

A CATALYTIC WET OXIDATION PROCESS FOR MIXED WASTE VOLUME REDUCTION/RECYCLING

Patrick M. Dhooge
Delphi Research, Inc.
Albuquerque, New Mexico

ABSTRACT

Mixed wastes have presented a challenge to treatment and destruction technologies. A recently developed catalytic wet oxidation method has promising characteristics for volume reduction and recycling of mixed wastes. The process utilizes iron (III) as an oxidant in the presence of homogeneous cocatalysts which increase organics' oxidation rates and the rate of oxidation of iron (II) by oxygen. The reaction is conducted in an aqueous mineral acid solution at temperatures of 373 - 573°K. The mineral acid should solvate a number of heavy metals, including U and Pu. Studies of reaction rates show that the process can oxidize a wide range of organic compounds including aromatics and chlorinated hydrocarbons. Rate constants in the range of 10^{-7} to 10^{-4} sec⁻¹, depending on the cocatalyst, acidity, type of anions, type of organic, temperature, and time. Activation energies ranged from 25. to 32. KJ/mole. Preliminary measurements of the extent of oxidation which could be obtained ranged from 80% for trichloroethylene to 99.8% for 1,2,4-trimethylbenzene; evidence was obtained that absorption by the fluorocarbon liners of the reaction bombs allowed some of the organics to escape exposure to the catalyst solution. The results indicate that complete oxidation of the organics used here, and presumably many others, can be achieved.

INTRODUCTION

Organic compounds are common matrices for mixed wastes, and many of these mixtures are difficult to handle effectively in present treatment systems. One method which might be used in lieu of present systems is wet oxidation. A recently developed wet oxidation method (1, 2) holds promise for effective treatment of mixed wastes. The method utilizes iron (III) as an oxidant in an aqueous mineral acid solution. A set of homogeneous cocatalysts increase the oxidation rate for organics, and the rate of oxidation of iron (II) to iron (III) by oxygen. Typically, these homogeneous cocatalysts are copper ions and one or more of the ions platinum (IV), palladium (II), and ruthenium (III). The aqueous acid oxidant solution is capable of solvating, containing and concentrating radionuclide metals. Although the method had been used to oxidize common biomass materials such as cellulose, lignin, proteins, starches, urea, and animal fats (3-8), it had not been applied to hazardous organic compounds such as aromatics and chlorinated hydrocarbons, nor had it been applied to petroleum-derived wastes such as used mineral oils. It was felt that it would be valuable to determine the ability of the method to destroy these compounds. The objective of the work described here was to determine the reaction rate constants for the organic components of scintillation fluids, vacuum pump oil, and trichloroethylene over a range of oxidation solution composition and temperature. Preliminary measurements of the extent of oxidation were also made.

EXPERIMENTAL

The reaction vessels for these studies were Parr Instrument Company Model 4749 standard acid digestion bombs, a stainless steel bomb with a fluorocarbon liner. The bombs were heated in a forced convection oven, and cooled using a shallow water bath.

The catalyst solution and other reagents were prepared from "reagent" or "ACS" grade materials and 10 Megaohm-cm deionized water. Samples of Hydrocount™ and Ready Value™ scintillation fluids, and Duoseal™ vacuum pump oil were provided by The University of California Los Alamos

National Laboratory (LANL) and were used as is. Benzene, toluene, and trichloroethylene were all "reagent" grade materials from stock at Delphi Research, Inc. (Delphi). Gases used were all "zero" grade.

For each oxidation the bombs were loaded with 10. ml of the primary catalyst solution, followed by addition of a weighed amount of cocatalyst and a measured amount of the organic. Amounts of organic varied from 1.0 ul to 100. ul and were measured out using micropipettes. Immediately upon addition of the organic the bomb was sealed. The bombs were placed into an oven preheated to the desired temperature. At the end of the allotted reaction time the bombs were removed from the oven and allowed to cool in a shallow (about 1.0 cm) water bath. The bombs were then opened and the oxidant solution titrated for iron (II) and in some cases analyzed for volatiles by gas chromatography.

Iron (II) was titrated with cerium (IV), using 1,10-phenanthroline as an indicator. Gas chromatographic analysis for volatiles was performed by purge-trap technique, using a standard EPA Method 624 packed column and an FID detector. Identification of the residual volatile material was by retention time.

RESULTS

Effect of Cocatalyst and Temperature

Table I lists the results of the rate tests with cocatalysts platinum (IV), ruthenium (III), and palladium (II) at 473°K. All of the reaction rate constant values were calculated from the amount of iron (II) formed in the reaction over a four (4) hour time period. As had been expected, the different cocatalysts are more effective at increasing the oxidation rate of differing types of organics. Platinum (IV) is a more effective cocatalyst with benzene, toluene, trichloroethylene, Hydrocount™ (o-xylene), and the Duoseal™ oil, but does not appear to have much, if any, catalytic effect on the oxidation of Ready Value™ fluid. Palladium (II) has a decided catalytic effect on the oxidation of Ready Value™, and ruthenium (III) has a somewhat lesser catalytic effect on the oxidation of this material.

TABLE I

Reaction Rate Constants for Oxidation of Organics
Oxidation Solution = 0.5 M Fe^{3+} , 1.0 M H_2SO_4
Temperature = 473°K

Organic	$K \cdot 10^6 \text{ SEC}$			
	No Cocatalyst	Pt^{4+}	Ru^{3+}	Pd^{2+}
Benzene	1.2	17.	0.77	2.5
Toluene	2.1	17.	1.7	4.4
TCE	1.9	19.	4.4	8.8
Hydrocount	11.	21.	19.	19.
Ready Value	12.	13.	16.	24.
Duoseal	7.3	22.	6.1	8.2

From the data on reaction rate constants over a range of temperature, average activation energies for the oxidations could be determined. It has been shown previously that the oxidation reaction is first order in iron (III)(9). The calculated average activation energies are given in Table II. These values are consistent with E_A values previously obtained for biomass materials, which have been in the range of 19. to 54. KJ/mole

Effect of Acidity

A brief series of experiments were conducted on the effects of acidity on the organics oxidation rate constants. At 0.2 N hydronium ion concentration there was no decrease in the reaction rates, but there was a significant amount of iron oxide precipitate observed at 473°K. At acidity levels of 10.0 N, reaction rate constants decreased by a factor of 2 to 5 times; a decrease in reaction rate constants at higher acidity is consistent with previous data obtained in the oxidation of biomass compounds.

Effect of Anions

Figure 1 shows plots of the reaction rate constants for the oxidation of benzene and trichloroethylene in the presence of a range of chloride concentrations. The "standard" oxidation solution here is a 1.5 M sulfate solution. For comparison purposes, the rate constants for the standard solution containing 1.0 M phosphate anion are also given. It is of interest to note that although the presence of chloride anion should increase the oxidation potential of iron (III), and thus increase

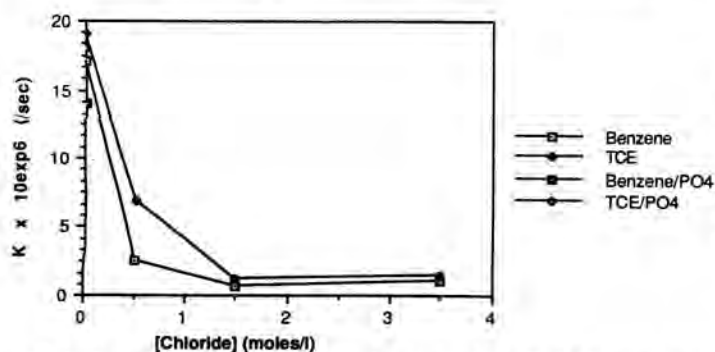


Fig. 1. Reaction rate constant vs [chloride] at 473 K Cocatalyst = platinum (IV).

TABLE II

Average Activation Energies for Oxidation of Organics by Iron (III)

Oxidation Solution = 0.5 M Fe^{3+} , 1.0 M H_2SO_4 , 0.001 M Pt^{4+}	
Organic	E_A (KJ/MOLE)
Benzene	31.
Toluene	32.
TCE	25.
Hydrocount	27.
Ready Value	28.
Duoseal	28.

its ability to oxidize organics, in fact the presence of chloride acts as an inhibiting influence on the oxidation reaction. The chloride anion as a ligand of iron (III) may not be able to transfer electrons as readily as a sulfate ligand. If the effect of the anion is on the iron (III), it would be expected that the same effect would be observed with other cocatalysts, and such is the case. For oxidation of trichloroethylene and Hydrocount™ in the presence of ruthenium cocatalyst, addition of chloride ion resulted in a decrease in the observed oxidation rate. Interestingly, for oxidations of benzene and toluene, where ruthenium had not exhibited a catalytic effect, the rate constants increased slightly; this would indicate that the mechanism which is being affected by chloride ion is the transfer of an electron from the cocatalyst complex (or the cocatalyst/organic complex) to the iron (III) complex.

Effect of the Ratio of Iron (III) to Iron (II)

A set of experiments were performed where the reaction times were one 1) and two 2) hours, to limit the amount of iron (III) consumed during the reaction. The ratio of iron (III) to iron (II) did not seem to have any noticeable effect on the rate constants over the range of ratios used. Of particular interest in these experiments are the rate constants for oxidation of benzene, toluene, and trichloroethylene over time. As shown in Fig. 2, all three compounds show an increase in reaction rate at longer reaction times, despite the reduction in oxidizing power of the solution over time. The increases in reaction rates at longer times can be attributed to the production of more reactive oxidation intermediates; during the oxidation of organics by the iron (III) solution, there will be a series of intermediates produced having progressively greater extents

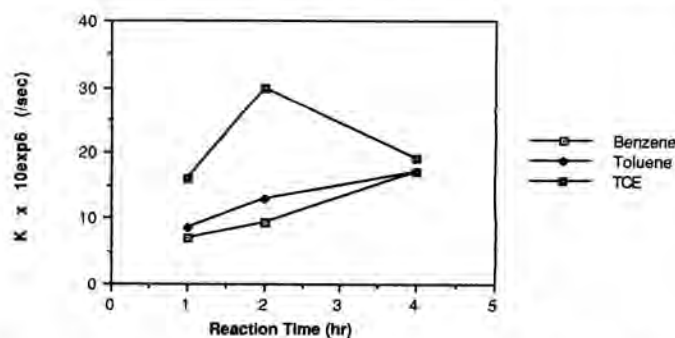


Fig. 2. Reaction rate constant vs reaction time at 473 K Cocatalyst = platinum (IV).

of oxidation and in many cases being progressively more reactive.

Preliminary Oxidation Efficiency Tests

Of crucial importance for any proposed hazardous organics destruction process is the ability of the process to achieve a high degree of destruction. Although previous experimental studies with biomass had shown apparent complete oxidation to carbon dioxide, no studies had been performed on more chemically stable compounds such as benzene or trichloroethylene, and no studies had looked for residual organics (either the parent compound or intermediates) after oxidation. It must be stressed here that these preliminary experiments were not designed to certify destruction efficiencies; what was desired was to demonstrate that the oxidation reaction did not stop at some point short of carbon dioxide, and that oxidation of most of the organic could be achieved.

The extent of oxidation was measured in two ways. The amount of iron (II) titrated after oxidation gave an approximate measure of the amount of oxidation which had taken place. The analysis of the post-oxidation solutions by gas chromatography gave a measure of any residual organics. The results are given in Table III.

It was found that for the iron (II) titration values of 100% oxidation were achieved for all compounds tested except trichloroethylene. Gas chromatographic analysis of the residues did not agree well with the iron (II) measurements for oxidation of benzene, toluene, and trichloroethylene. It was discovered that amounts of these more volatile organics had been absorbed into the fluorocarbon liners of the reaction bombs during previous experiments and were leaching into the oxidation solution during cooling.

Despite the problems encountered with absorbed organics in the reaction bomb liners, it is clear from the results obtained that complete oxidation to carbon dioxide is achieved for a variety of organic compounds in the oxidant solution.

CONCLUSIONS

All of the organic compounds or mixtures studied here can be completely oxidized at practical rates by the oxidation process studied here. The effects of different cocatalysts indicate that a mixture of cocatalysts may be appropriate for destroying multiple organic materials. Temperatures in the range of 473 - 523⁰K should be appropriate for an operating destruction system. At this present state of development, a 100 liter reactor would be capable of destroying 50 - 400 g/hr of organic materials. Although chloride ion was found to reduce the oxidation reaction rate constants, it is a more desirable anion for application to mixed wastes, since U and Pu chlorides are soluble. The effect of chloride anion needs to be investigated further, as does the solubility of radionuclide metals in the solution. More accurate values need to be obtained for the organics destruction efficiency of the solution.

TABLE III

Results of Preliminary Efficiency Measurements for Oxidation of Organics by Iron (III)

Oxidation Solution = 0.5 M Fe ³⁺ , 1.0 M H ₂ SO ₄ , 0.001 M Pt ⁴⁺ Temperature = 473°K, Reaction Time = 24 Hours		
Organic	%Oxidation (Fe ²⁺ Titration)	% Oxidation (GC Analysis)
Benzene	100.	81.
Toluene	100.	86.
TCE	87.4	80.
Hydrocount	100.	99.8
Ready Value	100.	99.1
Duoseal	100.	---

REFERENCES

1. United States Patent Number 4,925,540, "Method For Treating Organic Waste Material and an Oxidation Catalyst/Cocatalyst Composition Useful Therefor".
2. United States Patent Number 5,047,224, "Method For Treating Organic Waste Material and an Oxidation Catalyst/Cocatalyst Composition Useful Therefor".
3. "Hydrogen Production With The Electrocatalytic Oxidation System", Patrick M. Dhooge and Linda A. Henson, New Mexico Research and Development Institute Report NMRDI 2-73-4633, Santa Fe, NM, June, 1986.
4. "Final Report - Electrocatalytic Waste Reactor Phase II", Delphi Research, Inc., United States Air Force Report Number BMO-TR-87-101, December, 1987.
5. "An Electrocatalytic Waste Processing System For Closed Environments", Patrick M. Dhooge, Proceedings of the Eighth Princeton/AIAA/SSI Conference, Princeton, NJ, May, 1987.
6. "Infectious Waste Oxidation Using The HyPECOS Process", Nancy G. Drez, Terry W. Rogers, and Patrick M. Dhooge, New Mexico Research and Development Institute Report Number NMRDI 2-77-5617, Santa Fe, NM, November, 1989.
7. "Hydrogen Recovery From Organic Wastes By HyPECOS", Terry W. Rogers and Patrick M. Dhooge, Studiedag: Mesterwerking. Hoe En Hoeveel Kost Het?, Technologisch Instituut - K VIV, Antwerpen, Belgium, October, 1990
8. "Electrocatalytic Hydrogen Recovery From Organic Wastes", Patrick M. Dhooge, Proceedings of the National Hydrogen Association Second Annual U.S. Hydrogen Meeting, Washington, DC, March, 1991.
9. P.M. DHOOGHE, D.E. STILWELL, and S.-M. PARK, Journal of The Electrochemical Society, 129, 1719 (1982), also P.M. Dhooge and S.-M. Park, *ibid.*, 130, 1029 (1983).