

Photocatalytic Oxidation of Gas-Phase BTEX-Contaminated Waste Streams

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INTRODUCTION

Researchers at the National Renewable Energy Laboratory (NREL) have been exploring heterogeneous photocatalytic oxidation (PCO) as a remediation technology for air streams contaminated with benzene, toluene, ethyl-benzene, and xylenes (BTEX). This research is a continuation of work performed on chlorinated organics¹. The photocatalytic oxidation of BTEX has been studied in the aqueous phase,^{2,3,4} however, a study by Turchi et al.⁵ showed a more economical system would involve stripping organic contaminants from the aqueous phase and treating the resulting gas stream. Another recent study by Turchi et al.⁶ indicated that PCO is cost competitive with such remediation technologies as activated carbon adsorption and catalytic incineration for some types of contaminated air streams.

In this work we have examined the photocatalytic oxidation of benzene using ozone (O₃) as an additional oxidant. We varied the residence time in the PCO reactor, the initial concentration of the organic pollutant, and the initial ozone concentration in a single-pass reactor. Because aromatic hydrocarbons represent only a small fraction of the total hydrocarbons present in gasoline and other fuels, we also added octane to the reaction mixture to simulate the composition of air streams produced from soil-vapor-extraction or groundwater-stripping of sites contaminated with gasoline.

REACTOR ASSEMBLY

We performed benzene photocatalytic oxidation experiments using a single-pass annular reactor (Figure 1). The organic-contaminated stream was prepared by passing a humidified air stream through a heated water bath containing a diffusion tube filled with neat organic. This stream was then mixed with an ozone/oxygen stream produced by a corona discharge ozone generator (O₃ Associates). The ozone/oxygen stream made up approximately 5% of the total flow. Flowrates for both streams were controlled by mass flow controllers (Tylan General) and were adjusted to achieve specific initial O₃ and organic concentrations in the gas stream entering the reactor. The reactor was illuminated with an 8W near-UV lamp (Sylvania F8T5BLB), which also served as the inner wall of the annulus. The light intensity at the catalyst surface was estimated to be 15.7 n-einstein cm⁻² s⁻¹.

The inner wall of the reactor was coated with Degussa P25 titanium dioxide (TiO₂). The catalyst was applied to the reactor wall in a slurry of water or isopropyl alcohol. This catalyst is primarily of the anatase form with a Brunauer-Emmett-Teller (BET) surface area of 50±15 m² g⁻¹. The applied catalyst was then air dried and baked at 400°C for at least an hour. Prior to each set of experiments the catalyst was heated in place, and the air/oxygen/ozone mixture (without benzene) flowed through the reactor with the catalyst illuminated. This procedure ensured a clean, reproducible catalyst surface for each run.

Typical flowrates through the reactor were approximately 1 liter per minute (LPM). This corresponds to a Reynolds number of less than 50, indicating laminar flow. We have modeled the reactor system as a laminar-flow reactor with reaction occurring only at the outer wall. Our results indicate that no mass-transfer limitations exist for the range of reaction rates measured in this study. It may seem surprising that the reaction rate in a laminar flow reactor would not be mass-transfer limited, however the critical factor is not the absolute value of the mass transfer rate (represented by the dimensionless Sherwood number Sh), but the relative magnitudes of the mass transfer rate and the surface reaction rate (represented by the Damkohler number Da). As long as the mass transfer rate is much faster than the

surface reaction rate ($Sh \gg Da$), no mass transfer limitations are expected, regardless of the flow regime (i.e., laminar vs. turbulent).

The reaction mixture was analyzed with a portable gas chromatograph (MTI) equipped with dual chromatography column/thermal conductivity detector assemblies, which allowed us to measure organic disappearance and carbon dioxide (CO_2) production simultaneously. Ozone concentration was measured using a custom-built UV absorption cell loaned to our group by Edward Lovejoy at the National Oceanic and Atmospheric Administration (NOAA, Boulder, CO).

EXPERIMENTAL RESULTS

Initial photocatalytic oxidation studies using BTEX compounds without the addition of ozone have shown relatively low conversions. As the reaction is initiated, the outlet reactant concentration drops rapidly while the outlet CO_2 concentration increases sharply, indicating significant benzene adsorption and conversion. However, after several minutes, the outlet benzene concentration begins to increase while the outlet CO_2 concentration begins to decrease. When steady-state conditions are reached, only very low benzene conversions are observed. There is evidence that xylene and toluene have slightly greater conversion than does benzene under these conditions. Such low conversion rates compelled us to explore the use of additional oxidants (hydrogen peroxide and ozone). Experiments with added hydrogen peroxide did not result in a significant increase in conversion rate; however, experiments with added ozone improved the reaction rates considerably (3% conversion of 75 ppmv benzene stream without ozone, 40% conversion of same benzene concentration with 235 ppmv ozone). We have thus concentrated our efforts on the study of benzene degradation kinetics in the presence of ozone.

Unlike photocatalytic oxidation with other organics such as trichloroethylene and ethanol, no intermediate compounds have been directly observed during the oxidation of aromatics. Only unreacted aromatic compounds and carbon dioxide were observed in the reactor exhaust. It is likely the intermediate species formed are significantly less volatile than the original reactant, and they are unlikely to desorb from the catalyst surface.

In order to obtain kinetic data for this system we have performed experiments varying initial benzene concentration, initial ozone concentration, and residence time. For most of the reactions studied, greater than 90% carbon balance was observed. Figure 2 shows benzene conversion data as a function of initial ozone concentration. The effect of inlet benzene concentration on benzene conversion is shown in Figure 3. Figure 4 shows the effect of residence time on benzene conversion. The solid lines in these figures are model fits and are discussed below.

REACTION MECHANISM

PCO is a heterogeneous process in which an illuminated semiconductor catalyst produces photoexcited electron-hole pairs. In aqueous-phase PCO, the photogenerated electrons are scavenged by molecular oxygen, while the photogenerated holes oxidize water to hydroxyl radicals. These radicals react with organic contaminants. The mechanism of gas-phase PCO has not been studied as thoroughly, and is not currently well-understood.

It is certain that the gas-phase photocatalytic degradation of benzene (in the absence or presence of ozone) proceeds on the TiO₂ surface through the formation of a number of intermediates. These intermediates can then occupy reaction sites and compete for photogenerated oxidant species, slowing down the initial destruction of benzene. We hypothesize that the ozone oxidizes these intermediates, allowing further reaction of the benzene. Tabulated kinetic rate constants for the homogeneous reaction of aromatics show that the reaction of ozone with oxygenated aromatics (such as have been seen as intermediates in the aqueous-phase photocatalytic oxidation of benzene³) is many times faster than the reaction of ozone with non-oxygenated aromatics⁷. By analogy, we suggest that ozone serves to increase the rate of benzene conversion by reacting with oxygenated intermediates that would remain on the surface and occupy reaction sites otherwise available for benzene adsorption.

KINETIC MODEL

In our experiments, we detected no organic intermediates by gas chromatographic sampling of the gas phase. The likely intermediates (i.e., phenol, catechol) are significantly more polar than benzene, have very low vapor pressures, and are therefore unlikely to desorb from the catalyst surface. These strongly bound intermediates are not included in the model, however, because we cannot experimentally measure them.

We write the simplified reaction mechanism as the reaction of adsorbed benzene with and without adsorbed ozone to give CO₂. The CO₂ rapidly desorbs from the surface of the catalyst and is the only reaction product observed in the gas-phase in our experiments.



The simplified reaction rate expression is then the sum of the benzene reaction rates with and without ozone:

$$\text{rate} = -\frac{d[B]}{dt} = \frac{1}{6} \frac{d[CO_2]}{dt} = \frac{a_s I_0}{V} \cdot \left[\Phi_1 + \Phi_2 \frac{K_Z [O_3]}{1 + K_Z [O_3]} \right] \cdot \frac{K_B [B]}{1 + K_B [B]} \quad (3)$$

where a_s is the illuminated surface area, V is the reactor volume, I_0 is the light intensity at the catalyst surface, Φ_1 and Φ_2 are the quantum yields for the reaction of benzene in the absence and presence of ozone, and K_Z and K_B are the binding constants for ozone and benzene. We have assumed a Langmuir-Hinshelwood (L-H) adsorption isotherm for ozone and a modified L-H isotherm for benzene. The modified isotherm has a constant denominator, which accounts for the competition between original reactants and reaction intermediates for adsorption sites. This modification has been used for modeling PCO of aromatic compounds in the liquid phase⁸. We have used this kinetic equation to fit the data for the destruction of benzene as a function of ozone concentration, benzene concentration, and residence time. The model fits are shown in Figures 2-4.

This model significantly oversimplifies the reaction mechanism in a number of ways. It allows CO₂ evolution directly from benzene, with no kinetically important intermediates. The ozone destruction

equation (not shown) allows ozone loss only through reaction with benzene, although our preliminary data suggest that ozone does photocatalytically degrade in the absence of any organic. The model does not take into full account the inventory of adsorbed organics, which can be important in calculating accurate destruction rates in the case of significant organic adsorption, as shown by Sauer and Ollis⁹. Nonetheless, this simple model is a useful starting point for reactor design purposes.

MODEL RESULTS

The model equation shown above cannot be solved analytically because the concentrations of both benzene and ozone ($[B]$ and $[O_3]$) are changing over time. We integrated the model equation numerically using Euler's Method with a commercial spreadsheet (EXCEL 5.0). The results of the modeling effort are shown as solid lines in Figure 2-4. The values of the parameters in Eq. 3 (Φ_1 , Φ_2 , K_Z , K_B) were empirically chosen to fit the data.

Despite the theoretical shortcomings of the model, it fits the experimental results fairly well. This model has been used to estimate the cost of PCO treatment equipment for actual waste streams¹⁰. Further refinements in the model must include a more accurate treatment of the intermediates and the ozone. Currently, extrapolation to benzene and ozone concentrations outside the range used in the experiments is inadvisable.

EFFECT OF OCTANE ADDITION

In addition to exploring the fundamental chemistry of benzene PCO with secondary oxidants, NREL is interested in the near-term commercialization of PCO technology. Because of this, we have begun testing laboratory mixtures that simulate "real-world" waste streams. Data we have obtained regarding a soil-vapor-extraction vent from an abandoned gasoline station indicate the BTEX concentration in the vent is up to 600 ppmv, and the total petroleum hydrocarbon concentration is ~15,000 ppmv. These gasoline hydrocarbons are C5-C8 alkanes.

To explore how additional alkane hydrocarbons would affect the PCO of benzene, we performed experiments with octane as a model compound. Octane PCO in the absence of ozone is greater than that of benzene (20% conversion with an inlet concentration of 50 ppmv, 0.31 seconds residence time). Adding ozone (240 ppmv) increased the conversion (30% for 50 ppmv inlet octane concentration) but not as significantly as it does for the aromatic compounds. Fairly significant decreases in the rates of benzene conversion are observed when octane is added to the waste stream containing benzene and ozone (Figure 5). Note that the solid line in this figure is not a model prediction, but simply a best-fit curve.

These results indicate that the photocatalytic oxidation of BTEX waste streams will require characterization of all hydrocarbons. Reactor design will need to include additional capacity to compensate for the affects of these hydrocarbons, just as is currently required for activated carbon adsorption beds.

CONCLUSIONS

We have investigated the photocatalytic oxidation of BTEX-- an important groundwater and soil contaminant. Our studies have shown that the rates of reaction of the aromatic components are low. We assume that this results from a build up of organic intermediates on the surface. The addition of ozone is shown to increase the overall rate of reaction of our model compound (benzene), presumably by oxidizing these intermediates. We measured the kinetics of this process and have developed a simple kinetic model. We have also measured the effect of the other organic compounds that may accompany BTEX contamination.

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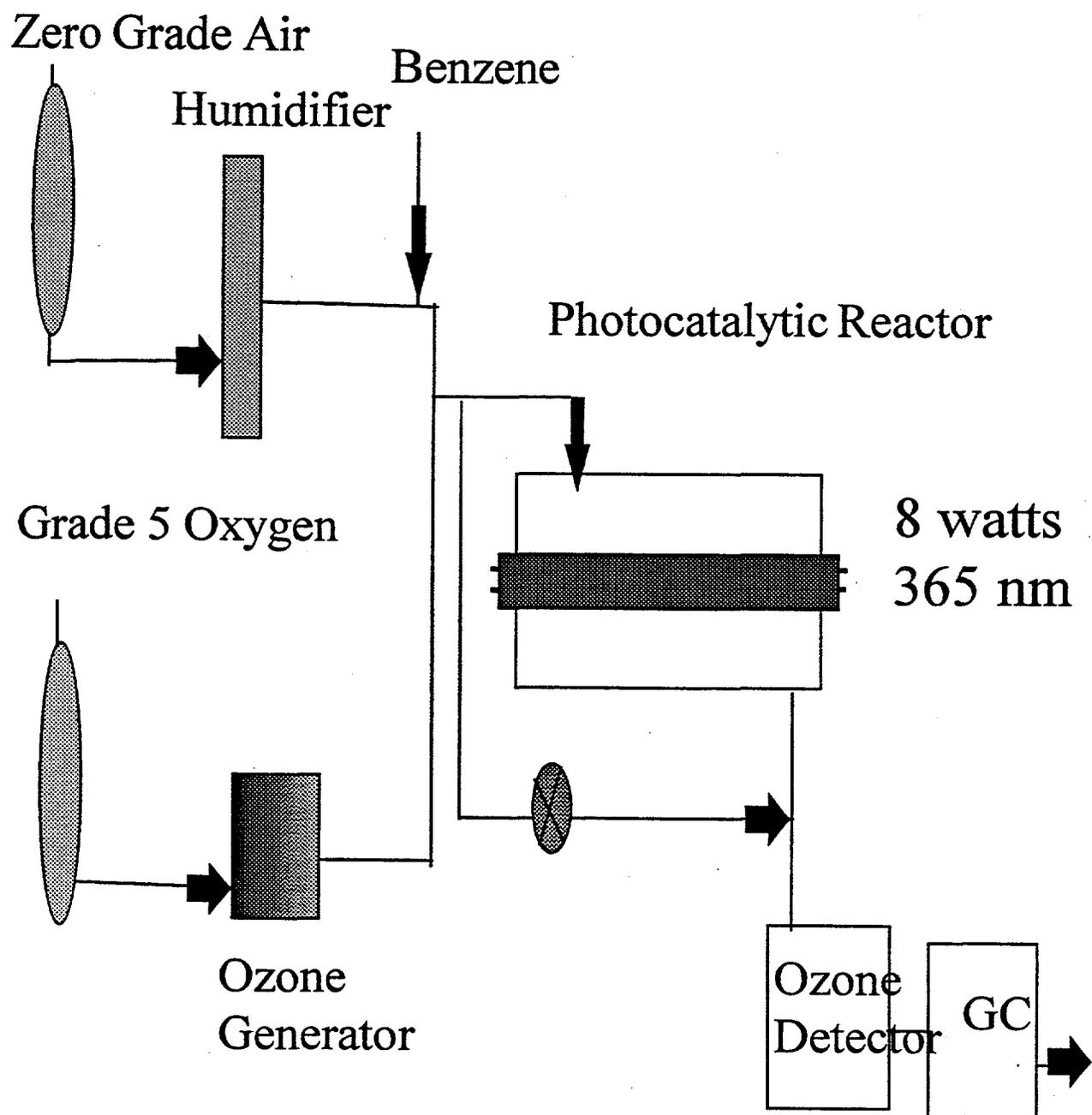


Figure 1. Schematic diagram of the photocatalytic oxidation reactor assembly.

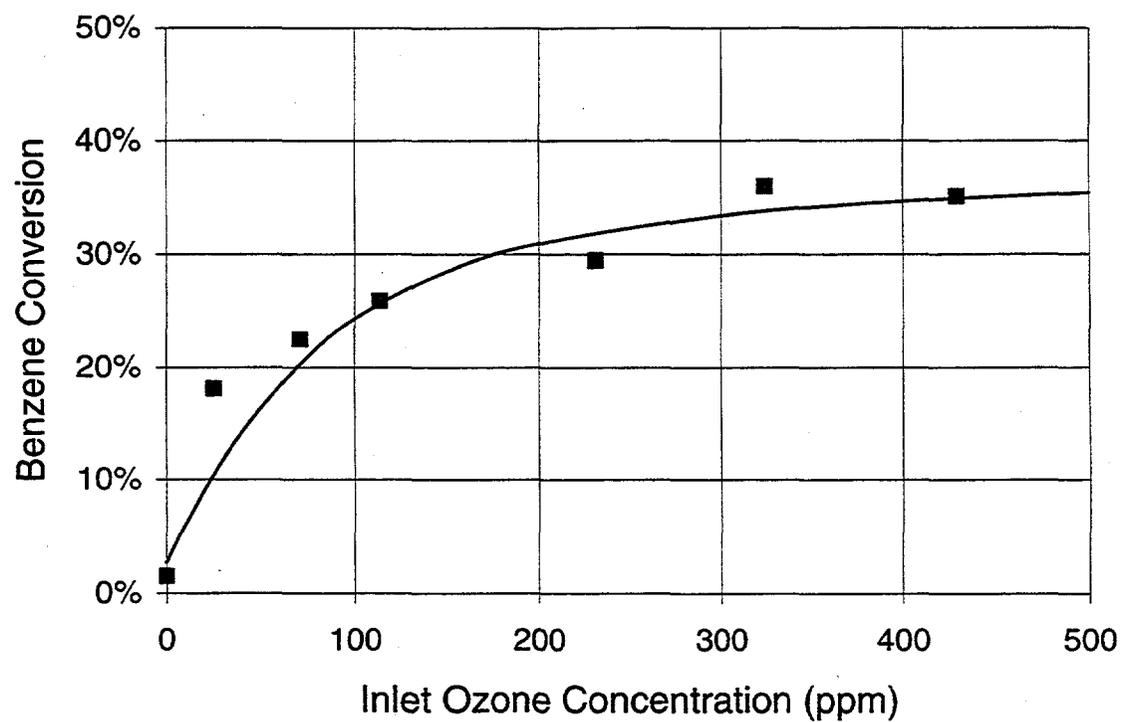


Figure 2. Benzene conversion (%) vs. inlet ozone concentration (ppmv). Inlet benzene concentration $[B]_{in}=88$ ppmv, residence time $t_{res}=0.61$ sec. Solid line is model fit (see text).

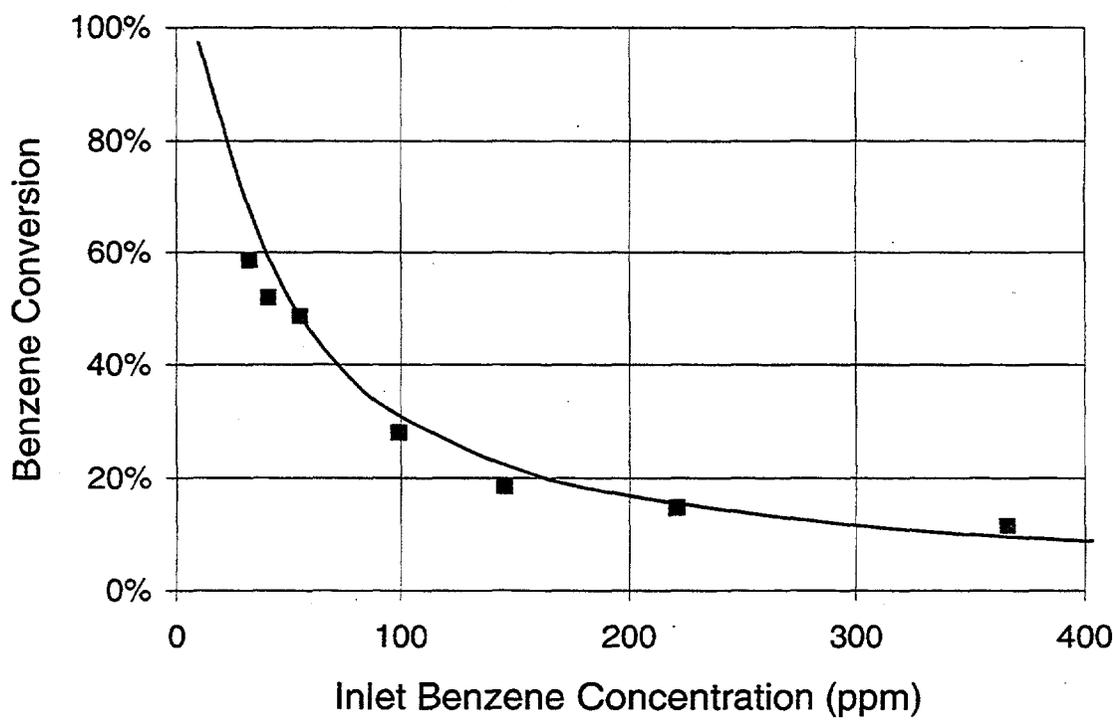


Figure 3. Benzene conversion (%) vs. inlet benzene concentration (ppmv). Inlet ozone concentration $[O_3]_{in} = 360$ ppmv, residence time $t_{res} = 0.61$ sec. Solid line is model fit (see text).

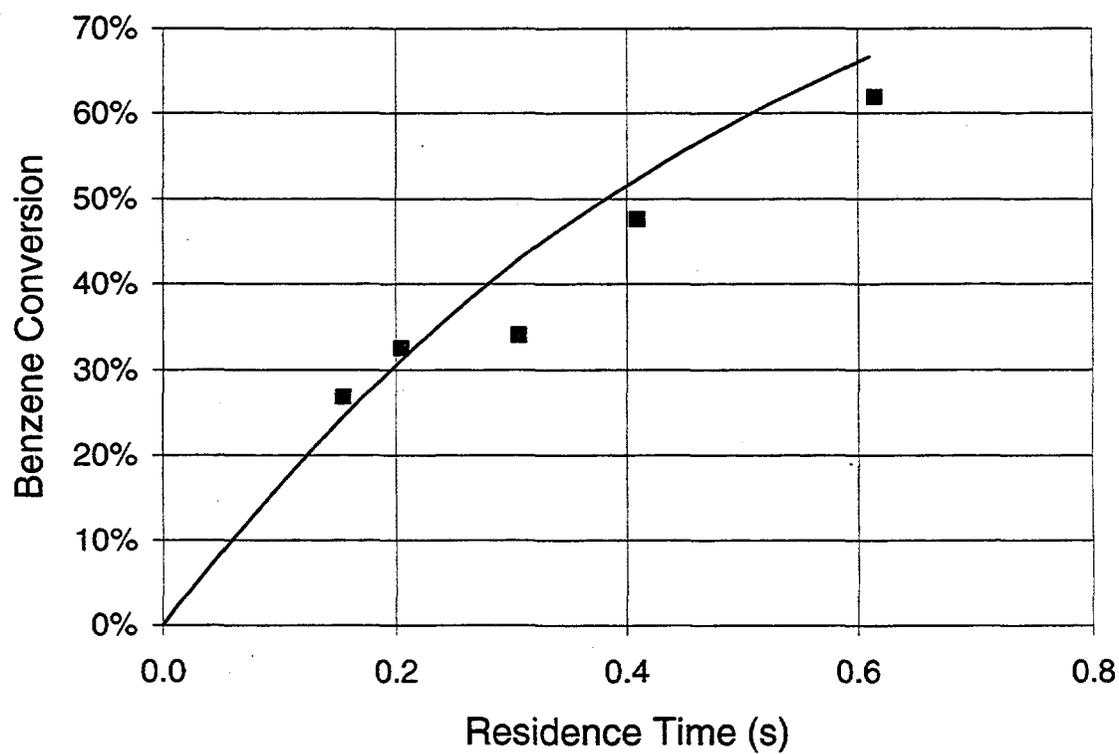


Figure 4. Benzene conversion (%) vs. residence time (s). Inlet benzene concentration $[B]_{in} = 33$ ppmv, inlet ozone concentration $[O_3]_{in} = 330$ ppmv. Solid line is model fit (see text).

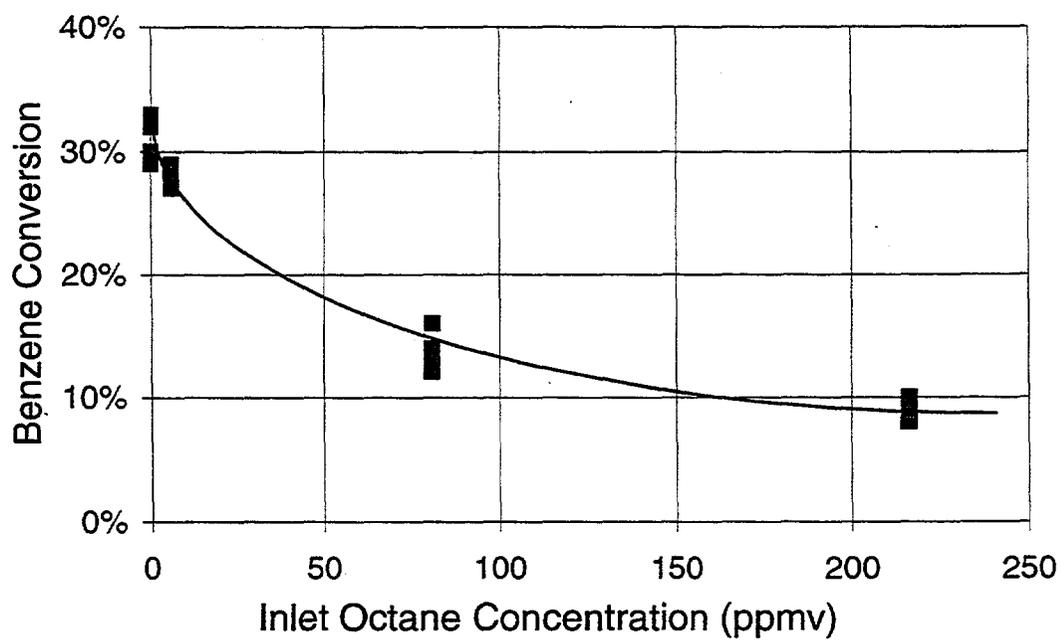


Figure 5. Benzene conversion (%) vs. inlet octane concentration (ppmv). Inlet benzene concentration $[B]_{in} = 50$ ppmv, inlet ozone concentration $[O_3]_{in} = 240$ ppmv, residence time $t_{res} = 0.61$ sec. Curve is best-fit line, not a model fit (see text).