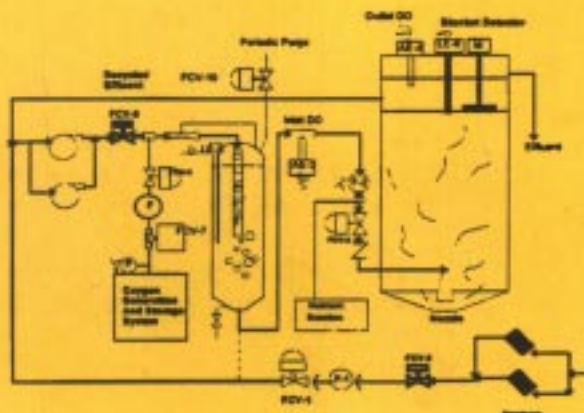


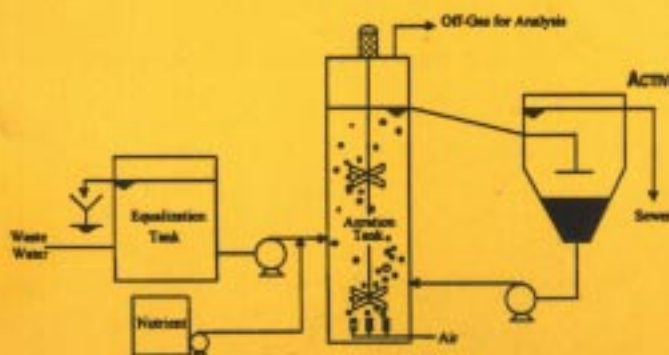
FIELD EVALUATION OF BIOLOGICAL AND NON-BIOLOGICAL TREATMENT TECHNOLOGIES TO REMOVE MTBE/OXYGENATES FROM PETROLEUM PRODUCT TERMINAL WASTEWATERS

Health and Environmental Sciences Department
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August 1997

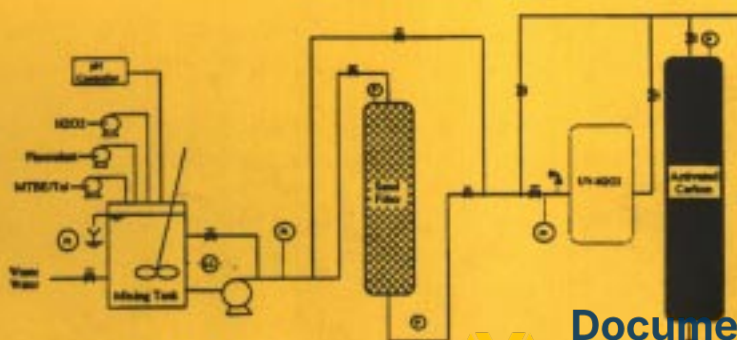
FLUIDIZED BED BIOLOGICAL REACTOR



ACTIVATED SLUDGE SYSTEM FOR THE TREATMENT OF MTBE CONTAMINATED WASTEWATER



UV-H₂O₂ GROUNDWATER TREATMENT PROCESS





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Field Evaluation of Biological and Non-Biological Treatment Technologies to Remove MTBE/Oxygenates from Petroleum Product Terminal Wastewaters

Health and Environmental Sciences Department

API PUBLICATION NUMBER 4655

PREPARED UNDER CONTRACT BY:

**W.T. TANG AND P.T. SUN
SHELL DEVELOPMENT COMPANY
ENVIRONMENTAL DIRECTORATE
HOUSTON, TEXAS**

AUGUST 1997



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API STAFF CONTACTS

Larry Magni, Manufacturing, Distribution & Marketing Department
Roger E. Claff, Health & Environmental Sciences Department

MEMBERS OF TERMINAL EFFLUENT TASK FORCE

Robert R. Goodrich, Chairman, Exxon Research and Engineering Company
Dave Pierce, Vice-Chairman, Chevron Research and Technology
Jeff Baker, Conoco Inc.
Terrie Blackburn, Williams Pipeline
Don Hitchcock, Texaco Refining and Marketing
LeAnne Kunce, BP Oil
Al Schoen, Mobil Research & Development
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PREFACE

The American Petroleum Institute (API), through its Marketing Terminal Effluent Task Force, has been conducting a multi-year research program to evaluate and identify practical and environmentally sound technology options for handling and treating waters generated at petroleum product distribution terminals. The results of this program are intended to provide industry and regulatory agencies with technical information to make informed decisions on appropriate alternatives for individual terminal facilities.

The Task Force has sponsored and published a significant amount of work in prior years on handling and treating terminal waters. The work contained in this report focuses on higher volume, low contamination waters, including those containing an oxygenated compound used in motor gasoline, namely methyl tert-butyl ether (MTBE). In this study, low contamination terminal waters, mostly groundwater, containing benzene, toluene, ethylbenzene and xylene (BTEX) and MTBE were tested in three pilot sized units—two biological systems and one chemical oxidation system—at a terminal. The results of the pilot test work showed that all systems were able to remove at least 95% of the MTBE and BTEX in the feed waters at the few ppm level (0.5-10 mg/L) to low effluent concentrations, less than 100 ppb.

The study concluded that any of the three systems could be applied to a terminal, if needed. The choice of a particular type of technology, a fluidized bed biological reactor (FBBR), an activated sludge type biological treatment system, or a combined ultraviolet light (UV) and hydrogen peroxide (H_2O_2) chemical oxidation system would depend on a life-cycle economics evaluation, expected time span needed for treatment (temporary vs. permanent treatment or remediation project), specific wastewater contamination, and operating staff capabilities at the individual terminal.

Prior studies sponsored by the Task Force have shown that operations and water characteristics at distribution terminals can vary significantly, as do regulatory

requirements in different geographical jurisdictions. Hence, it is recommended that terminal operators or engineers carefully review the terminal water characteristics and regulatory requirements for each facility before designing or installing treatment equipment. Also, other options such as pretreatment and discharge of waters to Publically Owned Treatment Works (POTWs), use of packaged, mobile units for temporary treatment needs, and integration of treatment with other existing petroleum or chemical facilities should be considered versus installation of equipment at the terminals. Other technologies, such as activated carbon adsorption and heated water/air stripping, should also be considered in addition to the treatment technologies tested in this research program.

The Task Force greatly acknowledges and appreciates the fine work performed by Shell Development Company, Houston, Texas in conducting this comprehensive and challenging technical study. In particular, we appreciate the dedication and expertise of Drs. W.T. Tang and P.T. Sun in completing this work.

ABSTRACT

A pilot/demonstration study was conducted on three treatment technologies—the fluidized bed biological reactor (FBBR) process, the activated sludge process incorporated with iron flocculation, and the ultraviolet light-hydrogen peroxide (UV-H₂O₂) process—to evaluate their effectiveness in the treatment of petroleum marketing terminal wastewater contaminated with methyl tert-butyl ether (MTBE). Contaminated groundwater was the primary constituent of the wastewater, which contained 3 to 4 mg/L of benzene, toluene, xylenes, and ethylbenzene (BTEX). MTBE in the wastewater varied from 0.5 to 10 mg/L.

All three technologies were shown to consistently remove BTEX (>99%) from this wastewater. Consequently, the study focused on the MTBE degradation kinetics. For the FBBR process, a start-up period of 3 to 4 weeks was necessary to build up sufficient MTBE degraders to exhibit effective MTBE biodegradation. Removal of MTBE to less than 100 µg/L was demonstrated in the FBBR for a MTBE volumetric loading rate of up to 40 mg per liter of reactor volume per day.

For the activated sludge process, incorporation of iron flocculation in the process enhanced the retention of biomass and allowed the system to sustain excellent MTBE biodegradation at a hydraulic detention time of three (3) hours. An effluent of less than 100 µg/L MTBE was achieved in the activated sludge system at a MTBE loading rate of 10 mg per liter of reactor volume per day.

The UV-H₂O₂ process was capable of degrading MTBE under high MTBE loading rates: using a photoreactor equipped with three 10-kW UV lamps, less than 100 µg/L MTBE in the effluent was achieved for a MTBE loading rate of 4800 mg/L/day. There was only a small reduction in the total organic carbon through the UV-H₂O₂ process, indicating that the organics were not completely oxidized to CO₂. In the presence of ferrous iron in the wastewater, lowering the pH to 3.5 enhanced the degradation efficiency of the UV-H₂O₂

process by increasing the hydroxyl radical generation through Fenton's reaction, and eliminated hydroxyl radical scavengers (carbonate/bicarbonate ions).

In summary, this study demonstrated that all three technologies can be applied at petroleum marketing terminals for the treatment of MTBE contaminated wastewater. Process selection depends on various factors, such as the wastewater flow, MTBE concentration in-and-out of the process, the concentrations of other relevant compounds in the wastewater, the estimated life span of the treatment required and the availability of competent operating man-power at the site.

In general, for the feed conditions evaluated, none of the technologies, when applied alone, will consistently and reliably meet effluent limits below about 100 µg/L. Some of the technologies exhibit significant operability concerns, especially slow response to upsets. In addition, development of cost data was not included in the scope of this study, thus no conclusions were drawn about the practicality of these technologies. Future application of these technologies for MTBE removal will have to take these factors into consideration.

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EXECUTIVE SUMMARY

The wastewater generated in a petroleum marketing terminal can generally be divided into two categories: the high-concentration-low-flow tank water bottoms and the low-concentration-high-flow contaminated groundwater and runoff. These wastewaters are contaminated with different levels of gasoline components including benzene, toluene, ethylbenzene, and xylenes (BTEX); gasoline additives such as methyl tert-butyl ether (MTBE); and inorganics. MTBE is added to gasoline as an oxygenate to reduce automobile tailpipe emission of carbon monoxide and hydrocarbons. MTBE has been shown to be more soluble in water, less strippable, less adsorbable, and more difficult to biodegrade than BTEX, and presents a significant challenge from a wastewater treatment standpoint.

This project investigates the feasibility of different treatment technologies for removal of BTEX and MTBE in low-concentration-high-flow marketing terminal wastewaters. Treatment technologies for MTBE removal include activated carbon adsorption, steam stripping, air stripping with and without off-gas control, air stripping at elevated temperature, biological processes, and advanced oxidation processes. Among these treatment technologies, much information has been available for the activated carbon adsorption and air stripping processes. This current study focuses on evaluating the effectiveness of MTBE removal in two biological processes—the fluidized bed biological reactor (FBBR) process and the activated sludge process, and a chemical process—the UV-H₂O₂ process.

The study was conducted at a petroleum product marketing terminal. Contaminated groundwater for that terminal made up the primary component of the wastewater used in the study. The wastewater contained about 3-4 mg/L BTEX and 0.5 mg/L MTBE. Additional MTBE was in some cases injected into the feed to vary the influent feed MTBE concentration.

In the FBBR study a 190-gallon reactor was used. It was filled with fluidized granular carbon particles on which bacteria could grow. The FBBR required a long startup time to build up a sufficient population of the MTBE degraders to exhibit effective MTBE biodegradation even

with an initial inoculation of a large quantity of the MTBE degrading mixed culture. The very slow buildup of the MTBE degrading bacteria in the FBBR was believed to result from the iron interference and the low temperature of the groundwater. Iron hydroxide deposited on carbon particles tended to flocculate the biomass. As the iron flocs sloughed off of carbon particles and elutriated out of the FBBR, loss of biomass from the FBBR resulted, thus slowing down the attachment of the culture. However, once the MTBE degraders were retained in the FBBR, the FBBR exhibited consistent MTBE removal and excellent stability against process upset. In lieu of the long startup time under field conditions, pre-immobilization of a large population of MTBE degraders onto the carbon particles before startup could be a viable alternative to ensure the success of the FBBR process for MTBE treatment.

This study demonstrated that removal of MTBE to less than 100 µg/L in the FBBR effluent could be achieved with a MTBE loading rate of approximately 40 mg MTBE/L-reactor/day. It is likely that the FBBR can handle higher MTBE loadings if sufficient time is allowed for the FBBR to accumulate enough of an MTBE degrader population.

In the activated sludge process, incorporation of iron flocculation in the activated sludge operation helped retain the MTBE degraders in the system. As a result, very good MTBE degradation and effluent quality can be achieved in the activated sludge system even at an influent biochemical oxygen demand (BOD) concentration as low as 11 mg/L. The removal of MTBE in the activated sludge system was largely due to biodegradation. Loss of MTBE through volatilization was determined to be only 0.5 to 9% of the influent MTBE loading. Based on the test data, an effluent of less than 100 µg/L MTBE could be achieved with a MTBE loading rate of less than 10 mg/day/L-reactor. This loading rate was considered a conservative value for sizing the MTBE biodegradation capacity in an activated sludge system. Overall, the activated sludge system does not possess as high a biomass concentration as the FBBR, and therefore requires a larger reactor to handle the same MTBE loading. The activated sludge system was also more prone to process upset than the attached film process used in the FBBR, and recovered at a slower pace. However, the activated sludge process could be started up (or re-started) rather

easily as compared to the FBBR, which was shown to be delayed by low temperature and iron interference.

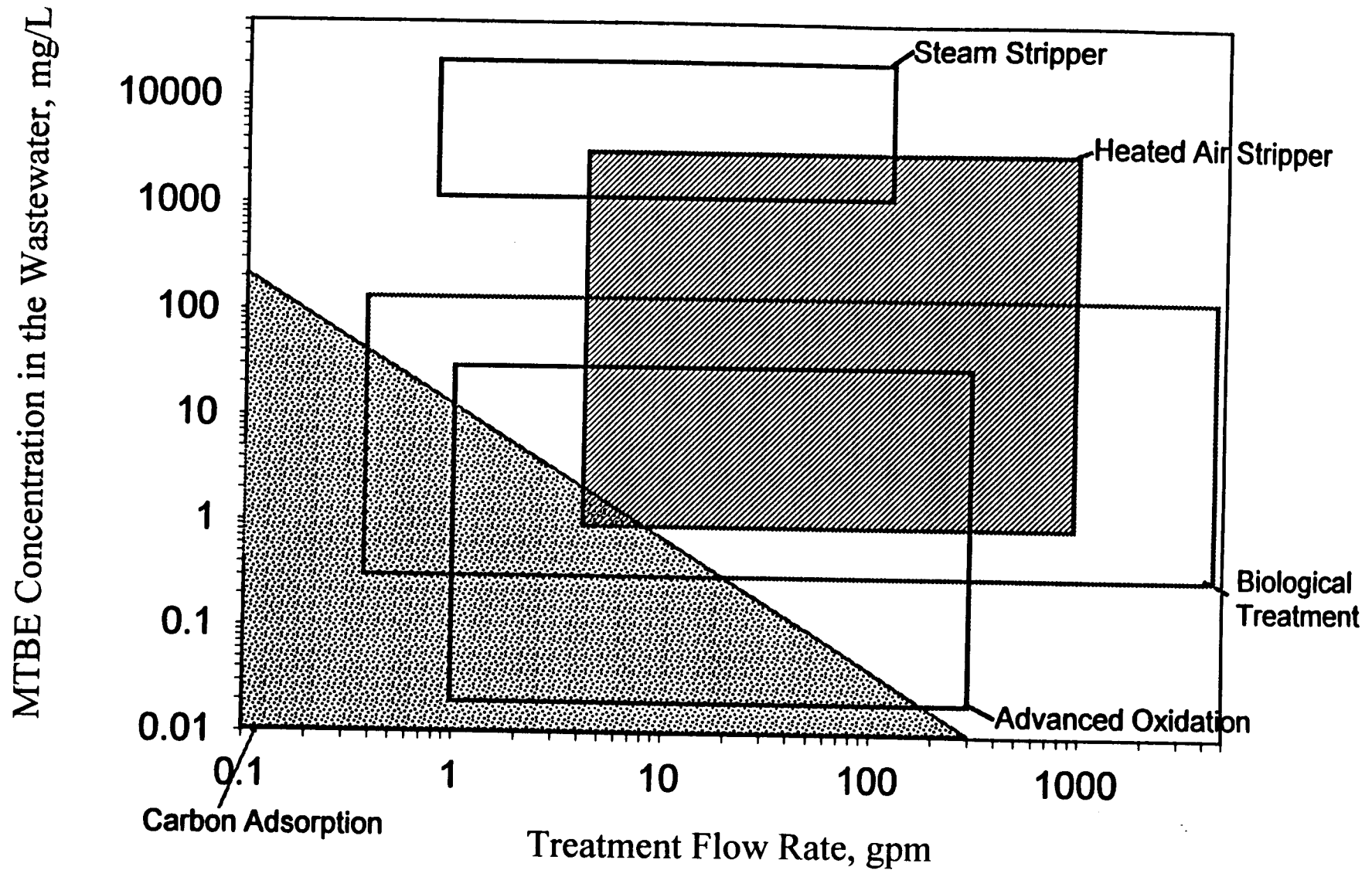
The UV-H₂O₂ process was capable of effectively degrading MTBE and other gasoline hydrocarbons under high MTBE and organic loading rates. Using a photoreactor equipped with three 10-kW UV lamps, less than 100 µg/L MTBE in the effluent could be achieved for a MTBE loading rate of up to 4800 mg/L-reactor/day. The hydraulic retention time used in the study ranged from 3 to 8 minutes. Despite its high degradation rate, there was only a small reduction in the total organic carbon through the UV-H₂O₂ process, indicating that most of the organic contaminants were not oxidized to CO₂. The by-products were likely to be alcohols, aldehydes and ketones. The aquatic toxicity of the treated effluent from the UV-H₂O₂ process was not addressed in this study, but should be carefully examined when choosing this technology.

The contaminated groundwater contained naturally occurring soluble iron. The soluble iron would compete with the target organic compounds for hydroxyl radicals rendering the process less effective. In addition, once iron was oxidized, it formed iron hydroxide flocs which adsorbed and scattered the UV light. Fouling of the UV lamp quartz sheath by iron deposition could also occur. Therefore, presence of iron in the feed water would significantly reduce the degradation efficiency of the UV-H₂O₂ process under neutral pH condition, and the UV-H₂O₂ process should incorporate an iron removal pretreatment step. However, if the pH of the feed water was lowered to 3.5 or less, the generation of hydroxyl radicals through Fenton's reaction was increased and the hydroxyl radical scavengers such as bicarbonate and carbonate were eliminated. As a result, the overall degradation efficiency of the UV-H₂O₂ process was significantly increased. The degradation of organic contaminants in the UV-H₂O₂ process involves complex chain reactions, of which most of the kinetic information is not known. Prediction of the reaction results will be difficult, and laboratory and/or pilot testing is strongly recommended before selecting the process and sizing of the equipment.

This study provided some engineering design data, such as E_{90} (energy consumed for 90% reduction of a targeted compound) and H_2O_2 consumption under different operating conditions, which may be used in the first-pass screening process for process selection.

In addition to the technologies considered in this study, several groundwater treatment techniques have been used to remove MTBE. They are carbon adsorption, steam stripping, and air stripping with and without heating the water (off gas control may or may not be required). Which technique to use for a specific wastewater treatment case depends on the following factors: water flow, MTBE concentration, MTBE discharge limit, off gas clean up requirement, other components in the wastewater (such as total organic concentration and/or iron content), the estimated duration of the treatment project, the variation of MTBE concentration during the pump-and-treat process, the available time for startup, and the availability of man power on-site. The treatment technology selection is a very complicated process and should be dealt with on a case-by-case basis. Nevertheless, general guidance can be provided based on knowledge gained from the study and from past experience. The following figure provides a screening guide for treatment technology selection based on cost and limitations of each process. The information provided in this figure is from general working knowledge and experience, and should not be used as a design tool.

ES-5



ES-1. Technology Application Range for MTBE Treatment

Section 1

INTRODUCTION

The wastewater generated in a petroleum marketing terminal can generally be divided into two categories: the high-concentration-low-flow tank water bottoms and the low-concentration-high-flow contaminated groundwater and runoff. These wastewaters are contaminated with different levels of gasoline components including benzene, toluene, and xylenes; gasoline additives such as methyl tert-butyl ether (MTBE); and inorganics. MTBE is added to gasoline as an oxygenate to help reduce automobile tailpipe emission of carbon monoxide and hydrocarbons. Among the organic contaminants, MTBE presents the greatest technical challenge from a treatment standpoint.

The use of MTBE in gasoline blending has increased significantly because of the recent mandate by the Clean Air Act Amendments of 1993 to increase the oxygenate content in gasoline products. MTBE has a moderately high solubility in water, approximately 50,000 mg/L at 25 °C. Consequently, high levels of MTBE are often detected in wastewater or runoff water that has been in contact with gasoline products. For example, the MTBE concentration in tank bottoms is in the range of several thousand mg/L. In groundwater or runoff water contaminated with gasoline, MTBE at the level of several hundred mg/L has been detected.

Current regulation on MTBE concentration in gasoline contaminated wastewater from marketing terminals varies with location. The Office of Water of the Environmental Protection Agency is currently developing a drinking water health advisory for MTBE in drinking water. Several states have set guidelines to regulate MTBE concentration in the groundwater discharge permit, ranging from 50 to 1000 µg/L. In some states, even though MTBE may not be regulated in the discharge permit for treated terminal wastewater, a discharge limit on the total volatile organic concentration (VOC) is usually specified at 100 µg/L. Since MTBE is detected in the VOC measurement, and since it is

more difficult to remove than the other components from gasoline contaminated water, MTBE is essentially the governing factor regulated under this blanket VOC limit.

API's Marketing Terminal Effluent Task Force has sponsored extensive research on the treatment of low-volume-high-concentration tank water bottoms (Voung *et al.*, 1993). Although the treatment processes evaluated have been successful in meeting certain treatment goals, these treatment processes cannot be readily adapted to the treatment of the high-volume-low-strength wastewaters, particularly when the wastewater contains MTBE. In 1991, API conducted another study to evaluate cost-effective, alternative treatment technologies for reducing the concentrations of MTBE and methanol in groundwater (API, 1991). The study evaluated five technologies: air stripping (with off-gas carbon adsorption or off-gas incineration), steam stripping, diffused aeration, biological treatment, and UV-catalyzed oxidation. Cost estimates showed that UV-catalyzed oxidation, air stripping with off-gas incineration, and air stripping with off-gas carbon adsorption were the most cost-effective of the MTBE treatment technologies considered. Most of the data used in this report were derived using some laboratory evaluations and theoretical calculation. Although a biological treatment option was evaluated, it was judged to be one of the most expensive options, in part because conservative design parameters were used.

Biodegradation of MTBE has since been demonstrated to be feasible, and hence, the API Marketing Terminal Effluent Task Force sponsored this current project to conduct field demonstration research to evaluate both biological and non-biological MTBE treatment processes for high-volume-low-concentration marketing terminal wastewaters. The biological treatment processes evaluated in this study included the fluidized bed biological process and the activated sludge process. The UV-hydrogen peroxide process was the non-biological process tested in this study. This study focuses primarily on assessing the capacity and the effectiveness of the biological and UV-peroxide processes on MTBE removal under different processing and operating conditions. The data obtained from this

study would provide guidelines on the selection and design of an appropriate MTBE treatment system.

This report documents, in separate sections, the experience and data acquired from the field tests of both the biological and non-biological treatment processes. Extensive literature review on various treatment technologies applicable to MTBE degradation has been provided in previously published API reports and will not be repeated here. However, relevant new literature information is included for discussion when appropriate.

SECTION 2

FLUIDIZED BED BIOLOGICAL PROCESSES

A. Introduction

Salanitro *et al.* (1994) first isolated a mixed culture that could degrade MTBE as sole carbon source. In their experiments, biodegradation of MTBE was clearly observed in an activated sludge process employing a mixed culture and receiving multiple organic substrates, including MTBE. They observed a few interesting characteristics of the mixed culture: (1) The MTBE degraders had a slow growth rate, and the MTBE biodegradation activity in the activated sludge system deteriorated if the sludge age was less than 30 days. (2) The MTBE biodegradation in an activated sludge system appeared to be susceptible to external disturbances, occasionally, the biodegradation efficiency of MTBE partially deteriorated for reasons not identified. (3) A pure culture of MTBE degrader could not be isolated. Since the MTBE biodegradation in this study was carried out using a mixed culture and multiple organic substrates, it was speculated that MTBE biodegradation might result from co-metabolism.

For the biological treatment of MTBE to be a viable process, the vulnerability of the MTBE degraders to the external disturbances needs to be further diminished. An attached film biological process appears to be a potentially superior alternative to the activated sludge process. An attached film biological process fixes the microbial cells onto solid carriers in a biological reactor. This process is capable of retaining a stable microbial population at a significantly higher cell concentration than the activated sludge process. The attached film process can thus improve both the operating stability and the biodegradation efficiency of the process on the basis of unit reactor volume. The configurations of an attached film biological process can be a packed bed biological reactor (including trickling filter), a fluidized bed biological reactor (FBBR), and a completely mixed reactor with solid carriers submerged and mixed in the reactor.

Tang and Wilcox (1993) used a laboratory-scale FBBR to address the operating stability and co-metabolism question encountered previously. In their study, the MTBE degraders were immobilized onto carbon particles in the FBBR to stabilize the MTBE degrader population in the reactor, and MTBE was used as the sole carbon source. MTBE biodegradation was clearly demonstrated without the presence of other organic compounds. This study also showed that MTBE could be consistently biodegraded to very low levels under well-controlled laboratory conditions (less than 20 µg/L). The study by Tang and Wilcox (1993) demonstrated some promising features of using the attached film biological processes for the practical treatment of MTBE contaminated wastewater. This current project intends to investigate the feasibility and performance of the attached film biological processes to the treatment of MTBE contaminated wastewater in petroleum product distribution terminals.

B. Review of the Results of MTBE Biodegradation From Previous Studies

Salanitro *et al.* (1994) first isolated a mixed bacterial consortium capable of degrading MTBE. The consortium was developed from seed microorganisms originating in a chemical plant biotreater sludge. It consisted of several bacterial species including coryneform-like species and species of *Pseudomonas* and *Achromobacter*. Through the study of the degradation of radiolabeled MTBE, $(\text{CH}_3)_3\text{-O-C}^{14}\text{H}_3$, they demonstrated that 40% of the MTBE biodegraded and was released as CO_2 , 40% was incorporated in cell mass, and the remaining 20% was present in solution as unbiodegraded MTBE or intermediate metabolites. The mixed culture was capable of degrading ethyl tertiary butyl ether, tertiary butyl formate, and tertiary butyl alcohol, in addition to MTBE. Very high nitrification activity was observed in the culture. However, addition of ammonium salt did not enhance MTBE biodegradation, suggesting that the initial cleavage of MTBE was not related to the ammonium-oxygenase system. The culture was maintained at a sludge age of 70 days during the study. When the sludge age was less than 50 days, loss of partial MTBE degradation activity was observed.

Sun *et al.* (1994) studied the kinetics of MTBE biodegradation in an activated sludge system. They observed the susceptibility of the mixed culture to external stresses such as anaerobic condition and sudden change in feed concentration, and its recovery was very slow after these upsets. A Monod type of kinetics was fitted to the data:

$$r_{su} = \frac{\mu_m X S}{Y_g (K_s + S)} \quad (2-1)$$

where:

- r_{su} = substrate utilization rate, mg MTBE/L day
- μ_m = maximum microorganism growth rate, day⁻¹
- X = microorganism concentration, mg mixed liquor volatile suspended solids (MLVSS)/L
- S = substrate concentration, mg MTBE/L
- Y_g = true biomass yield, mg MLVSS/mg MTBE
- K_s = half saturation constant, mg MTBE/L

The biokinetic and stoichiometric parameters were determined: $\mu_m = 0.2 \text{ day}^{-1}$ (maximum growth rate); $K_s = 0.05 \text{ to } 0.45 \text{ mg/L}$ (the half saturation constant); and $Y_g = 1.76 \text{ mg MLVSS/mg MTBE}$ (true biomass yield due to substrate removal). Based on these parameters and taking into account a design safety factor of 2, a minimum sludge age in the range of 20 to 30 days was suggested. The actual experimental data showed that a minimum sludge age of 25 days was required to achieve greater than 95% MTBE biodegradation. As the sludge age was reduced to less than 25 days, MTBE biodegradation deteriorated very rapidly. Biodegradation of MTBE was totally lost when the sludge age was reduced to 5 days.

Tang and Wilcox (1993) conducted an extensive study on MTBE biodegradation in a laboratory scale FBBR seeded with the mixed culture isolated by Salanitro *et al.* (1994). They investigated the effects of the following process and operating variables on MTBE biodegradation in a FBBR: carbon particle size, presence of other carbon sources in addition to MTBE in the feed, recycle ratio, oxygen requirements, and temperature. Their study showed that MTBE could be biodegraded consistently to less than 100 µg/L under the conditions of a loading of 100 mg MTBE/day/L-FBBR and a hydraulic retention time of 50 minutes (both the loading and hydraulic retention time, HRT, were based on the

total FBBR reactor volume). The MTBE biodegradation effectiveness was the same for the FBBR with MTBE as the sole carbon source or with the presence of either methanol or benzene in the feed at a weight ratio to MTBE of 4:1. The MTBE biodegradation appeared to be very sensitive to oxygen supply. As the dissolved oxygen concentration was reduced to less than 1.5 mg/L due to either the reduced oxygenation or increased competition for oxygen by ammonia nitrification, deterioration in the MTBE biodegradation was observed. If the depletion of oxygen lasted for only a short time, the MTBE biodegradation activity could be rapidly restored as soon as the dissolved oxygen at the exit was raised above 1.5 mg/L. The average ratio of oxygen consumption to MTBE biodegradation was about 2-3 mg O₂/mg MTBE.

The FBBR using a smaller carbon particle (300 µm) as carrier size did exhibit consistently lower effluent MTBE concentration than did the one with a large carbon particle size (600 µm) under the same feed and operating conditions. The difference, however, was not significant. Thus, the overall MTBE removal in FBBRs using different sizes of carbon particles was essentially the same. The MTBE degraders required a long adaptation time when the FBBR was switched from room temperature (23 °C) to a colder condition (17 °C). The effluent MTBE concentration increased immediately after the temperature shock. It took the FBBR about 2 weeks to return to the same MTBE biodegradation efficiency that existed prior to the temperature shock.

Based on these laboratory MTBE biodegradation results, the fluidized bed biological process appears to be a promising treatment technology for MTBE contaminated wastewater. This project was sponsored to further investigate the feasibility of this process under field conditions. The following sections describe the experimental setup and the results of the field-scale FBBR study.

C. Experimental Setup

Description of the Field FBBR Setup The simplified flow diagram of the pilot scale treatment system is shown in Figure 2-1. It consisted of a feed preparation skid, a skid-mounted fluidized bed biological reactor system, an effluent surge tank, a sand filter and a carbon bed adsorber. The feed preparation skid was simply a pump and a piping network designed to provide the flexibility to direct the feed flow to different treatment units and to allow the injection of additional organics into the feed. Since the groundwater well pump produced enough discharge pressure to push the feed through the influent skid to the FBBR, the pump in the influent skid was not used. Two sections of the pipes on the influent skid were installed with an in-line mixer to provide necessary mixing when concentrated MTBE solution was dosed into the feed.

The effluent surge tank had a volume of 80 gallons. The water in the effluent surge tank was pumped to the sand filter and the carbon adsorber before it was discharged to the sewer. The carbon adsorber was installed to remove any residual organic compounds that were not degraded in the FBBR so that the treatment system at the marketing terminal would not be impacted by the pilot test. The sand filter protected the carbon adsorber from plugging with biomass and iron flocs. It was also used to obtain field data for sand filter sizing in similar applications. The sand filter was 12 inches in diameter and 54 inches in height. The filter media included sand and anthracite.

A wastewater treatment laboratory trailer was installed on site next to the pilot scale test unit to provide analytical support. The trailer was equipped with Photovac portable gas chromatography for analysis of volatile organic compounds, CEM LabWave Moisture/Solids Analyzer and Muffle Furnace for measurements of total and volatile suspended solids, and other general water quality analytical equipment such as pH meter, balance, etc.

The pilot scale fluidized bed biological reactor system consisted of an air separation unit for oxygen production, an oxygen saturation unit, and the fluidized bed reactor column (Figure 2-2). The air separation unit was comprised of a compressor and a pressure swing adsorber (PSA). The pressure swing adsorber utilized two molecular sieve columns operated alternatively under about 100 psig to separate air into oxygen and nitrogen. The nitrogen gas was bled off to the ambient, while the oxygen (approximately 95% purity) was stored in an oxygen storage tank.

The release of oxygen to the wastewater was controlled by an adaptive controller that manipulated the oxygen feed rate through a control valve according to the deviation of the dissolved oxygen concentration in the FBBR effluent from the set point. When the oxygen control valve was open, oxygen was mixed with the incoming wastewater through an eductor that effectively dispersed and dissolved oxygen in the wastewater. The oxygen-water mixture entered the oxygen saturation tank through a draft tube. Any gas not dissolved in the wastewater would rise to the top of the saturation tank and form a gaseous space (i.e., a big gaseous bubble). The residual oxygen in the gaseous space was continuously recycled back to the eductor to mix with the wastewater for further dissolution.

The 95% purity oxygen gas contained nitrogen and argon. These gases would slowly accumulate in the gaseous bubble on top of the oxygen saturation tank. When the gaseous bubble grew over a certain size such that the liquid level in the tank was suppressed to a preset level, the level probe installed in the tank sent out a signal to the controller which opened up a control valve to vent off the gases accumulated in the saturation tank. The amount of gas thus released was very small and so was the emission of the organic compounds from the vent gas. This oxygen saturation system, therefore, very effectively utilized the oxygen. A dissolved oxygen concentration of 35 mg/L in the saturation tank could be obtained at its maximum design flow rate, 30 gpm. The oxygen saturation tank was grounded to eliminate the source of electrostatic ignition in case there was free product accumulated on the liquid surface in the saturation tank.

The fluidized bed column was 20 inches in diameter and 15 feet in height. The exit of the column was located at 14 feet from the column base. The working volume of the FBBR was thus approximately 200 gallons. The recycle port was located at 1 foot below the column exit. Both the feed and recycle merged before the intake of the reactor pump which delivered a constant 30 gpm flow. The recycle rate was therefore automatically adjusted according to the feed rate. Both the recycle and feed first passed through the oxygen saturation tank to saturate the water with oxygen before they entered the FBBR column. The feed could also bypass the oxygen saturation tank to merge with the recycle right before the FBBR column. This option was implemented in case of free product accumulation in the saturation tank.

Wastewater Characteristics The chemical composition of the feed, a contaminated groundwater, is shown in Tables 2-1 and 2-2. It was high in hardness and alkalinity, approximately 600 and 400 mg/L, respectively. The iron concentration in the feed water was about 10 mg/L. The wastewater was relatively low in organics: toluene was the highest in concentration among the typical hydrocarbon contaminants from gasoline. The polynuclear aromatic hydrocarbons were mostly below the detection limit (1 µg/L). During the field test, concentrated MTBE solution was dosed into the feed to evaluate the biodegradation efficiency of the biological system at different influent MTBE concentrations. Therefore, the concentration of MTBE in the feed varied with experimental conditions. This water also contained some level of di-isopropyl ether which was specific to this location.

Because the feed wastewater was deficient in nitrogen and phosphorus, a mixture of urea and diammonium phosphate was added to the feed to supplement the nitrogen and phosphorus requirements for biological growth. The nitrogen and phosphorus nutrients were dosed at a rate to give the nitrogen and phosphorus concentrations in the feed the relationship of COD:N:P=100:5:1.

Analytical Procedures During the field experiments, several parameters were monitored at a predetermined interval. Table 2-3 summarizes the monitoring parameters and frequency. The volatile organic compounds were analyzed using purge-and-trap gas chromatography. The quantification limits for the volatile components benzene, toluene, xylenes, ethyl benzene, MTBE and DIPE were 1 µg/L. The general water quality parameters such as Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), cations, anions, nitrogen, etc. were analyzed according to the *Standard Methods* (1985). The heavy metals were analyzed using graphite furnace atomic absorption spectrometry (GFAA). The polynuclear aromatic hydrocarbons were analyzed based on EPA Method 625 (EPA 1982).

D. Results and Discussion

FBBR Start-Up

The key to the success of the fluidized bed biological reactor process is to immobilize a high concentration of MTBE degraders onto carbon particles. The following startup procedure was therefore intended to provide a favorable environment to maximize the retention of the MTBE degrading mixture on the carbon particles. Before the startup, the adsorption isotherm of the carbon particles for MTBE was determined. At the startup, 360 lbs of carbon particles were loaded into the FBBR. Feed wastewater was then pumped through the FBBR to wash out the carbon fines. After the fines were removed, the feed wastewater was stopped, and the FBBR was converted to batch recycle mode. MTBE was then dosed into the FBBR to allow the carbon particles to adsorb MTBE. The amount of MTBE dosed was determined based on the MTBE adsorption isotherm data, the total carbon weight, and the MTBE concentration in the feed wastewater. The intent was to make the equilibrium MTBE concentration in the recycling water approximately the same as that in the feed wastewater. The reasons to pre-equilibrate carbon particles with MTBE are two fold: (1) create, through adsorption, an MTBE rich microenvironment on the carbon surface, encouraging the attachment of MTBE

degraders; and (2) exhaust the carbon so that once the FBBR was converted to continuous operation, any reduction of MTBE in the FBBR would indicate the biodegradation of MTBE.

After MTBE was dosed to the FBBR in recycling mode and the MTBE concentration in the water reached about 250 µg/L, 10 gallons of the MTBE degrading mixed culture with a mixed liquor volatile suspended solids (MLVSS) of 3000 mg/L were inoculated to the FBBR. This MTBE degrading mixed culture was maintained in the laboratory with MTBE as the sole carbon source. The FBBR was again left in recycle mode overnight to allow ample time for the bacterial species to attach to carbon surface. Due to the severe winter condition, the temperature of the water dropped to about 4 °C in the morning. The FBBR was then converted to continuous operation and started to receive 6 gpm of feed wastewater. The reactor temperature was about 15 °C under the continuous operation condition. The degradation data of benzene, MTBE, and DIPE during the startup period are shown in Figures 2-3 to 2-5.

As shown in Figure 2-3, benzene started to break through after 3 days of operation. However, the biodegradation of benzene started to take off in the same period, and the effluent benzene concentration was rapidly reduced to below the detection limit thereafter. The biodegradation of toluene, xylenes and ethyl benzene was very similar to that of benzene and is not shown here.

Despite the effort to pre-equilibrate the carbon with about 200 µg/L MTBE, adsorption of feed MTBE occurred after the continuous operation of the FBBR commenced. This adsorption was due to the fluctuation of the influent MTBE concentration between 200 and 450 µg/L. The difference between the influent and effluent MTBE concentrations during the first 20 days was believed to be mainly attributable to adsorption. The influent and effluent MTBE concentrations from the 20th to 30th days were essentially the same, indicating minimal biodegradation activity. Additional MTBE degraders were inoculated to the FBBR on Day-34 and Day-40. The feed rate was also reduced from 6 gpm to



2 gpm on Day-33. There was evidence of MTBE reduction immediately after the seeding of the MTBE degraders in both cases. The effluent MTBE concentration, however, slowly increased afterwards, suggesting that some MTBE degraders were not retained in the system. Two weeks after the last re-seeding, the FBBR started to display a more consistent removal of MTBE. The MTBE removal, however, was in the range of 25-50%. The effluent MTBE concentration appeared to level off at about 200 µg/L. The performance of DIPE biodegradation in the FBBR during the startup paralleled that of MTBE. The removal of DIPE during the first 25 days was attributed primarily to adsorption. After approximately 30 days of operation, the effluent DIPE concentration was slowly reduced to about 300 µg/L, and stabilized around that level without further improvement.

The removal of both MTBE and DIPE during the startup phase at best was only 50 to 60%. After biodegradation activity started, both the effluent MTBE and DIPE concentrations stayed at the 200-300 µg/L level without further declination. This is unusual, compared with the previous laboratory study which showed that greater than 95% of removal could be easily achieved once the MTBE biodegradation activity started to take off in the FBBR.

The results of the first two months of field study showed that an expedient startup and establishment of the FBBR to effectively remove MTBE under low initial MTBE concentration conditions was not satisfactory, especially during the cold weather. This run was thus terminated, and another startup with modification in the immobilization procedure was attempted.

Second Start-Up

Two factors might be related to the very low MTBE biodegradation activity in the first startup: (1) the carbon was equilibrated with only 200 µg/L MTBE concentration in the solution, which may not have created a sufficiently enriched micro-environment to

encourage effective attachment of most MTBE degraders on the carbon surface; and (2) the temperature of the water dropped to 4 °C during the batch recycle operating right after inoculation. It is not known whether this low temperature has a significantly adverse impact on the attachment of MTBE degraders.

Since the startup occurred during winter and the FBBR was not equipped to heat the water, the problem associated with low temperature during the attachment phase could not be resolved. During the second startup, MTBE was dosed so that at equilibrium the carbon was equilibrated with approximately 5 mg/L MTBE in the recycle water. The FBBR was subsequently inoculated with 10 gallons of the same MTBE degrading mixed culture with a MLVSS of 2000 mg/L. The lower MLVSS of the mixed culture was due to depletion of the culture stock. After inoculation, the FBBR was operated again in batch recycle mode. The temperature again dropped to approximately 2 °C after which the FBBR was fed with 1 gpm of feed wastewater.

Figure 2-6 shows the influent and effluent MTBE concentrations after the inoculation. Since the carbon was pre-equilibrated with 5 mg/L MTBE and since the influent MTBE concentration was less than 1 mg/L, desorption of MTBE from carbon occurred once the wastewater was fed through the FBBR. The desorption lasted for about 50 days after which the effluent MTBE concentration continued to drop until it stabilized at 100 to 150 µg/L. The difference between the influent and effluent MTBE concentration was definitely due to biodegradation. However, as also observed in the first startup, the effluent MTBE concentration was not further reduced to a very low level as did other easily biodegradable organic substrates (benzene, for example), suggesting that the MTBE biodegradation in the FBBR might be limited by either kinetics or other unknown factors. These questions will be addressed later in this report.

DIPE biodegradation data during the second startup are shown in Figure 2-7. As a result of carbon adsorption, DIPE was not detected in the effluent initially. Breakthrough of DIPE occurred after approximately 15 days of FBBR operation. The effluent DIPE

concentration did not rise significantly after breakthrough due to the concomitant removal of DIPE by biodegradation. The effluent DIPE concentration was eventually stabilized at approximately 50-70 µg/L. The DIPE removal across the FBBR was greater than 80% as compared with 30-50% in the first startup.

Figures 2-8 and 2-9 show the biodegradation of benzene and toluene in the FBBR. Both the effluent benzene and toluene concentrations were below the detection limit (1 µg/L) most of the time. The influent toluene concentration fluctuated significantly between the 30th and 50th days of operation due to the variability of groundwater characteristics. The effluent toluene concentration, however, was not impacted, showing the stability to the FBBR against feed concentration variation. The biodegradation behavior of xylenes and ethyl benzene was similar to those of toluene, and was not shown here. The raw data for the second startup were tabulated in the Appendix.

Effects of Loading on the Performance of FBBR Biodegradation

Once the biodegradation of MTBE was established in the FBBR, the focus of the test program was to establish the MTBE biodegradation capacity of the FBBR by gradually increasing the MTBE loading (i.e., by varying feed flow rate and MTBE concentration). The loading to the FBBR was changed according to the following sequence: The feed rate was first raised stepwise from 1 gpm to 2 gpm and finally to 3.5 gpm without dosing MTBE in the feed. Each of these test conditions lasted for 3 to 5 weeks. The hydraulic retention times corresponding to the feed rates of 1, 2, and 3.5 gpm were 3.17, 1.58, and 0.9 hours, respectively.

Subsequently, the influent MTBE concentration was increased from 400 µg/L to 1.1 mg/L while maintaining the feed rate at 3.5 gpm. Later, the influent MTBE concentration was further raised to 10 mg/L. During the last period, the field study of MTBE degradation in the UV-H₂O₂ process was carried out. Frequent shut down of the groundwater well was encountered due to overproduction of groundwater. The frequent shut down did not

adversely impact the UV-H₂O₂ test since it was not operated 24 hours continuously. However, it did introduce significant perturbation to the FBBR and it is doubtful that there was sufficient time to allow the FBBR to stabilize at a pseudo-steady state for the last loading condition. The data gathered in this period (i.e., 3 gpm and 10 mg/L influent MTBE concentration) are included in this report since they shed some light on the response of the FBBR to frequent perturbation in concentration shocks. However, the data are not interpreted due to the entangled effects of adsorption and biodegradation in transient states. The following sections present the results gathered under different loading conditions.

Figure 2-10 shows the chronological data of MTBE biodegradation in the FBBR under 3 different flow rate conditions. After one month's operation under 1 gpm, MTBE was reduced from 400 to about 100 µg/L. The average MTBE removal was 64%. As the flow rate was increased to 2 gpm, the effluent MTBE concentration was slightly increased and the average MTBE removal dropped marginally to 63%. At 3.5 gpm, the effluent MTBE concentration increased to about 200 µg/L, and the decrease of MTBE removal was more obvious, from 63% to 52%.

The net MTBE removal rate, however, increased with increasing MTBE loading (or feed flow rate) despite the deterioration of effluent quality (i.e., higher effluent MTBE concentration). Theoretically, as the net MTBE removal rate increases, the rate of the MTBE degrader population growth should also increase, leading to accelerated MTBE biodegradation. However, within the 3-4 weeks of operation for each flow condition, the improvement in the effluent MTBE concentration with time was not obvious. The results suggest that the growth or the retention of the newly proliferated MTBE degraders might be impeded in the FBBR by some factors yet to be identified; it is also possible that the growth rate of the MTBE degrading culture was so low that these short period runs might be too short to allow the FBBR to display its full capacity.

The biodegradation of benzene, on the other hand, was not affected at all by the increase in the benzene loading. In all three flow conditions, essentially all the benzene was removed: the effluent benzene concentration was below the detection limits (Figure 2-11). The biodegradation of DIPE in the FBBR was very similar to that of MTBE (Figure 2-12), and the effluent DIPE concentration increased and the overall DIPE removal decreased with increasing feed flow rate. The removal of DIPE was averaged at 90%, 77%, and 57% for the 1, 2 and 3.5 gpm conditions, respectively. The influent concentrations of MTBE and DIPE were about the same under these test conditions. The DIPE removal in the FBBR was significantly higher than MTBE, indicating that DIPE was more biodegradable than MTBE.

Starting June 2, 1994, concentrated MTBE solution was injected into the feed to raise the influent MTBE concentration to about 1 mg/L, representing an MTBE loading increase of 125%. There was no deterioration of effluent MTBE concentration immediately after the increase in the loading, due mainly to carbon adsorption. By the end of June, 1994, the effluent MTBE concentration slightly decreased with time. The increase in biodegradation rate suggests that there might be an increase, though at a very slow pace, in the population of MTBE degraders in the system.

As mentioned previously, well overproduction problems were encountered in mid-July. The well water flow rate fluctuated significantly with time. Figure 2-13 shows that there were significant fluctuations in the influent MTBE concentration due to erratic feed flow rate. It is difficult to segregate the effects of adsorption from biodegradation under such circumstances. Therefore, MTBE removal after mid-July might not be completely attributed to biodegradation. However, the plot of MTBE removal with time from June to mid-July (the middle plot in Figure 2-13) revealed a clear trend of continuous improvement in MTBE biodegradation with time.

During July 2 to July 8, the MTBE injection pump failed. The influent MTBE concentration dropped to the original 400-500 µg/L level. The effluent MTBE

concentration during that period was reduced to less than 30 $\mu\text{g/L}$ as compared with the greater than 100 $\mu\text{g/L}$ level previously measured. Similar phenomena were observed again on July 23 and August 3. These data strongly indicate that the growth and retention of the MTBE degraders in the FBBR did occur. However, the growth proceeded at a significantly slower rate than that expected from the MTBE biodegradation kinetics information obtained in the laboratory.

Figure 2-14 shows the biodegradation of DIPE in the FBBR after MTBE injection to the feed. Note that this set of data was the continuation of those of the last condition in Figure 2-11 (i.e., 3.5 gpm) since the influent DIPE concentration was maintained at the same level. The effluent DIPE concentration remained constant for a month after the feed flow rate was changed to 3.5 gpm, and slowly declined with time afterwards. The decline in the effluent DIPE concentration accelerated at the beginning of July with the effluent DIPE concentration reduced to less than 10 $\mu\text{g/L}$.

Figure 2-15 shows the benzene biodegradation data in the FBBR during June 2 to August 10. Biodegradation of toluene, xylenes, and ethyl benzene was similar to benzene in that they were consistently degraded to less than 1 $\mu\text{g/L}$ under all test conditions.

Effects of Low Temperature and Iron on MTBE Biodegradation in the FBBR

As previously discussed, it was a surprise that it took the field FBBR a significantly longer time than the laboratory units to achieve the desirable MTBE removal. The major differences between the laboratory and the field unit include the following: (1) The laboratory unit used 300 to 600 μm carbon particles as compared with the field FBBR which used 1.2 mm carbon particles. The particles in the field and the laboratory units obviously experienced different fluid shear, which might affect the attachment and retention of MTBE degraders on particle surface. (2) The laboratory unit was operated at 22 °C, while the water temperature in the field unit was between 14 °C in the winter and 17 °C in the summer. (3) The existing field FBBR data showed no effects of iron on

the biodegradation of the aromatic hydrocarbons. The potential impact of iron was therefore not investigated in the previous laboratory FBBR study on MTBE biodegradation. However, MTBE degraders had exhibited some unusual behavior such as susceptibility to environmental stresses. The potential iron interference with the attachment and retention of MTBE degraders should not be arbitrarily ruled out without further investigation.

A laboratory FBBR study was therefore initiated to evaluate the three factors described above. The study used three FBBR columns. Each column was 1 inch in diameter and 5 feet in height. Column 1 (designated as LFBBR-1) was loaded with 160 grams of carbon particles with an average size of 1.2 mm. Columns 2 and 3 (LFBBR-2 and 3) each used 100 grams of carbon particles with an average size of 0.75 mm. All three LFBBRs therefore had the same total external surface area onto which the microbial cells could attach. The carbon particles in LFBBR-1 and those in LFBBR-2 and 3 were from different carbon vendors: LFBBR-1 used the same carbon particles as the field unit, while the carbon particles used in LFBBR-2 and 3 were the same as those used in the previous laboratory study (Tang and Wilcox, 1993). LFBBR-1 and LFBBR-2 were operated at 22 °C, while LFBBR-3 was operated at 15 °C.

The initial phase of this study was to investigate the effects of particle size and operating temperature. Later, ferrous sulfate was injected in the feed to study the effects of iron. To simulate the fluid-particle shear condition in the field FBBR unit, the recycle rate for all three LFBBRs was 300 ml/min, which gave the same superficial upward liquid velocity as that in the field FBBR unit. All the carbon particles had been equilibrated with the intended influent MTBE concentration, approximately 400 µg/L, before the MTBE degrading mixed culture was seeded. Two hundred milliliters of MTBE degrading mixed culture with a MLVSS of 1950 mg/L was seeded to each of the LFBBRs.

The results of the laboratory study are summarized in Figure 2-16. MTBE biodegradation started almost immediately after seeding in LFBBR-1 and 2. The effluent MTBE

concentration was reduced consistently to below 20 µg/L and 10 µg/L for LFBBR-1 and 2, respectively. Since LFBBR-1 and 2 were operated under the same conditions except for the particle size and source, it is clear that those differences were not the cause for the significantly slower MTBE biodegradation in the field FBBR. However, it is interesting to note that the effluent quality of LFBBR-2 was consistently better than that of LFBBR-1, indicating effects of particle property could not be totally discounted.

The MTBE degraders seemed to require a long adaptation phase when subjected to low temperature shock as occurred in LFBBR-3. Very little MTBE biodegradation was observed within the first 20 days after the culture was seeded at 15 °C. MTBE biodegradation eventually took off after that, and achieved an even better effluent quality than LFBBR-1 after 2 months of operation. In comparison, for a FBBR which had an already established stable population of the MTBE degraders, the MTBE degradation deteriorated slightly when subjected to the same magnitude of temperature shock, but regained complete adaptation after 2 weeks (Tang and Wilcox, 1993). Therefore, it appears that the low temperature shock affected strongly the immobilization of the MTBE degraders onto carbon particles and their subsequent growth and development. This result also implies that if the carbon can be pre-immobilized with sufficient population of MTBE degraders, the startup of the FBBR for MTBE treatment can be greatly accelerated over what has been experienced in this field study.

Ferrous sulfate was injected at a concentration of 10 mg/L at the entrance of the LFBBR-2 column, to evaluate the effects of iron on MTBE biodegradation in the FBBR. After approximately 1 week of ferrous sulfate injection, the majority of the carbon particles were covered with reddish iron flocs. As shown in Figure 2-16, the effluent quality of LFBBR-2 was not impacted after continuous injection of ferrous sulfate for 1 month. It appears that once the MTBE degraders have been established on the carbon surface, the presence of iron and coverage of iron flocs on the carbon surface do not adversely affect the MTBE biodegradation in the FBBR.

On about Day-90, the influent MTBE concentration was increased from 500 µg/L to 4 mg/L for two purposes: (1) Additional growth and retention of the MTBE degraders would be needed to handle the extra MTBE loading. Therefore, this test allowed the effects of iron to be evaluated under conditions similar to the startup period. (2) The test would also provide a better controlled condition for observation of the effect of concentration shock on the MTBE biodegradation under a lower temperature, 15 °C.

Figure 2-16 shows that all three LFBBRs were adversely impacted by the concentration shock. Shortly after the shock, the effluent MTBE concentration in LFBBR-1 increased sharply to about 1 mg/L. It then stabilized at the 1 mg/L level for about 1 month, and improved slowly with time afterwards. At the time this test was terminated, the effluent MTBE concentration in LFBBR-1 had been reduced to less than 400 µg/L.

The effluent MTBE concentration in LFBBR-2, which was dosed with ferrous sulfate, increased drastically to 2 mg/L, and started to decrease at a very slow pace thereafter. The effluent MTBE concentration in LFBBR-2, which was consistently lower than that of LFBBR-1 before concentration shock, was significantly higher than LFBBR-1 throughout the concentration shock test.

For LFBBR-3 operated at 15 °C, the effluent MTBE concentration increased immediately after the concentration shock and maintained at a level very close to the influent concentration. The difference between the influent and effluent concentrations after the concentration shock was only slightly greater than that maintained before the shock, indicating that the magnitude of MTBE biodegradation remained about the same. Judging from the previous data that showed LFBBR-3 required three times longer than LFBBR-1 and 2 to achieve desirable MTBE biodegradation during the startup phase and that it took LFBBR-1 about 1.5 months after this concentration shock to display effective MTBE biodegradation, significant improvement in MTBE biodegradation in LFBBR-3 was not anticipated within 4 to 6 months. The laboratory tests were terminated at the conclusion of the field project.

Table 2-4 shows the total suspended solids (TSS) and volatile suspended solids (VSS) in the effluents of the three LFBBRs. The TSS in the effluent of LFBBR-2, which was dosed with 10 mg/L ferrous sulfate, was significantly higher than that in the effluent of LFBBR-1 and 3, primarily due to the iron flocs elutriated out of the unit. The VSS in the effluent of LFBBR-2 was also higher than LFBBR-1 and 3, suggesting that some biomass might be lost together with iron flocs from the system. It is possible that the biomass enmeshed with iron flocs on the carbon particle surface. Upon particle-particle collision or fluid shear, iron flocs were sloughed off of the particle surface, and were elutriated out of this LFBBR. It is possible that the loss of MTBE degraders with iron flocs might also occur in the field unit such that the increase in the MTBE degrader population in the FBBR was significantly delayed and hence partially contributed to the slow progress of MTBE biodegradation observed in the field unit.

Polishing of the Field FBBR Effluent

After a prolonged operation of the field FBBR, sloughing of biofilm from the carbon particles can occur particularly if the organic loading is high. Occasionally high total suspended solids (TSS) resulting from the dislodging of the biomass from the FBBR thus can occur in the effluent. In some cases, carbon adsorbers may be used downstream of the FBBR to ensure complete compliance of the discharge. Both of these two conditions require a polishing step following the FBBR to remove TSS and to prolong the operation of carbon adsorbers. During this study, two test runs of a sand filter were conducted to evaluate its performance as a polishing process for the FBBR effluent. The results are tabulated in Tables 2-5 and 2-6.

In the sand filter tests, the FBBR effluent was gravity-drained to a surge tank before it was pumped to the sand filter. The first test run was operated at a flow rate of 2 gpm and the second run at about 3.2 gpm. The sand filter had a cross-sectional area of 0.785 ft^2 .

Therefore, the filtration flux was 2.55 and 4 gpm/ft², respectively for Runs #1 and 2.

In Run #1, the TSS coming out of the FBBR were in the range of 8 to 10 mg/L. The constituents of the suspended solids were about 2 mg/L of biomass measured in terms of VSS and about 2-3 mg/L of iron (equivalent to 4-6 mg/L iron hydroxide). Approximately half of the iron in the FBBR effluent was in the soluble or non-filterable form. The filter was operated continuously for the 34-day period without backwash. The loading of solids increased dramatically at the end of the run, primarily due to the dislodging of solids adhered to the wall of the surge tank. The pressure of the sand filter increased to 20 psi around Day-34, the sand filter was shutdown for backwash. Throughout Run #1, the effluent TSS concentration had been maintained close to zero.

The TSS in the FBBR effluent in Run #2 were approximately 20 mg/L, significantly higher than that in Run #1. This is primarily due to higher organic loading into the FBBR as evidenced from the VSS data in Run #2. Interestingly, the iron in the FBBR effluent was primarily non-filterable iron since the concentration of the total iron was about the same as that of soluble iron. The pressure in the sand filter increased rapidly after 11 days of operation at 4 gpm/ft². The sand filter was shut down for backwash after 2 weeks of operation.

The total suspended solids loading to the sand filter before back wash were 10-11 lbs for both runs. The results of the sand filter test runs show that excellent effluent quality can be achieved with a sand filter operated under a solid loading of 10 to 20 mg/L and a filtration rate of 2 to 4 gpm/ft². The backwash frequency under such operating conditions is from 10 to 30 days.

The MTBE Biodegradation Capacity of the FBBR

Figure 2-17 summarizes the relationship between the influent MTBE loading and effluent MTBE concentration for all the MTBE biodegradation data obtained in the pilot FBBR study. It appears that the FBBR could achieve the desirable < 100 µg/L effluent MTBE concentration under a loading of up to 40 mg/day/L FBBR. This loading is substantially

lower than the 100 mg/day/L demonstrated in the laboratory study by Tang and Wilcox (1993). The difference in the maximum MTBE loading rate between the laboratory and the field unit could be attributed to the slow growth of the MTBE degraders at low temperature and the iron interference encountered in the field unit. Given sufficient time for the field unit to fully adapt to the low temperature and iron condition, there is no obvious reason why the field unit would not deliver the desirable effluent MTBE quality at a loading rate similar to that of the laboratory units.

E. Conclusions

1. Iron interference with the retention and accumulation of the MTBE degrader biomass on carbon particles should be further investigated. Iron interference together with low temperature of groundwater may have delayed the growth of the MTBE degrader population in the FBBR.
2. In lieu of the long startup time under the field conditions, pre-immobilization of a large population of MTBE degraders onto the carbon particles before startup could be a viable alternative to ensure the success of the FBBR process for MTBE treatment.
3. Once the MTBE degraders are retained in the FBBR, the FBBR exhibited consistent MTBE removal and excellent stability against process upset.
4. In this pilot study, an effluent of less than 100 µg/L MTBE could be achieved with a MTBE loading rate of approximately 40 mg MTBE/L/day. It is likely that the FBBR can handle even higher MTBE loading if sufficient time is allowed for the FBBR to accumulate enough MTBE degrader population.

Table 2-1. Chemical Characteristics of the Feed Wastewater
Single Sample Taken During Planing Phase

ANALYTIC PARAMETERS	Concentration (mg/L)
GENERAL	
BOD	9
COD	29.5
TOC	6
O&G (Gravimetric)	BDL (< 5 mg/L)
TSS	18
TDS	1758
Conductivity (µmho/cm)	3100
Sulfide	BDL (< 1 mg/L)
Cyanide	BDL (< 5 µg/L)
Ammonia N	BDL (< 1 mg/L)
Nitrate N	BDL (< 1 mg/L)
TKN	0.3
Total Iron	9
Soluble Iron	7
Alkalinity (as CaCO ₃)	430
Hardness (as CaCO ₃)	635
pH	7.2
VOLATILES	
Benzene	0.68
Toluene	1.396
Xylenes	0.307
MTBE	0.302
DIPE	0.483
METALS	
Arsenic	0.018
Beryllium	BDL (< 2 µg/L)
Cadmium	BDL (< 1 µg/L)
Chromium	0.005
Copper	0.011
Lead	BDL (< 1 µg/L)
Mercury	BDL (< 1 µg/L)
Silver	BDL (< 2 µg/L)
Zinc	0.02
OTHER CATIONS & ANIONS	
Chloride	270
Phosphate	< 1

Note: BDL - below detection limit

Table 2-2. Contents of Polynuclear Aromatic Hydrocarbons in the Wastewater

Polynuclear Aromatic Hydrocarbons	Influent ($\mu\text{g/L}$)
Naphthalene	4
Acenaphthylene	< 1
Acenaphthene	< 1
Fluorene	< 1
Phenanthrene	< 1
Anthracene	< 1
Fluoranthene	< 1
Pyrene	< 1
Benzo(a)Anthracene	< 1
Chrysene	< 1
Benzo(b)Fluoranthene	< 1
Benzo(k)Fluoranthene	< 1
Benzo(a)pyrene	< 1
Benzo(g,h,i)pyrene	< 1
Indeno(1,2,3-c,d)pyrene	< 1
Dibenzo(a,h)anthracene	< 1

Table 2-3. Monitoring Parameters for the Characterization of the Feed and the Treated Effluent

ANALYTIC PARAMETERS	Influent (mg/L)	Effluent (mg/L)
GENERAL		
BOD	1/week	1/week
COD	2/week	2/week
TOC	2/week	2/week
O&G (Gravimetric)	2/test conditions	2/test conditions
TSS	2/week	2/week
TDS	Initial sample	
Conductivity	1/week	1/week
Sulfide	initial sample	
Cyanide	initial sample	
Ammonia N	2/week	2/week
Nitrate N	2/week	2/week
Total Kjehdel Nitrogen (TKN)	initial sample	initial sample
Total Iron	daily	daily
Soluble Iron	daily	daily
Alkalinity (as CaCO ₃)	2/month	2/month
Hardness (as CaCO ₃)	2/month	2/month
pH	daily	daily
VOLATILES		
Benzene	daily	daily
Toluene	daily	daily
Xylenes	daily	daily
MTBE	daily	daily
DIPE	daily	daily
OTHERS		
Carbon Bed Height	2/week	2/week
Dissolved Oxygen (DO)	daily	daily

Note: This single sample was collected during the planning phase.