



Project Summary

Mixture Effects in the Catalytic Oxidation of VOCs in Air

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Most volatile organic compound (VOC) releases into the environment are mixtures. However, most fundamental studies of the catalytic deep oxidation of such compounds are usually confined to single components. This study examines the deep oxidation of organic mixtures over a heterogeneous catalyst in an attempt to explain earlier observations concerning the apparent inhibition or enhancement of destruction of some components to establish a scientific basis for the design and operation of catalytic incineration systems for VOC control. To elucidate these effects, the oxidation kinetics of n-hexane, benzene, ethyl acetate, and methyl ethyl ketone in air were examined over a commercial catalyst (0.1% Pt/3% Ni on γ -alumina.) Reaction rates of these components individually were determined at temperatures of 150 to 360°C from differential reactor studies. When these were compared to overall destruction efficiencies from integral reactor studies for both individual compounds and mixtures, the Mars/van Krevelen (MVK) reaction rate model satisfactorily represented the results for some single organic compounds at lower temperatures. By incorporating pore diffusion effects, the MVK model adequately explains the single component data over the entire temperature range for some of the compounds. A multi-component MVK model incorporating competitive adsorption effects is moderately successful in predicting the observed behavior for a binary

mixture of benzene and n-hexane; however, it cannot predict the apparently enhanced reaction rate observed for ethyl acetate at higher temperatures (>220°C). Other reaction pathways available for compounds with carbon-oxygen linkages and/or the advent of catalytically supported homogeneous combustion with free radical precursors may explain this phenomenon. The enhancement of ethyl acetate conversions in humidified air streams suggests that autocatalysis by-product water may be a possible mechanism.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The goal of this study was to establish a scientific basis for the selection and evaluation of heterogeneous catalysts and operating conditions for the control of gas streams containing mixtures of volatile organic compounds (VOCs). The research was devoted to both experimental evaluation of the catalytic oxidation of VOC-containing mixtures and the kinetic interpretation/modeling of the results.

Experimental

A schematic diagram of the experimental setup is shown in Figure 1. Table

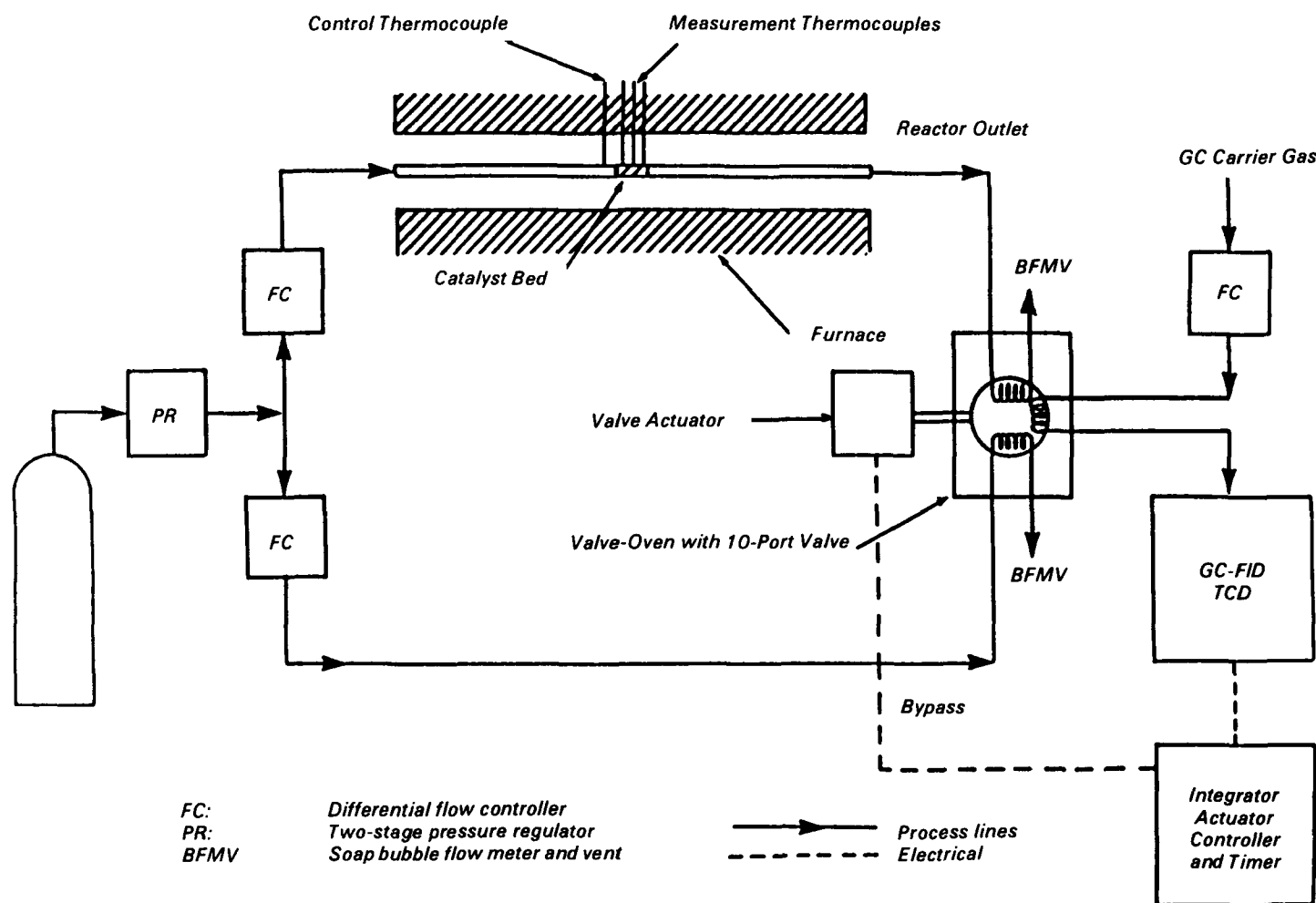


Figure 1. Microreactor system.

1 details the mixtures studied, and Table 2 describes the experimental conditions.

Results

Figure 2 shows the inhibition of n-hexane conversion in mixtures. Figure 3 shows the enhancement of ethyl acetate conversions in mixtures. Experiments were conducted in humidified air streams to ascertain if hydrolysis by-product water may be responsible for the enhancement. Figure 4 shows the enhancement of ethyl acetate conversions in humidified air streams.

Detailed experiments were carried out to obtain fundamental rate constants for the catalytic oxidation of the compounds in Table 1 as single components. These constants were incorporated into a reactor model based on the Mars/van

Krevelen kinetic mechanism to try and predict the observed mixture effects. Figure 5 represents the fit of the model to the single component benzene data. The fits for n-hexane and ethyl acetate were not as good. Mixture effects in a binary n-hexane/benzene mixture were also marginally predicted by the model.

Conclusions

- Conversions of components in a mixture of organics may be significantly higher or lower than when present by themselves.
- Mars/van Krevelen (MVK) kinetic mechanism is an adequate representation for the deep

oxidation of single organic compounds over the catalyst used in this study.

- A reactor model incorporating pore diffusion effects and MVK kinetics adequately explained single component benzene data over the entire temperature range of interest (150 to 360°C).
- A multicomponent reactor model incorporating pore diffusion effects and a simple proposed extension of MVK kinetics was marginally successful in predicting benzene/n-hexane mixture behavior.
- Conversions of oxygenated species such as ethyl acetate are higher in mixtures than in single component

Table 1. Test Gas Mixtures

Concentration in Air (ppmv)	
Single Hydrocarbon	benzene: 9, 69, 163, 375, 525 ethyl acetate: 53, 109, 238, 450 n-hexane: 201, 410, 566 methyl ethyl ketone (MEK): 25, 50, 70, 135, 190, 298
Binary Mixtures	193 ppm benzene + 172 ppm ethyl acetate 189 ppm benzene + 190 ppm n-hexane 184 ppm ethyl acetate + 190 ppm n-hexane 149 ppm n-hexane + 135 ppm MEK 160 ppm benzene + 135 ppm MEK
Ternary Mixtures	143 ppm benzene + 174 ppm ethyl acetate + 90 ppm n-hexane; 103 ppm n-hexane + 104 ppm benzene + 93 ppm MEK

ponents. The MVK model appears to explain the data in the kinetic regime. MEK oxidation shows lower apparent enhancement than ethyl acetate. Other reaction pathways, including thermally enhanced free radical mechanisms and the interactions of oxygen containing species with partially reduced

metal surfaces may explain the observed phenomena. Further experimentation is necessary before a specific model can be postulated for the oxidation of oxygenated compounds.

- The presence of water vapor in the gas stream increases the conversion of ethyl acetate

significantly. This suggests that autocatalysis by-product water may be responsible for the observed enhancement described above. The fact that MEK conversions are not significantly affected by the presence of water vapor lends credence to this theory.

Table 2. Experimental Conditions

Pressure:	1 atm
Temperature Range:	140 to 360°C (isothermal operation)
Space Velocity at Reaction Temperature:	50,000 to 1,000,000 h ⁻¹
Catalyst Bed:	17 to 20 mg
Hydrocarbon Concentration in Air:	10 to 600 ppmv
Catalyst Particle Size:	120 to 170 mesh
Ratio of Reactor Diameter to Particle Diameter	20:1

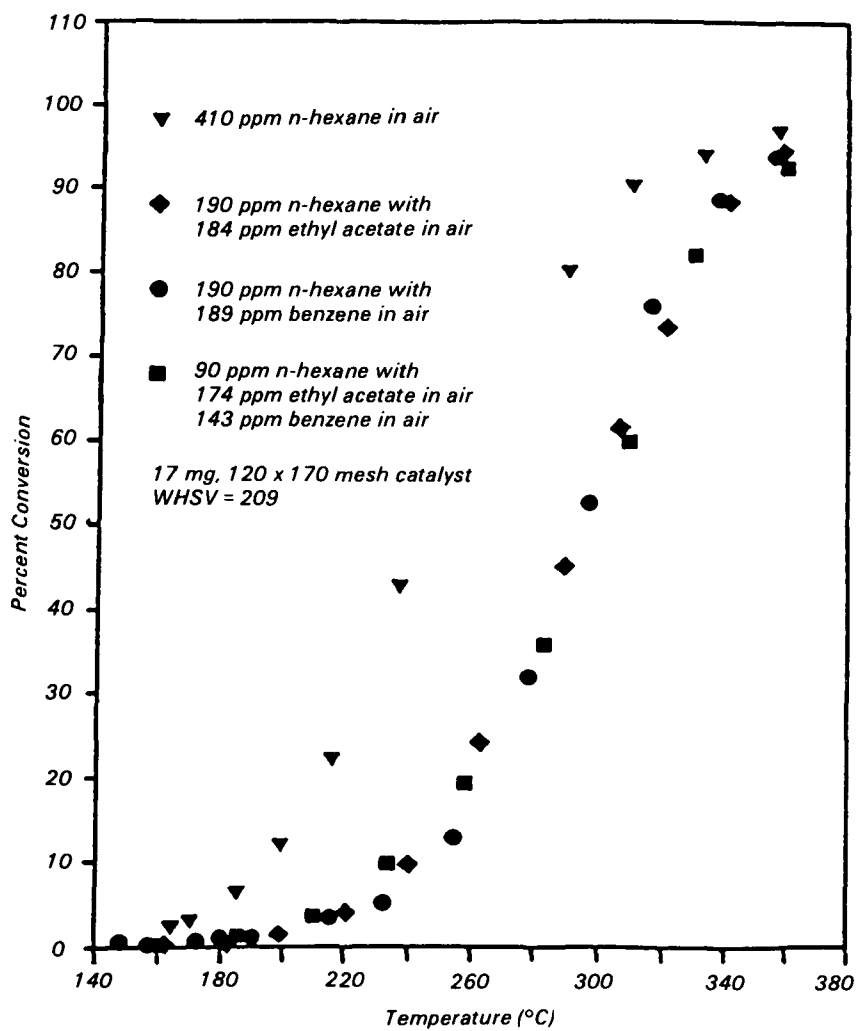


Figure 2. Effect of multicomponent mixtures on n-hexane conversion.

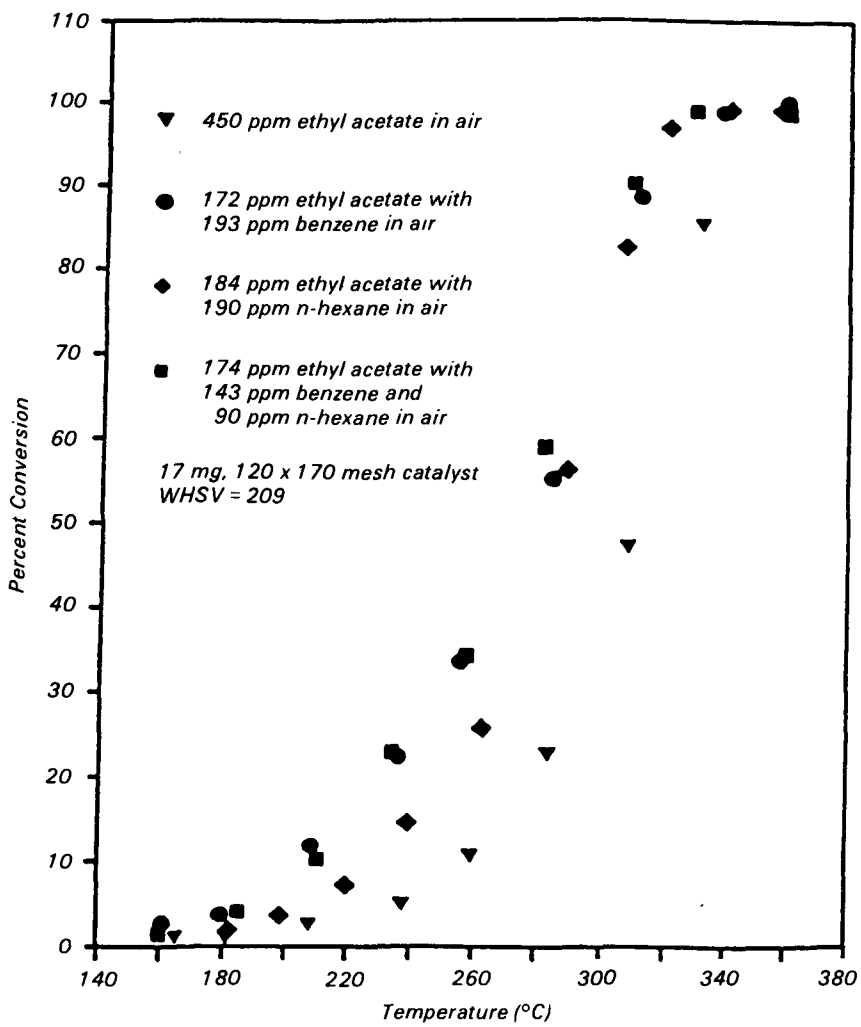


Figure 3. Effect of multicomponent mixtures on ethyl acetate conversion.

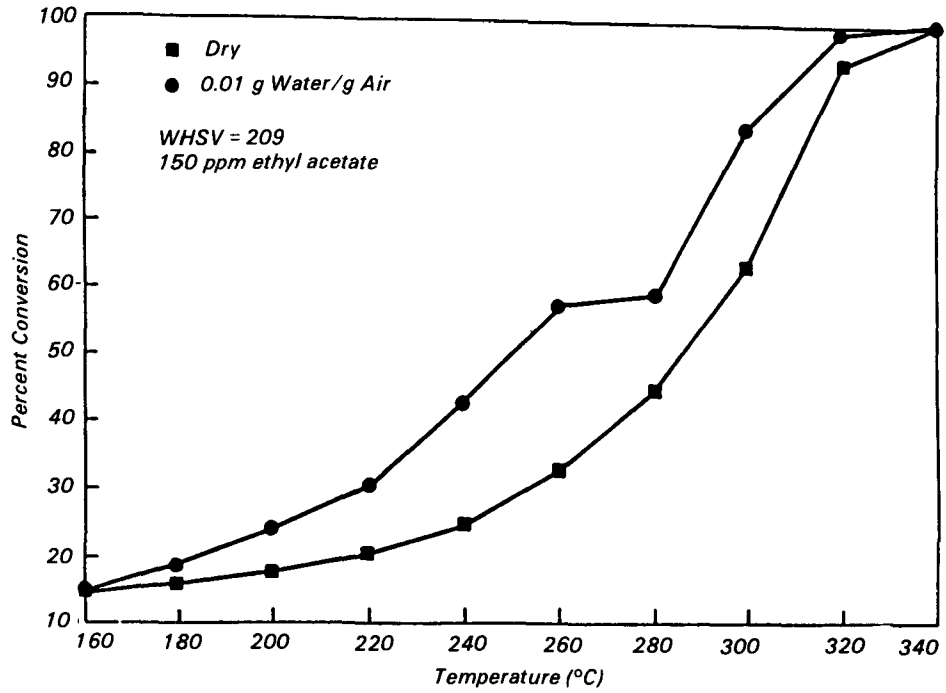


Figure 4. Comparison of ethyl acetate conversions in dry and humidified air streams.

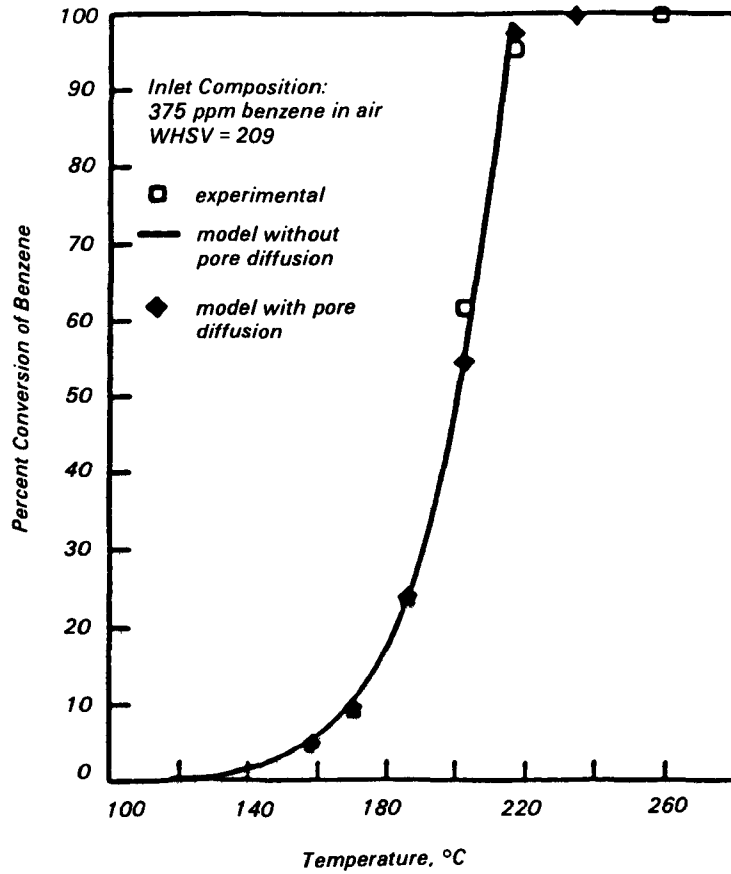


Figure 5. Comparison of model predictions and experimental data for benzene conversion as a single component.