



Modeling, design and operation of pilot plant for two-stage oxidation of methanol into formic acid



I.A. Zolotarskii^{a,*}, T.V. Andrushkevich^a, G.Ya. Popova^a, S. Stempel^b, V.O. Efimov^b, V.B. Nakrokhin^a, L.Yu. Zudilina^a, N.V. Vernikovskaya^{a,c}

^a Borekov Institute of Catalysis SB RAS, Novosibirsk, Russia

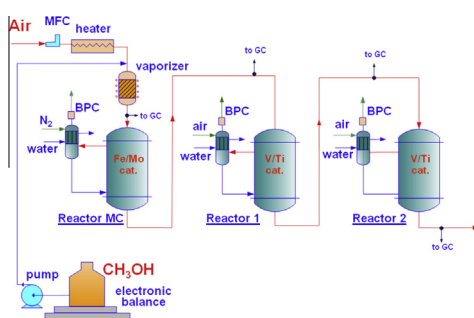
^b Safe Technologies Inc., St.-Petersburg, Russia

^c Novosibirsk State University, Novosibirsk, Russia

HIGHLIGHTS

- Tubular reactor for formaldehyde oxidation into formic acid was modeled.
- Process flowsheet with two reactors for formaldehyde oxidation is favorable.
- Pilot plant for formic acid production is designed and constructed.
- Formic acid yield of 87–88% based on formaldehyde is obtained.
- Methanol consumption is 0.75–0.80 kg per 1 kg of 85% formic acid.

GRAPHICAL ABSTRACT



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ABSTRACT

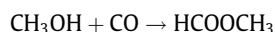
The new technology of formic acid production from methanol is developed. Methanol oxidation into formaldehyde in a tubular reactor with iron-molybdenum catalyst is carried out at the first stage similarly to existing technology of formalin production. Formaldehyde is oxidized into formic acid in a tubular reactor with an appropriate vanadia–titania catalyst at the second stage. Mathematical modeling of the process second stage is performed on basis of the detailed kinetic model. Design parameters and performance of large-scale multitubular reactors were determined and reproduced in the constructed pilot plant with a capacity of 2–3 kg of formic acid per hour. Process feasibility was confirmed by operation of the pilot plant. Formic acid yield at the second stage was shown to be 87–88%. The technology is ready for further scaling up to industrial level.

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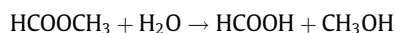
1. Introduction

Formic acid is a bulk chemical, its annual production being more than 500 thousand tons. Its major applications include silage and animal feed preservation, leather and tanning accounting for half of world consumption [1]. It is used in production of textiles, formate salts, pharmaceuticals/food chemicals, rubber chemicals (antiozonants and coagulants), catalysts and plasticizers also.

Formerly, formic acid was produced as a byproduct at liquid phase oxidation of butane and light gasoline into acetic acid. Nowadays formic acid is produced commercially by hydrolysis of methyl formate or formamide [2]. Raw material is carbon monoxide. It reacts with liquid methanol forming methyl formate in the presence of a strong base at elevated pressure:



Typical reaction conditions are 80 °C and 40 bar. Hydrolysis of methyl formate gives formic acid and methanol which is recycled.



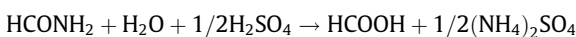
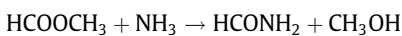
* Corresponding author. Tel.: +7 3833269409.

E-mail address: zol@catalysis.ru (I.A. Zolotarskii).

Nomenclature

A_c	relative catalyst activity	T_{in}	gas temperature at tube inlet (K)
$C_0 = P_0/RT_0$	gas molar concentration at normal conditions (mole m ⁻³)	T_W	tube wall (cooling agent) temperature (K)
C_p	total gas heat capacity (J mole ⁻¹ K ⁻¹)	T_0	temperature under normal conditions (K)
C_{pi}	heat capacity of gas component i (J mole ⁻¹ K ⁻¹)	u_l	superficial axial gas velocity (m s ⁻¹)
C_i	molar concentration of component i (mole m ⁻³)	u_l	superficial axial gas velocity (N m s ⁻¹), $u_l = \bar{u}_l T_0 P_i / TP_0$
d_p	diameter of equivalent-volume sphere (m)	u_0	superficial axial gas velocity at tube inlet (N m s ⁻¹)
d	diameter of the catalyst pellet (m)	u_r	superficial radial gas velocity (Nm s ⁻¹)
D_{ik}	binary diffusivity (m ² s ⁻¹)	V_i	hydrodynamic velocity of component i inside catalyst (N m s ⁻¹)
$D_{\rho i}^*$	effective generalized diffusivity in the catalyst (m ² s ⁻¹)	V_p	volume of catalyst pellet (m ³)
D_i^{Kn}	Knudsen diffusivity (m ² s ⁻¹)	W_j	rate of reaction j (mole m ⁻³ s ⁻¹)
D_r	effective radial diffusivity in the bed (m ² s ⁻¹)	X	conversion of formaldehyde (%)
D_{tube}	diameter of the catalyst tube (m)	y_i	molar fraction of component i
h	height of the pellet (m)	Y_{in}	inlet molar fraction of component i
ΔH_j	enthalpy change in reaction j (J mole ⁻¹)		
i	number of gas components		
J_i	flux of component i inside catalyst (mole m ⁻² s ⁻¹)	Greek letters	
l	tube length coordinate (m)	α	wall heat transfer coefficient (W m ⁻² K ⁻¹)
L	tube length (m)	ε	bed void fraction
P	pressure (atm)	ε_p	catalyst porosity
P_0	pressure under normal conditions (atm)	γ_{ij}	stoichiometric coefficient of component i in j th reaction
r	tube radius coordinate (m)	λ_r	effective radial thermal conductivity of the bed (W m ⁻¹ K ⁻¹)
R	universal gas constant (atm m ³ mole ⁻¹ K ⁻¹)	μ	gas viscosity (kg m ⁻¹ s ⁻¹)
S	selectivity of formaldehyde oxidation into formic acid (%)	ρ	space coordinate inside catalyst (m)
S_p	outer surface of catalyst pellet (m ²)	ρ_p	half-thickness of the catalyst slab (m)
T	temperature (K)	τ_p	tortuosity
		τ	residence time (s), $\tau = L/u_0$

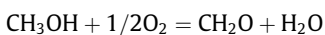
However, direct hydrolysis of methyl formate requires a large excess of water to proceed efficiently, thus causing high expenses on product separation. Some producers perform it by an indirect route, first reacting the methyl formate with ammonia to produce formamide, and then hydrolyzing the formamide with sulfuric acid to produce formic acid and ammonium sulfate as a byproduct:



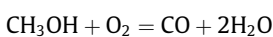
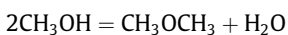
However all existing technologies still consist of several high capital and energy consuming stages resulting in high formic acid production cost.

The new method of formic acid production was developed by Boreskov Institute of Catalysis [3,4]. It contains two catalytic stages:

Stage 1. Methanol oxidation into formaldehyde on an iron-molybdenum catalyst.



Side reactions of dimethyl ether and carbon monoxide formation take place above the main one:



This reaction is common in industry and widely used in formalin plants. Methanol conversion is carried out in cooled tubular reactors at temperature of 270–400 °C, methanol concentration being kept under lower explosion limit.

Stage 2. Formaldehyde oxidation into formic acid on a vanadia-titania catalyst according the reaction:



Side reactions:



Methanol traces slipped from the first stage react with formic acid at the second stage with formation of methyl formate:



The key component of the technology is the appropriate V-Ti-O catalyst providing high reaction selectivity at temperature range 100–130 °C. Product selectivities versus formaldehyde conversion obtained in a bench scale continuous stirred tank reactor are shown in Fig. 1.

This paper presents results of mathematical modeling of formaldehyde oxidation reactors, designing and constructing the pilot plant and its operation.

2. Mathematical model of a tubular reactor for formaldehyde oxidation into formic acid. Problem formulation

Since the first stage of methanol oxidation is similar to conventional formalin plants, main attention in reactor design was paid to the second stage of formaldehyde oxidation into formic acid. For this purpose the detailed two-dimensional quasihomogeneous mathematical model of a tubular reactor developed in [5] was used. Mass balance in a catalyst pellet:

$$\frac{\partial}{\partial \rho} \left(D_{\rho i}^* \frac{\partial C_i}{\partial \rho} \right) - \frac{RT}{P} \frac{\partial}{\partial \rho} (V_i C_i) = \sum_{j=1}^4 \gamma_{ij} W_j \quad (5)$$

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