

Evaluation of Wastewater Treatment Requirements for Thermochemical Biomass Liquefaction

D. C. Elliott
*Pacific Northwest Laboratory
Richland, Washington*



National Renewable Energy Laboratory
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Golden, Colorado 80401-3393
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Contents

Acknowledgment	iii
Contents	v
Figures	vi
Tables	vi
Introduction	1
Thermochemical Biomass Liquefaction	1
Upgrading Biomass-Derived Liquids	3
Process Wastewater from Liquefaction	4
High-Pressure Liquefaction	4
Flash Pyrolysis	6
Process Wastewater From Upgrading Biomass Oils	8
Hydroprocessing Operations	8
Catalytic Cracking Operations	8
Identification of Environment, Safety, and Health Criteria	9
Statutes and Regulations that may be Applicable	10
Resource Conservation and Recovery Act of 1976 (RCRA)	10
Clean Water Act	11
Safe Drinking Water Act	11
Identification of Data Gaps and Research Needs	14
Proposed R&D Strategy	15
References	16

Figures

1. Conceptual High-Pressure Liquefaction Process	2
2. Conceptual Flash Pyrolysis Process	2

Tables

1. Typical Properties of Raw Products from Direct Liquefaction of Biomass	3
2. Organic Compounds Identified in Aqueous Phase from High-Pressure Liquefaction	5
3. Aqueous Phase Components from Flash Pyrolysis	7
4. Partial TCLP List of Maximum Concentration of Contaminants	10
5. List of Hazardous Constituents in Biomass Liquefaction Wastewaters	12

Evaluation of Wastewater Treatment Requirements for Thermochemical Biomass Liquefaction

Introduction

Biomass can provide a substantial energy resource. Liquids are preferred for use as transportation fuels because of their high energy density and handling ease and safety. Liquid fuel production from biomass can be accomplished by any of several different processes including hydrolysis and fermentation of the carbohydrates to alcohol fuels, thermal gasification and synthesis of alcohol or hydrocarbon fuels, direct extraction of biologically produced hydrocarbons such as seed oils or algae lipids, or direct thermochemical conversion of the biomass to liquids and catalytic upgrading to hydrocarbon fuels. This report is limited to a discussion of direct thermochemical conversion to achieve biomass liquefaction and the requirements for wastewater treatment inherent in such processing. A related report, prepared at the Technical Research Centre of Finland¹, provides similar information for biomass gasification systems. For the purposes of this report, biomass encompasses woody and herbaceous biomass, refuse-derived fuel (RDF), and peat.

Thermochemical Biomass Liquefaction

Direct liquefaction of biomass by thermochemical means has been studied continuously as a process for fuel production for the past 20 years. Modern development of the process can be traced to the early work at the Bureau of Mines as an extension of coal liquefaction research² and to the work on municipal solid waste at the Worcester Polytechnical Institute³. Ongoing work at universities and national laboratories in the United States, Canada, Scandinavia, and other European countries has resulted in much progress since the mid-1970s⁴. Currently the research focuses on two general processing configurations, high-pressure liquefaction and flash pyrolysis.

High-pressure liquefaction of biomass, shown conceptually in Figure 1, has been studied at a number of sites around the world and includes a number of process variations⁵. The processing temperature is generally in the range of 350°C with operating pressures in excess of 1000 psig. The feedstock is generally fed as a slurry, and the nature of the slurry vehicle is a major variable in the studies. The presence of added reducing gas or catalyst is an important variable. Most studies show that operation in the presence of alkali facilitates the formation of liquids with lower oxygen contents. Product recovery is also a major issue and is highly dependent on the slurry vehicle. Various systems of centrifugation, distillation, and solvent fractionation have been tested.

The flash pyrolysis concept, shown in Figure 2, has also been widely studied^{6,7}. Modern engineering methods have optimized the yield of liquid product through control of feedstock particle size, residence time, processing pressure, and processing temperature. The flash concept varies from the older technology of pyrolysis in which the biomass was slowly heated; thus, it produces lesser amounts of volatile gases and condensable vapors and more solid char product⁸. Current atmospheric pressure process development utilizes short residence time, <1 s, in isothermal, fluidized-, or entrained-bed reactors. The feedstock is carried by an inert gas carrier into the reactor where it thermally decomposes to tar vapors, water vapor, gases, and char solids.

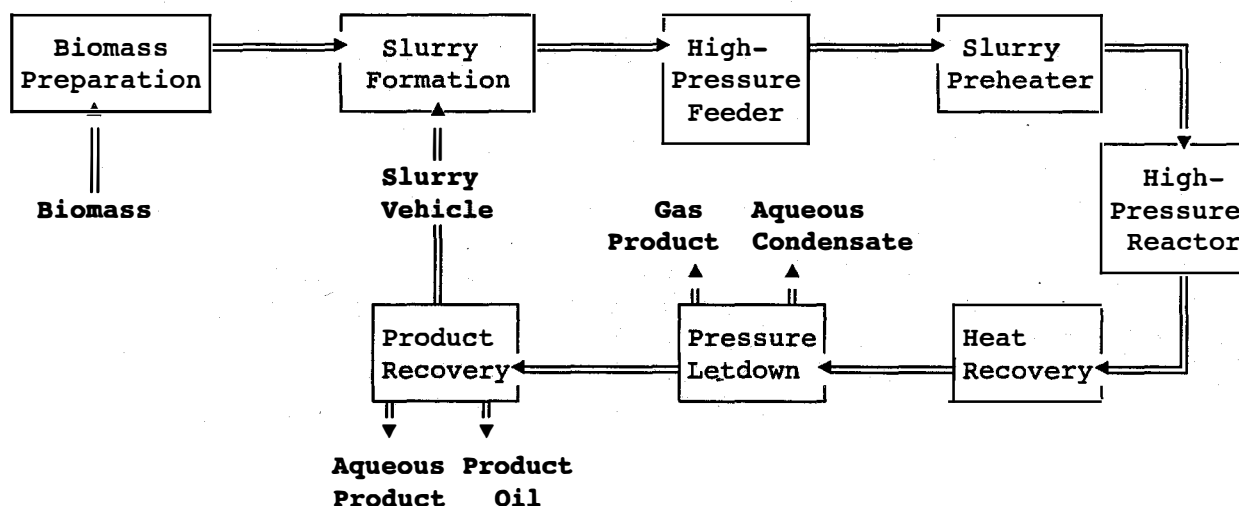


Figure 1. Conceptual High-Pressure Liquefaction Process

Various systems for vapor quench and recovery have used complicated condensing and coalescing systems including electrostatic precipitators, cyclones, filters, and/or spray towers. Another type of flash pyrolysis system operates at subatmospheric pressure to keep the vapor residence time to a minimum while controlling the rate of temperature increase in larger particle biomass feedstock⁹.

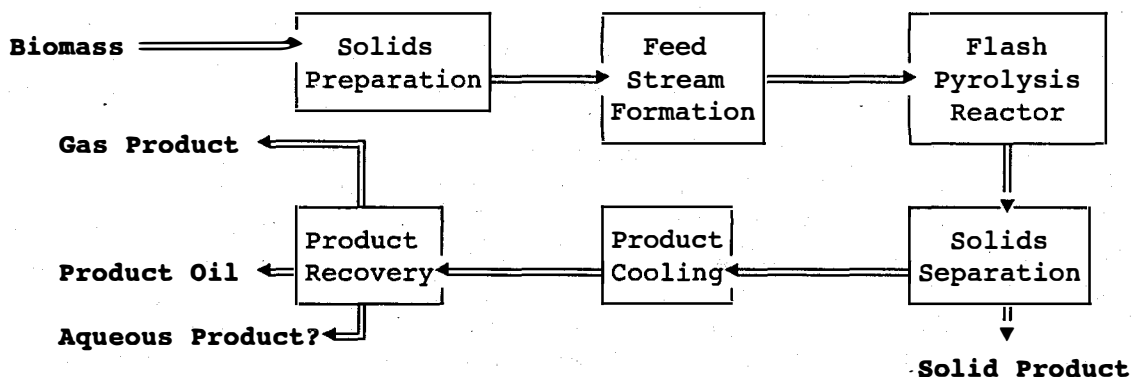


Figure 2. Conceptual Flash Pyrolysis Process

The products from the high-pressure liquefaction and atmospheric flash pyrolysis processes are quite different from each other. The properties of the two products are summarized in Table 1. The high-pressure product is a viscous, phenolic oil. Its physical properties of high viscosity, high boiling point, and limited water solubility are readily understood as resulting from the oxygenated and aromatic character of the product components. Because the water solubility is

limited, there is a separate aqueous product stream, which is usually recovered both from the condensed liquid product and also from the cooled gas product after pressure letdown.

The flash pyrolyzate is much more oxygenated and is more water soluble. The more oxygenated components in the product, acids and aldehydes/ethers, cause it to be more corrosive and more thermally unstable, respectively. As a result of the high level of dissolved water in the product, the flash pyrolyzate is much less viscous. In addition, the amount of aqueous phase byproduct is greatly reduced or eliminated entirely in most cases. However, the normal operation of vacuum pyrolysis, with staged condensation of the product, and slow pyrolysis, with extended reaction time, result in a separate aqueous byproduct stream in both cases. This effect is discussed more completely later in this report.

Table 1. Typical Properties of Raw Products from Direct Liquefaction of Biomass¹⁰

	<u>High-Pressure Liquefaction</u>	<u>Flash Pyrolysis</u>
Elemental Analysis (wet)		
Carbon, wt %	72.6	43.5
Hydrogen, wt %	8.0	7.3
Oxygen, wt %	16.3	49.2
Sulfur, ppm	<45	29
H/C atom ratio (dry)	1.21	1.23
Density, g/mL	1.15	1.23
Moisture, wt %	5.1	24.8
HHV, Btu/lb	15,340	9,710
Viscosity, cps	15,000 @ 61°C	59 @ 40°C
Distillation Range		
IBP - 225°C	8%	44%
225°C - 350°C	32%	coked
350°C - EP (°C)	7%	

Upgrading Biomass-Derived Liquids

Because of the chemical differences in the two products described above, different upgrading schemes have been derived for converting the products into usable hydrocarbon fuels. Catalytic hydroprocessing is an obvious choice based on the existing knowledge of sulfur removal from petroleum products. Catalytic hydrodeoxygenation of the products has been studied in several laboratories¹¹. Developments in further product refinement by catalytic cracking and hydrocracking have also been presented¹². This type of processing is most directly applicable to the high-pressure liquefaction products; however, a process has been identified that allows the use of catalytic hydroprocessing of the thermally unstable pyrolyzate product¹³. A refinement of this process is the use of a nonisothermal catalyst bed, which eliminates the intermediate step of product cooling and separation of a contaminated aqueous phase byproduct¹⁴.

Another alternative, which has been used successfully with the pyrolyzate products, is the catalytic cracking of the vapors over a zeolite catalyst without the intermediate quenching and recovery of the tars¹⁵. The process requires a bed of zeolite to crack the tar vapors to lighter components, including gasoline range hydrocarbons, and separates much of the oxygen in the pyrolysis oil as carbon oxide gases and water vapor. Byproducts from the cracking include fuel gas and coke, which can be burned to heat the process, and olefin gases, which can be reacted with the gasoline to increase the yield and octane rating. An important step in the process is the incineration of a water stream containing much of the unconverted pyrolysis material. Zeolite catalyst processing has the advantage of directly treating the pyrolysis vapors without condensing and allowing separation of an aqueous phase until after the oil components are hydrophobic and more easily recoverable from the water.

Process Wastewater from Liquefaction

Biomass liquefaction technology has had a relatively short developmental life. As a result, the limited amount of product analysis undertaken thus far has emphasized the oil phase material with much less analysis of the byproduct water phase. For example¹⁶, the extensive central analytical program undertaken in Canada in support of their biomass liquefaction program included only one aqueous sample in a slate of 62 different product samples. Because of the limited amount of work, collection of the information on the wastewaters from liquefaction did not produce a large field of data, although a large amount of literature was reviewed to find the available data. Much of the information was presented as a side issue in the articles of interest.

High-Pressure Liquefaction

Contamination of the byproduct water stream from high-pressure biomass liquefaction was recognized early on in the technology development. The earliest Bureau of Mines report on the CO-steam process utilization with municipal waste indicated that the aqueous phase carried considerable organic material that could be converted to separable oil product by recycle in the process¹⁷. No details of analysis of the water phase were reported, although organic contaminants were described as acids.

Later development of the process in the Biomass Liquefaction Experimental Facility at Albany, Oregon, also provided little insight into the composition of the wastewater components. The single reference to water analysis is a list of components identified in the aqueous condensate stream as part of supporting research at PNL¹⁸. The components listed are given in Table 2.

The concentration of the organic components can be significant. Limited analysis of the water phase in one test at the Albany Facility showed that TOC (total organic carbon) levels of 1% to 2% were produced in a liquefaction test using hydrolyzed wood chips at 10% solids concentration in water as the feedstock¹⁹. These dissolved components, effectively lost from the product yield, were reported to represent a significantly larger portion of the biomass liquefaction product than those lost to the water in operations with wood chips in oil as feedstock²⁰.

A related research effort at the Lawrence Berkeley Laboratory (LBL) provides detailed analysis for the aqueous phase products from high-pressure liquefaction²¹. Their TOC analyses show levels of 1.6% to 3.6% in single-pass experiments; recycle concentrations reached 14.3% of TOC.

Table 2. Organic Compounds Identified in Aqueous Phase from High-Pressure Liquefaction

methanol (18)* (22)	3-hydroxybutyric acid (22)
ethanol (18) (22)	acetone (18) (22)
2-propanol (18) (22)	2-butanone (18) (22)
1-propanol (18) (22)	2-pentanone (18) (21) (22)
2-butanol (18) (22)	cyclopentanone (18) (24)
2-methyl-1-propanol (18) (22)	cyclohexanone (18) (21) (22) (24)
1-butanol (18) (22)	methylcyclopentenone (21)
2-pentanol (18)	methylcyclohexanone (18) (24)
2 & 3-methyl-2-butanol (18)	methylisobutylketone (22)
2 & 3-methyl-1-butanol (18)	3-methylcyclopentanone (22)
1-pentanol (18)	
cyclopentanol (18) (22)	butylacetate (21)
2-methylcyclopentanol (18)	butyrolactone (21) (22)
cyclohexanol (24)	
methylcyclohexanol (18) (24)	2-acetylfuran (24)
ethylcyclohexanol (24)	tetrahydrofuran (18)
2,4-dimethyl-3-heptanol (21)	furfural (24)
tertiary-butyl alcohol (22)	2-methyltetrahydrofuran (18)
formic acid (18)	phenol (24)
acetic acid (21) (22) (24)	catechol (24)
propionic acid (21) (22) (24)	cresol (18) (24)
butyric acid (21) (22) (24)	methoxyphenol(18) (24)
isobutyric acid (21) (22)	1,4-benzenediol (21)
valeric acid (22) (24)	3-methyl-1,2-benzenediol (21)
2-and/or 3-methylbutyric acid (22)	dimethylphenol(18)
hexanoic acid (24)	ethyl guaiacol (24)
palmitic acid (21)	1,2-dimethoxybenzene (24)
succinic acid (21)	dimethoxyphenol (24)
glutaric acid (21)	Vanillin (24)
adipic acid (21)	Vanillyl alcohol (24)
methylsuccinic acid (21)	methoxycatechol (24)
2-methylglutaric acid (21)	naphthol (24)
4-oxohexanoic acid (21)	levulinic acid (21) (24)
	2,3-dihydroxybenzoic acid (21)

*Note: reference numbers are in parentheses

The components are similar to those reported at PNL (see Table 2) with a much larger fraction of organic acids identified.

Based on titrations of the aqueous phases, the actual masses of acids and anions were determined. The weight percentages of these materials ranged from 1.3% to 3.3% in single-pass tests and up to 27.0 wt % in a multiple-recycle test. Estimated neutral organic concentrations in the aqueous phase from single pass tests ranged from 1.2% to 6.0% but remained at only 3.2% in the recycle test. Apparently, the acids and anions, being less volatile, tended to concentrate in the aqueous phase during recycle operations while the neutral components tended to flash overhead

in the pressure letdown. The overhead aqueous condensate from the recycle test contained an estimated 6.7 wt % neutral organics and only 0.43 wt % acids and anions.

Other information that corroborates these results can be found in the literature from other biomass liquefaction research efforts in Canada and Europe. One important paper from the University of Saskatchewan deals specifically with the aqueous byproducts from biomass liquefaction in a high-pressure water slurry. The paper reports that up to a third of the biomass is lost to the aqueous phase²². Separation of the aqueous phase components was undertaken and analysis of two of the phases is reported in detail. The components identified are found in the list in Table 2. In addition to the two phases described in detail, the paper also mentions that the other two fractions contain low molecular weight phenolics.

Research results from the University of Toronto provide additional input from a batch catalytic hydrogenation of wood in water and batch steam pyrolysis of wood. Both systems show significant loss of organic to the aqueous phase. In the hydrogenation, batchwise recycle of aqueous was tested with final concentrations reaching 40-50 g/L TOC (4%-5%).

This level of contamination represents about 18% of the wood feed ending up in the aqueous stream²³. Aqueous recycle tests with the high-pressure steam pyrolysis gave similar results²⁴. A single pass resulted in 20 g/L TOC, which increased to 60 g/L after two recycles. During the recycle process, the increase in organic contamination was found to result from additional acetic acid in the aqueous phase while phenolic content increased only slightly. Numerous chemical components were identified (see Table 2) and quantitative yield information is provided. The major component in the aqueous phase was acetic acid.

The aqueous phase from one test at Toronto was the single aqueous phase analyzed in the Canadian centralized analysis effort in support of biomass liquefaction¹⁵. The dilute nature of the sample (4%-5% TOC) made the proton nuclear magnetic resonance (NMR) analysis nearly meaningless, but an extended time run on the carbon-13 NMR spectra showed a strong contribution from acetate (2.38% total acids by high-performance liquid chromatography). Many other components were suggested by the numerous strong resonances in the spectra. No sugars were detected by normal silylation procedures on a gas chromatograph.

From peat liquefaction tests at the Royal Institute of Technology in Stockholm, published results show high levels of water contamination by organics. In two experiments TOC is reported as 8.9 and 15.0 g/L. The yields of water and water solubles are lumped together with losses in the data, so the yield of water soluble organics from peat is probably less than the reported amount, 18% to 26% of carbon²⁵.

Flash Pyrolysis

One perceived advantage of flash pyrolysis systems for the production of liquid fuels from biomass is the absence of a byproduct aqueous stream with the inherent loss of organic product. The highly oxygenated (hydrophilic) oil components produced in flash pyrolysis allow more complete solubilization of the water into the oil product. As a result, all the leading flash pyrolysis process developers claim a stable single-phase product with no wastewater stream (see reference 6). In effect, the wastewater stream is dissolved in the oil product and is included in

the product stream. If the oil is used as turbine fuel, the wastewater is effectively incinerated with the oil product.

Lack of an aqueous phase is limited to operations with highly oxygenated biomass forms. Experiments with flash pyrolysis of peat²⁶ or municipal waste components (particularly plastics)²⁷ resulted in two phase products. The peat aqueous product has been analyzed to show 11.4 wt % carbon loading made up of a number of some oxygenates and anhydrosugars (see Table 3). These are the same components reported for cellulose and wood pyrolysis studies²⁸.

Table 3. Aqueous Phase Components from Flash Pyrolysis

Formic Acid	Methanol
Acetic Acid	Cellobiosan
Formaldehyde	Levogluconan
Glyoxal	Glucose
Hydroxyacetaldehyde	Fructose
Acetol	Glyceraldehyde
Ethylene Glycol	Methylglyoxal

Aqueous phase separation can be forced even with wood flash pyrolysis oils. If steam is used as the carrier in the pyrolysis reactor, a second aqueous phase is more likely to be produced. The effect is similar to that reported with the addition of water (to levels >25%) to flash pyrolysis oil to separate it into aqueous and tar phases²⁹. Such a procedure has been used to recover the chemicals that preferentially separate from the tar into the aqueous phase (see reference 7).

A more general consideration of pyrolysis of biomass would include the older slow pyrolysis systems, which produce more char and less oil. Because of more severe processing conditions (higher temperature, longer residence time), the oil products from these systems contain less chemically bound oxygen and are less hydrophilic. As a result, there is usually a two-phase liquid product: a less dense pyrolysis water phase that is highly contaminated with organics and a heavy tar phase that also contains a significant amount of dissolved water. If this oil product is used as boiler fuel, the wastewater stream is usually co-fired with the oil in the boiler.

Another variation of the flash pyrolysis system is the vacuum pyrolysis system being developed in Canada. This multiple-hearth reactor was envisioned as a useful fractionating system for the pyrolyzate oil. If chemicals are the product of the process, the separation is useful; if boiler fuel is the product from the process, the fractionation achieved may be less useful. Typical operations of the vacuum pyrolysis system result in a primary oil product and a secondary condensate product, which is a highly contaminated byproduct water³⁰. The organic content of the secondary condensate is reported to range from 45% to 55%, but process improvements (primarily in cooler design) are projected to lower the level to 10% to 20%. The characterization of the carboxylic acids in the aqueous phase has also been reported³¹.

Process Wastewater from Upgrading Biomass Oils

Hydroprocessing Operations

Upgrading biomass oils by hydroprocessing can lead to fewer water treatment requirements. The hydroprocessing reacts hydrogen gas with the oils to remove oxygen and make them more volatile. Both of these changes make the oil less water soluble, resulting in cleaner byproduct water streams. The more complete the hydroprocessing, the less contaminated the byproduct water. Unpublished data from our own research at PNL on hydrotreating high-pressure biomass liquefaction oils show that the carbon level in the byproduct water from hydrotreating operations is generally around 0.1 to 0.2 wt % when the product gasoline contains less than 1% oxygen. As less oxygen is removed from the oil, more oil is left dissolved in the water; i.e., 1% carbon in water at 2.5% oxygen in oil and 2% carbon in water at 5.5% oxygen in oil. The dissolved components were assumed to be oxygenated remnants of the biomass oil.

For the case of hydroprocessing pyrolysis oils, the single-step, nonisothermal procedure was developed, at least in part, to eliminate the wastewater treatment problem resulting from separating the aqueous condensate following the low-temperature hydroprocessing stabilization step. The recovered wastewater following low-temperature hydroprocessing is highly contaminated with up to 17 wt % carbon having been measured. Separation and loss of this material is detrimental to the process. By proceeding with the single-step upgrading, which produces a gasoline hydrocarbon product, the loss of feed carbon to the wastewater was much lower, 0.6% to 1.0% carbon in the water for products containing 0.8% to 1.5% oxygen (see reference 11). Intermediate levels of processing the pyrolyzates results in increased levels of wastewater contamination similar to the high-pressure oil processing. The numbers from PNL unpublished data range from 5% carbon in the water with a 16% oxygen content oil to 17% carbon dissolved in the water with a 34% oxygen content oil. As mentioned above, the dissolved components were assumed to be oxygenated remnants of the biomass oil.

Catalytic Cracking Operations

An advantage of the catalytic processing of the pyrolysis vapors is the elimination of the condensation step and potential for water phase separation. By processing the primary vapors immediately to the fuel components, the condensed product is a hydrophobic hydrocarbon rather than an oxygenated oil. Little information is available on the specifics of this product and the condensate streams. Most of the descriptive information suggests that all the aqueous condensate streams will be incinerated in the conceptual process.

An inherent quality of the cracking process is its less specific mechanism. Some of the primary pyrolysis product is deemed to be unreactive on the zeolite catalyst. This material, mostly phenolic, is expected to be concentrated in the aqueous byproduct and incinerated in the conceptual process. Other pyrolysis components will be reacted to coke on the catalyst and will be burned in a catalyst regeneration step. As a result, the process developers envision that no wastewater treatment will be necessary.

Identification of Environment, Safety, and Health Criteria

In general, the statutes and regulations discussed in this section protect human health and the environment by regulating discharges to the groundwater, surface water, and soil. To do so, 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 and design criteria that must be met to satisfy the regulatory standards. Some permits authorize discharges of substances to the environment; others 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 federal government's Environmental Protection Agency (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.

There are several overlaps in the process. Congress enacted federal environmental pollution control statutes that direct EPA to promulgate implementing regulations. These statutes may also direct or authorize the states to develop regulatory programs. As a result, the states can develop both "flowdown" statutes, which restate or are more stringent than the federal regulations, and "nonflowdown" statutes, which are regulations encompassing areas not covered by the federal regulations. All these regulations are subject to continual updating, which usually tightens the restrictions. In addition, Department of Energy (DOE) operations are subject to DOE orders that cover wastewater handling.

The procedure for obtaining permits to build and operate a biomass liquefaction plant will include a careful review of all the appropriate environmental regulations. First a Notice of Intent to file an environmental assessment will be given to EPA. The subsequent assessment will be made to determine whether a full-scale Environmental Impact Statement must be prepared or if a Finding of No Significant Impact can be made. The assessment will include a preliminary evaluation of environmental impacts of the proposed project, including effects on public health and welfare, archeological sites, historical values, endangered species concerns, and property values, along with any need for governmental permits. The Environmental Impact Statement is a more detailed evaluation of all these issues as well as an evaluation of alternatives to the preferred project plan. Preparation of each of these documents includes public input periods and governmental review.

This discussion is written from a federal government point of view as a reasonable baseline for consideration at this point in the development of biomass liquefaction. However, some states (Washington, for example) have implemented even more strict pollution control measures, as they are allowed under the federal legislation. Therefore, the specific site of the biomass liquefaction plant will determine the exact level of pollution control required. In addition, these regulations seem to be subject to continual change, which almost always leads to tighter control. As a result, when the biomass liquefaction plant is built, the level of pollution control required will almost certainly be more stringent than it is now.

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 purposeful or accidental. Therefore, plant design should take into account releases of all types. Maintenance procedures as well, especially equipment cleanout, need 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.

Statutes and Regulations that may be Applicable

Resource Conservation and Recovery Act of 1976 (RCRA)

RCRA provides for "cradle-to-grave" regulation of the generation, transportation, storage, treatment, and disposal of hazardous and nonhazardous solid waste. RCRA was amended and expanded in 1984 by the Hazardous and Solid Waste Act. "Solid waste" is broadly defined in RCRA to include almost all waste forms, including liquids and compressed gases. RCRA provides for the classification of waste as hazardous or nonhazardous based either on characteristics, source lists, or identifying criteria. Biomass liquefaction (or any type of biomass conversion) is not found on the source lists; therefore, the wastes could not be ruled hazardous on that basis. Some of the characteristics may apply to biomass liquefaction wastewaters in some cases. The characteristics include ignitability (flash point $<60^{\circ}\text{C}$), corrosivity ($\text{Ph}<2$ or $\text{Ph}>12.5$ or steel corrosion >0.25 in./yr @ 55°C), reactivity (numerous examples that do not apply), or TCLP (toxicity characteristic leaching procedure). TCLP toxicity includes a list of numerous elements and compounds with concentration limits. The concentration can apply to the extract of a solid waste (using the standard TCLP method) or the concentration of the liquid waste itself. The components of interest in biomass liquefaction in the current (March 1990) TCLP list are given in Table 4.

Table 4. Partial TCLP List of Maximum Concentration of Contaminants

Dangerous Waste Number	Contaminant	(Chemical Abstract Services	mg/L
D004	Arsenic	(7440-38-2)	5.0
D005	Barium	(7440-39-3)	100.0
D018	Benzene	(71-43-2)	0.5
D006	Cadmium	(7440-43-9)	1.0
D007	Chromium	(7440-47-3)	5.0
D023	ortho-cresol	(95-48-7)	240.0
D024	meta-cresol	(108-39-4)	240.0
D026	para-cresol	(106-44-5)	240.0
D026	Cresol (total)		240.0
D008	Lead	(7439-9201)	5.0
D009	Mercury	(7439-97-6)	0.2
D035	Methyl ethyl ketone	(78-93-3)	240.0
D038	Pyridine	(110-86-1)	5.0
D010	Selenium	(7782-49-2)	1.0
D011	Silver	(7440-22-4)	5.0

The balance of the TCLP list includes nitro-aromatics, chlorinated hydrocarbons, and pesticides. None of these is likely to be found in biomass liquefaction wastewaters. Phenol is a curious omission from this list in light of the inclusion of cresols.

The more general criteria for identifying hazardous wastes may also apply. These criteria include human toxicity at low doses or animal toxicity if human data are not available. The animal levels are oral LD50 (rat) at <50 mg/kg, inhalation LD50 (rat) at <2 mg/L, or dermal LD50 (rabbit) at <200 mg/kg. Secondly, the waste may contain any of a long list of components that may be present in such concentration as to be hazardous or that could degrade to a hazardous component. Consideration is given to the amount and disposal method for the waste and the impact on the environment, as well as evaluations from other governmental agencies or regulatory programs. Components likely to be found in biomass liquefaction effluent are in Table 5, a subset of the TCLP list.

This component list is apparently based on toxicity data in the literature. The specifics of why one component is listed and a similar component is not is not explained. Because this criteria basis for hazardous designation is a judgment call, similar components may be considered by the EPA in the designation process. The "P" numbered components at the top of the list are considered hazardous even at very low concentrations; the "U" numbered components are considered hazardous only at higher concentrations.

Clean Water Act

The Clean Water Act was enacted to protect surface waters from point and nonpoint sources of pollutants. Under this act, all discharges of pollutants must be in compliance with a National Pollutant Discharge Elimination System (NPDES) permit that is issued by the EPA or the state, if EPA has delegated NPDES authority to the state. Two general sets of standards that may be applicable have been promulgated under the Clean Water Act: categorical standards and water quality standards. Categorical standards are applicable to various categories of industrial discharges. Water quality criteria are not promulgated but are published as a separate document that is updated periodically.

To be allowed to dispose of wastewater outside of a hazardous waste disposal site, either a NPDES permit must be obtained or the wastewater must be accepted into a POTW (publicly owned treatment works). To obtain a NPDES permit for a wastewater stream, the flow volume and contamination level must be defined. The level of contamination allowed is subject to negotiation. Gaining acceptance by a POTW is similarly based on negotiation. Potential exists for higher levels of discharge to be allowed into the POTW because of the dilution of the stream with other waste streams. The POTW operates under a permit similar to a NPDES permit and must meet certain contaminant levels in its effluent. The same EPA or state organization will issue either the NPDES permit or the POTW's permit.

Safe Drinking Water Act

The Safe Drinking Water Act (SDWA) was enacted in 1974 and amended in 1986. To protect public drinking water sources, EPA is required to develop mechanisms to control bacterial and chemical contaminants and to regulate the underground injection of contaminants into groundwater. The SWDA mandates the creation of primary and secondary standards to regulate the

Table 5. List of Hazardous Constituents in Biomass Liquefaction Wastewaters

<u>Dangerous Waste Number</u>	<u>Contaminant</u>	<u>Chemical Abstract Number</u>
P005	2-propenol (allyl alcohol)	107-18-6
P054	Aziridine (ethylenimine)	151-56-4
P067	2-methylaziridine	75-55-8
P075	Nicotine	54-11-5
P003	2-propenal (acrolein)	107-02-8
P005	2-propen-1-ol (allyl alcohol)	107-18-6
U001	Acetaldehyde (ethanal)	75-07-0
U112	Ethyl acetate	141-78-6
U144	Lead acetate	301-04-2
U002	Acetone	67-64-1
U004	Acetophenone	98-86-2
U008	Acrylic acid (2-propenoic acid)	79-10-7
U113	Ethylacrylate	180-88-5
U118	Ethyl methacrylate	97-63-2
U162	Methyl methacrylate	80-62-6
U012	Aniline	62-53-3
U157	1,2-dihydro-3-methylbenz(j) aceanthrylene	56-49-5
U018	Benz(a)anthracene	56-55-3
U094	7,12-dimethylbenz(a) anthracene	57-97-6
U019	Benzene	71-43-2
U239	Dimethylbenzene (xylene)	1330-20-7
U201	1,3-benzenediol (resorcinol)	108-46-3
U220	Methylbenzene (toluene)	108-88-3
U055	1-methylethylbenzene (isopropylbenzene, cumene)	98-82-8
U022	Benzo(a)pyrene	50-32-8
U197	Quinone	106-51-4
U031	1-butanol	71-36-3
U159	2-butanone (methylethylketone)	78-93-3
U053	2-butenal (crotonaldehyde)	4170-30-3
U050	Chrysene	218-01-9
U051	Creosote	----
U052	Cresol (cresylic acid)	1319-77-3
U056	Cyclohexane	110-82-7
U057	Cyclohexanone	108-94-1
U063	Dibenz(a,h)anthracene	53-70-3
U064	Dibenz(a,i)pyrene	189-55-9
U094	7,12-dimethylbenz(a) anthracene	57-97-6

Table 5. List of Hazardous Constituents in Biomass Liquefaction Wastewaters (Concluded)

<u>Dangerous Waste Number</u>	<u>Contaminant</u>	<u>Chemical Abstract Number</u>
U101	2,4-dimethylphenol (2,4-xyleneol)	105-67-9
U120	Fluoranthene	206-44-0
U122	Formaldehyde	50-00-0
U123	Formic acid	64-18-6
U124	Furan	110-00-9
U213	Tetrahydrofuran	109-99-9
U125	Furfural	98-01-1
U137	Indeno(1,2,3-cd)pyrene	193-39-5
U140	2-methyl-propanol (isobutyl alcohol)	78-83-1
U151	Mercury	7439-97-6
U154	Methanol	67-56-1
U161	4-methyl-2-pentanone (methyl isobutyl ketone)	108-10-1
U165	Naphthalene	91-20-3
U166	1,4-naphthalenedione (naphthoquinone)	130-15-4
U188	Phenol	108-95-2
U196	Pyridine	110-86-1
U191	Methylpyridine	109-06-8

quality of water that is available to the public through community and noncommunity water systems. Primary standards protect public health by establishing maximum contaminant levels (MCL). MCLs are limits based on maximum contaminant level goals (MCLG), the levels at which public health will not be adversely affected. MCLs are set as close to the MCLGs as is technically feasible. Secondary standards, Secondary Maximum Contaminant Levels, protect public welfare by regulating the aesthetic qualities of water.

The MCLs currently in place apply only to a short list of inorganics and organic compounds. The inorganics are the metals found in the TCLP list in Table 4 plus nitrate analysis. The organics are the pesticide chemicals from the TCLP list and a total trihalomethanes analysis. The MCLs are two orders of magnitude in concentration below the TCLP levels. If the wastewater from biomass liquefaction was found to be a nonhazardous waste under RCRA (or was cleaned up to that level) it could then be discharged if it met the SWDA standards. A NPEDS permit would be needed so that flow volume of the waste could be controlled.

This discussion is limited to the liquid effluents from biomass liquefaction. Not discussed here are the gas emissions, which will also be regulated. Gas emissions will include leakage from equipment. RCRA regulations also apply to the solid waste streams that might be produced in biomass liquefaction.

Identification of Data Gaps and Research Needs

The category of direct biomass liquefaction covers processing conditions that lead to a range of product properties. The aqueous byproduct streams have received limited analysis because of the priority placed on the analysis of the complex organic liquid product. The aqueous byproducts will carry organic contaminants that directly correlate both in quantity and quality with the composition of the liquid oil product. Although the data in the literature can give a general feeling for the types and amounts of components expected in biomass liquefaction wastewater, the data are not sufficient to prepare a general model to predict the wastewater composition from any given liquefaction process. Therefore, further study will be needed on the wastewater from any specific biomass liquefaction process as the process moves forward in development. Analysis must address both the organic contaminants and inorganic residues.

It is possible to avoid a separate aqueous byproduct phase in the case of the flash pyrolysis processes, which produce a highly oxygenated oil that includes the aqueous phase as a dissolved component. In these cases, care must be exercised to maintain the single phase by controlling the amount of water introduced into the process stream and by making a total product collection in a single step without separation of an aqueous-rich stream. There is some conflict in the opinions as to the amount of water that will result in the formation of a separate water layer. More study is needed to define a model that considers the oil components and their source (feedstock and operating conditions) and can predict the amount of water that is soluble in the oil and at what level of dissolved water a second aqueous-rich phase will separate from the oil.

Much less is known about the aqueous byproduct streams produced in the upgrading of the biomass liquefaction products to turbine or engine fuels because much less research has been performed on these upgrading processes. In all the upgrading technologies, the common factor is the removal of oxygen from the liquid product, which results in the separation of an aqueous byproduct phase. Again, depending on the chemical properties of the upgraded product, the aqueous byproduct can contain a range of organic contaminants. Further analysis is needed to better define the aqueous byproduct contaminants. These contaminants will include both the organics and also catalyst residues.

In some process cases, it has been proposed that the aqueous stream has fuel value for the process and can be burned in an incinerator. No test data are available for such incineration systems based on biomass liquefaction wastewater. More complete analysis of the aqueous byproducts may allow an educated guess as to the incineration properties of these materials, but test incineration of the streams would be more convincing.

Alternative wastewater processing measures also need to be tested. Both biological and thermochemical processes have been proposed but none has yet been tested. Both aerobic and anaerobic biological systems as well as oxidative and catalytic reforming thermochemical systems should be considered.

A major gap in the information on biomass liquefaction wastewater treatment is a full understanding of the regulatory environment that applies to the process. The wastewater treatment regulations themselves are still subject to much revision. It is apparent that certain chemicals produced in biomass liquefaction will be of concern to regulators. Because the implementation time period and site for the biomass liquefaction process will have a strong impact on the

wastewater requirements, it seems inappropriate to try to further limit development of the processes based on perceived regulations at some unknown future time and place. However, process developers should maintain an awareness of the regulatory environment as it might apply to them.

Proposed R&D Strategy

Based on this review of the biomass liquefaction wastewater treatment requirements, a number of research needs have been identified. The following proposed R&D strategies are meant to address these needs. These strategies all require further operation of pyrolysis and upgrading units for production of product materials for study.

More analytical chemistry is needed to better understand the composition of biomass liquefaction wastewaters and their treatment requirements. This analytical chemistry should be focused on the process concepts deemed most useful; i.e., flash pyrolysis systems and oil upgrading processes. A perceived advantage of the flash pyrolysis systems is their lack of a separate aqueous phase. Thus, most of the analytical effort will be focused on the upgrading byproducts.

Treatment technologies need to be tested with biomass liquefaction wastewaters. Potential systems include oxidation and catalytic reforming as well as biological treatment systems. Oxidation systems include conventional incineration, wet oxidation, or chemical oxidants, such as ozone or chlorine. The catalytic reforming is a new technology for pressurized conversion of organics in water to fuel gases. Biological treatment systems, such as aerobic or anaerobic digestion, should also be tested on biomass liquefaction wastewaters. All of these systems should be evaluated for potential use in biomass liquefaction wastewater treatment. Bench-scale testing should be undertaken for those systems determined to be most applicable.

A third area of research is the elucidation of the phase properties of the flash pyrolysis oil/water system. Stability of the single phase oil is of paramount importance to the good handling properties of the pyrolysis oils. The effect of feedstock composition and moisture content on the oil composition and its water solubility needs to be better defined. Water solubility (true solubility? stable emulsion?) in the pyrolysis oil needs to be studied to be better understood. The effect of the product collection procedure on the oil properties and the use of steam in the process are both important in determining the stability of the single phase in the oil product and need to be studied further.

An ongoing, low-level effort needs to be maintained, probably at the program office level, to monitor the regulatory environment as it affects the wastewater (and other waste streams) treatment issue.

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