COMPARISON OF COMMERCIALLY AVAILABLE ELECTRON DONORS AND A NON-FLAMMABLE PROPRIETARY CARBON SOURCE MICROC™ FOR BIOLOGICAL NITROGEN REMOVAL BY DENITRIFICATION IN THE ONSITE AND DECENTRALIZED INDUSTRIES.

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Accumulation of various nitrogen species in surface and ground waters is linked to a number of ecological and human health concerns. These concerns include eutrophication of receiving waters including lakes, rivers, streams and estuaries. The Ecological Society of America reports that more than 60 percent of coastal rivers and bays in every coastal state of the continental United States are moderately to severely degraded by nutrient pollution. Other concerns include dissolved oxygen depletion in receiving waters due to discharge of un-nitrified effluents. Acute ammonia toxicity in fish and other aquatic life has been observed at levels as low as 0.1 mg/L to 10 mg/L. One public health concern affecting infants is methemoglobinemia, or “Blue Baby Syndrome”, caused by high nitrate levels in drinking water (US EPA, 1993). A report by the National Academy of Science in 1977 confirmed a value near 10 mg/L nitrate-nitrogen as a “maximum no-observed adverse-health-effect level” based on available evidence of methemoglobinemia in infants (NAS, 1977).

Nitrogen pollution from Onsite Sewage Disposal Systems (OSDS) accounts for a significant portion of the total nitrogen load to groundwater. Approximately ¼ of all households in the United States are served by OSDS. Within nitrogen sensitive states on the east coast, the percentage is nearly 30 percent (US Census, 1990). Moreover, new construction is disproportionately served by onsite or decentralized wastewater treatment systems. Approximately 1/3 of all new construction is served by these systems (WEF, March 05).

Effluent from OSDS typically contains 25-60mg/L of total nitrogen, most of this is in the form of ammonium-nitrogen. Ammonium nitrogen undergoes rapid nitrification (conversion of ammonium nitrogen to nitrate nitrogen) within the soil absorption system of OSDS (US EPA, 1993). A family of four can contribute up to 33kg of nitrogen to the groundwater annually depending on soil conditions, this is 200 times the amount that would be typically introduced via natural nitrogen loading by mineralization and precipitation (Hantzshe, 1992).

Onsite nitrogen removal performance varies by process design and operation. The majority of practical nitrogen-removal systems employ biological nitrogen removal (BNR), some of which are proprietary technologies. Many of these BNR systems use exogenous electron donor addition to achieve more complete nitrogen removal. Typical

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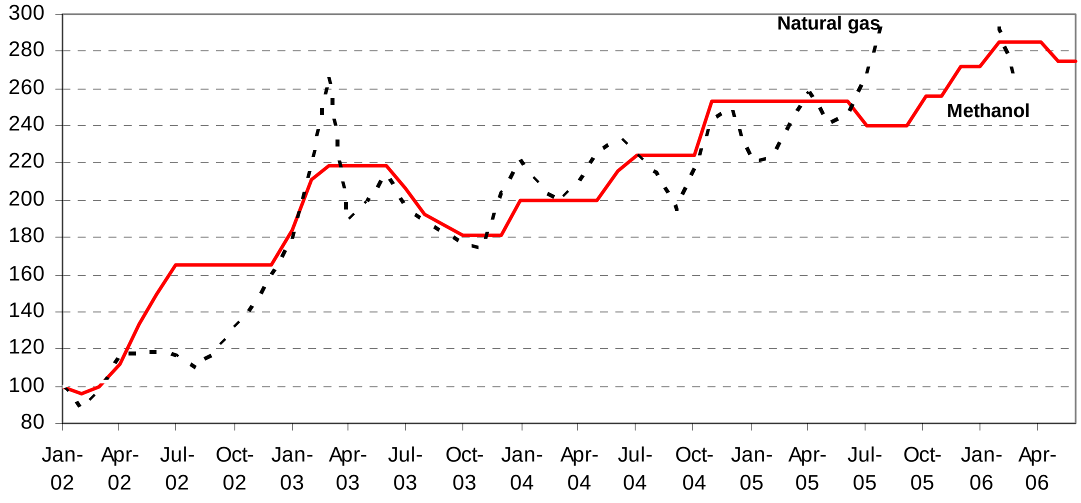
nitrogen removal rates for these technologies is 55-75% of total influent nitrogen (EPA, 2000). Other research indicates that TN reductions of greater than 70% are achievable without exogenous electron donor addition and 90% with exogenous carbon addition (Anderson, et al, 1998).

Where the addition of an exogenous electron donor is required, careful consideration of the available alternatives should be completed. A suitable electron donor for denitrification should have the following properties: the electron donor should be inexpensive, safe to handle, commercially available, free of nitrogen and phosphorus, free of non-biodegradable and toxic compounds such as VOC's, in liquid form or water soluble powder/crystals and have a low cell yield. Methanol, ethanol, acetic acid, sodium acetate, sucrose solutions, industrial wastes, food products and a proprietary chemical called MicroC™ are the most widely used electron donors for denitrification. The scope of this paper is to analyze the physical properties, safety and handling, economics and denitrification performance of the electron donors listed above.

Methanol

Methanol has been the industry standard for wastewater denitrification due to historically low cost, favorable kinetics, and low cell yield (US EPA 1993). As a result, there is an abundance of performance data for methanol in generic denitrification technologies such as suspended growth systems as well as proprietary denitrification technologies more relevant to the OSDS and decentralized industries. The supply of methanol is stable and easily procured from local chemical distributors, however the cost of methanol has increased almost three fold in the last four years due to rising natural gas costs (Figure 1).



[1] Methanex monthly average U.S. Gulf Coast price per gallon
[2] Energy Information Administration monthly average wellhead price

Figure 1: Indexed Methanol[1] and Natural Gas[2] Pricing (January 2002-May 2006)

Methanol poses an immediate fire hazard and human health hazard. Methanol liquid and vapor can ignite at temperatures as low as 55 degrees Fahrenheit and requires special explosion proof pumps, ventilation, electrical equipment and storage areas in wastewater treatment facilities. Despite the explosion proof infrastructure guidelines, there have been several accidents related to methanol fires and explosions in the wastewater treatment industry. The most recent and perhaps one of the more serious accidents occurred on January 11, 2006 at a wastewater treatment facility in Daytona Beach, Florida. The explosion and subsequent fire of a 6000 gallon methanol storage tank killed two operators and seriously injured a third (Wyland, 2006).

Methanol is classified as a poison and toxic chemical, inhalation and ingestion can cause blindness and death. The health and fire hazards of methanol suggest that other alternatives be sought for decentralized denitrification efforts, many of which are schools, nursing homes and housing developments. OSDS single dwelling denitrification systems should seek alternatives to methanol for the same reasons.

Ethanol

Pure ethanol or drinking alcohol is heavily regulated by the Alcohol and Tobacco Tax and Trade Bureau and therefore is not used for wastewater denitrification (WEF MOP30, 2005). Instead, denatured ethanol is more commonly used. Therefore all references to ethanol in this paper refer to denatured ethanol. Denaturants in ethanol often include methanol, methyl ethyl ketone, benzene, toluene and other organic compounds that render denatured ethanol toxic and therefore non-drinkable. Ethanol shares the same health, safety, handling and flammability characteristics as methanol and is more expensive than methanol per gallon. Despite a 125% increase in ethanol production since 2001 (ACE, 2005), prices have increased 83% (US DOE, 2006). Ethanol production increases are in part due to the increasing adoption of E85, an alternative to gasoline for automobiles. A second driver for increases in ethanol production is the replacement of MTBE in gasoline with an ethanol based gasoline additive. This trend indicates that although ethanol production will continue to increase, denatured ethanol prices will most likely not decrease due to increased demand for E85 fuels and ethanol fuel additives.

Despite having favorable kinetics compared to methanol, (Nyberg, 1996; Santos, 2004) the additional sludge production and cost per gallon compared to methanol is the determining factor for the preferential use of methanol over ethanol. A study completed by CH2MHill at the Blue Plains WWTF showed a 30% kinetic advantage for ethanol compared with methanol (represented as g electron donor/g NO3-N removed) however this kinetic advantage was not high enough to overcome the cost difference of $0.62 per gallon in 1997 (Jarrett, 2003).

Acetic Acid

Acetic acid is manufactured primarily from methanol via the Monsanto process and is linked to methanol and natural gas price. Some studies have shown that acetic acid has a higher kinetic rate compared with methanol (Akunna, 1993). Other studies have demonstrated the opposite conclusions (Jarrett, 2003). The cost of acetic acid is the foremost reason why methanol has historically been the preferred electron donor (WEF MOP30, 2005). Dilute acetic acid solutions are available. These dilutions have reduced safety and flammability hazards and are an attractive alternative to the operator and the community served, however costs are prohibitive.

There is a potential for phosphorus release from biological solids downstream of biological phosphorus removal treatment systems when acetic acid is used as an electron donor in denitrification. This could create potential problems for OSDS, decentralized and centralized facilities with very stringent nitrogen and phosphorus discharge permits (WEF MOP 30, 2005).

Sodium Acetate

Sodium acetate is manufactured primarily from acetic acid and therefore is linked to methanol and natural gas prices. Sodium acetate poses no flammability hazard and minor health hazards. As a result, it is an attractive alternative for wastewater denitrification. Sodium acetate is available in powder or crystalline form, both of which are water soluble. Handling the dry sodium acetate is a challenge logistically and requires additional labor and capital cost for tanks, mixers and the ability to receive bulk deliveries of sodium acetate. Sodium acetate and water solutions are prepared in concentrations from ten to thirty percent (w/w). A thirty percent solution of sodium acetate will begin to precipitate/freeze at 57 degrees Fahrenheit. This presents a serious problem for the onsite and decentralized industries in regards to winter storage, pumping problems, freezing in delivery lines, etc.

Thirty percent sodium acetate solutions are available from a limited number of chemical distributors, however these are not cost effective due to shipping and handling costs relative to the amount of sodium acetate present in these solutions.

Sucrose solutions

Sucrose solutions in the decentralized industry had been very common in the Northeast, specifically in New Jersey. A large operations firm, Applied Water Management in Hillsboro New Jersey (AWM NJ), had been using sucrose for denitrification in the majority of its plants due to safety concerns associated with methanol. Sucrose presents no health or flammability risk to the operator or community served and is typically prepared by mixing 3 to 4 lbs of sucrose per gallon of water. Sucrose solutions have some considerable disadvantages as well. Solutions are microbiologically unstable and will begin to ferment resulting in loss of carbon content in the form of carbon dioxide. Insects, rodents, odors and unwanted growth in pumps and lines as well as inconsistent denitrification results due to solution variability are other issues. Like sodium acetate, preparation of sucrose solutions requires capital cost for mixing equipment, additional labor, and delivery and logistics problems. As a result of these issues AWM NJ has implemented the use of a proprietary electron donor called MicroC™ (see below) in all of their decentralized facilities.

Industrial Wastes

Industrial wastes should be mentioned as an alternative electron donor for denitrification due to the rising costs of methanol and other commercially available electron donors. A study of 30 industrial waste carbon sources showed that 27 of the wastes exhibited denitrification rates equal to or greater than those observed for methanol (Monteith et al, 1980). At the time of the study, this resulted in an overall savings for plants of \$0.60 per kg NOX-N removed within a specified distance of the industrial waste supply. It is important to mention that the price point for methanol used in the study was \$0.176 per liter or \$0.67 per gallon. As of June 2006, methanol prices are close to double this price point.

The industrial source must be “clean”, i.e. free of metals, contaminants and nutrients. This is important because the denitrification process is generally at the end of the treatment process and untreated impurities may be discharged to the receiving groundwater or surface water. Carbon content consistency and stability is important for denitrification process control. Availability of the waste source should be considered and often varies due to seasonality or other variability within the industry itself (WEF MOP30, 2005).

Food Products

Other electron donor alternatives include food products such as molasses, corn syrup and sweeteners, caro syrup and other carbohydrates. Dog food and chicken feed have also been used for onsite and decentralized wastewater denitrification. There is very little literature and research available for these electron donors making their viability difficult to analyze. Handling and dosing problems associated with the physical properties of these electron donors create denitrification process control issues. The lack of research and implementation suggests that these alternatives are not viable options for electron donor feed for denitrification.

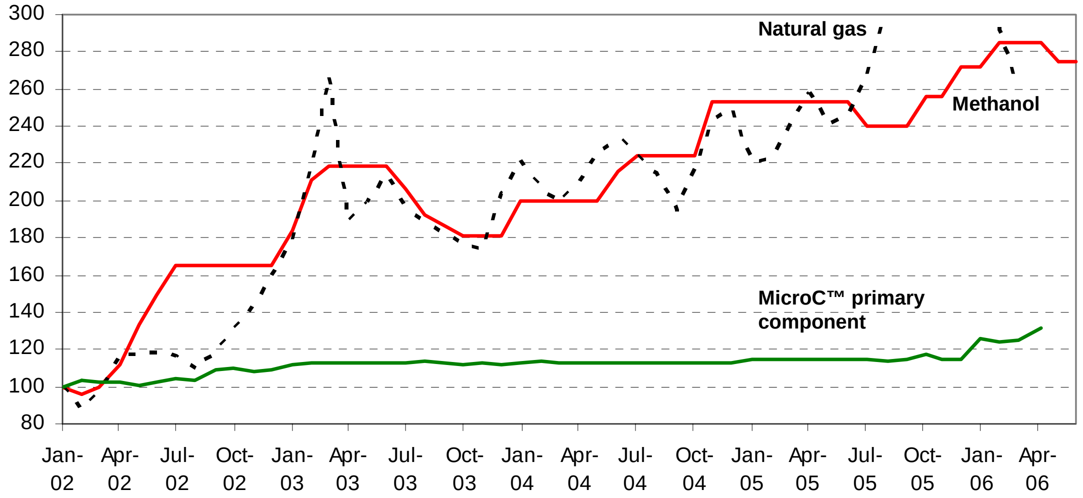
Table 1 summarizes the properties and limitations of the electron donors discussed thus far.

Table 1: Summary of Electron Donor Properties and Limitations

Limitation	**Limitation Explanation**	**Relevant Carbon Sources**
Toxicity	• Special requirements, including containment, ventilation and protection from high temperatures require expensive modifications • Poisonous liquid, harmful vapors, special handling and labeling requirements make use unnecessarily dangerous	• Methanol • Acetic Acid • Ethanol
Flammability-explosiveness	• Flammable liquid and vapors require expensive explosion proof containers, electrical components and metering pumps	• Methanol • Ethanol • Acetic Acid
Regulatory limitations	• State and local codes may prohibit storage at a site • Fire code(s) generally limit quantity of product stored at a site	• Ethanol • Methanol • Acetic Acid
Bacterial growth/ shelf life	• Significant product degradation over time by bacteria, yeasts and fungi • Bacterial and fungal growth issues within storage containers, pumps and distribution lines – including odors, clogged lines and problems with insects	• Sucrose • Industrial wastes
Handling/Mixing	• Capital cost required for storage tank and mixer • Additional handling required by operator to mix solutions • Variability in solution strength due to preparation errors	• Sucrose solutions • Sodium acetate
Freezing Point	• 30% sodium acetate solutions precipitate at 57 F • Sucrose solutions begin to freeze at temperatures below 32 F	• Sucrose solutions • Sodium Acetate
Impurities	• Electron donors may contain non-biodegradable impurities such as MEK, benzene, toluene and other volatile organic compounds • Potential for discharge of impurities to receiving waters and bacterial toxicity within the denitrification zone.	• Methanol • Ethanol • Industrial Wastes

MicroC™

One proprietary electron donor specifically designed for wastewater denitrification called MicroC™ exists. MicroC™ is an agriculturally derived electron donor resulting in greater price stability over time compared with natural gas derived electron donors (Figure 2). MicroC™ is in liquid phase and has a favorable freezing temperature of zero degrees Fahrenheit. MicroC™ does contain 5.5% methanol (w/w) and as a result is classified as a poison by the Occupational Safety and Health Administration and as a combustible liquid by the National Fire Protection Association. Despite the combustible classification, explosion proof equipment is not required (NFPA, 2003), resulting in considerable savings in capital expenditure for both new onsite and decentralized treatment system construction and upgrades to existing systems.



[1] Methanex monthly average U.S. Gulf Coast price per gallon

[2] Energy Information Administration monthly average wellhead price

[3] United States Department of Agriculture, Bureau of Labor Statistics

Figure 2: Indexed Methanol[1], Natural Gas[2] and MicroC™ Primary Component[3] Pricing (January 2002- May 2006)

MicroC™ has favorable kinetics in both laboratory studies and denitrification applications in industrial, municipal, decentralized and onsite systems. An analysis of nitrate removal performance was completed by a large engineering firm in 2005. The results of this analysis are summarized in Figures 3 and 4. The maximum specific removal rates for methanol and MicroC™ batch tests show slightly better results for MicroC™ (represented as mg NO3-N/mg VSS • day).

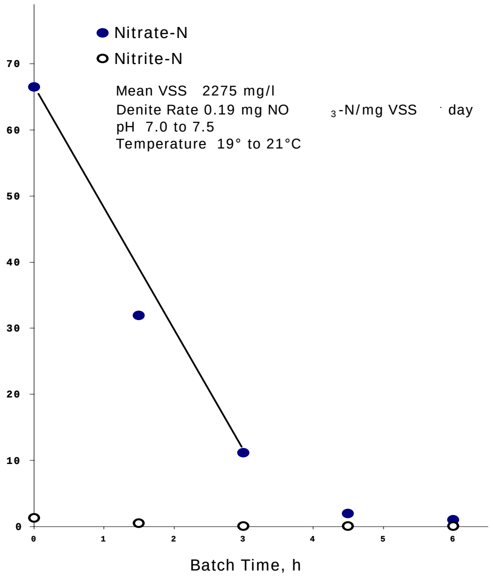


Figure 3- Batch Denitrification of Wastewater With Methanol as Carbon and Energy Source

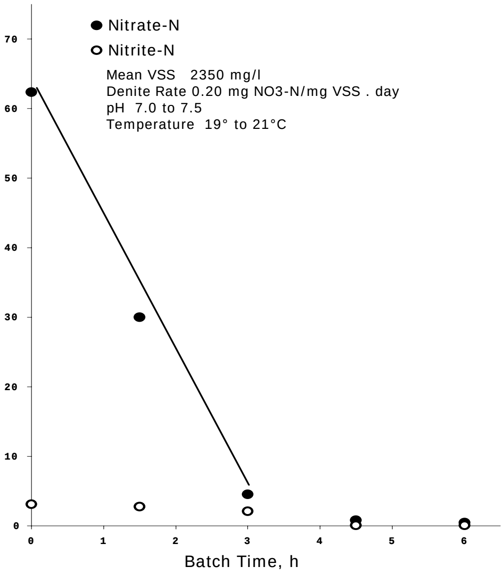


Figure 4- Batch Denitrification of Wastewater With MicroC™ as Carbon and Energy Source

As of June 1, 2006, MicroC™ is being used as an electron donor for denitrification in 92 facilities ranging in size from residential OSDS to large municipal facilities. MicroC™ is gaining acceptance as a viable alternative for denitrification for several reasons, as summarized in Table 2.

Table 2: Summary of MicroC™ Advantages Observed by Various Facilities

Plant Description/Technology	**MicroC™ Performance Results and Advantages**
• 18 MGD conventional activated sludge municipality in Connecticut • Plant unable to meet more stringent nitrogen discharge limits as part of the Long Island Sound nitrogen initiative • Discharge permit of approximately 4 mg/L TN	• MicroC™ put online in August 2005 • No capital cost was required • Facility is now able to meet the discharge permit for 2005 and 2006 and save money on nitrogen credits (CT program) • A methanol feed system for this facility would be in the millions of dollars
• 9500 GPD Decentralized facility serving condominium complex operated by Aquarion Operating Services • Aerobic RBC/Denitrification sand filter • Discharge permits for 10 mg/L TN. • Prior electron donor was 30% methanol solution.	• Switch to MicroC™ in December of 2004 • Cost savings realized due to kinetic advantage of MicroC™ • Removal of safety and fire hazard associated with methanol storage/utilization
• 13,000 GPD Decentralized facility serving residential community operated by Applied Water Management • Discharge permit for 10 mg/L TN • Zenon Zeeweed® membrane bioreactor • Prior electron donor was a sucrose solution	• Switch to MicroC™ in January 2005 • Plant remained in compliance using 1/3 the volume with a lower average NO3-N • Eliminated the logistics, handling and labor problems associated with sucrose
• 10,000 GPD Decentralized facility serving shopping complex operated by Earth Tech Inc. • Discharge permit for 10 mg/L TN • Aerobic RBC/Denitrification sand filter • Prior electron donor was methanol	• Switch to MicroC™ in February 2006 • Safety advantages of MicroC™ is highly regarded by operator • Operator is able to safely store more volume on site resulting in less frequent deliveries
• 0.36 MGD 5-Stage Bardenpho municipal plant • TN discharge permit is 5 mg/L • Prior electron donor was methanol	• Treatment plant is achieving lower TN discharge numbers with a reduced volume of MicroC™ compared to historical methanol usage
• Residential RUCK Filter System • TN discharge permit of 19 mg/L • Unable to meet permit without electron donor addition	• System is now in compliance for TN using MicroC™ as an electron donor. • Expensive methanol feed system was not necessary

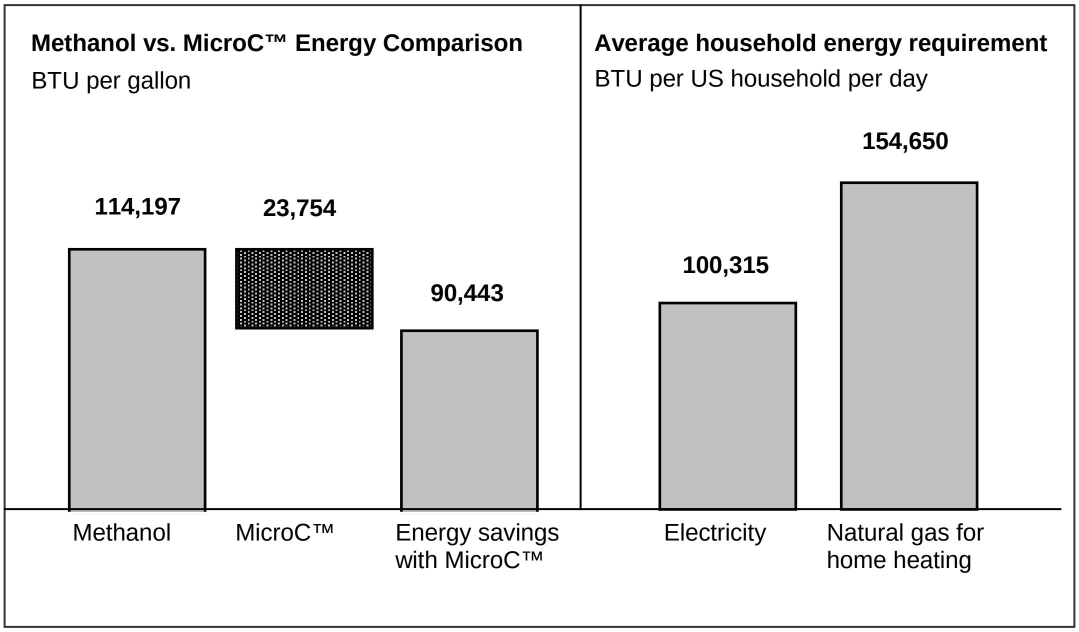
Many proprietary and non-proprietary OSDS technologies are unable to meet total nitrogen discharge permits without the addition of an exogenous electron donor. In some cases this is not a function of the specific technology but of variability in influent characteristics. In other cases the problem lies in the balance between providing an economical operations contract to homeowners while meeting stringent nitrogen discharge requirements.

Table 3 summarizes the technologies using MicroC™ as an electron donor in existing applications and those technologies currently investigating MicroC™ as an electron donor alternative.

Table 3: Summary of MicroC™ use by technology and industry

Denitrification Technology	**Denitrification Industry**
Advantex (Orenco Systems)	OSDS and Decentralized
Amphidrome (FR Mahoney)	
Bioclere (Aquapoint)	
FAST (BioMicrobics)	
RUCK (Holmes and McGrath)	
Generic denitrification filters	
Sequencing Batch Reactors	Decentralized
RBC (generic)	
Zenon Membrane Bioreactor	
Kubota Membrane Bioreactor	
US Filter Membrane Bioreactor	
Aquionics System	
Wetlands Denitrification	
Generic fixed film denitrification reactors	
Downflow Denitrification Filters	Centralized
Upflow Denitrification Filters	
Conventional Activated Sludge	
Bardenpho Process	
A20 Process	

Figure 5 shows the energy inputs of MicroC™ production relative to energy inputs for methanol production. Methanol production is significantly more energy intensive than MicroC™ production. For every gallon of methanol displaced by MicroC™ there is an overall energy savings of 90,443 Btu. This is approximately equivalent to the electrical requirements (represented as Btu) for a single US household for a single day.



Sources: US Department of Transportation, Methanol Institute, US Department of Agriculture, International Energy Studies (IES)

Figure 5: Comparison of Energy Input for Methanol and MicroC™ Production

Consideration of an electron donor for OSDS and decentralized denitrification should include a balance between cost, safety, ease of use, and denitrification performance. Flammable liquids should not be used for these types of systems when other non-flammable alternatives exist. Removal of flammable liquids from OSDS and decentralized systems decreases capital cost for explosion proof equipment as well as creating a safer environment for the operators, homeowners and community served. Industrial wastes are not a practical alternative for OSDS and decentralized systems. Sucrose and sodium acetate are safe alternatives but have considerable drawbacks related to handling and solution preparation, cost, sludge production, fermentation and freezing issues. MicroC™ offers a non-flammable, safe alternative for OSDS and decentralized electron donor feed for denitrification. MicroC™ has proven to be a cost competitive electron donor for denitrification, this fact is reinforced by the existing number of plants currently using MicroC™ for wastewater denitrification.

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