Thermophilic Biotrickling Filtration of Ethanol Vapors

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · JULY 2001

Impact Factor: 5.33 · DOI: 10.1021/es001764h · Source: PubMed

4 AUTHORS, INCLUDING:

Zarook Shareefdeen
American University of Sharjah
50 PUBLICATIONS **1,060** CITATIONS
SEE PROFILE

Marc Deshusses
Duke University
151 PUBLICATIONS **4,929** CITATIONS
SEE PROFILE

Environ. Sci. Technol. **2001**, *35,* 2612−2619

Thermophilic Biotrickling Filtration of Ethanol Vapors

HUUB H. J. COX, THOMAS SEXTON, ZAROOK M. SHAREEFDEEN, AND MARC A. DESHUSSES*

Department of Chemical and Environmental Engineering, University of California, Riverside, California 92521

The treatment of ethanol vapors in biotrickling filters for air pollution control was investigated. Two reactors were operated in parallel, one at ambient temperature (22 °C) and one at high temperature (53 °C). After a short adaptation phase, the removal of ethanol was similar in both reactors. At a bed contact time of 57 s, the elimination capacity exceeded 220 g m^{-3} h^{-1} at both temperatures. The experiments performed revealed that the process was most likely limited by biodegradation in the biofilm. The high-temperature biotrickling filter exhibited a higher degree of ethanol mineralization to CO_2 (60 vs 46% at ambient temperature); hence, a lower rate of biomass accumulation was observed. Plating and cultivation of biofilm samples revealed that the high-temperature biotrickling filter hosted a process culture composed of both mesophilic and thermotolerant or thermophilic microorganisms, whereas the ambient-temperature reactor lacked microorganisms capable of growing at high temperature. Consequently, the performance of the control biotrickling filter was significantly affected by a short incursion at 53 °C. The upper temperature limit for treatment was 62 °C. Overall, the results of this study open new possibilities for biotrickling filtration of hot gases.

Introduction

Biological treatment of contaminated air in biofilters and biotrickling filters is an established and cost-effective technology. The principle of biofilters and biotrickling filters is relatively similar: polluted air is passed through a porous packed bed on which pollutant-degrading mixed cultures form a biofilm. The pollutants are transferred from the waste gas to the biofilm where they are subsequently biodegraded. The difference between biofilters and biotrickling filters is the type of packing material (biofilters usually use a compost mixture, whereas biotrickling filters use an inert packing) and the presence of a free liquid phase continuously recycled over the packing in biotrickling filters. The recycle liquid enables a better control of the conditions; hence, biotrickling filters are usually more effective (on a volumetric basis) than biofilters. Also, biotrickling filters can be built taller than biofilters because of the better structural strength of their packing. Basic mechanisms and new developments in biofilter and biotrickling filter research have been recently reviewed (*1*−*3*).

As for any biological system, temperature is one of the parameters that has the most effect on performance. In most cases, biofiltration research and practical applications of biofilters have been limited to the treatment of waste gases with a temperature in the mesophilic range (15−40 °C) (*4*). However, many industrial waste gases have temperatures beyond this range, e.g., from the tobacco, (*4*) the pulp and paper, (*5*) and food industry (*6*). One option is cooling these gases to below 40 °C prior to biological treatment, which is costly especially when the gas is saturated with water. The use of thermophilic microorganisms active at temperatures over 40 °C would offer great savings and would greatly extend the applicability of biofilters and biotrickling filters.

Only a few studies exist on the biotreatment of waste gas at high temperatures. These were mostly with biofilters containing organic packing materials: treatment of NO_x at 55 °C, (*7*) co-treatment of methanol and α-pinene at 40 °C (*8*), and co-treatment of ethanol and ammonia at 65 °C (*6*) have been reported. However, certain problems are often observed in high-temperature biofilters that are normally not encountered at lower temperatures. High operating temperatures accelerate the degradation of the organic packing material, (*4*, *9*) causing bed compaction, higher pressure drop, air short-circuiting and preferential paths, and decreasing overall system performance. Also, there are a few unpublished reports that compost biofilters generated an offensive odor when operated at high temperature, which is very different from the usual pleasant earthy smell observed with ambient-temperature biofilters. This may be due to increased packing mineralization and/or organic acid production and could be similar to the odor problems associated with thermophilic sludge digestion (*10*).

The above problems are not likely to occur in biotrickling filters because of the different nature of the biotrickling filter packing material. Therefore, the objective of this research was to demonstrate for the first time the feasibility of using biotrickling filters for treatment at high temperature. However, while preparing this manuscript, we heard of a study with similar objectives but in which methanol was the primary pollutant of concern (*5*). In our study, ethanol was selected as the target pollutant as it is a major component in hot waste gases from bakeries. In the Los Angeles basin, it was estimated that pre- and postcontrol VOC emissions of large commercial bakeries were 6.6 and 3.0 tons/day as carbon, respectively, with most of the VOC being ethanol (*11*). Ethanol is also a good model compound removed at high rates in biofilters under mesophilic conditions (*12*). Hence, for the present study, two identical biotrickling filters were set up, one operated at ambient temperature, the other at 53 °C or higher so that mesophilic and thermophilic/thermotolerant ethanol removal in biotrickling filters could be compared.

Materials and Methods

Biotrickling Filter Setup and Operation. Two identical biotrickling filters were used in this study. They were operated in parallel: one at ambient temperature (22 °C) and the other one at an average temperature of 53 °C. The equipment was essentially the same as previously described (*13*), and operating parameters are summarized in Table 1. Figure 1 provides a schematic of the setup. Both reactors were operated with gas and recycle liquid flowing cocurrently. Cocurrent is better than countercurrent operation, since it avoids stripping of the pollutant at the gas outlet side of the reactor (*2*). Ethanol was the sole pollutant, and its gas phase concentration in the inlet air was controlled by injecting 200% proof ethanol (Gold Shield Chemical Co., Hayward, CA) at the desired rate directly into the main air stream with a 665 Dosimat titrator (Metrohm, Herisau, Switzerland) operated in the continuous mode. As no source of high-

* Corresponding author phone: (909) 787−2477; fax: (909) 787−2425; e-mail: mdeshuss@engr.ucr.edu.

10.1021/es001764h CCC: $20.00

Published on Web 05/18/2001

TABLE 1. Reactor Characteristics and Standard Operating Conditions

parameter	ambient-temperature reactor	high-temperature reactor
average temperature	22 °C	52.6 °C
packed bed dimension; volume	H × ID = 1.3 × 0.152 m; volume = 23.6 L	
packing	1-in. (2.54 cm) polypropylene Pall rings	
gas/liquid flow	cocurrent	
gas flow rate	1.5 $m^3\ h^{-1}$	
EBRT[a]	57 s	
ethanol gas inlet concentration	standard 2 g m^{-3}, up to 5 g m^{-3} in specific experiments	
liquid recycle rate	0.144 $m^3\ h^{-1}$	
recycle liquid volume[b]	3.7 L	
medium concentration and composition	2.0× concentrated as in Cox and Deshusses[13]	1.42× concentrated as in Cox and Deshusses[13]
medium feed rate[c]	250 mL h^{-1}	403 mL h^{-1}
water evaporation rate (mL h^{-1})[d]	29 mL h^{-1}	125 mL h^{-1}
recycle liquid purge rate (mL h^{-1})[e]	221 mL h^{-1}	278 mL h^{-1}

[a] Empty bed retention time = bed volume/gas flow rate. [b] Includes the dynamic liquid hold-up, estimated to be on average 2.1 L, and 1.6 L in the recycle liquid collection vessel, which was kept constant by an overflow purge outlet. [c] Average of 6, determined at regular intervals over the entire course of the experiment. [d] Estimation from psychrometric charts, see text. [e] Purge rate is the medium feed rate minus the evaporation rate.

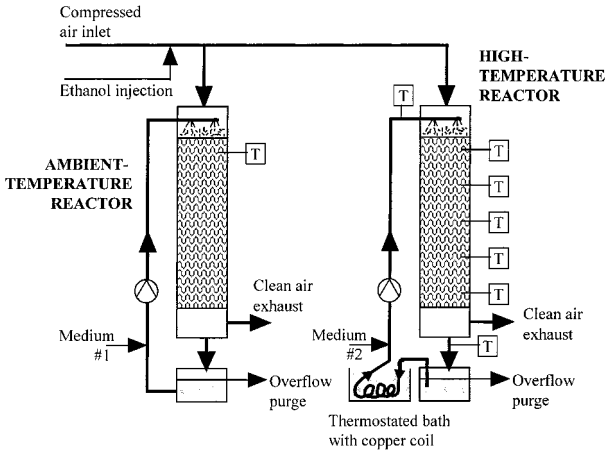

FIGURE 1. Schematic of the experimental setup. *T* = digital thermometer.

temperature gas was available, high temperatures were achieved by heating the recycle liquid through a coiled copper tubing submerged in a thermostated water bath. Analyses of the recycle liquid by atomic absorption spectrometry showed that copper dissolution from the heating coil was negligible. Therefore, possible inhibition of microbial activity in the high-temperature reactor by elevated copper concentrations could be excluded. The reactor was wrapped in plastic bubble sheet to minimize heat losses. Heating of the recycle liquid instead of the inlet gas turned out to be a simple and reliable method to control the temperature of the biotrickling filters.

A mineral medium was continuously fed to the reactors to supply nutrients for microbial growth and to supply water for compensation of water evaporation. From psychrometric charts, evaporation rates of 29 and 125 mL h^{-1} were calculated for the ambient and the high-temperature reactors, respectively. These numbers assumed average gas temperatures of 22 or 50 °C, a gas flow rate of 1.5 $m^3\ h^{-1}$, and relative humidities in the inlet and outlet gas of 0 and 100%, respectively. Operation at elevated temperature would therefore result in an additional 96 mL h^{-1} water evaporation. Therefore, the medium feed rate to this reactor was increased proportionally, and the nutrient concentration was decreased by the same, to maintain the same overall nutrient load. Details of nutrient feed and liquid purge rates are summarized in Table 1. Because of small variations in actual medium feed rates, reactor temperature, or relative humidity, the overall nutrient load to the high-temperature reactor was on average 14% higher than the nutrient load to the ambient-temperature reactor.

Both reactors were inoculated with a mixed microbial consortium obtained from an active green waste and food waste compost. The active compost sample was suspended in distilled water, large particles were removed by filtration over glass wool and 200 mL of the suspension was added to each reactor on day zero. Standard operation of the reactors was started immediately.

Experimental Design

After inoculation, start-up performance at standard operation with 2 g m^{-3} ethanol was followed by daily analysis of CO_2 production and the accumulation of wet immobilized biomass in the reactor. Because of problems with ethanol analysis during the startup phase, removal was determined only sporadically during the first 4 weeks. All other experiments, described in this section in chronological order, were done after 20 days, when a pseudo steady-state was obtained. After the biotrickling filter conditions were changed, new pseudo steady-states were usually obtained within 1−3 days.

The influence of the ethanol concentration on the removal rate was determined by stepwise increasing the inlet concentration up to 3.65 g m^{-3}. The air flow rate was kept constant at 1.5 $m^3\ h^{-1}$ (EBRT = 57 s). Average removal rates were calculated from daily analyses of inlet and outlet concentrations over periods of at least 3 days. Microbial analyses were done 26−29 days after inoculation: the number of mesophilic and thermophilic heterotrophs and ethanol degraders in biofilm and recycle liquid were determined by plate counting. Rapid accumulation of biomass in the reactors caused clogging and decreased performance (see Results for details). The reactors were opened on day 59 and longitudinal profiles of the wet and dry biomass concentration over the reactor were determined. That day, the reactors were repacked with a mixture of clean and old (containing the biofilm) Pall rings in a volumetric ratio of 92:8. Ethanol degradation started immediately, and constant performance was observed within a few days. Temperature shock experiments were done on days 134 and 137. The ambient-temperature reactor was subjected to an increase of the temperature from 22 to 53 °C for a period of 200 min, after which the reactor was cooled to ambient temperature. Similarly, the high-temperature reactor was temporarily subjected to a low-temperature shock at 19 °C. Cooling and heating were done by changing the temperature of the water bath. Constant temperatures in the reactors were obtained within 40−80 min. Performance before, during, and after the temperature shock was deter-

mined by analysis of ethanol in the inlet and outlet air and in the recycle liquid, CO_2 concentration in the inlet and outlet air, and the temperature inside the reactor. The upper operating temperature limit of the high-temperature reactor was determined between days 148 and 157 by gradually increasing the temperature from 50 to 70 °C. Ethanol removal and CO_2 production were determined at least 6 h after each change of the temperature.

Analyses. For gas-phase analysis, duplicate samples from the inlet and outlet air were taken with 10-L Tedlar bags. CO_2 was determined in triplicate using a gas chromatograph equipped with a thermal conductivity detector (*13*). Ethanol gas-phase concentration was determined by direct injection of 0.2−1 mL samples into a flame ionization detector (model 8860, SRI Instruments, Las Vegas, NV). The results of five determinations were averaged. Ethanol in the recycle liquid was determined as follows. Samples were taken from the liquid outlet and immediately mixed with 1 mL of a 2 M HCl solution/mL of sample. After centrifugation, the supernatant was analyzed in duplicate with a Hewlett-Packard 6890 gas chromatograph (Hewlett-Packard, Wilmington, DE). Conductivity and pH were determined with a portable, digital conductivity meter and an Accumet model 15 pH meter (both from Fisher Scientific, Pittsburgh, PA), respectively. Longitudinal temperature profiles in the high-temperature reactor were measured with five temperature probes inserted about 5 cm into the packed bed and located at regular distances over the reactor height. The amount of immobilized wet biomass was determined by weighing the reactor after draining the recycle liquid for 10 min and subtracting the known weight of the clean and dry reactor. Distributions of wet and dry biomass in the reactor were determined by random selection of three rings (with biofilm attached) per location. Each ring was weighed, dried to constant weight at 95 °C, cleaned, and dried again. The weights of wet or dry biomass per ring were calculated from weight losses at each step. Microbial counts were done in duplicate on Plate Count Agar (Difco, Detroit, MI) for total heterotrophs and solidified (8 g L^{-1} agarose) medium with ethanol in the gas phase for the number of ethanol degraders. Dilution series of biofilm and recycle liquid samples were prepared in 8.5 g L^{-1} NaCl. For each sample, two sets of counting plates were prepared for incubation at room temperature and at 52 °C. For counting ethanol degraders, the Petri dishes were placed in closed boxes with a small vial containing ethanol. Plates incubated at 52 °C were also placed in closed boxes to prevent drying out. All counts were related to the content of total carbon in the original sample, which was determined with a model 5050 Total Carbon analyzer (Shimadzu, Kyoto, Japan).

Results

Startup and Standard Performance. The operating conditions in the high-temperature reactor were quite homogeneous. The reactor temperature range was 49.0−56.5 °C with an average value of 52.6 °C. The temperature of the water bath for heating the recycle liquid was a few degrees higher. Heat losses from the reactor were minimal due to insulation of the reactor wall. The temperature difference at the inlet and outlet of the reactor was less than 2 °C. Temperatures of the high-temperature reactor reported hereafter are those measured at half-height of the reactor.

The production of CO_2 and the accumulation of wet biomass in both reactors during the initial 54 days are presented in Figure 2. The average ethanol inlet concentration was 2 g m^{-3}, but due to technical problems with the analysis of ethanol during the first 4 weeks, only a few reliable determinations of ethanol removal rates were available for this period. However, they indicated that ethanol removal was nearly complete in both reactors. This was consistent with biomass and CO_2 production data (Figure 2), which

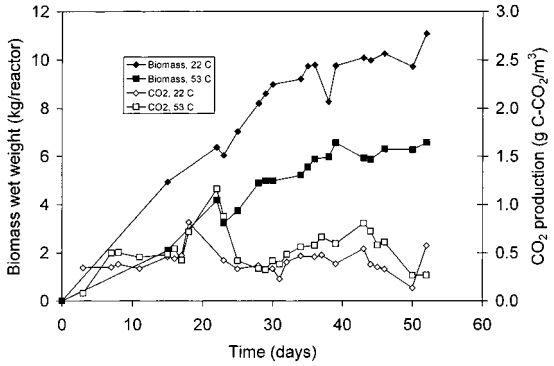

FIGURE 2. CO_2 production and wet biomass accumulation in the biotrickling filters operated at ambient temperature (22 °C) and at 53 °C; gas flow rate 1.5 m^3 h^{-1}, ethanol inlet 2 g m^{-3}. Day zero corresponds to the day of the inoculation.

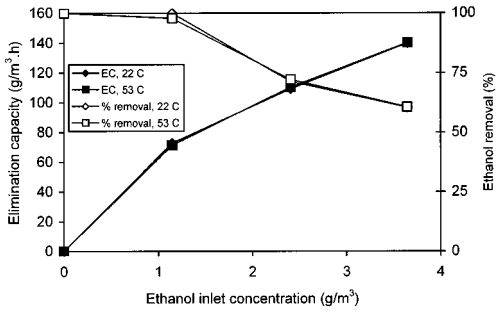

FIGURE 3. Influence of the ethanol concentration on the removal efficiency and elimination capacity at ambient temperature and 53 °C; gas flow rate 1.5 m^3 h^{-1}.

showed a rapid start-up and steady-state in both reactors within 5 days after starting both reactors. A CO_2 production of 0.5 gC m^{-3} corresponds to 1 g m^{-3} ethanol converted to CO_2. As discussed in the carbon balance section, some of the degraded ethanol was incorporated into biomass, and a small fraction left via the purge. Biomass accumulation was rapid and constant the first 5 weeks of operation but appeared to level off thereafter. Biomass accumulation did not result in increases in pollutant elimination, consistent with the observation made by others (*14*−*16*) that the majority of the biomass in biotrickling filter is inactive. Interestingly, although CO_2 production (Figure 2) and ethanol removal (see next paragraph) were relatively comparable in the ambient-temperature and high-temperature reactors, biomass accumulation was significantly slower in the reactor operated at 53 °C.

The temperature did not affect ethanol removal (Figure 3). Near complete removal at an empty bed contact time of 57 s was observed for ethanol concentrations up to 1.1 g m^{-3} in both reactors. Further increases of the ethanol concentration resulted in higher ethanol removal rates but lowered the removal efficiency. While elimination capacities of about 140 g m^{-3} h^{-1} were observed at inlet concentrations of 3.65 g m^{-3}, the maximum elimination capacity of each reactor was not determined. Later experiments reached elimination capacities up to 220 g m^{-3} h^{-1} at an inlet concentration of 5 g m^{-3} (see Figures 7 and 8).

Biofilters with a high ethanol load have been reported to accumulate acetic acid and possibly other acidic intermediates causing both the pH and the performance to decline (*17*). This was not observed in the present research. The average pH in the recycle liquid of the ambient-temperature and high-temperature reactor was 7.66 and 7.74, respectively, with little variation over time irrespective of the ethanol load. Measurements of the conductivity of the recycle liquid

TABLE 2. Plate Counts of Recycle Liquid and Biofilm Samples[a]

	ambient-temperature reactor		high-temperature reactor	
group	recycle liquid	biofilm	recycle liquid	biofilm
heterotrophs (grown at 22 °C)	1.8×10^7	6.4×10^7	2.6×10^5	2.6×10^7
ethanol degraders (grown at 22 °C)	1.7×10^8	3.7×10^8	7.6×10^5	5.8×10^6
heterotrophs (grown at 52 °C)	5.8×10^3	2.3×10^4	1.4×10^7	6.9×10^7
ethanol degraders (grown at 52 °C)	$<1 \times 10^2$[b]	4.0×10^3	5.2×10^7	9.1×10^7

[a] Number of colonies/g of total carbon. [b] No colonies observed at the lowest dilution.

TABLE 3. Distribution of Wet and Dry Biomass (± Standard Deviation) over the Reactor Height[a]

	ambient-temperature reactor		high-temperature reactor	
distance from inlet (cm)	wet biomass (g/ring)	dry matter content (%)	wet biomass (g/ring)	dry matter content (%)
10	7.92 ± 1.64	4.43 ± 0.12	8.58 ± 0.39	5.26 ± 0.18
38	9.24 ± 2.38	3.89 ± 0.06	6.15 ± 0.82	5.61 ± 0.84
65	6.98 ± 0.75	3.96 ± 0.20	5.87 ± 1.01	5.26 ± 0.34
93	8.58 ± 2.57	4.08 ± 0.27	5.87 ± 1.16	6.31 ± 2.47
110	8.43 ± 1.39	3.72 ± 0.22	4.75 ± 1.23	5.77 ± 0.63

[a] Average results of three determinations.

indicated that concentration of nutrients by evaporation occurred. Evaporation corresponded to our estimates using psychrometric charts and was not sufficient to cause inhibition of microbial activity. The conductivity was the highest in the recycle liquid of the high-temperature reactor, with the average value corresponding to that of 2.5 times concentrated medium.

Microbial Analyses. Microscopic observation of the recycle liquid and of the biofilm showed the development of different populations. While the recycle liquid in the ambient-temperature reactor contained high concentrations of a broad variety of bacteria, the population of the high-temperature reactor was less diverse and had a lower total concentration of organisms. The dominant microorganism at high temperature was a rod-shaped bacteria; yeasts and fungi were also observed, but not in significant numbers. Not unexpectedly, development of protozoa was faster and more diverse at ambient temperature than at 53 °C.

Within the same sample, cell counts of ethanol degraders were in general of the same order or slightly higher than the total count of heterotrophs. This indicates that in both reactors, microbial populations highly specialized in ethanol degradation had developed (Table 2). However, distinct differences were found in the temperature specificity for growth. The ambient-temperature reactor contained a mesophilic population with only a very small portion (0.001−0.01%) capable of growing at 52 °C. Apparently, operation of a biotrickling filter at ambient temperature resulted in selective enrichment of species in the mesophilic temperature range with low tolerance to high temperatures. The population in the high-temperature reactor was more diverse and adapted toward the growth at various temperatures. This reactor contained mostly species capable of growth at 52 °C, but 1−10% of the population could also grow at ambient temperature.

Biomass Accumulation and Carbon Balance. Although ethanol degradation was identical in both reactors (Figure 3), the results of Figure 2 show marked differences in the accumulation of wet biomass associated with statistically different (p > 98%) CO_2 production values. The distribution of biomass was homogeneous in the ambient-temperature reactor, whereas in the high-temperature reactor, a slight decrease of the biomass concentration was observed from the inlet to the outlet (Table 3). The amount of wet biomass per Pall ring was higher in the ambient-temperature reactor, as was expected from the higher biomass content at the time of sampling (Figure 2). A remarkable finding was that the dry matter content was significantly (at the 99% level) higher in the biofilm grown at 53 °C than in the one grown at ambient temperature. The dry matter content of the biofilm was on average 5.64 and 4.02% for the high- and ambient-temperature reactors, respectively. This may have been because of different populations in the biofilm (Table 2) or perhaps because operation at higher temperature caused an increased rate of evaporation of water from the biofilm.

TABLE 4. Biomass Accumulation and the Carbon Balance over the First 30 days of Operation[a]

parameter	ambient-temp reactor	high-temp reactor
Biomass		
wet biomass growth (g m^{-3} h^{-1})	530	294
dry biomass growth (g m^{-3} h^{-1})[b]	21.3	16.6
C-Balance		
C-ethanol removal rate (g m^{-3} h^{-1})[c]	56.3	56.3
C-CO_2 production (g m^{-3} h^{-1})	25.8	33.6
ethanol mineralization (%)[d]	46	60
C-biomass formation (g m^{-3} h^{-1})[e]	10.6	8.3
C not accounted for (%)	35 (10)[f]	26 (18)[f]

[a] All values are per m^3 reactor volume. [b] Average biofilm dry matter content of 4.02 and 5.64% at ambient temperature and 53°C, respectively (see Table 3). [c] Average inlet concentration 2 g m^{-3}; average outlet concentration of 0.3 g m^{-3} (see Figure 2). [d] Amount of C-CO_2 produced, divided by the amount of C-ethanol degraded. [e] 50% C in dry biofilm. [f] Estimated value calculated using the ethanol concentration in the liquid purge (2.86 and 0.66 g L^{-1}, for the ambient- and high-temperature reactors, respectively) from other experiments conducted under comparable conditions.

Table 4 summarizes the data on biomass accumulation and details of the carbon balance over the first 30 days, over which period the biomass accumulation rate was relatively constant (Figure 2). Biomass growth in the high-temperature reactor was 1.8 times slower on a wet basis and 1.3 times slower after correction for the lower biofilm water content. Carbon balances indicated that at 53 °C a significantly larger portion of removed ethanol was converted into CO_2. At the same ethanol removal rate, C-CO_2 production was 1.3 times higher at 53 °C than at ambient temperature. Hence, a major

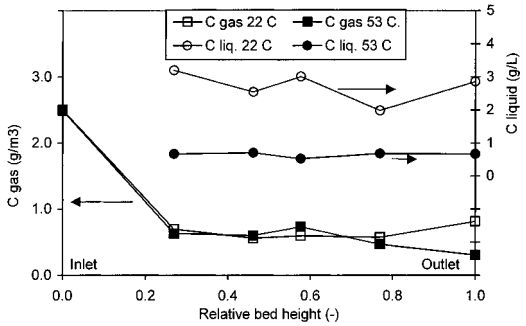

FIGURE 4. Ethanol gas and liquid concentration profiles for the ambient and high-temperature biotrickling filters.

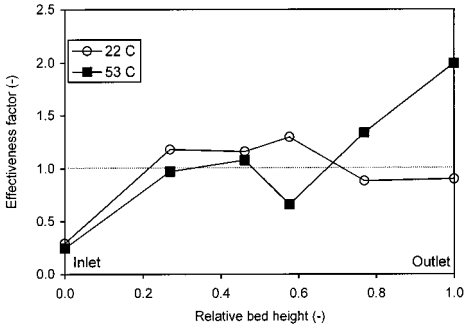

FIGURE 5. Local effectiveness factor $\eta_o = HC_{liq}/C_{gas}$ as a function of the height in the reactor for the data shown in Figure 4. An effectiveness of one indicates that gas and recycle liquid are in equilibrium.

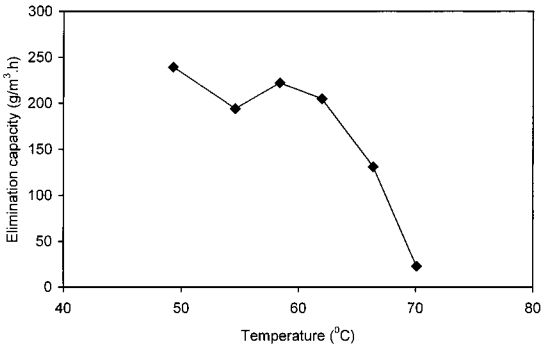

FIGURE 6. Influence of the temperature on the elimination capacity of the high-temperature reactor; gas flow rate 1.5 m^3 h^{-1}, ethanol inlet 5 g m^{-3}.

effect of the high temperature was the reduced biomass accumulation rate due to a higher conversion of ethanol to CO_2.

Determination of the carbon balances as shown in Table 4 unfortunately did not include analysis of the liquid purge. Carbon in the liquid purge may include biomass, dissolved ethanol, and ethanol intermediates and secondary microbial products, but these were not quantified. This may explain the relatively high fraction of unaccounted carbon (26−35%). Experiments described in the next section indicate that most of the unaccounted carbon can be attributed to ethanol in the liquid purge.

Gaseous and Liquid Ethanol Concentration Profiles. One possible concern with increasing the temperature of gas-phase bioreactors is the reduction of the pollutant or oxygen mass transfer rate due to the increase of Henry's constant with temperature. For ethanol, the dimensionless Henry's constant is 0.000257 at 22 °C (*18*) and 0.00092 at 53 °C (experimental value, determined by measuring air/water samples at equilibrium). In Figure 4, the gaseous and liquid ethanol concentrations are reported with respect to the height of the reactor. The gaseous ethanol concentration profiles for the low and high-temperature biotrickling filters were virtually identical, with most of the decrease occurring near the gas inlet port. For the liquid concentrations, a marked difference existed between the two reactors. Ethanol concentrations were on average four times lower at high temperature, still a relatively flat profile was again observed. This is partly due to the high trickling rate at which the biotrickling filters were operated. In fact, because of the low Henry's coefficient and the relatively low ratio of gas to liquid volume in the reactors, most (>99%) of the ethanol in the system is in the liquid phase. This is no longer true at very low trickling rates.

Simultaneous gas and liquid concentration measurements enable one to determine the local overall mass transfer driving forces and to calculate the effectiveness factor $\eta_o = HC_L/C_g$ defined by Lobo et al. (*19*) where C_g is the gaseous concentration, and C_L and H are the liquid concentration and the Henry coefficient of the pollutant being treated, respectively. The effectiveness factor varies from zero for gas−liquid mass transfer limitations, to one when the limitation is in the biofilm. In the latter case, η_o alone does not allow discrimination between diffusion or transfer limitation in (or into) the biofilm and a kinetic limitation. Still, η_o provides useful guidance as to the nature of the rate-limiting step of the process. In Figure 5, the local effectiveness factor is reported with respect to the height in the reactors. Examination of Figure 5 reveals that at the inlet port, the effectiveness is lower than one indicating some degree of transfer limitation. This was expected, since the effectiveness is calculated with the inlet gas and liquid concentration before they are contacted together. After gas and liquid are contacted, both phases reach concentrations close to equilibrium, as indicated by η_o values close to 1. Overall, Figure 5 shows that gas−liquid transfer was not the rate-limiting factor.

Upper Temperature Limit of the High-Temperature Reactor. The upper limit for effective treatment was determined. For this experiment, an inlet concentration of 5 g m^{-3} was selected to provide an excess of ethanol. At this high concentration, ethanol removal is not complete (see Figure 3); hence, temperature effects on the performance can be measured more accurately. Steady-state performance of the high-temperature reactor at increasing temperatures is reported in Figure 6. Up to a temperature of 62 °C, the ethanol elimination capacity remained constant at 200 g m^{-3} h^{-1}. Note that this value is corrected for ethanol removal via the liquid purge (7−16 g m^{-3} h^{-1} depending on the temperature) as the ethanol concentrations in the recycle liquid rose at an inlet concentration of 5 g m^{-3}. The ethanol elimination strongly decreased at temperatures above 62 °C, and the upper limit for detectable ethanol removal was close to 70 °C.

Temperature Shock Experiments. The effect of the temperature on ethanol removal was further investigated in temperature shock experiments. The high-temperature reactor was subjected to a 200-min low-temperature shock, and the ambient-temperature reactor was subjected to a 200-min high-temperature shock. The results are shown in Figures 7 and 8 and summarized in Table 5. They show the major impact of temperature on the observed pollutant removal. However, evaluation of the results of Figures 7 and 8 using a simple biotrickling filter mathematical model (results not shown) revealed that the changes observed in ethanol removal were mainly due to ethanol absorption−desorption effects. These were sufficiently important to mask any possible biological effects. The reason is that ethanol has a very low Henry's law coefficient; hence, the time required to

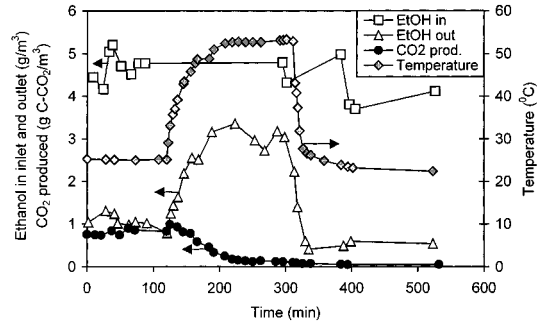

FIGURE 7. Response of the ambient-temperature reactor to a temporary increase of the temperature; gas flow rate 1.5 m^3 h^{-1}, ethanol inlet ~5 g m^{-3}.

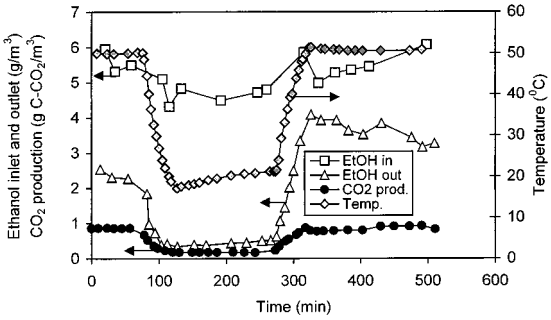

FIGURE 8. Response of the high-temperature reactor to a temporary decrease of the temperature; gas flow rate 1.5 m^3 h^{-1}, ethanol inlet ~5 g m^{-3}.

TABLE 5. Pseudo Steady-State Performances before, during, and 1−3 h after a Short-Term Temperature Shock of the Ambient-Temperature Reactor (High-Temperature Shock) and High-Temperature Reactor (Low-Temperature Shock)

	ambient-temperature reactor			high-temperature reactor		
parameter	before	during	after	before	during	after
Measured						
temp (°C)	24.9	53.0	24.2	50.4	19.2	51.1
ethanol inlet gas (g m^{-3})	4.70	4.46	4.15	5.59	4.71	5.43
ethanol outlet gas (g m^{-3})	1.09	3.05	0.51	2.37	0.43	3.65
CO_2 inlet gas (g C m^{-3})	0.020	0.020	0.020	0.020	0.020	0.020
CO_2 outlet gas (g C m^{-3})	0.818	0.160	0.080	0.885	0.196	0.859
ethanol recycle liq (g L^{-1})	2.98	1.73	2.47	2.72	2.75	2.70
Calculated						
ethanol removed (g m^{-3} h^{-1})						
total[a]	230	89	231	204	272	114
via purge[b]	28	9.2	24	31.8	44.1	31.8
% recovery as C-CO_2[d]	48	21	3.5	61	9.4	125

[a] Calculated from ethanol inlet and outlet gas concentrations. [b] Calculated from the liquid purge rate at the actual temperature during the experiment (Table 1) and the ethanol concentration in the recycle liquid. [c] Difference between the total elimination capacity and the amount removed via the liquid purge. [d] Ratio of the amount of C-CO_2 produced and the amount of C-ethanol removed (excluding the purge).

reach a new physicochemical equilibrium is very long (10−20 h). Examination of Figure 7 reveals that the outlet concentration of ethanol increased when the temperature was raised. This was because of the desorption of ethanol from the trickling liquid. When the temperature was returned to normal, ethanol absorption occurred, and low ethanol outlet concentrations were observed. Following a similar reasoning, the ethanol pattern of the high-temperature reactor can be explained by a transient absorption phase at ambient temperature, followed by a transient desorption phase when returning to a high temperature. This is consistent with the very low CO_2 recovery observed during the temperature shock (Table 5). While the absorption−desorption phenomena of Figures 7 and 8 are certainly relevant to the field application of biotrickling filters, they prevent using ethanol concentrations to describe the biological activity of the system.

A more representative indication of biological activity during the temperature shocks is the CO_2 production pattern. Because Henry's law coefficient of CO_2 is about 3 orders of magnitude higher than ethanol (*10*), the time to reach absorption−desorption equilibrium is in the order of minutes. Figure 7 reveals that CO_2 production decreased with increasing the temperature and remained low after the temperature shock. The reactor required about 24 h for effective ethanol treatment and normal CO_2 production to resume. The most plausible explanation for this is that the process culture in the ambient-temperature reactor was injured by the short incursion into high temperatures. This is further supported by very low CO_2 recoveries after the temperature shock (Table 5). The high-temperature reactor exhibited a markedly different behavior. It was only subject to a temporary inhibition for the duration of the temperature shock, and, after restoring standard conditions, effective treatment immediately resumed (Figure 8). This suggests that the process culture was only transiently inhibited and was not injured.

Discussion

Several studies have shown that small increases of the temperature within the mesophilic range generally improve pollutant removal in biofilters and biotrickling filters for waste gas treatment (*9*, *20*, *21*) However, little information exists on the biotreatment of waste gases in biotrickling filters at temperatures greater than 40 °C, i.e., temperatures above the optimum for mesophilic microorganisms. In a study that was conducted at the same time as this one, Allen et al. (*5*) reported effective removal of methanol and α-pinene in biotrickling filters maintained at temperatures between 40 and 70 °C. Both Allen et al. (*5*) and this study clearly prove that effective biotreatment can be obtained in biotrickling filters operated at temperatures exceeding 40 °C.

In the experiments reported herein, operation of the two biotrickling filters was identical, so that any observed effect could be directly attributed to the difference in reactor temperature. Ethanol removal rates were identical at ambient temperature and at 53 °C, and the maximum elimination capacity exceeded 200 g m^{-3} h^{-1} at an inlet ethanol concentration of 5 g m^{-3}. As a comparison, mesophilic biofilters packed with granular activated carbon exhibited a similar ethanol removal rate (*12*, *17*); however, long-term operation was affected by the accumulation of acetic acid resulting from the partial biodegradation of ethanol. Others have reported lower ethanol removal rates in peat or compost biofilters at ambient temperatures (*22*, *23*). In this context, our results are remarkable. They prove that biotrickling filters are very well suited for high rate ethanol treatment and that high temperatures are not detrimental to effective treatment.

Temperature effects in biotrickling filters are expected to be relatively complex. They involve both biological and physicochemical effects. The time constant for the latter is usually short (hours), while biological effects (other than shock responses), such as adaptation of the process culture to extreme conditions, can take months. In any case, the impact of temperature on treatment performance will depend

on the rate-limiting step of the process and the relative sensitivity of both mass transfer and biodegradation to changes in temperature. As the temperature rises, Henry's coefficient increases, which will result in a lower (maximum) driving force for interphase mass transfer and a lower pollutant availability to the process culture. Pollutant diffusivity increases with temperature, but the change estimated at a few percent is not significant. More important is the effect of the temperature on the process culture. Temperature will affect the composition of the process culture (Table 2), the metabolism, and both the rate of biomass accumulation (Figure 2, Table 4) and the rate of pollutant degradation (see e.g., Heitzer et al. (*26*)). These, together with the change in the availability of the pollutant, results in a complex, nonlinear and nonmonotonic behavior with temperature. Reliable models to predict biotrickling filter behavior over extended temperature ranges are lacking. Still our experiments provide some explanation as to why effective ethanol removal was maintained in the high-temperature biotrickling filter. This is discussed below.

As was presented in Figure 5, the local effectiveness factor was close to one throughout most of the reactor, indicating that gas−liquid mass transfer was not limiting. Thus the limiting step was in the biofilm, i.e., mass transfer or kinetic limitation. The relatively high concentrations at which the reactors were operated and the fact that the reactors responded to temperature shocks (see CO_2 pattern in Figures 7 and 8) suggest that both reactors were kinetically limited. Thus, the performance was solely depending on the microbial activity which remained high with increasing temperature. As discussed in the next paragraph, the sustained activity was a result of microbial adaptation. At this time, the exact reason for the kinetic limitation is unknown. It could be related to the maximum rate of pollutant turnover by the culture, or be related to oxygen, nitrogen, or another nutrient limitation.

As the process was kinetically limited, successful treatment in the high-temperature biotrickling filter required adaptation of the microbial population to high temperatures. The results of plate counting experiments (Table 2) showed that selective enrichment of specialized communities had indeed occurred. The biotrickling filter operated at ambient temperature contained only mesophilic microorganisms, and consequently, this reactor was severely inhibited when subjected to a temperature of 53 °C (Figure 5). Similarly, Lu et al. (*20*) observed decreasing performance of BTEX removal in a biotrickling filter when increasing the temperature from 30 to 50 °C. Interestingly, selective enrichment to high temperatures occurred relatively quickly (within days), whereas in other studies (*24*) on toluene removal at ambient temperature but low pH (<4), adaptation or enrichment took more than three weeks. Clearly, the time needed to obtain an effective treatment depends on both the nature and the extent of the stress imposed on the process culture. In both the present study and this on toluene, (*24*) the reactors operated under extreme conditions (high temperature or low pH) exhibited an increased CO_2 production and a slower rate of biomass accumulation. This is likely to be related to stress of the process culture under extreme conditions. A lower biomass yield coefficient at higher temperatures may be attributed to various phenomena such as increased maintenance energy requirements and temperature-induced growth uncoupling (*25*, *26*). From a practical point of view, reduction of the biomass yield is advantageous, as clogging is one of the greatest problems encountered in the application of biotrickling filters for waste gas treatment (*2*). Of course, controlling biomass accumulation by heating is not a viable option because of increase energy and water costs.

While the ambient-temperature reactor can be considered as truly mesophilic, classification of the high-temperature reactor as thermophilic is a matter of interpretation, since there is no agreement as to the minimum temperature for a thermophilic process. Using the criteria of Ingraham et al. (*27*) which specifies growth at $T > 50$ °C, plate counting of Table 3 indicates that the high-temperature biotrickling filter contained predominantly a thermophilic population. On the other hand, the fact that the upper temperature limit for effective biodegradation was only about 62 °C may suggest that a thermotolerant rather than a thermophilic process culture developed in our reactor. However, this point is rather academic, in light of the fact that the reactor contains a mixed population subject to complex dynamics with the operating temperature. Still, one can speculate that start-up and operation at a temperature higher than 53 °C would result in enrichment of a truly thermophilic population, capable of effectively removing ethanol at temperatures in the 60−80 °C range.

Overall, the results of the present study demonstrate the feasibility of treating waste gases in biotrickling filters operated well above the optimum temperature for mesophilic processes. While further studies are needed, for example, with other pollutants and at even higher temperatures, the results presented and discussed herein greatly extend the potential applicability of biotrickling filters for air pollution control.

Literature Cited

(1) Deshusses, M. A. *Curr. Opin. Biotechnol.* **1997**, *8*, 335−339.
(2) Cox, H. H. J.; Deshusses, M. A. *Curr. Opin. Biotechnol.* **1998**, *9*, 256−262.
(3) Devinny, J. S.; Deshusses, M. A.; Webster, T. S. *Biofiltration for Air Pollution Control*; CRC-Lewis Publishers: Boca Raton, FL, 1999.
(4) Van Lith, C.; Leson, G.; Michelson, R. *J. Air Waste Manage. Assoc.* **1997**, *47*, 37−48.
(5) Allen, D. G.; Fulthorpe, R. R.; Farhana, L. In *Proceedings of the 93rd Annual Meeting and Exhibition Air & Waste Management Association*; Air & Waste Management Association: Pittsburgh, PA, 2000; Paper #946.
(6) Heslinga, D. C.; Van Groenestijn, J. W. In *Biological Waste Gas Cleaning, Proceedings of an International Symposium*, Prins W. L., J. van Ham, J., Eds.; VDI Verlag: Duesseldorf, Germany, 1997; pp 353−358.
(7) Lee, B. D.; Apel, W. A. In *Proceedings of the 1998 Conference on Biofiltration (an Air Pollution Control Technology)*; Reynolds, F. E., Ed.; The Reynolds Group: Tustin, California, 1998, pp 51−59.
(8) Mohseni, M.; Allen, D. G. *J. Air Waste Manage. Assoc.* **1999**, *49*, 1434−1441.
(9) Arnold, M.; Reittu, A.; von Wright, A.; Martikainen, P. J.; Suihko, M. L. *Appl. Microbiol. Biotechnol.* **1997**, *48*, 738−744.
(10) Metcalf & Eddy, Inc., 3rd ed. revised by Tchobanoglous, G., and Burton, F. L. *Wastewater Engineering; Treatment, Disposal, and Reuse*; McGraw-Hill: New York, 1991.
(11) Joint Emission Inventory Program (JEIP) Study, Executive Summary, CH2M Hill Report, 1993.
(12) Hodge, D. S.; Devinny, J. S. *Environ. Progr.* **1994**, *13*, 167−173.
(13) Cox, H. H. J.; Deshusses, M. A. *Biotechnol. Bioeng.* **1998**, *62*, 216−224.
(14) Alonso, C.; Suidan, M. T.; Sorial, G. A.; Smith, F. L.; Biswas, P.; Smith, P. J.; Brenner, R. C. *Biotechnol. Bioeng.* **1997**, *54*, 583−594.
(15) Okkerse, W. J. H.; Ottengraf, S. P. P.; Osinga-Kuipers, B.; Okkerse, M. *Biotechnol. Bioeng.* **1999**, *63*, 418−430.
(16) Schönduve, P.; Sára, M.; Friedl, A. *Appl. Microbiol. Biotechnol.* **1996**, *45*, 286−292.
(17) Devinny, J. S.; Hodge, D. S. *J. Air Waste Manage. Assoc.* **1995**, *45*, 125−131.
(18) Mackay, D.; Shiu, W. Y.; Ma, K. C. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: IV Oxygen, Nitrogen, and Sulfur Containing Compounds*; Lewis Publishers: Boca Raton, FL, 1997.
(19) Lobo, R.; Revah, S.; Viveros-Garcia, T. *Biotechnol. Bioeng.* **1999**, *63*, 98−109.
(20) Lu, C.; Lin, M. R.; Chu, C. *J. Environ. Eng.* **1999**, *125*, 775−779.
(21) Sorial, G. A.; Smith, F. L.; Suidan, M. T.; Biswas, P.; Brenner, R. C. *J. Hazard. Mater.* **1997**, *53*, 19−33.

(22) Baltzis, B. C.; Wojdyla, S. M.; Zarook, M. Z. *J. Environ. Eng.* **1997**, *123*, 599−605.
(23) Auria, R.; Aycaguer, A. C.; Devinny, J. S. *J. Air Waste Manage. Assoc.* **1997**, *48*, 65−70.
(24) Cox, H. H. J.; Deshusses, M. A. In *Proceedings of the 93rd Annual Meeting and Exhibition Air & Waste Management Association*; Air & Waste Management Association: Pittsburgh, PA; 2000, Paper #773.
(25) Franks, P. A.; Hall, R. J.; Linklater, P. M. *Biotechnol. Bioeng.* **1980**, *22*, 1465−1487.
(26) Heitzer, A.; Kohler, H. P. E.; Reichert, P.; Hamer, G. *Appl. Environ. Microbiol.* **1991**, *57*, 2656−2665.
(27) Ingraham, J. L., In *The Bacteria*; Gunsalus, I. C., Stanier R. Y., Eds; Academic Press: New York, 1962; Vol. 3, pp 265−296.

Received for review October 12, 2000. Revised manuscript received March 27, 2001. Accepted March 27, 2001.

ES001764H