

DOE/ID/13548

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Final Report – 08/15/1997 – 02/14/2001

**H. D. Stensel
S. E. Strand**

March 2001

Work Performed Under Contract No. DE-FC07-97ID13548

**For
U.S. Department of Energy
Assistant Secretary for
Energy Efficiency and Renewable Energy
Washington, DC**

**By
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(#DE-FC07-971D13548)

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March 14, 2001

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1.0 INTRODUCTION AND BACKGROUND

The U.S. Environmental Protection Agency (EPA) "Cluster Rules" requires reduction and control of particulate and hazardous air pollutants (HAPs), which include organic and chlorinated organic compounds, and odor causing reduced sulfur compounds from pulp and paper facilities (Vice and Carroll 1998). The air regulations are based on applying maximum achievable control technology (MACT) to achieve 87 to 98 percent removal efficiency of hazardous air pollutants, depending upon the mill types and processes. Each mill can choose to participate in the Voluntary Advanced Technology Implementation Program (VATIP) or comply with MACT I and MACT III by April 15, 2001 (Anon 2000). MACT I air standards are applicable to chemical pulp mills while MACT III are applicable to mechanical, secondary fiber and non-wood pulping and paper making systems at mills.

Air emissions from pulp and paper mills can be categorized into either high volume low concentration gas streams (HVLC) or low volume high concentration gas streams. The low volume high concentration gas streams are generally handled by on-site incineration, and the high volume low concentration gas streams are the ones that will be most impacted by the cluster rules. The content and concentration of the gas streams vary for different processes. The most common organic compounds in HVLC gas streams, are methanol, chloroform, acetaldehyde, acrolein, formaldehyde, methyl-ethyl-ketone, toluene, benzene, xylenes, phenol, dichloromethane, carbon disulfide, hexane and terpenes (Mehta 1995). The major portions of the organic HAPs are methanol (100-500 ppm), formaldehyde (plywood industry) and acetaldehyde. EPA's cluster rules allow methanol to be used as a surrogate for HAPs with 98 percent reduction of methanol or an effluent concentration that does not exceed 20 ppm (Mehta 1995; Vice and Carroll 1998)

Reduced sulfur compounds (TRS) of interest in pulp and paper mill gas streams are hydrogen sulfide (HS), methyl mercaptan (MT), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS). The TRS concentration in pulp and paper gas emission streams was reported to be in the range of 20-50 ppm. However, these compounds have very low

odor threshold values (0.5-5 ppb for HS, 0.3-3ppb for MT, 1-15ppb for DMS and 1-20 ppb for DMDS (Jarvensivu et al. 1997).

Another important characteristic of pulp and paper mill gas emissions is their high temperature, which can be in the range of 40°C – 70°C.

1.1 Biological Treatment of Gas Emissions

While thermal incineration and carbon adsorption are established technologies for treating contaminated gas streams, biological treatment is of interest due to its potential for reduced cost. The most commonly used biological treatment process for gas streams is biofiltration, due to its simplicity and relatively low operating cost. The contaminated gas stream flows up through a media bed, which provides a surface for biomass attachment and growth. Various types of media have been used in biofilters, including compost, peat, perlite and activated carbon, for treating odor containing gases in sewage works, and organic compounds in gases from industrial emissions or hazardous waste remediation (Bielefeldt 1996).

Biofiltration has been evaluated in a limited number of bench scale and pilot plant studies for treating gas emissions from pulp and paper facilities. Mohseni and Allen (1998) studied α -pinene and methanol removal efficiency in a 28-cm diameter by 30-cm high biofilter at 40°C with the contaminated air fed in a downflow fashion from the top of the biofilter. In this study, two biofilters were tested in parallel with one packed with compost, small wood chips and perlite and the other with compost and small woodchips at influent concentration of 950 and 37 ppm for methanol and α -pinene, respectively. The results from both biofilters were very similar, indicating that perlite did not enhance the removal efficiency. The removal efficiency of methanol was 90% at a methanol loading rate of 280 g/m³-hr, based on empty bed volume (EBV). The maximum removal efficiency of α -pinene was 95% with an α -pinene loading rate of 45 g/m³-hr. The gas detention time based on EBV was 20 to 60 seconds. The methanol removal rate was not

affected by the presence of α -pinene, but the α -pinene removal rate decreased as the influent methanol concentration was increased.

In a second study using the same downflow lab biofilters (Mohseni et al. 1998) evaluated the effect of using granular activated carbon (GAC) versus perlite media on biofiltration performance treating air containing α -pinene. Both columns contained a mixture of wood chips (3.2 – 32 mm) and compost, which was mixed at a ratio of 3:1 with perlite pellets (4 mm) in one and GAC of similar size in the other. Both contained fertilizer pellets for nutrients and CaCO_3 at 10-15 kg/m^3 of bed volume for pH buffer. The columns were operated at 38-40°C and more than 90% α -pinene removal at the loading of 30-35 $\text{g/m}^3\text{-hr}$ (correspond to concentration of approximately 70-80 ppm) based on EBV. The gas detention time based on EBV was about 45 seconds. The pressure drop increased from 0.2 to 0.6 in H_2O in perlite biofilter and 0.4-0.8 to 1 in H_2O in GAC biofilter within 50 days. While the GAC adsorption provided higher α -pinene removal at start-up, it did not show any advantage for long-term operation after microbial acclimation.

A pilot-scale biofilter (2.13 m by 1.83 m and 2.24 m high) with downflow in an activated carbon media was tested for treating a gas stream from a press vent at an oriented strand board facility in the southeast USA (Pisotti 1997). The gas stream contained α -pinene, β -pinene, limonene, camphene, methanol, ethanol, acetic acid, acetaldehyde, phenol, formaldehyde and diphenyl-methane diisocyanate. The concentration of each VOC was not provided, but the total VOC concentration ranged from 40 to 220 ppm as propane with an average of 100 ppm. The inlet gas temperature was 54°C and the biofilter temperature was 30-31°C. The average gas application rate was 2.54 $\text{m}^3/\text{m}^2\text{-hr}$. The pilot plant was operated for 4 months and the total removal efficiency was 85-96%. The pressure drop across the media was only 19.1 mmH_2O . The study with various EBV gas retention times showed that the efficiency was higher at retention time of 30 sec than at 20 sec (90 vs. 82%).

Several studies showed the removal of TRS compounds from gas streams using biofilters. (Hirai et al. 1990) studied the removal rate of HS, MT and DMS in a 0.75 m high by 0.15 m diameter peat biofilter. The initial concentrations of HS, MT and DMS were 50, 30 and 30 ppm, respectively. The gas application rate ranged from 0.23-0.51 m³/m²-hr with EBV gas residence times of 198 sec. The pH ranged from 4.4 to 6.8 and the temperature was not reported. The removal efficiency of HS and MT was 70-90%, while that of DMS was only 20-30%.

Zhang et al (1991) inoculated a peat biofilter with *Hyphomicrobium* sp. I55. The biofilter was fed with a gas mixture of 30 ppm HS, 6 ppm MT and 63 ppm DMS at a constant flow rate of 200 mL/min. The pH of the system was 6.8, but the temperature was not reported. The removal efficiencies of HS, MT and DMS were 70-100%, 55-90% and 30-40%, respectively. However, when only DMS was fed to the biofilter at the concentration of 26 ppm, the DMS removal efficiency was 90%, suggesting that the DMS degradation was inhibited by the presence of HS and MT. A similar effect was observed in an experiment where a peat biofilter was inoculated with *Thiobacillus thioparus* DW 44 (Cho et al. 1991). The removal efficiency of HS, MT and DMS were 100, 100 and 45 % respectively, when the biofilter was fed with gas mixture (50 ppm HS, 30 ppm MT and 25 ppm DMS). However, when only DMS was fed at 25 ppm, the removal efficiency was 79%. The system was operated at 50 m³/m²-hr and pH was 6.8. The temperature was not reported.

A pilot-scale biofilter (0.5 m diameter, 0.85 m depth) with peat media inoculated with *Thiobacillus thioparus* DW44 was tested for treating exhaust gas from a night soil treatment plant in Japan (Cho et al. 1992). The gas application rate was 21 m³/m²-hr (EBV retention time 2.4 min). The temperature fluctuated from 8 to 20°C due to seasonal effects. The biofilter was operated for 185 days and the pH was 7.1. The initial concentration of HS, MT, DMS and DMDS were 1-45, 0.1-3, 0.3-3, and 0.02 to 0.2 ppm, respectively. The average removal efficiencies for HS, MT, DMS and DMDS were 99.8%, 99%, 89.5% and 98.1%, respectively. The removal efficiencies of HS and MT were fairly stable through out the experiment, while the removal of DMS and DMDS

fluctuated from 40 to 100%. The treatment efficiency for DMS and DMDS dropped when the temperature dropped below 8°C in the winter and increased when the biofilter inlet gas was heated to 8-10°C.

In biofilter applications with stringent treatment performance needs, more engineered approaches are needed in media selection and process design, including water recirculation, nutrient addition, and buffer addition to maintain more desirable conditions for biological growth. A major concern for biofiltration is media plugging from excess biomass growth or trapping water in the pore space, which cause the pressure drop to increase. When this happens the gas flow through the bed is not uniform, which can result in a decrease in treatment performance. Periodic media replacement may be necessary to overcome media plugging problems and these difficulties will be more significant for higher concentration gas streams and longer term operation.

An alternative to biofiltration for biological treatment of contaminated gas streams is a shallow suspended growth reactor (SSGR), which eliminates the use of media. In a previous laboratory study using the SSGR to treat gas contaminated with benzene, toluene, ethylbenzene, and o-xylene (BTEX), 99% of BTEX removal was achieved at 20°C using a reactor liquid depth of only 40 cm at volumetric loadings of 11 to 18 mg-BTEX/L-hr (Bielefeldt and Stensel 1998). In the SSGR the contaminated gas is dispersed into a shallow (less than 1 m depth) liquid suspension of biomass by fine bubble diffusers at the bottom of the reactor. The contaminants are transferred from the gas to the liquid phase, where biodegradation by the suspended biomass maintains a low liquid concentration to maximize gas-liquid transfer rates. The gas contact time is generally less than 1-2 seconds, and a high density diffuser design is used to maximize gas-liquid mass transfer in the relatively shallow liquid depth. The addition of nutrients and alkalinity is easily controlled and uniform, since the SSGR is a completely mixed liquid suspension. The reactor liquid can be removed periodically to control the biomass concentration and cell age. Though the SSGR requires more energy than a biofilter, the shallow depth used minimizes energy requirements. A number of SSGR units can be stacked to minimize land area requirements.

A mechanistic model to predict SSGR treatment performance, based on fundamental mass transfer processes and biodegradation kinetics, was developed and evaluated by Bielefeldt and Stensel (1999). The contaminant mass transfer rate from the gas to the liquid depends on the Henry's Law coefficient (H) and reactor gas-liquid mass transfer coefficient, (K_{La}). For the compound of interest, the K_{La} value was related to the K_{La} of oxygen, which can be easily determined for an SSGR system from clean water aeration tests. Lower H values and higher K_{La} values increase the mass transfer rate of compounds into the liquid, and thus result in a lower required liquid depth. The biokinetic part of the model was based on Michaelis-Menten substrate utilization kinetics, but can be modified to accommodate other biokinetic relationships.

1.2 Biological Description of HAPs at High Temperature

Reactor temperature is a significant issue for biotreatment of pulp and paper mill gas emissions. The organic compounds found in gas emissions from pulp and paper mills are reported to be easily biodegraded at mesophilic temperatures (Lund 1971). However, the temperature of the gas streams can be as high as 70°C (Mohseni and Allen 1998) requiring biodegradation by the microbial communities acclimated to thermophilic temperature (45-70°C), unless gas cooling is used.

Biodegradation experience at thermophilic temperature is limited. Biodegradation at 50°C to 70°C by several *Bacillus* strains in batch studies has been reported for methanol (Al-Awadhi et al. 1989; Dijkhuizen and Artman 1990; Arfman et al. 1992; Arfman et al. 1992). Biodegradation of BTEX compounds at 45°C to 77°C by a *Thermus* species in a batch reactor has been demonstrated (Chen and Taylor 1995; Chen and Taylor 1997). The aerobic degradation of selected monoterpenes; d-limonene, α -pinene, γ -terpinene, terpinolene and α -terpineol has been shown only at 23°C (Misra and Pavlostathis 1996; Misra and Pavlostathis 1997) and at 40°C for α -pinene and methanol (Mohseni and Allen 1997). The ability to biologically treat the range of organic compounds found in pulp and paper emissions at thermophilic temperatures needs investigation.

Degradation of TRS compounds has been widely reported, by both pure strain and mixed culture, but results at thermophilic temperature are limited. *Methylophaga sulfidovorans* (deZwart et al. 1996; deZwart and Kuenen 1997) was reported to oxidize HS and DMS in microbial mat at 17-35 °C, with the optimum growth temperature at 22°C ($\mu_{\max}=0.05 \text{ h}^{-1}$, $K_s=1 \text{ }\mu\text{mol}$). HS and DMS were completely consumed in the batch study with the initial HS concentration of 25 mM in gas phase and DMS concentration of 1.5 mM in liquid. *Thiobacillus thioparus* DW44 (Cho, Hirai et al. 1991), *Thiobacillus thioparus* TK-m (Kanagawa and Mikami 1989) and *Hyphomicrobium* sp. I55 (Zhang, Hirai et al. 1991) were able to degrade HS, MT, DMS and DMDS at 25°C and pH 6.8. The removal efficiency of 93-99% was observed with the initial concentration of 30 to 250 ppm. *Hyphomicrobium* EG was reported to degrade DMS and MT at 30°C (deBont et al. 1981; Suylen et al. 1987). The removal efficiency for DMS and MT was approximately 93%, when the liquid concentration of DMS and MT were 0.05 mmol/L and 0.3 mmol/L, respectively. *Pseudonocardia asaccharolytica* sp. nov. and *Pseudonocardia sulfidoxydans* sp. nov. were capable of degrading DMS and DMDS at 25°C, but the removal efficiency was not reported (Reichert et al. 1998).

Only HS degradation was studied at thermophilic temperature, and this was observed with two strains of pure cultures. *Thermothrix azorensis*, an obligate autotrophic aerobic microorganism was able to degrade HS at 63-86°C (Odintsova et al. 1996). *Thermothrix thiopara* is a facultatively autotrophic, microorganism that could oxidize HS and grow at a temperature range of 45-80°C and neutral pH (Brannan and Caldwell 1980; Brannan and Caldwell 1983; Brannan and Caldwell 1986; Odintsova, W.Jannaach et al. 1996).

2.0 OBJECTIVES

The overall objective of this research was to determine if the SSGR could provide sufficient treatment performance of organic and TRS compound at 50°C to meet the EPA cluster rule regulatory limits. The biodegradation of a mixture of organic compounds that could be present in pulp and paper HVLC gas stream was evaluated at 50°C in a bench-scale SSGR. The removal of methanol was followed in particular, and was mathematically modeled to evaluate the effect of process design and operating parameters on methanol removal. Additional tests were performed to obtain mass transfer and biodegradation kinetic parameters for the model. The acclimation of microbial populations capable of degrading TRS compounds from various seed sources was studied in batch reactors at 30 and 50°C. The degradation of TRS compounds in bench-scale SSGR was studied at 20-50°C. Also, the biodegradation kinetic and mass transfer coefficients for α -terpinene and γ -terpinene were studied. Finally, a pilot plant was constructed and operated at Simpson pulp and paper mill in Tacoma, WA.

3.0 MATERIALS AND METHOD

This research focused on the treatment of gas emissions from pulp and paper mills using a sparge suspended gas reactor (SSGR). The following studies were performed.

1. Bench scale SSGR study for removal of organic compounds from a gas stream
2. Bench scale SSGR study for removal of TRS compounds from a gas stream
3. Biological acclimation study using various seed sources for TRS degradation
4. Bench scale tests to obtain mass transfer and biokinetic parameters for methanol
5. Pilot plant construction and operation of the Simpson Mill in Tacoma, WA
6. Bench-scale acclimation, mass transfer, and biokinetic studies for terpene compounds

3.1 Description of Laboratory SSGR System

Figure 1 shows a schematic of the laboratory SSGR treatment system used for testing. The bioreactor and stabilizer units were 2-L glass graduate cylinders modified with ports for sampling and taps for attaching connecting tubing. The stabilizer contained deionized water, and the liquid depths for it and the bioreactor were maintained at 0.36 m. The reactor total height was 0.5 m, and its I.D. was 8 cm. Gas flow to the bioreactor and stabilizer was dispersed by air sparging stones located near the bottom of the reactors. The purpose of the stabilizer was to equilibrate the concentrations of the compounds fed to obtain more consistent bioreactor influent sample concentrations. The bioreactor and stabilizer were stirred by a TeflonTM-coated magnetic stir bar and ThermolyneTM stir plate. The bioreactor and stabilizer were wrapped with heating tapes, which were controlled by a temperature probe and input controller (Omega CN76000) to maintain constant operating temperature at 50°C.

Stainless steel tubes (6.35 mm diameter) were used between the stabilizer and the bioreactor, for the reactor effluent line, for the influent line to the stabilizer, and for GC sample lines from the reactor influent and effluent. All the tubes were heated by heat tape (Thermolyene silicone rubber) to prevent compound condensation in the lines.

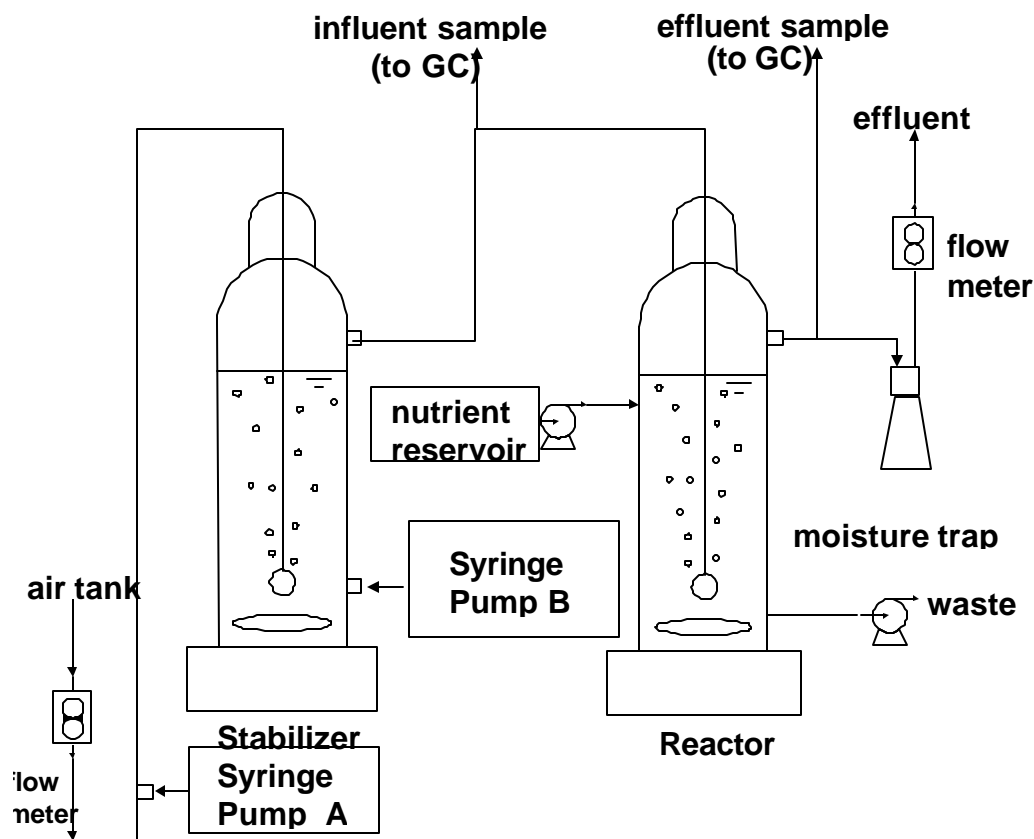


Figure 1 Schematic of laboratory SSGR system

A compressed air tank supplied a constant air stream flow rate, which was measured by a flowmeter before the stabilizer and in the effluent line after the reactor. Two syringe pumps (Cole-Parmer, 74900 series) were used for feeding chemicals into the reactor. Syringe pump A was used for feeding chemicals directly into the stabilizer feed line and syringe pump B was used for feeding chemicals into the stabilizer. The more volatile compounds were fed with syringe pump A.

3.2 SSGR Operation

The SSGR was operated at a gas feed rate of 150 mL/min during organic compound feeding and 220 mL/min during TRS compound feeding, which correlated to gas application rates of 1.8 and 2.6 m³/m²-hr, respectively. Equal volumes of nutrient

solution and reactor liquid were fed and removed daily. A ChronTrol™ timer was used to activate the peristaltic pumps used for nutrient feeding and reactor liquid withdrawal every 3 hours. The reactor solids retention time (SRT) was maintained by feeding and withdrawing a fraction of the reactor volume daily. For a 10-d SRT operation, 1/10th of the reactor volume was removed daily. Reactor wall growth was minimized by manually scraping the wall with a wire brush every other day. The nutrient media solution contained 1.9g/L KNO₃, 1.4 g/L KH₂PO₄, 2 g/L K₂HPO₄, 0.8 g/L NH₄Cl, 1.2 g/L NaHCO₃, 0.1 g/L CaCl₂, 0.06g/L MgSO₄, 0.2 g/L NaCl, 0.11 mg/L CuCl₂·H₂O, 0.3 mg/L ZnCl₂, 0.044 mg/L NiCl₂·6H₂O, 1.76 mg/L FeSO₄·7H₂O, 0.27 mg/L Al₂(SO₄)₃·18H₂O, 0.564 mg/L MnCl₂·4H₂O, 0.112 mg/L CoCl₂·6H₂O, 0.064 mg/L Na₂MoO₄·2H₂O, and 0.098 mg/L H₃BO₃.

Reactor influent and effluent gas flows were sampled daily. Organic and TRS compounds were analyzed by gas chromatograph (GC) using a flame ionization detector (FID) and a flame photometric detector (FPD), respectively. For organic compounds analyses, samples were taken through an electrically operated 3-way solenoid valve (Dayton®) that was manually connected to either the reactor influent or effluent flowlines. A peristaltic pump was used to pull the samples through the gas chromatograph sampling valve and a sample loop continuously. When the valve was rotated, the sample loop was disconnected from the sample line, and the GC carrier gas was directed through the sample loop, which flushed the sample to the GC separation column. A Chronrol™ timer controlled the valve rotation times. For TRS-compounds, the samples were taken manually by using 100-µL gas tight syringes (Hamilton). The gas samples were injected by syringe directly into the GC injection port, which was connected to the FPD detector.

Volatile suspended solids (VSS), total suspended solid (TSS) and soluble COD (sCOD) concentrations in the reactor liquid were measured 2-3 times per week. Dissolved oxygen (DO) concentration and pH were measured once per week. Liquid samples were obtained through reactor sampling ports equipped with Mininert valves.

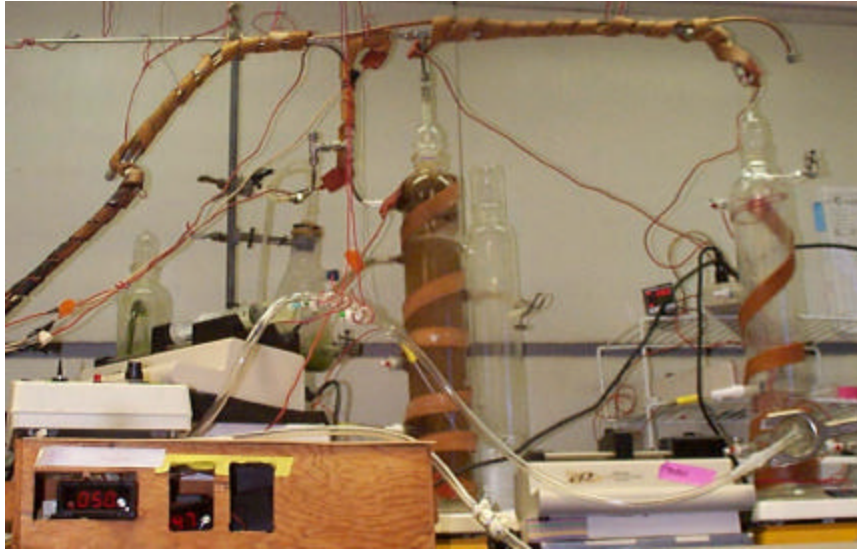


Figure 2 Laboratory SSGR system

3.3 Seed and Organic Compounds Used in Laboratory SSGR Studies

The seed for the biotreatment reactor for the tests treating organic compounds was obtained from an activated sludge lagoon at a Weyerhaeuser pulp and paper facility. Later it was also seeded with sludge from a high temperature (60°C) aerobic sludge digester at the Gig Harbor, WA municipal wastewater treatment plant. For the SSGR tests with TRS compounds, the seed was activated sludge from the wastewater treatment facility at the Simpson pulp and paper mill in Tacoma, WA. Benzene, toluene, p-xylene,

m-xylene and o-xylene were combined as a pure liquid phase and fed to the air feed line by syringe pump A. Methanol, acrolein, acetaldehyde and methyl-ethyl-ketone were combined as pure liquid phase and fed to the stabilizer by syringe pump B.

Benzene (99.9%), toluene (99.8%) and methanol (99%) were obtained from Fisher scientific. Acrolein (90%), acetaldehyde (98%), methyl ethyl ketone (99%), p-xylene(99+%), m-xylene (99%) and o-xylene (98%) were obtained from Aldrich.

For the laboratory SSGR system treatment of TRS compounds, HS and MT were fed as a pure gas phase through pump A to the gas feed line. DMDS, DMS, formaldehyde and methanol were fed in liquid phase through syringe pump B to the stabilizer.

HS (99.5%), MT (99.5%), DMS (99+%) and DMDS (98%) were obtained from Aldrich. Formaldehyde (37%) was obtained from Fisher scientific.

3.4 Enrichment Reactors for Terpene-Degrading Cultures at 35 °C and 50 °C

Alpha-terpinene- and gamma-terpinene- degrading enrichments were developed in separate enrichment reactors at 35 °C and 50 °C. Alpha-terpinene (1-isopropyl-4-methyl-1,3-cyclohexadiene) with purity of 89% and gamma-terpinene (1-isopropyl-4-methyl-1,4-cyclohexadiene) with purity of 99% were obtained from Sigma-Aldrich Co. The enrichment seed source was from the laboratory SSGR when it was treating the organic compound mixture.

Terpene-degrading cultures were initially grown in 125-mL serum bottles, and turbidity was used as an indication of biomass growth. After growth was observed the culture was transferred to one of two enrichment reactors (fed alpha or gamma terpinene) for growth with a constant feed supply. Terpene chemicals had been temporarily fed to the SSGR system stabilizer for approximately one month at a rate of 90 mg/L/day prior to removing SSGR mixed liquor for seed.

Figure 3 shows a schematic of the enrichment growth reactor design. The enrichment growth reactors were 4-L Erlenmeyer flasks with approximately 2-L of liquid volume and were connected by Teflon tubing in a closed system to a manometer containing oxygen. The enriched reactor operation was maintained at 35°C in a constant temperature room. Teflon mininert valves were used for the sampling and feed port on the reactor and the injection port on the manometer to prevent chemical losses due to adsorption. The reactor liquid was continuously mixed with a magnetic stir-bar controlled by a Thermolyne stir-plate. Mixing was sustained at the maximum level to create a vortex in the liquid, which enhanced gas transfer between the liquid and the headspace. An alkaline trap (60-mL of 10N KOH, with a glass fiber filter used as a wick) was attached to the reactor to remove carbon dioxide produced through bacterial respiration. By removing the carbon dioxide the oxygen consumed from the reactor headspace was replaced with oxygen from the attached manometer headspace. The oxygen consumption could then be determined by changes in the manometer liquid level. Pure oxygen was added as needed via syringe to the manometer to maintain an adequate reservoir of oxygen.

Based on a yield of 1.5 mg-VSS/mg-terpene (0.45 mg-VSS/mg-COD), the reactors were expected to use approximately 12 mL of oxygen daily. However, this rate of oxygen consumption was not indicated by the manometer liquid level measurements, which suggested that a small leak was present.

The reactors were maintained at an HRT and SRT of 5 days by manually wasting 400-mL once per day, which included sampling volumes. Nutrient solution was added daily to maintain a liquid volume of 2-L. The same nutrient recipe used for the SSGR biotreatment reactor was used here also.

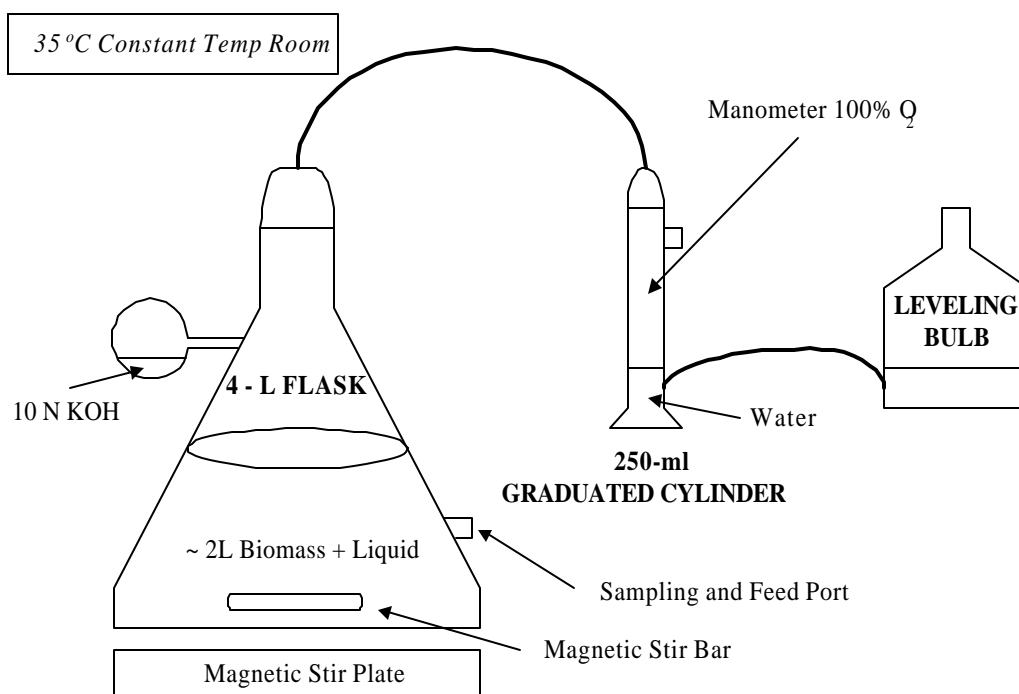


Figure 3 Schematic of terpene enrichment reactor maintained in 35°C constant temperature room

Each reactor was fed daily with 10 mg/L of the appropriate pure phase terpene chemical, which was injected manually with a Hamilton gas-tight 25- μ L glass syringe. The low solubility of the terpene compounds prevented feeding dissolved terpene in the nutrient solution. Liquid concentration of terpene was measured regularly to verify degradation. The VSS (volatile suspended solids) was measured weekly and used as an indication of acclimation and growth. Both reactors maintained approximately 40 mg/L VSS after the acclimation period. The reactor pH was maintained at about 7.5, slightly basic because of the alkaline trap and low CO₂ content in the gas phase.

For growth at 50 °C two enrichment reactors fed alpha-terpinene and gamma-terpinene, respectively, were seeded with the 35°C enrichment cultures. A 400- mL liquid volume from each of the 35°C reactors was centrifuged, washed with nutrient solution and centrifuged again. The concentrated biomass was added to 1-L of fresh nutrient media.

The reactor temperature was increased 1°C per day from 35°C to 50°C while being fed 10 mg/L of the terpene daily. The terpene liquid concentration was measured before feeding to verify terpene degradation, and it was always below the detection limit of 0.5 mg/L terpene.

The 50°C enrichment reactors were sealed 2-L Erlenmeyer flasks with approximately 1-L of liquid volume and were maintained at 50°C in a rotary shaker (140 rpm) incubator. Glass and Teflon stoppers were used to prevent terpene loss. The reactor headspace was flushed with pure oxygen every other day to provide oxygen and remove accumulated carbon dioxide.

After the initial acclimation of approximately 3 weeks, the reactors were maintained at an HRT and SRT of 5 days by removing 200-mL of reactor liquid each day (including sampling volumes) and replacing it with nutrient solution. Liquid terpene and VSS concentrations were measured regularly to monitor terpene degradation and enrichment acclimation. The enrichments maintained a VSS of approximately 15 mg/L after the acclimation period.

3.5 Batch Acclimation Tests for Sulfur Compounds

Seeds from different sources were tested for the ability to degrade HS, MT, DMS, and DMAS. The seed sources were municipal aerobic thermophilic digester sludge, Simpson Mill activated sludge, Simpson Mill pulp washer water, a high temperature lake sediment and a hot spring culture. Each sulfur compound degrading enrichment was acclimated in batch fed Erlenmeyer flasks at 35°C and 50°C. The flasks had a 400 mL liquid volume and 225 mL gas volume. The seeds were diluted in nutrient solution, and the flasks were capped with rubber stoppers. A side port, equipped with Mininert™ valve was added to the flask to allow the addition of sulfur compounds and sampling.

The 50°C flasks were incubated in a rotary shaker incubator, and the 35°C flasks were incubated in a walk-in environmental chamber. The 35°C flasks were stirred by a

TeflonTM coated magnetic stir bar and ThermolyneTM stir plate. HS and MT were added as pure gases, and DMS and DMDS were added as pure liquid phase by syringe. Target initial concentration were 100 ppm based on headspace concentration. Care was taken in the feeding and flask maintenance to prevent pressurization due to feed volumes. After the reduced sulfur compounds were added, each reactor was mixed and incubated at the desired temperature for 15 to 30 min to allow the system to reach equilibrium between liquid and gas concentration. Then, the initial headspace gas concentration was determined. The reduced sulfur concentrations were measured daily in the headspace until they were completely consumed. Each day, pure oxygen was replenished in each flask by inserting a needle connected to a lubricated glass syringe filled with pure oxygen. The vacuum created by oxygen consumption in the flasks automatically pulled in the oxygen. After the sulfur compound was completely consumed, the top of the reactor was removed and the liquid content of the reactor was sparged with clean air for 5 min to remove accumulated CO₂ or in the case of HS to replenish CO₂ used by the autotrophic bacteria. After every feeding 3-4 cycles, 50 ml of liquid sample was removed from the reactor to remove possible metabolite accumulation. The liquid was centrifuged. The biomass was separated and made up to the same volume by addition of nutrient solution. Then, the diluted biomass was returned to the bioreactor.

3.6 Gas-liquid Mass Transfer Characterization

3.6.1 Henry's Law Coefficient

Henry's Law coefficients of most compounds were available from the literatures. Otherwise the Henry's law coefficient was determined experimentally. The experimental procedure was done for methanol, toluene, terpenes, HS, MT, DMS and DMDS.

The most direct method for measuring the Henry's Law coefficient of a compound is to measure both the air and liquid concentrations of the compound in a closed system at equilibrium ($H=C_g/C_l$). However, this method is highly sensitive to the accuracy of the concentration measurements. It also requires the ability to accurately sample and measure both phases. Alternatively, the EPICS (Equilibrium Partitioning in Closed

Systems) method (Yuteri et al. 1987) is used to determine the Henry's Law coefficient. In this test, bottles with different liquid and gas volumes are prepared with the same mass of test compound added. The equation used in the EPICS method when only the gas phase concentration is measured is as follows:

$$H = \frac{C_{G1}}{C_{L1}} = \frac{C_{G2}V_{L2} - C_{G1}V_{L1}}{C_{G1}V_{G1} - C_{G2}V_{G2}}$$

where:

C_L = concentration in the liquid phase, mg/L

C_G = concentration in the gas phase, mg/L

V_L = liquid volume in the bottle, L

V_G = gas volume in the bottle, L

H = Henry's coefficient, L/L

and 1 and 2 denote the two different batch bottles

Similarly, if the liquid phase concentration is measure, the equation used is:

$$H = \frac{C_{G1}}{C_{L1}} = \frac{C_{L2}V_{L2} - C_{L1}V_{L1}}{C_{L1}V_{G1} - C_{L2}V_{L2}} \quad (2)$$

Using the EPICS method, Henry's Law coefficients were determined at 50°C for methanol and toluene, and at 20°C, 35°C and 50°C for alpha and gamma terpinenes. Two bottles with different gas-liquid volumes, but the same chemical mass, were compared at equilibrium using the EPICS method equation to calculate Henry's Law coefficient.

The Henry's Law coefficient experiments were performed in 125-mL serum bottles capped with Teflon-lined crimp-top seals. Initially, each bottle was weighed to 0.1-mg precision. DI water was added to each bottle of liquid volumes between 25 and 100-mL, and the bottles with the water addition were weighed again. Each batch was allowed to reach equilibrium with the assigned temperature before any chemical was added. To relieve the pressure in the 50°C bottles, a needle was inserted through the septa in order to equilibrate the bottle pressure with atmospheric pressure. A Hamilton 5- μ L gas-tight

syringe was used to inject an equal volume of pure phase compound into each bottle. The batch bottles were incubated at their respective temperatures on a rotary shaker (>100 rpm) for at least 48 hours to allow equilibrium of the compounds between the gas and liquid phases in the bottles prior to sampling. Two liquid volumes were used and three identical bottles set up for each volume to ensure reproducibility. Duplicate samples from each batch bottle were taken and measured. Concentrations of methanol, toluene and sulfur compounds were measured by gas samples, and the terpinenes by liquid samples.

3.6.2 Reactor Oxygen Mass Transfer (K_La) Coefficient

The volumetric mass transfer rate of oxygen (K_La) was determined at 35°C and 50°C in a 2-L sparged test reactor identical to the SSGR reactor. Deoxygenated DI water was sparged with air and the increase in dissolved oxygen (DO) was measured and recorded with time (Metcalf & Eddy, 1991). Multiple tests were conducted at different liquid volumes and airflow rates.

For the test reactor, a 2-L glass graduated test cylinder was modified by adding two ports for mininert sampling valves and a fitting for the sparge stone to be inserted from the side near the reactor bottom. Lab air was sparged through a 2.5-cm diameter spherical fritted sparge stone, and the gas flow rate was measured by a Gilmont GF-1160 flowmeter (range 0 to 289 mL/min). This is the same sparge stone design used in the SSGR test reactor. The target air flow rates were 50, 100 and 150 mL/min, and the flow varied ± 2 mL/min. Gas escaped through the top of the reactor that was open to atmospheric conditions. The reactor was heated to the appropriate temperature using a four foot Thermolyne heat tape attached to an Omega CN76000 digital temperature controller. A thermometer, as well as the temperature sensor on the DO probe, was used to verify accuracy and consistency of the temperature. The temperature varied $\pm 0.2^\circ\text{C}$. Total liquid volume in the reactor for each test was 1815 mL, and the liquid depth was 0.36 m.

A calibrated YSI DO probe and meter were used to measure DO concentration as a function of time. The probe was calibrated as described in the Indirect Method section. The probe was suspended in the liquid at about 5 cm below the water surface to measure DO concentration (0.01 mg/L precision). The probe was suspended with the membrane side up to prevent discrepancies in readings due to the air bubbles contacting the probe membrane.

After the DI water was heated to the designated temperature, deoxygenating chemicals were added to the liquid to remove the dissolved oxygen. The deoxygenating chemicals consisted of approximately 0.005 g/L $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ and 0.10 g/L Na_2SO_3 as demonstrated by Bielefeldt (1996). While dissolving the chemicals, and throughout the test, a magnetic stir-bar on a Thermolyne stir-plate set on speed 5 provided the necessary mixing. The aeration was continued through out the study, but the dissolved oxygen will drop due to the reaction rate of Na_2SO_3 and $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$. When deoxygenation achieved a stable DO concentrate near zero, about 0.03 mg/L, the airflow was started. The increase in DO concentration was manually recorded with time in 10 to 30 second intervals. Gas flow rate and temperature were also recorded for each test.

The DO concentration change with time can be related to the $K_L a$ as follows:

$$\ln \left[\frac{C_{\text{sat}} - C_t}{C_{\text{sat}} - C_o} \right] = -K_L a \cdot t \quad (3)$$

where:

C_t = DO concentration at time t, mg/L

C_{sat} = DO saturation concentration, mg/L

C_o = initial DO concentration in the system at $t = 0$, mg/L

$K_L a$ = oxygen mass transfer coefficient, min^{-1}

t = time, min

The value for $K_{L}a$ was determined from test data by a linear regression of $\ln(C_{\text{sat}}-C_t)$ versus t .

The DO saturation concentration (C_{sat}) was selected for the reactor temperature from the YSI meter saturated DO versus temperature calibration table at zero salinity. Salinity has minimal effects below 300 mg/L and the effect of depth on DO saturation is minimal in this case because of the shallow liquid depth. At 35°C, the saturated DO is 6.95 mg/L and at 50°C it is 5.47 mg/L. As recommended by the ASCE Standard Method (1984), the initial low DO values (less than 10% of C_{sat}) and the DO values near the C_{sat} (greater than 90% of C_{sat}) were not included in the slope calculation. The gas/liquid mass transfer coefficient for the other compounds can be related to the oxygen $K_{L}a$ by a factor equal to the ratio of the compound/oxygen diffusion coefficients (Bielefeldt and Stensel, 1999). Thirteen $K_{L}a$ tests were done with test reactor. One test was done with the lab SSGR reactor by temporarily replacing biomass liquid with clean water to determine if lab SSGR $K_{L}a$ was in the same range as the test reactor.

3.6.3. Terpenine Gas-Liquid Mass Transfer Coefficient in Sparged Reactor

Since diffusion coefficients for the terpene compounds were not available, their $K_{L}a$ values had to be determined experimentally. The mass transfer coefficient rate for each terpene in water was determined by a stripping test which was conducted as described by Bielefeldt (1996). A DO $K_{L}a$ test was performed immediately prior to the stripping $K_{L}a$ test at the same air flow rate in order to compare oxygen and terpene $K_{L}a$ values. Terpenine $K_{L}a$ experiments were done in the mass transfer test reactor and were conducted at 35°C and 50°C for both terpene compounds.

A single pure terpene compound was injected directly into DI water through a mininert valve using a Hamilton glass gas-tight syringe. Mixing was provided by a magnetic stir bar controlled by a Thermolyne stir plate on setting number five. The pure terpene chemical was allowed to dissolve for at least 30 minutes. Airflow was started after an initial liquid terpene concentration sample was taken, and decreasing terpene

concentrations were measured with time. Experimental conditions such as air flow, temperature and liquid volume were recorded for each test. Test target conditions were on air flow of 150 mL/min, temperature of 35°C or 50°C, and liquid volume of 1815 mL. A plot of $-\ln(C/C_o)$ versus time was plotted (C_o = initial concentration, C = concentration at time t). The slope of this plot was used in the following equation:

$$K_{La} = \frac{-Q_g \cdot H}{Vl} \cdot \ln \left[1 - \text{slope} \cdot \left(\frac{Vl}{Q_g \cdot H} \right) \right]$$

where: K_{La} = mass transfer coefficient, min^{-1}

Q_g = air flow rate, mL/min

H = Henry's coefficient, L/L

Vl = volume of liquid in reactor, mL

Slope = slope of $-\ln(C_t/C_o)$ versus time plot, min^{-1}

3.7 Biodegradation Kinetic Testing

The Michaelis-Menten model was used to describe biodegradation kinetics:

$$r_s = \frac{kSX}{K_s + S} \quad (5)$$

Where: r_s = substrate utilization rate, mg/L-d

S = substrate concentration, mg/L

X = biomass concentration, mg/L

K_s = half-velocity coefficient, mg/L

k = methanol specific substrate utilization rate, g/g-d

Biodegradation kinetic tests were conducted using two different methods to determine model coefficients, a direct method and an indirect method. For the direct method, batch serum bottle tests were inoculated with the enrichment culture and the concentration of the compound of interest was measured directly as a function of time. The indirect

method tests were also performed in batch serum bottles, with dissolved oxygen (DO) concentration measured with time instead of the actual compound concentrations. The concentration of the compound was assumed to decline in proportion to the amount of DO used, since a portion of the substrate was oxidized during substrate consumption to provide energy for growth. The advantages for the indirect method are that numerous data points can be obtained with time, and that reaction rates at very low substrate concentrations can be observed compared to the direct method.

3.7.1 Direct Method

Degradation rates were determined in batch tests conducted in 125-mL glass serum bottles capped with Teflon-lined crimp-top seals. The compound was pre-dissolved in 100-mL of nutrient solution that was added to the bottle, leaving a 25-mL headspace. The nutrient solution composition was the same as that used for the growth reactors. The test bottles were inoculated with biomass from the SSGR or enrichment reactors. The biomass sample was centrifuged and washed twice with nutrient solution to remove any residual chemical and to concentrate the biomass. The concentrated biomass was then added to the serum bottle using a syringe with volumes from 1 mL to 5 mL. Test bottle VSS concentrations were generally in the range of 40-100 mg/L. Bottles were incubated and shaken at the appropriate temperature. The 35°C experiments were performed on a shaker table in a 35°C constant temperature room. The 50°C biodegradation studies were performed in a rotary shaker incubator.

For tests with terpenine the terpenine concentration changes with time were determined from liquid samples taken about every 10 minutes. The first sample (time equal zero) was taken immediately after the concentrated biomass was injected into the bottle. The liquid samples were extracted into hexane immediately and later analyzed by gas chromatography (GC).

A linear plot of terpene concentration versus time was used to determine the specific substrate utilization rates (K') for different initial terpene concentrations. K' was

determined from the slope of the liquid terpene concentration versus time data divided by the biomass concentration in the bottle. The biomass concentration was measured at the end of each biodegradation test by VSS analysis. This rate was then corrected to determine the maximum specific substrate utilization rate (k) by accounting for the terpene partitioned into the headspace gas using Henry's Law coefficient and gas and liquid volumes in the serum bottle:

$$k = K' * (1 + H * V_g/V_L) \quad (6)$$

where:

k = maximum specific degradation rate, g Terp/g VSS-day

K' = maximum specific degradation rate from liquid concentrations,
g Terp/g VSS-day

V_g = gas volume in bottle, mL

V_L = liquid volume in bottle, mL

A limited number of control bottle tests were performed in order to conserve biomass. Bottles were set up as described above, then 5 mL of 37% formaldehyde was added to the control bottle to kill the biomass. Control bottles were run to confirm no leaks or abiotic losses of the chemical from the serum bottles.

3.6.2 Indirect Method

The indirect method of determining biokinetics involves a respirometric method modeled after that used by Ellis et al. (1994). The method assumes that the decline of dissolved oxygen in a closed batch system is directly proportional to the bacterial consumption of a single organic compound spiked into the system. This technique has been used to determine both k and K_S in the Michaelis-Menten model and was used here to determine methanol and terpinene degradation kinetics.

The test apparatus consisted of a modified 250-mL Erlenmeyer flask. The top of the flask was modified to a BOD bottle opening to accommodate a dissolved oxygen (DO)

probe. Two mininert ports were created for liquid sampling purposes. The liquid in the bottle was mixed by a TeflonTM coated magnetic stir bar and ThermolyneTM stir plate.

The seed culture for the biodegradation test was extracted from the selected reactor, washed with nutrient solution and centrifuged to concentrate the biomass. Then, the biomass was added to nutrient solution in the test apparatus that was pre-aerated with pure oxygen at the desired temperature. A calibrated YSI DO probe, connected to a YSI digital DO meter, was submerged into the flask and the data collection was started. Before the chemical was added, the dissolved oxygen concentration started dropping slowly due to the endogenous oxygen consumption. After approximately 15 min, a known amount of pure liquid methanol was injected into the test system.

The data collection procedure was automated to produce more consistent DO readings and reduce the labor time required. The data from the DO meter was logged into a computer continuously at 1-second increments with a program called Black Knight. It was then transferred to a spreadsheet in Microsoft[®] Excel. The large data set was compressed by taking a point every minute for graphing and interpretation purposes.

The test method requires subtracting the DO consumption due to endogenous respiration from the total DO consumption to determine the DO consumption related to substrate removal.

3.7 Simpson Mill Site Pilot Plant

A pilot plant was constructed and installed at the Simpson Pulp and Paper Mill in Tacoma, WA. Figure 4 shows the schematic of the pilot plant. The SSGR system reactor was an 8-ft diameter by 5-ft deep steel tank (Figure 5). The system was operated at a 4-ft. liquid depth. A fine bubble diffuser grid containing 37, 1-ft diameter Sanitaire[®] flexible membrane diffusers covered the tank floor (Figure 6). Contaminated air from the pulp washer operation was directed to the inlet of a positive displacement blower, which forced the air through the diffusers. The blower was supplied by Hoffman and was rated

at 7.5 HP, maximum pressure of 7 PSI, and maximum speed of 3600 RPM. The top of the tank was covered with plywood with an opening for exit gas.

The air flow rate to the bioreactor was controlled by a bleed valve down stream from the blower. High temperature 2 inch O.D. CPVC plastic piping was used for gas flow before and after the blower. A demister with 6-inch diameter by 6-inch high packing provided by Koch Engineer and a paper filter was installed upstream from the blower to trap foam, moistures and particle s.

The SRT of the bioreactor would be controlled by feeding and draining liquid from the tank. The feed and drain pipes were controlled by solenoid valves and timers.

Because of the excessively high temperature of the influent gas, it was necessary to cool the pilot plant reactor liquid to operate at 50°c or lower. Once the cooling system was installed, a 30°C temp was selected in an attempt to maximize DMS degradation. The temperature of the system was controlled by three loops of a 1" O.D. stainless steel cooling coil submerged along the tank well. The coil was connected to a tap water supply through a ¾" solenoid valve, which opened in the normal position. The solenoid valve was controlled by a temperature controller connected to a type K temperature probe (Cole Parmer) submerged in the reactor liquid. When the temperature was over the set point, the water valve was opened and water flowed through the cooling coil until the temperature dropped below the set point.

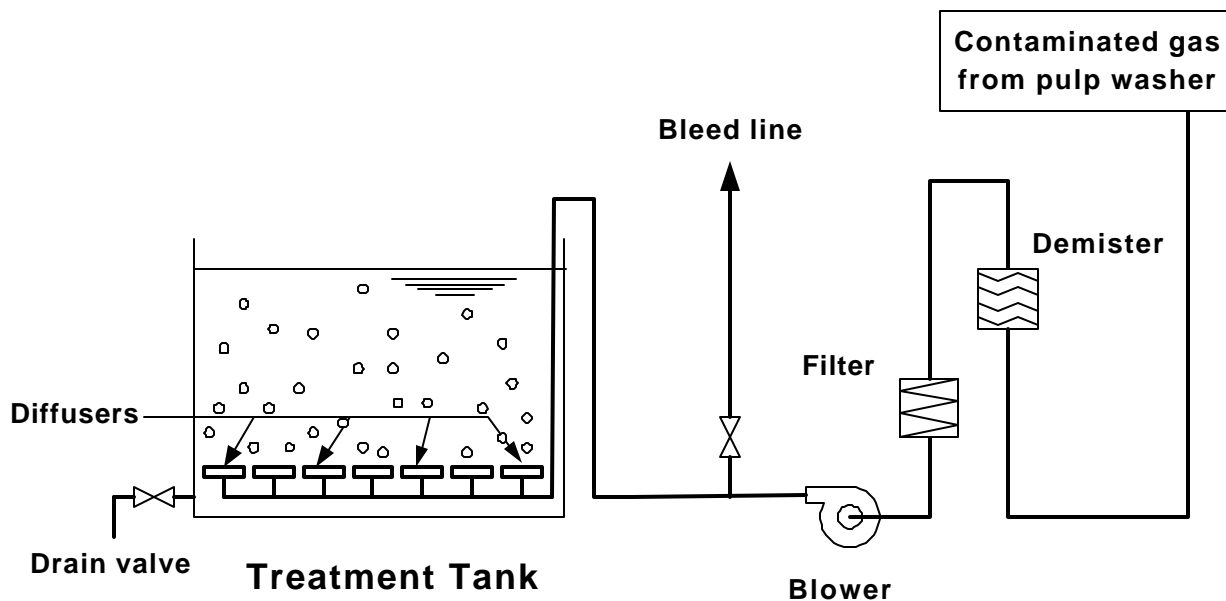


Figure 4 Pilot plant schematic

A gas influent sampling port was installed in the CPVC pipe section after the bleed line and before entering the tank. The influent sample was taken by connecting the Tedlar gas sampling bag (SKC) to the sampling port with a Teflon tube. The bag was filled by the gas pressure in the line. The effluent gas sample was collected in a Tedlar gas sampling bag located in a closed and sealed container. An air pump evacuated air from the container, which created a negative pressure allowing gas to flow from the headspace in the treatment reactor to the sample bag. This method eliminates problems of sample contamination from a sample pump. The samples were stored in an insulated and closed box to prevent light exposure and to minimize cooling. When the sample was brought back to the lab, it was heated in a water bath to the same temperature as the reactor gas. The sample was then analyzed for sulfur and organic compounds by injection into the GC-FPD and GC-FID respectively.

The feed gas flow rate to the reactor was measured using a hot wire anemometer inserted through a port on a pipe section prior entering the tank.



Figure 5 Pilot Plant at Simpson pulp and paper mill



Figure 6 Diffusers inside the pilot plant

Prior to system start up, oxygen transfer K_La tests were performed with different air flowrates. The K_La tests were done with the same procedure as that for the laboratory reactor.

The tank was seeded with activated sludge from the Simpson pulp and paper mill. Industrial grade sodium bicarbonate (Van Water and Roger) was added to the system to assure a minimum alkalinity of 100 mg/L as CaCO_3 . Nutrients were added as NaNO_3 and KH_2PO_4 to provide sufficient nitrogen and phosphorus for biogrowth.

3.8 Analytical Procedures

3.8.1 Organic Compounds

Organic compounds in the influent and effluent gases were analyzed on an SRI 8610C GC with a flame ionization detector (FID). The GC was equipped with a SUPELCOWAXTM-10 fused silica capillary column (60m × 0.53 mmID, 1.00 μ m film thickness). The oven temperature was set at 50°C for 2.5 minutes, then ramped 15°C/min for 7.5 min. PeaksimpleTM software was used to integrate the peak areas from the GC-FID. The gas concentration of the VOC was then determined from linear standard curves. The linear standard curves for each compound were developed from sampling and analysis of prepared gas standards. The standards were prepared by adding a known amount of pure compound into a gas bag, which was filled with a known volume of air. Five to seven standard values were prepared to obtain each standard curve for each compound ranging from 1 ppm to 500 ppm. Sample detection limits for methanol, methyl-ethyl-ketone, acetaldehyde, acrolein, benzene, toluene, and xylenes were 1, 1, 3, 2, 1, 1, and 1 ppm, respectively.

3.8.2 Sulfur Compounds

Sulfur compounds were analyzed on an SRI 8610C GC with flame photometric detector (FPD). The column used was SUPELPAK-S teflon column (30" × 1/8" OD). The oven temperature was set at 60°C for 1 min, then ramped 40°C/min for 3.25 min until the

temperature reached 190°C and held for 0.5 min. The standard curve was prepared similarly as with organic compounds. Seven to nine standard samples were prepared for each compounds ranging from 1 ppm to 500 ppm. The detection limits for HS, MT, DMS, and DMDS were 1, 2, 2, and 2 ppm, respectively.

3.8.3 Formaldehyde

The formaldehyde analysis method was adapted from NIOSH method 2541 (NIOSH, 1994). Influent and effluent gas stream was pumped through glass tube containing 10% (2-hydroxymethyl)piperidine on XAD-2 as a sorbent (SKC 226-118). The flow rate was 98 ml/min. The total volume of sample was 1728 mL. The sorbent were then desorbed by adding 1.0 ml toluene and placed in an ultrasonic water bath for 60 min. Then, 3 µl of aliquot was injected into a Hewlett Packard GC equipped with DB-WAX capillary column (30 m × 0.32mm ID, 0.5 µm film thickness). The injector temperature was 250°C, and the detector temperature was 300°C. The initial column temperature was held at 70°C for 1 min., was ramped at a rate of 15°C/min until the temperature reached 240°C, and held for another 10 min. The linear standard curve was prepared by injecting various concentrations of formaldehyde standard solution into vials containing sorbent. After 24 hr, the sorbent was desorbed and analyzed using the same procedure as the samples. Linear standard curves were developed. The percent recovery was determined by preparing gas standard in gas bag (as described in section 3.8.1) and sampled by pumping through sorbent tube, desorbed and analyzed. The recovery rate was 80%. The minimum detection limit was 5 ppm.

3.8.4 Terpenines

Liquid/liquid extraction and gas chromatography analysis was used to measure alpha-terpinene and gamma-terpinene concentrations. The method used was similar to that described by Misra et al. (1996) for measuring various monoterpene hydrocarbons with the modification of using hexane instead of isooctane for the extraction.

A 1-mL liquid sample was obtained with a 1-mL Hamilton glass gas-tight syringe. Samples were transferred to a 4-mL glass serum tube containing 1 mL of hexane spiked with approximately 10 mg/L bornyl acetate, which served as the internal standard. The glass serum tubes were sealed with screw-top, Teflon-lined rubber septa. Hexane extraction was facilitated by agitating with a vortex mixer for 6 minutes, then centrifuging for 5 minutes if needed to allow phase separation. A disposable pipette was employed to transfer 700- μ L of the solvent extract into a 2-mL crimp-top auto-sampler vial, and vials were immediately sealed with Teflon-lined crimp cap. Samples were analyzed the same day.

Hexane-extracted samples were analyzed using a Perkin-Elmer Auto System Gas Chromatograph (GC) equipped with a flame ionization detector (FID) and a DB-5 capillary column (30-m long, 0.548-mm inner diameter: J& W Scientific). The oven was operated under the following temperature program: 70°C for 3 min; 10°C/min to 180°C where it was held for 2 min (Misra et al. 1996). The injector and detector temperatures were maintained at 250°C and 380°C respectively. Omega integrating software on a Genesis computer was used to analyze the GC output.

Standards were prepared with pure terpene chemical dissolved in 1 L of DI water. Pure liquid phase terpene was injected with a glass, gas-tight Hamilton syringe into 1 L of DI water in a 1 L graduated flask. The air headspace was insignificant compared to the flask volume, and it was capped so that volatilization of terpene did not occur. The liquid was mixed for at least 30 minutes after the terpene was added with a magnetic stir-rod on a Thermolyne stir-plate. Standards were made for concentrations between 0.5 mg/L and 6 mg/L and at least 5 concentrations per standard curve. Concentrations higher than 6 mg/L would have approached the solubility limit of approximately 8 mg/L and resulted in inconsistent concentrations. Duplicate samples were taken at each concentration and averaged.

Standard curves were corrected for the internal standard response. The average response from the standards divided by the internal standard response was plotted versus terpene

concentration in a Microsoft[®] Excel spreadsheet. An equation of the best-fit curve was determined for the linear relationship. The equation was used to convert area responses of samples to concentration.

3.8.5 Conventional Reactor Parameters

Volatile suspended solids (VSS) and total suspended solid (TSS) were used as an indication of biomass concentration. The procedure for VSS and TSS analysis was taken from Standard Method (1995).

Soluble COD was used as an indicator of non-degraded compounds and the formation of intermediate compounds. Liquid samples from the growth reactors were periodically analyzed for soluble COD using Hach Low Range (0-150 mg/L COD) reagent vials and Hach DR/40000U spectrophotometer at 420 nm. Millipore 0.45- μm glass fiber syringe filters (47 mm) were used to eliminate biomass and suspended matter from liquid samples.

The pH of the growth reactors was periodically measured using Hydrion brand pH paper (range 6.0 to 8.0). Color change of the pH paper was compared to the color chart provided on the container. Visual judgement was estimated to be accurate to 0.2 pH units.

4.0 RESULTS

This section presents results on the laboratory SSGR experiments treating organic and reduced sulfur compounds, modeling of methanol removal in the SSGR , seed source acclimation studies for reduced sulfur compounds, mass transfer and biodegradation tests with terpenine, and pilot plant test observations.

4.1 Organic Compound Removal in the Laboratory SSGR

Table 1 Operating Conditions of SSGR

Period	I	II	III
# Days	21	26	7
SRT, Days	10	10	10
VSS, mg/L	692±21	647±12	642±16
TSS, mg/L	974±31	818±21	822±37
SCOD, mg/L	100±6	61±10	58±2
pH	6.4	6.4	6.9
DO, mg/L	6	6	6
Temp, °C	50	50	50
Gas Application (m ³ /m ² -hr)	1.8	1.8	1.8
Compounds Fed			
Methanol	1274 ±46	1077±46	1089±6.8
Acrolein	162±27	134±14	134±3.2
Acetaldehyde	191±21	170±14	161±4.0
Methyl-ethyl-ketone	174±16	134±9.5	134±3.7
Benzene	152±23	131±8.6	135±3.2
Toluene	135±19	121±11	128±3.7
p-xylene	14±1.6	16±1.7	19±0.6
m-xylene	16±1.9	16±0.9	19±0.6
o-xylene	15±2.1	16±1.2	18±1.0

Table 1 shows the steady-state operating conditions in three consecutive periods after a 106 day start up and operating period. The feed composition and concentrations were selected to simulate a HVLC stream from pulp and paper mills. The gas feed rate was set at $1.8 \text{ m}^3/\text{m}^2\text{-min}$ and the reactor was maintained at 50°C . Methanol, which is the major component in HVLC gas stream from pulp and paper mill was fed at a concentration of 1000 to 1200 ppm. Acrolein, acetaldehyde, methyl-ethyl-ketone, benzene and toluene were present at moderate concentrations (120 to 190 ppm). Xylenes were fed at around 20 ppm, since they have been observed at low concentration in pulp mill emissions. All three periods were operated at the same SRT (10 days) with similar VSS concentrations (642 to 692 mg/L). The reactor soluble COD concentrations were slightly different, which reflected the removal efficiency. The pH in phase I and II were 6.4. Period II is separated from period I based on the lower methanol feed concentration. In phase III, the pH was adjusted to 6.9 by adding NaOH solution to the reactor. The low pH in Phase I and II was suspected to be from nitrification. Therefore, in period III, the ammonia in nutrient feed was substitute with nitrate.

Since methanol is a cluster rule surrogate for treatment efficiency, its removal is reviewed separately here and shown in Figure 7 and Table 2. In period I and II, the methanol removal efficiencies were 94 and 96%, respectively. The average effluent concentrations in these periods were 71 and 49 ppm, above the 20 ppm treatment goal. However, after pH adjustment in period III, the removal efficiency increased to 99% and the average effluent concentration decreased to 10 ppm. During phase III the influent methanol concentration remained as high as that in phase II. The reactor VSS concentration was also similar, so that the only parameter that changed and appeared to be related to the improved methanol removal was pH. The surge of methanol feed concentration from 1000 ppm to 1200 ppm in Phase II, was followed by the decrease in the removal efficiency.

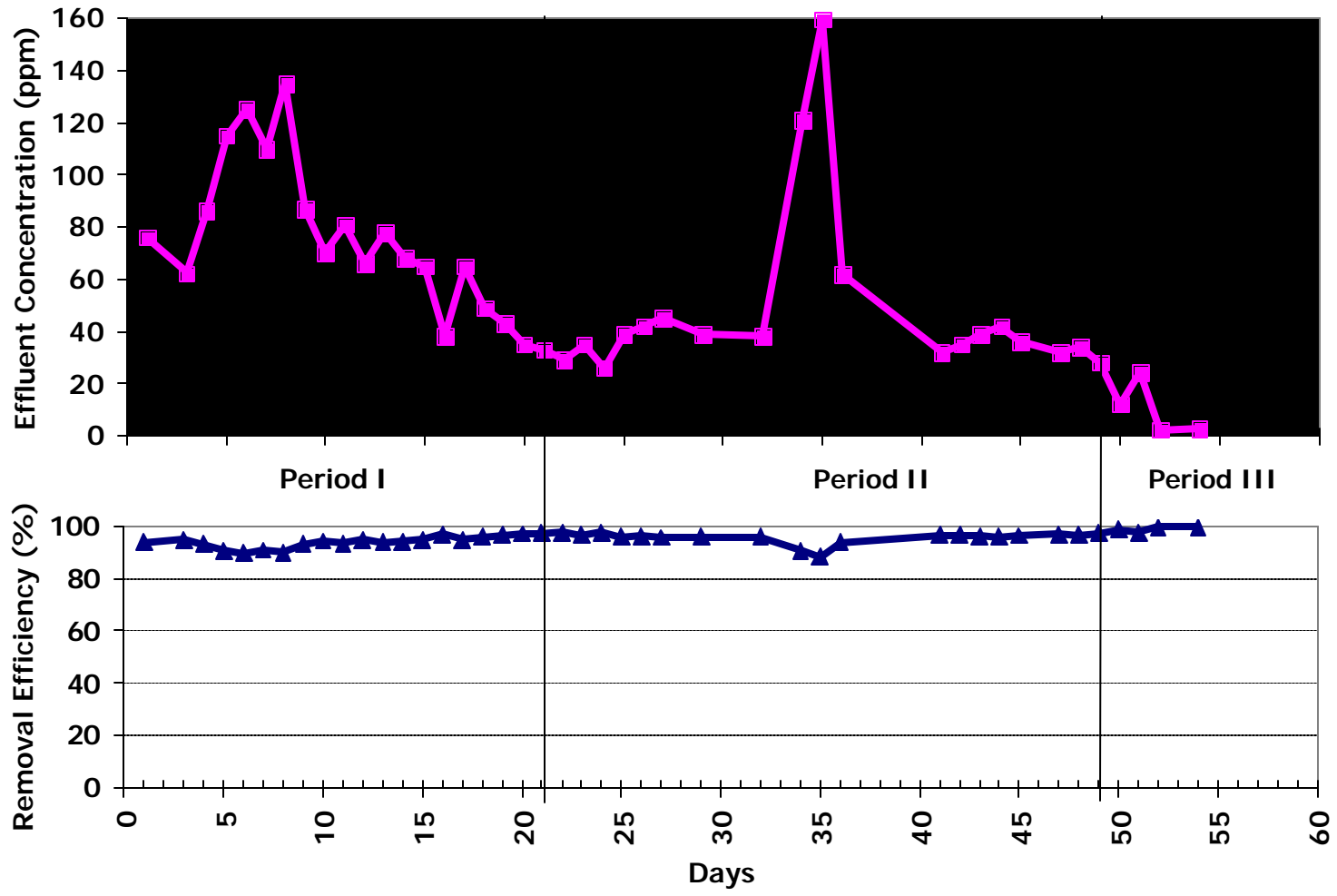


Figure 7 Methanol treatment performance in SSGR in 3 operation periods

Table 2 The average treatment efficiency for methanol in SSGR in periods I, II and III

Period	I	II	III
Influent, ppm	1275±46	1077±45	1089±7
Effluent, ppm	71±31	49±35	10±10
% Removal	94	96	99
Detection Limit, ppm	2	2	2
pH	6.4	6.4	6.9

The removal efficiencies for all other organic compounds are shown in Table 3. The removal efficiencies of acrolein, acetaldehyde, MEK, benzene and toluene were 99% in period I and above 99% in period II. For > 99% removal efficiencies, the compound was not detected so the detection limit concentration was used to calculate the removal performance. Since the removal efficiencies of these compounds were very high in periods I and II, the effect of the higher pH on their removal in period III could not be determined. Because of their lower treatment levels, the removal efficiencies of xylenes are shown in Figure 8 as well as in Table 3. The removal efficiency in period I was only 74-84%, which was substantially lower than other compounds. This may have been due to time needed for acclimation, because in period II, the removal efficiency increased to 86-94%. After the pH adjustment, the removal efficiency of xylene increased further, but was still lower than the target treatment. Despite the lower removal efficiencies, the actual effluent concentrations of xylenes were only 1-4 ppm, due to their low influent concentrations. It should be noted that BTX compounds are much more volatile than the other organic compounds, so that for the same liquid concentrations resulting from biodegradation in the SSGR, they will have higher effluent gas concentrations.

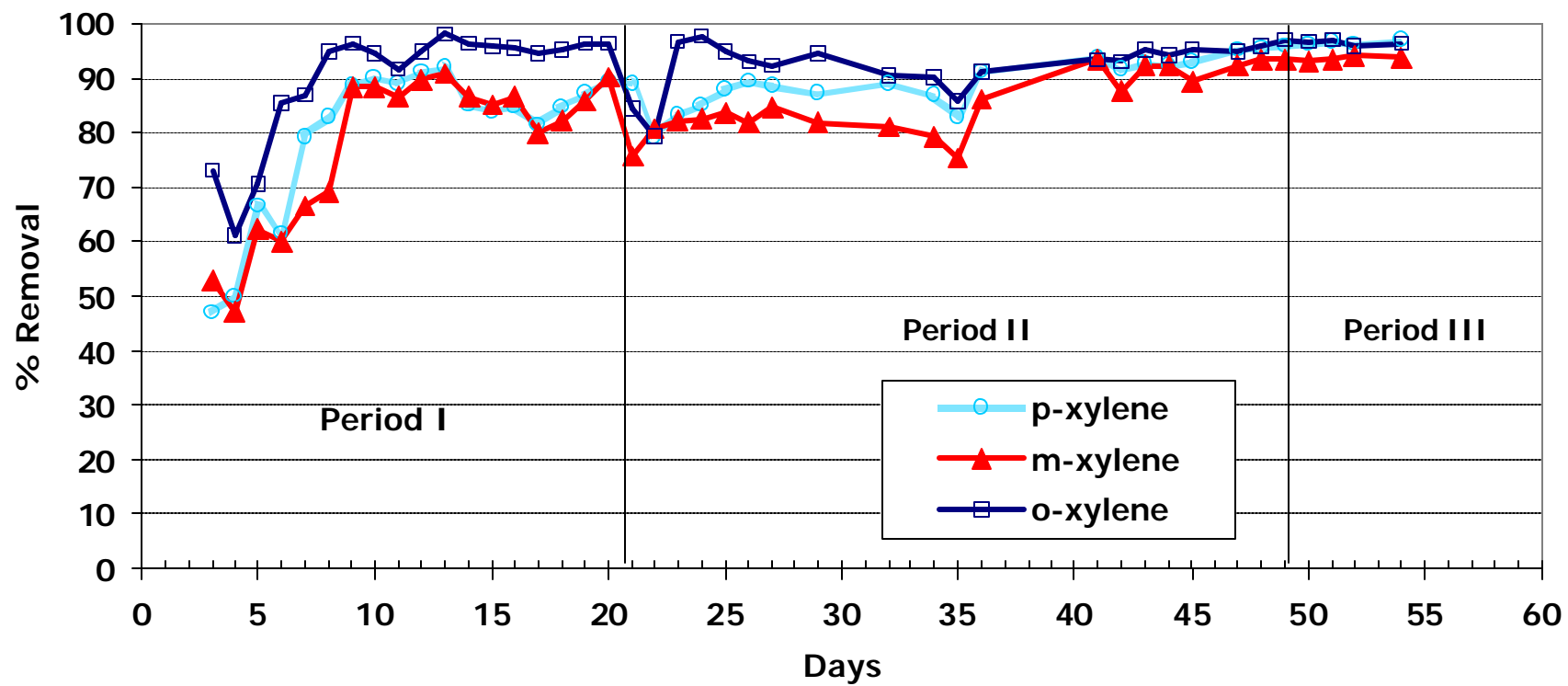


Figure 8 Treatment removal efficiency of xylene compounds in SSGR

Table 3 Treatment removal efficiencies of other organic compounds in SSGR for periods I, II and III

Compounds	Detection limits	% Removal		
	PPM	I	II	III
Acrolein	2	99	>99	>99
Acetaldehyde	3	99	>99	>99
MEK	1	99	>99	>99
Benzene	1	99	>99	>99
Toluene	1	99	98	>99
p-xylene	0.1	76	90	97
m-xylene	0.1	74	86	94
o-xylene	0.1	84	94	97

4.2 Application of SSGR Model for Methanol Removal

Since methanol can serve as a surrogate for gas emission organic compounds under the cluster rules, it was selected for the organic compound to be used in the mechanistic model evaluation. This section describes the gas treatment mechanistic model, provides mass transfer and biokinetic parameters for methanol for the model, and uses the model to analyze methanol removal performance in the SSGR system.

4.2.1 Model Description

The model has been developed and described by us previously (Bielefeldt and Stensel, 1999) and is summarized here. The first equation describes the effluent gas compound concentration as a function of the reactor liquid compound concentration, the air reactor application rate ($\text{m}^3 \text{ gas}/\text{m}^2 \text{ reactor area} - \text{hr}$), the mass transfer coefficients, $K_L a$ and H , the influent gas compound concentration, and liquid depth. This equation is based on a mass balance for gas/liquid transfer for a bubble traveling up through a liquid column.

An important, and valid assumption in this case, is that the reactor liquid is completely mixed so that C_L is constant.

$$C_{ge} = C_{go} e^{\frac{-KLa \cdot d}{H(Q_g/A)}} + C_L H \left[1 - e^{\frac{-KLa \cdot d}{H(Q_g/A)}} \right] \quad (7)$$

Where:

C_{ge} = Effluent gas compound concentration, mg/L

C_{go} = Influent gas compound concentration, mg/L

C_L = Liquid compound concentration, mg/L

H = Henry's coefficient, $\frac{air, mg / L}{H_2O, mg / L}$

K_La = Mass transfer coefficient, hr^{-1}

Q_g = Air flow rate, m^3/hr

Q_g/A = Air rate per unit area of reactor, $m^3/m^2 \cdot hr$

d = Liquid depth, m

The liquid concentration is controlled by biodegradation, which is a function of the biokinetic and growth coefficients (k , K_S , Y and b) and the reactor SRT. The biokinetic and growth parameters, k , K_S , Y and b must be known, estimated or obtained experimentally. At steady state conditions the fundamental and convenient equation that predicts the reactor liquid compound concentration is as follows:

$$C_L = \frac{K_S(1 + b \cdot SRT)}{SRT(Y \cdot k - b) - 1} \quad (8)$$

For the gas reactor the SRT can be controlled by how much reactor liquid is removed each day and replaced by liquid containing nutrients and alkalinity:

$$SRT = \frac{V}{Q_L} \quad (9)$$

Where:

C_L = Liquid concentration, mg/L

K_S = Michaelis-Menten half-velocity constant, mg/L

k = Max. specific substrate utilization rate, g/g-day

b = Cell decay coefficient, g/g-d

Y = Cell synthesis yield, g cell/g organic compound degraded

Q_L = Liquid removal rate, m³/d

V = Reactor volume, m³

The organic compound removal efficiency is given as follows:

$$\% R = 100 \cdot \left(1 - \frac{C_{ge}}{C_{go}} \right) \quad (10)$$

Where:

$\% R$ = Compound removal efficiency, percent

The maximum treatment potential for a given design would be at a long reactor SRT so that biodegradation reduces the liquid concentration to a minimal value, and the performance is then governed mainly by mass transfer. To study this limiting case and the effects of mass transfer, C_L in equation (7) is assumed to be very low (near zero). Therefore, the second term in equation (7) is less significant and can be eliminated for calculation purpose. Substituting (7) into (10) yields:

$$\% R = 100 \cdot \left(1 - e^{\frac{-K_L a d}{H \cdot (Q_g / A)}} \right) \quad (11)$$

The reactor depth required for a given $\% R$ is shown as follows:

$$d = \frac{H \cdot \left(\frac{Q_g}{A}\right) \cdot \ln\left(1 - \frac{\%R}{100}\right)}{-K_L a} \quad (12)$$

Given H and K_La values, equation (12) can be used to determine the reactor liquid depth for a specific removal efficiency where only mass transfer controls. The equation shows that for low H values or high K_La values, a lower liquid depth is needed for a given treatment performance.

4.2.2 Model Mass Transfer Coefficients

The compound gas/liquid mass transfer coefficient, K_La, and Henry's coefficients are critical elements of the model and reactor performance. The Henry's coefficient value depends on the compound's solubility and partial pressure, which are also temperature dependent. Henry's coefficient can be obtained experimentally or from calculation. Table 4 summarizes the Henry's coefficient values measured experimentally in this work for methanol, terpenes and the reduced sulfur compounds. Of these compounds, methanol has a relatively much lower H value, which means it is more readily transferred from the gas to liquid phase than the terpenes or sulfur compounds.

Table 4 Summary of Henry's Law Coefficient values measured by experiment (EPICS method)

Compounds	Henry's Coefficient (L water/L air)			
	20°C	25°C	35°C	50°C
Methanol				0.012 (0.002)
α-terpinene	1.3 (0.2)		2.4 (0.3)	3.5 (1.0)
γ-terpinene	1 (0.2)		1.6 (0.1)	3.5 (0.9)
HS		0.385		0.5
MT		0.18		0.48
DMS			0.115	0.15
DMDS				0.19

Henry's coefficient of a compound can also be calculated from the following equation (LaGrega et al. 1994):

$$H = \frac{e^{(A-B/T)}}{8.205 \times 10^{-5} \times T} \quad (13)$$

H = Henry's coefficient, $\frac{\text{air, mg / L}}{\text{H}_2\text{O, mg / L}}$

A, B = Constants

T = Temperature ($^{\circ}\text{K}$)

Calculated Henry's coefficient values at 50°C for the BTX test compounds were calculated and are summarized in Table 5.

Table 5 Calculated Henry's Law Coefficients for selected compounds

<u>Compounds</u>	A	B	Henry's Law Coefficient at 50°C
Benzene	5.53	3190	0.45
Toluene	5.13	3020	0.56
P-xylene	6.93	3520	0.71
O-xylene	5.54	3320	0.45

$K_{L}a$ value for oxygen and terpinenes were determined for the laboratory SSGR at different gas flow rates and temperature. Figure 9 shows an example of the oxygen concentration data for the aeration test to determine the oxygen $K_{L}a$ value. The oxygen $K_{L}a$ values for the SSGR tests are summarized in Table 6. The oxygen $K_{L}a$ of 21.1 hr^{-1} at 50°C for the 150 mL/min air flow rate at the 1.8 L volume is representative of the SSGR operating conditions. The other data show that $K_{L}a$ is not effected by depth (2.4 L versus 1.8 L was a result of increasing depth), and that $K_{L}a$ increases with temperature and air flow rate, as expected (U.S. EPA, 1985).

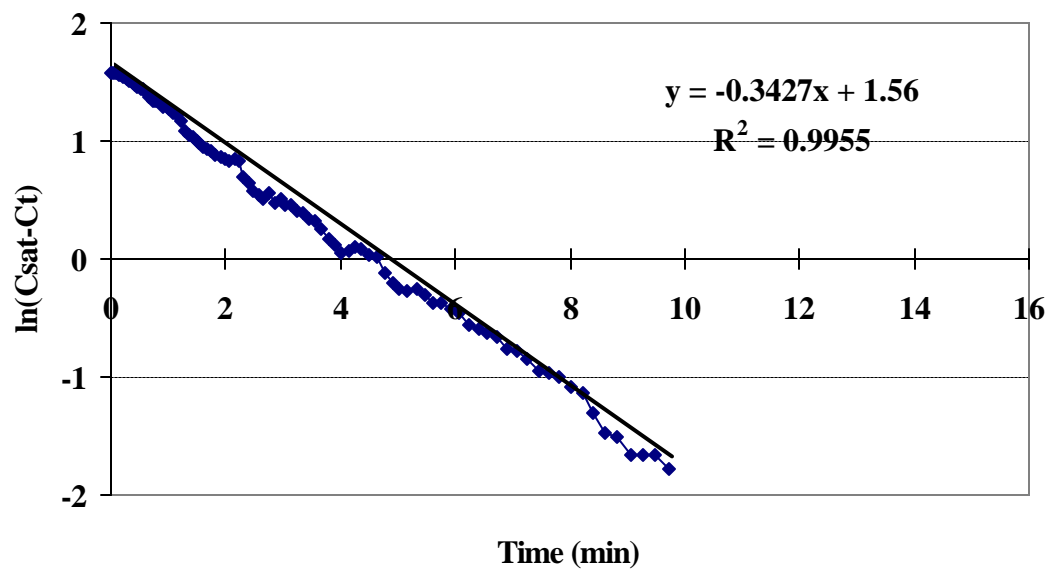
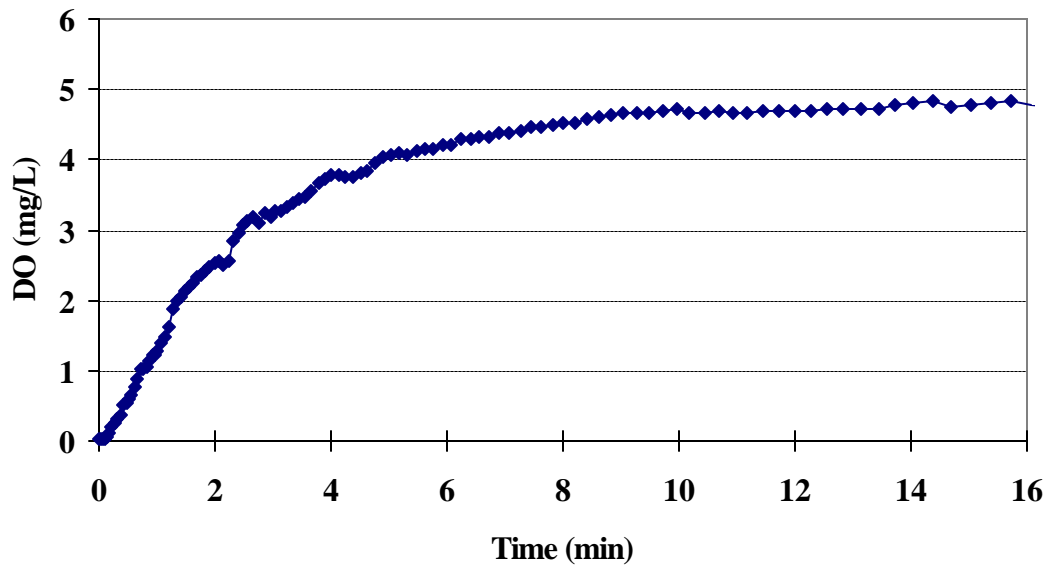


Figure 9 An example of $K_L a$ test result for oxygen at 50°C, liquid volume 2.4 L and flowrate of 150 mL/min

The $K_L a$ values of the terpene compounds was determined by air stripping tests with dissolved terpene concentration measured with time. Figure 10 shows an example of a terpene compound gas/liquid mass transfer test and linear regression fit to obtain $K_L a$. As the temperature was increased from 35°C to 50°C, the $K_L a$ increased by a factor of about 3.5, as shown in Table 6.

Table 6 $K_L a$ for oxygen, toluene, α -terpinene and γ -terpinene

	Temp	Vl (ml)	Flow rate (ml/min)	$K_L a$ (hr-1)	st dev
Oxygen	50	2.4	150	20.2	0.8
	50	1.8	150	21.1	0.6
	50	1.8	100	9.1	0.4
	50	1.8	48	7.4	0.5
	20	2.4	89.3	10.1	
Alpha-terpinene	35	1.8	150	5.4	0.6
	50	1.8	150	19.2	
Gamma-terpinene	35	1.8	150	7.8	1.2
	50	1.8	150	29.4	

Alternatively, when the $K_L a$ for oxygen is known, the $K_L a$ of another compound can be estimated using the ratio of the liquid diffusion coefficient of the compound to that for oxygen (Bielefeldt and Stensel 1998):

$$K_L a_{VOC} = K_L a_{O_2} \frac{D_{compd}}{D_{O_2}} \quad (14)$$

Where:

D_{compd} = Compound diffusion coefficient, cm^2/sec

D_{O_2} = Oxygen diffusion coefficient, cm^2/sec

$K_L a_{compd}$ = Compound mass transfer coefficient, hr^{-1}

$K_L a_{O_2}$ = Oxygen mass transfer coefficient, hr^{-1}

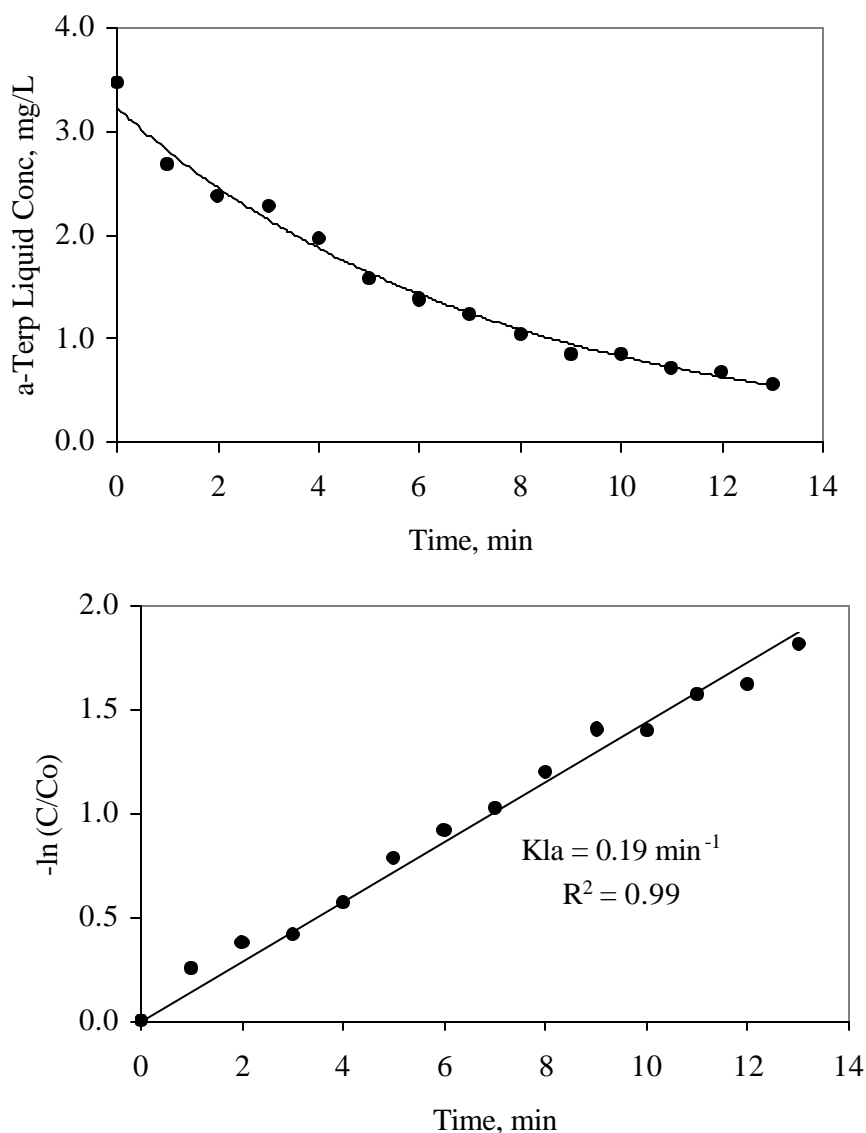


Figure 10 Alpha-terpinene liquid concentration versus time for a K_{La} test and K_{La} data fit at 50°C and gas flow rate of 150 mL/min

Estimated K_{La} values are summarized in Table 7 for methanol and BTX compounds based on the SSGR oxygen K_{La} of 21.1/ hr. Of these volatile compounds, methanol has the higher K_{La} value. In view of the intensive analytical effort that would be required to test the K_{La} of each HAP studied, the use of equation 14 should provide a reasonable estimate of the K_{La} for SSGR treatment application.

Table 7 Calculated $K_L a$ for methanol and other more volatile compounds tested in SSGR at 50°C. Based on oxygen $K_L a$ of 21.0/hr

Compounds	Diffusion coefficient ^a (cm ² /sec) × 10 ⁻⁵	Calculated $K_L a$ (hr ⁻¹)
Oxygen	2.50	21.0
Methanol	1.60	13.5
Benzene	1.30	10.9
Toluene	1.24	10.9
Para-xylene	1.15	9.7
Ortho-xylene	1.15	9.7

^a Chem.engr handbook (Perry, 1973)

The oxygen $K_L a$ was also measured by an in-situ, non-steady state test performed during the reactor treatment operation. In this test the oxygen concentration was perturbed by sparging with pure oxygen temporarily. The oxygen concentration was measured with a DO probe with time as it decreased to its steady state value under the normal aeration. A semi-log plot of DO concentration versus time yields the $K_L a$ value (Bielefeldt, 1996). The K_{LaO_2} at the reactor operating condition was 21/hr, which is similar to the aeration test $K_L a$ values at that operating condition.

The effect of temperature on the $K_L a$ of oxygen at 20°C and 50°C in the SSGR is compared to the $K_L a$ temperature relationship provided in the ASCE clean water standard (1984): (ASCE 1984)

$$K_L a_T = K_L a_{20} \cdot 1.024^{T-20} \quad (15)$$

Where:

$$K_L a_T = K_L a \text{ at temperature } T, \text{ hr}^{-1}$$

$$K_L a_{20} = K_L a \text{ at } 20^\circ\text{C}, \text{ hr}^{-1}$$

$$T = \text{temperature, } ^\circ\text{C}$$

Based on equation 15, the oxygen $K_L a$ at 50°C should be 2.04 times the oxygen $K_L a$ at 20°C. This compares well to the ratio of the $K_L a$ in table 6 of 20.2/10.1 or 2.0.

4.2.3 Biokinetic Coefficients

Since methanol is a surrogate parameter for the cluster rules, it was selected as the compound to be used in the SSGR model.

The Michealis-Menten biokinetics coefficients for methanol were obtained from a series of experiments using the indirect test procedure described in the methods section.

Kinetic tests were done using biomass taken directly from the SSGR system during testing for treatment of organic compounds.

Figure 11 shows an example of the oxygen consumption versus time during a methanol indirect kinetic test at 50°C. The oxygen concentration was elevated due to pre-aeration with pure oxygen. The initial oxygen consumption prior to substrate (methanol) addition was due to endogenous respiration of the bacteria. Following the substrate addition, the oxygen consumption rate increased due to substrate degradation. The degradation rate was constant for about 120 minutes, when the rate began to decline due to the effect of substrate concentration on the substrate removal rate. When the substrate was completely consumed, the oxygen consumption rate returned to near the initial endogenous oxygen consumption rate.

The oxygen consumption due to substrate degradation is calculated by removing the rate due to the endogenous respiration rate, which is shown in Figure 12. The oxygen consumption rate is then converted to a substrate consumption rate using the following equation (Ellis et al. 1994):

$$S_t = S_o - \left[\frac{DO_{int} - DO_t}{DO_{int} - DO_{fin}} \right] S_o \quad (16)$$

Where:

S_t = substrate concentration at time t, mg/L

S_o = initial substrate concentration, mg/L

DO_t = DO at time t corrected for endogenous respiration, mg/L

DO_{int} = initial corrected DO concentration, mg/L

DO_{fin} = final corrected DO concentration, mg/L

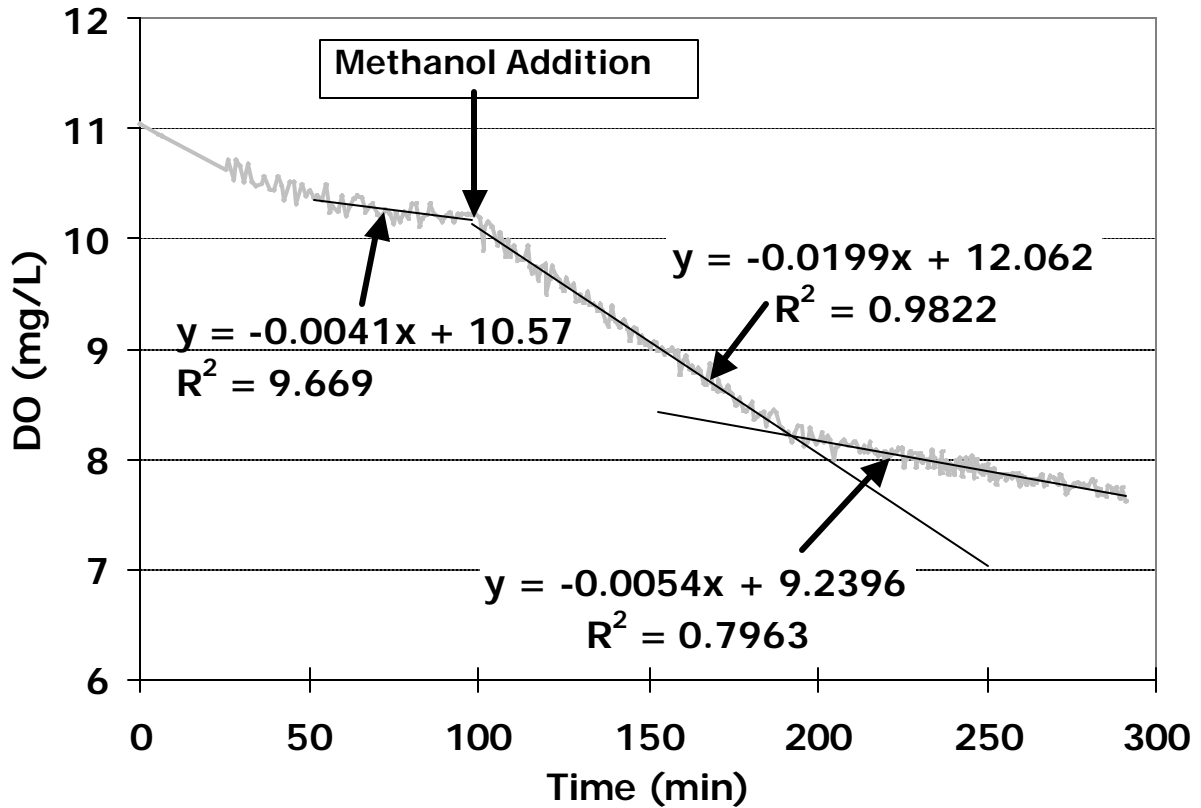


Figure 11 Example plot of DO consumption versus time for indirect test to determine methanol biokinetics (50°C)

Figure 13 shows the calculated substrate concentration versus time using equation 16, the initial substrate concentration added, and data in Figure 12. The results show a fairly constant methanol consumption rate until methanol level falls below 0.2 mg/L, after which time, the methanol concentration affected the methanol degradation rate.

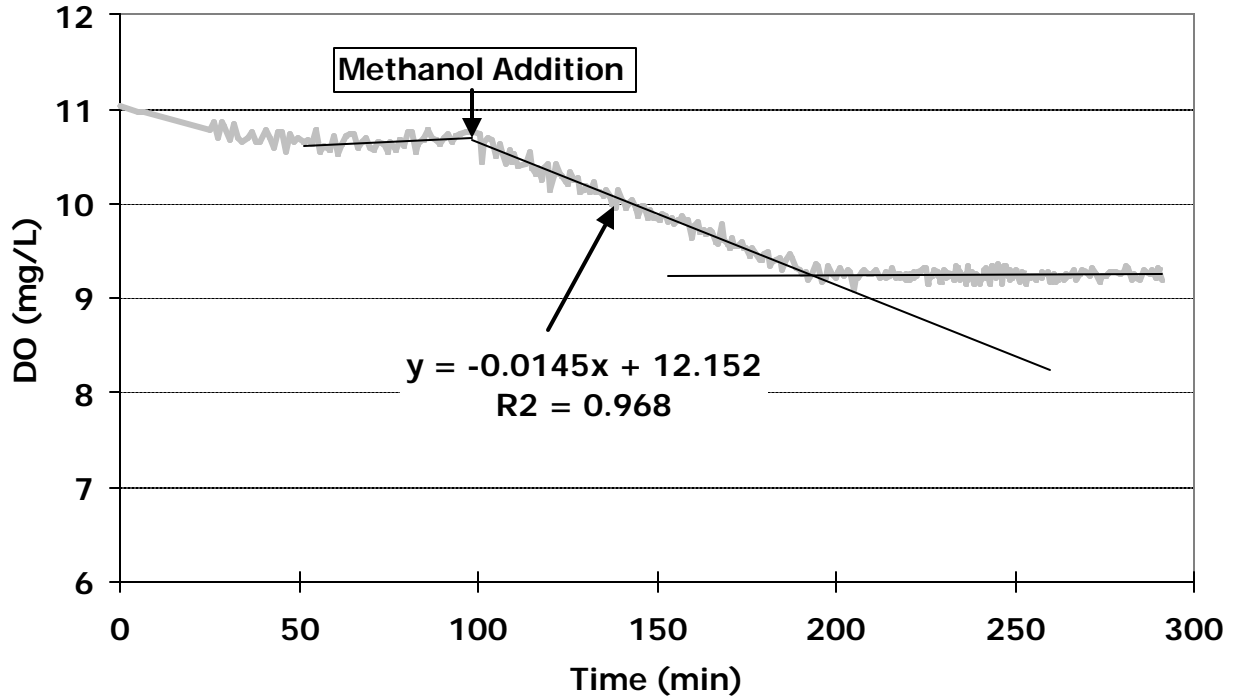


Figure 12 DO consumption curve from Figure 11 after removing endogenous DO consumption rate

The maximum specific substrate utilization rate (k) is determined by the slope of the linear portion of the curve in Figure 13 divided by the biomass concentration (VSS) estimated to be methanol degraders. The biomass in the test contained bacteria that were grown on compounds other than methanol, since the SSGR reactor was fed other compounds as well. The portion of VSS estimated to be methanol degrader is estimated from the ratio of methanol COD to the total COD fed to the reactor per day, which is 27%.

The K_S value is defined as the substrate concentration where the degradation rate (or slope) is half of k . To determine the experimental K_S value, the slope of methanol concentration versus time was calculated over small time intervals in a Microsoft[®] Excel spreadsheet. The K_S was assigned the value of the substrate concentration where the slope was half the maximum slope value.

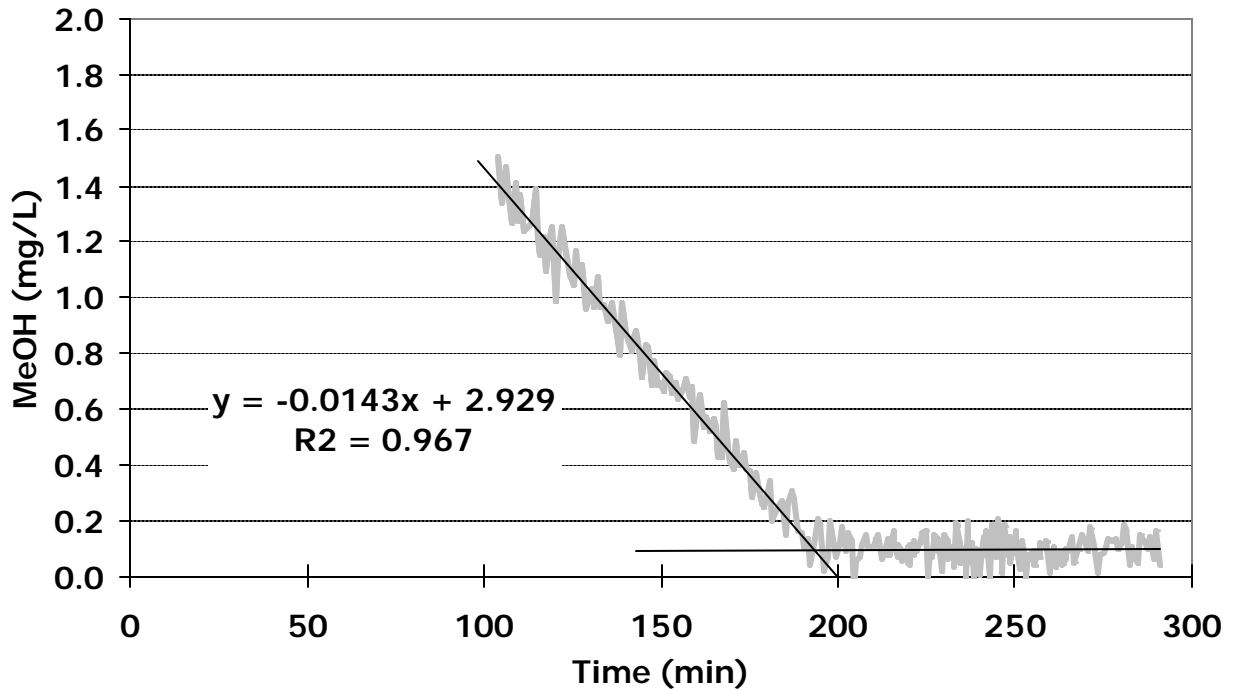


Figure 13 Methanol consumption rate based on DO consumption rate in Figure 12

The endogenous decay value, b , was estimated by dividing the slope of the final linear oxygen consumption rate in Figure 5, by $1.42 \text{ g O}_2/\text{gVSS}$, and dividing by VSS to get b as $\text{gVSS lost/g VSS present-day}$.

The results from four indirect kinetic tests for methanol done in the same week during the phase III steady state period are summarized in Table 8 along with the estimated methanol-degrading biomass concentration. The maximum specific methanol utilization rate (k) was higher when higher initial methanol concentration were used. This type of response is an indication of a possible substrate induction effect where higher initial substrate concentrations induce greater enzyme activity. The K_S values range from 0.1 to 0.3 mg/L and are comparable to the magnitude of K_S values observed for single substrates in the degradation of BTX compound by Bielefeldt (1996).

Table 8 Biodegradation kinetic parameters of methanol obtaining from indirect method test at 50°C

Initial MeOH conc. (mg/L)	VSS* (mg/L)	Observed maximum methanol utilization rate (mg /L-d)	k (mgMeOH/mgVSS-d)	K _S (mg/L)	b (g/g-d)
3.08	13.9	0.0226	2.33	0.30	0.18
3.08	13.1	0.0167	1.81	0.10	0.16
1.54	13.3	0.0145	1.54	0.15	0.16
1.54	13.4	0.0113	1.22	0.17	0.13

* estimated methanol-degrading biomass

4.2.4 Application of model to describe SSGR performance with laboratory results

The model described previously was used to evaluate methanol removal in the SSGR. Table 9 summarizes the conditions used to calibrate the model to the laboratory results. The operating conditions that resulted in an average effluent methanol concentration of 10 ppm during phase III are shown; the gas application rate was 1.8 m³/m²-hr, the influent methanol concentration was 1050 ppm, the SRT was 10 days, and the reactor liquid depth was 0.36 m. The mass transfer and biokinetic parameters were based on the results of the independent tests already described. The average K_S value and the higher k value from the kinetic tests was used, since those values would better represent the maximum rate possible at substrate saturation.

The only parameter not available for application in the kinetic model equations is the synthesis yield coefficient (Y), g VSS/g methanol used. Thus, the model was calibrated to determine a value for Y, where the model predicted an effluent gas methanol concentration of 10 ppm. For this fit, a Y value of 0.12 g VSS/g methanol was obtained. This is a reasonable yield value for aerobic degradation of methanol at thermophilic temperatures.

Table 9 Operating conditions and model parameters used to calibrate gas treatment model for methanol removal in the SSGR

Model Parameters for Methanol	Value
Qg/A	1.8 m ³ /m ² -hr
Cgo	1050 ppm (1.37 mg/L)
SRT	10 day
Depth	0.36 m
Temperature	50°C
Cge	10 ppm
H	0.011
K _{La}	13.5 hr ⁻¹
k	2.33/d
K _S	0.14 mg/L
b	0.15 d ⁻¹

The effect of reactor liquid depth and operating SRT was evaluated with the calibrated model (Figure 14), using the same gas application rate and influent methanol concentration as shown in Table 9. The depth was varied from 0.05 to 0.4 m and the SRT was varied from 8 – 30 days. The figure shows that the performance under these conditions is not mass transfer limited, but biodegradation limited. If it were mass transfer limited, increasing depth would improve the treatment performance. At longer SRTs the effluent gas concentration is lower, since at longer SRTs, a higher biomass concentration is present in the reactor. Thus, a lower liquid methanol concentration is possible, which results in a lower effluent gas concentration (see equations 7 and 8).

Long SRTs are feasible in the SSGR system, since there are no solids separation limitations. An upper limit on SRT would result when the biomass concentration is sufficiently high to cause reactor oxygen utilization rate, that is high enough to prevent a dissolved oxygen concentration sufficient to support efficient biodegradation and low substrate liquid concentration.

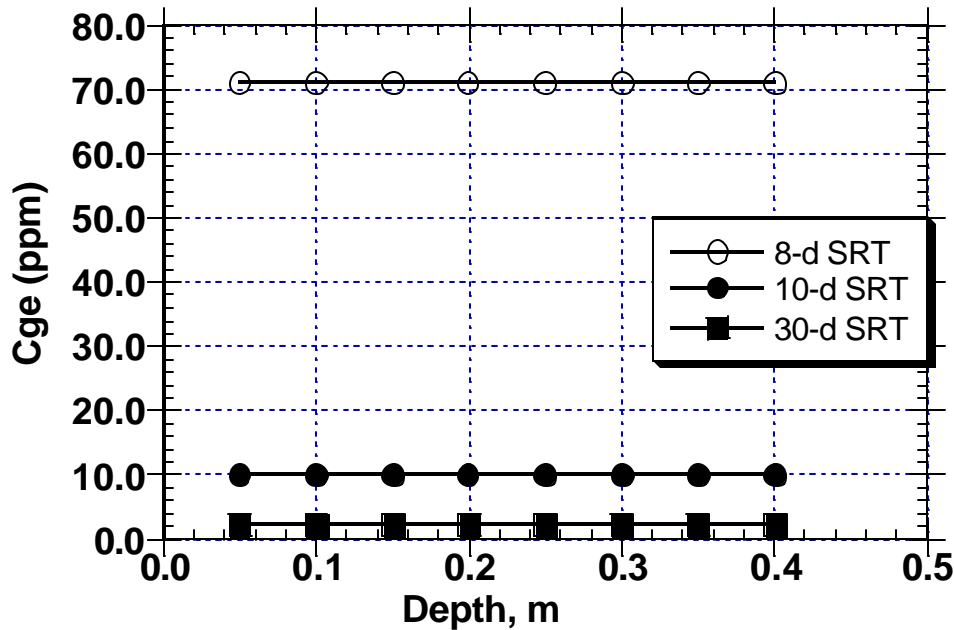


Figure 14 Laboratory SSGR model evaluation; effect of depth and SRT on Effluent gas methanol concentration at 50°C

The model example shows only an evaluation of depth and SRT for the laboratory SSGR operation. For the pilot plant operation, a much higher gas application rate was used versus the laboratory system, which would affect the mass transfer characteristics of the SSGR and treatment performance. However, at the higher gas application rate, a higher K_{La} would occur. This aspect of the model application and evaluation of the SSGR system for methanol removal in full scale designs will be presented after the pilot plant results.

The model was used to evaluate methanol removal at higher gas application rates, ranging from a practical design range of $0.5 \text{ m}^3/\text{m}^2\text{-hr}$ to $2.5 \text{ m}^3/\text{m}^2\text{-hr}$, based on possible diffuser densities. In Figure 15, the model prediction of effluent gas methanol concentration is shown as a function of gas application rate for a reactor liquid as shallow as the lab reactor (0.4 m) and assuming the same K_{La} of the lab reactor (13.5/hr). The K_{La} would increase at higher gas flow rates, so the results in Figure 15 are only illustrative of the possible treatment level for methanol with an unrealistically low K_{La} value. The results show that even in this case, with such a shallow liquid depth, the

effluent methanol gas concentration of 20 ppm can be met with a 30-d SRT operation at gas application rates of $2.0 \text{ m}^3/\text{m}^2\text{-hr}$ or less.

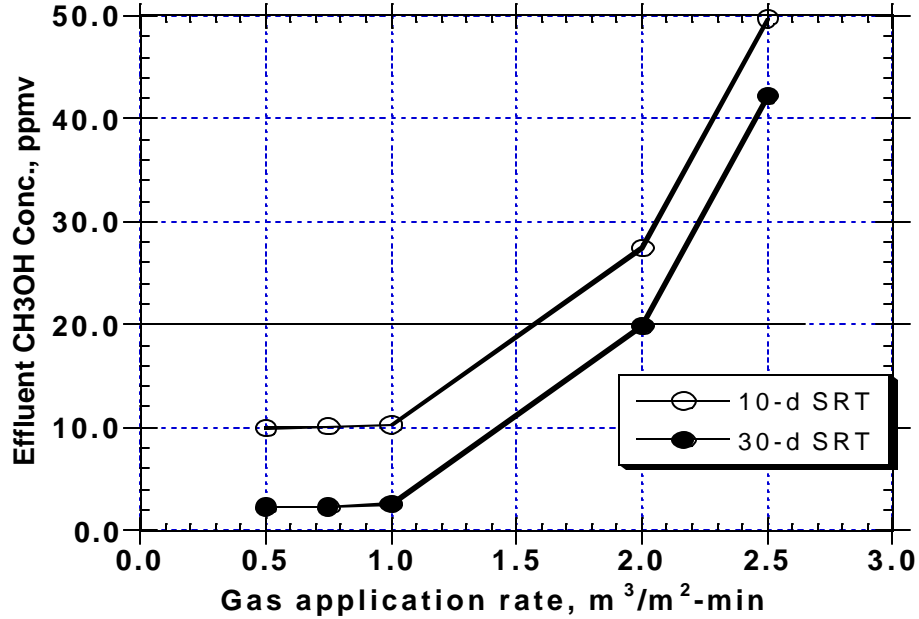


Figure 15 Model simulation on the effect of gas application rate on effluent gas methanol concentration (ppm) for 10-day and 20-day SRT operation at 50°C . K_{La} of only 13.5/hr assumed. Reactor liquid depth equal 0.40 meter.

Figure 16 shows results of a similar simulation using a K_{La} value of 50/hr, which is a more realistic mass transfer condition for a full-scale facility. (The pilot plant results (section 4.4) show that a K_{La} of 50/hr is possible.) At this K_{La} , Figure 16 shows that methanol removal, even at the high end of practical gas application rates, is not mass transfer limited. The effluent gas concentration is equal to that calculated for the lab reactor at a lower gas application rate but at about the same liquid depth. These results and simulation illustrated that methanol can be easily removed to low effluent gas concentrations using very shallow reactor depth for the SSGR.

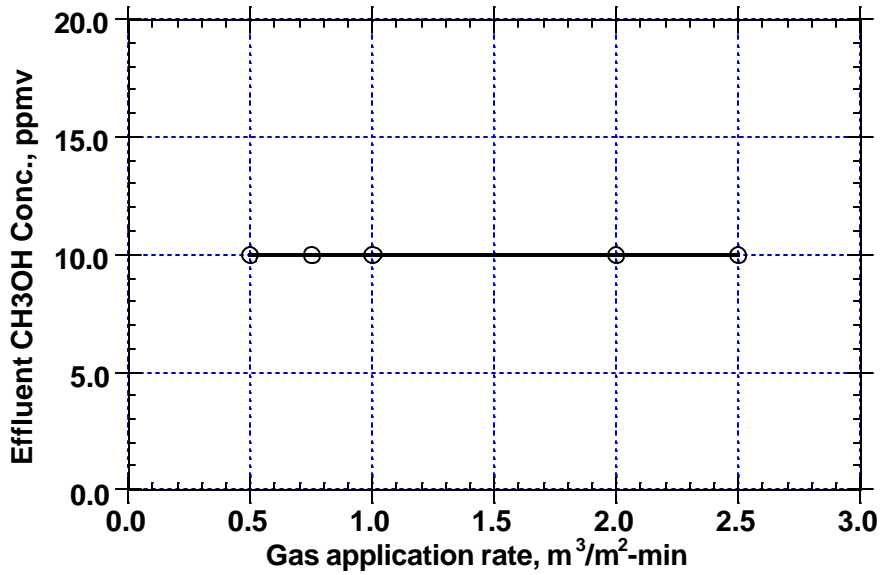


Figure 16 Model simulation of the effect of gas application rate on effluent gas methanol concentration for 10-day SRT and K_{La} of 50/hr at 50⁰C operation. Reactor liquid depth equal 0.40 meter.

4.2.5 Model Evaluation of BTX removal in SSGR

Since the BTX compounds are much more volatile than methanol, their removal potential in the SSGR is of interest. BTX removal was modeled by considering mass transfer limitation only, since they are very biodegradable. Equation (11), (12) and (13) were used for modeling the effect of depth versus % removal and the results are shown in Figure 17. The removal efficiency increases with the increase of depth and 98% removal is possible for all the compounds except p-xylene at a liquid depth of only 0.4 m. The model showed that in order to achieve 98% removal of p-xylene, the reactor depth must be more than 0.6 m, still a relatively shallow liquid depth.

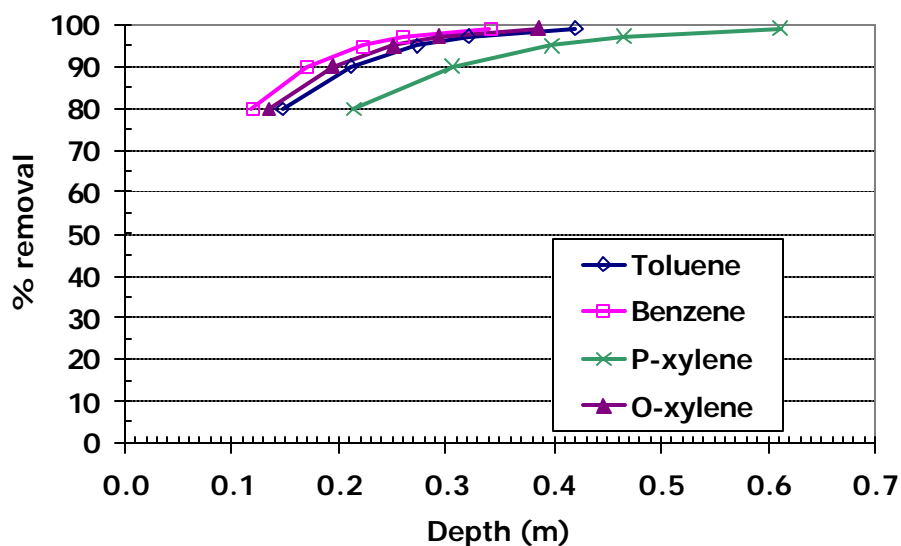


Figure 17 Model simulation of the effect of depth on percent removal of benzene, toluene, and p- and o-xylenes, based on mass transfer limitation only

4.3 TRS Compounds

4.3.1 Acclimation Test

The first step in studying the treatment of TRS compounds in the SSGR was to develop a microbial population capable of degrading all the TRS compounds. Batch acclimation tests were performed as described in the method section with inocula from a municipal aerobic thermophilic sludge digester, activated sludge from the Simpson Mill, Simpson Mill pulp waster water, high temperature lake sediment, and cultures from a hot spring located on the Olympic peninsula, WA.

Each batch reactor was fed a single compound and incubation continued for up to 120 days.

A summary of the acclimation test results is shown in Table 10. HS and MT degrading populations were easily developed in every seed source. The degradation was fast and no lag time was observed for both compounds. DMDS degradation populations were slower to develop in 50°C reactors. A lag time of 4-10 days was observed for all 50°C

incubations except for the high temperature lake sediment and Olympic hot spring culture, which degradation started without a lag time. In the 35°C incubation, no lag time was observed for DMDS degradation, except for the reactor seeded with high temperature lake sediment, which had a lag time of 8 days. In the beginning, DMDS degradation rate was slower than HS and MT. Figure 21 shows DMDS degradation at 50°C after 160 days of incubation. It took 4-5 days to completely degrade approximately 450 ppm of DMDS, where as a HS degrading culture degraded 3700 ppm of HS overnight, as shown in Figure 18.

Table 10 Summary of batch acclimation tests for degradation of reduced sulfur compounds

Seed Source	HS		MT		DMS		DMDS	
	50°C	35°C	50°C	35°C	50°C	35°C	50°C	35°C
Municipal Aerobic Thermophilic sludge digester	+	+	+	+	-	-	+	+
Activated sludge from Simpson Mill	+	+	+	+	-	+	+	+
Simpson Mill pulp washer water	+	+	+	+	-	-	+	+
High temperature lake sediment	+	+	+	+	-	-	+	+
Olympic Hot Spring (40-50°C) cultures	+	N/A	+	N/A	-	N/A	+	N/A
Maximum concentration degraded (ppm)	6500	900	400	1100	-	800	475	100

+ degraded, - not degraded, N/A no test was performed

DMS was difficult to degrade. No DMS degradation occurred in any of the 50°C incubations. The only reactor that showed DMS degradation was a 35°C reactor seeded with activated sludge from Simpson Mill. After 120 days, the culture degraded a maximum DMS concentration of 800 ppm overnight. An attempt was made to slowly increase the temperature of this culture. However, the degradation activity decreased when the temperature exceeded 45°C. After repeated feedings at 45°C, the activity stopped altogether.

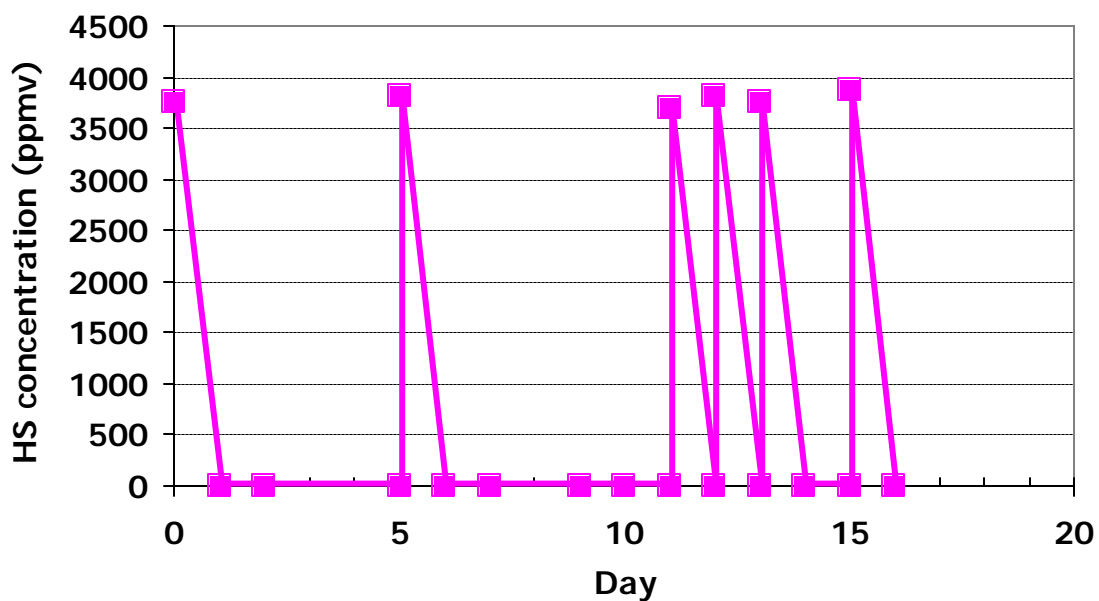


Figure 18 HS degradation in a batch-fed reactor at 50°C after 160 days of incubation and repeated feeding of HS

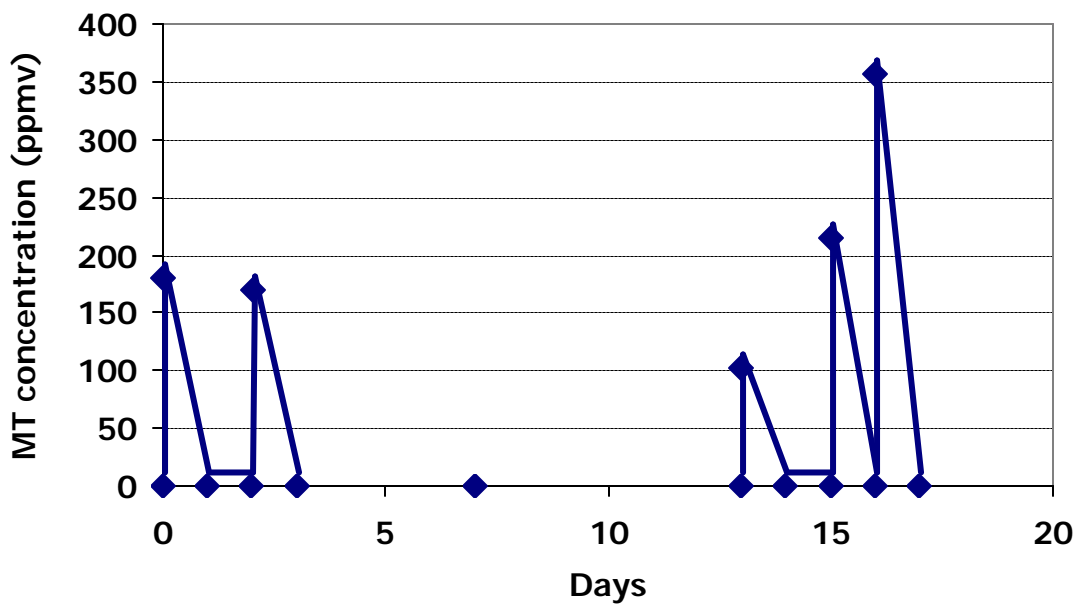


Figure 19 MT degradation in a batch-fed reactor at 50°C after 160 days of incubation and repeated feeding of MT

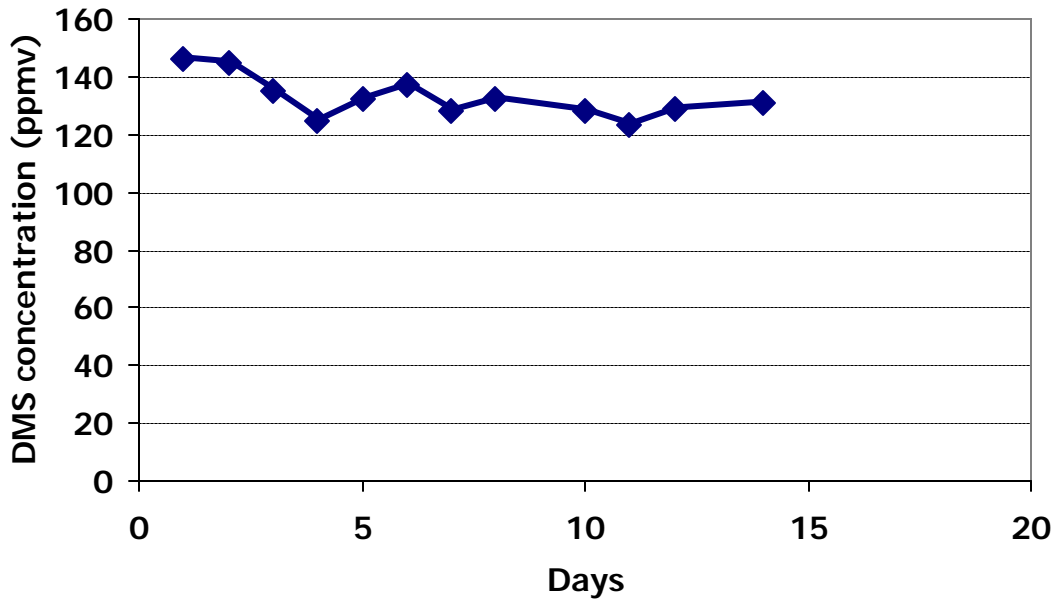


Figure 20 Lack of DMS degradation in a batch reactor at 50°C after 75 days of incubation

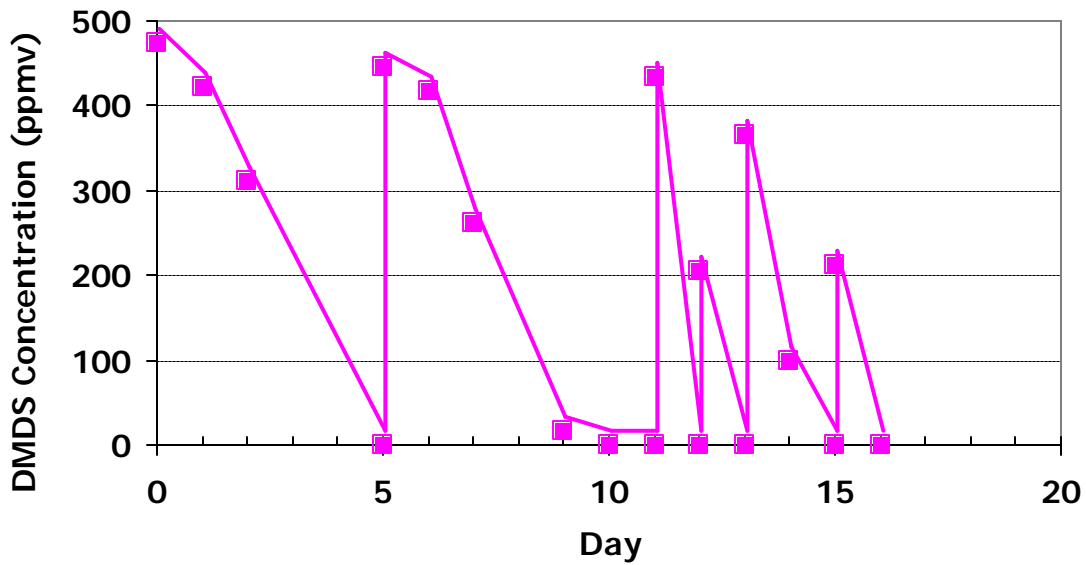


Figure 21 DMDS degradation in a batch-fed reactor at 50°C after 160 days of incubation and repeated feeding of DMDS

Once the populations were acclimated to HS, MT, DMDS and in the case of the 35°C reactor, DMS, the initial TRS concentrations were increased. The highest concentrations fed and completely degraded for HS, MT and DMDS in the 50°C reactors were 6500, 400 and 475 ppm, respectively. The highest concentrations fed in the 35°C reactors for HS, MT, DMS and DMDS were 900, 1100, 800 and 100 ppm, respectively.

Since HS can also ionize to H^+ and S^- abiotically, the abiotic transformation of HS was tested. Biomass and nutrient from the HS batch reactor was added to two 125-mL serum bottles. In one bottle, formaldehyde was added to kill the biomass. The same amount of HS was added to both bottles. The rate of HS disappearance in the bottle with active biomass was about 5 times higher than that with the killed control, indicating that HS transformation in the batch reactor was mainly biological (data not shown).

Occasionally, DMDS was observed in the reactor fed MT, indicating that MT can be transformed to DMDS. To investigate if this reaction was biotic or not, a study was set up to compare the reaction in the presence of active and inactive biomass. MT was added to two 125-mL serum bottles containing biomass and nutrient solution. Formaldehyde was added to one bottle as a killed control. Without the active biomass, DMDS accumulated in the system. In the active bottle, the MT disappeared while DMDS appeared and then decreased. The test confirmed that MT can be transformed to DMDS abiotically. However, it was unclear whether the microbes consume MT directly or wait for MT to transform to DMDS first or both.

4.3.2 SSGR treatment performance with TRS compounds

The SSGR for treating TRS compounds was seeded with return activated sludge from the Simpson wastewater treatment facility. Methanol and formaldehyde were fed along with TRS compounds in order to simulate composition of a pulp mill HVLC gas stream. The gas feed rate was $2.4 \text{ m}^3/\text{m}^2\text{-hr}$ and the system was started with a 30-day SRT at 50°C. The SRT and temperature were varied during 4 periods of operation as shown in Table 11. The temperature was decreased from 50°C in periods I and II, to 30°C in period III,

and to 20°C in period IV, in an attempt to increase DMS removal efficiency. The feed composition was similar in all 4 periods.

Table 11 SSGR operating conditions and feed concentrations of TRS compounds, formaldehyde and methanol

Period	I	II	III	IV
# days	170	50	50	13
SRT, days	30	10	30	30
Temp, C	50	50	30	20
VSS, mg/L	343+/-7	134+/-6	482+/-10	487+/-17
TSS, mg/L	445+/-14	198+/-12	721+/-15	731+/-21
COD, mg/L	102+/-10	42+/-4	82+/-11	65+/-10
pH	7	7	7	7
Gas application rate, m³/m²-min	2.4	2.4	2.4	2.4
Compounds fed				
HS	60+/-20	67+/-3	79+/-8	79+/-5
MT	58+/-20	67+/-6	77+/-6	81+/-5
DMS	41+/-14	51+/-8	62+/-12	53+/-3
DMDS	43+/-20	38+/-18	55+/-12	52+/-2
Formaldehyde	60+/-10	64+/-7	n/a	n/a
Methanol	90+/-18	90+/-20	87+/-6	91+/-7

Nearly complete removal of HS and MT was observed in all 4 periods. The effluent concentrations for both compounds were below detection limits most of the time.

DMS and DMDS were more difficult to treat. Figure 22 -Figure 25 show the removal efficiencies of DMS and DMDS in the 4 operation periods. DMDS removal improved as the temperature declined. In period I, only 46% was removed. In period II, even though the SRT was decreased to 10 days, the removal efficiency of DMDS increased to 60%. In period III and IV, the SRT was increased to 30 days, while the temperature was decreased from 50 to 30°C and 20°C, respectively, which resulted in improved DMDS

removal efficiencies (82 and 91%, respectively). DMDS was degraded much better at mesophilic temperatures than at thermophilic temperatures.

DMS was the most difficult to degrade. Only 25% of the DMS was degraded in period I. In period II, the SRT was decreased from 30 to 10 days, and the removal efficiency of DMS dropped to 16%. When the SRT was brought back to 30 days and the temperature was dropped to 30°C, the removal efficiency increased to 47%. The removal efficiency increased further to 63 % when the temperature was dropped to 20°C. The trend in temperature effect on DMS degradation was similar to DMDS. Significantly improved degradation of DMS was observed at mesophilic temperatures than at thermophilic temperatures.

Methanol was removed effectively in all 4 periods with over 99% efficiency observed. Formaldehyde was also efficiently removed. No formaldehyde could be detected in the effluent gas in period I and II, which were the only periods in which its degradation was studied.

Table 12 The influent, effluent concentrations and removal efficiency of TRS compounds, formaldehyde, and methanol for different operating periods

Period I, SRT = 30 D, Temp = 50°C						
Compounds	Inf. (ppm)		Eff (ppm)		% removal	
	Aver	SD	Aver	SD	Aver	SD
HS	60	20	0	0	100	0
MT	58	21	0.85	4	97	14
DMS	41	15	31	13	25	17
DMDS	44	21	22	10	46	19
Formaldehyde	61	11	0	0	100	0
Methanol	91	19	0	0	99	1
Period II, SRT = 10 d, Temp= 50°C						
Compounds	Inf (ppm)		Eff (ppm)		% removal	
	Aver	SD	Aver	SD	Aver	SD
HS	68	4	0	0	100	0
MT	68	6	0	0	100	0
DMS	51	9	43	8	16	8
DMDS	39	18	18	18	60	29
Formaldehyde	64	7	0	0	100	0
Methanol	90	20	1	3	99	3
Period III, SRT = 30 d, Temp = 30°C						
Compounds	Inf (ppm)		Eff (ppm)		% removal	
	Aver	SD	Aver	SD	Aver	SD
HS	79	8	0	0	100	0
MT	77	5	0	0	100	0
DMS	62	42	30	10	47	15
DMDS	56	33	9	4	82	11
Formaldehyde	n/a	n/a	n/a	n/a	n/a	n/a
Methanol	77	6	1	1	99	2
Period IV, SRT = 30 d, Temp = 20°C						
Compounds	Inf (ppm)		Eff (ppm)		% removal	
	Aver	SD	Aver	SD	Aver	SD
HS	79	5	0	0	100	0
MT	81	4	0	0	100	0
DMS	53	3	19	6	63	11
DMDS	52	2	4	1	91	2
Formaldehyde	n/a	N/a	n/a	n/a	n/a	n/a
Methanol	91	7	1	1	99	2

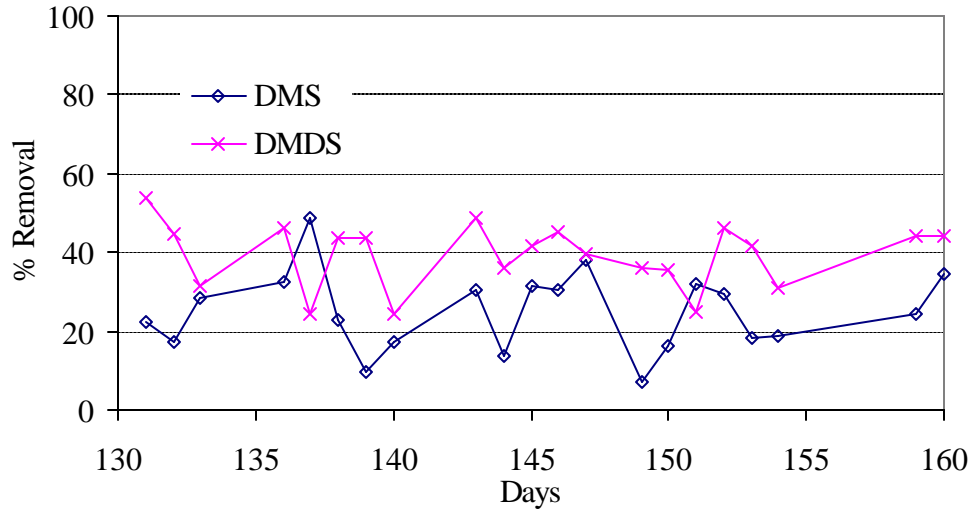


Figure 22 Percent removal of DMS and DMDS in the SSGR in period I, SRT = 30 day, Temperature = 50°C

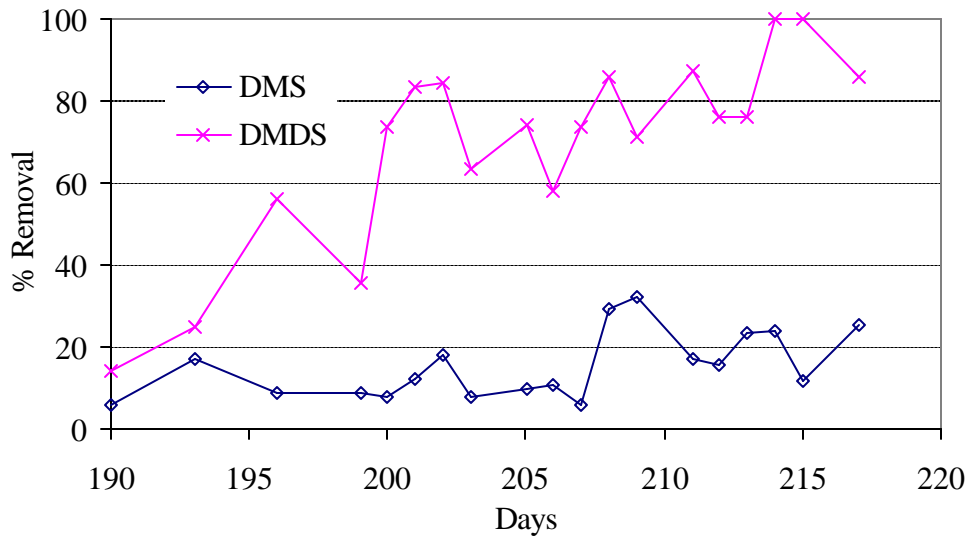


Figure 23 Percent removal of DMS and DMDS in the SSGR in period II, SRT = 10 day, Temperature = 50°C

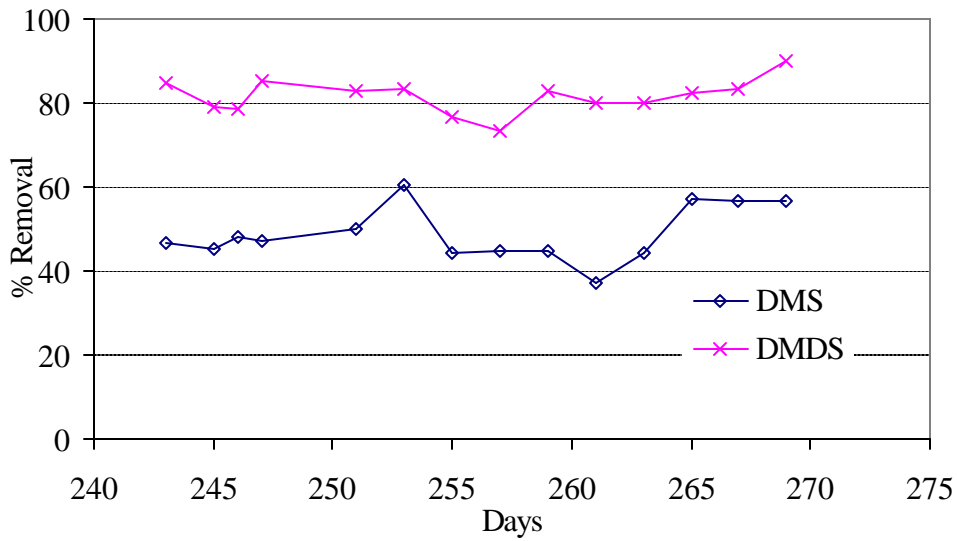


Figure 24 Percent removal of DMS and DMDS in the SSGR in period III, SRT = 30 day, Temperature = 30°C

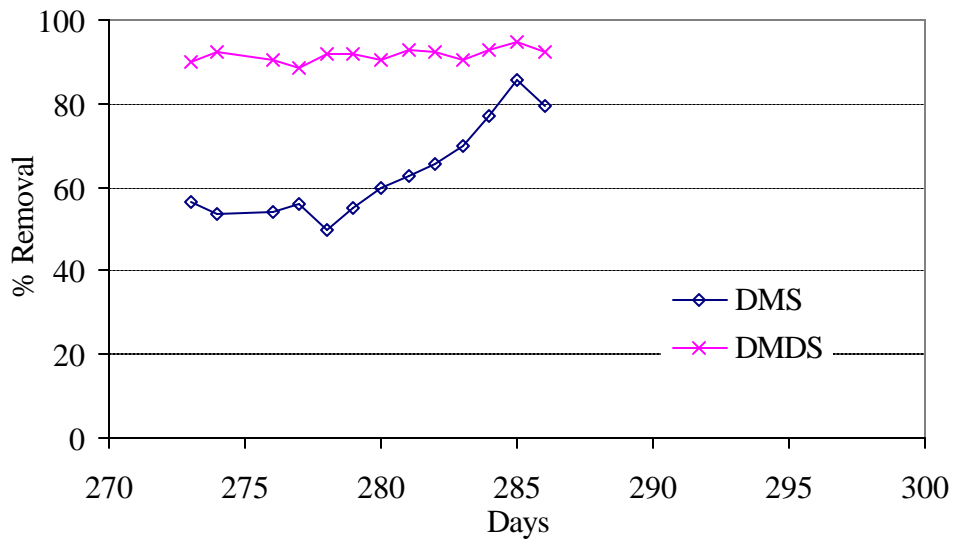


Figure 25 Percent removal of DMS and DMDS in the SSGR in period IV, SRT = 30 day, Temperature = 20°C

4.4 Pilot Plant Results

Before starting contaminated gas treatment at the Simpson mill, the mass transfer effectiveness of the SSGR pilot plant was tested. The K_{La} test were done at 1.2 m (4ft) water depth, blower feed air temperature of 52°C, a reactor water temperature of 45°C and ambient temperature of 27°C. Table 13 shows the test conditions and results. Figure 26 shows an example K_{La} test result at an air flow rate of 157.15 ft³/min. The K_{La} of the pilot plant was in the range of 17.4 to 93 hr⁻¹ and increased linearly with the air flow rate. The high K_{La} values were the result of high diffuser density design developed for the pilot system. Based on the model evaluation, such a high K_{La} value would assure efficient treatment at shallow depth.

Table 13 Summary of pilot plant K_{La} test conditions and results

Pilot Plant K_{La} test

Water depth	1.2 m (4 ft)
Fed air temperature	52 °C
Water temperature	45 °C
Ambient temperature	27 °C

Test #	Gas Application rate (m³/m²-min)	Air Flow Rate (ft³/min)	K_{La} (1/hr)
1	0.36	60	17.4
2	0.5	83	55.8
3	0.55	90	39
4	0.55	90	42
5	0.90	150	80.4
6	0.90	150	81.6
7	0.97	160	88.2
8	0.97	160	93

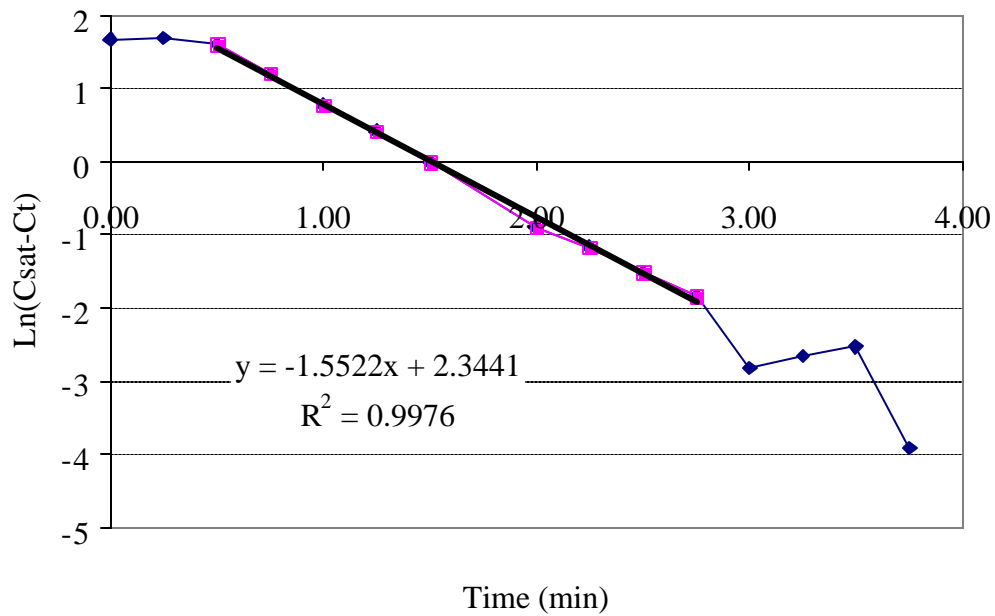
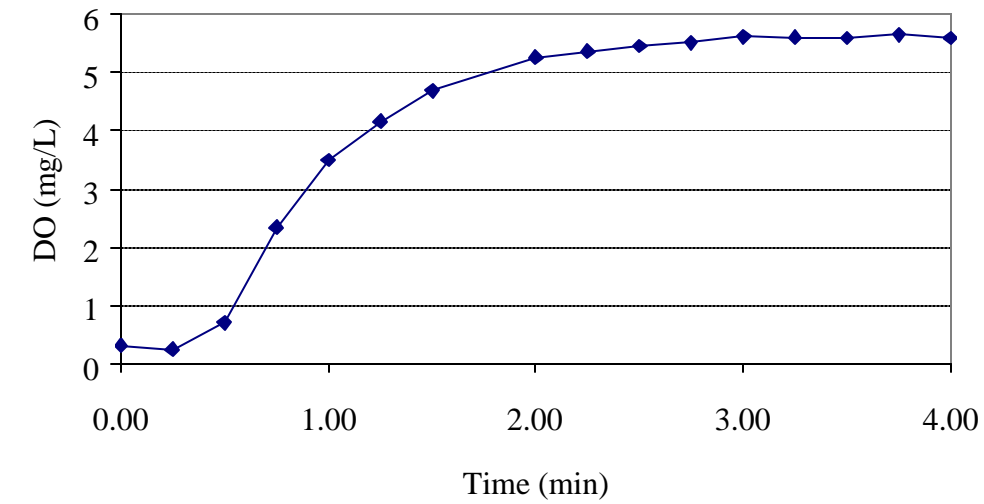


Figure 26 Example of time course of DO for an oxygen K_La test and oxygen K_La data fit of the pilot plant at flow rate of $157.5 \text{ ft}^3/\text{m}$

Return activated sludge from the Simpson wastewater treatment plant was used for seeding the pilot plant. The initial VSS was 474 mg/L and the pH was 7.2. Sodium bicarbonate was added to ensure a minimum alkalinity of 1000 mg/L. The temperature of the gas stream coming into the pilot plant was 60-70°C. A cooling system was used to lower the temperature to 30°C to provide a better condition for DMS removal. The gas application rate was approximately 0.95 m³/m²-min.

The pilot plant gas feed source was from a pipe located above the pulp washers. This location was chosen out of convenience with some awareness that foam from the pulp washer off gas flow could be carried into the pipe. A significant amount of foaming and water did pass through the limited demister design, (indicated by water in the gas flow measurement port). This issue raised an important point about the need to consider the gas source and the potential for contaminants that could give rise to foaming and formation of particulates, affecting the diffusers and operation of the SSGR. Each site will have specific issues about the gas source and quality, and will require appropriate engineering to provide a gas stream that is compatible with the biological treatment process.

The pilot plant was operated for a brief time period from 8/31/00 to 9/5/00 after seeding with a small amount of Simpson mill activated sludge. A thermostat failure and a leak in the cooling system forced the premature shutdown of the pilot plant. Influent and effluent samples were taken during the operation. The average influent and effluent concentration and the percent removals are presented in Table 14.

With the exception of acetaldehyde, DMDS and the terpene compounds, the treatment performance conformed to the SSGR laboratory results, with high removal of methanol, HS, MT and the BTX compounds and low removal for DMS. The poor acetaldehyde removal was most likely due to the lack of sufficient time for acclimation. DMDS and terpinene removal was better than expected.

Table 14 The influent, effluent and removal efficiency of TRS and organic compounds of the pilot plant

Compounds	Influent (ppm)	Effluent (ppm)	% Removal
HS	0	0	n/a
MT	0	0	n/a
DMS	956	605	37
DMDS	41	0	100
Acetaldehyde	1379	450	67
Methanol	59	2	97
Toluene	2	0	100
P-xylene	4	0	100
M-xylene1	82	0	100
M-xylene2	44	0	100
Alpha-terpinene	31	0	100
O-xylene1	107	0	100
O-xylene2	109	0	100
Gamma-terpinene	29	0	100

4.5 Evaluation of Terpenes Removal

Alpha- and gamma-terpinene compounds were selected as representative chemicals from the group of terpene compounds of evaluation for biotreatment in an SSGR system. To evaluate removal efficiency in an SSGR the mass transfer characteristics (H coefficient and K_{La}) and biokinetic parameters must be determined or estimated. The EPICS method was used to determine the H coefficients of the alpha- and gamma-terpinenes. Reactor stripping tests in clean water were carried out at the same air sparge rate as the laboratory SSGR operation to obtain K_{La} values. Terpinene degrading enrichments were maintained and used to measure biodegradation kinetics. With this information, the removal of these terpinene compounds in an SSGR operation was assessed.

Table 15 summarizes the H coefficient values determined for the terpinene compounds at 20°C, 35°C, and 50°C. The H coefficient values are very high, and almost a magnitude

higher than that for such highly volatile compounds such as HS (0.50) and benzene (0.45) at 50°C. Such a high H coefficient suggests that these compounds will not be removed well in a biotreatment application, whether it be the SSGR design or a biofilter.

Table 15 Summary of Henry’s Law Coefficient values measured by EPICS method for terpene compounds

<u>Compounds</u>	Henry’s Coefficient (L/L)		
	20°C	35°C	50°C
α-terpinene	1.3 (0.2)	2.4 (0.3)	3.5 (1.0)
γ-terpinene	1 (0.2)	1.6 (0.1)	3.5 (0.9)

Table 16 summarizes the K_{La} for the terpinene compounds at 35°C and 50°C. The effect of temperature on the K_{La} value is higher than expected in comparing the 50°C K_{La} to the 35°C K_{La} , but the magnitude of the change was similar for both compounds.

Table 16 Summary of K_{La} values for terpene compounds

	Temp	Vl (ml)	Flow rate (ml/min)	K_{La} (hr ⁻¹)	st dev
Alpha-terpinene	35	1815	150	5.4	0.6
	50	1815	150	19.2	
Gamma-terpinene	35	1815	150	7.8	1.2
	50	1815	150	29.4	

In batch bottle biokinetic testing the initial specific terpinene degradation rate was observed for different initial terpinene concentrations. The biodegradation rate increased with concentration and a substrate-saturated, maximum degradation rate (as defined by the maximum specific substrate degradation rate in the Michaelis-Menten model) was not observed before the solubility concentration limit for the compounds was approached. Thus, a first-order model was used to describe the terpinene degradation kinetics. The first-order degradation rate coefficients are summarized in Table 17. The degradation

rates of the two compounds were similar and no significant improvement in rate was found for this enrichment at 50°C.

Table 17 Specific substrate utilization rate (K) values at 35°C and 50°C for the first-order model

	K, L/mg-VSS-day	
	35°C	50°C
Alpha-terpinene	0.18	0.16
Gamma-terpinene	0.13	0.14

The mass transfer and biokinetic data were used with the SSGR performance model to evaluate the removal of the terpinene compounds under the same operating conditions as the laboratory reactor (air application rate of 1.8 m³/m²-d and 30-d SRT). Since first-order kinetics were used instead of the Michaelis-Menten model, equation 8, which calculates the steady state reactor liquid organic compound concentration, was modified as follows:

$$C_L = \frac{1 + bSRT}{YKSRT} \quad (17)$$

Where:

K = first order kinetic coefficient, L/mg-d

The model evaluation found that no significant terpinene removal was possible with the 0.36 m reactor depth. Even at depths in the range of meters, little removal is predicted at both 35°C and 50°C. The main reason for this result is the high value of the terpinene Henry's coefficient.

Table 18 Summary of K_S value for alpha- and gamma-terpinene

<u>Compounds</u>	<u>K_S, mg/L</u>	
	K _S at 35°C	K _S at 50°C
Alpha-terpinene	0.14 ± 0.06	0.17*
Gamma-terpinene	0.15 ± 0.08	0.15*

*one observation

4.6 Evaluation of Full Scale SSGR Designs

The results from the laboratory bench scale studies, mechanistic model evaluations, and pilot plant operation are incorporated here in an assessment of full scale SSGR designs, in terms of reactor sizing, operating needs, and pretreatment considerations. An SSGR design example for a 5000 cfm gas flow is presented.

A variety of gas streams from different sources will be candidates for a biological treatment alternative to meet the Cluster Rule regulations. The testing program showed that the HAPs and TRSs expected for pulp and paper gas emissions were removed at high levels with the SSGR, with the exception of DMS and the two terpinenes tested. The high Henry's coefficient value for the particular terpenes evaluated make biological treatment impractical, but there are a range of other terpene compounds for which mass transfer characteristics are not known, and thus may have potential for removal in biological treatment.

Removal of DMS, which was present at significant levels in the feed gas at the Simpson Mill pilot plant, was limited and improved with decreasing reactor temperature. Based on the batch incubation tests, which showed higher degradation rates at lower temperatures, the improved removal of DMS in the SSGR at lower temperature was due to improved biological degradation and not related to a mass transfer limitation. Since DMS was biodegradable, further research may develop cultures or treatment conditions that provide more favorable degradation rates. Biological inocula obtained from hot natural environment with high sulfur activities may offer a rich source of bacteria capable of degrading DMS at higher temperatures. Within the time and resources of this project, the effect of temperature on DMS degradation was observed to be significantly inhibited at temperatures greater than 35°C.

The inability to achieve acceptable DMS removal efficiency does not mean that the SSGR is not a feasible process for pulp and paper mill gas emissions. High removal

efficiency was observed for other compounds and the cluster rule level for the surrogate HAP, methanol, can be easily met at thermophilic temperatures. Other methods can be used in conjunction with the SSGR to remove DMS at an overall lower cost. Activated carbon adsorption could be used to treat the SSGR effluent gas stream. Treatment with the SSGR before carbon adsorption would assure long carbon life and reduced costs for carbon regeneration. Another approach would be to add powdered activated carbon (PAC) or other efficient sorbent to the SSGR reactor, removal of a side stream for biodegradation of organic compounds on the PAC, and recycling the PAC to the SSGR. This is illustrated in the following schematic.

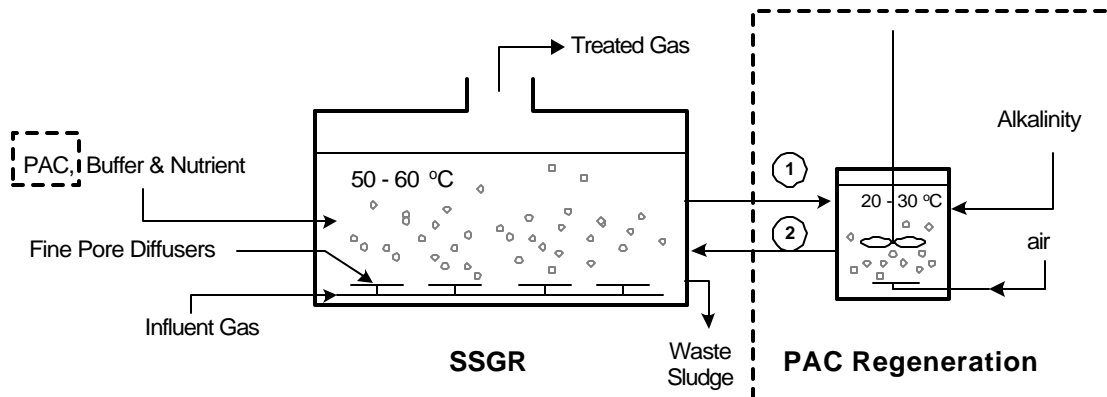


Figure 27 Schematic of Shallow Suspended Growth Reactor (SSGR) for Gas Treatment. (Dashed boxes indicate powdered activated carbon addition to SSGR with biological regeneration of PAC. Mixed liquor with spent and regenerated PAC represented by lines 1 and 2.)

The SSGR alone is not the only solution to pulp mill emission problems, and a proper site evaluation would be needed to produce optimal results. Consideration of pretreatment of the gas and temperature are necessary. Depending on the site conditions, pretreatment of the gas may be needed before the SSGR to prevent fouling of the fine bubble diffusers used to disperse the feed gas. In some cases, a standard filter on the gas feed blower may suffice. In other cases where the gas is highly contaminated with particulates and/or foam, the gas must be pretreated before it is fed to the SSGR. Temperature control may

also be considered for some locations, depending on the variability of the temperature and operating temperature possible for the SSGR system. For streams without DMS, a higher temperature can be tolerated for biotreatment in the SSGR.

4.7 SSGR Design

For this analysis a gas treatment reactor with a treatment capacity of 5,000 cubic ft/min (cfm) flow was assumed. This could represent a significant size module for a pulp and paper mill gas treatment system where total HVLC flows may be in the range of 20,000 cfm.

The laboratory results and model evaluation showed that very shallow liquid depths can be used to meet the cluster rules for methanol. A reactor liquid depth of less than 0.4 m and air application rate of 1.0-2.0 m³/m²-min were shown to be feasible by the modeling results. The pilot plant showed that a diffuser density of 37 diffusers (each was 30 cm or 1.0 ft diameter) in a 4.65-m² area was feasible. This resulted in a diffuser density of 0.58-m² diffuser area/m² floor area. Using a reasonable design gas application rate of 0.14 m³/min-diffuser (5 scfm/diffuser), the gas application rate 1.1 m³/m²-min. At a gas flow rate of 5,000 cfm (141.7 m³/min), the SSGR required floor area is 129 m² (1384 ft²). Assuming a 1.2 m (4 ft) reactor depth, a 4.8-m (16-ft) tall system could contain 4 stacks of SSGR reactors to minimize the floor area needed. This would result in a 6.4-m (21-ft) diameter unit. Thus, the SSGR for a 5000 cfm gas flow would be 6.4-m diameter by 4.8-m high and contain 1000 diffusers. Assuming a 0.90 m liquid depth and a blower efficiency of 70%, a 50 Hp compressor would be sufficient to feed the air to the SSGR.

4.8 Cost Analysis

A cost analysis is provided to compare the cost of the SSGR system to that for thermal treatment for the design and gas flow rate described above.

4.8.1. Capital Cost

The capital cost of the SSGR are compared to that for thermal treatment based on a report by Govind, 1993. ("Development of novel biofilters for the treatment of volatile organic

compounds (VOCs).", Presented at the IGT Symposium on Gas, Oil, and Environmental Biotechnology, Colorado Springs, CO.)

Capital Costs, 5,000 cfm units

Biological Reactor (SSGR)	\$110,000
Incineration (with scrubber)	\$200,000

4.8.2. Non Variable operating costs

Based on maintenance costs at 5% of capital costs and labor for operations at 1 person-day (\$40,000/year with overhead) for incineration and ½ person-day for biological treatment operations.

Biological Reactor (SSGR)	\$25,500/year
Incineration (with scrubber)	\$50,000/year

4.8.3. Energy costs

The following table compares the energy costs for biotreatment versus thermal treatment.

Table 19 Comparison of energy cost to treat 5000 scfm

Fuel Type	New Technology (SSGR)	Thermal Treatment	Comments
Electricity (million kWh)	0.392	-	
Natural Gas (million cu. Ft.)	-	91.4	1700°F temperature
Annual Energy Costs	\$24,000	\$338,000	*

*Assuming electricity at \$0.06/kWh and gas at \$3.70/1000 cu. Ft. of gas

4.8.4 Total annual costs

The capital cost was amortized over 10 years at a 7% interest rate. The annual operating costs for biotreatment compared to incineration is \$64, 800 versus \$415,900, with the major cost savings related to energy consumption in thermal treatment.

5.0 SUMMARY AND CONCLUSIONS

The overall goal of this project was to develop and evaluate a shallow suspended growth reactor (SSGR) biotreatment system to provide an economical alternative to remove contaminants from high volume, low concentration (HVLC) gas streams at pulp and paper facilities. Of particular interest was the ability to treat a range of organic and reduced sulfur compounds at high temperature. Tests were performed with a bench-scale SSGR for treating a gas stream containing organic contaminants at 50°C, followed by tests of the treatment of a gas stream with reduced sulfur compounds, formaldehyde, and methanol. The latter laboratory SSGR was operated at temperatures ranging from 30°C - 50°C. A 2.4-m diameter by 1.5-m high pilot plant was designed, fabricated, and installed at the Simpson Mill in Tacoma, WA. The pilot plant was fed exhaust gas from a pulp washer, and was operated for a short period at 30°C in September 2000, before a mechanical failure in the gas cooling system prevented further operation.

The following conclusions resulted from this study:

1. The use of a suspended growth shallow reactor to destroy contaminants in pulp and paper gas streams is a feasible process and reactor liquid depths of 1.0 m or less are practical.
2. A wide range of hazardous air pollutants that are expected to be common for pulp and paper emissions were found to be readily biodegradable at 50°C by the cultures developed, except dimethyl sulfide and dimethyl disulfide. Of these two, the DMS was the most difficult to degrade and DMDS removal rates significantly improved at mesophilic operating temperatures.
3. The Cluster Rule treatment requirements for organic compounds were met in the bench-scale SSGR operation when the pH was controlled to near 7.0. The removal efficiencies were methanol, 99%, acrolein, >99%, acetaldehyde, >99%,

methyl-ethyl-ketone, >99%, benzene, >99%, toluene, >99%, p-xylene, 97%, m-xylene, 94%, o-xylene, 97%, formaldehyde, 99%, hydrogen sulfide, 99%, methyl mercaptan, 99%, and dimethyl disulfide, 85%. Of particular importance for these results is that the bench-scale reactor liquid depth was only 0.36 m (14 inches). A full-scale system, with a 0.6 to 1.2 m (2-4 ft.) depth, would have improved treatment performance where mass transfer limitations exist. Even at this extreme shallow depth the Cluster Rule requirements for 98% methanol removal and less than 20-ppm methanol effluent concentration were met.

4. Activated sludge from the Simpson Mill provided a sufficient seed source to degrade all of the reduced sulfur compounds at 35⁰C, and all except DMS at 50⁰C.
5. Biodegradation rates for DMS and DMDS increased at mesophilic versus thermophilic temperatures. However, the DMS degradation rate was still low enough at 30⁰C to result in poor treatment efficiencies in the SSGR.
6. Biokinetic and mass transfer experimental data was used to calibrate a mechanistic model to predict the removal of methanol in the SSGR. Methanol can be almost completely removed in an SSGR at liquid depths of 0.4 m or less, and at practical gas application rates of 1.0 – 2.0 m³/m²-min.
7. The SSGR mechanistic model with sufficient mass transfer and biokinetic data can provide a reasonable estimate of the treatment performance of an SSGR system.
8. Alpha- and gamma- terpinene degradation were found to be readily biodegradable at 35⁰C and 50⁰C. However, they had extremely high Henry's law coefficients, which suggest little removal of these compounds in a biotreatment reactor.
9. Further research is needed to develop bacteria cultures or environmental conditions that would increase the biodegradation rates of DMS and DMDS.

10. Future use of the SSGR treatment technology should include pilot plant studies at specific sites with consideration of the particular site characteristics and gas pretreatment needs or temperature control.

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