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Kinetics of anaerobic degradation of glycol-based Type I aircraft deicing fluids

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Abstract

The kinetics of anaerobic degradation of glycol-based Type I aircraft deicing fluids (ADFs) were characterized using suspended-growth fill-and-draw reactors. Both Type I ADFs tested showed near-complete anaerobic degradability. First-order degradation rate constants of 3.5 d^{-1} for the propylene glycol-based Type I ADF and 5.2 d^{-1} for the ethylene glycol-based Type I ADF were obtained through continuous-culture means under mesophilic conditions (35 °C). Fill-and-draw operation at lower temperatures affected anaerobic degradability only minimally down to 25 °C but substantially below 25 °C. High Type I ADF feed concentrations substantially affected degradability. Batch testing of fill-and-draw reactors resulted in first-order degradation rate constants of 1.9 d^{-1} for propylene glycol-based Type I ADF and 3.5 d^{-1} for ethylene glycol-based Type I ADF.

Introduction

Aircraft deicing is usually accomplished by chemical means using aircraft deicing fluids (ADFs). Type I ADFs are used for removing snow, frost, and ice from aircraft surfaces. The ADFs are comprised primarily of either ethylene glycol (EG) or propylene glycol (PG) (Mericas and Wagoner 1994). (Diethylene glycol-based fluids are commonly used in Europe (e.g. Nitschke et al. 1996)). The balance of the fluids are composed of corrosion inhibitors, wetting agents, surfactants, thickeners, and other chemicals (Cancilla et al. 1997).

Ethylene glycol has a theoretical oxygen demand (ThOD) of 1.29 g/g, or around 1.4×10^6 mg/L. Propylene glycol has a ThOD of 1.68 g/g, or around 1.7×10^6 mg/L. For perspective, the typical chemical oxygen demand (COD) of untreated domestic wastewater is 250–1000 mg/L (Metcalf & Eddy, Inc. 1993). Both compounds are highly degradable aerobically (e.g. Fincher and Payne 1962, Kaplan et al. 1982, Strong-Gunderson et al. 1995). Deicing runoff from several northeastern U.S. airports were measured for chemical oxygen demand and glycol content during the 1966–7 deicing season. One sample from a centralized deicing facility had a COD of 6.0×10^5 mg/L. The COD of all samples was attributed almost entirely to glycol (CHA Technical Services LLC 1998).

The primary environmental concern with deicing/anti-icing operations has been attributed to the glycols. Their copious use, high organic strength, and aerobic biodegradability threatens to deplete oxygen from surface waters receiving uncontrolled runoff. In addition, attention has shifted to the potential toxic effects from additives, specifically corrosion inhibitors (Cancilla et al. 1997; Cancilla et al. 1998). Airports have become increasingly responsible for managing their runoff and have numerous options for recovery and treatments (e.g. Bremer 1993; Mericas & Wagoner 1994; Betts 1999; Switzenbaum et al. 1999).

One option for treating collected ADF wastes is anaerobic treatment (Switzenbaum et al. 1999). Anaerobic treatment is suitable for high strength wastes (McCarty 1964) and also lends itself to the intermittent generation of deicing wastes (Jewell 1987). Anaerobic treatability has been demonstrated for EG-based and PG-based ADFs (Veltman et al. 1998a) and for ADF wastes (CHA Technical Services LLC,

1998). A pilot-scale anaerobic fluidized bed reactor successfully treated PG-based deicing wastes effectively (Komisar et al., 1998) and led to the construction and operation of a full-scale system at the Albany International Airport, NY.

The metabolic pathways for anaerobic degradation of EG (Dwyer and Tiedje 1983) and PG (Veltman et al. 1998b) have been illustrated. EG undergoes an initial disproportionation reaction into ethanol and acetate, and ethanol is subsequently oxidized to acetate. Aceticlastic methanogens split acetate into methane and carbon dioxide; hydrogen-oxidizing methanogens produce methane from hydrogen liberated during ethanol oxidation. PG undergoes an initial disproportionation reaction into *n*-propanol and propionate, *n*-propanol is oxidized to propionate (liberating hydrogen), and propionate is oxidized to acetate (also liberating hydrogen). Aceticlastic and hydrogen-oxidizing methanogenesis proceeds. Anaerobic glycol degradation is thus a collection of metabolic processes occuring in series (formation and subsequent degradation of metabolic intermediates) and in parallel (hydrogen oxidation; start of degradation of intermediates as they are being formed). Propionate oxidation is especially prone to hydrogen-induced thermodynamic limitations (McCarty 1981).

While several studies have been conducted which evaluated the pathway and extent of anaerobic degradation of glycols and glycol-based ADFs, very little information exists concerning the rates of degradation of these products. Information on kinetics is important for the rational design of an anaerobic treatment system (Speece 1996) and to evaluate the fate in natural systems when high oxygen demands, such as exerted by deicing fluids, lead to oxygen-depleted conditions. A summary of anaerobic treatment kinetics has been presented by Pavlostathis and Giraldo-Gomez 1991. The paper here presents results from experiments designed to quantify the kinetics of anaerobic glycol-based Type I ADF degradation. First-order kinetics constants were determined for anaerobic degradation of both EG- and PG-based Type I ADFs. Both continuous-culture and batch measurements were made. These kinetics values describe the overall degradation of the glycols in the Type I ADFs and are thus a summarization of all serial and parallel metabolic processes accomplished by the Type I ADF-degrading microbial consortia and the thermodynamic conditions to which they were exposed.

Materials and methods

Type I aircraft deicing fluids

The EG-based Type I ADF used was Union Carbide Type I ADF Concentrate. The PG-based Type I ADF used was ARCO Chemical Company concentrated Type I ADF and ARCOPLUS® Dilute Type I ADF.

Continuous-culture reactors

Fill-and-draw reactors were constructed to approximate continuous-flow stirred tank reactors (CFSTRs). One EG-based and one PG-based Type I ADF reactor was operated. Each reactor consisted of a 2-liter Erlenmeyer flask with fittings for feeding, withdrawing effluent, and exhausting process gas. Each reactor contained 1.5 L of an anaerobic suspended-growth culture developed previously from wastewater treatment plant anaerobic digester sludge to degrade either EG-based or PG-based Type I ADF (Veltman et al. 1998a). The exhaust line was connected to a glass submarine-shaped gas reservoir 20 cm long and 4.5 cm in diameter, with glass hose connectors at each end and a screw top from a 12 mL glass vial (National Scientific Company) fashioned onto the top. A 15 mm Mininert™ valve cap (Dynatech Precision Instruments, Baton Rouge LA) was affixed onto the screw top to allow for penetration by a syringe needle for process gas analysis. The reservoir was connected in-line with a 500 mL Erlenmeyer flask containing water, which prevented oxygen from seeping into the gas reservoir and greatly enhanced the ability to withdraw contents from the reactor.

Each reactor was fed once per day; the initial residence time was 15 days. The reactor was vigorously shaken, 100 mL of effluent was withdrawn, then an equal volume of feed solution containing Type I ADF, nutrients, and buffer was added. The reactors were kept in an insulated room heated to 35 °C (±1 °C) with an electric floor heater. The substrate feed concentration was approximately 9000 mg COD/L. The reactors were operated for at least three residence times to attain steady-state.

The reactors were routinely monitored for pH, TSS, VSS, and dissolved COD to verify the attainment of steady-state operation and obtain data used to quantify CFSTR-based kinetics. Monitoring was performed on effluent collected in 125 mL Erlenmeyer flasks just prior to feeding. Effluent pH was measured using an Orion® Model 520A pH meter (Orion Research, Inc., Beverly, MA) fitted with an Orion®

Triode^{TM} pH electrode. Other parameters were measured in accordance with Standard Methods (APHA, 1995), sections 2540 D (TSS), 2540 E (VSS) using residue from TSS analyses, and 5220 D (dissolved COD). Whatman® 934AH glass microfibre filters (Whatman, Inc., Clifton, NJ) were used for TSS; dissolved COD refers to effluent passed through these filters.

After attaining steady-state, measurements for dissolved COD, TSS, and VSS were made daily for 5 days; samples were also prepared for analyzing metabolic intermediates. Additionally, process gas was analyzed for percent methane (CH_4). Following these steady-state measurements, the residence time was decreased and the process to obtain and measure steady-state performance repeated. These reactors were designated EG_X and PG_X. (The subscript X refers to the progressively decreasing residence time.)

Temperature-effects fill-and-draw reactors

A second pair of fill-and-draw reactors was operated similarly to the kinetics fill-and-draw reactors, except the temperature was incrementally decreased while the residence time was kept constant. The reactors were initially operated to steady-state at a 15 day residence time, temperature of 35 °C (±1 °C), and feed concentration of 9000 mg COD/L. After steady-state measurements, the reactors were moved to a 30 °C incubator. Subsequent temperature drops were made after steady-state was attained and characterized in both reactors.

Substrate concentration-effects fill-and-draw reactors

A third pair of fill-and-draw reactors was operated similarly, except the feed strength was incrementally increased while the residence time and temperature were kept constant. The reactors were initially operated to steady-state at a 15 day residence time, 35 °C (±1 °C) temperature, and 9000 mg COD/L feed concentration. Following attainment of steady-state, the feed concentration was increased to 12,000 mg COD/L. Subsequent increases in feed concentration were made after steady-state operation was achieved and measured.

Intrinsic (batch) kinetics

Batch kinetics studies were implemented to highlight the intrinsic kinetics of each methanogenic consortium (EG- and PG- based Type I ADF). Since fill-and-draw operation amounted to a series of daily batch feedings, a fill-and-draw reactor could also be measured in batch mode simply by measuring reactor dissolved COD concentrations periodically after a daily feeding. The formation and disappearance of metabolic intermediates could also be observed.

Steady-state operation at 15 day residence time, 35 °C (±1 °C), and 9000 mg COD/L feed concentration resulted in near- complete COD conversion following start-up in all reactors. Therefore these conditions were known to result in stable performance and provided the basis for intrinsic kinetics testing.

Two new fill-and-draw reactors, one EG- and one PG-based Type I ADF, were brought to steady-state at these same start-up conditions. Batch kinetics information was then obtained by measuring reactor dissolved COD immediately after feeding and periodically thereafter over a 24 hour period. Each measurement incurred the net removal of only 5 mL of reactor material, which only minimally increased headspace volume. Metabolic intermediates samples were drawn from the filtered reactor material used for dissolved COD analyses.

Metabolic intermediates

Filtered effluent (from dissolved COD analyses) was drawn through a Corning® 13mm disposable syringe filter containing a cellulose acetate membrane and transferred into a Target DP^{TM} vial (National Scientific Company) or Target Micro-Sert^{TM} vial insert placed in a Target DP^{TM} vial. This was then acidified to pH < 2 to preserve samples and to ensure VFAs were in their un-ionized form for GC detection. The vial was then capped with a Target DP^{TM} cap with Teflon/rubber septum and then refrigerated at approximately 2 °C until analyzed by GC/FID.

Metabolic intermediates (alcohols and volatile fatty acids) were analyzed using gas chromatography with flame ionization detection (GC/FID). The instrument and sample injection procedures described by Veltman et al. (1998b) were used here except that a different column temperature program was used. The column temperature was kept at 40 °C for one minute, then increased at 50 °C/min up to 100 °C, held there for 2.8 minutes, then increased at 10 °C/min up to 140 °C and held there for one minute, at which point the temperature program was complete. Samples were analyzed only after they had been acidified.

Degradation rate constant determination

A simple first-order degradation model was adopted to determine a first-order degradation rate constant k (time^{-1}). The general first-order expression to express the change in concentration of a substance C with time t is given as follows:

$$\frac{dC}{dt} = -kC. \quad (1)$$

The rate expression for a given reactor configuration is derived by employing mass balance principles around the reactor and considering special conditions such as steady-state. For a CFSTR operating at steady-state the effluent concentration S from the reactor is given as follows:

$$S = \frac{S_0}{1 + k\theta} \quad (2)$$

where S_0 = concentration introduced into the reactor (i.e. feed concentration) and θ = hydraulic residence time. A plot of the ratio S_0/S versus the residence time would therefore give a line whose slope is k. For a batch reactor, the degradation rate expression for the decrease in concentration C at time t is given as follows:

$$C = C_0 e^{-kt} \quad (3)$$

where C_0 refers to the concentration in the reactor at time $t = 0$.

Results

PG-based Type I ADF, continuous culture (PG_X)

Steady-state effluent dissolved COD for the PG-based Type I ADF continuous-culture reactor PG_X is provided in Figure 1. (A steady-state effluent dissolved COD of 7350 mg/L resulted at a 4 day residence time; this was left out of Figure 1 to preserve scale.) The effluent dissolved COD and levels of metabolic intermediates are provided in Table 1. There was a noticeable discontinuity in steady-state dissolved COD at around an 8 day residence time and again at about a 4 day residence time, which likely indicates the washing out of critical methanogenic populations. The ratio of theoretical COD contributed by metabolic intermediates listed in the table to the dissolved COD measured in the effluent is quite low at low steady-state dissolved COD levels, suggesting a background dissolved COD

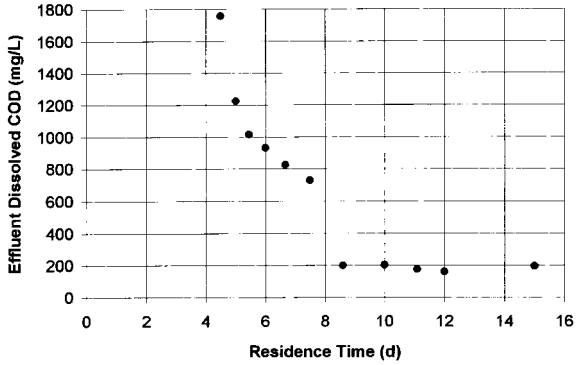

Figure 1. Steady-state effluent dissolved COD levels in reactor PG_X.

of approximately 150 mg/L was present. This background dissolved COD was most likely contributed by dissolved methane, other compounds not detected by the GC/FID method used (e.g. sulfides), and soluble microbial products (SMPs).

Since the reactors incorporated suspended-growth cultures, the solids and hydraulic residence times were virtually identical and have been referred to simply as residence time. Equation 2 was applied separately to the data between an 8 and 15 day residence time and from 4 to 8 day residence time, since the 8 day residence time appears to represent where the growth rate of a critical methanogenic species was exceeded. In each region the ratio S_0/S was plotted versus residence time. The point defined by $S_0/S = 1$ for a residence time θ of zero days was also included in the plot for each region because, independent of mechanistic circumstances governing the demarcations in effluent dissolved COD, this point would be expected from Equation 2. A least-squares linear regression using Microsoft Excel was applied to each plot. The resulting kinetics constants were 3.52 d^{-1} for the region between 15 and 8 days, and 1.52 d^{-1} between 8 and 4 days.

EG-based Type I ADF, continuous culture (EG_X)

The steady-state results obtained from reactor EG_X are summarized in Table 2. A lower background dissolved COD appears to have been present, since a significant portion of measured dissolved COD at 10 day residence time was contributed by propionate even though the measured dissolved COD was only around 100 mg/L. The data are limited since operation at a residence time of six days led to unstable operation. An attempt was made to recover the reactor by reverting to

Table 1. Effluent dissolved COD and metabolic intermediates in reactor PG_X at steady-state. SRT = solids residence time; COD_{Eff} = measured dissolved chemical oxygen demand of reactor effluent; ND = not detected; COD_{Int} = chemical oxygen demand calculated from intermediates listed in table; Ratio = COD_{Int}/COD_{Eff}

SRT (d)	COD_{Eff} (mg L^{-1})	*n*-Propanol (mg L^{-1})	Acetate[a] (mg L^{-1})	Propionate[a] (mg L^{-1})	Butyrate[a] (mg L^{-1})	COD^{b}_{Int} (mg L^{-1})	Ratio
15	194	ND	<5	<5	ND	<13	<0.07
12	160	ND	7.2	ND	ND	7.7	0.05
11	176	ND	<5	<5	ND	<13	<0.08
10	202	ND	<5	ND	ND	<5.3	<0.03
8.6	198	ND	5.3	ND	ND	5.7	0.03
7.5	730	ND	91	300	5.9	560	0.77
6.7	825	<5	59	320	5.7	560	0.68
6.0	933	ND	56	370	5.7	630	0.68
5.5	1020	ND	34	460	9.4	750	0.74
5.0	1220	29	20	550	9.6	940	0.77
4.5	1760	42	21	960	10	1600	0.90
4.0	7350	400	42	4000	8.1	7100	0.97

[a]Volatile acids are listed in ionized forms due to circumneutral pH in reactors.
[b]Does not include small contributions from longer-chain volatile fatty acids or from compounds detected at less than 5 mg/L.

Table 2. Effluent dissolved COD and metabolic intermediates in reactor EG_X at steady-state

SRT (d)	COD_{Eff} (mg L^{-1})	Ethanol (mg L^{-1})	Acetate (mg L^{-1})	Propionate (mg L^{-1})	Butyrate (mg L^{-1})	COD_{Int} (mg L^{-1})	Ratio
15	124	ND	<5	<5	ND	<13	<0.10
10	109	ND	<5	17	ND	26	0.24
7.5	220	ND	52	45	<5	120	0.55

a 10 day residence time, but the reactor did not recover to pre-upset levels.

A CFSTR-based first-order kinetic constant of 5.24 d^{-1} was determined for reactor EG_X for the region 7.5–15 day residence time. This value is roughly 1.5 times that from reactor PG_X for a similar range of residence times.

Temperature effects reactors, continuous culture ($PG_{15}(T)$ and $EG_{15}(T)$)

The steady-state performance of reactors $PG_{15}(T)$ and $EG_{15}(T)$, which had been operated at a constant feed concentration (9000 mg COD/L) and residence time (15 d) but at progressively lower temperatures, is summarized in Tables 3 and 4. The data clearly show low temperature dependence on anaerobic degradation of both PG and EG from 35 °C down to 25 °C, and substantial temperature dependence below 25 °C. A sharp delineation between balanced operation and upset conditions, rather than a progressive decline, was observed in both reactors. The lower temperatures clearly upset the metabolic balance in both reactors.

Substrate feed concentration effects, continuous culture ($PG_{15}(N)$ and $EG_{15}(N)$)

Tables 5 and 6 summarize the steady-state performance of reactors $PG_{15}(N)$ and $EG_{15}(N)$, in which temperature (35 °C) and residence time (15 d) were constant but in which the feed concentration was progressively increased. Sharp delineations in steady-state effluent dissolved COD were seen in both reactors according to the data in these tables.

Batch kinetics, standard feed conditions

The batch tests involved new 1.5 L fill-and-draw reactors operating at steady-state under the standard feed conditions (15 d residence time, 35 °C, and 9000 mg

Table 3. Effluent dissolved COD and metabolic intermediates in reactor PG_{15}(T) at steady-state

Temp. (°C)	COD_{Eff} (mg L^{-1})	*n*-Propanol (mg L^{-1})	Acetate (mg L^{-1})	Propionate (mg L^{-1})	Butyrate (mg L^{-1})	COD_{Int} (mg L^{-1})	Ratio
35	204	–	–	–	–	–	–
30	235	ND	40	8.3	<5	55	0.23
25	344	ND	80	18	<5	110	0.32
20	5350	ND	450	2300	80	4200	0.78
15	7350	300	130	4200	15	7200	0.97

Table 4. Effluent dissolved COD and metabolic intermediates in reactor EG_{15}(T) at steady-state

Temp. (°C)	COD_{Eff} (mg L^{-1})	Ethanol (mg L^{-1})	Acetate (mg L^{-1})	Propionate (mg L^{-1})	Butyrate (mg L^{-1})	COD_{Int} (mg L^{-1})	Ratio
35	128	–	–	–	–	–	–
30	111	ND	<5	5.7	ND	<14	<0.13
25	245	ND	64	41	<5	130	0.55
20	6820	150	5600	69	ND	6400	0.93

COD/L feed concentration from deicing fluid glycol). Reactor dissolved COD measurements were periodically made after a daily feeding of 100 mL feed (containing 9000 mg COD/L from glycol), up until the next feeding around 24 hours later.

Since the primary focus of these batch tests was to determine first-order degradation rate constants for the reduction of COD derived from glycol in the added feed, the background dissolved COD was subtracted from each measured dissolved COD value. The background dissolved COD was the steady-state dissolved COD of the reactor measured just prior to conducting the batch test experiments. The background-corrected dissolved COD values, represented as the ratio C/C_0, are provided in Figure 2. The value for C_0 used in Figure 2 was the background-corrected dissolved COD immediately following feeding.

The simple first-order degradation model given in Equation 3 was adopted. COD reduction during the initial stages of anaerobic glycol degradation is minimal while the glycol undergoes an initial disproportionation reaction. Therefore, for kinetic constant determination, the starting point was taken to be the data point where COD reduction began in earnest. To facilitate the determination of kinetic constants, the dissolved COD value and time point were assigned as C_0 (adjusted) and t_0 (adjusted), respectively. All subsequent values were similarly adjusted. The final point for kinetic constant determination was taken to be the point at which no further degradation appears to have occured. With these adjustments, an exponential decay curve was fitted through a plot of adjusted C/C_0 versus adjusted time. A value of 1.94 d^{-1} was determined for PG-based Type I ADF. The

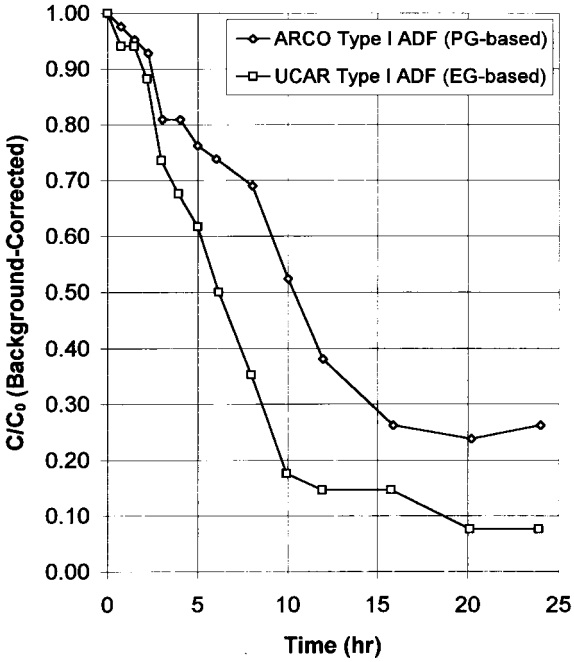

Figure 2. Background-corrected batch test results, standard feed conditions.

Table 5. Effluent dissolved COD and metabolic intermediates in reactor PG_{15}(N) at steady-state

Feed Conc. (mg COD/L)	COD_{Eff} (mg L^{-1})	*n*-Propanol (mg L^{-1})	Acetate (mg L^{-1})	Propionate (mg L^{-1})	Butyrate (mg L^{-1})	COD_{Int} (mg L^{-1})	Ratio
9000	176	–	–	–	–	–	–
12,000	338	ND	8.7	ND	ND	9.3	0.03
15,000	347	ND	11	<5	ND	<19	<0.06
20,000	14600	53	80	10200	<5	15700	1.08

Table 6. Effluent dissolved COD and metabolic intermediates in reactor EG_{15}(N) at steady-state

Feed Conc. (mg COD/L)	COD_{Eff} (mg L^{-1})	Ethanol (mg L^{-1})	Acetate (mg L^{-1})	Propionate (mg L^{-1})	Butyrate (mg L^{-1})	COD_{Int} (mg L^{-1})	Ratio
9000	88	–	–	–	–	–	–
12,000	179	–	5.7	6.4	ND	16	0.09
15,000	261	–	7.0	7.4	ND	19	0.07
20,000	726	<5	160	180	ND	440	0.61
25,000	16900	650	13800	81	ND	16200	0.96

"delay" period before active COD reduction began was 0.094 d. A batch first-order degradation rate constant of 3.49 d^{-1} was determined for EG-based Type I ADF, preceded by a delay period of 0.061 d before active COD reduction began.

Metabolic intermediates, batch kinetics tests, standard feed conditions

The metabolic intermediates from these batch tests were measured for each time point at which a reactor dissolved COD measurement was made. The results for the PG-based Type I ADF batch test are shown in Figure 3. (Unfortunately glycols were not detected during these analyses.) Figure 3 shows that n-propanol and propionate were simultaneously formed, although the maximum molar n-propanol concentration only reached one-fourth that of propionate rather than one-half if disproportionation proceeded to completion prior to subsequent degradation. Oxidation of n-propanol probably occurred as it was formed; oxidation of propionate proceeded much more slowly. This may be expected given the relative sensitivities to hydrogen between anaerobic oxidation of n-propanol ($\Delta G^{\circ\prime} = +2.9$ kcal/mol) and propionate ($\Delta G^{\circ\prime} = +18.3$ kcal/mol), plus the fact that *n*-propanol releases hydrogen as it is anaerobically oxidized.

The metabolic intermediates for the batch test of EG-based Type I ADF is shown in Figure 4. Here

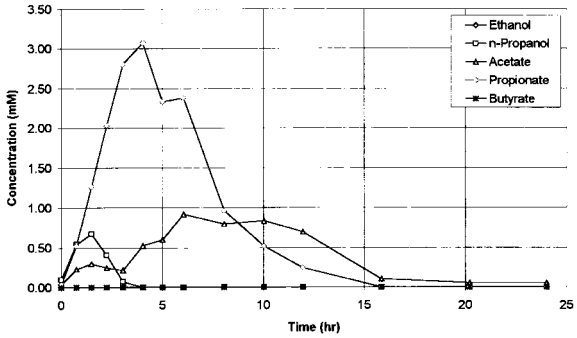

Figure 3. Metabolic intermediates, PG-based Type I ADF batch test, standard feed conditions.

the maximum molar concentration of ethanol was almost as high as that for acetate. This indicates acetate oxidation proceeded as ethanol was being formed during disproportionation. This would be expected since anaerobic ethanol oxidation is sensitive to hydrogen ($\Delta G^{\circ\prime} = +2.3$ kcal/mol) whereas acetate conversion to methane is not nearly so ($\Delta G^{\circ\prime} = -7.4$ kcal/mol). Figure 3 and 4 both illustrate that the first-order degradation rate constants determined here characterize the overall metabolic and thermodynamic complexities of anaerobic degradation of these glycols.

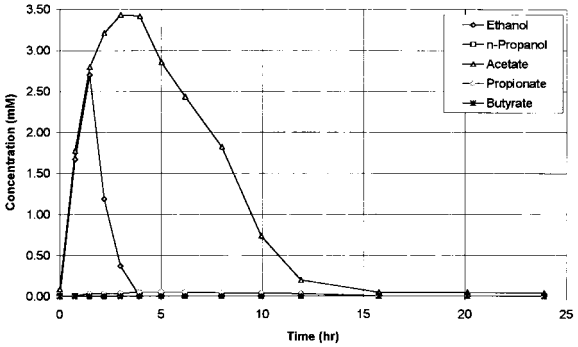

Figure 4. Metabolic intermediates, EG-based Type I ADF batch test, standard feed conditions.

Discussion

Comparison of PG and EG kinetics constants

Both glycol-based Type I ADFs tested showed near-complete degradability, therefore degradation rate constants most likely reflected glycol degradability. The lower experimental kinetic constant for PG-based Type I ADF derived from both continuous-culture and batch experiments was most likely due to the higher complexity involved in anaerobic propylene glycol degradation, particularly the formation of propionate directly from PG (during disproportionation) and *n*-propanol (product from disproportionation). Propionate represents an additional metabolic step. Anaerobic propionate degradability is especially sensitive to hydrogen levels ($\Delta G^{\circ\prime} = +18.3$ kcal/mol). The anaerobic oxidation of *n*-propanol ($\Delta G^{\circ\prime} = +2.9$ kcal/mol) during PG degradation and ethanol ($\Delta G^{\circ\prime} = +2.3$ kcal/mol) during EG degradation indicate both reactions are affected by hydrogen concentrations relatively equivalently, and both reactions release similar amounts of hydrogen. Therefore the additional step of propionate oxidation, especially with its high sensitivity to hydrogen levels, is most likely responsible for the lower first-order degradation rate observed for anaerobic degradation of PG-based Type I ADF.

The anaerobic conversion of propionate to acetate is favorable only at low hydrogen levels and is thus particularly dependent on hydrogen-oxidizing methanogens to consume hydrogen. However, the favorable conditions for hydrogen-oxidizing methanogenesis include high hydrogen concentrations. A narrow range of favorable conditions exist for propionate conversion and hydrogen consumption in the same environment (McCarty 1981). The suspended-growth cultures would not have allowed for shielding against environmental hydrogen conditions, as might be realized in the inner layers of anaerobic consortium granules (Guiot et al. 1992).

Other potential differences between degradation rate constants could stem from additive packages. The exact ADF formulations are proprietary. However, benzotriazole and tolytriazole have been isolated from ADFs as Microtox®-active compounds (Cancilla et al. 1997). Benzotriazole and 5-methyl-*H*-benzotriazole (a primary component of tolytriazole) were conserved in our reactors (data not shown). The concentrations in the PG-based Type I ADF were around 10 times those in the EG- based Type I ADF. It is possible this was a factor in the lower degradation rate constants for PG-based Type I ADF. However, the additives did not appear to affect degradability under balanced operation. Additionally, the transition from balanced to unbalanced operation under increased substrate loading occurred at similar feed concentrations (Tables 5 and 6). Other manufacturers' formulations might contain different levels of these particular additives or contain different additives that may affect degradability.

Reduced performance in fill-and-draw reactors under stressed conditions

An interesting feature is the sharp delineations in steady-state dissolved COD in all fill-and-draw reactors (except EG_X, where only limited data were obtained). It is possible this reflected the washing out of critical organisms; however, no evidence of this was obtained. Under the most stressed conditions in these reactors, alcohol was present. This suggests thermodynamic limitations set in under the most stressed conditions; hydrogen was not being scavenged quickly enough to allow even for complete alcohol oxidation. However, this was just as likely a reflection of metabolic imbalance as it was a cause. Other factors could include product inhibition, particularly acetate inhibition of anaerobic propionate degradation (Gorris et al. 1989; Fukuzaki et al. 1990; Kus and Weismann 1995).

The performance in the temperature-effects reactors declined only slightly down to 25 °C. Operators of reactors designed to reduce the COD from deicing fluid wastes may be able to operate reactors to temperatures somewhat lower than 35 °C without reducing treatment efficiency. The fixed-film nature of operational reactors may allow for enhanced acclimation to lower temperatures.

One ramification of temperature-effects testing has to do with degradation of glycols in the subsurface, where glycols may reside due to overspray and drippage from aircraft surfaces. The drastically limited reduction of COD at temperatures below 25 °C in these experiments could indicate that glycols trapped in the subsurface, where temperatures stay relatively cool, may experience limited degradation once anaerobic conditions set in (after available oxygen is depleted).

The substrate concentration effects discussed here may be lessened in an actual operational reactor that incorporated attached-growth. The results presented here merely illustrate the effects overloading may cause.

Conclusions

Both PG-based and EG-based Type I deicing fluids were almost completely degradable anaerobically. The degradation rate constants determined here were a reflection of the difference in complexity between the anaerobic metabolic pathways of EG and PG accomplished by their respective microbial consortia, rather than other differences in the Type I ADF formulations. The lower degradation rate constant obtained for PG-based Type I ADF through both CFSTR and batch testing reflects the thermodynamic challenges of maintaining anaerobic propionate oxidation and hydrogen oxidation under the same conditions, in addition to the added number of steps in anaerobic PG degradation.

Deicing fluids are constantly being reformulated (USEPA 1999). The establishment of anaerobic degradability has been accomplished for fluids which contain levels of additives which are uninhibitory to the anaerobic cultures. Future formulations may contain additive packages or base compounds which have different effects on the cultures designed to treat the deicing wastes.

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References

APHA (1995) Standard methods for the examination of water and wastewater, 19th Edition. American Public Health Association, Washington D.C.

Betts KS (1999) Airport pollution prevention takes off. Environ. Sci. Technol. 33: 210A–212A.

Bremer K (1993) The double deicing dilemma, available at http://www.airportnet.org/depts/publications/airmags/am91093/deicing.htm, September–October 1993.

Cancilla DA, Holtkamp A, Matassa L & Fang X (1997) Isolation and characterization of Microtox®-active components from aircraft deicing/anti-icing fluids. Environ. Toxicol. Chem. 16: 430–434.

Cancilla DA, Martinez J & Van Aggelen GC (1998) Detection of aircraft deicing/antiicing fluid additives in a perched water monitoring well at an international airport. Environ. Sci. Technol. 32: 3834–3835.

CHA Technical Services, LLC (1998) Anaerobic treatment of aircraft deicing wastes: a technology assessment. Final Report 98-13 for the New York State Energy Research and Development Authority (NYSERDA), September 1998.

Dwyer DF & Tiedje JM (1983) Degradation of ethylene glycol and polyethylene glycols by methanogenic consortia. Appl. Environ. Microbiol. 46: 185–190.

Fincher EL & Payne WJ (1962) Bacterial utilization of ether glycols. Appl. Microbiol. 10: 542–547.

Fukuzaki S, Nishio N, Shobayashi M & Nagai S (1990) Inhibition of the fermentation of propionate to methane by hydrogen, acetate, and propionate. Appl. Environ. Microbiol. 56: 719–723.

Gorris LGM, van Deursen JMA, van der Drift C & Vogels GD (1989) Inhibition of propionate degradation by acetate in methanogenic fluidized bed reactors. Biotechnology Letters 11(1): 61–66.

Guiot SR, Pauss A & Costerton JW (1992) A structured model of the anaerobic granule consortium. Water Sci. Technol. 25(7): 1–10.

Jewell (1987) Anaerobic sewage treatment. Environ. Sci. Technol. 21: 14–21.

Kaplan DL, Walsh JT & Kaplan AM (1982) Gas chromatographic analysis of glycols to determine biodegradability. Environ Sci. Technol. 16: 723–725.

Komisar SJ, Veltman S, Switzenbaum MS & Hickey RF (1998) Complete on-site treatment of aircraft deicing wastewater using a sequential anaerobic fluidised bed – slow sand filter system. Proceedings WEFTEC, Orlando, Florida, October 1998.

Kus F & Wiesmann U (1995) Degradation kinetics of acetate and propionate by immobilized anaerobic mixed cultures. Water Res. 29: 1437–1443.

McCarty PL (1964) Anaerobic waste treatment fundamentals. Public Works 95(9): 107–112.

McCarty PL (1981) One hundred years of anaerobic treatment. Presented at the Second International Conference on Anaerobic Digestion, Travemünde, Germany, September 7, 1981.

Mericas D & Wagoner B (1994) Balancing safety and the environment. Water Environ. Technol. 6(12): 38–44.

Metcalf & Eddy, Inc. (1993) Wastewater engineering: treatment, disposal, and reuse, 3rd Edition. McGraw-Hill, Inc., New York.

Nitschke L, Wagner H, Metzner G, Wilk A & Huber L (1996) Biological treatment of waste water containing glycols from deicing agents. Water Res. 30: 644–648.

Pavlostathis SG and Giraldo-Gomez E (1991) Kinetics of anaerobic treatment: a critical review. Critical Reviews in Environmental Control 21: 411–490.

Speece RE (1996) Anaerobic biotechnology for industrial wastewaters. Archae Press, Nashville.

Strong-Gunderson JM, Wheelis S, Carroll SL, Waltz MD & Palumbo AV (1995) Degradation of high concentrations of glycols, antifreeze, and deicing fluids. In: Hinchee RE (Ed), Microbial Processes for Bioremediation. Battelle Press, 1995.

Switzenbaum MS, Veltman S, Schoenberg T, Durand CM, Mericas D & Wagoner B (1999) Best management practices for airport deicing stormwater. Manual for workshop held at University of Massachusetts Amherst, July 28, 1999.

USEPA (1999) Draft: effluent guidelines, airport deicing operations guidelines. EPA 812-D-99-002.

Veltman S, Schoenberg T & Switzenbaum MS (1998a) Potential for anaerobic treatment of airport deicing fluids. Proceedings of the 1998 ASCE Conference on Environmental Engineering.

Veltman S, Schoenberg T & Switzenbaum MS (1998b) Alcohol and acid formation during the anaerobic decomposition of propylene glycol under methanogenic conditions. Biodegradation 9: 113–118.