1. MASS TRANSFER AND CHEMICAL REACTION ASPECTS CONCERNING ACETALDEHYDE OXIDATION IN AGITATED REACTOR

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MASS TRANSFER AND CHEMICAL REACTION ASPECTS CONCERNING ACETALDEHYDE OXIDATION IN AGITATED REACTOR

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Abstract

Experimental investigation has been carried out concerning acetaldehyde oxidation with oxygen/air using homogenous catalyst mangan acetate. Two steps of work have been carried out. Firstly, hydrodynamic of reactor has been evaluated by measuring gas-liquid mass transfer coefficient using oxygenation dynamic method. This work gave empirical correlation of the coefficient in term of rotation speed and gas flow rate. Secondly, the evaluation of acetaldehyde oxidation reaction was carried out in mechanically agitated reactor at atmospheric pressure, where impeller rotation speed, air flow-rate, and temperature were varied. This research showed that increasing impeller rotation speed could not increase acetaldehyde conversion. On the other hand, the selectivity of acetic acid decreased with increasing impeller rotation speed. The observation also showed that the conversion of acetaldehyde and selectivity of acetic acid increased with the increasing of gas flow rate and temperature. The maximum conversion was 32.5 % and the highest selectivity was 70.5 %.

1. INTRODUCTION

Liquid phase oxidation of acetaldehyde using air and homogeneous catalyst mangan acetate is one of processes in industrial scale production of Acetic Acid wide spread in the world. To utilize molasses, by product of sugar industry, abundantly produced in Indonesia, in 1989 Acetic Acid Plant have been built using the above process. In United States, production of acetic acid from acetaldehyde was applied since 1960 [6]. We observe that even the process of acetaldehyde oxidation to produce Acetic Acid has been applied in industry long time ago, however detailed phenomena occurring in the reactor has not been studied by previous researchers. The performance of process was affected by kinetic and hydrodynamic factors. Hydrodynamic and mass transfer characteristic in stirred tank gas-liquid reactor were determined by the interaction between impeller rotation speed and gas flow rate factors as has been studied by several workers [4, 5, 7, 10]. Venugopal et al. [12] studied the kinetic of acetaldehyde oxidation and reported that the reaction follows second order kinetic.

The present research was focused on the study of acetaldehyde oxidation using air with aqueous mangan acetate catalyst in mechanically stirred tank reactor.

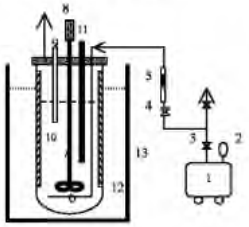
2. METHODOLOGY

The research has been carried out in two steps:
1. Evaluation of reactor hydrodynamics by measuring gas-liquid mass transfer coefficient

2. Evaluation of acetaldehyde oxidation reactor especially by determining reaction conversion and selectivity.

2.1. Equipment and Method

This research used mechanically agitated tank reactor system shown in Fig. 1. The reactor, 102 mm in diameter and 165 mm in height, was made of transparant pyrex glass and was equipped with four baffles, 120 mm in length and 8 mm in width, and six blades disc turbine impeller 45 mm in diameter and 12 mm in width. The impeller was rotated by electric motor with digital impeller rotation speed indicator. Waterbath thermostatic, equipped with temperature controller was used to stabilize reactor temperature. Gas-liquid mass transfer coefficient $k_l a$ was determined using dynamic oxygenation method as has been used by Suprapto et al. [11].



1. Air compressor
2. Pressure indicator and controller
3. Main control valve
4. Air flow Needle Valve
5. Flowmeter
6. Air Distributor
7. Agitator
8. Motor
9. Liquid sampling tap
10. Baffle
11. Thermometer
12. Reactor
13. Thermostatic Water-bath

Fig. 1. Equipment Apparatus

The evaluation of acetaldehyde oxidation process was carried out by aeration of acetaldehyde solution and analyzing the concentration of acetic acid using gas chromatography HP 5890 with detector FID equipped with PEG Column in 15 minutes time interval. The gas flow rate (*Qg*), impeller rotation speed (*N*) and temperature (*T*) were varied.

2.2. Mathematical Model Development

Acetaldehyde oxidation reaction comprise of a main reaction and several side reaction as follow;

Main reaction : $CH_3CHO + \frac{1}{2} O_2 \xrightarrow{k1} CH_3COOH$

Side reaction : $CH_3CHO + O_2 \xrightarrow{k2} CH_3OH + CO_2$

$CH_3OH + CH_3COOH \xrightarrow{k3} CH_3COOCH_3 + H_2O$

These reactions were carried out in semi batch stirred tank reactor. The governing equations for this process were :

$$da'/d\tau = E\,\xi\,(a^* - a') - (\tfrac{1}{2} + \alpha)\,a'\,b' \quad (1)$$

$$db'/d\tau = -(1 + \alpha + \gamma)\,a'\,b' \quad (2)$$

$$dc'/d\tau = a'\,b' - \beta\,c'\,d' \quad (3)$$

$$dd'/d\tau = \alpha\,a'\,b' - \beta\,c'\,d' \quad (4)$$

$$de'/d\tau = \beta\,c'\,d' \quad (5)$$

$$a_k\,y_{AG}^3 - b_k\,y_{AG} + c_k = 0 \quad (6)$$

where $a^* = C_A^*/C_{Bl} = (1 - \delta)\,a_p$, $a' = C_A/C_{Bl}$; $b' = C_B/C_{Bl}$; $c' = C_C/C_{Bl}$; $d' = C_D/C_{Bl}$; $e' = C_E/C_{Bl}$; $\alpha = k_2/k_1$; $\beta = k_3/k_1$; $\xi = k_L a/(k_1\,C_{Bl})$, δ = fraction of gas film resistance, $a_p = P_{AG}/(H_A$

C_{Ai}), H_A = Henry constant, k_La = volumetric gas-liquid mass transfer coefficient., C_{Bi} = initial concentration of B in bulk of liquid, and P_{AG} = partial pressure of A in bulk of gas, $a_k = E\ \varphi\ (1 - \delta)\ (P/(H_A\ C_{Bi})$, $b_k = E\ \varphi\ (1-\delta)[P/(H_A\ C_{Bi})] + y_{Ai}/(1-y_{Ai}) + 1$, $c_k = y_{Ai}/(1-y_{Ai})$, $\varphi = k_La\ V\ C_{Bi}/G$, P = operating pressure, G = molar gas flow rate, A= O_2, B = CH_3CHO, C = CH_3COOH , D = CH_3OH , F = CH_3COOCH_3. Equation (6) can be written as $y_{AG} = c_k/(b_k - a_k\ y_{AG})$, where y_{AG} mole fraction of A in bulk gas phase can be determined iteratively, y_{Ai} = mole fraction of A in gas inlet. Equations (1) to (6) were solved using fourth order Runge-Kutta method [1, 8]. The value of enhancement factor, E, was predicted using equation of Van Krevelen and Hoftijzer [2].

The computation result yield acetaldehyde concentration as function of time. The value of kinetics parameters, k_1, k_2, k_3 were adjusted to minimize the sum of square of error between the predicted and measured concentration using Hooke Jeeve method [3].

3. RESULTS AND DISCUSSION

The measurement of liquid side gas – liquid mass transfer coefficient k_La, showed that the value of k_La increase with increasing rotation speed (N) and gas flow rate (Qg). In the present research, the effect of impeller rotation on mass transfer coefficient was more significant than the effect of gas flow rate. The following correlation was obtained $k_La = 1.7 \times 10^{-3}\ N^{0.98}\ Qg^{0.22}$. Pedersen et al. [9] who carried out the measurement of k_La using tracer ^{85}Kr, gave almost the same prediction as the present work.

The value of k_La predicted above and kinetic data obtained by Venugopal et al. [12] were used for simulation of acetaldehyde oxidation reaction. The present study obtained the expression of kinetic konstants as follows: $k_1 = 6.64.10^{10}$ exp(-12709/RT), $k_2 = 244.17$ exp(-1.8/RT) and $k_3 = 3.11.10^{7}$ exp(-13639/RT) $m^3.kmol^{-1}.s^{-1}$. The value of k_1, obtained in this research are almost the same as that obtained by Venugopal. Venugopal neglected the side reactions. The value of E and Hatta Number $\sqrt{M}$ were greater than 3, so that the reaction system can be considered as pseudo-first order reaction with respect to oxygen and the process was controlled by mass transfer aspect.

Fig. 2 and 3 showed that increasing gas flow rate (Qg) and temperature (T) at 500 rpm rotation speed (N), will increase the acetaldehyde conversion. Fig. 2 also showed that the reaction is in kinetic regime at low temperature, while at higher temperature (Fig.3), the reaction approach the equilibrium condition or in thermodynamic region.

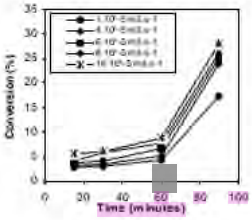


Fig. 2. The effect of Qg on conversion (N= 500 rpm, 35°C)

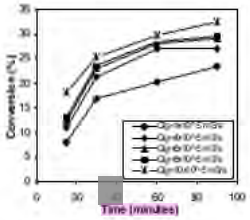


Fig. 3. The effect of Qg on conversion (N= 500 rpm, 55°C)

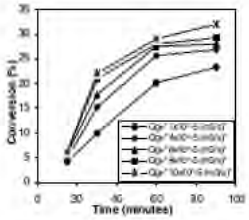


Fig. 4. The effect of Qg on conversion (N= 900 rpm,55°C)

In the range of 500 to 900 rpm, Fig. 3 and 4 showed that impeller rotation speed does not affect significantly on reaction conversion for relatively long reaction time (above 60 minutes). Apparently, the hydrodynamic condition of liquid in the reactor was sufficiently turbulent by aeration.

Increasing of temperature and gas flow rate can enhance the selectivity, however the selectivity decrease with increasing impeller rotation speed (Fig. 5 and 6). In general, increasing selectivity was followed by decreasing of conversion, as shown in Fig. 7.

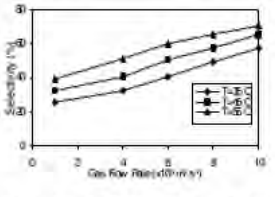


Fig. 5. The Effect of T and Q_g on Selectivity (for N= 500 rpm)

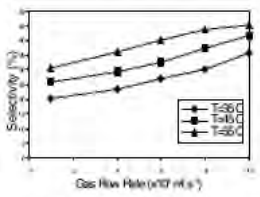


Fig. 6. The Effect of T and Q_g on Selectivity (for N= 900 rpm)

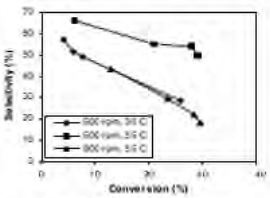


Fig. 7. Relation between conversion and selectivity

4. CONCLUSION

Liquid phase oxidation reaction of acetaldehyde with Mn acetate catalyst can be considered as pseudo first order irreversible reaction with respect to oxygen, and the reaction occurred in liquid film. The value of kinetic constant as follow : $k_1 = 6.64.10^{10}$ exp(-12709/RT), $k_2 = 244.17$ exp(-1.8/RT) and $k_3 = 3.11.10^{7}$ exp(-13639/RT) $m^3.kmol^{-1}.s^{-1}$. The conversion can be increased by increasing gas flow rate and temperature, however the effect of impeller rotation on the conversion is not significant. The highest conversion 32.5% was obtained at the rotation speed of 900 rpm, temperature 55 °C, and gas flow rate 10^{-4} $m^3.s^{-1}$. The selectivity of acetic acid was affected by impeller rotation speed, gas flow rate and temperature. The highest selectivity of acetic acid was 70.5% at 500 rpm rotation speed, temperature of 55 °C and 10^{-4} $m^3.s^{-1}$ gas flow rate.

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