0273-2289/94/4546—0917$03.00

The Removal of Alkanes in a Liquid-Continuous Gas-Phase Bioreactor: Preliminary Considerations

Scientific Note

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ABSTRACT

Columnar bioreactors are being tested for the treatment of volatile organics. The bioreactors contain microorganisms that are able to remove and degrade the dilute gaseous hydrocarbons (*n*-pentane and isobutane) from effluent air streams by biological action. Columnar bioreactors, including a liquid continuous packed column, were continuously operated for over 18 mo with sustained degradation of the gaseous hydrocarbons. In these systems, the hydrocarbons, pentane, and isobutane are the sole carbon and energy sources for the microbes. The overall conversion rate was increased by operating at higher gas flow rates. This indicates the importance of improving mass transfer and gas contact in these systems.

Index Entries: Degradation; VOC; pentane; isobutane; gas-phase bioreactor.

INTRODUCTION

Volatile organic compounds (VOCs) are air pollution emissions of increasing concern. Even emissions of gaseous hydrocarbons, such as alkanes, are becoming of increasing regulatory concern. When VOCs are present in dilute concentrations, adsorption on activated carbon followed

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by incineration can be used, but is very expensive; for this reason, biodegradation has been proposed as a viable alternative (*1–3*). Advantages include lower capital and operating costs, minimal maintenance, and greater inherent safety, and no production of secondary pollution. Many microorganisms can degrade various hydrocarbons yielding carbon dioxide, water, and biomass. In our previous work, a microbial mixed culture was enriched that consumed pentane and isobutane as the sole carbon and energy source for extended periods of time (*4*). Here we identify several limiting factors for the enhanced efficient operation of a liquid continuous columnar bioreactor for gaseous substrates. The removal of hydrocarbon gases from a model effluent gas streams is of particular interest with the primary emphasis on *n*-pentane and isobutane. These gases are sparingly soluble in water. Therefore, good mixing and high surface area between the gas and liquid phases are required. Several of the liquid continuous columnar bioreactors now have been in operation for over 18 mo with continued degradation of pentane and isobutane as sole carbon and energy source.

MATERIALS AND METHODS

The experimental system, media, and columns were described earlier (*4*). A mixture of 5000 ppm pentane and 5000 ppm isobutane in air was used. The gas phase was bubbled through the 90-mL liquid-filled column packed with ceramic berl saddles, operated with rapid gas recirculation, and maintained with a slow bleed of fresh gas ($\sim$ 5 mL/min). The total gas volume in the system was 0.2 L. The loss of VOCs through the tubing was measured to be negligible relative to the degradation rates.

For VOC consumption rate measurements, the reactor's gas loop was first sparged with fresh gases. The system was then sealed off and operated in complete recycle (as a batch system) while monitoring the change in gas composition on a GC. The gas flow rate was varied between 20 and 85 mL/min. The gas bubbles rose through the liquid continuous packed column. The increase in gas flow rate increased the number of bubbles, and likewise the surface area, the mass transfer, and thus the consumption rates. Triplicate experiments were performed at each condition. Several milliliters of culture were removed before and after the entire series of experiments, and the biomass dry weight determined.

RESULTS AND DISCUSSION

At the gas circulation rates used and with the low gas holdup within the column, the system operated as a differential batch reactor for the VOC consumption tests. The effect of gas flow rates was studied. In Figs. 1 and 2, representative results are shown for two of these gas flow rates.

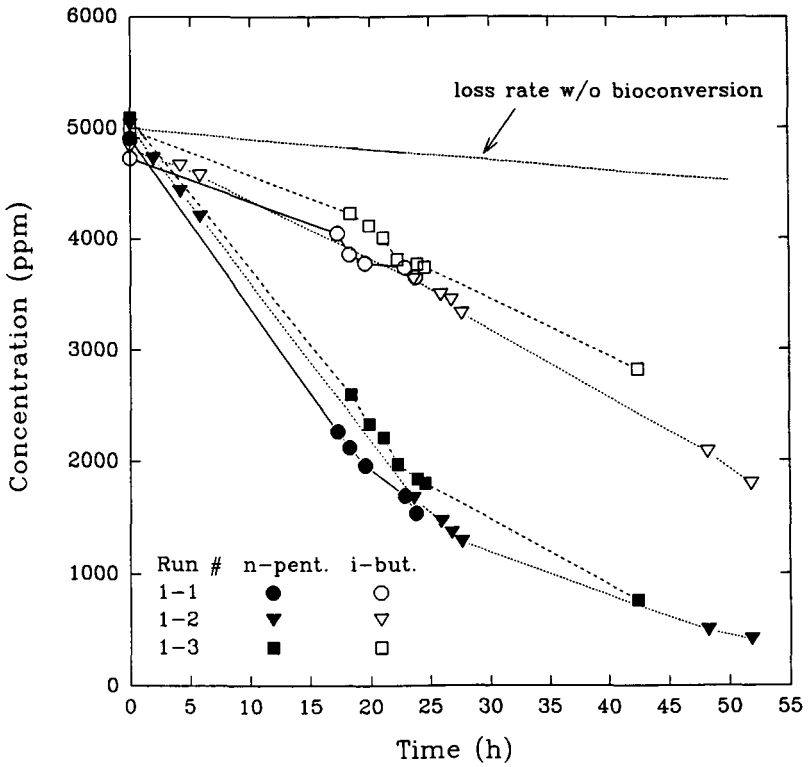

Fig. 1. Consumption of hydrocarbons in a gas bioreactor. The reactor was charged with a mixture of pentane, isobutane, and air, and then placed in complete recycle. The figure shows three successive runs. The gas flow rate was 18 mL/min.

Data for three successive runs performed in immediate succession are shown in each figure. It should be noted that some of the scatter between experiments was the result of each run having a slightly different initial gas-phase concentration. Significant portions of the curves above 1000 ppm appear linear. In all cases, when the pentane concentration in the gas phase fell below about 1000 ppm, the consumption rates decreased. One of the experiments was operated for longer periods of time and showed continued degradation of both gases (Fig. 3). The linear rates were estimated in each experiment by a least-squares regression analysis using the data above 1000 ppm. The correlation coefficients were 0.99 to 0.97 with a mean standard error of about 110 ppm. At the lowest gas flow rate (*see* Fig. 1), the data for the three runs are in excellent agreement. During some triplicate experiments (as the gas flow rate was increased), the rates decreased steadily between the first, second, and third repeat. This may be an experimental artifact owing to the development of gas channels in the packed column over time, or from an undetermined effect on the kinetics or mass transfer.

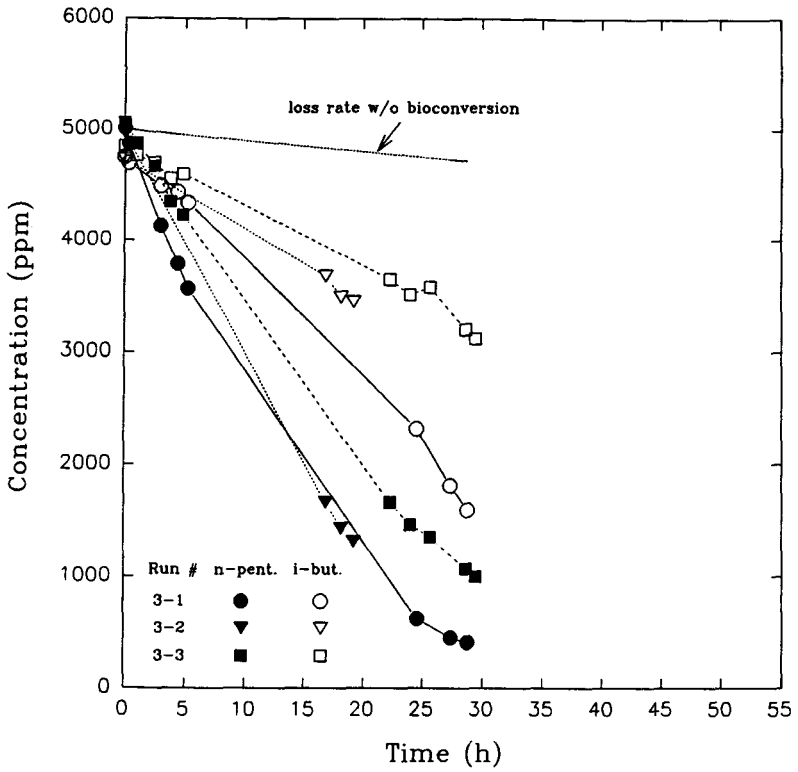

Fig. 2. Consumption of hydrocarbons in a gas bioreactor. The reactor was charged with a mixture of pentane, isobutane, and air, and then placed in complete recycle. The figure shows three successive runs. The gas flow rate was 34 mL/min.

In Fig. 4, the initial degradation rates are shown. There is a linear increase in the degradation of both pentane and isobutane followed by a leveling off at the higher gas flow rates. This leveling off of the degradation rate at higher gas flow rates may indicate that the highest gas flow rates used did not increase the mass transfer rate and surface area further. This may be because of larger individual bubbles or channeling. The improved mass transfer doubled the overall degradation rates in this system to 0.4 g pentane $h^{-1}m^{-3}$. The evidence supports mass-transfer limitation of the hydrocarbons. Further work is needed to elucidate and separate the mass-transfer and kinetic effects.

Oxygen is present in excess; thus, the system is hydrocarbon-limited. Using Henry's law constants reported in the literature (*5,6*), it was estimated that the initial aqueous molar ratio of oxygen to pentane was more than 60. Only 9 and 7 mol of oxygen are needed to degrade completely 1 mol of pentane or isobutane, respectively. No other carbon or energy source is added. This culture prefers pentane as a carbon source, but uses both substrates simultaneously at a consistent ratio of about 2.5 pentane/1 isobutane. Microscopic observation indicates only the presence of small

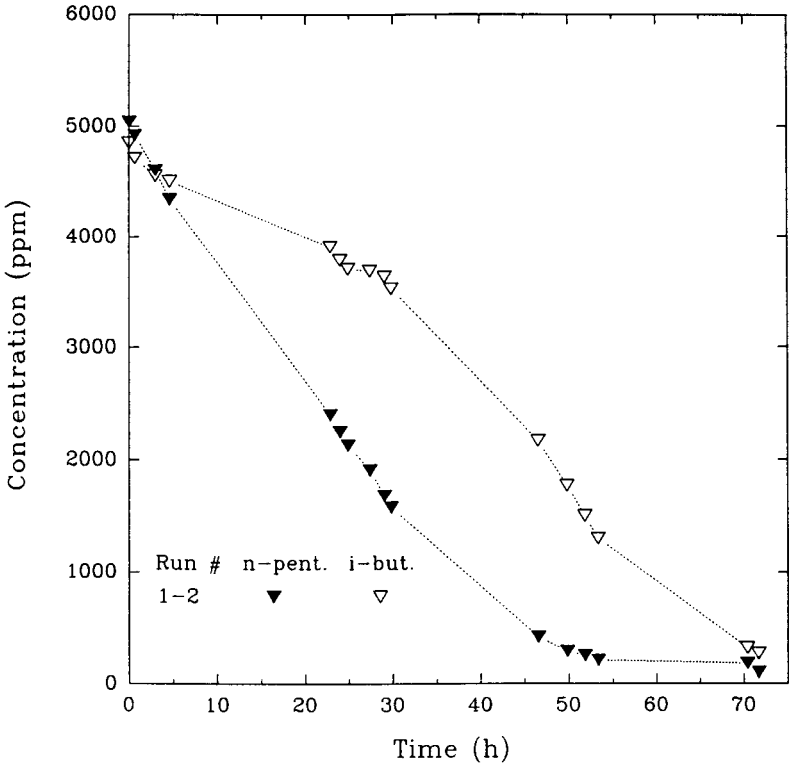

Fig. 3. Extended consumption of hydrocarbons in a gas bioreactor. The gas flow rate was 26 mL/min.

motile rods, which in bulk are yellow; these have been tentatively identified as a *Flavobacterium* species. The biomass has reached a stable population (0.01 g dry wt/mL) and has not changed significantly over 6 mo. This biomass value does not include biomass that may have become entrapped on the ceramic packing; however, visual observation does not indicate any biofilm on the packing. Attempts to grow a biofilm on this ceramic packing as part of a trickle-bed reactor were unsuccessful. The stable biomass values may indicate that the growth on the VOCs is poor enough that growth equals the death rate plus the removal by monthly sampling. An alternative is that there may be trace nutrient limitation or some by-product inhibition.

For better design, it is necessary to determine whether (1) the microbes are at a kinetic limit and the system is biomass-limited, or (2) the system is limited by the rate of mass transfer of hydrocarbons across the gas–liquid interface. The linear or zero-order rates may imply a reaction-controlled system, whereas the first-order rates may be expected for mass transfer controlled by the gas-phase concentration. The data from the "batch" degradation experiments (Figs. 1–3) may also be fit to an exponential curve

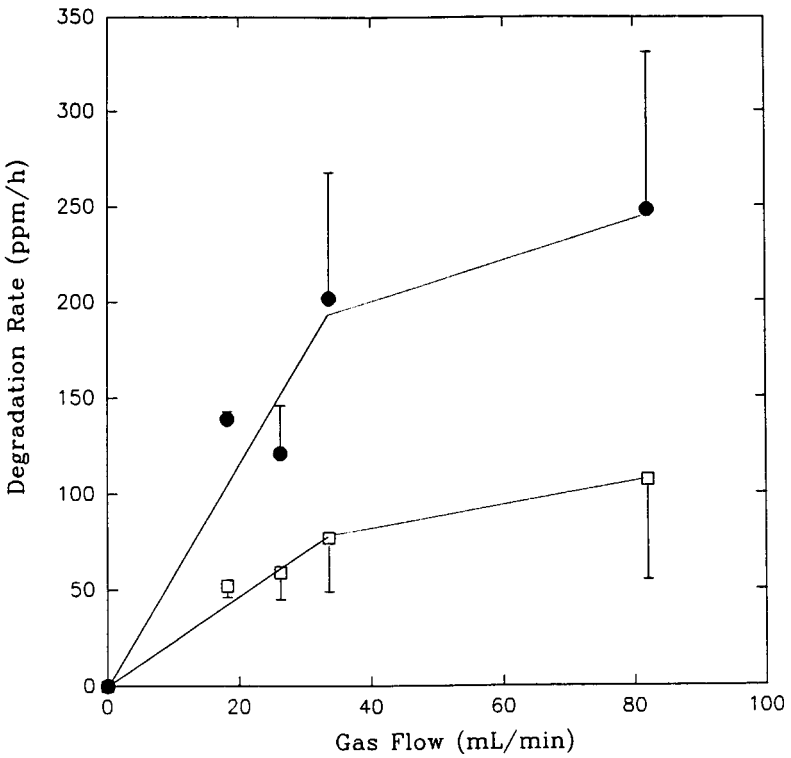

Fig. 4. The effect of the gas recycle flow rate on the degradation rate of *n*-pentane (□) and isobutane (●) in the gas bioreactor. Error bars indicate magnitude of variation among triplicate tests.

as well as the linear fit used above. The linear curves tend to fit the data better both visually and statistically, especially for the isobutane data. However, the exponential curve is able to fit data points from a wider concentration range, and the difference is not great enough to eliminate first-order rates conclusively. However, attempts to increase the mass-transfer rate by increasing gas contact with the same biomass level were successful in increasing the consumption rates (Fig. 4). The system may also be in transition from a reaction-limited regime above 1000 ppm and a mass-transfer-limited regime at lower VOC concentrations. Additional experiments are being planned at different biomass concentrations to elucidate the system better.

CONCLUSIONS

The manipulation of the operating conditions in a gas-phase bioreactor was shown to have a significant impact on the overall VOC consumption rate. The system has a stable and active, but moderate biomass concentration capable of consuming alkane VOCs for extended periods of time.

Evidence indicates that this system may be operating under mass-transfer limitations under some operating conditions, but further testing is necessary to confirm this and to determine the intrinsic reaction kinetics separate from the mass-transfer effects. Further increases in the overall rate will be needed to make this system economic (2). One avenue for further improvements is to increase the biocatalyst concentration through culturing and addition or through immobilization on surfaces; another is to test and design the system for rapid mass transfer of the sparingly soluble gaseous substrates.

ACKNOWLEDGMENT

Research was supported by the Advanced Industrial Concepts Division—Biological and Chemical Technologies Research, US Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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