



REMOVAL OF METHYL TERTIARY BUTYL ETHER FROM SYNTHETIC WASTEWATER

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ABSTRACT

Methyl tertiary-butyl ether (MTBE) is the most fuel additive used through the world. Thus, it has been reported that MTBE is the second high concentration contamination found in ground water.

Study of the effect of reaction time and reaction temperature of 25 to 55° C on the kinetic of chemical oxidation has been done with 3000 ppm MTBE in water at pH range 3 to 7 and 1:1 hydrogen peroxide to Fenton's reagent ratio.

Also, Kinetic analysis was carried out to determine reaction order and activation energy for the reaction of MTBE disappearance during the reaction with Fenton's reagent.

الخلاصة

مثيل رباعي بيثيل اثير هو من اشهر المضافات الى الوقود حول العالم. و سجل كثاني أعلى ملوث في المياه الجوفية. تم دراسة تأثير كل من زمن و درجة حرارة التفاعل من 25 الى 55° مئوية على حركية تفاعل الاكسدة لمحلول مصنع ذو تركيز 3000 جزء بالمليون من مثيل رباعي بيثيل اثير في الماء لمدى اس هيدروجيني بين 3 و 7 و بأستعمال نسبة بيروكسيد الهيدروجين الى معاملة فينتون 1:1. حسبت من تحليل حركية التفاعل كل من درجة التفاعل و طاقة التنشيط.

KEYWORDS: Methyl tertiary butyl ether, wastewater, organic chemistry, oxidation, reaction rate, activation energy.

INTRODUCTION

Methyl tertiary butyl ether (MTBE) is a synthetic chemical that was historically used as an octane booster additive to gasoline. Increasingly there have been concerns about its toxicity and potential carcinogenicity.

Because of its chemical characteristics, MTBE contaminated sites are difficult to remediate. MTBE readily dissolves and spreads in water. Additionally, MTBE resists biodegradation, does not sorb to soil, and has a low Henry's Law constant. As a result, the extent of MTBE contamination is usually much greater than that of the other common gasoline components. Because of these factors, remediation of MTBE-impacted groundwater can be very difficult and costly.

Methyl tertiary butyl ether (MTBE) is a synthetic chemical that was historically used as an octane booster additive to gasoline due to its many properties which including low production cost, ease of production, high octane rating [Shelly and Fouhy, 1994]. Increasingly there have been concerns about its toxicity and potential carcinogenicity [Carver and Brown, 2008]. The addition of MTBE to gasoline improves fuel combustion and reduces the resulting concentrations of carbon monoxide and un-burn

hydrocarbons. Accordingly, MTBE was added to about 30% of the gasoline nationwide at an average concentration of about 11% by volume [USEPA, 1994].

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 (about 50 g/L). 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 [Schirmer and Barker, 1998]. It is resistant to biological degradation with a half-life of 10,000 days. 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].

National Water-Quality Assessment Program reported that MTBE was a second higher concentration component (after trichloromethane) out of 60 volatile components in different groundwater, rainwater of United State and eight other urban areas during 1993 to 1994 [Delzer, et al., 1996].

Chemical oxidation of organic component is the most practical and effective process to convert organic components (usually in aqueous solution) into carbon dioxide and water. Ray, et al. [2003] was summarized chemical oxidation techniques efficient for the reduction of organic components in water, these techniques including chemical oxidizing agent with and without catalyst and irradiation with and without chemical oxidizing agent.

Greater than 99% reduction of MTBE was achieved with initial concentrations of 170 and 196 ppm in pH region between 7.7 and 8.8 by using chemical oxidation with hydroxyl radical technique [Tornatore, et al., 2000].

Many metals have special oxygen transfer properties which improve the utility of hydrogen peroxide (H_2O_2). The most common of these is iron which, when used in a prescribed manner, results in the generation of highly reactive OH ion. The reactivity of this system was first observed in 1894 by its inventor H.J.H Fenton. The procedure requires to adjusting pH of the wastewater (aqueous solution of MTBE in water) from 3 to 5, then addition the iron catalyst (as a solution of $FeSO_4$) and finally addition of H_2O_2 slowly to finish the reaction. 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) [Ray, et al., 2003].

The reaction of aqueous MTBE with the hydroxyl radical generated by UV/ H_2O_2 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. The results also show that about 85 % reduction of initial MTBE concentration of about 87 ppm was noticed during 10 hours reaction time and the results reported that MTBE was disappear after 40 hours reaction time. In all cases, the decay of MTBE was found to follow first-order reaction kinetics with a pseudo first-order rate constant. The value of pseudo first-order rate constant increased with the decreasing concentrations of MTBE. Byproducts of the UV/ H_2O_2 degradation of MTBE were found to be tert-butyl formate (TBF), tert-butyl alcohol (TBA), methyl acetate, acetone, a per-oxy compound, formaldehyde, alkanes, and acetic and formic acids [Stefan, et al., 2000].

Ray, et al. [2003] studied the effect of hydrogen peroxide to Fenton's reagent ratio (0.1:1 to 100: 1), pH (3 to 7), 25° C temperature and time (up to 60 minutes) on the reduction of initially 1300 mg/l (ppm) MTBE concentration in groundwater and the probability of reduce this amount to regular accepted level of 20 mg/l (ppm) or less (as reported by USEPA [1997]). This goal was achieved at hydrogen peroxide to Fenton's reagent ratio of 1:1 and reaction pH of 5 and contact time about 10 minutes.

Carver and Brown [2008] compared four methods for producing TBA from MTBE which are: Fenton's reagent, permanganate, ozone and uncatalyzed persulfate. Fenton's reagent method done by using 500 mg/L H_2O_2 and 100 mg/L Fe^{+2} at a pH of 2.8 to reduce MTBE to less than 10 % from its initial value (250 ppm) in 10 minutes.

The aim of this work is to study the effect of reaction time (up to 60 minutes) and reaction temperature (25 and 55° C) on the concentration of MTBE in treated solution and study the kinetic of chemical oxidation of 3000 ppm MTBE in water at pH range 3 to 7 and 55° C and 1:1 hydrogen peroxide to

Fenton's reagent ratio.

EXPERIMENTAL WORK

• Materials

The following materials were used in this work:

MTBE: 99.5 wt. %, molecular weight of 88, boiling point 53.6° C and refractive index is 1.3692 (Aldrich).

Hydrogen peroxide: 35 wt. % solution in water (Annular).

H₂SO₄: 98 wt. % (Annular).

FeSO₄: White crystal, molecular weight 151.9, melting point 400° C (decomp.) and the density is 2.841 g/cm³ (Aldrich).

• Experimental Setup

MTBE was mixed with Fenton's reagent in 3-neck, 500 ml glass flask. The flask necks were fitted with thermo-meter (to measure temperature), condenser (to insure that no loss of solution due to heating occurs) and syringe to take samples (as shown in Figure 1). The flask was heated by magnetic-stirred type Hinotik-79-1 (rotation speed 0-2400 rpm, power of motor 40 W and heating power 300 W).

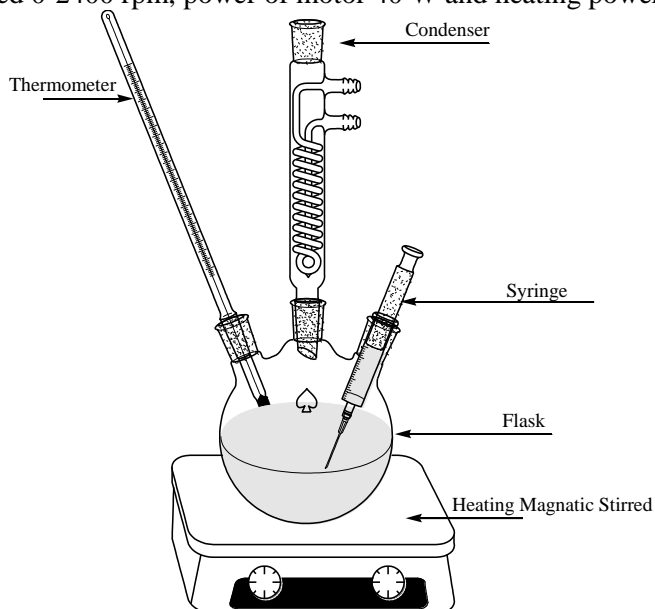


Fig. 1 Experimental setup

• Tests

pH: OAKION PH2100 Series pH-meter was used to measure solution and sample pH.

MTBE concentration: UVD-3500/UVD-3400 spectro-photometer was used to measure concentration of MTBE in sample.

RESULTS AND DISCUSSION

• Effect of Temperature, pH and Time on MTBE Conversion

The effect of temperature, pH and time on MTBE conversion (disappearance) was studied in the range of temperature from 298 to 333 K, and pH range from 2 to 6 with a period of time up to 60 minutes, and this effect illustrated in Figures 2 to 4.

It is obvious from these figures, in the mentioned range of temperature, that MTBE conversion generally increasing with time and temperature and gives maximum value of 0.99 (about complete conversion of MTBE) at 333 K and 60 minutes in pH solution 5. This result is in good agreement with that reported by Carver and Brown [2008] who used Fenton's reagent method of 500 mg/L H₂O₂ and 100 mg/L

Fe^{+2} at pH of 2.8 and temperature of 298 K to reduce MTBE to less than 10 % from its initial value (250 ppm) in 60 minutes.

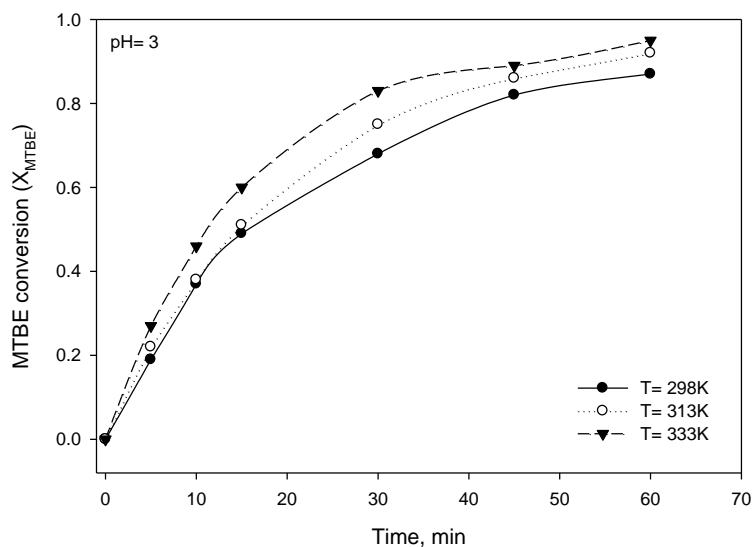


Fig. 2 Effect of time and temperature on MTBE conversion at 3 pH solution

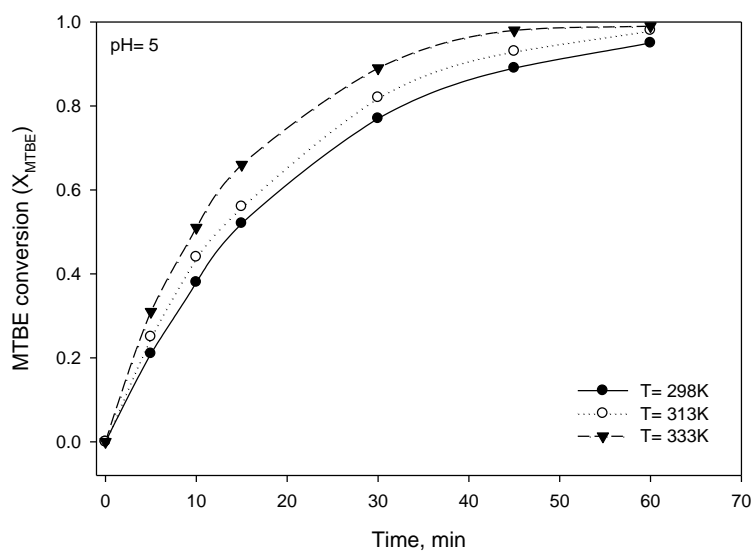


Fig. 3 Effect of time and temperature on MTBE conversion at 5 pH solution

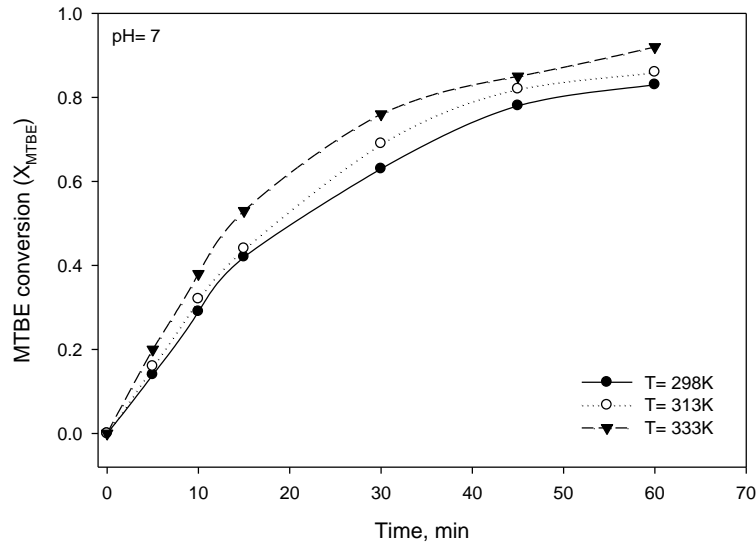


Fig. 4 Effect of time and temperature on MTBE conversion at 7 pH solution

The solution pH increases from 3 to 5 increases MTBE conversion, but more increasing in solution pH to neutral value (7) causes decrease in MTBE conversion, this effect shown in Figure 5.

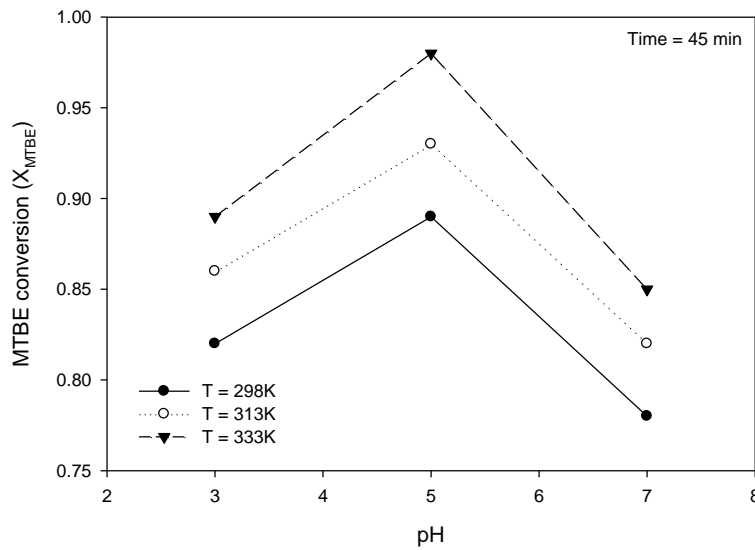


Fig. 5 Effect of pH and temperature on MTBE conversion and 45 minutes time

Hydrogen peroxide in the presence of ferrous iron (Fe^{2+}) reacts to form hydroxyl radicals (OH^\cdot), ferric iron (Fe^{3+}), and hydroxyl ions (OH^-). The hydroxyl ions are very powerful oxidizers, and react particularly with organic compounds. The generation of highly reactive ion (OH^\cdot) affects the oxygenation of MTBE, this ion is generated according to the following equilibrium chemical equations [Ray, et al. 2003]:



When the pH decreasing (below 5), hydrogen ion H^+ increasing, and the equilibrium reaction (Eq. 2) shifts backward and more amount of Fe^{+3} ion appears which cause also shifting backward in equilibrium reaction (Eq. 1) and the amount of reactive ion (OH^*) available to react with MTBE decreases. The increasing in pH value of the reaction media more than 5, forced both equilibrium reactions (Eq. 1 and 2) forward and also the amount of reactive ion (OH^*) available to react decreases.

This result is in good agreement with Ray, et al. [2003] who find that 20 ppm MTBE solution can be obtained from 1300 ppm solution at hydrogen peroxide to Fenton's reagent ratio of 1:1 and reaction pH of 5 but contact time about 10 minutes.

• KINETIC OF MTBE CONVERSION

Data obtained from the bench-scale for the MTBE conversion (disappearance) were analyzed by available kinetics models [Levenspiel, 1972].

First order reaction analyses show more accurate model to describe MTBE conversion variation with time.

$$-\ln(1 - x_{MTBE}) = \ln\left(\frac{C_{MTBE0}}{C_{MTBE}}\right) = kt \quad (3)$$

The reaction rate coefficients at each temperature can be easily evaluated from the straight lines slope of $-\ln(1 - x_{MTBE})$ versus t as shown in Figures 6 to 8.

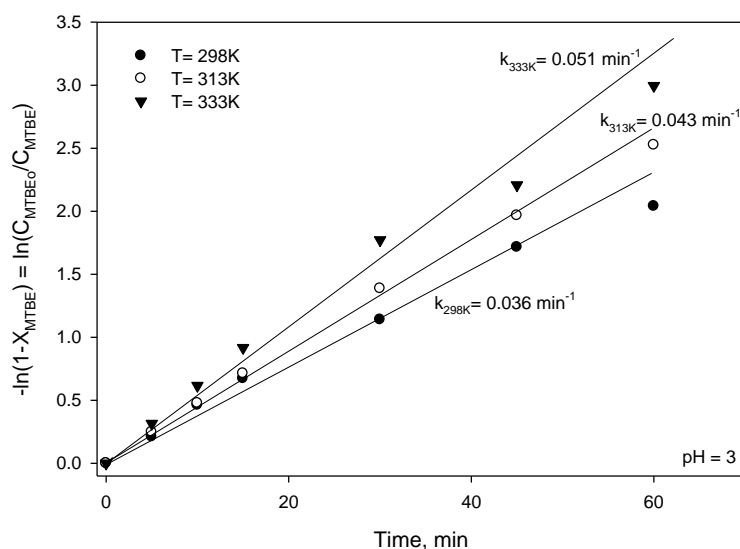


Fig. 6 First order reaction model of MTBE conversion at different temperatures and 3 pH

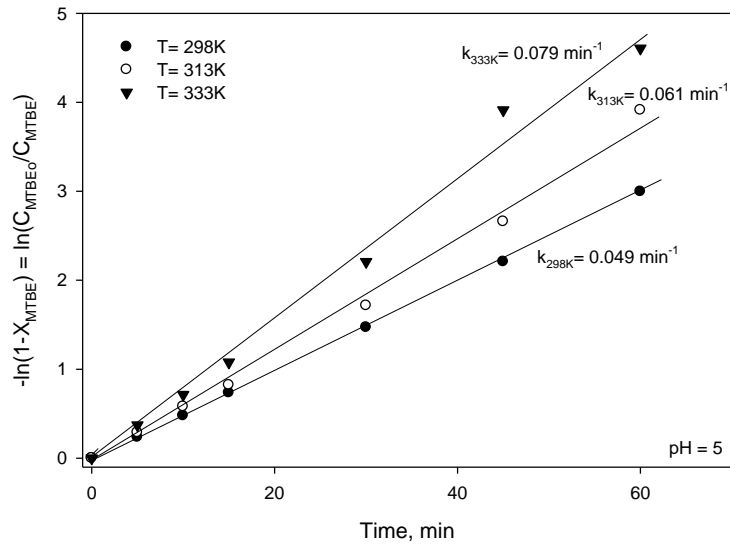


Fig. 7 First order reaction model of MTBE conversion at different temperatures and 5 pH

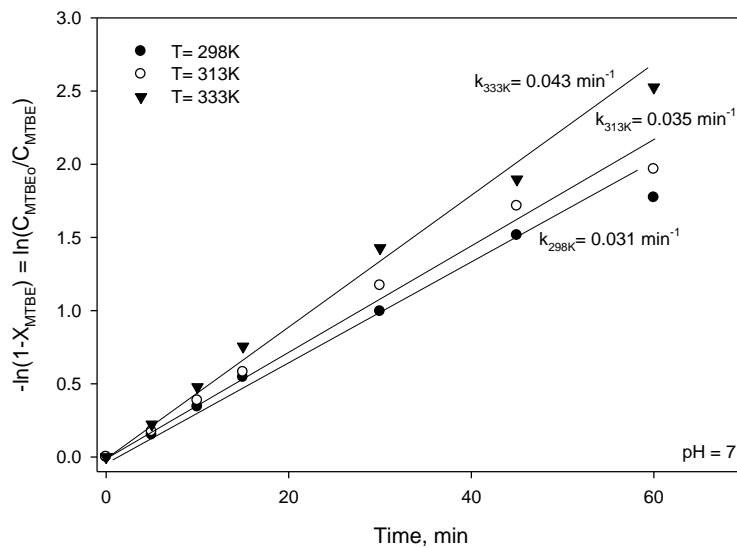


Fig. 8 First order reaction model of MTBE conversion at different temperatures and 7 pH

The values of the reaction rate coefficients for MTBE conversion appears to increase with temperature but increasing with pH in the range of 3 to 5 and then decreases when pH get neutral (pH=7), the reaction rate coefficient values are summarized in Table 1.

Table 1 Reaction rate coefficient values at different reaction conditions

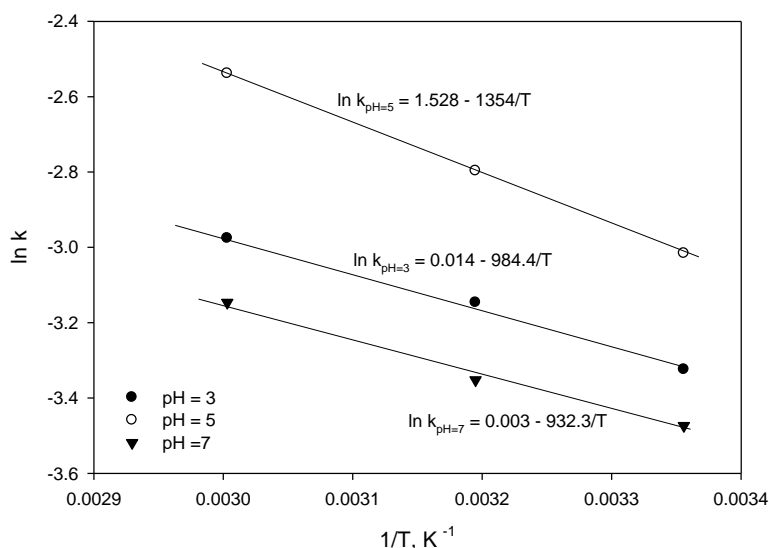
Temperature, K	Rate coefficient, min ⁻¹ at 3 pH	Rate coefficient, min ⁻¹ at 5 pH	Rate coefficient, min ⁻¹ at 7 pH
298	0.036	0.049	0.031
313	0.043	0.061	0.035
333	0.051	0.079	0.043

Reaction rate coefficient is “pure” function to temperature, but the difference in reaction rate coefficient values with pH variation is due to variation of reactive ion (OH⁻) amount with pH as a result of reactions equilibrium shifting (Eq. 1 and 2).

The activation energy for MTBE conversion reaction was calculated by using Arrhenius equation, which satisfies the relation between reaction rate coefficient and the reaction temperature [Levenspiel, 1972].

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (4)$$

A plot of $\ln k$ versus $\frac{1}{T}$ gives a straight line with a slope equal to $\frac{-E}{R}$ from which the activation energy was calculated, as shown in Figure 9 and the extracted activation energy and frequency factor values are summarized in Table 2.

**Fig. 9 Arrhenius plot of first order reaction model of MTBE conversion at different pH**

**Table 2 Activation energy and frequency factor values at different pH**

Solution pH	E, kJ/mole	ln A	R ²
3	8.18	0.014	0.9962
5	11.26	1.528	0.9992
7	7.75	0.0003	0.9908

Activation energy results show that reaction is more sensitive to temperature at pH 5 (high activation energy values reported) [Levenspiel, 1972]. No reported values of activation energy of MTBE conversion are found in literature survey.

CONCLUSIONS

- MTBE conversion increases with time (up to 60 minutes) and temperature (between 298 and 333 K).
- The increasing in solution pH from 3 to 5 increases MTBE conversion, but more increasing in neutral solution pH causes decrease in MTBE conversion.
- MTBE conversion of 0.99 (about complete conversion of MTBE) was achieved at 333 K and 60 minutes in pH solution 5.
- The reaction of MTBE conversion (disappearance) was first order with activation energy of 11.26 kJ/mole and natural logarithm of frequency factor was 1.528 (frequency factor equal to 4.61 min^{-1}) for the reaction at 5 pH solution.

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NOMENCLATURES

A	Frequency factor, min^{-1}
C_{MTBE}	Concentration of MTBE at any time(t), ppm
$C_{\text{MTBE}0}$	Initial concentration of MTBE, ppm (=3000 ppm)
E	Activation energy of reaction, J/mole
k	Reaction rate Coefficient, min^{-1}
R	Universal gas constant, (=8.314 J/mole. K)
T	Reaction temperature, K
t	Reaction time, min
X_{MTBE}	Conversion of MTBE, (dimensionless)