Oxidation of Methanol in Supercritical Water

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Abstract: Oxidation of methanol in supercritical water has been studied in an isothermal flow reactor over the temperature range 400~500 °C at 250 bar. The reaction kinetics were estimated and the oxidation rate was first order with respect to methanol concentration and proportional to oxygen concentration raised to the power of 0.1. The activation energy for methanol oxidation was 193.7 kJ/mol (46.3 kcal/mol) over the temperature range of 400~475 °C. The model gave reasonable predictions of the concentrations of methanol, oxygen, carbon monoxide and carbon dioxide. However there were large errors involved with the prediction of hydrogen concentration.

Keywords: supercritical water (SCW), methanol, oxidation, kinetics

1. Introduction

For the past decade, a considerable attention has been paid to the application of supercritical water (SCW) as a processing medium in chemical reaction processes, especially in the area of oxidation of organics. SCW displays quite different properties to those of water at ambient conditions. In addition to the typical properties of conventional supercritical fluids (SCFs) such as wide variation in density and viscosity with small changes in pressure and temperature, SCW also has a high propensity for dissolving organics, a low solvating power for inorganics and a low dielectric constant. The gases such as oxygen, methane and nitrogen are fully miscible with SCW. These properties enable to proceed the oxidation reaction in a single homogeneous phase without the complications of diffusion controlled kinetics. A variety of organics have been oxidized in SCW [1-4]. Although the SCW oxidation process has been successfully used for the destruction of some hazardous chemical wastes, the reaction kinetics and mechanisms of the reactions involved have not been fully understood. The available information in the literature is focused on the efficiencies of the destruction of the specific compounds. Little information on fundamental studies of SCW oxidation is available.

Kinetic data for oxidation in SCW were first reported by Wightman [5], for phenol and acetic acid. The oxidation kinetics of carbon monoxide and ethanol in SCW were studied with an isothermal plug-flow reactor [6-8]. The oxidation of methane in SCW was studied by several workers [9-14]. Webley and Tester [10] reported that CO and CO₂ were the only carbon-containing oxidation products, and no methanol and formaldehyde were detected. However, although the methanol was not yielded from the oxidation of methane, it was reported that there were the formation and oxidation steps of methanol in free-radical reaction pathways developed from elementary reaction model [10]. The oxidation of methanol in SCW was studied over the temperature range of 430 to 590 °C [15-18]. A developed rate-expression by Tester and coworkers [16] was proportional to the oxygen and methanol concentrations raised to the powers of 0.12 and 0.89 respectively.

The purpose of the present study is to investigate the kinetics of the methanol oxidation in SCW, and to substantially expand the present database for SCW oxidation kinetics.

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2. Experimental

2.1. Apparatus

A schematic flow diagram of the experimental apparatus is shown in Figure 1. The tubular reactor used was 0.73 m of 0.25 inch O.D. x 0.18 inch I.D. of Hastelloy C-276 tubing immersed in a temperature-controlled fluidized sand bath. The aqueous methanol solutions were delivered to the reactor with two high pressure water pumps. A gas booster and a mass flow controller were used to deliver oxygen to the reactor. The solution and oxygen feeds were combined in a stainless steel cross-piece. In order to enhance mixing, oxygen was passed through a sparger which was located at the inlet of the cross. An Inconel sheathed type-K thermocouple was sealed in the cross. A water-cooled double-pipe heat exchanger was used to cool down reactor effluent to high pressure ambient water. The cooled effluent was then depressurized through a back-pressure regulator and fed to a gas-liquid separator. An in-line oxygen analyzer was used to measure the oxygen concentration of gasous effluent. More details have been described in elsewhere [18].

2.2. Laminar Flow Reactor

A tubular reactor system was used for this study. Under the experimental conditions investigated in the present study, the Reynold’s numbers of the flow ranged from 300 to 1700 and in this range flow regime is considered to be laminar. In addition, a residence time distribution experiment, as described in detail elsewhere [18], has shown that the flow regime was laminar at a flowrate corresponding to a value of 1700 for the Reynold’s number. The flow was also checked against the characteristic times criteria by the plug flow idealization model [19] and the results showed that the flow regime could be assumed to be laminar. The reactor was therefore considered as a laminar flow reactor. In the laminar reactor the fluid passes through the tube in the form of streamlines and radiative velocities of these stream-lines generate a parabolic velocity profile. Hence the laminar velocity profile can be assumed to approximate a series of annuli. The velocity of each annulus is constant. If there is no radial and axial diffusion in the reactor, each annulus can be considered to be plug flow. The velocity profile in a laminar flow reactor is:

\[ \tau = V_0 \cdot \left(1 - \frac{r^2}{R^2}\right) \]  

(1)

If time (t) is the residence time of the fluid at radius (r) in the reactor of length (L):

\[ t = \frac{L}{V_0 \cdot \left(1 - \frac{r^2}{R^2}\right)} \]  

(2)

From the Equations (1) and (2),

\[ t \cdot dr = \frac{L \cdot R^2}{2V_0} \cdot \frac{dt}{t^2} \]  

(3)

If the reaction is B+nM → products, the disappearance rate of component B is represented as below:

\[ -\frac{dC_B}{dt} = k \cdot C^n_B \cdot C_M^k \]  

(4)

Since the mean conversion of total flow is equal to the sum of fractional conversion of each annular element, the mean fractional conversion of component B over the exit plane \((f_{B,\text{avg}})\) is:

\[ f_{B,\text{avg}} = \sum \frac{4\pi \cdot r \cdot dr}{R^2 \cdot t} \cdot f_{B,r} \]  

(5)

2.3. Procedure

The oxidation of methanol in SCW was investigated over the temperature range of 400 to 500 °C at 250 bar with residence times of 8 to 40 seconds. Methanol and oxygen feed concentrations ranged from 5.4 × 10⁻³ to 2.5 × 10⁻² gmol/liter and 2.4 × 10⁻² to 0.11 gmol/liter respectively. A stoichiometric excess of oxygen
was used, ranging from 50% to 200% excess with the assumption that oxidation is \( \text{CH}_3\text{OH}+3/2\text{O}_2 \rightarrow \text{CO}_2+2\text{H}_2\text{O} \). One experimental run was conducted in the absence of oxygen to determine the significance of methanol pyrolysis reactions.

Prior to each experiment, the system was tested for leaks. The start-up procedure for each experiment involved first pressurizing the system to desired reaction pressure at room temperature by pumping in feed solution and oxygen. The heaters were then turned on. During the heat-up time, the system was maintained at the reaction pressure. After the reactor attained the desired temperature, the feed solution and compressed oxygen were fed to the preheaters and the heated solution and oxygen were mixed at the inlet of the reactor. The reactor effluent was cooled quickly by the heat exchanger. The cooled effluent passed through a regulator and then entered a gas-liquid separator. Some of the gas effluent was used to measure the oxygen concentration with an in-line oxygen analyzer. Before collecting the samples, the system was operated for 3–6 hrs, depending on the pumping rate, to establish a steady state. Samples were taken in triplicate at intervals of 20–30 mins. The collected gas and liquid samples were analyzed by gas chromatography.

3. Results and Discussion

3.1. Data Analysis and Interpretation

Methanol was oxidized to carbon monoxide, carbon dioxide and hydrogen with conversions ranging from 0 to 99% (based on the disappearance of methanol). No formaldehyde was detected in the reactor effluent. These results are consistent with those of Webley and Tester [15]. However contrary to the present results, Brock and coworkers [17] reported that formaldehyde was a primary product of the methanol oxidation in SCW and it’s yield was always less than 24% with residence time of 0.2–1.2 secs. These results can be explained on the basis of the residence time of 8–40 secs in the present study. Since formaldehyde is more active than methanol, a much longer residence time results in the oxidation of produced formaldehyde. In addition the methanol concentration in this study was about 20 times higher than in the study of Brock and coworkers [17], and this means that the heat released by the methanol oxidation might result in local hot points and, thus enhance to oxidize the produced formaldehyde.

For 0.3 mol % methanol feed solution, the conversions of methanol with 200% excess \( \text{O}_2 \) are plotted as a function of mean residence time at different temperatures in Figure 2. The conversions of methanol increased as the temperature and mean residence time increased. All of the other data (50% and 100% excess \( \text{O}_2 \)) have shown a similar trend. The conversion of methanol as a function of the \( \text{O}_2 \) excess is shown in Figure 3. Under oxygen-rich conditions, the conversion of methanol is almost independent of the \( \text{O}_2 \) concentration for the temperature range of 410–500 °C. This suggests that the concentration of oxygen has a small effect on the methanol oxidation rate. Under the experimental conditions investigated in the present study, selectivities to \( \text{CO} \) and \( \text{CO}_2 \) ranged respectively from 0 to 91% and 9 to 100% of the methanol consumed. The selectivity to \( \text{CO}_2 \) generally increased as the conversion of methanol and mean residence time increased. The selectivity to \( \text{CO} \) has shown the reverse characteristic of the selectivity to \( \text{CO}_2 \).

From the pyrolysis/hydrolysis experiment, methanol was found to be stable in SCW at 500 °C and no \( \text{CO} \) and \( \text{CO}_2 \) were detected in the reactor effluent. It was suggested that SCW did not directly participate in the oxidation reaction and only enabled to proceed the oxidation reaction in a single homogeneous phase without the complications of diffusion controlled kinetics. It was therefore confirmed that all of the obtained \( \text{CO} \) and \( \text{CO}_2 \) in the outlet were produced from the oxidation of methanol. Webley [20] reported that at 544 °C, 2.1% of methanol was converted to \( \text{CO} \), \( \text{CO}_2 \) and \( \text{H}_2 \) with a residence time of 6.6 sec in the absence of oxygen. This suggests that up to 500 °C methanol is stable in SCW and at higher temperatures it starts to slowly react with SCW.

A trace amount of hydrogen was detected in the products of oxidation. Previously, hydrogen was also
detected in the products of SCW oxidation [7,20] and it was suggested that the water-gas-shift reaction is the most likely mechanism for hydrogen gas formation. In the present study, as with the methane oxidation [18], it is also assumed that hydrogen formation occurs via the water-gas-shift reaction.

• water-gas-shift reaction: CO + H₂O = CO₂ + H₂

Liquid samples were analyzed for formaldehyde and acetaldehyde. No aldehydes were detected in the products of oxidation. Under the conditions investigated, CO and CO₂ were the only carbon containing products for the oxidation of methanol in SCW.

3.2. Rate Expression

Since the mole fractions of methanol are less than 0.01 in SCW, the water concentration can be considered to be constant during the oxidation. It is therefore assumed that the rate of methanol oxidation is independent of the water concentration. The form of global rate expression is assumed as:

\[- \frac{d[\text{MeOH}]}{dt} = k \cdot [\text{MeOH}]^{0.9} \cdot [\text{O}_2]^{0.1}\]  (6)

To use Equation (6), it is necessary to change the concentration terms to the initial concentration and conversion terms which can be determined directly from the experiments. And to derive the rate expression, it is required to solve Equation (5) numerically. More details have been described in elsewhere [14,18].

From a FORTRAN program using the optimization routine IMSL, the oxidation rate of methanol was estimated by regression of the data at 400~475 °C.

\[- \frac{d[\text{MeOH}]}{dt} = 10^{13.45} \cdot \exp(-133.7/R \cdot T) \cdot [\text{MeOH}]^{0.9} \cdot [\text{O}_2]^{0.1}\]  (7)

The activation energy is in kJ/mol and the parameter uncertainties are at the 97% confidence level which is estimated using a propagation of errors approach. However, since the obtained experimental measurements were the mean of three samples and the estimates of errors in the experimental data were themselves uncertain, a 97% confidence level was approximated as X ± 2σ. The oxidation rate of methanol is proportional to the O₂ and CH₃OH concentrations raised to the powers of 0.1 and 1.0 respectively at 400~475 °C. Under the oxygen-rich conditions, reaction rate mainly depends on the concentration of methanol. The predicted and observed conversions are represented in Figure 4. At the temperatures of 400~425 °C, it is experimentally difficult to maintain reaction conditions because small changes in temperature and pressure can cause large changes in the density of SCW. In addition with relatively higher methanol concentrations, the heat released by the oxidation might form local hot points and thus result in higher reaction rate. These may account for some of the scatter in the data in Figure 4.

Tester and coworkers [16] reported that methanol oxidation kinetics were proportional to the oxygen and methanol concentrations raised to the powers of 0.12 and 0.89 respectively. This is in good agreement with the present work. However the values of A and E_a evaluated by Tester and coworkers [16] are 10^{12.8±10.5} and 447±125 (kJ/mol) and these values are quite different from those obtained in the present work. If
Table 1. Rates and Rate Constants for the global mechanism of methanol oxidation

<table>
<thead>
<tr>
<th>rates</th>
<th>rate constants</th>
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<tbody>
<tr>
<td>(\frac{d[CH_3OH]}{dt}) = (-k_1[CH_3OH]^4(O_2)^{3/2})</td>
<td>(k_1 = 10^{13.8} \cdot \exp(-19537/RT))</td>
</tr>
<tr>
<td>(\frac{d[CO]}{dt}) = (-k_2[CO]^{1/2} - k_3[CO]^{3/2} + k_4[CH_3OH])</td>
<td>(k_2 = 10^{23} \cdot \exp(-238/RT))</td>
</tr>
<tr>
<td>(\frac{d[CO_2]}{dt}) = (-\frac{d[CO]}{dt} - \frac{d[CH_3OH]}{dt})</td>
<td>(k_3 = 10^{25} \cdot \exp(-42.9/RT))</td>
</tr>
<tr>
<td>(\frac{d[H_2]}{dt}) = (k_5[CO]^{1/2} - k_6[H_2])</td>
<td>(k_5 = 10^{17} \cdot \exp(-372/RT))</td>
</tr>
</tbody>
</table>

Activation energy in kJ/mol, [C] in gmol/L.

it is assumed that both results are correct, then the reaction mechanisms must be different under the experimental conditions investigated in both studies. A temperature range of 400 \(\sim\) 475 \(^\circ\)C was used in this study and 450 \(\sim\) 550 \(^\circ\)C in the study of Tester and coworkers [16]. As the methanol concentrations in the fuel for this study were also much higher than those for Tester and coworkers [16], these differing experimental conditions may account for the discrepancy.

3.3. Oxidation Mechanism

Although it was reported that formaldehyde was a primary product of the methanol oxidation in SCW [17], no formaldehyde was detected in the present study. The methanol oxidation mechanism, proposed by Webley [20], is therefore adapted and is shown in Figure 5. However, the rate expression for the methanol oxidation is the one obtained in this study and the rate of hydrogen oxidation is based on the work of Holgate and Tester [21]. The proposed rates and rate constants are shown in Table 1.

The differential equations in Table 1 were solved with an IMSL routine for first-order differential equations. Since the rate expression for methanol oxidation has been developed by optimization of the data, the calculated conversions of methanol have been already compared with the experimental conversions in Figure 4. The calculated \(O_2\) concentrations in the reactor exit are compared with the observed \(O_2\) concentrations in Figure 6. There is a close agreement between the experimental and predicted data for the whole range of oxygen concentration.

The calculated selectivities to carbon monoxide and carbon dioxide in the reactor exit are shown as a function of the experimental data in Figures 7 and 8 respectively. At a temperature of 400 \(\sim\) 425 \(^\circ\)C there is a good agreement between the data, while at the temperatures of 450 \(\sim\) 475 \(^\circ\)C (higher methanol conversion (>85%) was achieved) the data are scattered. At this temperature range, the model overpredicted the selectivities to CO and underpredicted the selectivities to CO\(_2\). This means that either the direct oxidation of CO is relatively slow at higher temperatures or the water-gas-shift reaction or both of the reactions are relatively slow under these conditions. The rate expression for CO was determined by Helling and Tester [7]. There are some differing concentrations of species and this may account for the small over
4. Conclusions

It was found that methanol was stable in SCW upto 500 °C. The methanol was oxidized to carbon monoxide and carbon dioxide with the conversions ranging from 0 to 99% (based on the disappearance of methanol). No formaldehyde was detected. The conversions of methanol increased with the increasing temperature and mean residence time. Under oxygen-rich conditions, the conversion of methanol was almost independent of the O₂ concentration.

The rate expression for methanol oxidation was evaluated. The rate is proportional to the oxygen concentration raised to the power of 0.1 and proportional to the methanol concentration raised to the power of 1.0. The activation energy is 193.7 kJ/mol (46.3 kcal/mol). The model gave reasonable predictions of the concentrations of methanol, oxygen, carbon monoxide and carbon dioxide. However there were large errors involved with the prediction of hydrogen concentration.

Nomenclature

- A : pre-exponential factor
- E₀ : activation energy (kJ/mol)
- fB,avg : mean fractional conversion of component B over the exit plane
- fB,i : fraction conversion of component B of each annular element
- k : rate constant
- L : reactor length
- r : radius in the reactor
- R : reactor radius
- t : residence time of the fluid at any radius (r)
- V(r) : velocity of the fluid at any radius (r)
- V₀ : velocity at the center line of the reactor
- X : conversion
- σₓ : standard error in X
- α, β : reaction orders

References

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