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# Treatment of Acetonitrile by Catalytic Supercritical Water Oxidation in Compact-Sized Reactor

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## Abstract

The objective of this research was to study the treatment of acetonitrile by catalytic supercritical water oxidation in a compact-sized tubular reactor, with an internal volume of 4.71 mL. Manganese dioxide was used as the catalyst and $H_2O_2$ was used as the oxidant. The oxidation of acetonitrile in supercritical water was studied at 400-500 °C, 25-35 MPa, the flow rate of 2-4 mL/min, the initial concentration of acetonitrile 0.077-0.121 M and the %excess $O_2$ of 50-200%. As a result, the products were mainly $N_2$, $CO_2$ and CO and acetonitrile can be decomposed > 93 % within a very short contact time (1.45-6.19 s). The oxidation process was carried out with respect to the conversion of acetonitrile by $2^5$ factorial design. Regression models were obtained for correlating the conversion of acetonitrile with temperature and flow rate. The complete oxidation can be achieved at a condition as moderate as 400 °C, 25 MPa with the flow rate of 2 mL/min.

**Keywords:** Acetonitrile, Supercritical Water Oxidation, Compact-Sized Reactor

## 1. Introduction

Laboratory wastes, which contain various types of hazardous chemicals generated from scientific research, have become a serious problem both financially and environmentally. Thus, two important and fundamental concepts of "treatment at the origin" and "self-responsibility for waste", brings about a development of a compact-sized reactor for an on-site laboratory wastewater treatment. Supercritical water oxidation (SCWO) has been proposed as a promising candidate for the treatment of various organic wastes. Organic compounds and permanent gases (such as oxygen) are completely miscible in supercritical water, so the oxidation occurs in a single-phase aqueous environment. It was reported that, above the critical point of water (374 °C, 22.1 MPa), most organic compounds can be converted into $CO_2$ and $H_2O$ by SCWO in a very short residence time [1–3]. Recently, there has been increasing interests in the use of heterogeneous catalysts in SCWO. Many catalysts can increase the oxidation rate, reduce the residence time and temperature requirement, and possibly provide a better selectivity for competing reaction pathways, which is difficult to achieve in noncatalytic processes [4].

Acetonitrile ($CH_3CN$) is widely used as a solvent for the synthesis of many chemicals such as perfumes, acrylic nail removers, pharmaceuticals, rubber products, pesticides and in the manufacturing of photographic film. It is also used as a solvent in various extraction processes and HPLC analysis technique [5]. In recent years, there have been a number of studies in literature demonstrating processes for the treatment of acetonitrile wastewater [6–8]. For incineration of nitrogen-containing organic compounds, the byproducts may include NO and $NO_2$. At lower temperatures as required in SCWO, however, thermodynamics favor nitrogen conversion into $N_2$ and $N_2O$, rather than NO or $NO_x$. In addition, any $NO_x$ formed would remain in the supercritical water, rather than being emitted to the atmosphere [9].

Thus, we have examined the oxidation of $CH_3CN$ in supercritical water using $MnO_2$ as a catalyst in a compact-sized reactor [10]. The reaction is of great interest since nitrile groups are commonly found in many commercial products and they are major constituents of waste streams.

## 2. Methods

### 2.1. Apparatus and Procedure

The SCWO experiments were performed in a custom-

made tubular reactor system schematically shown in **Figure 1**. It was designed to be a compact reaction system with a similar size to a gas chromatograph, so that it can be installed in a limited space of a general laboratory. The experimental apparatus consists of a tubular reactor (0.1 m x 3/8" I.D. with an internal volume of 4.71 mL), which is heated by a 200 W vial heater. A commercial catalyst, bulk $MnO_2$ was packed in the reactor. The wastewater and oxidant pre-heating line (180 cm x 1/8" I.D.) is heated by a 100 W electrical heater. All wetted parts (tubing, fittings, etc.) from the feeding pumps to the gas–liquid separator, were made of SUS316 stainless steel. The oxidant feed stream was prepared by dissolving hydrogen peroxide with deionized water in a feed tank. Another feed tank was loaded with a mixture of hydrogen peroxide (oxidant) and acetonitrile solution as a simulated wastewater. The two feed streams were fed in different lines using two HPLC pumps (Jasco) and were brought together at a SUS316 stainless steel mixing tee, prior to entering the pre-heater section. Hydrogen peroxide decomposes into oxygen and water completely when it is heated in the pre-heater section (150-200 $^{\circ}$C) as verified by previous experiments [11]. After pre-heating, the solution was fed into the reactor. The reactor inlet and outlet temperature were measured using thermocouples. The experiments were carried out at 400-500 $^{\circ}$C, 25-35 MPa, the initial concentration of acetonitrile 0.077-0.121 M and the % excess $O_2$ of 50-200 %. Upon exiting the reactor, the effluent was cooled rapidly by passing through a heat exchanger. Then, the effluent was flowed through a 0.5 μm inline filter, before being depressurized by a back-pressure regulator (GO REGULATOR Inc.). The product stream was then separated into liquid and vapor phases. The liquid products were collected in a graduated cylinder. It was assumed that the liquid and vapor phases were in equilibrium in the phase separator, and Henry's law was used to calculate the amount of each gas dissolved in the liquid. The flow rates of both the gas and liquid phases were measured at the ambient laboratory condition.
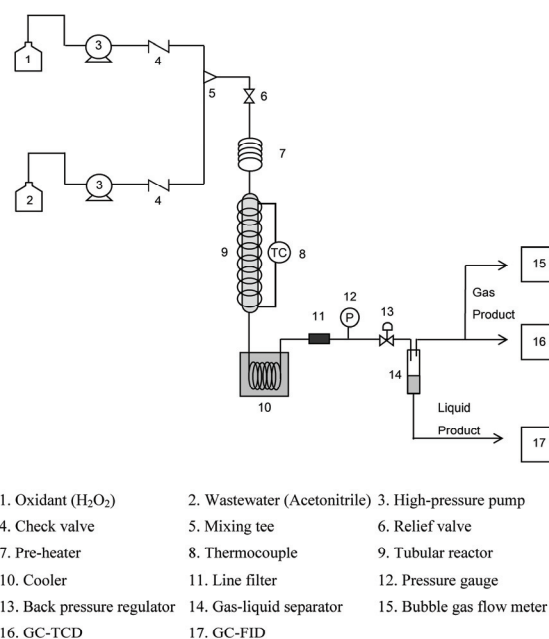
## 2.2. Materials and Analytical Methods

The oxidant is oxygen which was produced by the thermal decomposition of hydrogen peroxide (Fisher, 30 %, w/v aqueous solution). Acetonitrile (Lab scan, > 99 % purity) was used as the organic compound to be oxidized in the catalytic SCWO experiments.

The effluent liquid phase was collected and then analyzed by a Shimadzu 7AG gas chromatograph with a flame ionization detector. The on-line gas samples were analyzed using a Shimadzu 2014 gas chromatograph with a thermal conductivity detector.

## 2.3. Experimental Design

A full $2^5$ factorial design was performed to evaluate the



| 1. Oxidant ($H_2O_2$) | 2. Wastewater (Acetonitrile) | 3. High-pressure pump |
| 4. Check valve | 5. Mixing tee | 6. Relief valve |
| 7. Pre-heater | 8. Thermocouple | 9. Tubular reactor |
| 10. Cooler | 11. Line filter | 12. Pressure gauge |
| 13. Back pressure regulator | 14. Gas-liquid separator | 15. Bubble gas flow meter |
| 16. GC-TCD | 17. GC-FID | |

**Figure 1. Schematic diagram of the compact-sized reactor.**

**Table 1. Factors and levels used in the $2^5$ factorial design.**

| Factor | Parameter | Level | |
| --- | --- | --- | --- |
| | | (-) | (+) |
| A | Temperature ($^{\circ}$C) | 400 | 500 |
| B | Pressure (MPa) | 25 | 35 |
| C | Flow rate (mL/min) | 2 | 4 |
| D | Initial acetonitrile concentration (M) | 0.077 | 0.121 |
| E | Excess $O_2$ concentration (%) | 50 | 200 |

effects of 5 factors; temperature, pressure, flow rate, initial acetonitrile concentration and % excess $O_2$ concentration on conversion of acetonitrile. **Table 1** summarizes these factors and their respective levels. The statistical analysis of variance, ANOVA, was carried out to determine the significance and impact of each factor as well as their interactions on the conversion. The relationships linking the main factors and interactions with the conversion were determined and presented as a quadratic equation of the general form in the following equation.

$$Y = \text{mean} + \sum\text{main effects} + \sum\text{interactions} \quad (1)$$

The equation coefficients were calculated using the coded values, thus the effects of various terms can be compared directly regardless of their actual magnitude. The coding used throughout the statistical analysis denotes that −1 was taken as the lower level and +1 as the upper level. Therefore, a positive coefficient of a pa-

rameter indicates that the conversion increases with increasing level of the parameter, while a negative coefficient indicates that the conversion increases with decreasing level of the parameter.

The conversions of acetonitrile were calculated using the following equation.

$$X = (1 - C_t / C_o) \times 100 \qquad (2)$$
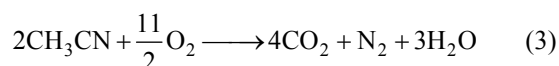
where: $X$ = acetonitrile conversion (%)

$C_t$ = concentration of acetonitrile at a given time $t$ (M)

$C_o$ = initial concentration of acetonitrile (M)

## 3. Results and Discussion

The experimental data using full $2^5$ factorial design were listed in **Table 2**, 32 factorial points and 4 central points included. The experiments were executed in a random order to correctly evaluate experimental errors [12]. The conversions were obtained to be between 93.63 % and

100 % at the contact times ranging from 1.45 to 6.19 s under various reaction conditions. The gas phase products were detected as CO, $CO_2$, $CH_4$, $N_2O$, $N_2$, $H_2$ and $O_2$ by GC analysis. The liquid phase products were clear and colorless. The analysis of gas and liquid products showed that acetonitrile was completely degraded and transformed into intermediate products, $CO_2$, $H_2O$ and $N_2$. The decomposition of $CH_3CN$ in the SCWO can be expected to follow the oxidation reaction,

$$2CH_3CN + \frac{11}{2}O_2 \longrightarrow 4CO_2 + N_2 + 3H_2O \qquad (3)$$

Although catalytic SCWO was carried out at high pressures and temperatures, its advantages of short reaction time and environmental friendliness overcame its shortcomings. In comparison with other treatment techniques such as nitrile-degrading microorganisms [6,8], which needed more than 10 h of reaction time, catalytic SCWO required only in the order of seconds with the

**Table 2. Results and reaction parameters for SCWO of acetonitrile.**

| Run order | Temperature (°C) | Pressure (MPa) | Flow Rate (mL/min) | Initial Concentration of Acetonitrile (M) | Excess Oxygen (%) | Conversion (%) |
|---|---|---|---|---|---|---|
| 1 | 402 | 34.8 | 4 | 0.121 | 50 | 99.75 |
| 2 | 398 | 24.2 | 4 | 0.121 | 50 | 96.16 |
| 3 | 408 | 26 | 2 | 0.077 | 50 | 98.32 |
| 4 | 453.5 | 30.5 | 3 | 0.099 | 125 | 99.11 |
| 5 | 503.5 | 34.9 | 4 | 0.121 | 200 | 99.90 |
| 6 | 389 | 25.2 | 4 | 0.077 | 200 | 93.65 |
| 7 | 502.5 | 25.5 | 2 | 0.077 | 200 | 99.85 |
| 8 | 410 | 35 | 2 | 0.121 | 50 | 98.82 |
| 9 | 389.5 | 25 | 4 | 0.121 | 200 | 95.18 |
| 10 | 396 | 25 | 4 | 0.077 | 50 | 95.44 |
| 11 | 451.5 | 30.6 | 3 | 0.099 | 125 | 98.37 |
| 12 | 504 | 35.3 | 2 | 0.077 | 50 | 99.84 |
| 13 | 408.5 | 35 | 2 | 0.121 | 200 | 97.74 |
| 14 | 402.5 | 35.5 | 4 | 0.077 | 50 | 97.86 |
| 15 | 506 | 35 | 2 | 0.121 | 200 | 99.88 |
| 16 | 401 | 35.3 | 4 | 0.121 | 200 | 97.00 |
| 17 | 499.5 | 24.7 | 2 | 0.077 | 50 | 99.98 |
| 18 | 507 | 34.8 | 2 | 0.121 | 50 | 99.87 |
| 19 | 501.5 | 35 | 4 | 0.077 | 200 | 99.82 |
| 20 | 501 | 25 | 4 | 0.077 | 50 | 99.72 |
| 21 | 503 | 35.5 | 4 | 0.121 | 50 | 99.74 |
| 22 | 407.5 | 36 | 2 | 0.077 | 200 | 99.47 |
| 23 | 496 | 24 | 2 | 0.121 | 50 | 100.00 |
| 24 | 404 | 34 | 4 | 0.077 | 200 | 97.35 |
| 25 | 496.5 | 25 | 4 | 0.077 | 200 | 99.90 |
| 26 | 449 | 30.5 | 3 | 0.099 | 125 | 98.85 |
| 27 | 403.5 | 25.3 | 2 | 0.121 | 50 | 100.00 |
| 28 | 498.5 | 25 | 4 | 0.121 | 200 | 99.99 |
| 29 | 405 | 35.4 | 2 | 0.077 | 50 | 99.50 |
| 30 | 448.5 | 30 | 3 | 0.099 | 125 | 98.31 |
| 31 | 505.5 | 25.3 | 4 | 0.121 | 50 | 99.93 |
| 32 | 504.5 | 34.6 | 2 | 0.077 | 200 | 99.93 |
| 33 | 495.5 | 35 | 4 | 0.077 | 50 | 99.83 |
| 34 | 400 | 25 | 2 | 0.077 | 200 | 99.16 |
| 35 | 506.5 | 25.6 | 2 | 0.121 | 200 | 99.99 |
| 36 | 437.5 | 24.5 | 2 | 0.121 | 200 | 100.00 |

same conversion. In terms of environmental impact, catalytic SCWO generated less toxic components as supposed to NO or $NO_x$ emitted from incineration [7].

The $2^5$ factorial study revealed that the conversion was not significantly influenced by the initial acetonitrile concentration, pressure and % excess oxygen, while temperature, and flow rate influenced the conversions at 95 % confidence interval. A mathematical model for the conversion of acetonitrile can be written in terms of the statistically significant effects on conversion in (4) and (5) [12,13].

$$\%Conversion = 98.9 + 0.989T' - 0.529F' + 0.545T'F' \quad (4)$$

where: $T'$ = coded value of temperature
$\quad\quad F'$ = coded value of flow rate
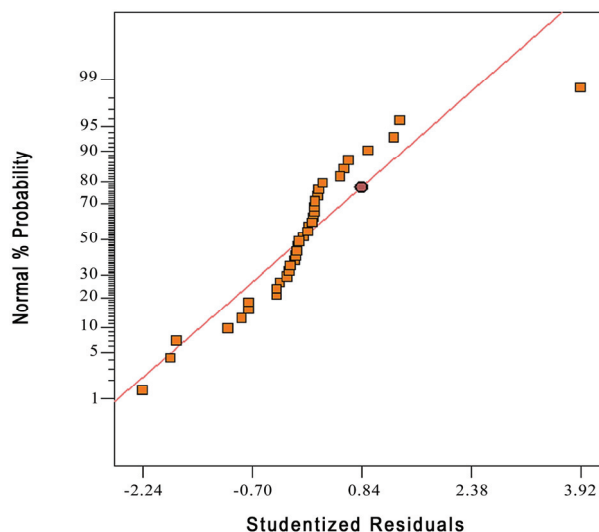
$$\%Conversion = 106 - 0.013T - 5.48F + 0.011TF \quad (5)$$

where: $T$ = actual value of temperature ($^{o}$C)
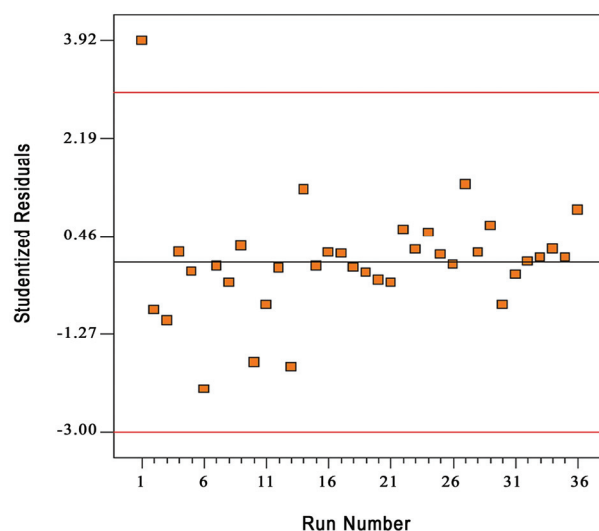$\quad\quad F$ = actual value of flow rate (mL/min)

A positive sign of the coefficient represents a synergistic effect, while a negative sign indicates an antagonistic effect. The temperature and flow rate have a negative relationship with the conversion, so with an increase of those factors, there will be a decrease in the conversion. However, the interaction term has a positive sign indicating that with a change in temperature and flow rate in the same direction from the central point, there will be an increase in the conversion. **Figure 2** shows a comparison between the experiment and predicted conversion for acetonitrile decomposition. The high value of the coefficient of determination, $R^2 = 0.8$ indicates a good correlation between the observed and the predicted values of conversion.



**Figure 2. Comparison of the experimental and the predicted conversion.**



**Figure 3. Normal probability plot of the difference between the observed and the predicted value.**



**Figure 4. The residuals versus the run number when the variance is constant.**

The normality of the data can be checked by plotting the normal probability plot (NPP) of the residuals. The normal probability plot is a graphical technique for assessing whether or not a data set is approximately normally distributed [14]. The residual is the difference between the observed and the predicted values (or the fitted values from the regression). **Figure 3** shows the normal probability plot of residuals. The residuals fall fairly close to the diagonal line, so the data are normally distributed. **Figure 4** illustrates the residuals for each run number. The residuals scatter randomly about zero with no specific trend, confirming that the residuals are the random error that have a normal distribution.

## 4. Conclusions

A compact-sized tubular reactor was designed to treat the aqueous solution of acetonitrile at the origin using catalytic supercritical water oxidation. The oxidation of acetonitrile was studied using $2^k$ factorial experimental design. The significant factors were found to be temperature and flow rate. The mathematical models correlating the conversion to temperature and flow rate were formulated and evaluated. The results demonstrated that the SCWO process can treat acetonitrile efficiently, with the contact times between 1.45 and 6.19 s, and the acetonitrile concentration between 0.077 and 0.121 M. It was found that acetonitrile was completely degraded and transformed into its intermediate products, $CO_2$, $H_2O$ and $N_2$. The liquid phase products were clear and colorless. The advantage of catalytic supercritical water oxidation is the rapid oxidation of organics and the nitrogen conversion into $N_2$ and $N_2O$ rather than NO or $NO_x$.

## 5. Acknowledgment

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