L/L feed oil	0.10	0.24	0.19	0.12
Aqueous phase, L/L feed oil	0.85	0.59	0.58	0.42
H ₂ consumption, L/L feed oil	379	318	352	72
Carbon conversion to gas, wt%	30.9	42.2	33.3	7.9
Carbon in aqueous phase, wt%	0.05	0.01	1.3	7.8

PRODUCT INSPECTIONS

Oxygen, wt%	-0-	-0-	3.9	11.1
H/C ratio, mole/mole	1.79	1.84	1.47	1.49
Carbon conc. in aqueous, %	0.03	0.01	1.10	9.00

BALANCES

Material	99	93	86	53
Carbon	46	76	61	32

The results of these tests must be viewed with consideration of the poor carbon balances and less-than-complete mass balances. These shortcomings result primarily from the limited time on stream, resulting in a less than steady-state operation. However, some preliminary conclusions can be drawn from these results. First, there appears to be a relationship between space velocity and the product quality and distribution. At higher space velocity, the oxygen content of the product oil goes up; the amount of carbon dissolved in the aqueous byproduct stream increases; and the gas yield drops with a lower consumption of hydrogen. These are reasonable and expected effects.

Catalyst analysis after the tests indicated some changes occurred during the test. There was clear evidence in some of the catalyst pellets of the reaction of the alumina support to the hydroxide (boehmite). We have seen this reaction in aqueous processing under similar conditions,¹² and the effect has been reported by others.¹³ The high-surface-area aluminas (gamma and delta) are not stable in the presence of water at 350°C. The stability of the sulfide phases was not quantified, but no nickel or molybdenum oxide was evident by x-ray diffraction, while the sulfides were both identified.

The program for the second year of operation had an ambitious plan to address the relationships of processing conditions and product quality to determine the extent of hydrotreating required to produce useful product from fast pyrolysis oil. This plan included study of residual alkali in the product, catalyst stability effects including reaction of the alumina support with water, and alternative catalyst supports.

PYROLYSIS OIL HYDROTREATING IN FY 1994

Another test was performed in the single-reactor, upflow mode in late 1993. This test was also terminated prematurely with plugging in the overhead line. After this test, the reactor system was rebuilt with shortened and less convoluted overhead lines by the removal of the recycle system (left from earlier gasoline production tests). At this same time, a small reactor was added prior to the main catalytic reactor to allow total separation and control of the two temperature stages of the reaction. A schematic of the rebuilt hydrotreater is shown in Figure 3. These changes were required to move the research program forward and address the issues of operating parameter effects on product quality and catalyst stability. Without

Figure 3. Schematic of Continuous-Flow, Bench-Scale Hydrotreater
- Rebuilt Configuration

these changes the reactor system could not be operated for sufficient periods to bring the system to steady state before plugging occurred.

Test results at near-steady-state conditions were achieved in the rebuilt reactor configuration. The results for several time periods during the HT 57 test are presented in Table 2. The fast pyrolysis oil feedstock for these tests was a sample provided to NREL by Ensyn Engineering Associates. As seen in the earlier tests, a significant period of non-steady-state operation precedes the near-steady-state operation. The oxygen content of

Table 2. Upgrading of Pyrolysis Oil, 1994 Results

PROCESSING CONDITIONS

Temperature, top/bottom, °C	359/218	357/210	358/218	358/240
Pressure, MPa	14.2	14.2	14.0	13.8
LHSV, vol oil/vol cat/h	0.42	0.42	0.33	0.22

YIELDS

Total oil, L/L feed oil	0.24	0.45	0.43	0.42
Aqueous phase, L/L feed oil	0.47	0.46	0.41	0.45
H ₂ consumption, L/L feed oil	264	243	149	242
Carbon conversion to gas, wt%	19.7	6.9	9.0	12.4
Carbon in aqueous phase, wt%	6.9	8.6	5.4	5.5

PRODUCT INSPECTIONS

Oxygen, wt%	10.7	20.5	23.4	22.4
H/C ratio, mole/mole	1.51	1.37	1.40	1.44
Carbon conc. in aqueous, %	6.2	7.9	5.6	5.2

BALANCES

Material	82	89	85	90
Carbon	60	79	73	76

the oil product continually increases during the initial period of the test and then stabilizes at the onset of near-steady-state operation as shown in Figure 4. The test results in Figure 4 are all from experiment HT57 (as is Table 2). Experiment HT56 ended with plugging in the overhead lines and pressure control valve as did experiment HT58 (three different starts on three different days, after cleaning out the overhead lines and pressure control valve).

Figure 4. Product Oil Oxygen Content During Experiment HT57

The products from the near-steady-state operations appear much heavier than expected as a result of the fractionation occurring during the initial period of the experiments. A

significant period of non-steady-state operation occurs at the beginning of the tests in which product recovery is incomplete, while volatile products are swept from the reactor and heavier (liquid-phase) products slowly build up in the catalyst bed. Eventually (after several hours on line) the catalyst bed fills with liquid phase and the "whole" product oil begins to exit the reactor and a near-steady-state operation is achieved. However, there remains the accounting of the light products recovered in the early stages of the test. These must be added back to the heavy "whole" products to account for a true mass balance. These initial-period products are the type of light fuel oil being sought after for the desired turbine fuel product. In experiment HT57 they represent 1/4 of the organic oil recovered during the test and may represent a significant fraction of the turbine fuel grade material produced from the pyrolysis oil.

In these tests wherein the vapor phase product and the liquid phase product are so different, it is difficult to bring short-term tests to steady-state operation. The fixed-bed reactor in an upflow mode of operation naturally allows the product fractionation. In addition, the difference in product properties makes control of the process equipment and recovery of the product more difficult than in gasoline production tests with a totally vapor-phase product.

The oil products produced in these tests have a range of physical properties as suggested by the range of oxygen contents. Viscosity measurements were made on the oils to quantify the differences. As seen in Figure 5 the viscosity of the oils at near ambient conditions is a function of the oxygen content. The viscosity of these hydrotreated products is actually higher than

the fast pyrolysis oil itself as a result of the removal of the water. The viscosity of the 26.5% oxygen content oil may be lower because of remaining dissolved water in this heavy tar product. Only by reducing the oxygen content to less than 10% can a hydrotreated product with a viscosity approaching conventional turbine fuel be produced. Otherwise, preheating the fuel will be required to reduce the viscosity to an acceptable range.

Figure 6 shows that the viscosity of the oxygenated oils over a range of temperatures. The viscosity of these products only falls in the turbine fuel range (1 to 2 cSt @ 20°C) at much higher temperature. By extrapolation of the viscosity of the lowest oxygen content product tested, one can conclude that preheating in the range of 70°C to 80°C should be adequate.

Figure 5. Relation of Viscosity to Oxygen Content

Figure 6. Viscosity as a Function of Temperature

An important byproduct issue arising from this type of low severity processing is the amount of oxygenated material which ends up in the aqueous byproduct phase. The amount of dissolved organic is also a function of the space velocity as it directly relates to the amount of oxygen in the product oil. Figure 7 shows the relationship. The dissolved organic is a wastewater disposal problem and will require treatment.

Figure 7. Relationship of Water Contamination to Oil Composition

Catalyst analysis after the tests gave no new insights. The x-ray diffraction analysis of the two catalyst beds showed no significant differences. The samples produced poorly resolved patterns with many unidentified peaks. The alumina of the support was evident as was the nickel sulfide catalyst phase. No other phases could be identified. The spent catalyst had carbon levels of from 7.8 to 14.5 in one test and from 5.9 to 12.1 in the other. These amounts of residual carbon on a used catalyst after hydrotreating are normal.

CONCLUSIONS AND RECOMMENDATIONS

The fixed-bed catalytic reactor system can be used to hydrotreat fast pyrolysis oil to produce product oils of varying oxygen contents and physical properties. Sulfided catalysts can be used, at least in short-term tests. The oxygen content of the product varies with processing rate, as does the amount of hydrogen requirement and byproduct gas production. The increase in processing rate, reduced hydrogen requirement, and reduced byproduct gas production with increased oil yield should contribute to improving the process economics compared with gasoline production cases.

It is difficult to operate the catalytic reactor in the up-flow mode because of the tendency of the product to fractionate and the plugging in the reactor by high-viscosity products. The products with oxygen contents less than 15% were low viscosity, as good or better than the feed oil. The products with 15% to 25% oxygen were several orders of magnitude higher in viscosity and difficult to recover from the reactor system. In the upflow mode there is a tendency for the low-viscosity (and also high-volatility) products to fractionate from the more viscous, low-volatility products and leave the reactor with the excess hydrogen. In this manner, the catalyst bed slowly fills with high-viscosity oil which exits the reactor in disproportionately high yields later in the experiment.

It is recommended to continue the hydrotreating processing research in a downflow reactor configuration. It is apparent that the pyrolysis oil cannot be used directly as turbine fuel

because of its high viscosity and alkali content. Hydrotreating remains the primary means of upgrading fast pyrolysis oil to a turbine fuel quality.

Modification of the PNL Continuous Hydrotreater to a down-flow mode of operation can be accomplished with a minimum of investment and no capital requirement. The reactor modified system will include all existing components with only a minor amount of piping changes. Use of the existing equipment and expertise will make this a cost-effective research effort.

Downflow operation will allow the operation to come to steady state to be reached more readily and will maximize the experimental results. With this system, we can study the effect of flow rate and other operating parameters on the product quality. Furthermore, longer-term tests will be possible and will allow catalyst stability to be studied.

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APPENDIX B

ASSESSMENT OF REGULATORY REQUIREMENTS FOR PROCESS EFFLUENTS FROM
THERMOCHEMICAL BIOMASS CONVERSION

**ASSESSMENT OF REGULATORY REQUIREMENTS
FOR PROCESS EFFLUENTS FROM
THERMOCHEMICAL BIOMASS CONVERSION**

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ABBREVIATIONS

BAT	-	best available technology
BDAT	-	best demonstrated available technology
CAA	-	Clean Air Act
CEQ	-	Council of Environmental Quality
CFR	-	Code of Federal Regulations
CWA		Clean Water Act
DCG		derived concentration guide
DOE		United States Department of Energy
EA		environmental assessment
EIS		environmental impact statement
EPA		United States Environmental Protection Agency
FONSI		finding of no significant impact
FWPCA		Federal Water Pollution Control Act
ICRP		International Council on Radiation Protection
ICS		individual control strategies
LDR		Land Disposal Restrictions
MCL		maximum contaminant level
MCLG		maximum contaminant level guideline
NAAQS		National Ambient Air Quality Standards
NEPA		National Environmental Policy Act
NESHAP		Nat'l Emission Standards for Hazardous Air Pollutants
NPDES		National Pollutant Discharge Elimination System
NREL		National Renewable Energy Laboratory
NSPS		New Source Performance Standards
POTW		publicly owned treatment works
PSD		Prevention of Significant Deterioration
RCRA		Resource Conservation and Recovery Act
SDWA		Safe Drinking Water Act
SMCL		secondary maximum contaminant level
TSD		treatment storage and disposal facility

1 INTRODUCTION

This report contains a listing of potential hazardous process effluent components from thermochemical biomass conversion and reviews the regulation of these materials. The review of regulations is an extensive coverage of all federal regulations and U.S. Department of Energy (DOE) directives important to the operation and activities of a biomass conversion facility located at a DOE site.

The following federal regulations are discussed: The National Environmental Policy Act of 1969; the Resource Conservation and Recovery Act; the Clean Water Act; the Safe Drinking Water Act; the Clean Air Act; and DOE Order 5400.5. The information from the review of these regulations was combined with information on components of biomass conversion effluents [Elliott 1992, Fagernas 1992] to produce two tables listing applicable regulations per contaminant; one for organics and one for inorganics. Future updates potentially affecting biomass thermochemical conversion are also discussed here based on possible regulatory changes.

2 APPLICABLE FEDERAL STATUTES AND REGULATORY ISSUES

This section provides the review of federal regulations.

2.1 THE NATIONAL ENVIRONMENTAL POLICY ACT OF 1969, 42 USC 4321 et seq.

The National Environmental Policy Act (NEPA) is often called the "cornerstone" of national environmental policy. It established the tone for future environmental legislation. When NEPA was passed in 1969, it established a national environmental policy that ensures full consideration of the potential environmental impacts of major federal activities in the decision-making process. Section 2 of the Act states that the role of NEPA is to establish an environmental policy and "to promote efforts which will prevent or eliminate damage to the environment and biosphere and stimulate the health and welfare of man; to enrich the understanding of the ecological systems and natural resources important to the nation." It is included in this discussion, not because it contains specific discharge limits itself, but because it will apply (to varying extent) to any decision to build or locate a treatment facility at a DOE site.

Section 102(2)(C) is the primary governing provision of NEPA. It states that all agencies of the federal government shall review proposed major federal actions to determine whether they may have a significant effect upon the environment. For those actions that have the potential for significant

environmental effects, an environmental impact statement (EIS) must be prepared.

Once an agency has identified a proposed action, it must gather the data necessary to determine whether that action is a major federal action that could significantly affect the quality of the human environment [NEPA Section 102(2)(C)]. Council of Environmental Quality (CEQ) implementing regulations define "human environment" to include the natural and physical environment and the relationship of people to the environment. When answering this question, agencies have traditionally developed several supporting documents. These documents are not specifically required by the statute.

If uncertainty exists in the "level of impact" of the proposed action, an environmental assessment (EA) must be completed. CEQ created the EA as a means of gathering sufficient data to determine whether an EIS is necessary. According to CEQ regulations, the EA must include the need for the proposed action, alternatives to the proposed action, the environmental impacts of the action and its alternatives, and a listing of agencies and persons consulted.

Upon examination of the EA, if it is determined that the action will not have a significant impact on the environment a "finding of no significant impact" (FONSI) is prepared. The FONSI must include the EA or a summary of the EA (40 CFR 1508.13).

If an action is determined to be "major" and its impact on the environment could be significant, the EIS is completed. The EIS is the foundation of NEPA, and is the document required by Section 102(2)(C). The purpose of the EIS is to provide decision makers with the information they need to make sound, environmental decisions, and to inform the public and provide them with an opportunity to participate in the process.

The environmental consequences section of the EIS contains a scientific analysis of the direct and indirect environmental effects of the proposed action and alternatives (46 FR 18026, 1981, Q.7). The narrative must include a discussion of the proposed action's direct effects and their significance, the proposed action's indirect effects and their significance, and the environmental effects of each alternative.

Following the description of the alternative actions and their environmental impact, an environmentally preferable alternative is identified. The environmentally preferable alternative is usually the one that causes the least damage to the biological and physical environment, and that also best protects and preserves historic, cultural, and natural resources (46 FR 18026, 1981, Q. 6a). The environmentally preferred alternative is not necessarily the alternative chosen in the final "Record of Decision." The comparison of alternatives must be done in a consistent manner that allows each alternative to be "fairly" compared with each other.

A draft EIS is published in the Federal Register to request and receive public comment. In response to the comments, DOE may

need to conduct further research, including additional target ecological risk assessments. Some comments may not be incorporated into the final EIS. If a comment is not incorporated, an explanation should be prepared as to why the comment did not warrant further response on the part of the agency (40 CFR 1503.4). At this point the final EIS is published, and a final preferred alternative is stated. NEPA does not require that the most environmentally preferred alternative be chosen, but rather that environmental consequences be accounted for in the decision-making process. A Record of Decision is then published.

Despite its 25 years of existence, the language within NEPA remains vague and often results in confusion about how to meet regulatory requirements. Case law continues to lead to new interpretation. Of the issues that have repeatedly arisen as a result of vague language, the decision on the threshold determination [Section 102(2)] is the most critical and difficult to resolve.

2.2 THE RESOURCE CONSERVATION AND RECOVERY ACT, 42 USC 6901 et seq.

The Resource Conservation and Recovery Act (RCRA) was enacted by Congress to establish a "cradle to grave" system to control the generation treatment, storage, and/or dispose of hazardous waste. Through the provisions of RCRA and subsequent amendments, Congress required EPA to promulgate an expansive body of regulations which would protect "human health and the

environment." EPA's implementing regulations define solid and hazardous waste; establish standards and a manifest system for hazardous waste generators and transporters; establish standards and permit provisions for facilities that treat, store, and/or dispose of hazardous waste; and establish requirements for state delegation of RCRA implementation authority. Many states have been delegated implementation authority and have adopted even more stringent requirements. RCRA also requires facility owners to carry out corrective actions for releases of hazardous substances.

RCRA is divided into 10 subtitles, the most significant being Subtitle C, which establishes the hazardous waste management program. EPA's RCRA implementation regulations appear in 40 CFR 260-268 and 270-272. Generators of hazardous waste have the responsibility to determine whether their wastes are hazardous; notify EPA that they are managing a hazardous waste; obtain an EPA identification number for the generating facility; and verify that transportation, treatment, storage, and disposal of the waste is conducted only by those who have obtained EPA numbers. The generators must also prepare a Uniform Hazardous Waste Manifest to track waste to ensure that hazardous waste actually reaches its destination.

RCRA requires every owner or operator of a treatment, storage and/or disposal (TSD) facility to obtain a permit. (Section 3005). Permit applications must show the facility will be in compliance with TSD standards. These standards cover such topics as waste analysis, security, inspections, local standards and compliance with the manifest system (40 CFR 264 and 265).

Permit applications will be issued by states authorized under RCRA and by the EPA regional administrator in other states. Some general ongoing requirements for operation and monitoring of a RCRA facility include the maintenance of records for all hazardous wastes handled by the facility, reporting, monitoring, inspection, and compliance with the manifest system, contingency plans, maintenance and operation of the facility, and compliance with RCRA Section 3005 relating to permits.

The RCRA regulatory standards that have been promulgated pursuant to RCRA and that are of interest to DOE are found in 40 CFR 261, Regulations for identifying Hazardous Waste; 40 CFR 264/265, Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities; and 40 CFR 268, Land Disposal Restrictions (LDR).

2.2.1 Identification of Hazardous Waste

The land disposal restrictions are used by EPA to protect the environment and public health from hazardous waste. In order to implement the requirements imposed upon them by RCRA, EPA had to further define "hazardous waste" and adopted a two-fold approach to defining hazardous waste. Certain wastes were specifically listed as hazardous and four "hazardous characteristics" identified that make a waste hazardous if one or more of them apply. A complete listing of the hazardous wastes can be found in 20 CFR 261.

The listed hazardous wastes have been divided into three subcategories:

- hazardous waste from nonspecific sources
- hazardous waste from specific sources
- acute hazardous wastes or toxic waste discarded from commercial chemical products, off-specification species, container residues, and spill residues.

Each listed hazardous waste is assigned an EPA Hazardous Waste Code number. These codes are used to identify the specific hazardous waste constituents. The codes are then assigned a specific treatment technology or a maximum constituent concentration level. Table 1 contains the three categories of listed wastes, the applicable CFR section, and the range of hazardous waste codes assigned to the particular group.

Table 1. Listed Hazardous Waste EPA Codes

Listed Hazardous Waste Subcategory	CFR Section	EPA Code #'s
1. Hazardous waste from nonspecific sources	20 CFR 261.31	F001 -- FXXX
2. Hazardous waste from specific sources	20 CFR 261.32	K001 -- KXXX
3a. Acute hazardous waste from discarded commercial chemical products, off-spec. species, & container/spill residues	20 CFR 261.33(e)	P001 -- PXXX
3b. Toxic waste from discarded commercial chem. products, off-spec. species & container/spill residues	20 CFR 261.33(f)	U001 -- UXXX

The four hazardous characteristics are grouped into subcategories: 1) ignitability, 2) corrosivity, 3) reactivity, and 4) toxicity. Table 2 shows the hazardous waste code number assigned to each of these characteristics, the CFR code section which discusses it, and the actual characteristic.

Table 2. Characteristic Hazardous Waste EPA Codes

Waste Code #	CFR # (20 CFR 261)	Characteristic	Description of Substance
D001	261.21(a)(1)	Ignitability	Liquid, other than aqueous solution containing < 24% alcohol by volume and has a flash pt < 60 degrees C
D001	261.21(a)(2)	Ignitability	Not a liquid & is capable under standard temperature & pressure of causing fire through friction absorption of moisture or spontaneous chem. changes and, when ignited, burns so vigorously & persistently that it creates a hazard
D001	261.21(a)(3)	Ignitability	Ignitable compressed gas (49 CFR 173.3)
D001	261.21(a)(4)	Ignitability	Oxidizer (49 CFR 173.151)
D002	261.22(a)(1)	Corrosivity	Aqueous & pH less ≤ 2 or ≥ 12.5
D002	261.22(a)(2)	Corrosivity	Liquid which corrodes steel (SAE 1020) at a rate > 6.35 mm/yr @ a temp. of 55 degrees C.
D003	261.23(a)(1)	Reactivity	Normally unstable & readily undergoes violent change w/o detonating

D003	261.23(a)(2)	Reactivity	Reacts violently with water
D003	261.23(a)(3)	Reactivity	Forms potentially explosive mixtures with water
D003	261.23(a)(4)	Reactivity	When mixed with water, it generates toxic gases, vapors, or fumes in dangerous quantity
D003	261.23(a)(5)	Reactivity	Cyanide or sulfide bearing waste that, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors or fumes in dangerous quantities.
D003	261.23(a)(6)	Reactivity	Capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement
D003	261.23(a)(7)	Reactivity	Readily capable of decomposition or reaction at standard temperature & pressure
D003	261.23(a)(8)	Reactivity	Forbidden explosive as defined in 49 CFR 173.51; or a Class A or B explosive.
D004-DXXX	261.24 Tbl 1	Toxicity	This range of numbers assigned to wastes that exhibit the toxicity characteristic. The CFR cited specifically describes the numerous substances considered toxic.

2.2.2 Treatment Standards

40 CFR 268 prohibits land disposal of certain hazardous waste. Accordingly, RCRA required EPA to establish treatment standards for each restricted hazardous waste to allow for disposal. The treatment standards established by EPA were based on the performance of the best demonstrated available technology (BDAT) to treat the waste. EPA used the various BDATs to establish treatment standards as either specific technologies or

maximum constituent concentration levels. If a specific technology is expressed as the treatment standard, that technology must be used. If the standard is expressed only as a concentration level, the regulated community may use any technology not otherwise disapproved by EPA. For example, it is not permissible to merely dilute a waste to meet a concentration level.

Hazardous waste code numbers are used to identify and assign the required treatment standard(s). EPA has expressed the treatment standards in essentially three different manners:

- Treatment standards expressed as waste extract constituent concentrations
- Treatment standards expressed as specified technologies
- Treatment standards expressed as waste concentrations

It is not uncommon for a particular hazardous waste to carry more than one waste code and the applicable treatment standard for each waste code must be met. For example, if a waste is assigned both a D001 and D002 waste code (i.e., ignitable and corrosive hazardous waste characteristics), the waste must meet the treatment standard applicable for both D001 and D002 wastes. This applies to both characteristic hazardous waste and to the listed hazardous waste. However, if a listed hazardous waste exhibits one or more hazardous characteristics and the characteristic constituent or property is specifically addressed in the treatment standard for the listed waste, only that treatment is required.

2.2.3 Hazardous Chemicals

Commercial chemical products, manufacturing chemical intermediates, off-speciation commercial chemical products, or manufactured chemical intermediates, per 40 CFR 261.33, are identified as either acute hazardous wastes and assigned a P001-P123 EPA hazardous waste number or toxic wastes and assigned a U001-U243 EPA hazardous waste code.

2.3 CLEAN WATER ACT, 33 USC 1251 et seq.

The basic regulatory framework for water pollution control was established by the adoption of the Federal Water Pollution Control Act (FWPCA) in 1972. This act has been amended several times (most recently in 1987) and was renamed the Clean Water Act (CWA) in 1977. Section 101 of the CWA describes its purpose as "to restore and maintain the chemical, physical, and biological integrity of the Nation's waters." The requirements under the CWA are directed at uniform discharge standards from both existing and new sources even if the discharges do not result in violation of water quality standards.

The current form of the CWA contains five elements covering its objective:

1. minimum effluent standards for each industry
2. water quality standards
3. a discharge permit program
4. toxic chemical and oil spill provisions
5. a revolving construction loan program for publicly owned treatment works (POTW)

The discharge of "pollutants" from a point source must be in compliance with a National Pollutant Discharge Elimination System (NPDES) permit. Pollutants under the CWA include biological oxygen demand, suspended solids, fecal coliform bacteria, and pH. Discharges not from a point source or those from dredge/fill activities (Section 404) or discharges to a POTW are regulated under different sections of the CWA.

The NPDES permit for point source discharges can be issued by the EPA or the state. The EPA has based its permit requirements upon two general sets of standards: categorical standards and water quality criteria. Application of the appropriate standards can often depend upon the state's classification of the water receiving the discharge.

Categorical standards are technology-based standards that are applicable to various categories of industrial discharges. These standards are based upon and in reference to pollution control technology. Standards vary depending upon the nature of the point source and the type of pollutant being discharged (40 CFR Parts 304, 405-471).

Section 304(a)(1) of the CWA [33 USC 1314(a)(1)] requires EPA to publish ambient water quality criteria or standards. These standards will include a designated use or uses for a particular body of water and water quality criteria will be assigned based upon these uses. The criteria are not rules and do not in themselves have regulatory impact. However, they do present scientific data on the effects of various contaminants on plants and animals, and establish nonbinding criteria for

concentrations of contaminants in effluent streams. This information can then be used to derive the regulatory requirements that may be incorporated into permit conditions, thereby becoming binding standards. In some cases, limitations more stringent than the technology-based requirements can be imposed.

2.3.1 Human Health Standards-Water, Fish and Carcinogen

Standards set to prevent adverse health effects in humans and minimize exposure to carcinogens. Level below which no adverse health effect to humans is expected, based on tests assuming an ingestion rate of 2 liters of water and 6.5 grams of fish per day. The limit represents the human health criteria for carcinogens at the $1.0E-06$ level, assuming a lifetime consumption of 6.5 g/day average of contaminated fish and/or shellfish for a 70-kg male person.

2.3.2 Chronic Freshwater Limits - Lowest Effect Level

Standards set to prevent acute or chronic effects on aquatic life. Concentration below which chronic or latent adverse effects will not appear in freshwater biota. The data are insufficient to derive criteria. The stated limit is the lowest observed effect level.

2.3.3 Chronic Freshwater Limits - 96-Hour Average

Standards set to prevent acute or chronic effects on aquatic life. Concentration below which chronic or latent adverse effects will not appear in freshwater biota. The limit is the

maximum 96-hour average, not to be exceeded more than once every 3 years.

2.3.4 Human Health Standards - Water and Fish Ingestion

Standards set to prevent adverse health effects in humans and minimize exposure to carcinogens. Level below which no adverse health effect to humans are expected, based on tests assuming ingestion rate of 2 liters of water and 6.5 grams of fish per day.

2.3.5 Chronic Marine Limits - Lowest Effect Level

Standards set to prevent acute or chronic effects on aquatic life. Concentration below which chronic or latent adverse effects will not appear in freshwater biota. The data are insufficient to derive criteria. The stated limit is the lowest observed effect level.

2.3.6 Chronic Freshwater Limits

Standards set to prevent acute or chronic effects on aquatic life. Concentration below which chronic or latent adverse effects will not appear in freshwater biota.

2.4 SAFE DRINKING WATER ACT, 42 USC Section 300, et seq.

The Safe Drinking Water Act (SDWA) establishes maximum contaminant levels (MCLs) and secondary maximum contaminant levels (SMCLs) for discharges to public drinking water in 40 CFR 141 and 40 CFR 143. The SDWA is often incorporated into other regulations by reference. MCLs protect the health of persons by

regulating the maximum level of the contaminant permitted in community drinking water. Secondary MCLs protect the public welfare by regulating the aesthetic qualities of water in community and noncommunity water systems. In addition, the SDWA (40 CFR 148) regulates the underground injection of hazardous wastes. These limits correspond to the land disposal restrictions contained in RCRA (40 CFR 268).

2.4.1 MCLs-Inorganics

40 CFR 141 establishes MCLs for public drinking water. This regulation protects the health of persons by regulating the inorganic contaminants in community and noncommunity drinking water systems. Turbidity in drinking water is also regulated by 40 CFR 141.

2.4.2 MCLs-Organics

40 CFR 141 establishes MCLs for public drinking water. This regulation protects the health of persons by regulating the organic contaminants in community and nontransient noncommunity drinking water. Turbidity in drinking water is also regulated by 40 CFR 141.

2.4.3 SMCLs - Organics

40 CFR 143 establishes SMCLs which are unenforceable federal guidelines regarding taste, odor, color, and certain other nonaesthetic effects on drinking water.

2.5 CLEAN AIR ACT, 40 USC 7401 et seq.

The federal Clean Air Act (CAA), originally enacted in 1970, has been amended several times over the years. It is one of the most complex environmental statutes existing.

The intent of the act is to protect and enhance the quality of the nation's air resources in order to promote the public health and welfare and the productive capacity of its population. To achieve this goal, the act requires that EPA establish air quality standards, and states develop state implementation plans. Since the act was substantially amended in 1990, many of EPA's implementing regulations have yet to be promulgated. These standards control air quality through various mechanisms including the National Ambient Air Quality Standards (NAAQS) and emission limitations.

Section 112 of the CAA and EPA's implementing regulations (40 CFR 61) provide control of the emission of hazardous pollutants to the atmosphere. This control is through the adoption of National Emission Standards for Hazardous Air Pollutants (NESHAP). Approval to construct a new facility or to modify an existing one may be required by these regulations. NESHAPs apply to existing as well as new sources. Pollutants regulated under NESHAPs may not be emitted from enough sources to justify a NAAQS and thus are controlled through this separate provision.

The NAAQS manage air pollution through the use of controls based on ambient air concentrations of pollutants in an area

(Section 109 of the CAA). The NAAQS establish the maximum allowable concentration for certain criteria pollutants and compel the degree of source control to meet the standard. The NAAQS are not directly enforceable; rather they set the standards on which other enforceable requirements, such as emission limitations and permit requirements, are based. The standards are classified as either primary or secondary.

Primary standards are set to protect human health with an "adequate margin of safety." Secondary standards are set to protect the "public welfare." The definition of Public welfare is extremely broad, including "effects on soils, water, crops, vegetation, man-made materials, animals, wildlife, weather, visibility, and climate..." [42 USC section 7602(h) and 40 CFR 50)]. In general, if an area is currently attaining the NAAQS standards established, the Prevention of Significant Deterioration (PSD) permit program will apply. If an area is a "non-attainment" area, then a permit must be sought under the non-attainment permit program. New sources of emissions must comply with New Source Performance Standards (NSPS) (Section 111 of CAA and 40 CFR 60). The NSPS are technology driven and may incorporate and require use of PSD permits.

2.6 DOE ORDER 5400.5 - RADIATION PROTECTION OF THE PUBLIC AND THE ENVIRONMENT

DOE Order 5400.5, Radiation Protection for the Public and the Environment, establishes standards and requirements for operations of the DOE and DOE contractors with respect to

protection of members of the public and the environment against undue risk from radiation.

2.6.1 Air Inhalation DCG - 0.5 Days Retention

The Derived Concentration Guide (DCG) values for inhalation of air assume that under conditions of continuous exposure, members of the public will to inhale 8400 cubic meters of air. The DCG values are based on a committed effective dose equivalent of 100 mrem for the radionuclide taken into the body by inhalation during 1 year, and are assigned to lung retention class "D", which has a removal half-time of 0.5 days [See International Council on Radiation Protection (ICRP) Publication 30 for the Task Group Lung Model]. If more than one limit is given for a contaminant, the most restrictive or smaller is reported.

2.6.2 Air Inhalation DCG - 50 Days Retention

The DCG values for inhalation of air assume, under conditions of continuous exposure, members of the public are assumed to inhale 8400 cubic meters of air. The DCG values are based on a committed effective dose equivalent of 100 mrem for the radionuclide taken into the body by inhalation during 1 year, and are assigned to lung retention class "W", which has a removal half-time of 50 days (See ICRP Publication 30 for the Task Group Lung Model). If more than one limit is given for a contaminant, the most restrictive or smaller is reported.

2.6.3 Air Inhalation DCG - 500 Days Retention

The DCG values for inhalation of air assume, under conditions of continuous exposure, members of the public are

assumed to inhale 8400 cubic meters of air. The DCG values are based on a committed effective dose equivalent of 100 mrem for the radionuclide taken into the body by inhalation during 1 year, and are assigned to lung retention class "Y", which has a removal half-time of 500 days (See ICRP Publication 30 for the Task Group Lung Model). If more than one limit is given for a contaminant, the most restrictive or smaller is reported.

2.6.4 Water Ingestion DCG

The DCG values for ingestion of water assume, under conditions of continuous exposure, members of the public are assumed to ingest 730 liters of drinking water. The DCG values are based on a committed effective dose equivalent of 100 mrem for the radionuclide taken into the body by ingestion during 1 year and are not release limits but, rather, are screening values for considering best available technology (BAT) for discharges and for making dose estimates.

For liquid wastes containing radionuclides from DOE activities which are discharged to surface water, the BAT is the prescribed level of treatment if the surface waters contain, at the point of discharge and prior to dilution, radioactive material at annual average concentrations greater than the DCG values given. Additional treatment is not required for waste streams that contain radioactive concentrations of not more than the DCG values at the point of discharge to a surface waterway. For liquid waste streams containing more than one type of radionuclide, the DCG shall be the sum of the fractional DCG values and, if more than one limit is given for a contaminant, the most restrictive or smaller is reported.

3 SPECIFIC COMPONENT REGULATIONS

Two tables of applicable regulations were prepared from this review and from lists of components identified in biomass conversion process effluents [Elliott 1992, Fagernas 1992]. These tables were derived from searches using the ReOpt™ software [White & Bryant 1992]. The tables list the components determined to be regulated based on any of the regulations described above. These tables can be used as a reference for determining required actions relative to process effluents which might contain any of the listed components.

Tables 3 and 4 provide a basis for evaluation of biomass thermochemical conversion process effluents. Some of the regulations do not specifically apply to these effluents, partly because the processes are not yet commercialized and have not been regulated. In addition, there are no stream specific definitions of the biomass conversion effluents yet designated; however, it is possible that such designation will be forthcoming based on the amounts and types of hazardous chemicals that have been identified in the biomass conversion effluents. The information in Tables 3 and 4 should be helpful in the future definition of applicable regulations for these effluents.

ReOpt™ Version 2.0, Pacific Northwest Laboratory, Richland, WA

TABLE 3. APPLICABLE FEDERAL REGULATIONS

ORGANIC CONTAMINANTS

Contaminant	CAS No.	Statute	Regulation	Limit
Acetaldehyde (ethanal)	75-07-0	RCRA	LDR/physical characteristic	specified technol. 1000 mg/kg
Ethyl Acetate	141-78-6	RCRA	LDR/physical characteristic Hazardous Chemical/HW* No. U112	specified technol. NA#
Lead Acetate	301-04-2	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U144	specified technol. NA
Acetone	67-64-1	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U002	specified technol. NA
Acetophenone	98-86-2	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U004	specified technol. NA
Acrylic Acid (2-propenoic acid)	79-10-7	RCRA	LDR/physical characteristic	specified technol. 1000 mg/kg
Ethylacrylate	180-88-5	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U113	specified technol. NA
Ethylmethacrylate	97-63-2	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U118	specified technol. NA
Methylmethacrylate	80-62-6	RCRA	LDR/physical characteristic	specified technol. 1000 mg/kg
Aniline	62-53-3	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U012	specified technol. NA
Benzene	71-43-2	RCRA	Toxicity characteristic/HW No. D018 LDR/physical characteristic Hazardous Chemical/HW No. U019	0.5 mg/L specified technol. NA
		CWA	Human health standards-water, fish, & carcinogen	0.66µg/L
		SDWA	MCL - Organics	0.005 mg/L
Methylbenzene (Toluene)	108-88-3	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U220	specified technol. NA
		CWA	Chronic marine limits-lowest effect level	5000µg/L
		SDWA	MCL-Organic	1.0 mg/L
Dimethylbenzene (xylene)	1330-20-7	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U239	specified technol. NA
		SDWA	MCL-Organic (xylenes total)	10 mg/L

TABLE 3. APPLICABLE FEDERAL REGULATIONS, cont.

ORGANIC CONTAMINANTS

Contaminant	CAS No.	Statute	Regulation	Limit
1-Methylethylbenzene (isopropylbenzene, cumene)	98-82-8	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U055	specified technol. NA
1,2-Dihydro-3-methylbenz(j) aceanthrylene (3-methylcholanthrene)	56-49-5	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U157	specified technol. NA
Benz(a)anthracene	56-55-3	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U018	specified technol. NA
7,12-Dimethylbenz(a) anthracene	57-97-6	RCRA	LDR/physical characteristic	specified technol. 1000 mg/kg
Benzo(a)pyrene	50-32-8	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U022	specified technol. NA
1-Butanol	71-36-3	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U031	specified technol. NA
2-Butenal	4170-30-3	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U053	specified technol. NA
Chrysene	218-01-9	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U050	specified technol. NA
Creosote	8001-58-9	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U051	specified technol. NA
Cresol (cresylic acid)	1319-77-3	RCRA	Toxicity characteristic/HW No. D026 LDR/physical characteristic Hazardous Chemical/HW No. U052	200 mg/L specified technol. NA
ortho-Cresol	95-48-7	RCRA	Toxicity characteristic/HW No. D023 LDR/physical characteristic	200.0 mg/L specified technol.
meta-Cresol	108-39-4	RCRA	Toxicity characteristic/HW No. D024 LDR/physical characteristic	200.0 mg/L specified technol.
Cyclohexane	110-82-7	RCRA	Toxicity characteristic/HW No. D026 LDR/physical characteristic Hazardous Chemical/HW No. U056	200 mg/L specified technol. NA
Cyclohexanone	108-94-1	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U057	specified technol. NA

TABLE 3. APPLICABLE FEDERAL REGULATIONS, cont.

ORGANIC CONTAMINANTS

Contaminant	CAS No.	Statute	Regulation	Limit
Dibenz(a,h)anthracene	53-70-3	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U063	specified technol. NA
Dibenz(a,i)pyrene	189-55-9	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U064	specified technol. NA
2,4-Dimethylphenol	105-67-9	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U101	specified technol. NA
Fluoranthene	206-44-0	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U120	specified technol. NA
		CWA	Chronic marine limits-lowest effect level	16µg/L
Formaldehyde	50-00-0	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U122	specified technol. NA
Formic acid	64-18-6	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U123	specified technol. NA
Furan	110-00-9	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U124	specified technol. NA
Tetrahydrofuran	109-99-9	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U213	specified technol. NA
Furfural	98-01-1	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U125	specified technol. NA
Indenal(1,2,3-cd)pyrene	193-39-5	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U137	specified technol. NA
2-methyl-propanol	78-83-1	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U140	specified technol. NA
Methanol	67-56-1	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U154	specified technol. NA
Methylethylketone	78-93-3	RCRA	Toxicity characteristic/HW No. D035	200 mg/L
			LDR/physical characteristic Hazardous Chemical/HW No. U159	specified technol. NA
4-Methyl-2-pentanone (methylisobutylketone, MIBK)	108-10-1	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U161	specified technol. NA

TABLE 3. APPLICABLE FEDERAL REGULATIONS, cont.

ORGANIC CONTAMINANTS

Contaminant	CAS No.	Statute	Regulation	Limit
Naphthalene	91-20-3	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U165	specified technol. NA
		CWA	Chronic freshwater limits-lowest effect level	620µg/L
1,4-Naphthalenedione (naphthoquinone)	130-15-4	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U166	specified technol. NA
Phenol	108-95-2	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U188	specified technol. NA
1,3-Benzenediol (resorcinol)	108-46-3	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U201	specified technol. NA
2-Propenol (allyl alcohol)	107-18-6	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. P005	specified technol. NA
2-Propenal (acrolein)	107-02-8	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. P003	specified technol. NA
		CWA	Chronic freshwater limits-lowest effect level	21µg/L
Quinone (2,5-cyclohexadiene- 1,4-dione)	106-51-4	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U197	specified technol. NA
Pyridine	110-86-1	RCRA	Toxicity characteristic/HW No. D038 LDR/physical characteristic Hazardous Chemical/HW No. U196	5.0 mg/L specified technol. NA
Methylpyridine	109-06-8	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. U191	specified technol. NA
Aziridine (ethylenimine)	151-56-4	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. P054	specified technol. NA
2-Methylaziridine	75-55-8	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. P067	specified technol. NA
Nicotine	54-11-5	RCRA	LDR/physical characteristic Hazardous Chemical/HW No. P075	specified technol. NA

* HW = hazardous waste.

NA = not available.

TABLE 4. APPLICABLE FEDERAL REGULATIONS

INORGANIC COMPONENTS

Contaminant	CAS No.	Statute	Regulation	Limit
Arsenic	7440-38-2	RCRA	Toxicity characteristic/HW(a) No. D004	5.0 mg/L
			LDR/toxicity characteristic-wastewater/HW No. D004	5.0 mg/L
			LDR/physical characteristic	specified technol.
			LDR/CA(b) list-metals	500 mg/L
			LDR/toxicity characteristic-nonwastewater extract/HW No. D004	5.0 mg/L
		CWA	Human health standards-water, fish, & carcinogen	0.0022µg/L
		SDWA	MCL - inorganic	0.05 mg/L
		DOE Order 5400.5	Air Inhalation DCG-50 days retention	0.5µCi/mL
Barium	7440-39-3	RCRA	Toxicity characteristic/HW No. D005	100.0 mg/L
			LDR/toxicity characteristic-wastewater/HW No. D005	100.0 mg/L
			LDR/physical characteristic	specified technol.
			LDR/toxicity characteristic-nonwastewater extract/HW No. D005	100.0 mg/L
		CWA	Human health standards-water & fish ingestion	1000µg/L
		SDWA	MCL - inorganic	2.0 mg/L (c)
		DOE Order 5400.5	Air Inhalation DCG-0.5 days retention	0.1µCi/mL
Cadmium	7440-43-9	RCRA	Toxicity characteristic/HW No. D006	1.0 mg/L
			LDR/toxicity characteristic-wastewater/HW No. D006	1.0 mg/L
			LDR/physical characteristic	specified technol.
			LDR/CA list-metals	100 mg/L
			LDR/toxicity characteristic-nonwastewater extract/HW No. D006	1.0 mg/L
			LDR/toxicity characteristic-specified technology	specified technol.
		CWA	Chronic freshwater limits-96 hour average	1.1µg/L
		SDWA	MCL - inorganic	0.005 mg/L
		DOE Order 5400.5	Air Inhalation DCG-0.5 days retention	0.05µCi/mL
			Air Inhalation DCG-50 days retention	0.05µCi/mL
			Air Inhalation DCG-500 days retention	0.05µCi/mL
Chromium	7440-47-3	RCRA	Toxicity characteristic/HW No. D007	5.0 mg/L
			LDR/toxicity characteristic-wastewater/HW No. D007	5.0 mg/L
			LDR/physical characteristic	specified technol.
			LDR/CA list-metals	500 mg/L
			LDR/toxicity characteristic-nonwastewater extract/HW No. D007	5.0 mg/L
		SDWA	MCL - inorganic	0.1 mg/L
		DOE Order 5400.5	Water Ingestion DCG	0.01µCi/mL
			Air Inhalation DCG-0.5 days retention	0.1µCi/mL
			Air Inhalation DCG-50 days retention	0.1µCi/mL
			Air Inhalation DCG-500 days retention	0.1µCi/mL

TABLE 4. APPLICABLE FEDERAL REGULATIONS, cont.

INORGANIC COMPONENTS

Contaminant	CAS No.	Statute	Regulation	Limit
Lead	7439-92-1	RCRA	Toxicity characteristic/HW No. D008	5.0 mg/L
			LDR/toxicity characteristic-wastewater/HW No. D008	5.0 mg/L
			LDR/physical characteristic	specified technol.
			LDR/CA list-metals	500 mg/L
			LDR/toxicity characteristic-nonwastewater extract/HW No. D008	5.0 mg/L
			LDR/toxicity characteristic-specified technology	specified technol.
		CAA	NAAQS primary standards - calendar quarter	micro-gm/m ³
			NAAQS secondary standards - calendar quarter	1.5 µg/m ³
		CWA	Chronic freshwater limits-96 hour average	3.2 µg/L
		SDWA	MCL - inorganic	TT (d)(e)
Mercury	7439-97-6	RCRA	Air Inhalation DCG-0.5 days retention	0.2 µCi/mL
			Toxicity characteristic/HW No. D009	0.2 mg/L
			LDR/toxicity characteristic-wastewater/HW No. D009	0.2 mg/L
			LDR/physical characteristic	specified technol.
			LDR/CA list-metals	20 mg/L
			LDR/toxicity characteristic-nonwastewater extract/HW No. D009	0.20 mg/L
			LDR/toxicity characteristic-specified technology	specified technol.
		CWA	Chronic freshwater limits-96 hour average	0.012 µg/L
		SDWA	MCL - inorganic	0.002 mg/L
		DOE Order 5400.5	Air Inhalation DCG-0.5 days retention	0.02 µCi/mL
			Air Inhalation DCG-50 days retention	0.02 µCi/mL
Selenium	7782-49-2	RCRA	Air Inhalation DCG-0.5 days retention	0.02 µCi/mL
			Toxicity characteristic/HW No. D010	1.0 mg/L
			LDR/toxicity characteristic-wastewater/HW No. D010	1.0 mg/L
			LDR/physical characteristic	specified technol.
			LDR/wastewater-mixtures/HW No. F039	0.82 mg/L
			LDR/CA list-metals	100 mg/L
			LDR/toxicity characteristic-nonwastewater extract/HW No. D010	5.7 mg/L
		CWA	Human health standards - water & fish ingestion	10 µg/L
		SDWA	MCL - inorganic	0.05 mg/L
		DOE Order 5400.5	Water ingestion DCG	0.05 µCi/mL
			Air Inhalation DCG-0.5 days retention	0.8 µCi/mL
			Air Inhalation DCG-50 days retention	0.8 µCi/mL

TABLE 4. APPLICABLE FEDERAL REGULATIONS, cont.

INORGANIC COMPONENTS

Contaminant	CAS No.	Statute	Regulation	Limit
Silver	7440-22-4	RCRA	Toxicity characteristic/HW No. D011	5.0 mg/L
			LDR/toxicity characteristic-wastewater/HW No. D011	5.0 mg/L
			LDR/physical characteristic	specified technol.
			LDR/toxicity characteristic-nonwastewater extract/HW No. D011	5.0 mg/L
		CWA	Chronic freshwater limits	0.12µg/L
		SDWA	SMCL - inorganic	0.1 mg/L
		DOE Order 5400.5	Air Inhalation DCG-0.5 days retention	0.05µCi/mL
			Air Inhalation DCG-50 days retention	0.05µCi/mL
			Air Inhalation DCG-500 days retention	0.05µCi/mL

(a) HW = hazardous waste

(b) CA = California

(c) Effective date: January 1, 1993

(d) Effective date: December 7, 1992

(e) TT = Treatment technique requirement in effect.

4 FUTURE UPDATING OF THE REGULATORY ENVIRONMENT

Evaluation of the regulatory environment surrounding biomass thermochemical conversion processes is an ongoing activity in this project. This report is the revised version of the original report issued in January 1993, updated in August 1993 with the updates for June 1993 through February 1994 included here. This report will be updated on a semi-annual basis to include changes in the regulations that might affect a biomass thermochemical conversion facility. Significant changes in some of the regulatory requirements have been proposed and may become effective within the next year. The following text highlights a portion of the anticipated regulatory changes.

4.1 Resource Conservation and Recovery Act Update:

- EPA proposes to revise the existing small-scale treatability studies Subtitle C exclusions to allow up to 10,000 kg of soil and debris contaminated with non-acute hazardous waste from a single waste stream to be treated (40 CFR 261).
- EPA plans to establish air emission standards for emissions of volatile organics from tanks and impoundments at hazardous waste TSD facilities and require that organic emissions controls be installed and operated (40 CFR 264/265).
- EPA plans to amend Subpart F groundwater monitoring regulations to foster the early detection of leaks and to

better tailor the current groundwater monitoring regulations to site-specific conditions (40 CFR 264/265).

- EPA proposes treatment standards under the RCRA LDR program for certain newly listed wastes and contaminated debris pursuant to a proposed consent decree and finalize revised treatment standards for other hazardous debris (40 CFR 268).
- EPA proposes procedures and technical requirements for implementing corrective action at RCRA solid waste management units. The proposal would create a new Subpart S to define requirements for conducting remedial investigations, evaluating potential remedies, and selecting and implementing remedies at RCRA facilities.

4.2 Clean Water Act Update:

- EPA proposes two options for determining which facilities newly identified under CWA section 304(1) are required to have individual control strategies: 1) require ICSs only for point sources originally subject to such a requirement or 2) give the state discretion to determine eligibility on a case-by-case basis (40 CFR 130).

4.3 Safe Drinking Water Act Update:

- Primary Drinking Water Regulations - Radionuclides: EPA has proposed MCL guidelines (MCLGs) of zero and the MCLs for several radionuclides as well as additional monitoring, reporting, and public notification requirements (final rule 10/94).

- EPA set MCLs and MCLGs for 18 synthetic organic chemicals and five inorganic chemicals. The primary drinking water regulations consist of MCLs and monitoring, reporting, and public notification requirements (40 CFR 141/142/143, effective 1/17/94).

4.4 Clean Air Act Update:

- EPA proposes to revise the maximum allowable increases for particulate matter under the requirements for prevention of significant deterioration (40 CFR 51/21).
- EPA proposes general provisions for NESHAPs under Sect. 112 which codify procedures and criteria to implement emission standards for stationary sources that emit one or more of the 189 substances listed as hazardous air pollutants. The general provisions eliminate the need to repeat general information and requirements within the standards (40 CFR 60, 61, and 63).
- EPA has proposed to control emissions of hazardous organic chemicals from storage tanks, process vents, equipment leaks, transfer operations, and wastewater treatment of synthetic organic chemicals manufacturing plants (40 CFR 63).
- List of substances and threshold quantities for accidental release prevention: EPA proposed a list of regulated substances as required under Sect. 112(r) of the CAA. Included are 100 toxic substances, 62 flammable substances,

and commercial explosives. Threshold quantities for accidental releases for each substance listed were also proposed (40 CFR 68).

5 CONCLUSIONS AND RECOMMENDATIONS

In general, the statutes and regulations discussed in this report protect human health and the environment by regulating discharges to the air, groundwater, surface water, and soil. Accordingly, the regulations contain performance and design standards and criteria that must be met by plant operators. Permits may also be required; these permits prescribe the specific performance, design, and siting criteria that must be met to satisfy the regulatory standards. Some permits authorize direct discharges of substances to the environment. In other cases, additional permits are required before waste management and other facilities are allowed to operate. The permits for a facility may be issued by several regulatory agencies, such as the EPA, state departments of ecology or social and health services or local agencies, such as county health districts, city sewer systems, or pollution control authorities.

Any DOE biomass conversion operation is subject to DOE orders that cover waste management and disposal and protection of workers, the public, and the environment. For the most part, the DOE orders add procedural requirements, but the 5400.5 order described in this report specifies actual effluent limits. In the case of biomass, the limits specified are expected to be well above the effluent amounts.

The multiple levels of governmental involvement derive from the high level of public interest in environmental regulation. State regulatory agencies often play major roles in implementing

and enforcing environmental laws. A number of the federal environmental statutes provide for a dual federal-state regulatory program where the states are given the opportunity to enact and enforce laws. While these laws must meet congressionally mandated minimum criteria, states are generally free to adopt and enforce even more stringent environmental requirements. In states that have been delegated and accepted responsibility for enforcing various federal environmental laws [such for the Resource Conservation and Recovery Act (RCRA)], the state becomes the primary permitting and enforcement mechanism. All of these regulations are subject to continual updating, which usually tightens the restrictions. Therefore, the specific site of any biomass conversion operation will determine the exact level of pollution control required, and may be different from a similar operation in another location.

It is important to note that the release specifications described below apply to both normal operations and off-normal operations. That is, releases of any type over the set limits can result in fines and other legal retribution, whether the releases were on purpose or accidental. Therefore, plant design should take into account releases of all types. Maintenance procedures as well, especially equipment cleanout, needs to be considered in the plant design. Allowance must be made for collection of all waste streams from the plant, including off-spec startup products, spent maintenance materials, and feedstock storage pile runoff.

6 REFERENCES

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Statutes:

Clean Air Act (CAA), 40 USC 7401, et seq.

Clean Water Act (CWA), 33 USC 1251, et seq.

National Environmental Policy Act (NEPA), 42 USC 4321, et seq.

Resource Conservation and Recovery Act of 1976 (RCRA), 42 USC 6901, et seq.

Safe Drinking Water Act (SDWA), 42 U.S.C. 300, et seq.

Regulations:

40 CFR 60. 1992. "Standards of Performance for New Stationary Sources," U.S. Code of Federal Regulations.

40 CFR 61 "National Emission Standards for Hazardous Pollutants." U.S. Code of Federal Regulations.

40 CFR 104-149 "Subchapter D - Water Programs," U.S. Code of Federal Regulations.

40 CFR 141 "National Primary Drinking Water Standards," U.S. Code of Federal Regulations.

40 CFR 257 "Criteria for Classification of Solid Waste Disposal Facilities and Practices.

40 CFR 261 "Identification and Listing of Hazardous Waste," U.S. Code of Federal Regulations.

40 CFR 262 "Standards Applicable to Generators of Hazardous Waste," U.S. Code of Federal Regulations.

40 CFR 264 "Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities," U.S. Code of Federal Regulations.

40 CFR 266 "Standards for the Management of Specific Hazardous Wastes and Specific Types of Hazardous Waste Management Facilities," U.S. Code of Federal Regulations.

40 CFR 268 "Land Disposal Restrictions," U.S. Code of Federal Regulations.

40 CFR 270 "EPA Administered Permit Programs: The Hazardous Waste Permit Program," U.S. Code of Federal Regulations.

49 CFR 171-180 "Hazardous Materials Regulations," U.S. Code of Federal Regulations

57 FR 60920-60921, December 22, 1992. "Water Quality Standards," Federal Register.

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The report covers information on thermochemical conversion which is limited to fast pyrolysis, upgrading of fast pyrolysis, upgrading fast pyrolysis oils, and gasification. Environmental impacts of all types were considered within the project, but primary emphasis was on discharges to the land, air, and water during and after the conversion processes.

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