

Treatment of Methyl Tertiary-Butyl Ether (MTBE)-Contaminated Waters with Fenton's Reagent

Asim B. Ray, Ariamalar Selvakumar, and Anthony N. Tafuri
Urban Watershed Management Branch
United States Environmental Protection Agency
2890 Woodbridge Avenue
Edison, NJ 08837

ABSTRACT

Methyl tertiary-butyl ether (MTBE) has been commonly used as a fuel additive because of its many favorable properties that allow it to improve fuel combustion and reduce resulting concentrations of carbon monoxide and unburnt hydrocarbons. Unfortunately, increased production and use have led to its introduction into the environment. Of particular concern is its introduction into drinking water supplies. Accordingly, research studies have been initiated to investigate the treatment of MTBE-contaminated soil and water. In this study, experiments were conducted to demonstrate the effectiveness of Fenton's reagent ($\text{H}_2\text{O}_2:\text{Fe}^{+2}$) to treat MTBE-contaminated groundwater. The concentration of MTBE was reduced from an initial concentration of 1,300 F g/L (14.77 F moles) to the regulatory level of 20 F g/L (0.23 F moles) at a $\text{H}_2\text{O}_2:\text{Fe}^{+2}$ molar ratio of 1:1, with 10 minutes of contact time and an optimum pH of 5. The byproducts, acetone and tertiary butyl alcohol, always present in MTBE in trace amounts, were not removed even after 60 minutes of reaction time.

INTRODUCTION

Several oxygenates have been used in the United States since the 1970s as octane-enhancing replacements for tetraethyl lead. These include ethanol, methanol, ethyl tertiary-butyl ether (ETBE), and tertiary-butyl alcohol (TBA) as well as methyl tertiary-butyl ether (MTBE). MTBE is the most commonly used fuel oxygenate because of its many favorable properties, including low production cost, ease of production, high octane rating, and favorable transfer and blending characteristics (Ainsworth, 1992; Shelly and Fouhy, 1994). The addition of MTBE to gasoline improves fuel combustion and reduces the resulting concentrations of carbon monoxide and unburnt hydrocarbons. The use of MTBE in gasoline at levels in excess of 10% by volume began in November 1992 when the requirements of the 1990 Clean Air Act Amendments (CAAA) mandated the use of oxygenated gasoline during the winter to help meet standards for carbon monoxide emissions. Furthermore, since January 1995, the CAAA also required nine metropolitan areas that have the most severe ozone pollution to use, year-round, reformulated gasoline that contains fuel oxygenates. Accordingly, MTBE was added to about 30% of the gasoline nationwide at an average concentration of about 11% by volume (USEPA, 1994). Since 1993, MTBE has been the second most produced organic chemical manufactured in the United States (USEPA, 1998).

The increased production and physical properties of MTBE have led to its introduction into the environment. MTBE can enter the environment in several ways: leaks from above- and below ground storage and conveyance facilities, incomplete combustion in internal combustion engines, spillage and evaporation during the manufacture and transportation of MTBE and gasoline containing MTBE, and watercraft exhaust (especially from two-cycle engines). MTBE has been detected both in groundwater (Squillace *et al.*, 1996) and stormwater (Delzer *et al.*, 1996). Of the 60 volatile organic compounds (VOCs) analyzed in samples of shallow ambient groundwater collected from eight urban areas during 1993 to 1994, as a part of the United States Geological Survey's National Water-Quality Assessment Program, MTBE was the second most, after trichloromethane, frequently detected compound.

Both the physical and chemical properties of MTBE control its fate in the environment. MTBE is a liquid with a molecular weight of 88 and a boiling point of 55°C under atmospheric pressure. It is soluble in all common solvents and is highly soluble in water (~50 g/L or 575 F moles). Therefore, MTBE is highly mobile, undergoing little or no retardation as it travels through a groundwater system. MTBE, through co-solvent effects, increases the solubility of other petroleum derivatives, such as benzene, toluene, ethyl benzene, and total xylenes (Schrimmer and Barker, 1998). It is resistant to biological degradation with a half-life of 10,000 days (27 years). Laboratory studies have shown that MTBE is recalcitrant to all forms of aerobic as well as anaerobic biodegradation, key components in the natural attenuation process (Vance, 1998).

The U.S. Environmental Protection Agency has tentatively classified MTBE as a possible human carcinogen and has issued a drinking water advisory, based on taste and odor thresholds, of 20 µg/L (0.23 F moles) (USEPA, 1997).

Treatment of MTBE

A number of techniques have been investigated for the remediation of MTBE from aqueous media. Because of MTBE's low Henry's law constant and high water solubility, air stripping (a routine practice for the removal of volatile organic compounds from groundwater) is unsatisfactory for MTBE removal. In addition, the process produces contaminated air byproducts that require further treatment.

Biodegradation of MTBE has also been explored. In a study by Eweis *et al.* (1997), a culture capable of degrading MTBE, both as a fixed film on a solid matrix and in liquid culture, was isolated from a bio-filter from the County Sanitation District of Los Angeles County Joint Water Pollution Control Plant in Carson, California. Another aerobic microbe consortium capable of biodegrading MTBE was isolated from two waste air bio-trickling filters (Fortin and Discusses, 1999). Further studies are, however, needed to assess the feasibility of biodegradation of MTBE-contaminated aqueous media. Natural attenuation of MTBE, although intrinsically feasible, is a very slow process (Schrimmer and Barker, 1998) and may not be suitable for situations where immediate corrective action is required.

In a study by Tornatore *et al.* (2000a), both granulated activated carbon (GAC) and synthetic adsorbents (Ambersorb 563 and Ambersorb 572– Rohm and Haas) were evaluated for their ability to remove MTBE from drinking water. Because of its electrophilic nature, MTBE is weakly adsorbed by GAC and consequently requires larger quantities of GAC for removals equivalent to other organic pollutants such as trichloroethylene (TCE). Montgomery Watson (1996) observed that using activated carbon to remove MTBE from aqueous streams is about 21 times more expensive than removing the same mass of TCE. Although the synthetic adsorbents performed better than activated carbon, they are 5 to 10 times more expensive than GAC. Consequently, the use of GAC or other synthetic adsorbents is not practical for the treatment of large volumes of MTBE-contaminated water.

Chemical oxidation is an efficient technique for the remediation of organic compounds. It is the most practical and effective way to convert, in aqueous media, organic compounds such as MTBE into innocuous carbon dioxide and water. The relevant oxidation techniques can be broadly sub-divided into:

- chemical oxidizing agents;
- chemical oxidizing agents with a catalyst;
- irradiation; and
- irradiation with a chemical oxidizing agent.

Chang and Young (1998) evaluated the chlorination (sodium hypochlorite) of MTBE-contaminated water at pH 4 and 7 and found that even after 24 hours of contact, there was no significant reduction in MTBE concentration. The same authors also found that using hydrogen peroxide or UV radiation alone did not result in a significant reduction in MTBE.

Farooq *et al.* (1993) used a high energy electron beam to disinfect wastewaters containing raw sewage. The disinfection mechanism involved the generation of the hydroxyl radical (OH^\bullet) by the photolysis of water:



The hydroxyl radical is one of the most powerful oxidizing chemicals known. Tornatore *et al.* (2000b) used this technique in their studies on the reduction of MTBE in water from deep water wells. Greater than 99% reduction of MTBE was achieved with initial concentrations of 170 and 196 $\mu\text{g/L}$ (1.96 and 2.25 μmoles) and a pH between 7.7 and 8.8. The MTBE reduction was found to be dose-dependent and the major byproducts tert-butyl formate (TBF) and TBA were present in small quantities.

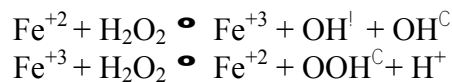
Barreto *et al.* (1995) investigated the photo-catalytic degradation of MTBE. Several reaction products including TBF, TBA, acetone, and acetic and formic acids, in addition to gaseous CO_2 , were identified. A small quantity of α -hydroperoxy methyl-tert-butyl ether was tentatively identified. An exposure of 4 hours was needed to completely degrade an aqueous

solution containing MTBE at a concentration of 88 mg/L (1.012 F moles). Complete elimination of TBF, TBA, and acetone required 10 hours of reaction time.

The reaction of aqueous MTBE with the hydroxyl radical generated by UV/H₂O₂ was investigated by Carter *et al.* (2000). Results indicated that the rate of destruction of MTBE is influenced by the initial concentrations of both hydrogen peroxide and MTBE. In all cases, the decay of MTBE was found to follow first-order reaction kinetics with a pseudo first-order rate constant, k_1 . The value of k_1 increased as the concentration of MTBE decreased. Byproducts of the UV/H₂O₂ degradation of MTBE were found to be TBF, TBA, methyl acetate, acetone, a peroxy compound, formaldehyde, alkanes, and acetic and formic acids (Stefan *et al.*, 2000). A 4-hour reaction time was required to remove 86.9 mg/L (1 milli mole) of MTBE, and after 10 hours, approximately 85% of the initial organic carbon was mineralized.

Fenton's Reagent

Many metals have special oxygen transfer properties which improve the utility of H₂O₂. By far, the most common of these is iron which, when used in a prescribed manner, results in the generation of highly reactive OH[•]. The reactivity of this system was first observed in 1894 by its inventor H.J.H Fenton. The chemistry involved in the generation of OH[•] by the Fenton's reagent can be summarized by the following equations:



The procedure requires:

- adjusting the wastewater to a pH of 3 to 5;
- adding the iron catalyst (as a solution of FeSO₄); and
- adding the H₂O₂ slowly.

Fenton's reagent is used to treat a variety of industrial wastes containing a range of toxic organic compounds (phenols, formaldehyde, BTEX, and complex wastes derived from dyestuffs, pesticides, wood preservatives, plastic additives, and rubber chemicals). The process may be applied to wastewaters, sludges, or contaminated soils, with the effects being:

- organic pollutant destruction;
- toxicity reduction;
- biodegradability improvement;
- BOD/COD removal; and
- odor and color removal.

OBJECTIVE

The overall objective of this study was to determine the optimum conditions for using the OH[•] radical to treat MTBE-contaminated waters frequently found at “hot spots” such as fueling depots, petro-chemical facilities, parking lots and garages, and gasoline stations. These contaminated streams are often carried by stormwater runoff via combined and separate stormwater sewers to drinking water sources. Because of the potential contamination and the volume of water involved, a fast, efficient, and cost-effective technology is needed. Early studies (Barreto *et al.*, 1995; Carter *et al.*, 2000; Stefan *et al.*, 2000; Ray and Selvakumar, 2000) suggest that OH[•] radicals generated by Fenton’s reagent are capable of treating MTBE contaminated waters quickly and effectively. However, major byproducts such as TBA, TBF, and acetone, and small quantities of 2-methyl-1-propene (isobutylene) have been identified in some studies (Ray and Selvakumar, 2000). Because of the potential end-use of these waters, the MTBE content must be at or below 20 mg/L (0.23 mg moles) and free from major byproducts. Therefore, a secondary objective of the study was to monitor, over time, the concentrations of the reported major byproducts of the treatment as well as their subsequent degradation by the OH[•] radical.

EXPERIMENTAL DESIGN

Reagents and Materials

All chemicals used in the study were of American Chemical Society analytical grade or better.

Apparatus

A 3-necked septum-fitted flask (1.5-L capacity) with various attachments (Exhibit 1) was used for this study. Using a syringe, reagents were introduced into the center neck; pH samples and other samples for analysis were withdrawn through the outer necks. A magnetic bar was used to agitate the liquid reagent mixture. Gas samples were collected through the gas sampling port.

Analytical Methods

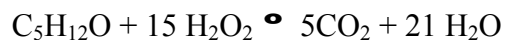
- MTBE and its degradation products were analyzed by USEPA Method 624. The GC/Mass system used consisted of a HP 5890 Series II GC with a Model 5971A mass spectrometer.
- Organic acids (formic and acetic) were analyzed by USEPA Method 300 using a

Dionex DX-100 ion chromatograph equipped with a column (AS4-A) for separation.

- H₂O₂ was analyzed by a HACH (Model 5000) scanning spectrometer at a wavelength of 276 nm. Hydrogen peroxide strongly absorbs at this wavelength; neither NaHSO₃ nor any other analyte of interest has any absorption at this wavelength.
- The CO₂ that evolved was analyzed by gas chromatography using a thermal conductivity detector. The volume of gases collected was measured by a gas burette as shown in Exhibit 1.
- All calibrations were carried out with a five-point calibration procedure.

Experimental Procedure

A total of twelve experiments was performed to determine the optimum pH, Fe⁺² to H₂O₂ ratio, and contact time for the degradation of MTBE without major byproducts. Reaction stoichiometry of these tests was based on the assumption that complete mineralization of MTBE takes place according to the equation:



In all cases the total volume of the reactants was 1 L. One liter of deionized water was added to the flask and purged with oxygen-free nitrogen gas to remove all air and any dissolved oxygen from the system. Predetermined quantities of MTBE, FeSO₄ solution, and H₂O₂ from stock solutions, were sequentially added to the flask. Prior to the addition of H₂O₂, the pH of the reaction medium was adjusted by either a dilute sulfuric acid or sodium hydroxide solution. Liquid samples for analyses were withdrawn from the flask every five minutes over a period of 1 hour. Excess NaHSO₃ solution was added to the collected samples to remove any residual H₂O₂ and to prevent further reaction. The samples were then cooled to 4⁰C and analyzed for MTBE and byproducts. The quantity of H₂O₂, CO₂, and O₂ was determined at the beginning and end of each experiment. All H₂O₂ and pH measurements were conducted before the addition of NaHSO₃ solution.

The initial concentration of MTBE, in most cases, was approximately 1,300 F g/L (14.77 μ moles). Because of an earlier observation that MTBE reduction by the Fenton's reagent appeared to depend on the H₂O₂:Fe⁺² molar ratio (Ray and Selvakumar, 2000), the ratio of these chemicals was also varied in the study. The quantity of H₂O₂ used in all cases was the same; i.e., twice the amount specified in the above equation. All reactions were carried out at three different pH values of 3, 5, and 7. The reaction conditions are summarized in Exhibit 2.

Reasons for this approach are as follows:

- Contaminated groundwater often contains organic matter which can consume H_2O_2 and thereby affect the concentration of H_2O_2 in the Fenton's reagent. Hence,

the effect of varying the $\text{H}_2\text{O}_2:\text{Fe}^{+2}$ ratio of the efficiency of Fenton's reagent in removing MTBE was investigated.
- Although Fenton's reagent works best in strongly acidic media (pH 2 to 4), it is somewhat impractical to lower the groundwater pH to such a low value. Because of this, additional tests were performed at more natural pH values of 5 and 7.

As previously mentioned, a total of twelve tests were conducted; however, details of only those tests in which significant amounts of MTBE reduction occurred are discussed.

RESULTS

Test Series A ($\text{H}_2\text{O}_2:\text{Fe}^{+2} = 0.1:1$)

In Test Series A, it was observed that the reaction of MTBE with Fenton's reagent was pH dependent. At pH ~3, the MTBE concentration was reduced by 75% after 20 minutes of reaction time. At the end of one hour, the initial MTBE concentration was reduced by 82% from 1,367 to 251 F g/L (15.53 to 2.85 F moles). The byproducts, at the end of one hour, were acetone (33.64 F g/L or 0.58 F moles), TBA (7.4 F g/L or 0.10 F moles), and TBF (10.2 F g/L or 0.10 F moles). Although both formate and acetate ions were detected after 10 minutes of reaction they disappeared after 30 minutes. The highest concentration of formate ions (286.2 F g/L or 6.36 F moles) and acetate ions (404.15 F g/L or 6.85 F moles) were observed at 20 and 30 minutes, respectively. In addition to the above compounds, 58.96 F g (1.34 F moles) of CO_2 gas were produced. The pH of the mixture also decreased from the initial value of 2.9 to a final value of 2.4. No residual H_2O_2 was detected at the end of the reaction. These results are shown in Exhibits 3 and 4. No significant change in MTBE concentration, however, was observed when the reaction was carried out either at pH 5 or 7.

Test Series B ($\text{H}_2\text{O}_2:\text{Fe}^{+2} = 1:1$)

In contrast to Test Series A, Test Series B exhibited a rapid reduction in MTBE concentration at pH 5. MTBE concentration was reduced by 99% within five minutes of reaction. After 10 minutes, no detectable amount of MTBE was found. These results are shown in Exhibit 5 and graphically represented in Exhibit 6. No significant change in MTBE concentration occurred when the oxidation reaction was carried out at pH 3 and 7.

Test Series C and D ($\text{H}_2\text{O}_2:\text{Fe}^{+2} = 10:1$ and $100:1$)

In Test Series C and D, no significant change in MTBE concentration occurred at any of the three pH values of 3, 5, and 7.

DISCUSSION

This study demonstrated that Fenton's reagent was successful in reducing MTBE concentration in water from approximately 1,300 F g/L (14.77 F moles) to the proposed regulatory level of 20 F g/L (0.23 F moles) or lower without generating significant amounts of undesirable byproducts. This reduction was achieved with a contact time of 10 minutes or less. The reaction was found to be dependent both on the pH of the reaction medium and on the ratio of $\text{H}_2\text{O}_2:\text{Fe}^{+2}$ in the Fenton's reagent.

These findings are in contrast to some of the earlier studies. Wagler and Malley (1994) found that pH had only a minor role in UV/ H_2O_2 treatment of MTBE in low-alkalinity groundwater. Yeh and Novak (1995) found that the oxidation process using Fenton's reagent is influenced by pH, H_2O_2 concentration, and the presence of Fe^{+2} , but is independent of the iron concentration. This disagreement is probably due to the different methods used to generate OH^\bullet radicals. In the UV/ H_2O_2 process, the OH^\bullet radical is generated by the photocatalysis of H_2O_2 ($\text{H}_2\text{O}_2 + h\nu \rightarrow 2 \text{OH}^\bullet$) and hence is independent of the pH of the medium.

A drop in pH of the reaction medium during the progress of the reaction was also reported in the photocatalytic degradation of MTBE in TiO_2 slurries (Barreto *et al.*, 1995). This drop in pH, which agrees with the results of this study, was attributed to the formation of formic and acetic acid byproducts.

Observations of Barreto *et al.* (1995) that the oxidation of MTBE by H_2O_2 and Fe^{+2} iron is independent of iron concentration are also in contrast to previous findings (Ray and Selvakumar, 2000) and the findings of the present study. Optimum conditions for generating the OH^\bullet radical by Fenton's reagent requires not only acid conditions but also a molar ratio of $\text{H}_2\text{O}_2:\text{Fe}^{+2}$ of 1:1 (Fischer and Fisher). The most rapid oxidation of MTBE was achieved in this study using Fenton's reagent with a 1:1 ratio of $\text{H}_2\text{O}_2:\text{Fe}^{+2}$. However, the inability of Fenton's reagent to oxidize MTBE with this molar ratio at pH 3 requires further study, especially in view of the fact that Fenton's reagent with a 0.1 to 1 ratio of $\text{H}_2\text{O}_2:\text{Fe}^{+2}$ was able to achieve a substantial and fairly rapid reduction of MTBE at pH ~3 (Exhibit 3).

Of the byproducts studied (Exhibits 4 and 6), only the concentration of acetone remained almost constant during the 60-minute time periods of the reaction. Both formate and acetate ions reached their peak concentrations at 20 and 25 minutes of the reaction, respectively, and disappeared shortly thereafter. TBA and TBF, although in small concentrations, persisted after

60 minutes of reaction. Incomplete mineralization of these byproducts is probably due to the lack of the necessary amount of H₂O₂ since no residual amount of it was found at the end of the reaction. During the reaction, a total volume of 186.56 F g/L (4.24 F moles) of CO₂ gas evolved.

Results of this study indicate that any significant change in MTBE concentration is always accompanied by the evolution of a substantial quantity of CO₂ gas, formation of acetone and TBF, and loss of TBA (almost always present as an impurity in MTBE). Conversely, in all cases where no significant change in MTBE concentration occurred, no change in the concentrations of the original impurities (acetone, TBF, and TBA) present in MTBE nor any evolution of CO₂ was observed. The byproducts, acetone and TBA could not be removed even after 60 minutes of reaction time. Other byproducts such as formates and acetates, although originally absent, appeared after 10 minutes of reaction but disappeared after 40 minutes.

CONCLUSION

Fenton's reagent can be used to remediate, at ambient temperature, MTBE-contaminated groundwater. MTBE concentration was reduced from an initial concentration of 1,300 F g/L (14.77 F moles) to the regulatory limit of 20 F g/L (0.23 F moles) or less. This study established that this can be achieved by Fenton's reagent under the following conditions:

- H₂O₂:Fe⁺² molar ratio of 1:1 in Fenton's reagent
- Reaction pH of 5
- Contact time less than 10 minutes

Evolution of CO₂ confirmed mineralization of MTBE and other byproducts. A drop in pH and evolution of CO₂ can be used as an indication of the progress of the mineralization of MTBE.

REFERENCES

- Ainsworth, S. 1992. Oxygenates Seen as Hot Market by Industry. *Chemical Engineering News*, Vol. 70, pp. 26-30.
- Barreto, R.D., K.A. Gray, and K. Anders. 1995. Photo-catalytic Degradation of Methyl-tert-Butyl Ether in TiO₂ Slurries: A Proposed Reaction Scheme. *Water Res.*, Vol. 29, No.5 pp. 1243-1248.
- Carter, S.R., I. Stefan Mihaela, J.R. Bolton, and A. Safarzadeh-Amiri. 2000. UV/H₂O₂ Treatment of Methyl-tert-Butyl Ether in Contaminated Waters. *Environ. Sci. Technol.*, Vol. 34, pp. 659-662.
- Chang, P. and T. Young. 1998. Reactivity and By-products of Methyl Tertiary Butyl Ether

Resulting from Water Treatment Processes. Report to the California State Legislature under S.B. 521, Volume V. University of California, Davis. Civil and Environmental Engineering.

Delzer, G.C., J.S. Zogorski, T.J. Lopes, and R.L. Bosshart. 1996. Occurrence of the gasoline oxygenate MTBE and BTEX compounds in urban storm water in the United States, 1991-95.

U.S. Geological Survey Water Resource Investigations Report No. 96-4145.

Eweis, J. B., D.P.Y. Chang, E.D. Scroder, K.M. Scow, R.L. Morton, and R.C. Caballero. 1997. Meeting the Challenge of MTBE Biodegradation. Air & Waste Management Association's 90th Annual Meeting & Exhibition, June 8-13, Toronto, Ontario, Canada.

Farooq, S., C.N. Kurucz, T.D. Waite, and W.J. Cooper. 1993. Disinfection of Waste waters: High-Energy Electron Vs. Gamma Irradiation. *Water Res.*, Vol. 27, No.7. pp. 1177-1184.

Fischer, L.F. and M. Fisher. Reagents for Organic Synthesis. John Wiley and Sons.

Fortin, N.Y. and M.A. Discusses. 1999. Treatment of Methyl-tert-Butyl Ether Vapors in Biotrickling Filters. 1. Reactor Startup, Steady-State Performance, and Culture Characteristics. *Environ. Sci. Technol.*, Vol. 33, pp. 2980-2986.

Montgomery Watson. 1996. Treatment Alternatives for MTBE in Ground Water. Applied Research Department. Technology Transfer Note No. 11.

Ray, A.B. and A. Selvakumar. 2000. Treatment of MTBE Using Fenton's Reagent. *Remediation*, Vol. 10, No. 3, pp. 3-13.

Schrimer, M., and J.F. Barker. 1998. A Study of long-term MTBE attenuation in the Borden aquifer, Ontario, Canada. *Ground Water Monitoring and Remediation*, Vol. 8, No. 2, pp. 113-112.

Shelly, S. and K. Fouhy. 1994. The Drive for Cleaner Burning Fuel. *Chemical Engineering*, Vol. 101, No. 1, pp. 61-63.

Squillace, P.J., J.S. Zogorski, W.G. Wiber, and C.V. Price. 1996. Preliminary Assessment of the Occurrence and Possible Sources of MTBE in Groundwater in the United States, 1993-1994. *Environ. Sci. Technol.*, Vol. 30, pp. 1721-1730.

Stefan M.I., J. Mack, and J.R. Bolton. 2000. Degradation Pathways During the Treatment of Methyl-tert- Butyl Ether by the UV/H₂O₂ Process. *Environ. Sci. Technol.*, Vol. 34, pp. 650-658.

Tornatore, P.M., S.E. Powers, W.J. Cooper, and E.G. Isacoff. 2000a. Synthetic Adsorbents Show Promise for Removing MTBE from Drinking Water. *Water Online*. June 28.

Tornatore, P.M., S.E. Powers, W.J. Cooper, and E.G. Isacoff. 2000b. High Energy Electron Injection System Destroys MTBE in Drinking Water. *Water Online*. July 28.

USEPA. 1994. Health Risk Perspectives on Fuel Oxygenates. EPA/600/R-94/217. Office of Research and Development, Washington, D.C.

USEPA. 1997. "Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl tertiary-Butyl Ether (MTBE)." EPA 822-F-97-008. Office of Water, Washington, D.C. December.

USEPA. 1998. MTBE Fact Sheet #3. Use and Distribution of MTBE and Ethanol. EPA/510-F-97-016. Office of Solid Waste and Emergency Response.

Vance, D.B. 1998. MTBE: Character in Question. *Environmental Technology*. January/February.

Wagler, J.L. and J.P. Malley. 1994. *J. N. Engl. Water Works Assoc.*, Vol. 108, pp. 236.

Yeh, C.K. and J.T. Novak. 1995. The effect of hydrogen peroxide on the degradation of methyl and ethyl tert-butyl ether in soils. *Water Environment Research*, Vol. 67, No.5, pp. 828-834.

About the Authors

Dr. Asim B. Ray is a Technical Scientist with the Senior Environmental Employee Program with the USEPA, National Risk Management Research Laboratory, Water Supply and Water Resources Division, Urban Watershed Management Branch, 2890 Woodbridge Avenue, Edison, NJ 08837. Dr. Ariamalar Selvakumar and Mr. Anthony Tafuri are Environmental Engineer and Senior Environmental Engineer, respectively, with the same Branch.

Disclaimer

Although the research described in this article has been funded wholly by the USEPA through Contract No. 68-C7-0008, it has not been subjected to the Agency's peer review. Therefore, it does not necessarily reflect the views of the Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Exhibit 1. Schematic Diagram of Experimental Apparatus

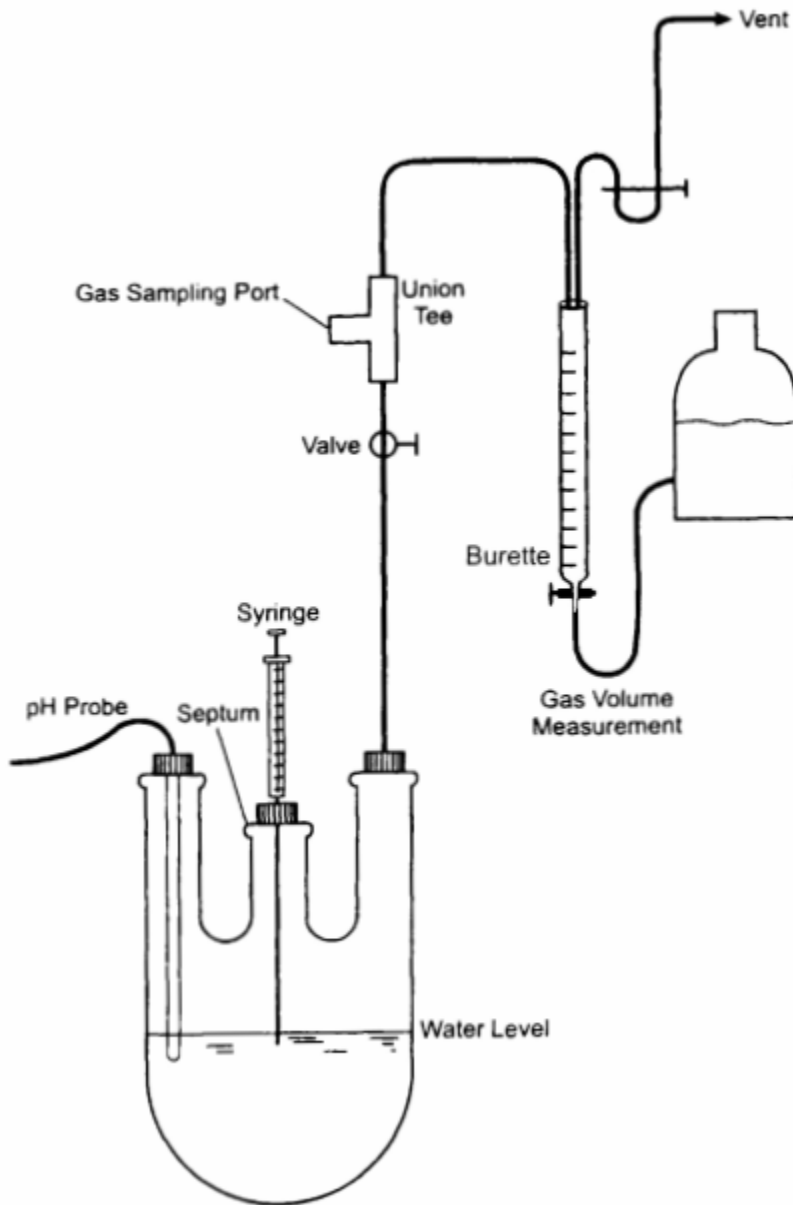


Exhibit 2. Test Conditions for MTBE Degradation

Test Designation	H ₂ O ₂ :Fe ⁺² (molar ratio)	pH
A	0.1:1	3, 5, 7
B	1:1	3, 5, 7
C	10:1	3, 5, 7
D	100:1	3, 5, 7

Exhibit 3. Test Series A: $\text{H}_2\text{O}_2:\text{Fe}^{+2} = 0.1:1$; pH 2.9 to 2.4

Time (minutes)	MTBE (F moles)	Acetone (F moles)	TBA (F moles)	TBF (F moles)	Formate (F moles)	Acetate (F moles)
0	15.53	0.19	0.49	0.05	ND	ND
5	NA	0.42	0.63	0.08	ND	ND
10	3.61	0.47	0.21	0.01	2.22	3.05
15	NA	0.56	0.39	0.05	0.67	3.56
20	3.77	0.56	0.30	0.01	6.36	1.59
25	3.41	0.55	0.22	0.01	4.36	5.08
30	3.17	0.51	0.20	0.01	4.53	6.85
35	3.16	0.51	0.20	0.01	1.51	ND
40	2.85	0.46	0.18	0.01	ND	ND
45	2.88	0.47	0.19	0.01	ND	ND
50	3.23	0.56	0.20	0.01	ND	ND
55	3.39	0.57	0.22	0.01	ND	ND
60	2.85	0.48	0.01	0.01	ND	ND

At the end of the reaction 1.34 F moles of CO_2 gas was collected.

NA = not analyzed.

ND = not detected.

Note: Testing at pH 5 and 7 showed no significant change in MTBE concentrations.

Exhibit 4. Change in MTBE/MTBE Byproducts Concentrations with Time (Test Series A)

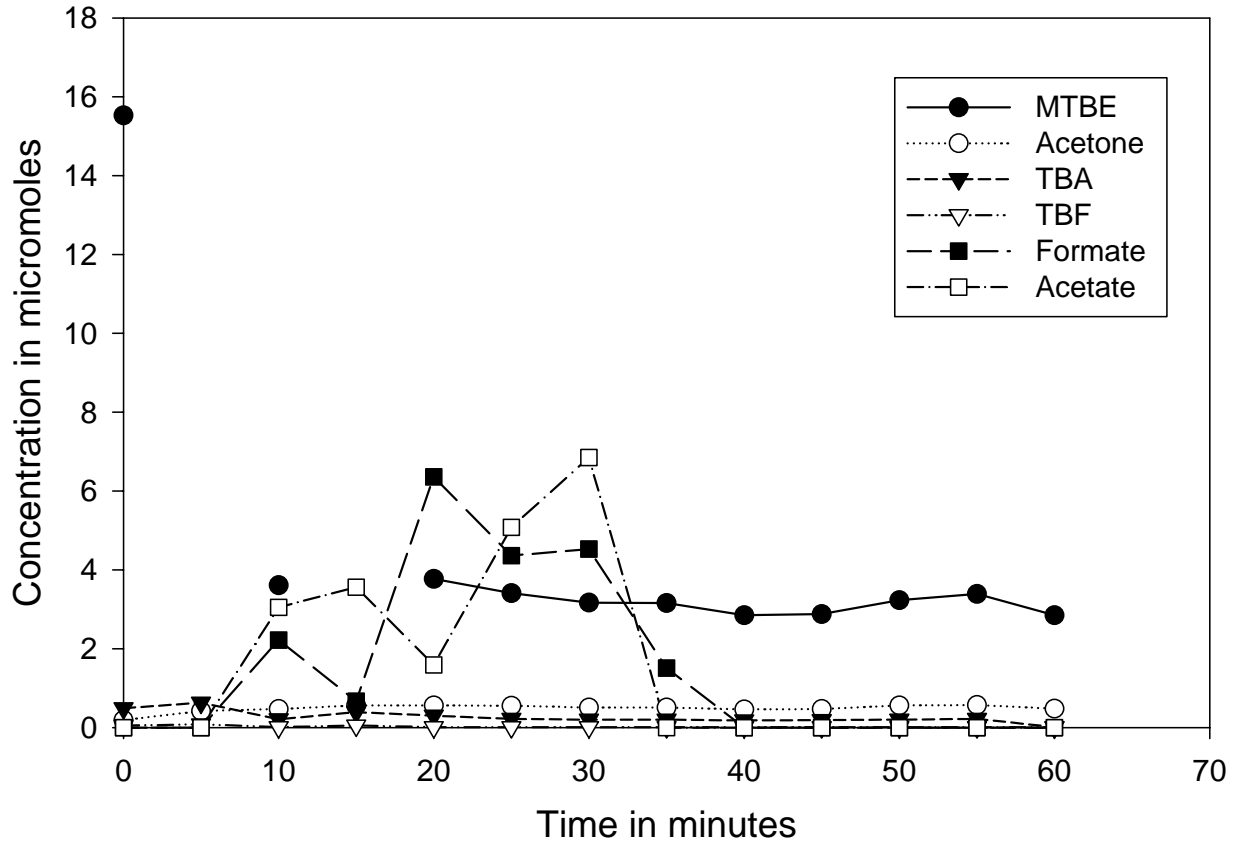


Exhibit 5. Test Series B: H₂O₂:Fe⁺² = 1:1; pH 5.2 to 3.3

Time (minutes)	MTBE (F moles)	Acetone (F moles)	TBA (F moles)	TBF (F moles)	Formate (F moles)	Acetate (F moles)
0	15.10	0	3.08	0	ND	ND
5	0.19	4.10	1.69	1.86	ND	ND
10	0	4.78	1.16	1.41	5.24	ND
15	0	4.31	0.91	1.11	8.00	2.98
20	0	4.50	0.68	0.89	12.84	5.36
25	0	4.93	0.54	0.54	4.36	12.14
30	0	4.60	0.62	0.70	ND	9.19
35	0	4.66	0.55	0.70	ND	7.12
40	0	5.22	0.55	0.66	ND	3.76
45	0	5.28	0.50	0.62	ND	ND
50	0	5.38	0.50	0.51	ND	ND
55	0	4.31	0.38	0.43	ND	ND
60	0	4.74	0.27	0.29	ND	ND

ND = not detected.

After 60 minutes of reaction 4.24 F moles of CO₂ evolved.

Note: Testing at pH 3 and 7 showed no significant change in MTBE concentrations.

Exhibit 6. Change in MTBE/MTBE Byproducts Concentrations with Time (Test Series B)

