ORNL/CP-95200

CONF-971180--

Estimation of Mass Transfer and Kinetics in Operating Biofilters for Removal of VOCs*

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For presentation at
The Annual Meeting on
Advances in Environmental Biotechnology
Los Angeles, California
November 16-21, 1997

Preferred session: Bioremediation

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* This work was supported by the Environmental Management Science Program of the Offices of Energy Research and Environmental Management, U.S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

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Estimation of Mass Transfer and Kinetics in Operating Biofilters for Removal of VOCs

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Prepared for presentation at the 1997 Annual Meeting
Los Angeles, CA Nov. 16-21
Advances in Environmental Biotechnology: Bioremediation

November 18, 1997

UNPUBLISHED

ABSTRACT

Long-term, stable operation of trickle-bed bioreactors remains desirable, but is difficult to achieve for industrial processes, which generate continuous streams of dilute gaseous hydrocarbons. Mass transfer and kinetic parameters are difficult to measure, complicating predictive estimates. Two methods are presented which were used to predict the importance of mass transfer versus kinetics limitations in operating trickle-bed biofilters. Both methods altered the overall kinetic activity of the biofilter and estimated the effective mass transfer coefficient ($K_l a$) by varying the VOC (volatile organic contaminant) loading rate and concentration. The first method, used with developing biofilters possessing low biomass, involved addition of cultured biomass to the recirculating liquid to effect an overall change in VOC removal capacity. The second method altered the total bed temperature of a well-established biofilter to effect a change. Results and modeling from these experiments are presented for a mixed culture biofilter which is capable of consuming sparingly soluble alkanes, such as pentane and isobutane. Methods to control overgrowth are dicussed which were used to operate one reactor continuously for over 24 months with sustained degradation of VOC alkanes with a rate of 50 g/h/m^3.

INTRODUCTION

Biological air pollution control of volatile organic contaminants (VOCs) is based on the process of moving contaminated gas through a biologically active matrix or bed where microorganisms convert the contaminants to carbon dioxide, water, biomass, and inorganic salts. Many compounds have previously been treated by means of biofiltration, e.g., hydrogen sulfide, odors, acetylene, ethylene, aliphatics, toluene, ammonia, aldehydes, ethanol, ketones, esters, styrene, etc. (Govind and Bishop, 1993) Trickle-bed bioreactors have also been used for conversion of gas components to fuels, such as hydrogen and methane, from other gaseous components (Cowger et al., 1992; Kimmel et al., 1991, Klasson et al., 1990). Treatment of dilute gaseous hydrocarbon waste streams remains important for many industries due to increasingly stringent environmental regulation. Alkanes, such as butane and pentane, are used as propellants and blowing agents; petroleum cracking generates a wide variety of alkanes, many of which are released into air streams; paper industries seek processes to treat off-gases from pulping operations. Natural extensions of engineering principles and reactor designs as applied to biotreatment of gaseous hydrocarbons include areas of higher concern as well, such as bioremediation of aromatic and chlorinated hydrocarbons. As an alternative to traditional treatment methods (e.g., incineration, adsorption), bioreactors which are properly designed to remove sparingly soluble gaseous substrates from effluent air streams hold promise for providing low-cost treatment methods for industries and government agencies. Increasing understanding of the engineering principles of these systems will broaden their applicability and acceptance.

Although biofiltration of volatile organic contaminants (VOCs) has received much attention in the past decade (Klasson et al., 1990; Andrews and Noah, 1995; Davison and Thompson, 1993, 1994; Leson and Winer, 1991), several challenges associated with this process make optimization difficult. First, rates of removal are much slower than incineration or adsorption. Second, bacteria grow in an aqueous environment, and some VOCs are only sparingly soluble in water; difficulty thus arises in transferring gases into the aqueous phase. Overgrowth of biomass and channeling can also reduce performance. To address these problems, improved bioreactor designs are required which have a high active biocatalyst concentration and efficient mass transfer of the VOC from air to the liquid medium. Optimization necessitates a better understanding of the mechanisms by which biofilters function and can be approached through modeling and maximizing appropriate conditions for removal.

Among trickle-bed designs there are many variations, mainly related to the chosen packing material. A well-designed biofilter operates close to mass-transfer limited conditions (from gas to liquid), meaning a large active biomass must be available to carry out rapid degradation (Andrews and Noah, 1995). The most effective strategy for maintaining a high biomass in the system is to use a trickle-bed filter with a type of packing which supports biomass attachment. In doing so, however, overgrowth may cause fouling and high pressure drops which in turn result in extended shut-down periods. This was noted quickly by Sorial et al. (1994) who were forced to design a high flow flushing system for periodic (twice a week) removal of biomass. Other biofilters, such as compost filters, use the packing to provide nutrients for biomass growth. These biofilters can foul due to growth or lose activity when nutrients are eventually depleted. Other characteristics of a packing material should include channel-free flow, high surface area, resistance to microbial degradation, and ease of cleaning/replacement.

Although predictive mathematical models have been available for a wide variety of biological systems, development and verification studies of models for trickle-bed bioreactors remain sparse in the literature. Shareefdeen and Baltzis (1994), assuming mass-transfer limitation, successfully applied a steady state model to a peat/perlite biofilter constructed to remove toluene. Diks and Ottengraf (1991), assuming negligible mass-transfer limitation for a sparingly soluble gas, successfully applied a model for removal of dichloromethane from waste gases in a biofilter based on zeroth-order biological uptake. Little consideration has been given thus far as to how the possible operating regimes associated with the processes of mass transfer and biological removal can be identified during bioreactor operation. The extent to which each plays a role in biofiltration is further clouded by difficulty in the measurement of the necessary parameters required to incorporate both processes into a successful mathematical model.

MATERIALS AND METHODS

The initial consortium used for these studies was taken from a methanotrophic mixed culture. Identified bacterial species included *Citrobacter freundi*, *Pseudomonas da*, *Alcaligenes paradoxus*, *Xanthomonas maltophilia*, and *Flavobacter indologenes*. Unidentified yeast species were also found to be present. The culture was fed n-pentane and isobutane and was self-maintained by using these VOCs as sole carbon sources (Davison and Thompson, 1993, 1994). The consortium no longer displayed methanotrophic activity during these studies.

A well-defined mineral medium [NATE medium (Palumbo et al., 1991)] containing 10.0 g $MgSO_4$-H_20, 2.0 g $CaCl_2$, 10.0 g KNO_3, 1.0 g NH_4Cl, 2.7 mg $FeCl_3$, 0.44 g KH_2PO_4, 0.56 g K_2HPO_4 and 10 mL of a trace element solution per liter was used for all studies except those in which non-growth associated degradation was being studied. The trace element solution contained 50 mg $CuSO_4$-$5H_20$, 10 mg $MnSO_4$-H_20, 70 mg $Zn(NO_3)_2$-$6H_20$, 10 mg $CoCl_2$-H_2O, and 10 mg MoO_3. Nitrogen (as ammonium) was found to be the limiting supplemental nutrient in systems using NATE medium in batch experiments. The medium contained no carbon-containing compounds from which energy or carbon could be acquired.

Trickle-bed reactors contained a structured polyethylene packing (Sulzer™ packing, Koch Industries, Houston, TX) to maximize surface area and minimize pressure drops. The structure also provided a stable support for a biofilm, which developed on the surface. Humidified gas was fed into the top of the reactors containing 500 to 5000 ppm n-pentane and/or 500 to 5000 ppm isobutane; gas exited at the bottom for a single pass. These systems ran with gas flow rates of 5 to 500 mL min^{-1}, with a maximum degradation rate of approximately 60 g h^{-1} m^{-3}. Columns were 50 cm long, with an internal diameter of 5.0 cm (see Figure 1). Within each column were placed three packing units, for which the surface area of each was known. The liquid media, which itself contained a substantial level of biomass, was recirculated (Masterflex™ peristaltic pumps) and distributed on the mesh packing at the top of the vertically-mounted column. The packing material was sterilized by soaking it in ethanol for 24 hr and the other components of the reactor were autoclaved for one hour at 121 °C before use. The liquid medium fed to the reactor was also sterilized. Provision was made for a continuous supply of fresh sterile mineral nutrients to encourage growth and consumption. Strict aseptic conditions were not maintained after bioreactors had developed a substantial level of VOC-degrading biomass. Column temperature was maintained as desired using a constant temperature recirculating water bath and heating/cooling jacket.

Gas chromatography of VOCs was performed on a Varian Instruments (McFarland, WI) Model 3700 Gas Chromatograph with a Supelco (Bellefonte, PA) Model #2-17204 packed column equipped with flame ionization detection. Injector, oven, and detector temperatures were 160°C, 160°C, and 270°C respectively. Integration was performed by a Hewlett Packard (Greenville, NC) Model HP3396 Series II Integrator. Gas-phase concentrations of isobutane and n-pentane were monitored at inlet, outlet, and mid-length ducts of the column using 1.0 mL samples in gas-tight syringes (Hamilton Co., Reno, NV). Calibrations were performed using standardized gases purchased from Matheson Gases and Equipment (Morrow, GA). Liquid-phase concentrations were not detectable with the above analytical techniques; liquid phase concentrations are expected to be at most (using Henry's law assumption) about 300 ppb. The actual concentration, considering significant biological uptake, is suspected to be much lower.

Modeling. To mathematically describe the system, we considered two processes: mass transfer of VOCs into the liquid phase, and kinetic conversion of VOCs by the bacteria. The rate of mass transfer is proportional to the difference between the VOC concentration in both the gas and liquid phases. The latter of these will be directly affected by microbial degradation of the VOC within the liquid phase which causes the concentration in liquid phase to decrease. Microbial removal was assumed to follow simple Monod kinetics. One-dimensional model equations describing trickle-bed reactors have been presented elsewhere (Barton et al., 1997). Numerical solutions to the 1-D model equations were obtained by using finite difference techniques available in MathCAD 7.0 for Windows™ (MathSoft Inc., Cambridge, MA). Two-dimensional solutions were obtained via finite element codes written in FORTRAN. Values of the uptake constant and saturation constant were measured independently in batch flasks.

RESULTS AND DISCUSSION

Predictive models in the literature for trickling bed biofilters often assume that the system being described is kinetics- or mass transfer-limited (with steady, high biological uptake in the unit) with little evidence to support this claim. Separating these two processes can indeed be difficult, and many have reported values for 'effective mass transfer coefficients', which lump resistances due to each effect into one parameter. These parameters can work very well for describing the system from which they were derived, but can fail for alternative systems which might operate at a different mass transfer or kinetic rate. In most cases, both mass transfer limited and kinetics-limited conditions result in first-order removal processes which resemble each other phenomenologically. We have separated and quantified these competing factors to facilitate the development of one- and two-dimensional mathematical models which can be used to predictively describe a variety of biofiltration systems under a variety of operating conditions.

In order to determine whether our biofiltration units were kinetics- or mass transfer-limited, an initial assumption of mass-transfer limitation was made. Other common assumptions which were made included constant molar gas flow throughout the columns, negligible pressure drop , and negligible wall effects. A first-order mathematical model (mass transfer-based) was then used to calculate the overall mass transfer coefficient for the trickle beds. Well-defined geometry and boundary conditions of the reactors facilitated this type of analysis. A plot of ln[outlet concentration] versus reciprocal flow rate yields a straight line [even if kinetics are actually limiting] and the slope is proportional to the overall mass transfer coefficient. It must be noted that the systems which we have examined are generally *not* completely limited by mass transfer of the gases into the liquid phase, even though the gases used (pentane and isobutane) are sparingly soluble in water. If these types of measurements are made at different temperatures (e.g. 15 °C and 30°C), quick determination is possible regarding whether the system is mass transfer- or kinetics limited. If the system is kinetically-limited, the slopes of the lines generated at both temperatures will be different due to the effect of temperature on the biological specific uptake. If the system is mass transfer limited, the slopes of the lines will be somewhat different (because solubility, diffusion, and Henry's constant are somewhat temperature sensitive), but not markedly so. Measurements in our biofilters at different temperatures suggest that at low loading (gas feed concentrations were approximately 500 ppm at the inlet) and lower temperatures, kinetic limitations occur within the column (see Figure 2). Overall effective mass transfer coefficients at T = 15 °C were estimated to be 28 h^{-1} and 47 h^{-1} for isobutane and n-pentane respectively. At T = 30 °C, the values measured were 82 h^{-1} and 260 h^{-1}. Values were corrected for temperature effects (such as the effect of temperature on the Henry's law constants) according to standard relationships. For comparison, Shareefdeen et al. (1992) reported a value of 0.8 h^{-1} for the overall transfer coefficient in a peat/perlite packed biofilter removing toluene. Whitmore and Corsi (1994) reported several values of K_l for VOCs in sewage streams, ranging from 0.01 to 0.15 m h^{-1}. These values are similar to values measured in the trickle-bed systems, which ranged from 0.05 to 0.5 m h^{-1} (interfacial area ~ 500 m^{-1}). Since the values at both temperatures differ distinctly from each other, even when the appropriate temperature corrections were applied to temperature-sensitive parameters such as the Henry's law coefficient, significant kinetic limitations must exist with filters (the initial assumption is negated). These limitations are more likely to dominate at conditions of higher gas flow rate, high feed concentrations, and lowered temperatures.

As an alternative to the initial assumption made above (complete mass-transfer limitation), complete kinetics limitation may also be assumed and equations describing uptake within the trickle bed reactor may be written. As above, outlet concentrations plotted versus reciprocal flow rate yield straight lines proportional to biomass concentration. The most accurate method for determining the validity of this assumption would be to conduct trickle bed experiments using varying levels of biomass; thus, if removal rates change proportionately with changing biomass concentration, a bioreactor can be said to be kinetically limited. In practice, however, modifying (and subsequently quantifying) biomass levels in trickle bed reactors is difficult at best. Thus, the technique of applying a mass-transfer limited assumption, followed by its mathematical negation, reveals more information about the system than assuming complete kinetics limitation alone.

An alternative method which can work in some biofilters is that of changing the biomass concentration present in the recirculating liquid. This method is easily implemented as compared with changing biofilm concentrations in the reactor. If changes in rates are noted with changing biomass liquid loading, kinetics limitation is implied. Results from these types of experiments are displayed in Figure 3.

Mathematical modeling of the reactor can also enable a better understanding of trickle-bed bioreactors, particularly if the reactors operate at the boundary between mass-transfer and kinetics-limited conditions. We have used both one-dimensional and two-dimensional models, incorporating mass transfer and kinetic uptake, to predict VOC profiles both along the column axis and within the biofilm and liquid layers. These results (data not shown) suggest that under normal operating conditions, our columns operate under a mixture of both conditions.

SUMMARY

Separation of the competing effects of mass transfer and kinetic uptake may require the employment of a variety of experimental and mathematical modeling techniques to understand and describe the biofilter being used. The trickle beds used in this study operated in a mixed regime, under which both kinetics and mass transfer played significant roles. Alteration of bed temperature and biomass liquid loadings were used to determine operating regimes. Predictive models supported this conclusion and allowed estimation of both axial and biofilm VOC concentration profiles.

ACKNOWLEDGMENTS

This research was sponsored by the Environmental Management Science Program - U.S. Department of Energy. Prior research was sponsored by the Advanced Industrial Concepts Division--Biological and Chemical Technologies Research Program - U.S. Department of Energy.

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FIGURE CAPTIONS

Figure 1. Schematic of trickle-bed bioreactor. Fresh humidified gas feed entered the top of the reactor and passed over a structured plastic packing which acted as a solid support for a biofilm. Volatile organic contaminants were removed as they transferred into the liquid phase by the microbial consortium. Trickling mineral media containing no added carbon and/or energy source was recirculated through the reactor to keep the biomass moist. Gas and/or liquid samples were taken at various points to analyze for isobutane and/or n-pentane concentrations.

Figure 2. Slopes of lines are proportional to the effective overall mass transfer coefficient, $K_l a$. Measurements at different temperatures suggest that at low loading (gas feed concentrations of 0.05 mol % n-pentane and 0.05 mol.% isobutane) and lower temperatures, kinetic limitations occur within the column. Coefficients at T = 15 °C were estimated to be 28 h^{-1} and 47 h^{-1} for isobutane respectively, while at T = 30 °C, the values measured were 82 h^{-1} and 260 h^{-1}. Values have been corrected for temperature effects; differences are statistically significant.

Figure 3. Solutions of varying cell density were prepared by centrifuging cell mass, followed by resuspension to a specific optical density. Recirculating liquid in the biofilter was replaced by the suspension and allowed to reach steady-state conditions. Inlet concentrations of n-pentane and isobutane were 5100 and 6400 ppm respectively, and are indicated above by dotted lines. The column used for this experiment *did not* possess a substantial biofilm coating on the packing material. Drops in the outlet concentration as a function of biomass density in the recirculating liquid indicate kinetic limitation.

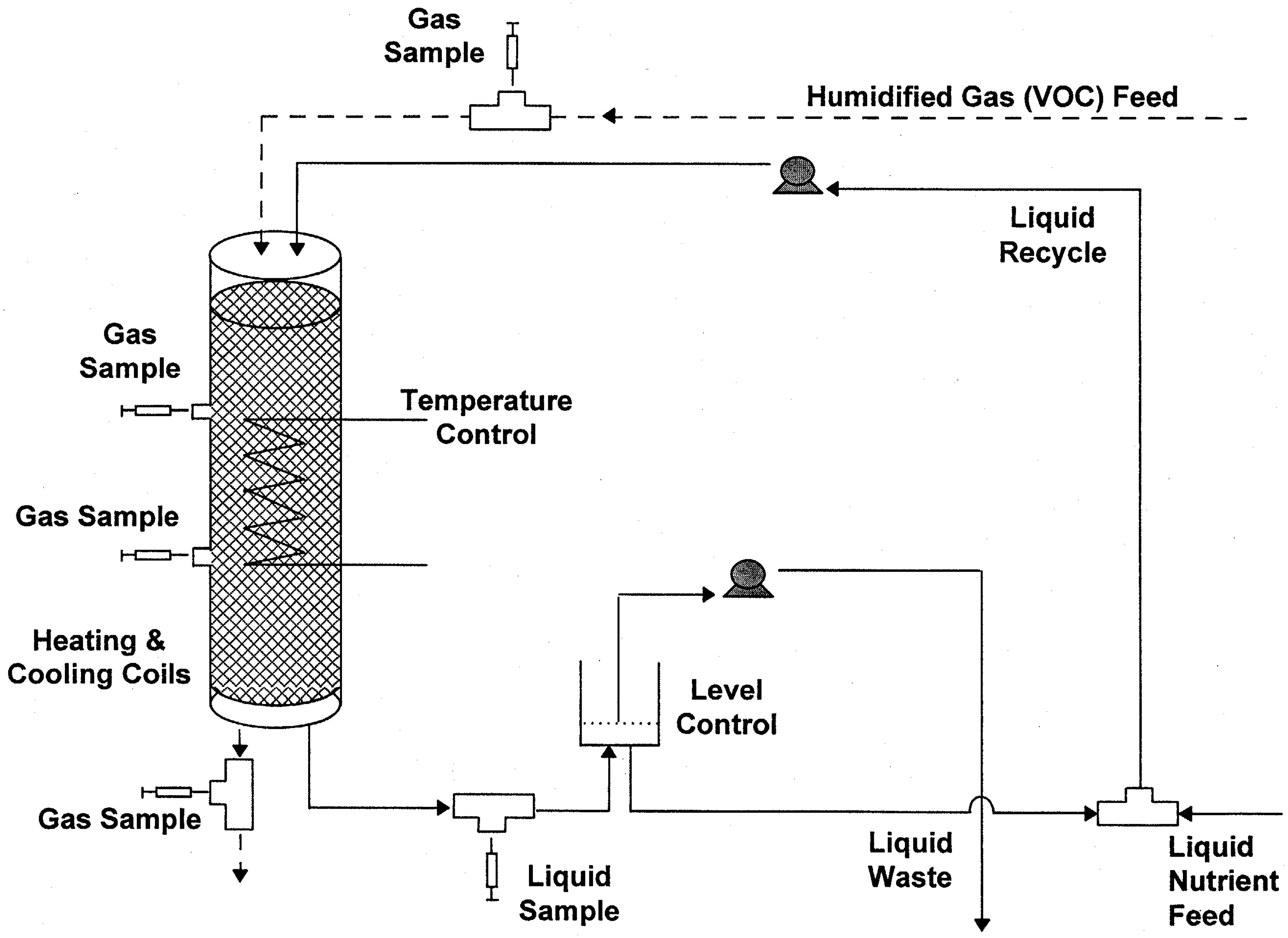
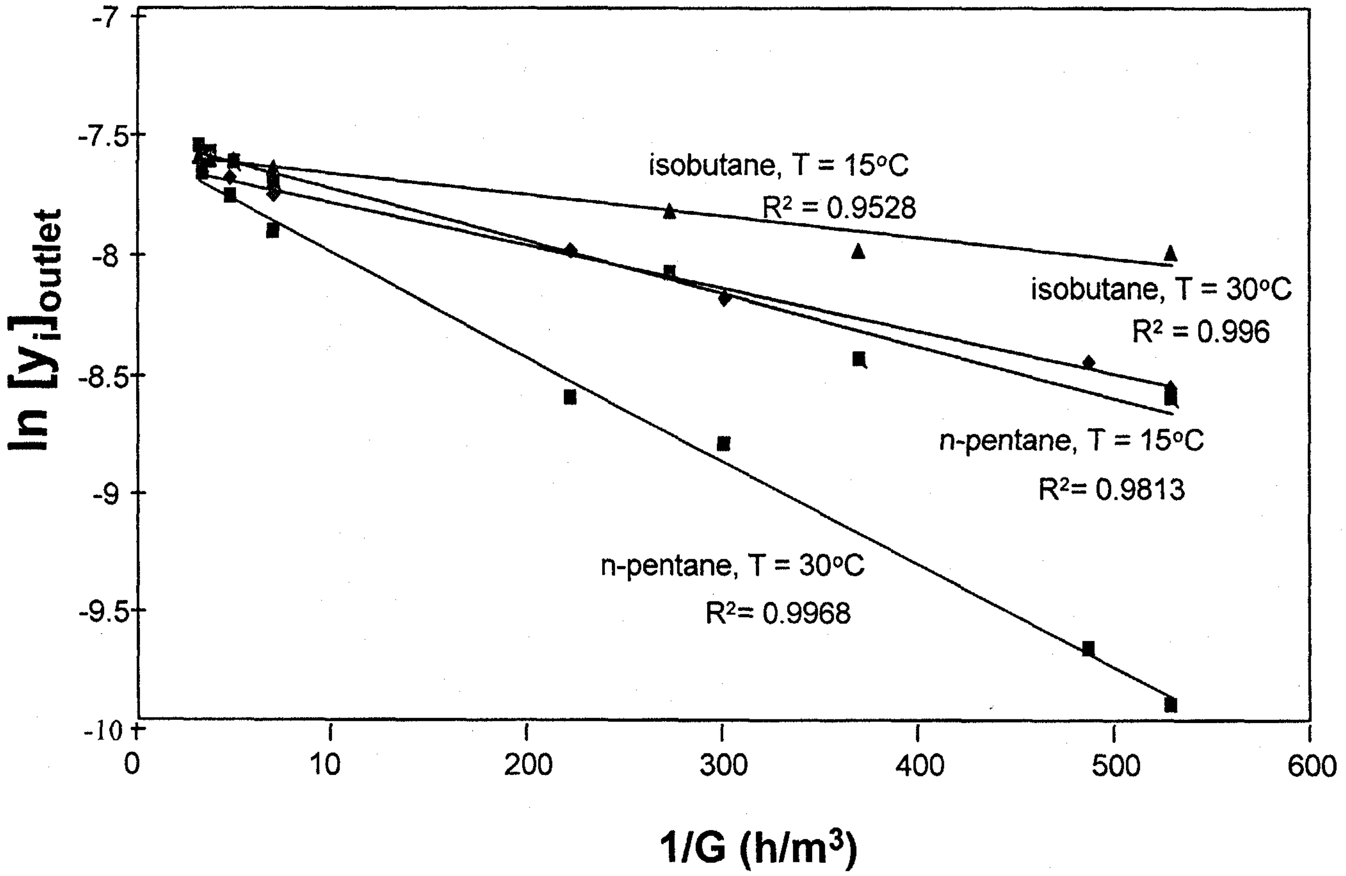

Gas Sample
Humidified Gas (VOC) Feed
Liquid Recycle
Gas Sample
Temperature Control
Gas Sample
Heating & Cooling Coils
Level Control
Gas Sample
Liquid Sample
Liquid Waste
Liquid Nutrient Feed

Figure 1



-7
-7.5
-8
-8.5
-9
-9.5
-10
0
10
200
300
400
500
600
ln [y$_i$]$_{outlet}$
1/G (h/m^3)
isobutane, T = 15°C
R² = 0.9528
isobutane, T = 30°C
R² = 0.996
n-pentane, T = 15°C
R²= 0.9813
n-pentane, T = 30°C
R²= 0.9968

Figure 2

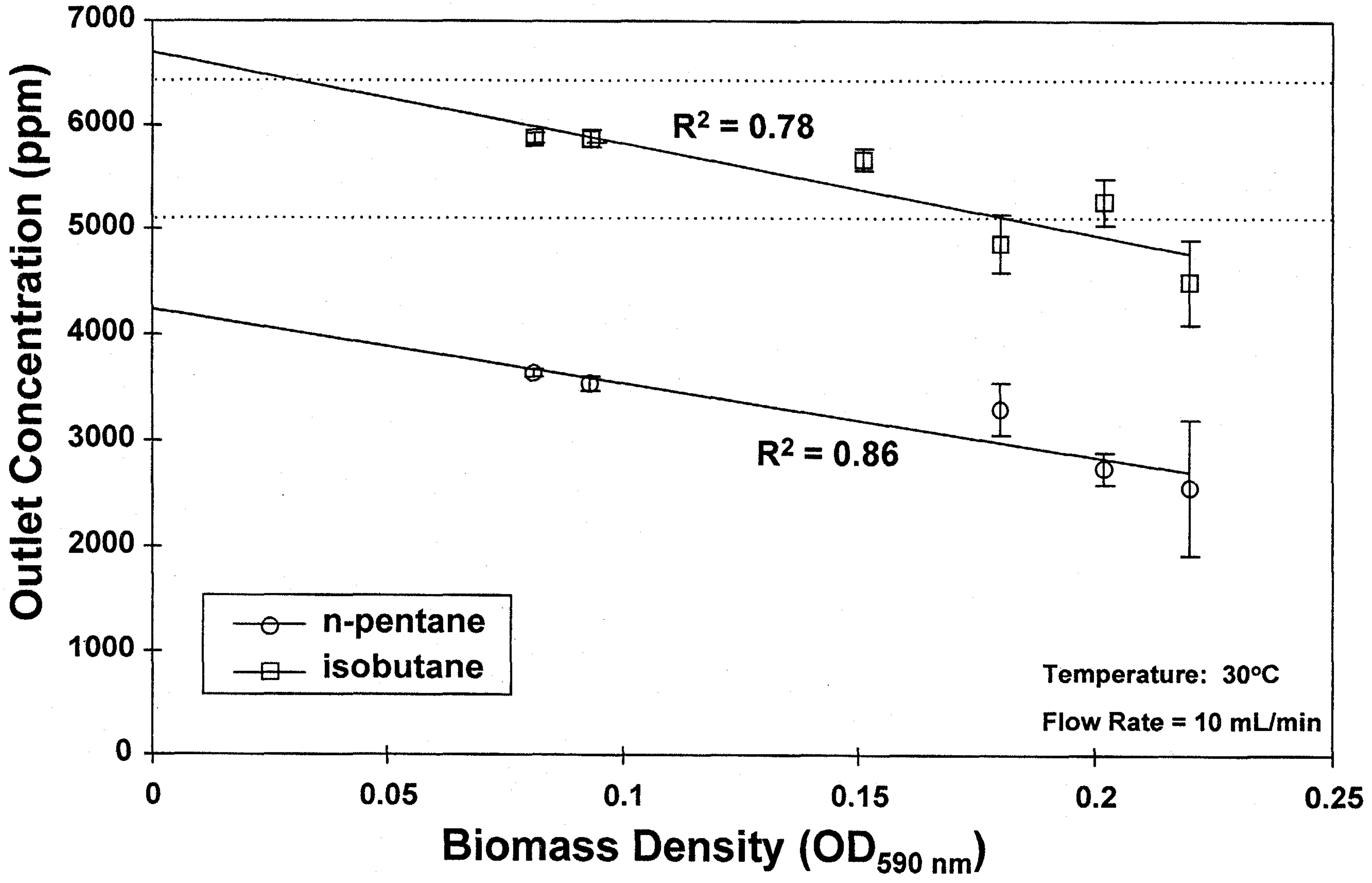

Outlet Concentration (ppm)
7000
6000
5000
4000
3000
2000
1000
0
0
0.05
0.1
0.15
0.2
0.25
Biomass Density ($OD_{590\ nm}$)
$R^2 = 0.78$
$R^2 = 0.86$
n-pentane
isobutane
Temperature: 30°C
Flow Rate = 10 mL/min

Figure 3