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Computer simulation of methanol oxidation in supercritical water

F.Esmaeilzadeh*, M.Kordnejhad, S.Zareie

Chemical Engineering Department, Shiraz University, Shiraz, (IRAN)

E-mail : esmaeil@shirazu.ac.ir

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ABSTRACT

Supercritical solvent is used as a reaction medium in which the solvent either actively participates in the reaction or functions solely as the solvent medium for the reactants, catalysts and products. A mathematical model has been developed and tested with experimental data for methanol oxidation in supercritical water. The model is based on a material balance in a differential element of reactor and is subjected to constant temperature and pressure through the reactor length. In this work, Runge-Kutta of fourth order is used to solve the differential equations and obtain the concentration profiles through the reactor length. The agreement between calculated concentrations and methanol conversion with experimental data confirms the validity of the developed model. Once the validity of the model is checked, the effects of variables such as the residence time, temperature and feed ratio upon the conversion of methanol are surveyed. © 2008 Trade Science Inc. - INDIA

INTRODUCTION

With an supercritical fluid medium it may be possible to increase the selectivity of a reaction while maintaining high conversions, to dissolve reactants and catalyst in a single fluid phase and carry out the reaction homogeneously, and to capitalize on the solvent characteristics of the supercritical fluid to separate the product species from the reactants, catalyst, and unwanted by-products. Reaction rates may also be enhanced while the process is operating in the mixture critical region as a result of the potentially favorable effect of applied hydrostatic pressure. Supercritical conditions for water is above 374°C (705°F) and 22.1 MPa(3200psia).

Under supercritical conditions, water behave like a dense gas with a high solubility of organics^[1], complete miscibility in all proportions with oxygen^[2], high diffusivities^[3], low viscosity^[4], and low solubility and dissociation of inorganics, particularly ionic salts^[5,6].

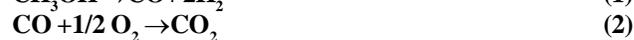
Several studies have been done to determine the fundamental reaction kinetics in supercritical water^[7-11]. Richard K.Helling and Jefferson W.Tester^[9] determined

the oxidation kinetics of dilute carbon monoxide in supercritical water and conditions in the isothermal, plug-flow reactor and temperature between 400 and 540°C, pressure around 24.6 MPa(3550 psia), and residence time 6-13s.

Jefferson W.Tester, Paul A.Webley H.Richard Holgate^[10] have been investigated the oxidation of methanol in supercritical water over the temperature range 450-550°C at 246 bar(3550 psia). Methanol concentration ranges from 1.28×10^{-3} to 5.68×10^{-3} mol/L and oxygen feed concentration ranges $< 0.04 \times 10^{-3}$ to 5.07×10^{-3} mol/L and water concentration is 4.33-5.98 mol/L. Reactor residence time 6.7 to 9.6 s. Experiments were carried out in the Inconel 625 tubular system with outside diameter of 1/4-in.(6.35mm) and 1/16-in.(1.71 mm)^[11].

2. Rate expressions

In the reactor three chemical reactions happen :



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The kinetic of methanol oxidation in supercritical water that is used in this work was determined by Jefferson W. Tester, Paul A. Webley and H. Richard Holgate^[10] that can be expressed as follows:

$$\frac{d[\text{CH}_3\text{OH}]}{dt} = -10^{26.2 \pm 5.8} \exp\left(\frac{-408.8 \pm 85.4}{RT}\right) [\text{CH}_3\text{OH}] \quad (4)$$

Where the activation energy of 408.8 is in kJ/mol (or equivalently 97.7 kcal/mol); R= universal gas constant, 8.31 J/mol.K; T=absolute temperature K and [CH₃OH]=methanol concentration, mol/L.

The oxidation kinetics of carbon monoxide in supercritical water was determined by Richard K. Helling and Jefferson W. Tester^[9] shown as follows:

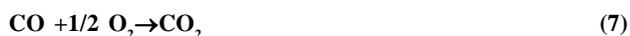
$$\frac{d[\text{CO}]}{dt} = -10^{7.25 \pm 0.53} \exp\left(\frac{-120 \pm 7.7}{RT}\right) [\text{CO}]^{1.014 \pm 0.09} [\text{O}_2]^{0.03 \pm 0.04} \quad (5)$$

Where the activation energy of 120 is in kJ/mol; R=universal gas constant, 8.31 J/mol.K; T=absolute temperature, K; [CO]=carbon monoxide concentration, mol/L and [O₂]=oxygen concentration mol/L.

This equation is a global rate expression and can not separate contribution to the production of CO₂ of the water gas shift pathway:



And the direct oxidation of carbon monoxide pathway is:



The kinetic of gas shift reaction (9) can be also expressed as follows:

$$\frac{d[\text{CO}]}{dt} = -10^{1.6 \pm 3.57} \exp\left(\frac{-62.9 \pm 8.6}{RT}\right) [\text{CO}]^{0.568 \pm 0.107} \quad (8)$$

And the kinetic of direct oxidation^[9] is:

$$\frac{d[\text{CO}]}{dt} = -10^{17.4 \pm 1.63} \exp\left(\frac{-238 \pm 24}{RT}\right) [\text{CO}]^{1.87 \pm 0.02} [\text{O}_2]^{0.03 \pm 0.06} \quad (9)$$

3. Mathematical model

The model is developed based on material balance at constant temperature and pressure throughout the reactor length with negligible mass and heat transfer in radial direction.

The reactor is divided into 100 equal compartments

in which, $V_i = V_t/100$.

where V_i =volume of one compartment, m³, V_t =total volume of reactor, m³

The residence time in reactor can be obtained from the following relation:

$$t = V_t/Q \quad (10)$$

Where t=residence time in reactor, s. V_t =total volume of reactor, m³. Q=volumetric flow rate, m³/s.

The value of Q can be assumed to be constant due to having higher concentration of water with respect to concentration of methanol, carbon monoxide, carbon dioxide and hydrogen. Therefore, the value of residence time in each compartment is equal to $t/100$. The effect of O₂ concentration in calculation of rate equation was negligible due to having very small order. As a result shown in several tests, it can be omitted.

The schematic diagram of each compartment was shown in figure 1. On basis of above assumptions, material balance equation that describe the evaluation of the composition along an isothermal reactor can be written as:

$$X_2 = X_1 \times dt \times \left(-10^{17.4}\right) \exp\left(\frac{-238}{R \times T}\right) \times X_1^{1.87} \quad (11)$$

$$Y_2 = Y_1 \times dt \times \left(-10^{1.6}\right) \exp\left(\frac{-62.9}{R \times T}\right) \times Y_1^{0.568} \quad (12)$$

$$X_1 + Y_1 = C_{\text{CO}(i)} \quad (13)$$

$$X_2 + Y_2 = C_{\text{CO}(i+1)} \quad (14)$$

$$r_1 = \frac{d[\text{CH}_3\text{OH}]}{dt} = -10^{26.2} \exp\left(\frac{-408.8 \pm 85.4}{RT}\right) [\text{CH}_3\text{OH}] \quad (15)$$

$$r_2 = \frac{d[\text{CO}]}{dt} = -10^{7.25} \exp\left(\frac{-120 \pm 7.7}{RT}\right) [\text{CO}]^{1.014} \quad (16)$$

$$r_{\text{CO}_2} = r_1 + r_2 \quad (17)$$

Where: r_1 =rate equation of methanol, r_2 =rate equation of carbon monoxide consumption, r_{CO_2} =net rate equation of carbon monoxide, X_1 =initial concentration of CO for direct oxidation, X_2 =final concentration of CO for direct oxidation, Y_1 =initial concentration of CO for water gas shift reaction, Y_2 =final con-

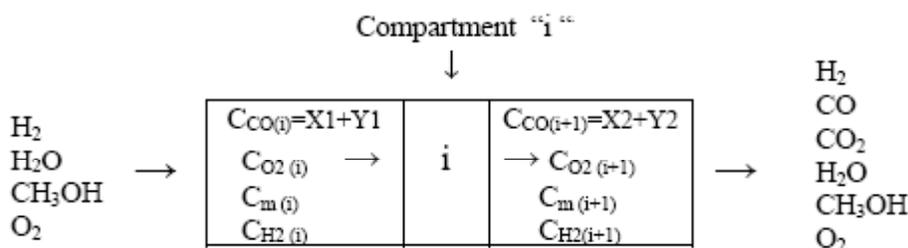


Figure1 : Schematic diagram of material balance for each compartment

centration of CO for water gas shift reaction.

The concentration of O_2 , H_2 and CO_2 can be obtained from the following relation by knowing the values of X_1 , X_2 , Y_1 and Y_2 .

$$C_{CO_2(i+1)} = C_{CO_2(i)} + (X_1 - X_2) + (Y_1 - Y_2) \quad (18)$$

$$C_{H_2(i+1)} = C_{H_2(i)} + (Y_1 - Y_2) \quad (19)$$

$$C_{O_2(i+1)} = C_{O_2(i)} + 1/2(X_1 - X_2) \quad (20)$$

Where: $C_{CO_2(i+1)}$ = outlet concentration of CO_2 from compartment I, $C_{CO_2(i)}$ = inlet concentration of CO_2 to compartment i, $C_{H_2(i+1)}$ = outlet concentration of H_2 from compartment I, $C_{H_2(i)}$ = inlet concentration of H_2 to compartment I, $C_{O_2(i+1)}$ = outlet concentration of O_2 from compartment I, $C_{O_2(i)}$ = inlet concentration of O_2 to compartment i.

4. Method of solution

To solve the material balance equations (Eqs. 11-20), the reactor is divided into 100 compartments.

Knowing the inlet temperature, pressure and composition of the first compartment, the solution of the material balance equation gives the extent of reaction and as a result, the inlet composition of the second compartment.

In this way the composition profile can be obtained throughout the reactor length. The Rung-Kutta method of fourth order has been used for the solution of mass balance equations.

RESULT AND DISCUSSION

The calculation results, including the effect of conversion of methanol for a methanol oxidation reactor in supercritical water are presented, along with experimental data^[10], in TABLE 1, in figure 2 to 3. The result in TABLE 1 shows that, in general, the calculation values are in good agreement with experimental data.

Maximum and minimum difference in experimental data and calculated method conversion are 11% and 0% respectively. The total average absolute deviation in calculation of methanol conversion is 2.8 percent and well within the expected range of error.

Once the validity of proposed model is confirmed by experimental data, the concentration profile along the reactor is obtained. Figure 2 shows the CO_2 , CH_3OH and CO concentration profile at different temperature along the reactor length. Figure 3 shows the conversion profile of methanol throughout the reactor length. In addition, the effect of inlet temperature, feed ratio and residence time are also shown in figures 4 to

TABLE 1: Comparison of experimental and calculated results

Temp °C	ts	[CH ₃ OH] ₀ 10 ³ mol/L	[O ₂] ₀ 10 ³ mol/L	Feed ¹ ratio	Conversion , X%		Absolute ² error %	
					Cal.	Exp.		
474	8.2	3.63	4.27	1.16	3.3	4.2	0.9	
524	7	2.78	3.49	1.25	83.2	94.2	11.0	
503	7.4	2.27	3.56	1.57	29.9	20.7	9.2	
493	7.6	2.40	3.72	1.55	14.8	15.7	0.9	
493	7.6	1.28	3.48	2.71	14.8	15.9	1.1	
493	7.5	5.68	3.04	0.54	14.6	14.7	0.1	
493	7.6	4.65	3.42	0.74	14.8	10.8	4.0	
493	7.4	3.30	3.33	1.01	14.4	9.6	4.8	
493	7.4	2.52	2.82	1.12	14.4	12.7	1.7	
493	7.5	2.47	1.10	0.45	14.6	9.0	1.7	
530	6.7	1.97	3.43	1.74	93.4	96.0	2.6	
522	6.9	2.03	1.92	0.94	77.8	78.4	0.6	
522	6.9	2.05	1.92	0.93	77.8	78.3	0.5	
453	8.7	2.76	2.47	0.90	0.5	0.5	0.0	
							Absolute error _{Ave} %	2.8

¹Feed ratio : $[O_2]_0/[CH_3OH]_0$; ²Absolute error: The absolute value of difference between calculated conversion and experimental conversion.

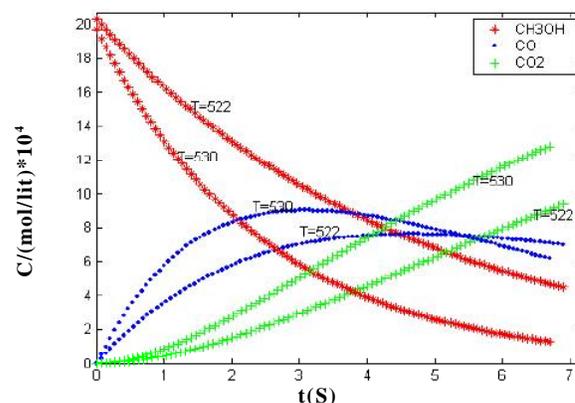


Figure 2 : Concentration profile in reactor at below condition: Temperature: 522°C, residence time : 6.9s, initial methanol concentration: 2.03×10^{-3} (mol/lit) & initial oxygen concentration: 1.92×10^{-3} (mol/lit).

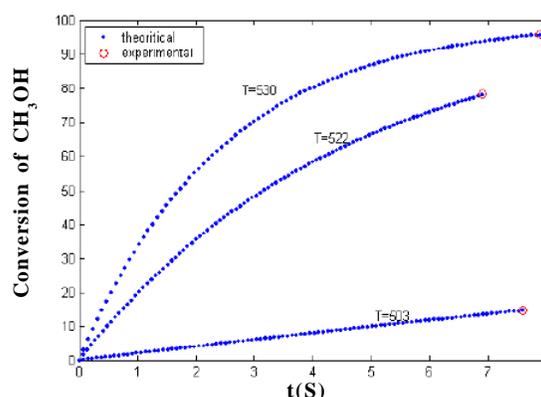


Figure 3: Conversion of methanol in reactor at different temperature

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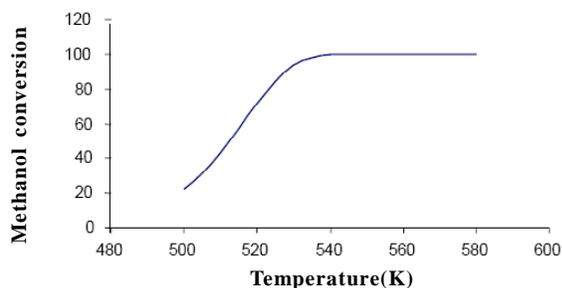


Figure 4: Effect of reactor temperature upon methanol conversion on the below conditions: residence time :6.9s, initial methanol concentration: 2.03×10^{-3} (mol/lit) & initial oxygen concentration: 1.92×10^{-3} (mol/lit).

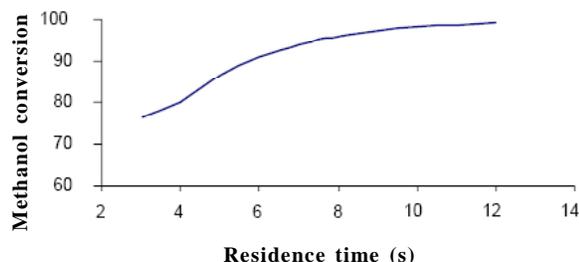


Figure 5: Effect of residence time upon methanol conversion on the below conditions: reactor temperature 530°C , residence time :6.9s, initial methanol concentration: 2.03×10^{-3} (mol/lit) & initial oxygen concentration: 1.92×10^{-3} (mol/lit).

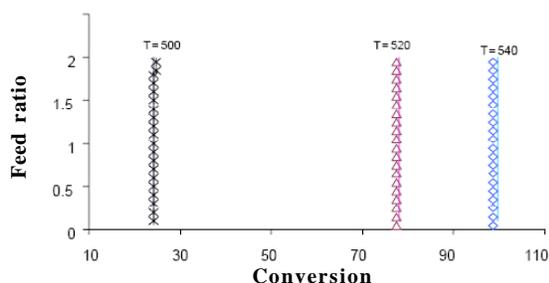


Figure 6 : The effect of feed ratio upon methanol conversion at different temperature

6. Increasing the effect of temperature and residence time cause an increase in effluent conversion of methanol. The result shows that the optimum values of conversion, residence time and temperature are 96% , 8 s and 530°C respectively.

ACKNOWLEDGMENT

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Symbols used

$C_{\text{CO}_2(i)}$ -[mol/L] inlet concentration of CO_2 to compartment i ; $C_{\text{CO}_2(i+1)}$ - [mol/L] outlet concentration of CO_2 from compartment i ; $C_{\text{H}_2(i)}$ - [mol/L] inlet concentration of H_2 to compartment i ; $C_{\text{H}_2(i+1)}$ - [mol/L] outlet concentration of H_2 from compartment i ; $C_{\text{O}_2(i+1)}$ - [mol/L] outlet concentration of O_2 from compartment i ; $C_{\text{O}_2(i)}$ - [mol/L] inlet concentration of O_2 to compartment i ; $[\text{CH}_3\text{OH}]$ - [mol/L] initial methanol concentration; $[\text{CO}]$ -[mol/L] carbon monoxide concentration; $[\text{O}_2]$ -[mol/L] initial oxygen concentration; $[\text{O}_2]$ - [mol/L] oxygen concentration; Q -[m^3/s] volumetric flow rate; R -[$\text{J}/\text{mol}\cdot\text{K}$] universal gas constant; r_1 - [mol/L.s] rate equation of methanol; r_2 -[mol/L.s] rate equation of carbon monoxide consumption; r_{CO} -[mol/L.s] net rate equation of carbon monoxide; T -[K] absolute temperature; t -[s] residence time in reactor; V_i -[m^3] volume of one compartment ; V_r - [m^3] total volume of reactor; V_t -[m^3] total volume of reactor; X_1 -[-] initial concentration of CO for direct oxidation; X_2 -[-] final concentration of CO for direct oxidation; Y_1 -[-] initial concentration of CO for water gas shift reaction; Y_2 -[-] final concentration of CO for water gas shift reaction

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