Wastewater Treatment Options for the Biomass-To-Ethanol Process

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By:
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DRAFT REPORT
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I. Introduction

NREL (National Renewable Energy Laboratory) contracted with Merrick & Company (Merrick) to provide expertise in evaluating Waste Water Treatment Alternatives for various ethanol manufacturing processes. Three Lignocellulosic Biomass-to-Ethanol processes are currently under development by NREL. Each could require different treatment depending on various characteristics of the waste water stream volume and strength. To initiate the evaluation, Merrick met with NREL engineers and scientists in interactive meetings, where the appropriate designs were developed for each of the processes.

II. Waste Water Treatment Processes

Initial designs for the processes showed the potential for large waste water streams which could require extensive treatment systems. During discussions, Merrick showed the trend in the current, similar ethanol and pulp and paper industries to recycle various water streams internally in the process and to reclaim waste water with appropriate treatment to allow recycle. Especially over the past 20 years, once-through water systems have been replaced with minimum discharge systems. This is due not only to the cost of treatment for waste water, but also minimization of environmental impact, cost and availability of makeup water, etc.

In order to guide the selection of the best alternatives for waste water treatment, Merrick created a "map" of potential alternatives and potential internal process changes that would change the volume and strength of the system discharge. The map is shown in Appendix A. The map shows the effects of incorporating various subsystems into the process to minimize waste water generation. A few of the important aspects considered were:

- Elimination of combining all or most waste waster streams into one grand glop for simultaneous treatment. Previous flow schemes routed most waste water streams to a single Waste Water Tank. From this tank water was sent to treatment and then part of the treated water was recycled to the process. By selecting waste water streams which can be recycled individually upstream of treatment the treatment systems become much smaller and overall plant efficiency is greatly increased. Since some waste water streams are cleaner than others, it is better to do minor treatment of the relatively cleaner streams to allow reuse or recycle within the process. This both lowers the volumes of waste water and makeup water and also minimizes the treatment costs for the easily treatable streams.

Also, the objective of waste water treatment is to concentrate contaminants into a relatively small stream, leaving the major stream sufficiently clean for reuse or discharge. If a waste water stream is already somewhat concentrated, it will cost more to re-concentrate the contaminants if it becomes diluted due to mixing with less contaminated streams. Combining the centrifugation of the stillage with evaporation is advantageous in optimizing the recycle.

- Centrifugation of stillage, after the first stage of evaporation, removes the easily recoverable solids before they are combined with any other stream. Combining the streams would make the solids recovery more difficult and expensive. The recovered solids can be used as fuel or sold as byproducts rather than requiring treatment.

- Evaporation of stillage/centrate (the second and third evaporation stages are downstream of centrifugation) using heat integration with the distillation section of the process. The heat available in the required ethanol distillation section would otherwise require extra cooling (water).

Using these and other recycle options, two developments significantly minimized the size of the waste water treatment systems.

1. NREL developed with another contractor an integrated water recycle design intimately associated with the distillation system design. ***Both centrifugation and evaporation were incorporated into the design.***

2. Merrick simultaneously evaluated the application of four alternatives to treatment with various degrees of recycle. Merrick specifically evaluated:
    1. Evaporation (and Incineration)
    2. Stream Discharge
    3. Land Application
    4, Discharge to a Publicly Owned Treatment Works (POTW).

The result is shown in Appendix B, which gives the costs to accomplish treatment of waste water without the improvements listed above (centrifugation and evaporation). As can be seen, the cost for treatment of the full volume of waste water is prohibitive.

Therefore, ***Merrick and NREL reduced the stream volume to that which could be expected from maximization of recycle, evaporation and centrifugation within the process.*** The flow scheme for water and reuse is shown in Appendix C. The waste water system now has significantly reduced flow, making onsite treatment easily achievable with conventional treatment systems.

Below is an explanation of the fully developed systems available for the past 10-20 years to treat these “high strength biologically treatable” streams. In actuality, the current sizing and strength of ***the waste water streams for the three NREL processes are all within the same typical treatment methodology: Anaerobic Treatment followed by Aerobic Treatment.*** Appendix D shows the reasons for application of these treatment steps as developed by industry.

III. Evaporator Syrup Disposition

The concentrate or syrup from the evaporator can be sent to the boiler directly or to the anaerobic digester. Merrick assumed that the syrup could be sprayed or mixed with the lignin cake and sent to the boiler as fuel in a first option. If the evaporators use all of the waste heat in the distillation section the syrup is predicted to contain 7.5 to 8% solids. Using a heat of combustion for the syrup solids of 8000 BTU/lbs. the syrup will have a negative heating value in the boiler. The syrup must be concentrated to about 12.5% solids for a break-even heating value.

The second option would be to send the syrup to the anaerobic digester. The digester and all downstream equipment becomes larger including the aerobic unit but this is somewhat offset by the production of more methane gas (boiler fuel) in the anaerobic digester.

Appendix G contains the comparison that was conducted. Various configurations of the anaerobic/aerobic units were considered and judged based on simplicity (ease of operation and maintenance) and cost. The decision was to burn the syrup at approximately 7.7% solids with the lignin in the boiler.

IV. Flows and Strength of the waste:

The stillage from the three processes qualifies as "high-strength" waste. At the beginning of the project, the CODs and BODs (Biological and Chemical Oxygen Demand) of each process were presented by NREL based on testing simulated stillage (Pinnacle 1998; Evergreen Analytical 1998) and an initial mass balance. These initial estimates are presented in Table 1.

Table 1

PROCESS	**FLOW (Kg/hr)**	**COD (Mg/L)**	**BOD (Mg/L)**	**Ratio BOD/COD**
Enzymatic	307,221	27,000	13,400	.496
.				
Softwood	438,113	37,000	18,300	.495
Counter-current	668,314	54,000	29,400	.544

Upon evaluation of these initial estimates, a revised general waste treatment flow schematic was developed. This followed the typical evolution of ethanol plant designs over the past 15-20 years. To minimize costs of wastewater treatment and to minimize any makeup water requirements, the ethanol plant designs have incorporated various water recovery/cleanup/reuse schemes. Merrick developed with NREL, a typical scheme which used centrifugation and evaporation to concentrate waste into smaller stream flows.

The revised process(es) developed by others (Delta-T design for evaporation and dehydration, a separate project currently underway) similarly integrate the distillation step with waste treatment processes including evaporation and centrifugation for concentration of solids in the distillation column stillage.

The revised flow schematic includes various streams being recycled (or "backset" in the language of the ethanol industry). The new flow schematic also includes waste treatment streams from ion exchange (detoxification), pretreatment flash vents, syrup and condensate from the evaporator. The new schematic also includes waste waters from boiler and cooling tower blowdown to be included in the overall waste treatment process.

Following these revisions, a preliminary estimate of the strengths of the wastewater was performed. This estimate assumed that the removal of most of the soluble components from the stillage would reduce the COD of the wastewater to 3,000-7,000 mg/L. The assumed parameters for each case are shown below in Table 2.

Table 2

PROCESS	Projected Flow (Kg/Hr.) (MGD)	Projected COD (Mg/L.)
Enzymatic	126,631 (0.8 MGD)	2,938 Mg/L to digester, 235 Mg/L to aerobic
Softwood	173,835 (1.1 MGD)	4,173 Mg/L to digester, 334 Mg/L to aerobic
Countercurrent	250,767 (1.6 MGD)	6,510 Mg/L to digester, 520 Mg/L to aerobic

As can be seen by the stream flows and strengths, the designs will now be suitable for typical industrial "high strength biologically treatable waste water." These waste water streams can be economically treated in either package plants of standard designs or in small custom plants with standard processes. Costs for each system were then projected by vendors and are contained in Appendix F. After the initial cost estimate was completed, the ASPEN model was completed. The ASPEN model used the soluble chemical constituents to project a COD loading into wastewater treatment. The estimate assumed that COD was a measure of the amount of oxygen required to convert all of the carbon in a specific compound to carbon dioxide. For example, the COD of glucose is 1.07 kg oxygen/kg compound and is calculated as follows:

$C_6H_{12}O_6 + 6\ O_2 \;=\; 6\ CO_2 \;+\; 6\ H_2O$

COD of glucose = (6 kgmol O2*32 kg/kgmol)(1 kgmol glucose*180 kg/kgmol)

COD of glucose = 1.07 kg oxygen/kg glucose

The COD values calculated for the components in the NREL process using this methodology are summarized in Table 3.

Table 3
Component COD Factors

Component	COD Factor (kg COD/kg)
C-6 and C-5 Sugars and Oligomers	1.07
Cellobiose	1.07
Ethanol	2.09
Furfural	1.67
Lactic Acid, Acetic Acid	1.07
Glycerol	1.22
Succinic Acid	0.95
Xylitol	1.22
HMF	1.52
Soluble Solids	0.71
Soluble Unknown	1.07
Corn Oil	2.89
Acetate Oligomers	1.07
Acetate	1.07

As shown on the table, the COD for most components is slightly greater than unity. This approximation agrees well with practice; CODs of sugar-based streams generally range from 1 to 1.1 (kg COD/kg component) (Nagle 1998a). This method of approximation, however, did not agree well with the initial estimates of the strength of the wastewater; it resulted in COD loadings that were 5 to 10 times higher than the earlier projections. This discrepancy was due, in part, to the different methods used to determine COD. The initial, lower COD values, were based on a rule-of-thumb estimate where 1 pound of soluble solids was equivalent to 1 pound of COD (Ruocco 1998). This method did not take into account any soluble liquids (e.g., furfural) or the relative flowrates of the soluble solid components. In addition, initial stream flows on PFDs did not include all soluble solids (e.g., ammonium acetate) in its calculation of the soluble solid percentage.

In any case, a reliable method of projecting the COD of the wastewater needed to be developed. Thus, as noted earlier, NREL sent out samples of SSCF effluent from each of the 3 processes to determine the COD content and to test each samples digestibility (Pinnacle 1998; Evergreen Analytical 1998). In addition, a component analysis of the samples was conducted (McMillan 1998). To simulate distillation, all samples were stripped of ethanol using a constant volume technique so that concentration of the species would not occur. Copies of the test results are contained in Appendix G, Attachment 4.

Because these samples were not subjected to evaporation or ion exchange, they do not represent the composition of the streams to the wastewater treatment. However, they can be used to test the methods of COD projection. The predicted COD using the factors in Table 2 and the composition (without ethanol) for the enzyme process (McMillan 1998) is 28,398 mg/l. The average of 3 measured values for the enzyme process (Pinnacle 1998; Evergreen Analytical 1998) is 27,199 mg/l, an error of less than 5%. Thus, the method used in the ASPEN model appears reasonable.

A more detailed compositional analysis of the enzyme sample was also conducted. However, these values were not used due to possible contamination (McMillan 1998a). In addition to the reported values, Attachment 4 of Appendix G contains a spreadsheet that calculates the projected COD value.

Using the methodology outlined for the ASPEN model and using the W9809i model, the strength of the wastewater for the enzyme case is projected to be 32,093 mg/L with a total flowrate 188,129 kg/hr. Since the ASPEN models of the other 2 processes are not yet complete, no new estimate of the strengths and flows of these processes can be made. These parameters were then used to obtain an updated cost estimate for the wastewater treatment process. These costs are contained in Appendix J.

In the initial model, the BOD is calculated as 70% of the COD for all waste streams. This approximation agrees well with published ranges for COD and BOD for similar wastewater (Perry 1998). Although data on SSCF effluent predicts a lower BOD/COD ratio, with an average value of 52% for all technologies (Evergreen Analytical 1998), the wastewater in the model, will have a different composition than that analyzed due to detoxification and evaporation. It is also expected that this ratio will change through each treatment step.

Based on the projected wastewater compositions and the proposed treatment system, the estimated BOD/COD ratio is 0.50 for the influent to anaerobic digestion, 0.20 for the influent to aerobic treatment and 0.10 for the system effluent (Ruocco 1998). Since BOD is a laboratory test and cannot be specifically predicted, the ratios provided above are estimates based on experience with other wastewater systems. The FORTRAN blocks CODCALC1, CODCALC2 and CODEND in the ASPEN model should be updated with the new BOD/COD ratios.

The COD calculations outlined above correspond to the COD loadings for anaerobic digestion. In aerobic treatment, nitrogen-containing compounds such as ammonium acetate will have a significant oxygen demand (e.g., 4.43 kg O_2 required per kg of NH_3).

Since ammonia is not converted in anaerobic digestion, the contribution of the reduced nitrogen compounds is not included in the overall COD calculation. In aerobic treatment, however, these compounds cannot be ignored. This fact requires two significant changes to the model. The first is that reduced nitrogen compounds that are converted in anaerobic digestion (i.e., ammonium acetate and ammonium sulfate) must be treated differently in the ASPEN model. Currently, the carbon and sulfur portions of these compounds are converted to biogas and hydrogen sulfide, respectively, and the other portion is converted to water. This system incorrectly ignores the nitrogen in the effluent from anaerobic digestion. The second major change is in the FORTRAN block CODCALC2. The current COD values are the same as those listed above in Table 3. As discussed, these COD do not include the contribution of reduced nitrogen. This contribution must be accounted for in aerobic treatment.

To remedy this situation, the following specific changes should be made to the ASPEN model:

1. The reduced nitrogen compounds should be carried through the wastewater treatment system as their component ions. Thus, an RSTOIC block should be added prior to the anaerobic system. Here, ammonium acetate would be converted to ammonia and acetate and ammonium sulfate would be converted to ammonia and sulfuric acid.

2. The FORTRAN block CODCALC1 would then need to be modified such that the COD value for acetate was 1.07.

3. Within the anaerobic digestion subroutine, no significant changes would be required except that ammonium sulfate would no longer be converted to hydrogen sulfide and ammonium acetate would no longer be converted to methane, carbon dioxide and water. The new substances, acetate, sulfuric acid and ammonia are already correctly handled in the subroutine. That is, acetate is converted to biogas; sulfuric acid is converted to hydrogen sulfide and water; and ammonia is not changed.

4. As noted earlier, the FORTRAN block CODCALC2 must be modified so that all reduced nitrogen compounds are included in the COD calculation. Since most of these compounds are now noted as ammonia, a new COD factor of 4.43 should be added and applied to ammonia. Ammonium hydroxide should also be added and will have a COD demand of 2.15.

5. The FORTRAN block that calculates the air addition, AERAIR, should be modified so that there is no excess air.

6. The aerobic reactor should be modified so that the ammonia-containing compounds are converted to nitrates as follows:

   $NH_3 + 2.25\ O_2 = NO_3 + 1.5\ H_2O$
   A conversion efficiency of 98% should be used for this reaction.

7. Finally, the FORTRAN block POWER should be modified so that the work stream for the aerators is correct. Each kg of oxygen required uses 2 hp-hr of energy. This should be added to the FORTRAN block as well as an appropriate work stream. The current system comprised of a compressor with an associated work stream should be deleted and replaced as outlined above.

If these changes are made, it is expected that the ASPEN model will correctly simulate the wastewater treatment system. Other strategies would also likely work, but this appears to be the most straightforward method.

V. Waste Water/Sludge Processing

The process flow schematic in the revised recommended configuration retains a burner (sludge incinerator) to combust suspended solids produced by the centrifuge and to probably combust the syrup produced by the evaporator.

The inclusion of a waste burner system is to be compared with alternate sludge processing options in this report. These other options include land application of the sludge, with or without first composting the sludge. Also, this analysis includes the evaluation of the alternatives of evaporation and final treatment by a Publicly Owned Treatment Work (POTW). As can be seen in Appendix B, the relative costs of evaporation and POTW treatment appear to be typically more expensive than onsite treatment of the Ethanol Facility effluent.

VI. Evaporation

Combustion of Fuel for Evaporation or Incineration

The typical methods of evaporation of waste water effluent include energy sources of solar, fuel or waste heat. The alternative of incineration is similar to direct evaporation, especially with respect to the fuel requirements. For an average 1 MGD load of Waste Water (Option I for the Enzymatic Process; higher flows are expected for the other two processes), the energy requirement is about 1 x 8.33 pounds/gallon x 1,000,000 gallons x 1100 Btu per pound (to evaporate at low temperature only) per day. If the energy source is fuel at about $2.20 per million Btu, the cost would be about $20,000 per day or over $7 million per year. Over a 20-30 year life of the project, the fuel cost alone could total over $100 million, or more if fuel costs rise. The capital cost for the evaporation or incineration equipment and the operating and maintenance cost will be additional to this. ***Since the anticipated cost for other alternatives such as treatment by a POTW or on-site treatment is expected to be one-half this cost or less, we will not consider this alternative further.***

Solar Evaporation

If the site has adequate space and adequate solar energy, the costs may be less. Typically solar evaporation is used where there is a net evaporation from a shallow pond after new rainfall adds to the evaporation load. The typical range of net evaporation is 1 to 10 inches of exposed surface per month (1 inch in winter, 10 inches in summer). This translates to 27,154 gallons per acre per month at the minimum. Actual land space required to pond the waste water safely will be about 120-130% of the evaporation surface to allow for dikes, access, etc. In addition, the design should include a holdup volume for storage of excess (peak) waste water and for extended winter evaporation rates.

With a typical net winter evaporation rate of 27,154 gallons per acre per month, even the well integrated Enzymatic Biomass-to-Ethanol facility (about 1 MGD waste water average; about 1.5 MGD design for peak flows) would require well over 1000 acres of land dedicated to solar evaporation. This would include a combination of peak storage for winter and adequate surface area for summer evaporation of average flow plus part of the stored volume. At a cost of about $1200 per acre plus an additional $800 per acre for diking, pumping and piping, etc., this would cost over $2,000,000 for the land alone, if such a large area could be located near the facility. Operating and Maintenance costs, including removal of accumulated solids, would be additional to this. The other Biomass-to-Ethanol processes would require larger acreage and a resulting higher capital and operating cost. ***It is not expected that sufficient land space will typically be available due to the expectation that the location of a biomass facility will not be in an arid, hot, flat region. If a biomass facility is located in such a region, this alternative should be reevaluated using local design information.***

Waste Heat Evaporation

If the Biomass-to-Ethanol facility has any waste heat available, it should already be recovered for other duties in the process if it is economical. This is evident by the sophisticated integration around the evaporator and distillation systems for the developed ethanol plant designs. If excess waste heat is available, it is expected to be at a low level, requiring a vacuum evaporation system with its associated capital and operating costs. The size/cost of this equipment is highly dependent on the available heat level. There may be some significant heat available in the boiler exhaust portion of the facility. However, this heat is most properly integrated into a lignin or other biomass fuel or product drying operation to minimize the fuel required to fire the boiler and to provide boiler feed water preheating.

VII. Irrigation

Another land application alternative is to apply a waste water stream directly to the land in an irrigation situation. This is different than solar evaporation and the application rate to the ground is typically higher since the water is used for a crop. Typical crops could eventually be part of the biomass feed stock for the ethanol facility. However, at present for an existing site, sufficient land and the associated growing season and crop farming operators may not exist.

Handbook of Applied Hydrology by Ven Te Chow, and Wastewater Engineering Treatment, Disposal, and Reuse by Metcalff and Eddy, (the McGraw Hill series in water resources and environmental engineering) were used to ascertain some data contained herein.

Some important aspects of land application for irrigation are:

- Large storage capacity is typically required to accommodate the times when application will not be allowed. This includes about 3-4 months of storage for the winter months, especially if the ground freezes. Land application is not allowed if the land surface is frozen. Also, there may be additional storage required, or additional land required, to accommodate the harvesting of the crop. Overall, full application rates to the soil may be limited to less than one-half the year.
- Concentrations of various contaminants may severely restrict the potential crop choices. Actual experience with a Front Range brewery waste water applied to alfalfa caused cattle feed problems. As a result, the waste water is now applied only to turf farms. This does not appear to be a reasonable design choice for continuous discharge of the waste water.
- Large land areas must be dedicated to the application of waste water. Certainly, in hot and arid regions, waste water is applied to golf courses or park land. However, these areas are typically not adjacent to forest products plants.

VIII. Other Wastewater and Sludge Treatment Alternatives

Another sludge disposal option could be the development of commercial markets for these materials. Such markets could be envisioned as a market for their chemical constituents, a market for these materials as animal feeds or as soil enhancement additives. This co-product development is beyond the scope of this report, however is highly recommended by the contractor for further development to enhance project economic viability.

IX. Suggested Treatment Options:

As can be seen from Table 2, the reduced flows from the three processes average between 1.0 and 2.2 MGD of total flow to the waste treatment block on the process flow schematic. Actual design flows will be higher than these daily averages to account for variations in operation and unexpected equipment unavailability. The attached Appendix E shows typical actual design sizing to accommodate peak daily, weekly, etc. flows.

The suggested treatment system should be a combination of anaerobic biological treatment followed by aerobic biological treatment. This recommendation is based on the calculated flow rates as well as the suggested waste strength.

Anaerobic and aerobic facilities in the 1 to 5 MGD range can be obtained in a variety of process and facility types ranging from custom engineered and constructed “municipal” facilities to vendor distributed and installed package type plants.

For the first draft of this report, contact was made with vendors of “off-the-shelf” package type anaerobic and aerobic plants.

Anaerobic units were selected by Phoenix Biosystems of Colwich, KS, and aerobic units of the sequential cell, aerated, fabric lined earthen pond type were provided by Globe Sampson Associates, Englewood, CO.

These two vendors each provided a table listing the basic equipment and installed cost for their respective units. The tables in Appendix F summarized the two vendor submittals for this draft report.

X. Discussion of Expected Effluent Quality

In general, with influents over 1000 Mg/L BOD, anaerobic digestion (treatment) is the preferred first treatment step. Anaerobic treatment of soluble organics will average over 90% reduction on a COD basis.

For effluents from the anaerobic treatment as influent to the aerobic treatment step of up to 400 Mg/L BOD, the effluent from the aerobic treatment system will average below 10 Mg/L BOD and TSS (Total Suspended Solids).

For effluents from the anaerobic treatment as influent to the aerobic treatment step of between 400 Mg/L to 800 Mg/L BOD, the effluent from the aerobic treatment system will average below 20 Mg/L BOD and TSS.

For effluents from the anaerobic treatment as influent to the aerobic treatment step of up to 1000 Mg/L BOD, the effluent from the aerobic treatment system will average below 30 Mg/L BOD and TSS.

As the site of the proposed facility and therefore the ultimate discharge of the effluents from the waste water treatment facility are unknown, 30 Mg/L BOD and TSS are suggested targets for maximum discharge parameters. 30 Mg/L BOD and TSS are usual stream discharge requirements for the average Western US stream. For the analysis in this report, the discharge standard of 30 Mg/L BOD and TSS are used as the required treatment standard for effluent from the Biomass-to-Ethanol facility. The fact that a particular project effluent could be higher quality than the regulation of 30 Mg/L BOD and TSS does not typically change the requirement for both an anaerobic and an aerobic treatment step. However, if the typical "treatment step" appears over-designed, the design should be evaluated for potential cost savings by reducing the size (residence time) of the equipment to match system performance to the effluent requirement.

Other parameters for waste water discharge requirements such as toxins, metals, nitrogen and phosphorous will have a bearing on treatment steps in the waste treatment scheme finally selected. ***confirm that the list of contaminants does not contain high concentration constituents -- and note this here*** The selected site specific discharge point will have a large effect on the difficulty of treatment and the discharge requirements for these parameters. Since the expected effluent from an unspecified location with a Biomass-to-Ethanol facility does not contain unusually high levels of normally suspect contaminants, this analysis will not have any adjustments for isolated contaminants. However, if a project has a new feed stock with significant levels of regulated contaminants, the project economics should include additional capital and operating costs to properly treat these contaminants.

XI. ASPEN Model

A waste water treatment model was developed and incorporated into an NREL base model (W9806F). The resulting model, P9808B, has been checked into the Basis database. Appendix G gives a detailed description of the model development plus a listing of changes and subroutines.

XII. Treatment of Anaerobic Digester Off Gas

Anaerobic digester off gas is primarily a mixture of methane and carbon dioxide. It is burned in the boiler to recover the heat of combustion of the methane. Late in Task 3 it was noticed that the waste water contains sulfates which will convert to hydrogen sulfide in the digester. The resultant hydrogen sulfide concentration in the off gas is approximately 1800 ppm (wt.). At this concentration the gas must be considered toxic. Further the boiler stack will emit approximately 1.14 tons/day of sulfur to the atmosphere (tons/day of SO2). It is believed that this emission rate would not be permitted in the U.S. EPA regulations are site specific but a useable rule of thumb is less than 100 tpy of SO2 emissions is allowable. Also the anaerobic off-gas will meet toxicity definitions in OSHA 29 CFR 1910.119 and EPA 40 CFR.

It should be noted that the fluidized boiler which burns the anaerobic off-gas may include limestone addition for other sulfurous components in the lignin fuel. If this is the case treatment in the combustion chamber may be more economical than the options described below. The boiler is not in Merrick's work scope.

Two potential treating options were briefly considered to remove hydrogen sulfide from the off gas:

1. Iron Sponge Process and SulfaTreat Process

SulfaTreat is a proprietary process licensed by the SulfaTreat Company, Chesterfield, MO. The process is a vast improvement over the generic iron sponge process. However, because of the large flow rate and daily sulfur tonnage, the SulfaTreat Company found that their process is not practical for the 2000 bone dry tons per day plant size. This is because the process reacts hydrogen sulfide with beads impregnated with ferric oxide. As the ferric oxide is consumed the beads must be changed out. The beads cannot be regenerated but are suitable for landfill. At the large plant size 6500 cubic feet per month of beads are consumed which is impractical. Plant sizes under 1000 bdt/d should consider the SulfaTreat process.

2. Direct Oxidation Processes

U.S. Filter was contacted concerning their Lo-Cat process for the direct oxidation of hydrogen sulfide to elemental sulfur. Lo-Cat is a well known process in the natural gas processing industry and also has extensive application to anaerobic off gas. Several companies offer similar direct oxidation processes.

Lo-Cat can produce the elemental sulfur in several physical forms depending on the market for this material. Most elemental sulfur produced in the U.S. is consumed by the fertilizer industry. The price obtainable for this byproduct is highly site specific and has not, as yet, been included in the plant economics.

U.S. filter estimates the bare equipment cost the Lo-Cat equipment will be $1,500,000 which is a considerable increase over the previous allocation of approximately $56,000 for off gas handling (M-606).

XIII. Plant On-stream Factor

The capital to be invested in equipment sparing must be carefully evaluated against the predicted increase in on-stream factor for the entire plant including the waste treatment sections. The flowsheets and model currently indicate a number of the pumps to be spared yet certain services such as P-611, Clarifier Feed Pump, do not have a spare. Merrick feels it may be possible to delete all installed spares downstream of the aerobic lagoon as the lagoon can be made marginally larger and provide the necessary surge time for equipment repairs. In each case the investment in warehouse spares must be considered based on availability and delivery time for parts. This must be evaluated against the potential for boiler upset due to sudden load variations and against the cost of the larger lagoon. The filter press is in this part of the process and is considered a high maintenance service.

The large decanting centrifuges, S-601 A/D, are key equipment items and each machine is very expensive ($750,000 each, not installed). However this is a difficult service and will have significant individual machine off-stream maintenance. High Plains Corp. at York, NE (corn to ethanol) has multiple spares in a very similar service and list these decanters as one of the three highest maintenance services in the plant.

Rotating machinery of nearly all types tends to have relatively high maintenance. The York plant also listed long-shaft tank agitators in their fermentors and all of the solids/cake conveyors.

Many of the pumps in the plant are moving slurries and these pumps have a much higher maintenance history than pumps moving only liquids provided that the temperatures and pressures are in a normally encountered operating range.

An evaluation of predicted failure frequency, duration of repairs and cost of lost production versus the cost of installed or warehouse spares is the classic method of determining if a spare equipment should be purchased, provided the necessary performance data is available. This evaluation is beyond the scope of the current work.

XIV. General Plant Considerations

The High Plains Corp. of York, NE uses variable speed electric drives in many of their rotating equipment services. They have found this a superior method of process control. Alternatives have maintenance and efficiency drawbacks:

1. Throttling control valves in mixed phase (solid/liquid) service are subject to erosion and plugging. They are considered high maintenance items.
2. Pump arounds can be made practical when properly sized but waste energy in the discharge to suction loop.

3. Belt and screw conveyors can also use recycle (spill-over) control methods but suffer from the same inefficiencies.

It is advisable to consider variable speed drivers for NREL designs. The cost of variable speed electric drives is higher than fixed speed but this may be justified by avoiding expensive specialty control valves, avoiding recycle loops, increasing operating ease, enhancing start-up reliability etc. In this regard, depiction of control methods would enhance the flow sheets and allow more meaningful pressure profiles, hydraulics and pump sizing.

XV. Environmental Emissions

The biomass to ethanol facility is a specific group of chemical processes which in general, break down cellulose and lignin complexes in to sugars. The sugars are subsequently fermented by yeast or bacterial action into ethanol and other left over compounds and biomass.

The basic steps include pretreatment processes which break down the cellulose and lignin complex to simpler compounds and finally with suitable chemicals or enzymes into sugars. These sugars are fermented by either yeast or bacteria yielding ethanol, biomass and left over molecules. The weak beer is consequently distilled and otherwise treated to yield high proof ethanol which is the main product of this process and leftover compounds in the form of suspended and dissolved solids in liquid streams. The leftover compounds become either byproducts worth money, or must be treated as liquid or solid wastes. The biological based feedstocks make the production of most hazardous compounds not an issue. However, some compounds classified as toxic will have to be treated in the waste treatment processes associated with the biomass to ethanol facility.

The biomass compounds which make up the feedstocks for these facilities may be as simple as sugar or ethanol solutions, or as complex as hardwoods, and the leftover molecules from the processing steps will be varied as well.

The fate of left over molecules:

Emissions from sewage treatment plants are in the form of odors and VOC's emitted from the various treatment processes. Molecules not emitted can be "bioconverted" into other molecules and compounds which may be emitted or form part of the biomass or sludge left over from the treatment process. Finally molecules not emitted or bioconverted can be reported as liquid borne emission in the effluent liquids or as semi solid sludge from the waste treatment process. The **FATE** of the produced molecules and compounds in the waste treatment process is the subject of this section of the report.

To discover the FATE of the many potential compounds and molecules that a biomass to ethanol facility can generically produce is beyond the scope of this general section. The authors of this report have had success using one of the many computer models which can trace the fates of molecules in a sewage treatment facility.

Computer models such as “BASTE” (Bay Area Sewage Toxic Emissions), “CHEMDAT 7”, and “SIMS” are examples of commercially available computer models which can be tailored to the exact series of processes that comprise the sewage treatment plant in question. The models each contain embedded data bases containing many chemical compounds which have been found in sewage influents at actual sewage systems. The data bases have bioconversion constants for the biotreatability and Henry’s Constants for the emission and or solubility or each compound.

The model consists of a series of mass transfer algorithms coupled with bioconversion formula which taken in a series consistent with the sewage treatment plant being modeled, allow the concentration of the sewage stream to be calculated for each process in the sewage treatment train. Thus the environmental emissions of any sewage treatment process can be approximated.

Releases to the air, land ,water and other:

Project designers typically use check lists specifically tailored for the biomass to ethanol plant designer. The check lists for air, land, water, and other emissions, will allow the designer to be aware of specific emissions from the plant in each release category. This will allow the designer to begin a permitting process in an early stage in the plant design. Construction permits from Environmental agencies typically require as much as a year of effort to obtain, depending on the specific site of the proposed facility.

Air releases:

An example of such a check list is as follows:

Release	Relevant to the Site	Relevant to the facility	Permitted amount.
Sulfur dioxide	X	X	100 TPY
NOX	X	X	
CO	X	X	
PM10	X	X	25 TPY
Lead			
VOC	X	X	
CO2			
CH4			
Acetaldehyde			
Formaldehyde			
Other toxics			
Radionuclides			
Thermal emissions			

The expected concentration of each compound identified in the waste stream would be entered into the properly configured BASTE or SIMS model of the sewage system for the ethanol facility. The actual calculation of emissions for that compound both in the air and in the effluent would be the output of the model. In this way, the checklist can be filled and the permit process initiated.

Water releases (releases with effluent):

Release	Relevant to the Site	Relevant to the facility	Permitted amount
BOD			
TSS			
NH4			
NO3			
Oil and grease			
Priority pollutants			
Thermal emissions			

As with air, the amounts of compounds can be entered into the table and the calculated resultant emissions can be included as part of the permit process and the eventual permit for the ethanol facility.

Land concerns:

Land area to dispose of the solid and semisolid residue of the plant will be a concern to the plant designer. Typically, nutrients contained in the sludges will determine how many pounds of the material can be applied to an acre of land during a crop season. In colder climates, sludges cannot be applied to frozen ground and require storage for 180 days, provision for such storage will have to be part of the initial plant design.

Other concerns:

Other concerns of the plant designer will be Health and Safety, Noise, Odors, Catastrophic Events and Aesthetics. Each item should be addressed by the facility designers to match the local requirements.

Emission measurements at operational ethanol facilities:

Emission measurements may be required by the regulatory authorities. Such measurements may be in the form of “stack tests” at the boiler and other vent stacks. Such tests usually monitor for PM10, VOC’s and toxics. Measurement of the emissions from the waste treatment facility can be avoided by careful configuration and operation of the BASTE or SIMS models which provide an answer for the regulatory agencies which has been accepted by the agencies when applied. Typically operation of the computer model is much less expensive than is the field testing required to actually measure actual emissions. The result of the model is frequently a better look at actual emissions than is the "snap-shot" look that results from field testing.

Emission treatment at operational ethanol facilities:

Sewage plant VOC emissions can be easily controlled by covers over the emitting unit operations. Weir covers and covers over manholes and other sewage structures where waste streams come in contact with the air are the treatment choices due to the low cost of such control measures. Typically unit operations where odors are emitted in sewage plants are also the areas where VOC’s are emitted. Odor control usually provides some measure of VOC control.

The sludge incinerators, spent grain driers, and/or the steam boilers employed at ethanol facility, are all subject to PM10 and VOC emission controls. Waste gas flares for biogas from anaerobic processes must also be designed for low emissions. For very large power plant boilers, NOX control such as low NOX burners must be employed.

XVI. Environmental Regulations and Permits

Similar to the Report Section XV on Emissions from Ethanol Plants, this report Section will address the Regulations and Permits required to construct and operate a typical facility in the USA.

This section addresses the regulations and permits required to release discharges into the air, into a water body/stream, and onto land. Each of these areas has had regulations issued at the Federal, State and Local levels. Permits associated with these regulations are often managed at the State or a Local level as directed by the Federal and State Statutes. Sometimes the authorizing agency may be the State itself, a Regional District or Agency, a County, and/or a City or other smaller entity. Whichever discharges are contemplated, the first step is to determine the agency(ies) having jurisdiction for the actual plant location and for each discharge contemplated.

Most local or state governments maintain an "Assistance Center" to guide the new Facility Owner through the applicable regulations and how to obtain the required permits for construction and operation. The particular "center" may be called a "Permit Assistance Center" or "Technical Assistance Center" or a similar title. Local county agencies will be able to determine the best method of establishing the jurisdictional agencies for the emissions from the new Ethanol Facility.

For construction and operation of a new Ethanol Facility that will be co-located at an existing host site, the discharges may become part of the existing host discharges with modifications to existing permits. Therefore, in addition to determining the agencies having jurisdiction, the new Ethanol Facility Project Owners must also determine if the Facility will be operated as a separate entity or as an addition (modification) to an existing facility. This report will not address specifically the permit requirements of a co-located, co-owned Facility, since the permit requirements will be determined by the (modification of the) existing permits for the host site. However, the comments about the emissions (previous Section XV - Environmental Emissions and Effects) and the related permits for an Ethanol Facility (below) will be applicable to the modifications of the existing permits.

<u>Other Regulations</u>

The Wastewater Treatment Systems at a new Ethanol Facility will be subject to many regulations other than the air, water and solid waste regulations. Typical of these will be the Occupational Health and Safety Act (OSHA) regulations about personnel safety. These regulations will address standard safety aspects of such things as ladders, personnel access, confined spaces, etc. Another series of regulations will be the National Fire Protection Association and the American Petroleum Institute standards regarding the methane and hydrogen sulfide gases evolving from the anaerobic treatment of wastewater. Also, the electrical devices used in the wastewater treatment systems may require Underwriters Laboratories (UL) certification for certain components. This report will not address these specifically since these regulations and standards will apply to the whole Ethanol Facility.

<u>Air, Water and Solid Waste Regulations and Permitted Quantities of Emissions</u>

For each type of environmental emission, the Owner must <u>determine the type and quantity of each specific regulated constituent</u> that may be contained in the intended discharge. For example, the air emissions may contain particulates (PM10), Volatile Organic Compounds (VOC's), and other similarly regulated constituents.

The Owner must estimate to a sufficient degree the maximum, the average, and/or the total expected emission of each category of release to the atmosphere, the water, and the land. Sufficient controls (engineered equipment and operating procedures) and monitoring/reporting must be put into place at the Facility to ensure that the Owner will be able to comply with the limits of his proposed emission types and quantities.

<u>Location of Ethanol Facility</u>

The regulations require permits for construction and operation of an Ethanol Facility that depend on the facility location. Basically, this may range from an undisturbed "greenfield" site to a previously occupied or existing industrial site. Also, and this may be equally important, the facility site may have no nearby neighbors or may be surrounded with residential or other neighbors. The presence of a local population may impact allowable limits for such emissions as odors (even during emergency situations), visual aesthetics, etc. Thus, even though odor is not currently regulated under any federal program, state and local regulations may require that odor control be specifically addressed (to the satisfaction of the local populace).

As a location for the Ethanol Facility is determined, the local authorities should be contacted to establish the various requirements for the Permitting of the Facility. Planning Departments of the City/County or similar entity sometimes offer an organized approach to permitting with a "Permit Assistance Center" or similar organization. These organizations should be contacted to determine which agencies participate at that one location. These organizations also provide checklists of required permits and compliance information, including ongoing operational monitoring and reporting requirements. These checklists should be utilized to set up the Operation and Maintenance procedures for the Ethanol Facility. An example is available on the Internet at *http://smallbiz-enviroweb.org/htm/regchecklist.asp*.

<u>Air Emission Regulations and Permits</u>

Federal Clean Air Act and Amendments

The Federal Clear Air Act, originally promulgated in 1963, has been modified and upgraded in content and requirements by various Amendments in 1967, 1970, 1977 and 1990. The Act and its Amendments require State Implementation Plans or the Federal Environmental Protection Agency (EPA) will provide the implementation. States that have implemented the requirements of the Clean Air Act may also allow the participation of local governments in controlling air pollution within their territorial jurisdictions.

While the wastewater treatment section of the Ethanol Facility typically controls the wastewater in piping and tanks, etc., any storm water that is received by the Facility must also be contained and addressed as required. Storm water on the Facility site may fall into various categories requiring different treatments. For example, storm water on roads and parking lots may only require a surge volume control before slow, controlled release to the natural receiving water. However, storm water in the main process units may require hydrocarbon separation treatment steps to remove any spillage existing on the contained process area. Also, storm water on an uncovered wood chip storage pile will produce a leachate that contains material which will settle and that must be removed before discharge of the storm water. The design of the Facility should incorporate a coordinated approach of equipment and procedures for containment and treatment of all storm water received by the Facility.

Water Emission Regulations and Permits

The information below has been adapted from the reference item "Wastewater Engineering Treatment, Disposal and Reuse" and gives typical guidelines for the discharge of wastewater to a receiving body.

A National Discharge Elimination System (NPDES) program was established based on uniform technological minimums with which each point source discharger had to comply.

Pursuant to Section 304(d) of Public Law 92-500, the U.S. Environmental Protection Agency published its definition of secondary treatment. This definition, originally issued in 1973, was amended in 1985 to allow for additional flexibility in applying the percent removal requirements of pollutants to treatment facilities serving separate systems. The current definition of secondary treatment is reported in the table below. The definition of secondary treatment includes three major effluent parameters: 5-day BOD, suspended solids, and pH. The substitution of 5-day carbonaceous BOD ($CBOD_5$) for BOD_5 may be made at the option of the NPDES permitting authority. Special interpretations of the definition of secondary treatment are permitted for publicly owned treatment works (1) served by combined sewer systems, (2) using waste stabilization ponds and trickling filters, (3) receiving industrial flows, or (4) receiving less concentrated influent wastewater from separate sewers.

Minimum national standards for secondary treatment[b]

Characteristics of	Unit of	Average 30-day	Average 7-day

discharge	measurement	concentration	concentration
BOD_5	mg/L	30[c,d]	45[c]
Suspended solids	mg/L	30[c,d]	45[c]
Hydrogen-ion concentration	pH units	Within the range of 6.0 to	9.0 at all times[e]
$CBOD_5$ [f]	mg/L	25[c,d]	40[c]

[b] Present standards allow stabilization ponds and trickling filters to have higher 30-day average concentrations (45 mg/L) and 7-day average concentrations (65 mg/L) BOD/suspended solids performance levels as long as the water quality is not adversely affected. Exceptions are also permitted for combined sewers, certain industrial categories, and less-concentrated waste water's from separate sewers.
[c] Not to be exceeded.
[d] Average removal shall not be less than 85 percent.
[e] Only enforced if caused by industrial wastewater or by in-plant inorganic chemical addition.
[f] May be substituted for BOD_5 at the option of the NPDES permitting authority.

In 1987, Congress completed a major revision of the Clean Water Act. Important provisions of the WQA are (1) the strengthening of federal water quality regulations by providing changes in permitting and adding substantial penalties for permit violations, (2) significantly amending the CWA's formal sludge control program by emphasizing the identification and regulation of toxic pollutants in sludge,

In response to the provisions of the Water Quality Act, new regulations have been promulgated or proposed for controlling the disposal of sludge from wastewater treatment plants.

In 1989, the EPA proposed new standards for the disposal of sludge from wastewater treatment plants. The proposed regulations established pollutant numerical limits and management practices for (1) application of sludge to agricultural and non-agricultural land, (2) distribution and marketing, (3) monofilling or surface disposal, and (4) incineration.

Trends in Regulations

Regulations are always subject to change as more information becomes available regarding the characteristics of wastewater, effectiveness of treatment processes, and environmental effects. It is anticipated that the focus of future regulations will be on the implementation of the Water Quality Act of 1987. Receiving the most attention will be the pollutional effects of storm water and nonpoint sources, toxics in wastewater (priority pollutants), and as noted above the overall management of sludge, including the control of toxic substances. Nutrient removal, the control of pathogenic organisims, and the removal of organic and inorganic substances such as VOCs and total dissolved solids will also continue to receive attention in specific applications.

Other Regulatory Considerations

In addition to the requirements established under the 1987 Water Quality Act and enforced by the U.S. Environmental Protection Agency, other federal, state, and local agencies prescribed by the Occupational Safety and Health Act (OSHA) which deals with safety provisions to be included in the facilities' design. State, regional, and local regulations may include water quality standards for the protection of the public healthy and the beneficial uses of the receiving waters, air quality standards for the regulation of air emissions (including odor) from treatment facilities, and regulations for the disposal and reuse of sludge. Because all of these guidelines and regulations affect the design of wastewater treatment and disposal facilities, the practicing engineer must be thoroughly familiar with them and their interpretation and be aware of contemplated changes. Contemplated changes and current interpretations of the regulatory aspects of water pollution control are summarized in various weekly publications.

XVII. Summary and Conclusions

Several important results were disclosed during this work, among those were:

1. The waste water streams for the three NREL processes (co-current enzyme, softwood, hardwood) are all within the same typical treatment methodology: Anaerobic Treatment followed by Aerobic Treatment.

2. Waste water minimization through judicious water recycling is economically advantageous compared to once-through water use.

3. Although treatment must be judged anew for each specific plant site, the anaerobic followed by aerobic treating processes appear to be, most often, advantageous.

4. The anaerobic digester off gas is potentially laden with hydrogen sulfide in sufficient quantities to require sulfur removal processing.

5. The capital cost estimate resulted in a total installed cost for the 2000 bdt/y feed rate case of $11,362,700. Please refer to Appendix F for the structure and backup of this estimate.

Further Work

Several areas indicate the need for more development :

1. Treatment of the anaerobic off gas stream for the enzymatic process. This stream may contain sulfur (as hydrogen sulfide) in concentration to be toxic and to require clean-up prior to combustion.
2. The methane to carbon dioxide ratio in the anaerobic digester off gas is variable with the operation and the proprietary license. This ratio needs to be established for the plant economic assessment.
3. A 1986 EPA regulation includes a classification of “ethanol for fuel”. This regulation needs to be analyzed for potential benefits.
4. The waste water section should be considered for a environmental model to assist in design and to replace on-site sampling when plants are built.
5. Some waste streams were not considered which may have significant impact. Namely : periodic vessel drains for maintenance, storm water falling within curbed areas, chip stock pile leachate, etc. Additionally the effects of listed chemical inventories are not fully developed. These chemicals include natural gasoline denaturant, BFW chemicals, WWT chemicals, lube oils, various acids and bases.
6. VOC emissions for the above chemicals should be evaluated.

XVIII. References

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