GIVE YOUR DENITRIFICATION BUGS A SUGAR HIGH

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ABSTRACT

An alternative substrate to methanol was sought for tertiary denitrification. High fructose corn syrup (HFCS) was identified as the most cost effective alternative, which would also be much safer to handle. This should also render HFCS subject to less legislation at all levels of government. A pilot scale test was conducted. The test confirmed that HFCS is a suitable substrate. A dose of 7.4 g HFCS/g nitrate-nitrogen (NO_3-N) removed was achieved and effluent NO_3-N was reduced from 8.1 to 3.3 mg/L. Excluding a period of upset conditions, the dose was 5.9 g HFCS/g NO_3-N, and the reduction was from 8.8 to 2.7 mg/L. This compares to a theoretical dose of 4.2 g HFCS/g NO_3-N based on stoichiometry and a typical methanol dose of 3 g/g NO_3-N. Factors that may have contributed to the high dose include variability of the feed NO_3-N concentration and occasionally insufficient NO_3-N for the available substrate. A preliminary cost estimate indicated that the simple payback for a methanol dosing system would be between 5 and 17 years, depending on the actual HFCS dose.

KEYWORDS

Tertiary denitrification, methanol, high fructose corn syrup, fluidized bed denitrification towers.

INTRODUCTION

Methanol is commonly used as a substrate in tertiary denitrification systems. The addition of methanol for denitrification is based on its biodegradability and availability, but methanol also has some disadvantages, including its potential for evaporative loss, a resulting danger of spark ignition, and the effect of evaporative losses on the surrounding air quality. These concerns have resulted in increasingly strict legislation in Southern California regarding the storage and use of methanol.

Temecula Valley Regional Water Reclamation Facility (TVRWRF) is one of four wastewater treatment plants (WWTP) operated by Eastern Municipal Water District (EMWD). TVRWRF has an existing tertiary denitrification system that consists of methanol storage and dosing facilities as well as six fluidized bed denitrification towers. Methanol has been classified a hazardous air pollutant under Section 101(14) of the Comprehensive Environmental Responses Compensation and Liability Act (CERCLA). This means that existing methanol storage facilities would have had to add a number of safety and leakage prevention features. In December 2002 the methanol storage tank was removed from the site.

EMWD decided to investigate alternatives that might meet most of methanol's advantages, while avoiding some of the disadvantages. One alternative carbon source that was identified is HFCS, a sweetener used in the food industry.

The results of pilot testing using HFCS and evaluating the cost to retrofit the current denitrification towers to a system capable of using HFCS is the subject of this paper.

BACKGROUND

The add-on approach of a tertiary denitrification system leaves the secondary treatment process unchanged and allows a higher degree of denitrification than what is typically achieved by secondary treatment alone. Denitrification occurs when biomass growing on a substrate uses nitrate as an electron acceptor as a substitute for oxygen. As oxygen is the preferred electron acceptor, nitrate is only used in the absence of oxygen, and a readily biodegradable carbon source as an electron donor. In the process, the nitrate is reduced to nitrogen gas, which is released into the environment.

The denitrification reaction rate is affected by:

- Type and concentration of readily biodegradable carbon source (soluble BOD).
- Concentration of nitrate.
- Concentration of residual dissolved oxygen.
- Temperature, biomass concentration, and other factors affecting the growth of biomass.

The chemical reaction for denitrification using methanol (but excluding biological growth) can be presented as:

$$5\ CH_3OH + 6\ NO_3^- + 6\ H^+ \rightarrow 5\ CO_2 + 3\ N_2\uparrow + 13\ H_2O$$

The stoichiometry of this reaction indicates that 1.9 grams of methanol is needed for each gram of nitrate-nitrogen (NO_3-N) that is reduced. In practice, the ratio is increased to 3.0 to 3.5 grams methanol per gram of nitrogen reduced (Tchobanoglous et al., 2003), or increased by approximately 58 percent to 84 percent to allow for biological growth.

When using HFCS, the chemical reaction can be presented as:

$$5\ C_6H_{12}O_6 + 24\ NO_3^- + 24\ H^+ \rightarrow 30\ CO_2 + 12\ N_2\uparrow + 42\ H_2O$$

Here the stoichiometry indicates that 2.7 grams of sugar is required per gram of NO_3-N reduced. Increasing this ratio by the same 58 percent to 84 percent used for methanol results in a dose of 4.2 to 5.0 grams fructose per gram of NO_3-N.

Typical systems available for add-on denitrification are denite filters and fluidized-bed denitrification towers. These units employ a bed of sand as a carrier material for denitrifying microorganisms that are maintained under anoxic conditions and fed with readily biodegradable carbon source. The TVRWRF has a fluidized-bed system.

SELECTING HIGH FRUCTOSE CORN SYRUP

In theory, there are several other alternative substrates to methanol that may also achieve tertiary denitrification. Alternative substrates would include volatile fatty acids (VFAs), other low molecular weight organic acids, lower alcohols, and simple carbohydrates. A preliminary cost comparison of a number of substrates was completed. The substrates were selected based on sufficient solubility in water and their absence from the list of hazardous air pollutants under Section 101(14) of CERCLA.

The stoichiometric requirement for a given substrate can be calculated from its Theoretical Chemical Oxygen Demand (TCOD). For a generic organic substrate with the empiric formula $C_xH_yO_z$ TCOD (gram TCOD/gram substrate, i.e. dimensionless) can be calculated according to the formula:

$$TCOD = 32(x + 0.25y - 0.5z)/(12x + y + 16z)$$

Thus methanol (CH_3OH or CH_4O) would have a TCOD of:

$$TCOD = 32(1 + 0.25(4) - 0.5)/(12 + 4 + 16) = 1.50$$

Similarly, sugar ($C_6H_{12}O_6$ or empiric CH_2O) would have a TCOD of 1.067. The stoichiometric required consumption of a substrate would be inversely proportional to its TCOD value. Hence, the theoretical sugar requirement, based on a methanol dose of 3.0 g/g N would be

$$\text{Theoretical Dose} = 3(1.5.TCOD) = 4.5/1.067 = 4.2 \text{ g/g N}$$

confirming the number calculated above.

The consumption of the alternative substrates can be determined using the same methods, establishing a relative comparison of the consumption of other substrates to methanol.

The only substrates that would be cheaper to dose than HFCS are ethanol, isopropanol, and isobutanol. These lower alcohols all have relatively high vapor pressures, which means they would be subject to evaporative loss. The vapors also cause safely concerns and are likely to be the subject of an extensive list of federal, state, and local regulations. Hence, it was concluded that in spite of its higher operating cost, HFCS had other advantages that warranted further investigation.

HIGH FRUCTOSE CORN SYRUP CHARACTERISTICS

HFCS is produced from corn through wet milling and a three-step enzymatic conversion of the resulting cornstarch:

- First the starch (a polymer of glucose) is partially hydrolyzed using an α-amylase to yield a solution consisting of some glucose and higher saccharides.
- Next the hydrolysis is completed (93- to 96-percent glucose) using a glucoamylase to produce a glucose syrup, also known as corn syrup or dextrose syrup in the food industry.
- The glucose is partially converted to fructose (typically 42-percent fructose) using an isomerase.

The corn syrup that is produced by the first two steps could also be used as a substrate for denitrification and, from a microbiological point of view, it would actually be superior to HFCS. Glucose is a fundamental carbon source in the sense that other sugars must be converted either to glucose or a glucose-degradation product. A bacterium growing in a mixture of sugars would selectively consume glucose and only then start consuming other sugars. However, at the low substrate concentrations that would be used in the denitrification tower, selective substrate utilization would be suppressed.

The reason for converting glucose to fructose is that glucose is only 70 percent as sweet as sucrose (table sugar) whereas fructose is 130 percent as sweet as sucrose. The conversion has some benefits in terms of the physical properties of the resulting syrup, for example fructose is twice as soluble as glucose at low temperatures.

HFCS is available in three different grades, depending on the fructose content; 42-percent, 55-percent, and 90-percent fructose. All syrups are produced at high solids concentrations so that the osmotic pressure is sufficient to prevent the growth of yeast and mold in the syrup. The physical properties and prices of glucose syrup and HFCS, at 42-, 55-, and 90-percent fructose, are compared in Table 1.

Table 1 Physical Properties of Different Syrups

Syrup	Corn Syrup	HFCS 42%	HFCS 55%	HFCS 90%
Constituents, %				
Fructose	-	42	55	87
Glucose	95	52	42	8.5
Maltose	3	3	2	-
Higher Saccharides	2	3	2	1.5
Solids, %	80	71	77	77
Specific Gravity, g/L				
27°C		1.344	1.382	
38°C		1.337	1.374	
49°C	1.328	1.330	1.367	
Viscosity, cP				
16°C	-	-	-	1,900
27°C	-	220	760	575
38°C	-	95	360	220
49°C	57	55	160	-
Recommended Storage Temperature, °C	43 - 54	32 - 38	27 - 32	21 - 29
Cost				
$/tote	196.01(1)	733.15	845.71	(2)

Table 1	Physical Properties of Different Syrups			
Syrup	**Corn Syrup**	**HFCS 42%**	**HFCS 55%**	**HFCS 90%**
kg/tote	295(1)	1,340	1,380	-
$/t solids	831	772	794	-

Notes:
(1) Price for drum, product not available in totes on the West Coast.
(2) Not available in totes or drums on the West Coast.

As can be seen in the table, the syrups all have high viscosity and all require storage at an elevated temperature to prevent crystallization. The higher the fructose content of a particular syrup, the lower the required storage temperature. This is of primary importance in selection of the appropriate syrup to use. Corn syrup is ruled out based on its high storage temperature requirements.

Based on prices for larger quantities, the highest fructose content syrup (HFCS 90 percent) is approximately 50 percent more expensive than either HFCS 42 percent or HFCS 55 percent. Its use is, therefore, not recommended due to its high cost compared to the other syrups. Thus the recommended product is the HFCS 55 percent, which is marginally more expensive than the other syrups, but easier to handle and requires lower storage temperatures.

There are three challenges for using HFCS as a substrate for tertiary denitrification:

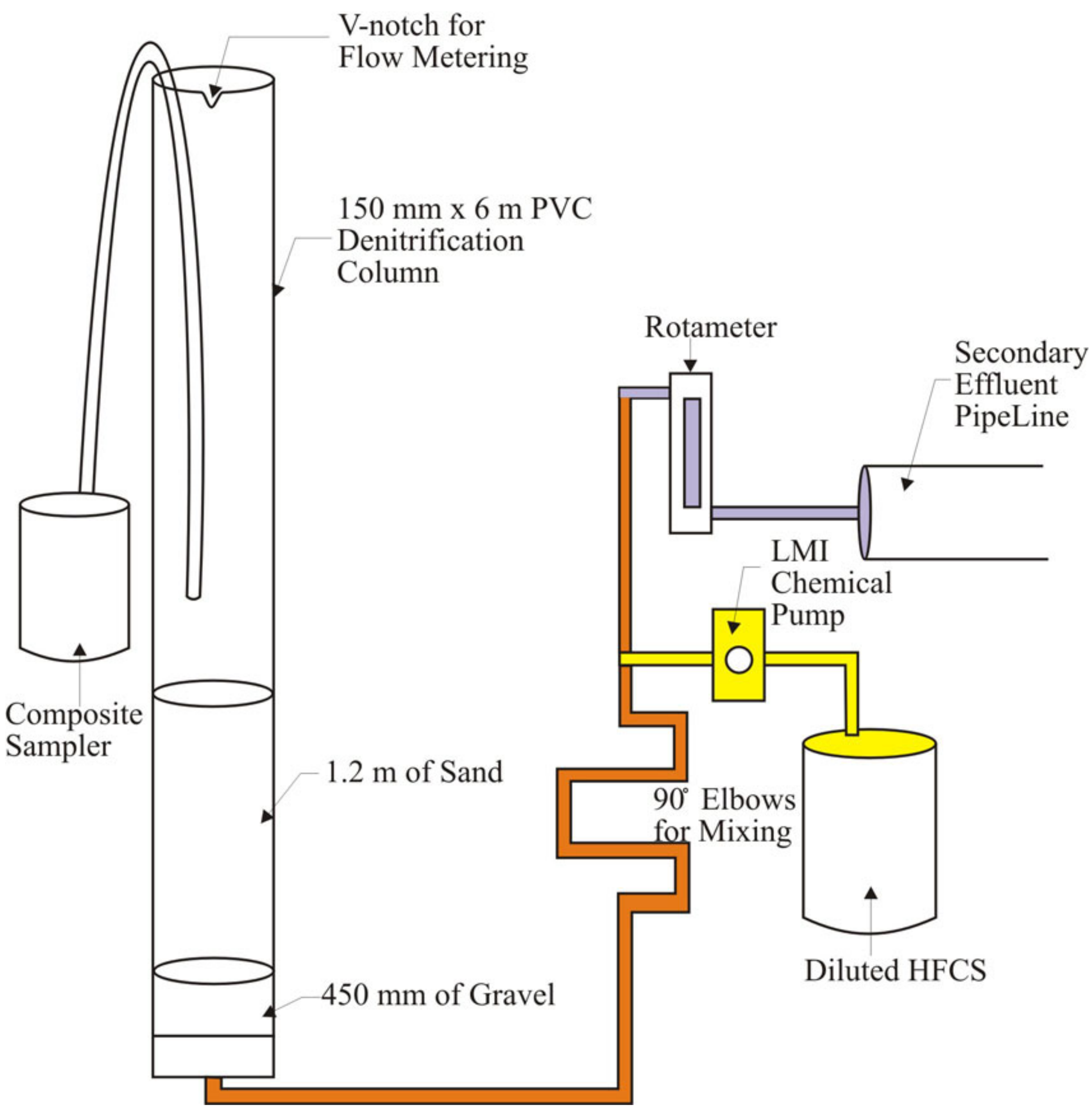
1. The requirement for storage at an elevated temperature, as discussed above.
2. The viscous liquid must be pumped to the point where it is mixed with the effluent.
3. The mixing must be sufficient to ensure that the thick syrup fully dissolves in the effluent.

Alternatively, the HFCS could be diluted to 66-percent solids, at which point crystallization is no longer a concern. Unfortunately, this concentration would permit the growth of yeast and mold. In the absence of oxygen, the growth of yeast and mold would not reduce the BOD or COD of the syrup. Dilution would increase the equipment required for dilution and pumping and would complicate operations. Dilution is not recommended for these reasons.

MATERIALS AND METHODS

A pilot-scale model of the existing fluidized bed denitrification column was set up for testing with HFCS 42 percent as substrate (Figure 1). Although HFCS 55-percent would be preferred, the HFCS 42-percent was donated to EMWD and was therefore used during the pilot testing.

Figure 1 - Pilot Scale Denitrification Column



The column consisted of a 100-mm diameter pipe with a 1.2-m deep bed of sand media on top of an 450-mm gravel bed. The system was operated in an up-flow mode at an expanded empty bed contact time of 10 minutes and a hydraulic loading of 0.004 $m^3/m^2.s$, similar to the existing denitrification towers.

The system was fed with secondary effluent. A 20-fold dilution of HFCS (42-percent fructose, 71-percent solids, SG of 1.35) was prepared and pumped into the secondary effluent feed pipe, upstream of a series of 90-degree elbows, which served as inline mixers. The solution was pumped at a constant rate of 0.23 L/h (approximately 5.5 L/d). The HFCS dose was based on a reduction of approximately 8 mg/L of NO_3-N. The actual final dose corresponded to a reduction of 7.8 mg/L of NO_3-N.

A composite sample of secondary effluent and pilot bed effluent was collected and analyzed for ammonia-nitrogen and NO_3-N. Effluent flow from the bed was measured every day to ensure that the feed flow remained in the target range.

RESULTS

The results from the test are shown graphically in Figure 2 and summarized in Table 2.

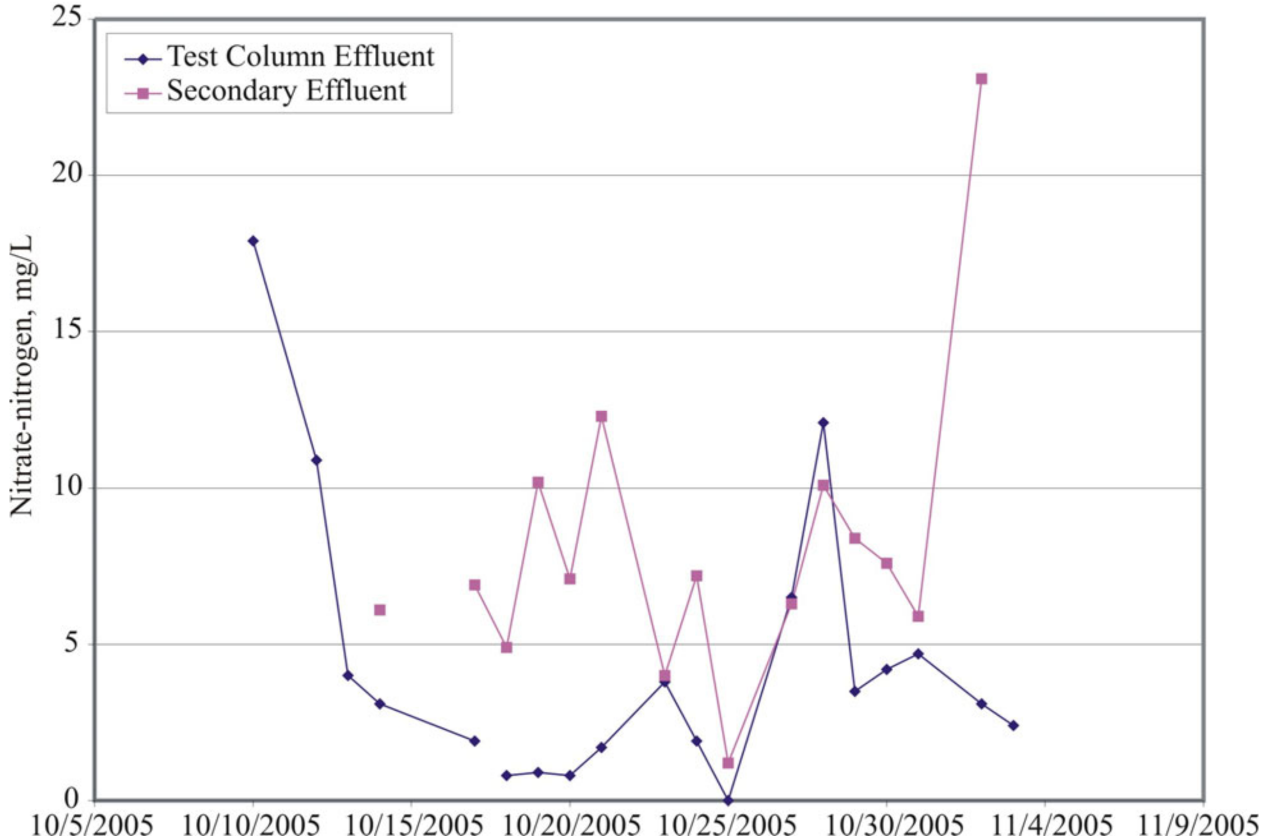
Table 2 Test Results

	Secondary Effluent		Test Column Effluent	
	NH_4-N, mg/L	NO_3-N, mg/L	NH_4-N, mg/L	NO_3-N, mg/L
Average, entire test	1.4	8.1	1.7	3.3
Average, excl. upset	1.2	8.8	1.5	2.7

HFCS was successfully used as a substrate for tertiary denitrification. The table shows that, on average, a removal of 4.8 mg/L NO_3-N was achieved, at a sugar requirement of 7.4 grams of sugar per gram of NO_3-N. A period of upset conditions occurred during the test between October 23 and October 27. When this period is excluded from the analysis, the removal increased to 6.1 mg/L NO_3-N, at a sugar requirement of 5.9 grams of sugar per gram of NO_3-N.

It was assumed that the secondary effluent NO_3-N concentration would be approximately 10 mg/L. During the test, it averaged 8.1 mg/L and on one occasion it was as low as 1.2 mg/L. It is therefore fair to assume that denitrification was limited, at times, by lack of available NO_3-N. In addition, the relatively short duration of the test (approximately 1 month) did not allow this dose to be optimized, and it is quite possible that an actual dose of 4.2 grams of sugar per gram of NO_3-N could be delivered, the equivalent of dosing 3.0 grams of methanol per gram of NO_3-N. A longer test run would potentially allow the biomass to stabilize and produce a lower effluent NO_3-N concentration.

Figure 2 - Results of Pilot-Scale Denitrification



DISCUSSION

Since the conversion to HFCS (55 percent) would not be a long-term application, the design approach was based on a low capital cost/temporary application. Table 3 summarizes the design requirements for the tertiary denitrification system.

Table 3 Design Requirement for Tertiary Denitrification

Parameter	Value
Feed flow to towers, L/s, each	95
Number of towers in operation	6
N reduction required, mg/L	6.0[(1)]
N load requiring reduction, lb/d	295

Notes:
(1) Assuming the aim is to reduce secondary effluent N from 8 mg/L to 2 mg/L.

The consumption of HFCS will depend on the load of NO_3-N that would be reduced, as well as the actual dosing requirement. As mentioned above, the results from the pilot work indicated that the sugar dose requirement may be as high as approximately 6.0 grams of sugar per gram of NO_3-N reduced, or even as high as 7.5 grams of sugar per gram of NO_3-N (approximately what was achieved when upset conditions are included). It is possible that the sugar dose requirement may be as low as 4.2 grams of sugar per gram of NO_3-N. Table 4 summarizes the sugar requirements for all three dose requirements.

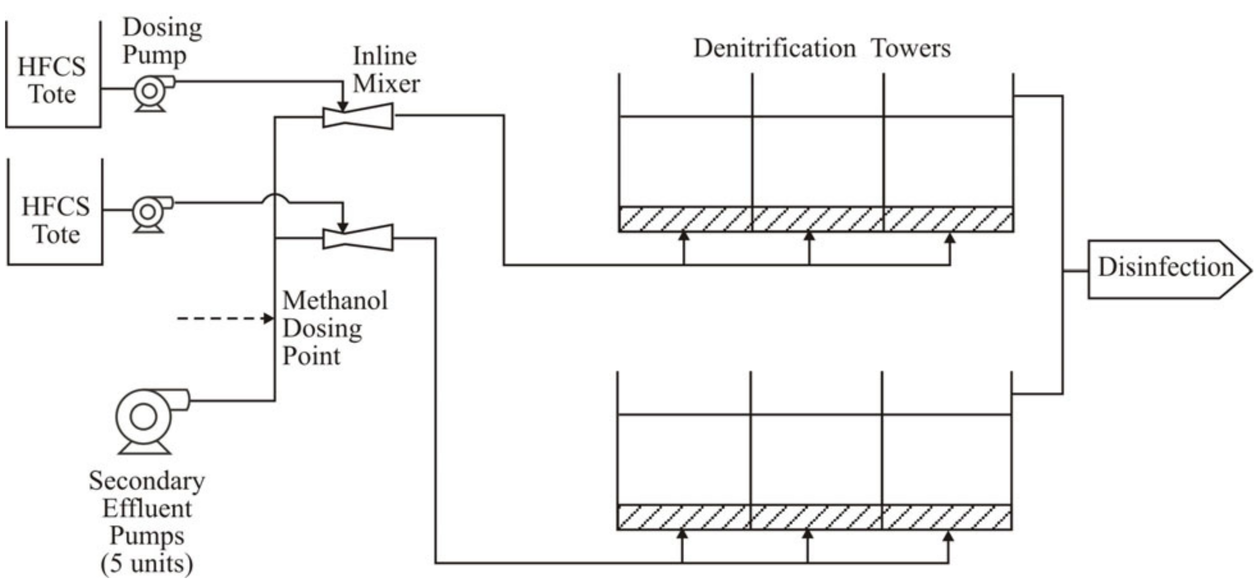
Table 4 Sugar Requirement for Tertiary Denitrification

Sugar Dose Requirement, g/g NO_3-N	4.2	6.0	7.5
Sugar requirement			
kg/d, dry	1,240	1,770	2,210
L/d, as syrup @ SG = 1.36(1)	1,180	1,690	2,110
Totes required per week, approximate	8.1	11.6	14.5

Notes:
(1) A minimum expected SG for HFCS 55%, at 77% solids.

Figure 3 shows a process flow diagram of the proposed HFCS dosing system. The syrup would be delivered to site in 1,000-kilogram (approximately) totes.

Figure 3 - Tertiary Denitrification Process Flow Diagram



Mixing the viscous syrup with water will require a dedicated mixer. An inline static mixer would offer the most appropriate solution. The physical layout of the denitrification tower feed pumps and piping limits the options available for placing such a device and two inline mixers are required. The syrup would be injected directly upstream of the inline mixers, so that there would be two syrup injection points.

Two electronic metering pumps would be used to feed the syrup to the two injection points. The totes that are in service would be located as close to the dosing points as possible to minimize the risk of cooling and the associated concerns of crystallization as well as increased viscosity in the pipe. All piping would be lagged and contain heat trace to keep it warm.

The inline mixer would add approximately 6 meters of water column head loss to the secondary effluent pump delivery. Since these pumps are equipped with variable frequency drives (VFDs), the loss can be overcome by adjusting the VFD, based on the flow signal from the magnetic flowmeter downstream of the inline mixer. The additional head loss would add to the operating costs for the HFCS denitrification system.

FINANCIAL ANALYSIS

The decision to remove the methanol storage tank from the site was made partially based on the high capital cost required to upgrade the storage tank to meet the new regulatory requirements. To reinstall the tank with the necessary upgrades would probably cost in the order of $3 to $4 million.

The infrastructure requirements for implementing the HFCS as a substrate in the existing denitrification towers are the following:

- Three electronic chemical dosing pumps, two duty, one standby. The standby unit could also be used to transfer syrup between totes. This would allow the operators to manage the syrup inventory in the duty tote such that replacement would not be required after hours. Each duty pump would also be equipped with a diaphragm valve on the suction and discharge ends.
- Suction piping to connect to the female connection in the tote and discharge piping to connect the pump discharge to the injector upstream of the inline mixer. It is proposed to keep this pipe as short as possible, no more than 1.5 meters in length for the suction side and 3 meters for the discharge side. It is proposed to use a 50-millimeter diameter carbon steel pipe. The retention time in a 5-meter length of pipe would be less than 30 minutes.
- Two inline mixers, including injection points, to ensure proper mixing of viscous syrup with secondary effluent.
- To avoid crystallization, each tote should be covered to minimize heat loss during cool weather. The 50-millimeter steel pipe would also require insulation and a heat trace.
- Electrical power connections for the three chemical dosing pumps.

The estimated capital cost for the infrastructure requirements is approximately $385,000.

Operating Costs

The operating costs depend to a large degree on the dose that is required. To indicate the effect of the dose, the operating cost was determined for all the doses shown in Table 4. The operating cost also includes the energy required to mix the viscous syrup with the secondary effluent and was compared to dosing methanol at 3.0 grams per gram of NO_3-N. Using an inline mixer, as proposed, means that this energy is supplied by the secondary effluent pumps. The operating costs for treating 49 mL/d (95 L/s per tower) are summarized in Table 5.

Table 5	Estimated Operating Cost for Using Different Substrates, $/year			
	Methanol	HFCS, Low Dose	HFCS, Medium Dose	HFCS, High Dose
Substrate Cost	177,500	359,500	511,300	639,700
Mixing Cost	-	37,100	37,100	37,100
Total	**177,500**	**396,600**	**548,400**	**676,800**

Notes:
Based on a methanol cost of $0.55/kg, HFCS cost of $0.79/dry kg and electricity of $0.125/kWh. Treating 49 mL/d (95 L/s per tower).

The table shows how sensitive the actual operating cost is to the dosing requirement. At the higher dose, the cost is approximately 280 percent higher than using methanol. On the other hand, at the low dose HFCS is approximately 120 percent more expensive. At the medium dose, the cost is 240 percent higher. This illustrates the need for further testing to determine the actual dosing requirements more accurately. The cost of methanol depends partly on crude oil prices (Austin, 1984) and may be volatile in the near future.

Not included in the operating cost analysis, are such items as the cost of complying with Air Quality Management District regulations for storage and handling of methanol, labor required for moving HFCS totes around, etc.

Life-Cycle Cost

The capital cost required for converting to HFCS as a substrate for tertiary denitrification is low compared to the annual cost of substrate. Based on a capital cost of $3 to $4 million to reinstall the methanol storage tank, the simple payback period would be between 5 and 17 years (depending also on the actual operating cost of dosing HFCS). The range is large due to the uncertainty in both the capital cost required for methanol storage and the operating cost for HFCS. However, the minimum would exceed the expected operating life of tertiary denitrification. Hence HFCS would have a lower life cycle cost than methanol even at the highest HFCS, partly due to the short project life of 3 years.

CONCLUSIONS

It has been demonstrated that HFCS 42 percent can be used as an alternative substrate to methanol for tertiary denitrification. Test results indicate that overall a 4.8 mg/L reduction in secondary effluent NO_3-N was achieved at a dose of 7.4 grams of sugar per gram of NO_3-N reduced. When upset conditions were excluded, the removal improves to 6.1 mg/L. The corresponding sugar dose was 36.4 mg/L. It was demonstrated that a dose of 5.9 grams of sugar was required per gram of NO_3-N reduced.

The secondary effluent fed to the system had a NO_3-N concentration of less than 7.8 mg/L on several occasions, which would suggest that denitrification may have been limited by a lack of nitrate. Comparing HFCS to methanol, it is expected that the HFCS requirement may be as low as 4.2 grams sugar per gram of NO_3-N reduced, based on the equivalent requirement of 3.0 grams methanol per gram of NO_3-N reduced.

The operating cost for using HFCS is higher than using methanol, even if HFCS can be dosed at the equivalent dose as methanol. However, even using the most conservative HFCS dose (7.5 grams of sugar per gram of NO_3-N), the payback for using methanol is likely to exceed the expected period for which tertiary denitrification would be required.

HFCS appears to be feasible but the crystallization issue would require further investigation to confirm that heat lagging would resolve this issue.

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