

FORMALDEHYDE SYNTHETIC SIMULATION OF A FIXED BED REACTOR OVER SILVER CATALYST

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Abstract— A plug flow tubular reactor model for the oxidation of methanol in a fixed-bed reactor over silver catalyst has been presented in this paper. The model performs the dynamic behavior for the oxidation reaction of methanol and formaldehyde throughout the reactor length. The literature data are used to validate the model accuracy. The effect of time and the amount of water in feed are studied in the simulation study. The model gives the acceptable prediction of the formaldehyde yield, especially at reaction temperature 500-975 K. In addition, the simulation confirms that the high yield is achieved by increasing the amount of water in feed.

Index Terms— Fixed-bed reactor, Formaldehyde, Fully explicit, Simulation

I. INTRODUCTION

The whole formaldehyde production amounts 32.5 million tons per year in 2012, While demand increase similarly due to the versatility of formaldehyde which is intermediate in chemical synthesis such as the many resin product for example urea formaldehyde, melamine formaldehyde, phenol formaldehyde, polyoxymethylene and methylenediphenol diisocyanate etc. These resins are used to plywood production and the property adaptation. Furthermore the formaldehyde solution (formalin) can destroy bacteria and fungi for conservation of dead creature.

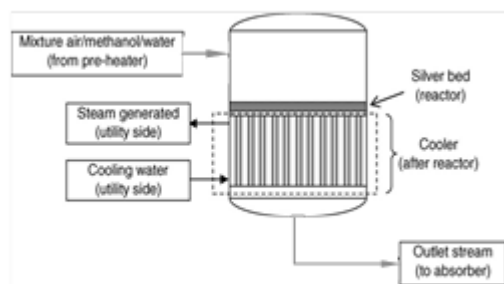


Fig. 1. A typical silver catalyst reactor, showing the fixed bed and the downstream cooler

The formaldehyde was discovered in 1859 by Russian chemist named Aleksandr Butlerov. Then in 1869, it was ultimately identified by the German chemist August Hofmann. Who synthesized formaldehyde by passing methanol over a heated platinum spiral. The generally formaldehyde process has 2 processes that is air deficiency process or silver contact process, passing methanol more than 37.5% by volume over silver catalyst in fixed-bed reactor at temperature 873-923 K under atmospheric pressure. The second process is air excess or formox process by passing methanol less than 7% by volume over iron-molybdenum-vanadium oxide or metal oxide in multitubular reactor under 573-673 K. The disadvantage of formox process is larger equipment in process

design when compared to the original silver catalyst process design for achieved purpose of yield 88-92%

The numerous utilizable silver contact process amounts 80% of total formaldehyde process. The contact process has 2 types that is methanol ballast process (example: Degussa process, ICI, etc), conversion of this process isn't complete. Second process is water ballast process (example: BASF's process, etc), which has conversion and selectivity better than methanol ballast process. The silver contact process is addable steam for preventive deactivation catalyst because of sintering and fouling so catalyst life of fresh catalyst more than methanol ballast process [7, 10]. Furthermore the steam removes heat in reactor which forms hot spot in finally runaway reaction. The steam is decrease side of reaction is carbon dioxide and formic acid.

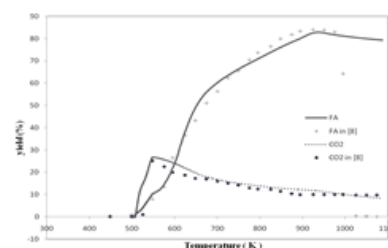


Fig. 2. the formaldehyde and carbon dioxide synthetic simulations compare [8]

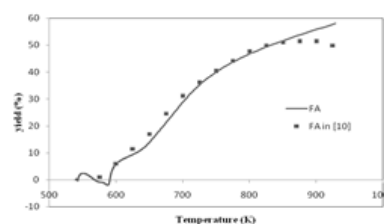


Fig. 3. the formaldehyde synthetic simulation compares [10]

The formaldehyde productive reactor shows in Fig. 2, feed streams include air, methanol and water in suitable composition for explosive prevention to adiabatic fixed-bed reactor under atmospheric pressure and 873-923 K [1]. The purpose of general reactor is desirous product which depends feed quantity [5, 8] and reactor temperature [7, 10, 13]. The active oxygen over surface catalyst reacts with methanol. Formable reactions, including oxidation reaction to formaldehyde and water express in Eq.(1) and dehydrogenation reaction express in Eq.(2) but restricted formaldehyde synthesis by reaction in Eq.(3)-(5)



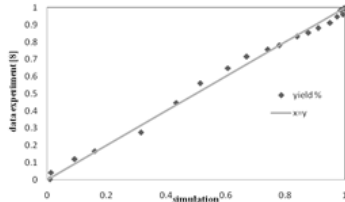
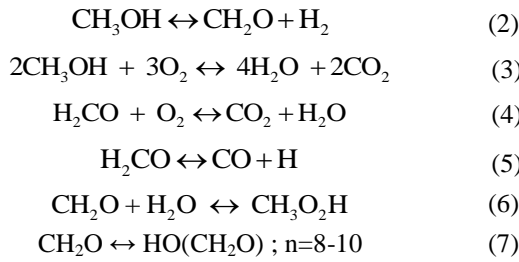


Fig. 1. simulate prediction of yield towards to formaldehyde plots against prediction of experiment data of [8]

Step i	Reaction mechanism
1	$\text{CH}_3\text{OH} (\text{g}) + * \leftrightarrow \text{CH}_3\text{OH}^*$
2	$\text{O}_2 (\text{g}) + * \leftrightarrow \text{O}_2^*$
3	$\text{O}_2^* + * \leftrightarrow 2\text{O}^*$
4	$2\text{CH}_3\text{OH}^* + \text{O}^* \leftrightarrow \text{CH}_3\text{O}^* + \text{H}_2\text{O}^*$
5	$\text{CH}_3\text{O}^* + * \leftrightarrow \text{H}_2\text{CO}^* + \text{H}^*$ (slow)
6	$\text{H}_2\text{CO}^* \leftrightarrow \text{H}_2\text{CO} (\text{g}) + *$
7	$2\text{H}^* \leftrightarrow \text{H}_2 (\text{g}) + 2*$
8	$\text{H}_2\text{O}^* \leftrightarrow \text{H}_2\text{O} (\text{g}) + *$
9	$\text{H}_2\text{CO}^* + \text{O}^* \leftrightarrow \text{H}^* + \text{HCOO}^*$
10	$\text{HCOO}^* + * \leftrightarrow \text{H}^* + \text{CO}_2^*$ (slow)
11	$\text{CO}_2^* \leftrightarrow \text{CO}_2 + *$

The * signifies a surface site and X* is an adsorbed species.

The products in gas phase from reactor are cooled to decrease formaldehyde decomposition in Eq. (5) [7, 8]. The products are fed in absorber to formaldehyde 37% by mass called 'formalin' in (6) [4, 7, 13]. However the formalin in the room temperature isn't stable and formability to polymer which is called 'paraformaldehyde' in Eq.(7). The paraformaldehyde formation is formaldehyde concentration, life time of formalin in storage and temperature in storage. So usually formalin has methanol 1-14% by mass for more stable in solution and temperature more than 313 K. Figure 2, including 2 part that is part of reactor formaldehyde synthesis part at temperature 873-923 K and part of heat exchanger for cool product in gas phase from first part to temperature 453-523 K.

The process simulation study output variables from input variables as experiment but experiment more expensive than simulation. A model derives process behavior simulation in form of mathematic model. The any assumption formation assists simple model for model solution. The model solution in this work is fully explicit finite difference method that calculates by MATLAB programming

In this work purposes is simulation of adiabatic fixed-bed reactor for formaldehyde synthesis at atmospheric pressure. A reaction occurrence is oxidation reaction of methanol and formaldehyde. Thus entire heat of formaldehyde reaction Eq. (1) and (2) is exothermic reaction. The carbon dioxide appears in low temperature but the carbon monoxide appears in high temperature more than 900 K [1, 7].

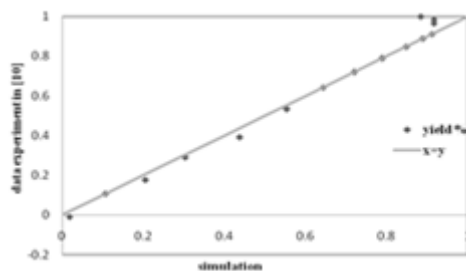


Fig. 2. simulate prediction of yield towards to formaldehyde plots against prediction of experiment data of [10]

TABLE I. THE REACTION MECHANISM

II. THE METHODOLOGY.

A. The fixed-bed reactor model in BASF's process

The fixed-bed reactor model is explained by plug flow tubular reactor model, only z-direction is considerate in cylindrical coordinate but this axis doesn't consider mixed substance. An assumption in the model which is a few pressure drops in a packed-bed can evaluates constant pressure [11], the properties of substance are constant. The gas phase behavior based on ideal gas. The model doesn't describe catalyst deactivation term, following the fixed-bed reactor model shows in (8)-(9).

- The component balance

$$(\varepsilon + (1-\varepsilon)\varepsilon_p) \frac{\partial C_i}{\partial t} = u \frac{\partial C_i}{\partial z} + \sum_k (1-\varepsilon_p) v_{ik} r_{ik} \quad (8)$$

- The energy balance

$$(\varepsilon \rho_{\text{gas}} C_{p_{\text{gas}}} + (1-\varepsilon) \rho_{\text{solid}} C_{p_{\text{solid}}}) \frac{\partial C_i}{\partial t} = G_{\text{gas}} C_{p_{\text{gas}}} \frac{\partial C_i}{\partial z} + \sum_k (-\Delta H_{ik}) (1-\varepsilon) v_{ik} r_{ik} \quad (9)$$

- Parameters

C_i = Component i (mol/m³ void space)
 $C_{p_{\text{gas}}}$ = Specific heat capacity of gas (kJ/kgK)
 $C_{p_{\text{solid}}}$ = Specific heat capacity of solid or catalyst (kJ/kgK)
 G_{gas} = Mass flux of gas (kg/m³s)
 r_{ik} = Rate of reaction K (kJ/s m³ catalyst)
 t = time (s)
 T = Temperature in reactor (K)
 U = $G_{\text{gas}} / \rho_{\text{gas}}$ = Superficial velocity (m/s)
 z = Axial position (m)
 ε = Bed void fraction
 ε_p = Catalyst void fraction

TABLE II. THE ENTHALPY AND ENTROPY CHANGE FOR ELEMENTARY REACTION STEP I

Step i	The enthalpy and entropy change for elementary reaction	
	ΔH_i (KJ/mol)	ΔS_i (J/molK)
1	-32.955	-82.317
2	-37.735	-120.500
3	-83.069	-44.969
4	42.843	-89.129
5	-52.856	71.413
6	19.324	75.059
7	51.250	132.15
8	47.478	103.27
9	-26.153	-78.897
10	-238.98	92.782
11	15.082	51.745

$\rho_{\text{gas}} = (\text{MW})_{\text{mean}} \cdot (\text{P}/\text{RT}) = \text{Density of gas phase (kg/ m}^3 \text{ void space)}$

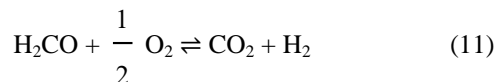
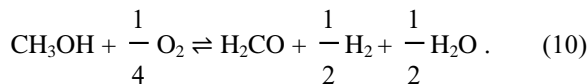
$\rho_{\text{solid}} = \text{Density of silver catalyst (kg/ m}^3 \text{ catalyst)}$

$v_i = \text{Stoichiometric coefficient of component i in reaction K}$

$\Delta H_{\text{rk}} = \text{Heat of reaction K (kJ/mol)}$

B. The kinetic model

The fixed-bed reactor model in this work explain rate of reaction by the kinetic model in [8, 9]. The model description is Langmuir-Hinshwood mechanism in tale 1. O* in table 1 is active oxygen. Equation (8)-(9) shows totally reaction. The kinetic model based on work of Wachs and Madix in UHV condition, parameters obtain from many surface science experiments on silver catalyst.



Two limiting step including reaction mechanism is step 5 and step 10 .Step 5 is decomposition of methoxy to formaldehyde, this step controls oxidation reaction of methanol. Step 10 that is decomposition of formate, this step controls combustion of formaldehyde. Another step assumes equilibrium, following the kinetic model shows in (12)-(13)

$$r_5 = \frac{k_5 K_A \left(\frac{P_{\text{O}_2}}{p^0}\right)^4 \left(\frac{P_{\text{CH}_3\text{OH}}}{p^0}\right) \left(\frac{P_{\text{H}_2\text{O}}}{p^0}\right)^{-\frac{1}{2}}}{\left(1 + K_c \left(\frac{P_{\text{O}_2}}{p^0}\right)^{\frac{1}{2}}\right)^2} \quad (12)$$

$$r_{10} = \frac{k_{10} K_B \left(\frac{P_{\text{O}_2}}{p^0}\right)^{\frac{1}{2}} \left(\frac{P_{\text{H}_2\text{CO}}}{p^0}\right) \left(\frac{P_{\text{H}_2}}{p^0}\right)^{-\frac{1}{2}}}{\left(1 + K_c \left(\frac{P_{\text{O}_2}}{p^0}\right)^{\frac{1}{2}}\right)^2} \quad (13)$$

$$K_i(T) = \exp\left(\frac{\Delta S_i}{R}\right) \left(\exp\left(\frac{\Delta H_i}{RT}\right)\right) \quad (14)$$

$$k_i(T) = A_i \exp(-E_{a_i} / RT) \quad (15)$$

$$E \cong U = H - RT \quad (\text{For ideal gas}) \quad (16)$$

- The kinetics model parameters
- A_i = Pre exponential factor of reaction i (s^{-1})
- E_{a_i} = The activation energy of reaction i (J/mol)
- H_i^\ddagger = The activity enthalpy
- k_i = Rate constant of reaction i (s^{-1})
- K_A, K_B and K_C = Lump constant when:
- $K_A = K_1 (K_2 K_3)^{1/4} K_4^{1/2} K_8^{1/2}$
- $K_B = (K_2 K_3 K_7)^{1/2} K_6 K_9$
- $K_C = K_2 K_3$
- K_i = Equilibrium constant of reaction i
- P_j = Partial pressure of component j (Pa)
- P^0 = Thermodynamic reference pressure amount 10^5 Pa

R = Gas constant amount 8.314 J/molK

ΔH_i = The enthalpy changes of reaction i (J/mol)

ΔS_i = The entropy changes of reaction i (J/molK)

The findable equilibrium constant of reaction i from ΔH_i and ΔS_i show in table.2. Rate of reaction for step 5 and 10 based on Arrhenius equation that has A_i and The activity enthalpy (H_i^\ddagger) of reaction i shows in table 3.

C. The Fully explicit finite difference

The differential equation can evaluate to the difference equation that shows in (22).

$$\frac{df(x)}{dx} \approx \lim_{\Delta x \rightarrow 0} \frac{\Delta f(x)}{\Delta x} \approx \frac{\Delta f(x)}{\Delta x} \quad (17)$$

Equation (22), the difference equation as the differential equation when Δx nearly to zero. Some familiar basic formulas of difference equation that can be used:

$$f'(x) \approx \frac{1}{h} [f(x+h) - f(x)] \quad (18)$$

TABLE III. THE ENTHALPY AND ENTROPY CHANGE FOR LUMP CONSTANT

Lump constant	The enthalpy and entropy change for Lump constant	
	ΔH_i (KJ/mol)	ΔS_i (J/molK)
K_A	-117	-18
K_B	-171	-80
K_C	-165	-121

$$f'(x) \approx [f(x+h) - f(x)] \quad (19)$$

$$f''(x) \approx \frac{1}{h^2} [f(x+h) - 2f(x) + f(x-h)] \quad (20)$$

Using equation (23) and (24) apply to the fixed bed reactor model in equation (10) - (11) following expression

$$(\varepsilon + (1-\varepsilon)\varepsilon_p) \frac{C_{j,i}^{n+1} - C_{j,i}^n}{\Delta t} = \frac{u}{\Delta z} \left(\frac{C_{j,i+1}^n - C_{j,i-1}^n}{2} \right) + \sum_k (1-\varepsilon) v_{jk} r_{ki} \quad (21)$$

$$\left(\varepsilon\rho_{\text{gas}}C_{p_{\text{gas}}}+(1+\varepsilon)\rho_{\text{solid}}C_{p_{\text{solid}}}\right)\left[\frac{T_i^{n+1}-T_i^n}{\Delta t}\right]=\frac{G_{\text{gas}}C_{p_{\text{gas}}}}{\Delta z}\left(\frac{T_{i+1}^n-T_{i-1}^n}{2}\right)+\sum_k(-\Delta H_{rk})(1-\varepsilon)v_{jk}r_{ki} \quad (22)$$

The simulation both component i and temperature used feed and temperature inlets, process designs and operation conditions that depend on time called “dynamic simulation”.

III. Results and discussion

In this section refers formaldehyde synthetic process simulative comparison with the previous literature for demonstration of mathematics model can simulate nearly true process. Figure 2, an expression of formaldehyde synthesis and byproduct (carbon dioxide) that depends operation temperature compares between the process simulation and [8], a few increment of formaldehyde synthesis because of decomposition to carbon dioxide. When temperature higher than 548 K, the vary increment of formaldehyde synthesis and highest at 948 K, the temperature of formaldehyde synthesis decline due to formaldehyde decomposition to carbon monoxide, in this work doesn't explain to carbon monoxide because of complicated formation mechanism.

The carbon dioxide synthesizes at low temperature when temperature higher than 548 K, carbon dioxide synthesis decline of temperature so carbon dioxide synthetic reaction occurs at low temperature. Figure 3, the comparison of process simulation and the experiment data of [10], this expression as figure 2. Thereby demonstrative simulation of mathematic model can describes formaldehyde synthesis in reactor under industrial conditions. Figure 2 and 3, results of simulation has high accuracy at low temperature but lower accuracy in higher temperature because rate of reaction in [1, 2] describes formaldehyde synthesis at low temperature, an accuracy describes by least square amount 10.01% and 8.49%

TABLE IV. ARRHENIUS PARAMETERS FOR TWO LIMITING STEPS

Step i	Arrhenius parameters	
	$A_i (A^{-1})$	$H_i (J/molK)$
1	-32.955	-82.317
2	-37.735	-120.500

respectively (500-975K). So model application in rang of temperature 500-975 K that can describes in industrial condition.

Figure 4 and 5, an experiment data normalization of [9] and [11] respectively plots against simulated data experiment, both figure expression is yield from experiment (y-axis) and simulation (x-axis) closed to y-x line. Therefore a few mistake exhibits acceptable model for used simulation.

IV. Conclusion

The formaldehyde synthetic simulation from mathematic model in the adiabatic fixed-bed reactor under UHV condition used many assumptions as flow pattern of fluid depends only z-direction and disregard mixed of fluid, property constant, process has two reaction that is oxidation reaction of methanol and formaldehyde. The mathematic solution is fully explicit method that is simpler method for partial differential equation. The simulation nearly evaluate with experiment data of previous literature. The model can used in rang 500-975 K

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