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TSA-CATOX FOR AIR PURIFICATION AND PURGE EFFLUENT DETOXIFICATION

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The removal of toxic chemical vapors from air and the subsequent treatment of those chemicals is an ever-growing environmental problem. A unique system has been developed which is capable of removing toxic chemical vapors from air and detoxifying these chemical vapors, *in situ*. Temperature Swing Adsorption (TSA) is used to continuously remove the toxic constituents from the incoming air stream using a two-bed cyclic operation. During the desorption (purge) step in the TSA cycle, a hot, concentrated effluent is generated which is fed to a catalyst reactor to decompose the toxic vapors. The design and operation of the TSA makes the system unique and is the focus of this work. During the purge step, energy is introduced into the system by heating the adsorbent directly. This permits heating without flow, which is not possible using the traditional TSA methods of purge gas or steam regeneration. An important consequence of this capability is that purge-step, vapor-phase concentrations may be increased by orders of magnitude over the feed concentrations. Parameters such as the power input and the purge flow rate may be adjusted to achieve the desired purge effluent quality, while maintaining the required product air purity. These design improvements allow the TSA to (1) satisfy even the most stringent air quality requirements and (2) generate a TSA purge effluent (both concentration and flow rate) tailored to optimize catalyst system performance.

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PREFACE

The work described in this report was authorized under Project No. 1O162622A553, CB Defense/General Investigation. This work was started in June 1994 and completed in January 1995.

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TSA-CATOX FOR AIR PURIFICATION AND PURGE EFFLUENT DETOXIFICATION

1. INTRODUCTION

An important and ever-growing problem is removing volatile organic compounds (VOC's) from effluent air streams and the subsequent post-processing (recovery for reuse or destruction) of these VOC's in an energy efficient and environmentally acceptable manner. The standard approach used in most applications is a single-pass carbon filter. In most cases this would appear to be the simplest and most cost-effective means of treating the problem. However, there are significant problems with this approach. To insure that performance specifications are met, single-pass filters must be designed to remain on-stream for at least several days of operation. If no method of monitoring the effluent concentration of contaminate(s) is provided, then filters typically must be sized for the worst case situation. This results in filters which are excessively large, thereby increasing both capital costs and waste generation.

A system capable of purifying air and treating the chemical waste at the point of production is shown in Figure 1. Temperature Swing Adsorption (TSA) is used to remove chemical vapors from air and generate a concentrated purge effluent stream. A catalytic (Cat-Ox) reactor is used to subsequently decompose these vapors. A purge air heater is not required for the TSA operation because a relatively new, more efficient method is employed. Using an activated carbon adsorbent, an electrical potential is induced across the bed. Since carbon can conduct electricity and has a measurable resistance, electrical energy supplied to the bed is converted to resistive heat. Most importantly, the energy introduced into the system goes directly to the point where it is required, the adsorbent, as opposed to traditional TSA purge gas techniques which require a heat transfer step. Consequently, the flow rate of purge gas is no longer important in determining the heating rate, thus the heating time and cycle time may be proportionately reduced.

The regeneration step in the TSA cycle is typically composed of a heating and a cooling stage. Invariably the regeneration step is the time limiting step of the TSA cycle. It is also the most complex and the least understood. Friday and LeVan (1, 2) performed a theoretical analysis of the purge step for two systems, (1) benzene on activated carbon and (3) water on 4-A molecular sieve. They also conducted an experimental study of the regeneration of an activated carbon bed with adsorbed octane using a hot nitrogen purge (4) and compared measured data with model results. However, their analysis did not include mass transfer resistances which could be significant for complete VOC removal. Shoofs (5) has studied the behavior of the regeneration step of a TSA process to purify ammonia synthesis make-up gas. He reports that monitoring temperature behavior at the exit and within the beds can allow one to estimate the effectiveness of the desorption step. Some qualitative information regarding the magnitude of concentrations within the bed is also obtained.

In-bed resistive heating was suggested by Petkovska et al. (5). In their experiments, activated carbon cloth was placed between two electrodes. Trichloroethane was used as the test chemical. Regeneration experiments were

performed and the following conclusions about direct electrical heating were reached: (1) it is both interesting and applicable, (2) it is rapid, and (3) it is superior to conventional heating methods from an energy point of view.

2. MATHEMATICAL MODEL

The only way to estimate the performance improvements in the TSA system is by using a mathematical model. The basis of the simulation is given by the material and energy balances as described below. A full discussion of the assumptions used to develop the material and energy balances along with the complete list of parameter definitions is given by Friday and LeVan (1).

Material balance

$$\rho_b \frac{\partial q}{\partial t} + \frac{\partial(\varepsilon v c)}{\partial z} = 0 \qquad (1)$$

Energy Balance

$$\rho_b \frac{\partial h_s}{\partial t} + \frac{\partial\left(\varepsilon v \rho_f h_f\right)}{\partial z} = Power\ Density \qquad (2)$$

The power density is expressed as J/(s m^3). The mathematical model also includes an internal particle mass transfer resistance, Equation (3), and an external particle heat transfer resistance, Equation (4).

$$\rho_b \frac{\partial q}{\partial t} = k_p a\left(q^* - q\right) \qquad (3)$$

$$\rho_b \frac{\partial T_s}{\partial t} = ha\left(T_f - T_s\right) \qquad (4)$$

q^* is the equilibrium adsorbed-phase concentration, T_f is the fluid-phase temperature, T_S is the solid-phase (particle) temperature, $k_p a$ is the mass transfer rate constant and ha is the heat transfer rate constant.

3. EXPERIMENTS

The main purpose of this paper is to demonstrate the capability of the TSA system not only to purify air streams, but to provide a mechanism for more efficient downstream processing of the chemical vapors of interest. The most important characteristic of the TSA operation is the concentration increase achieved during the purge step. Two experiments are performed which demonstrate both the increase in concentration and the flexibility the system has to control the purge effluent concentration profile. The test chemical is 1,1 dichloro, 2,2,2 trifluoroethane (R-123) and the adsorbent is 12x30 mesh BPL carbon manufactured by Calgon Corporation. The most important feature of the experimental system is the in-bed heating configuration depicted in Figure 2. For both experiments, the voltage is held constant at 26V. The bed depth is 50 cm, the bed diameter is 33 cm and the mass of

adsorbent is 22.5 kg. In-bed temperatures are measured using Resistance Temperature Detectors (RTD's) approximately 6.5 cm from each end of the bed. Experiments are compared with mathematical model results to better understand the purge step temperature and concentration behavior.

The feed-step procedure used for both experiments is the same. A clean bed is partially saturated with chemical by feeding 500 ppm (0.38 torr) of R-123 at 100 SCFM for 4 hours. Based on the equilibrium loading for R-123 of 0.182 g/g at 500 ppm and 300 K, this results in the bed being about 1/2 filled with adsorbed chemical. After the 4-hour adsorption step, two different purge steps are employed. For Experiment 1, the purge step consists of 30 minutes of power input at 1.77 kW with no purge flow. The purge flow rate of 15 Standard Cubic Feet per Minute (SCFM) is not initiated until the power is turned off (30 minutes). For Experiment 2, the purge step consists of 15 minutes of power input at 1.65 kW with no purge flow, followed by 15 minutes of power input at 1.65 kW with 15 SCFM purge flow. After 30 minutes the power is turned off while the purge flow continues. For both experiments the purge flow direction is counter-current to the feed flow direction.

Shown in Figure 3 are the purge effluent partial pressure profiles for both experiments. Both experiments show that the purge effluent partial pressure is increased by one to two orders of magnitude over the feed step partial pressure. In addition, these results demonstrate that heating with no flow provides another level of capability to control the purge effluent partial pressure with time. This can be particularly valuable for optimizing a downstream Cat-Ox reactor. Shown in Figure 4 are the in-bed temperatures for both experiments. These results demonstrate the differences in temperature achieved if heating is performed with and without flow. For example, the temperature at the purge outlet probe in Experiment 1 is about 40 K higher than in Experiment 2 at 30 minutes. The temperature behavior of the purge inlet is also different. When the purge flow is started at 15 minutes in Experiment 2, the temperature at the purge inlet rises for about five minutes, then drops as the purge gas cools the bed. The temperature for Experiment 1 however continues to rise reaching a temperature more than 40 K greater than in Experiment 2. The second rise in the in-bed temperatures near the purge outlet for each experiment result from hotter regions of the bed upstream of the probe. This may have been caused by the differences in bed resistance when material is adsorbed versus the bed resistance when the adsorbent is clean.

To further understand the behavior of the system, the experimental results are compared to the mathematical calculations. The mathematical model results are obtained using $D_E = 2.0 \times 10^{-6}$ cm^2/s and a particle diameter (d_p) of 0.15 cm in the following expression for $k_p a$.

$$k_p a = \frac{60 D_E}{d_p^2} \qquad (5)$$

The heat transfer coefficient, ha, was calculated using standard engineering correlations for the Prandtl and Nusselt numbers with a thermal conductivity of 0.0216 J/(s m K) and a particle heat transfer area per mass of adsorbent of 6.96 m^2/kg. Adsorption equilibria for R-123 on BPL activated carbon was measured

using a closed-loop isotherm system described in detail by Mahle et al. (9). These data are shown in Figure 5 correlated using the following five-parameter virial expression,

$$\ln(p) = \ln(q) + K_0 + \frac{K_1}{T} + \frac{B_1 q}{T} + \frac{C_1 q^2}{T} + \frac{D_1 q^3}{T} \qquad (6)$$

where q is expressed in g adsorbate per g adsorbent and p in torr. Parameter values obtained from a least squares best fit of ln(p) are $K_0 = 20.240$, $K_1 = -7134.5$, $B_1 = 13594$, $C_1 = -39117$, and $D_1 = 45762$.

Shown in Figure 6 are the purge effluent partial pressure profiles for Experiment 2 compared to the model results. The model seems to be reasonably close initially, but the model predicts a much more rapid drop in the effluent partial pressure than is measured. This discrepancy may be explained by examining the in-bed temperature results for Experiment 2 shown in Figure 7. The predicted temperatures for the purge inlet and the measured temperatures for the purge inlet are in reasonable agreement. However, the additional rise in the measured purge outlet temperature at about 40 to 50 minutes is not accounted for in the model. This is the reason the measured purge effluent partial pressure remains fairly constant at an elevated level. More work to identify the mechanism for the hotter upstream temperatures is required.

The design model was used to examine the purge step behavior of the TSA system with a more realistic feed concentration profile. Using the same bed dimensions and the same adsorbate adsorbent system, a 3-part feed was introduced. The feed concentration was 500 ppm (0.38 torr) for 2 hours, followed by 0 ppm for 2 hours and finally 50 ppm (0.038 torr) for 2 hours. The purge step was the same as in Experiment 1, 30 minutes of heating with no flow, followed by 15 SCFM purge flow. Shown in Figure 8 are the in-bed partial pressures during the heating stage of the purge step. The bed profile at 0 minutes shows the condition of the bed at the conclusion of the 3-part feed step. Although there is a noticeable drop in the partial pressure at about $z/L = 0.1$, the 3-part feed step has been smeared considerably. The maximum partial pressure in the bed is about 0.06 torr (6 times less than the 0.38 torr feed) and it exists near $z/L = 0.6$. When the potential is applied the partial pressures rise by more than 2 orders of magnitude. At the end of the heating step the in-bed profiles are nearly uniform. Figure 9 shows the effluent partial pressures and temperatures starting at 30 minutes when the 15 SCFM purge flow begins. Although the concentration drops continually from a high value of about 25 torr, it remains above 0.38 torr until about 60 minutes and above 0.038 torr for more than 80 minutes. The temperatures are also more than 50 K above ambient until about 70 minutes into the purge step.

4. CONCLUSIONS

The TSA system provides a mechanism for more efficient downstream processing by increasing the concentration and reducing the flow rate of a contaminated air stream. In-bed resistive heating allows the purge effluent concentration to be tailored to optimize a downstream process, e.g., Cat-Ox. The mathematical model results demonstrate that the TSA system is relatively insensitive to wide variations in feed concentrations.

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Figure 1.

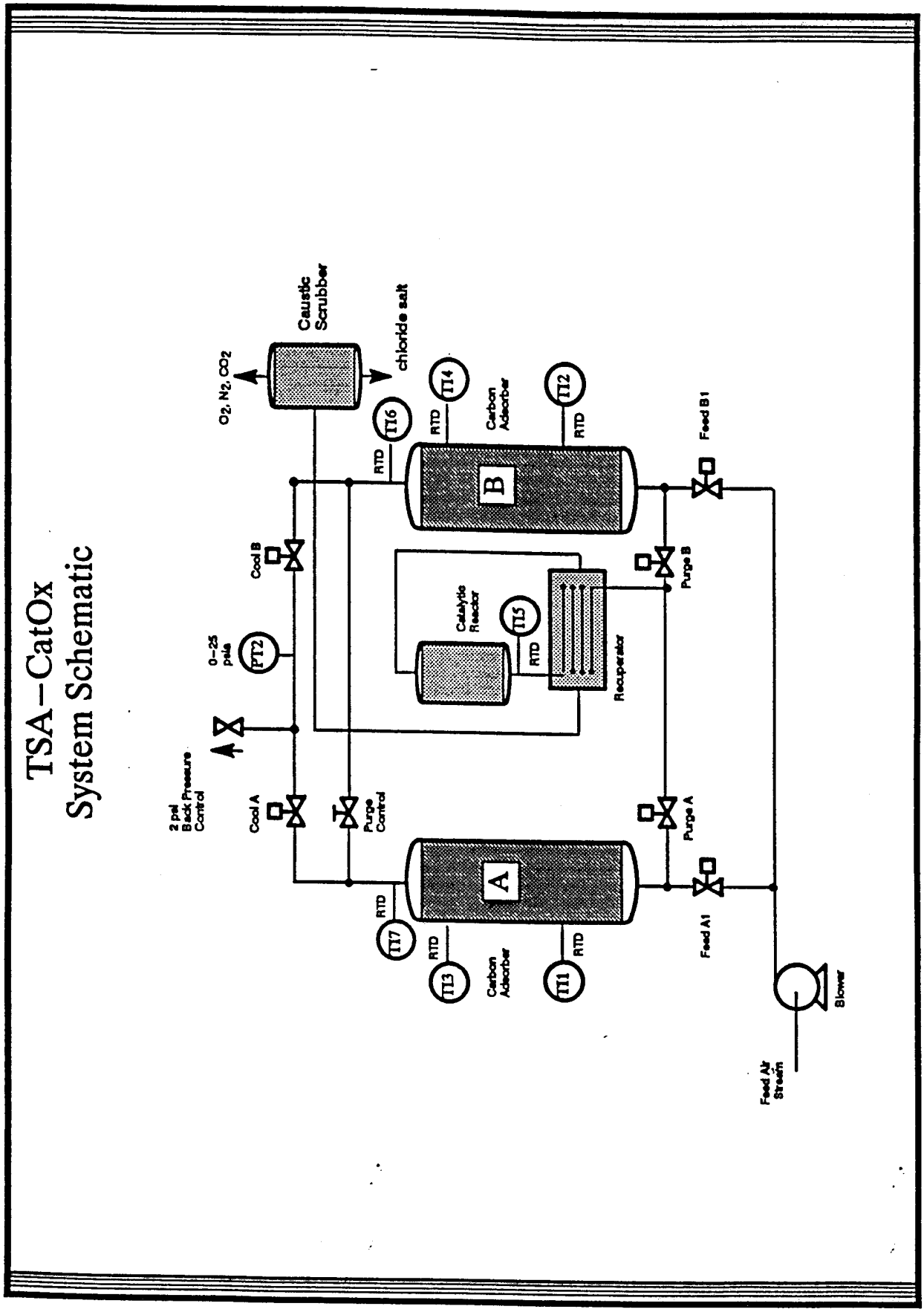

TSA–CatOx
System Schematic
Caustic Scrubber
chloride salt
O_2, N_2, CO_2
RTD
T16
T14
T12
Carbon Adsorber
B
Feed B1
Purge B
Cool B
0–25 psia
PT2
Catalytic Reactor
T15
Recuperator
2 psi Back Pressure Control
Cool A
Purge Control
Purge A
A
T17
T13
T11
Feed A1
Blower
Feed Air Stream

Figure 2.

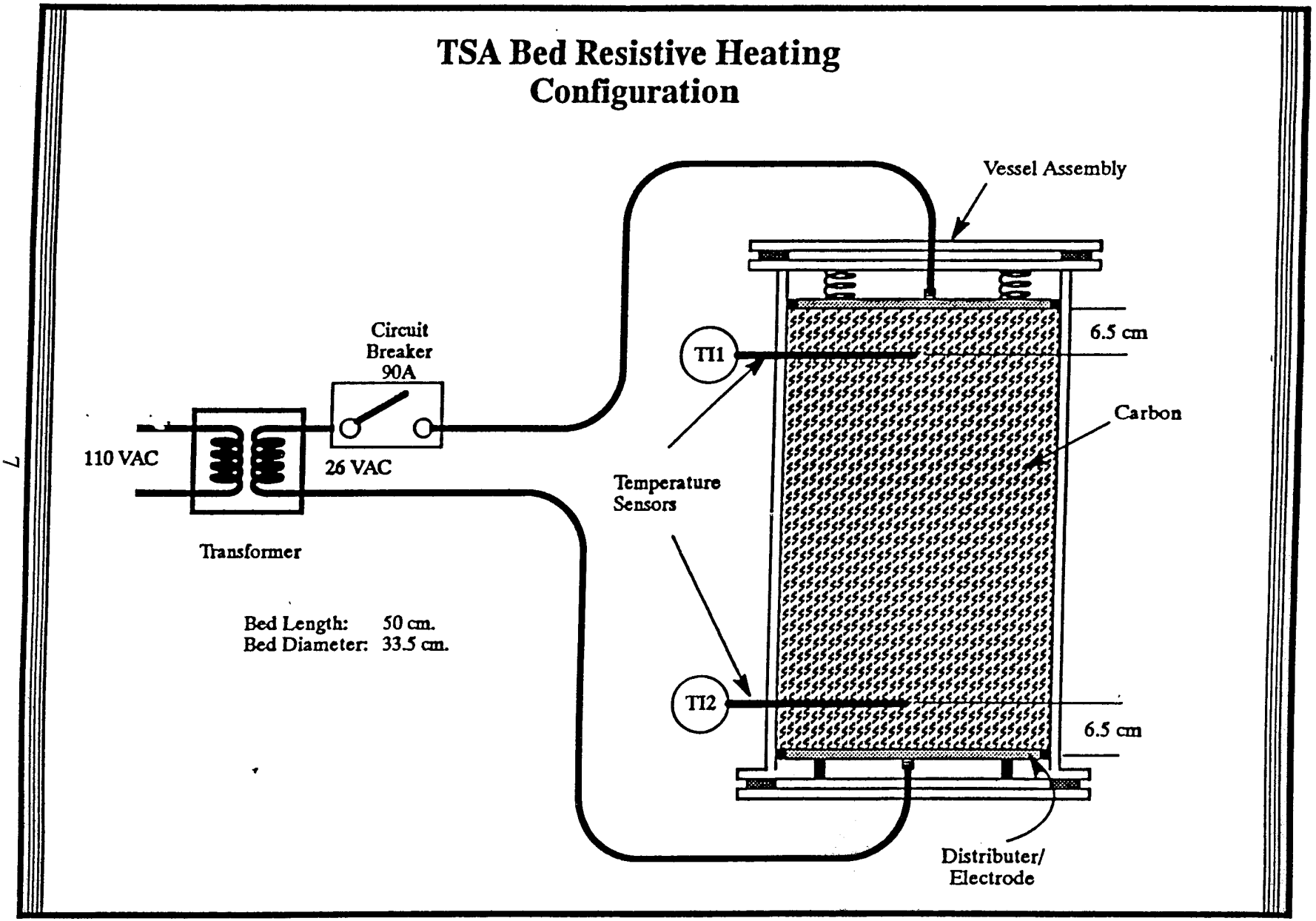
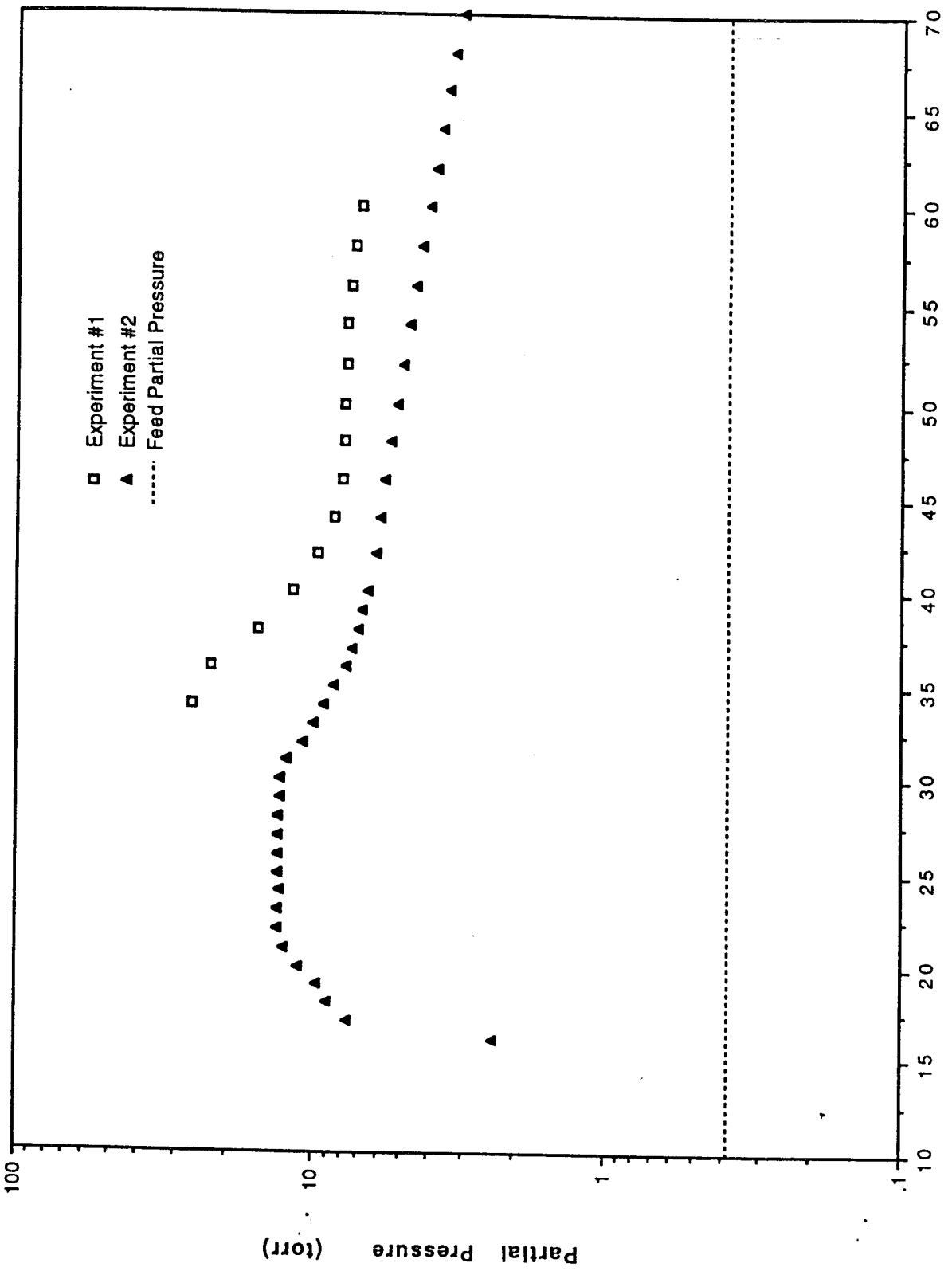

TSA Bed Resistive Heating Configuration
Vessel Assembly
Circuit Breaker 90A
110 VAC
26 VAC
Transformer
TI1
TI2
Temperature Sensors
6.5 cm
Carbon
6.5 cm
Distributer/ Electrode
Bed Length: 50 cm.
Bed Diameter: 33.5 cm.

Figure 3. Purge Effluent Partial Pressures for Experiments 1 and 2



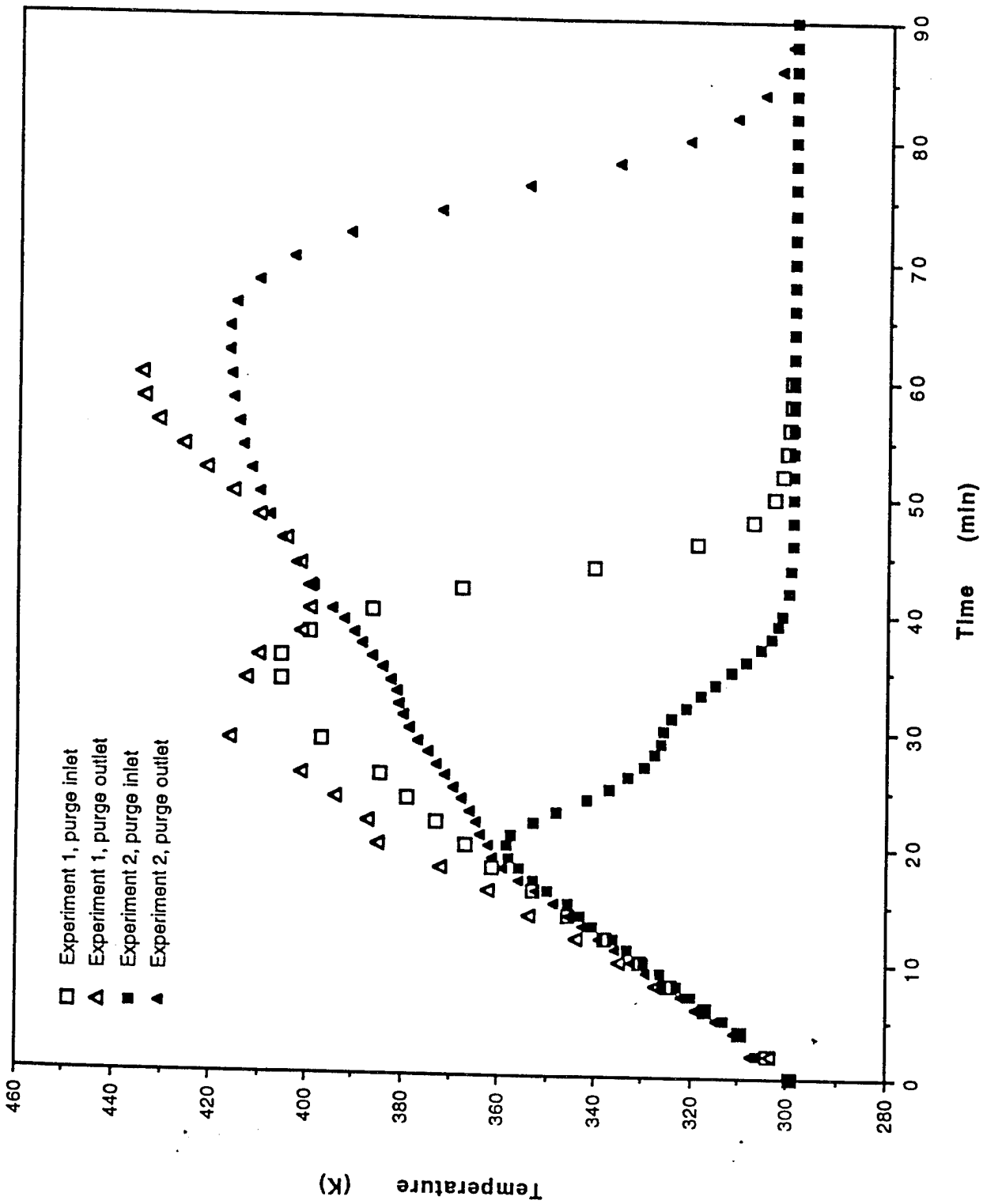
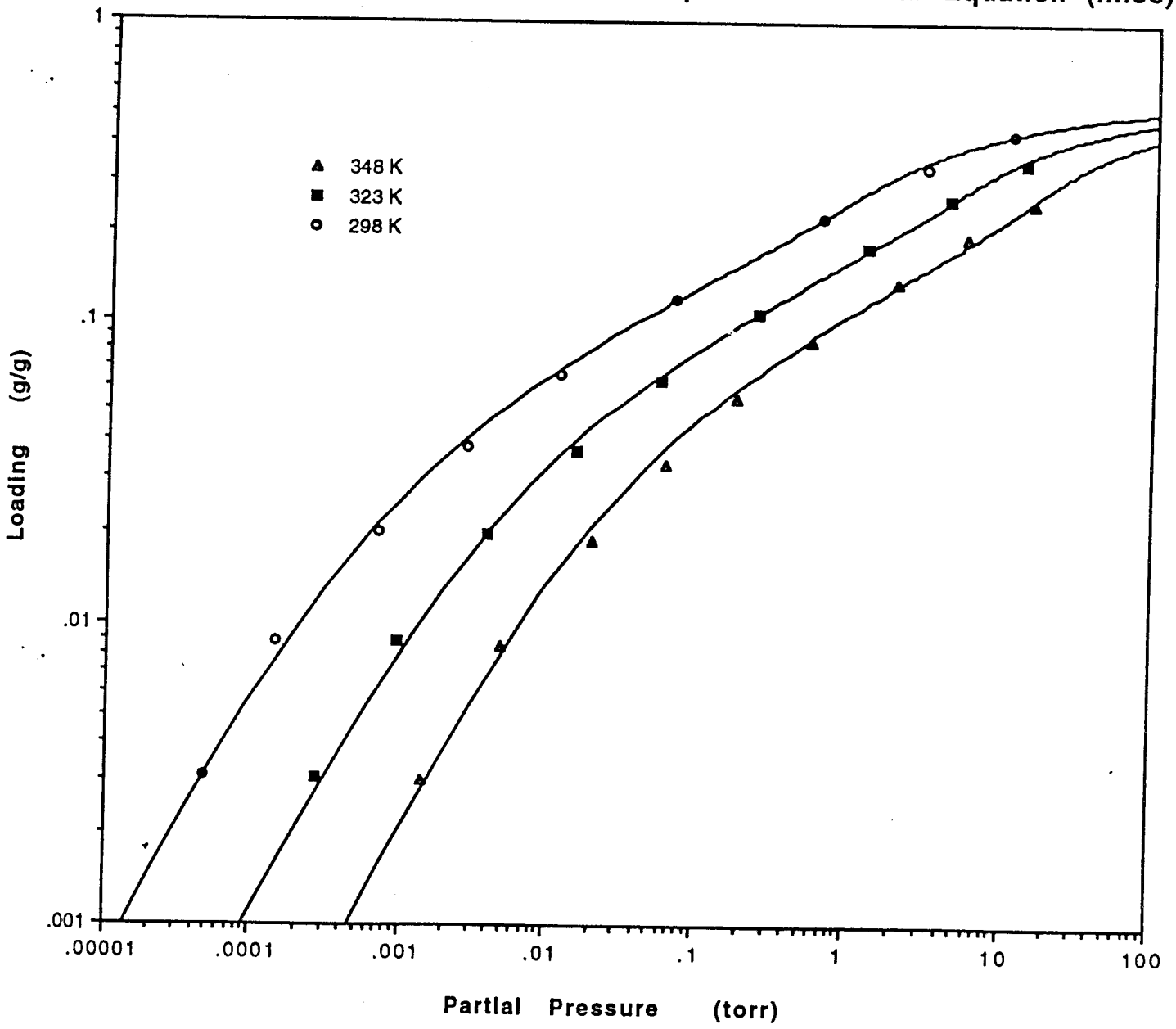


Figure 4. In-bed Temperature Data for Experiment 1 and Experiment 2

Figure 5. R-123 on BPL Activated Carbon Isotherm Data (symbols) with the Best Fit 5-parameter Virial Equation (lines)



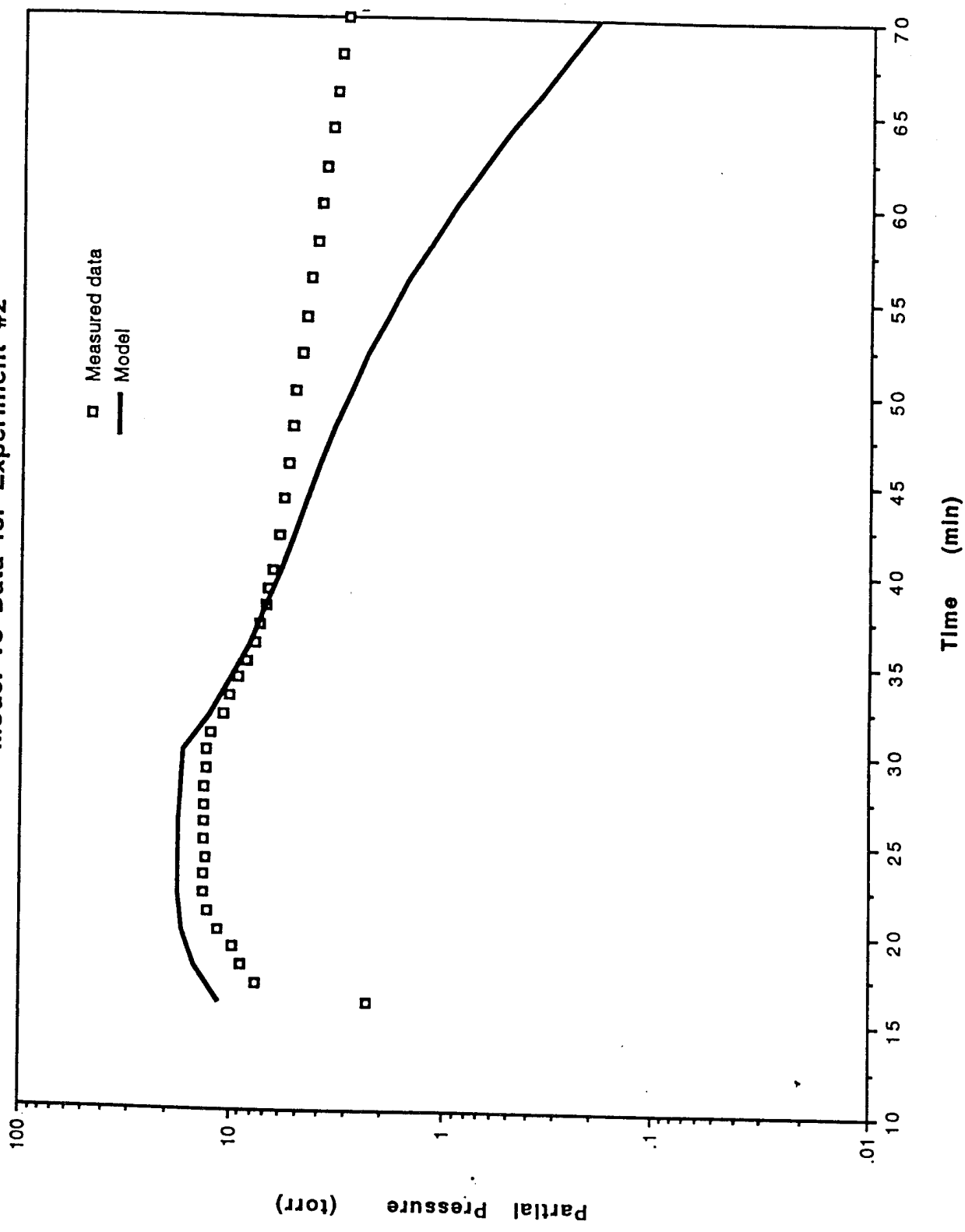
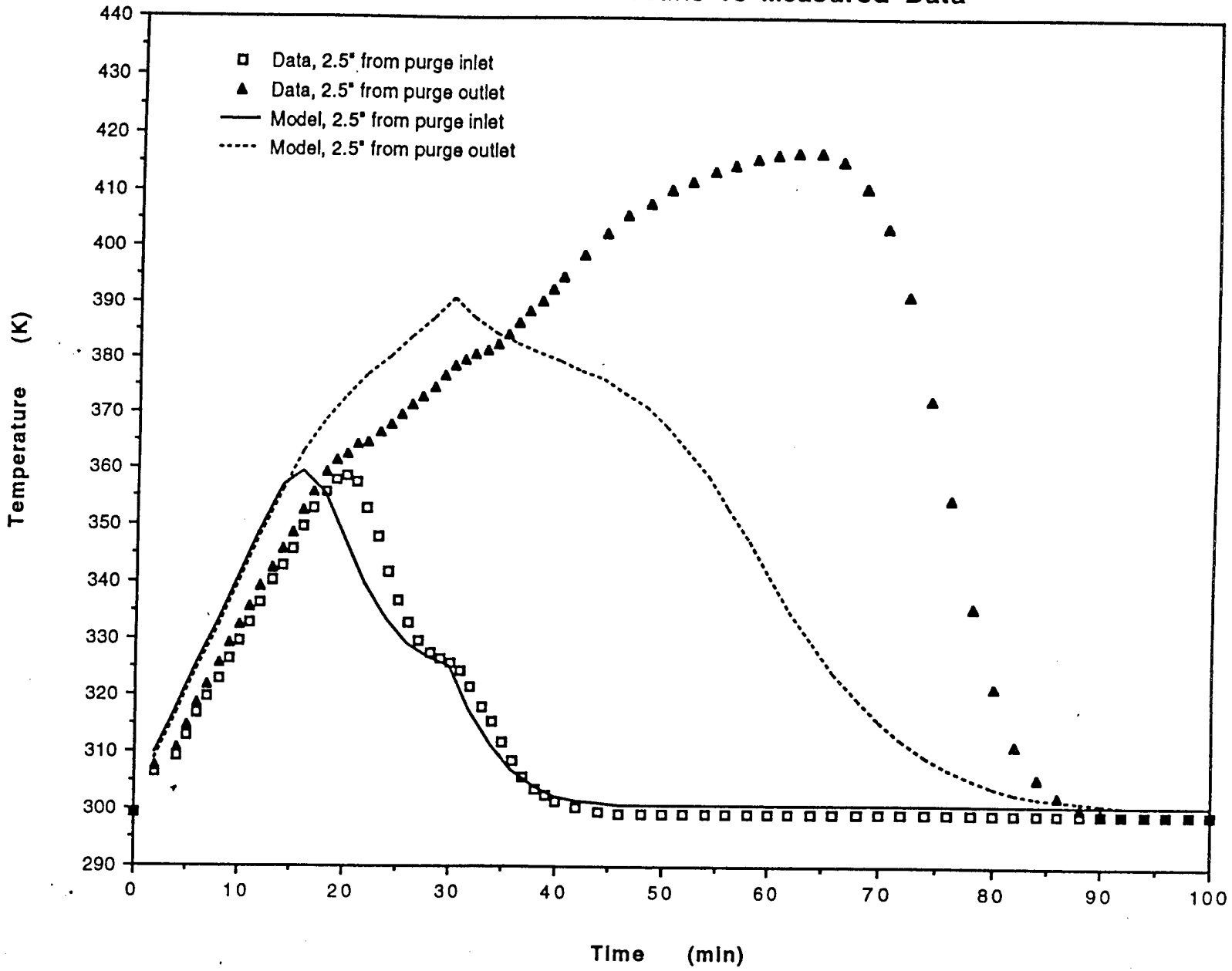


Figure 6. Purge Effluent Partial Pressures with Time. Model vs Data for Experiment #2

Figure 7. In-bed Temperatures for Experiment 2. Model Results vs Measured Data



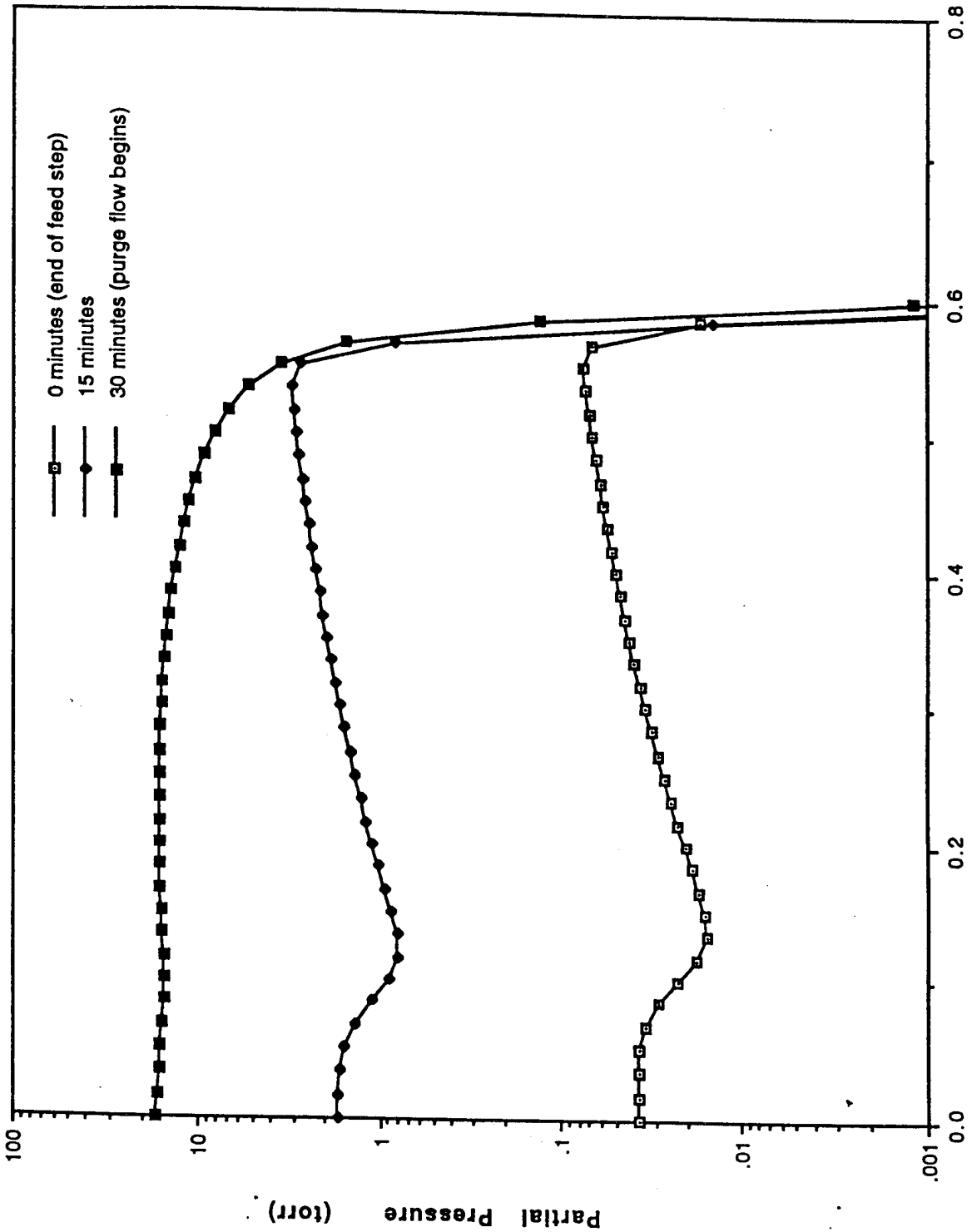


Figure 8. Design Model In-bed Partial Pressure Profiles for 3-step Feed Simulation. 0, 15, and 30 Minutes Into Purge Step

Figure 9. Design Model Purge Effluent Temperatures and Partial Pressures for 3-step Feed Simulation