

1,2-Dichloroethane production by two-step oxychlorination reactions in a fluidized bed reactor

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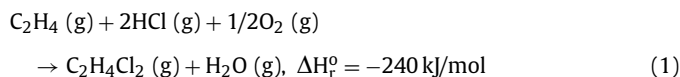
ABSTRACT

The reaction characteristics of two-step oxychlorination to produce 1,2-dichloroethane as a feedstock of PVC production were determined in a fluidized bed reactor. The effects of superficial gas velocity and gas composition on the reactivity and fluidization stability have been determined to find the optimum operating conditions in the continuous fluidized bed reactor system. It has been found that the average ethylene conversion is 94% with ethylene dichloride (EDC) selectivity of 97–98%, the average HCl conversion is 97.4%, the solid reactant conversion is 54% and a solid inventory ratio for the optimum reaction conversion is 3.3 in the process.

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1. Introduction

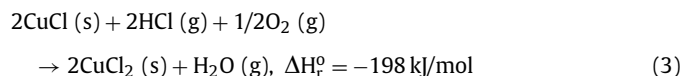
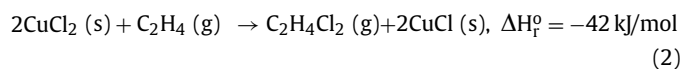
Polyvinyl chloride (PVC) is one of the most mass producing thermoplastics in chemical industries of the world. As a feed stock for PVC production, 1,2-dichloroethane (also called ethylene dichloride, EDC) is manufactured by the oxychlorination reaction of ethylene. In commercial ethylene oxychlorination reactors, gaseous ethylene, hydrogen chloride, and air react with catalyst at a temperature range of 473–573 K and a pressure of 0.4–0.6 MPa (Naworski and Velez, 1983; Mallikarjunan and Hussain, 1983; Magistro and Cowfer, 1986). Under these conditions, typical feedstock conversions are reported to be 94–99% for ethylene and 96–99% for HCl with EDC selectivity of 93–96% (Ullmann, 1986). Since this reaction (Eq. (1)) is highly exothermic, conventional reactors are accompanied with internal cooling coil or some other heat-transfer medium for heat removal (Smallwood et al., 1987):



However, local hot spots may still remain and it creates some problems. For example, copper chloride (CuCl_2) as a catalyst can be evaporated above 673 K and it was reported that the product distribution can change from high yields of 1,2-dichloroethane to a mixture of

more highly chlorinated hydrocarbons such as 1,1,2-trichloroethane, trichloroethylene, vinyl chloride, and 1,2-dichloroethylene with increasing temperature (Magistro and Cowfer, 1986; Pan et al., 1994; Wachi and Asai, 1994).

To solve these problems, the oxychlorination reaction is divided into two individual reactions (Wachi and Asai, 1994; Leofanti et al., 2001, 2002) in this study. It is composed of ethylene chlorination by the reduction of cupric chloride (Eq. (2)) and re-oxidation of the cuprous chloride by hydrogen chloride and oxygen (Eq. (3)).



It can be anticipated that the risk of sublimation of catalyst can be reduced due to heat of reaction and the separation of gases in the downstream would become very simple. In addition, flammability of the reaction of ethylene and oxygen can be basically excluded and selectivity of EDC could be improved without any hydrocarbon compounds in the reactions.

However, the two individual reactions in the practical chemical process have not been reported in literatures except for some kinetic studies (Kominami et al., 1965; Allen and Clark, 1971; Hall et al., 1984; Wachi and Asai, 1994). To maximize the product efficiency of EDC using the two-step reactions in the continuous process with catalyst circulation through both reactors, a systematic study is needed. In this regard, a fluidized bed reactor system is introduced since the

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reactor system has smooth liquid-like flow of particles which allows continuous solid circulation operation with rapid mixing of solids (Kunii and Levenspiel, 1991). The solid inventory ratio for the reduction and oxidation reactions is an important factor to maintain the mass balance in the continuous fluidized bed reaction system.

In this study, the two-step oxychlorination reaction for EDC production was carried out in a batch fluidized bed reactor. First of all, the fluidization stability was determined based on the variation of bed pressure drop during the reaction. The optimum gas velocity and the feeding compositions were determined at 523 K. With these optimized values, solid reactant conversion and solid inventory ratio were determined for the continuous fluidized bed process.

2. Experimental

The catalyst was prepared from the commercial product copper chloride by impregnating on γ -alumina powder. The catalyst had the mean particle diameter of 70 μm with a density of 2000 kg/m^3 . The amount of copper loaded on the alumina carrier was 4.12 wt% that was determined by inductively coupled plasma (ICP) analysis. Minimum fluidizing gas velocity (U_{mf}) of the catalyst was determined to be 0.0014 m/s at 523 K. The experimental apparatus is schematically shown in Fig. 1. The reactor was made of Inconel 600 having inside diameter of 40 and 995 mm in high. The reactor was heated by electric heaters around the reactor walls to attain a desired temperature. Streams of gaseous reactants of ethylene on the reduction step and the combined hydrogen chloride and oxygen on the oxidation step were introduced into mass flow controllers. Nitrogen gas was used to maintain the minimum fluidization state. Reactivity of the reduction and oxidation reactions were analyzed by gas chromatography (J and W GC Capillary Columns and FID analysis) and pH meter (ISTEK 735p). The fluidization stability in the bed was determined by the ratio of the measured bed pressure drop and its theoretical pressure balance value, where the pressure was measured by pressure transmitters (Sensys) at 1 and 15 cm from the distributor plate (ΔP_{1-6}). The fluidization stability is defined as in Eq. (4) where $Q = 1$ indicates the best stable fluidization state, $Q > 1$ is forming a solid packed bed without channeling, and $Q < 1$ indicates particle sintering at the walls of the bed and not in the bulk, or bulk agglomeration

occurs with channeling (Compo and Preffer, 1987).

$$Q = \Delta P / \Delta P_0 \quad (4)$$

where ΔP_0 is the pressure drop by the bed weight and ΔP is pressure drop at any time.

The catalyst of 170 g (bed length/column diameter = 3) was packed in the reactor and fully oxidized before reaction. After the reaction, the sample of catalysts was observed by optical microscope (EgTech, Korea).

3. Results and discussion

3.1. Fluidization stability in two-step oxychlorination reaction

During the reactions of oxidation and reduction at a gas velocity of 0.0028 m/s ($2U_{\text{mf}}$), the fluidization stability as a function of variation of the bed pressure drop ratio (Q) is shown in Fig. 2. As can be seen, a stable fluidization stability condition having $Q = 1$ in the whole reduction stage can be observed while a severe defluidization can be seen with decreasing Q values in the initial oxidation reaction without inert gas and its stability is recovered with time to the normal stable fluidizing state. Since no particle agglomeration can be observed after the reaction, this result can be elucidated by volume change of the gas that accompanied in the oxidation reaction (Eq. (3)). However, the defluidization due to the gas volume change can cause local hot spots and lowering mixing between gas and solids in the real process. Therefore, the inert gas of 60% in the total flow rate was needed into the bed to maintain the stable fluidization state in the oxidation stage in the present system. At the minimum fluidization state by using the inert gas, the effect of molar ratio of O_2/HCl on the fluidization stability was determined and the particle agglomeration was observed at the O_2/HCl molar ratio below 0.33. Images of the solid particles before and after the oxidation reaction are shown in Fig. 3. As can be seen, the particle agglomeration can be observed having larger particle diameter in Fig. 3(b). This fact coincides with the increase of the standard deviation of the bed pressure drop (ΔP_{2-4}) as can be seen in Fig. 4. With decreasing O_2/HCl molar ratio, the deviation of pressure drop in the bed increases and this pattern can be represented obviously below the stoichiometric molar ratio of O_2/HCl . This is attributed to the

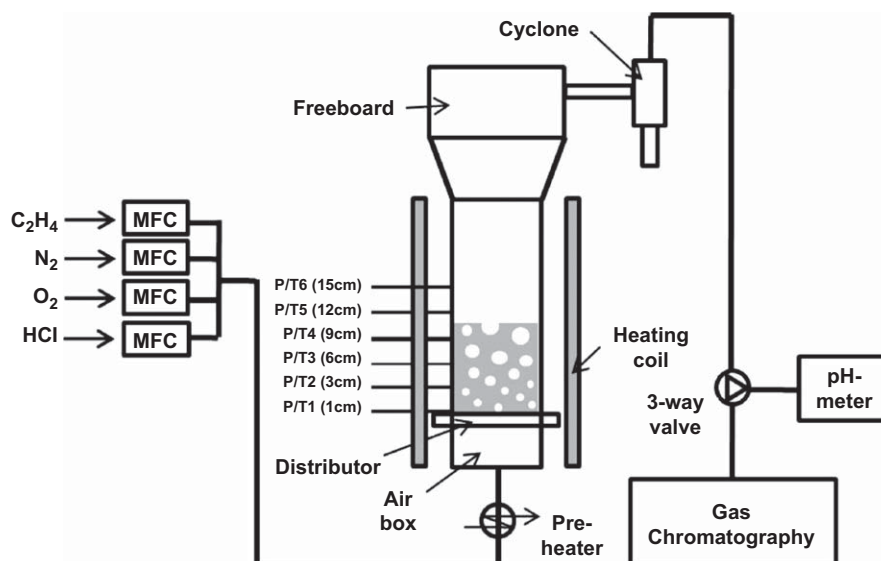


Fig. 1. Schematic diagram of the fluidized bed reactor for oxychlorination reaction (P/T: pressure tap).

increase of bubble size and bubble formation frequency in the bed of larger particle size. Also, Pan et al. (1994) reported that deactivation of the catalyst can be prevented at the O_2/HCl ratio in the range of 0.3–0.75 in the oxidation stage so that it may be claimed that the O_2/HCl molar ratio of 0.5 is a desirable one for the reaction.

3.2. Effects of gas velocity and ethylene concentration on the reduction reaction

After oxidizing the fresh catalyst completely, the reduction reaction was carried out. At an ethylene feeding concentration below the stoichiometric value, the effect of gas velocity (0.004–0.024 m/s) in terms of gas residence time in the bed on the ethylene conversion and EDC selectivity in the reduction reaction was determined as shown in Fig. 5. As can be seen, the ethylene conversion increases with increasing gas residence time or decreasing gas velocity in the bed since bubble size is smaller at the lower gas velocities that may improve the contacting area between the gas and solid phases. However, the effect of gas residence time of ethylene is insignificant to the EDC selectivity at approximately 98% that is acceptable range in the present reaction system.

At a gas residence time of 10 s, the effect of ethylene feeding concentration on the ethylene conversion and EDC selectivity with the

reaction time is shown in Fig. 6 where the reactivity of reduction depends on ethylene feeding concentration and the reaction rate approaches to its maximum value above 50% concentration of ethylene and the EDC selectivity is mainly dependent on the ethylene conversion. The average EDC selectivity is found to be 97–98% in the ethylene conversion range above 90% while it decreases with increasing unreacted ethylene. With the constant supply of ethylene in the reactor, the amount of $CuCl_2$ to participating in the reaction becomes smaller which may cause unreacted ethylene in the reactor. For this reason, decreasing EDC selectivity can be interpreted by increase of the byproducts from the side-reaction between the unreacted ethylene and EDC.

3.3. Effect of gas velocity and hydrogen chloride concentration on the oxidation reaction

After the reduction reaction, the oxidation reaction was carried out at a O_2/HCl molar ratio of 0.5. At a hydrogen chloride feeding concentration below the stoichiometric value, the effect of gas velocity (0.003–0.012 m/s) in terms of gas residence time in the reactor on hydrogen chloride conversion was determined as shown in Fig. 7.

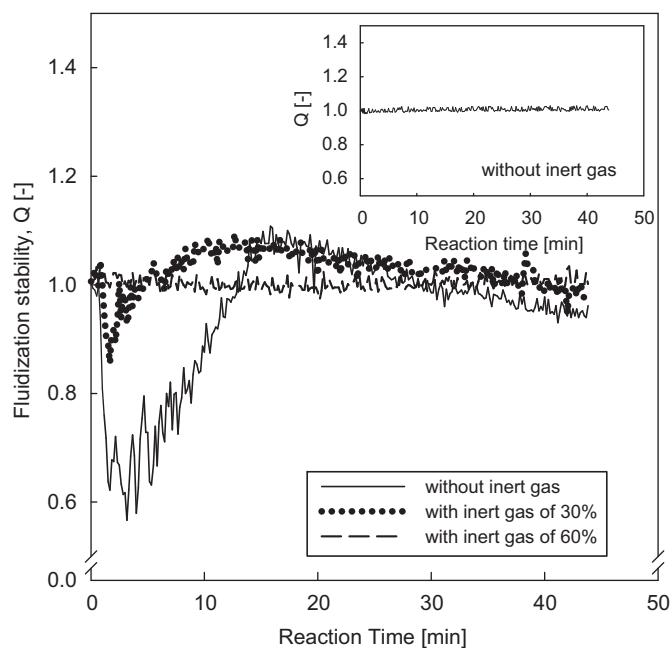


Fig. 2. Fluidization stability of the oxidation and the reduction reactions.

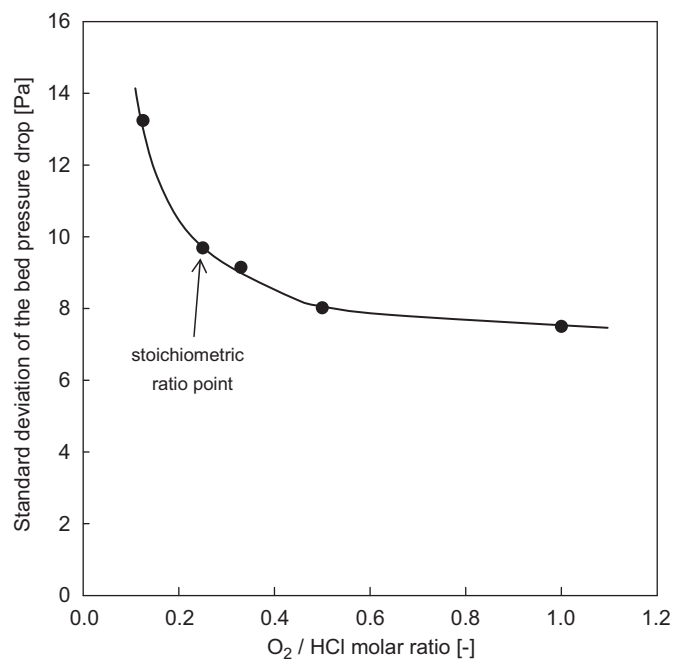


Fig. 4. Effect of O_2/HCl molar ratio on fluidization stability.

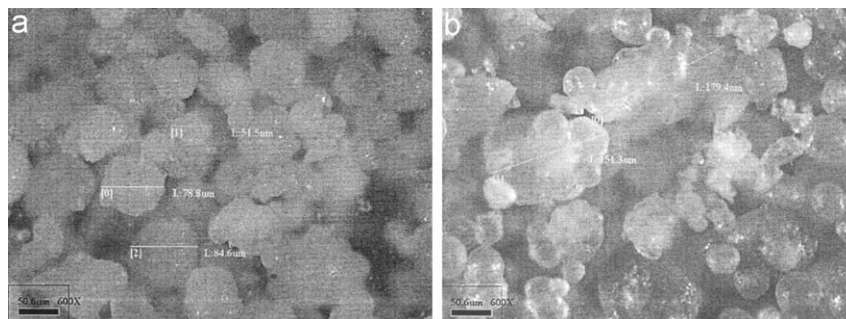


Fig. 3. Optical microscope images of the reactant particles (a) before and (b) after oxidation.

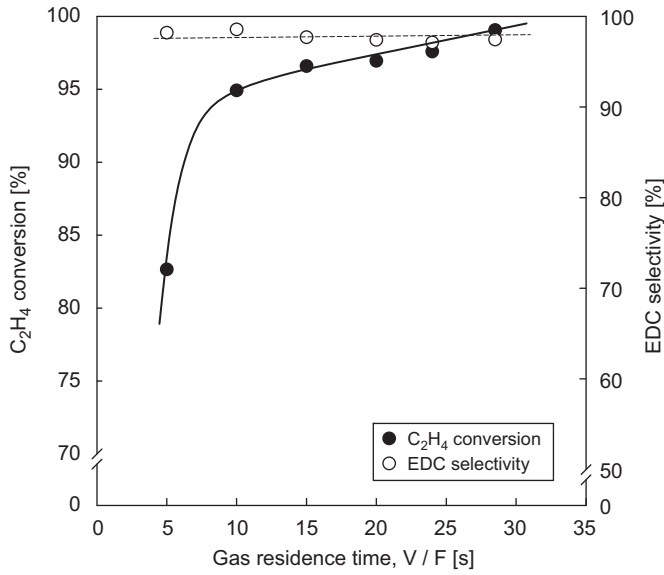


Fig. 5. Effect of gas residence time on ethylene conversion and EDC selectivity.

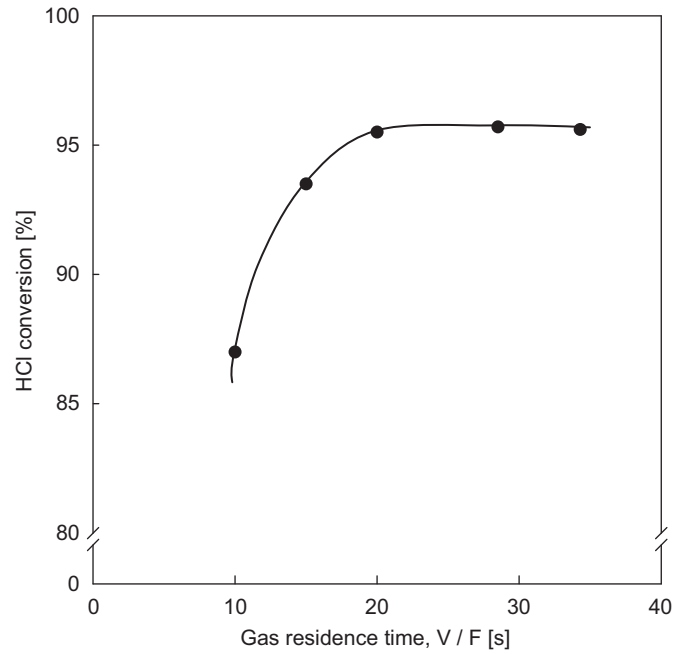


Fig. 7. Effect of residence time of hydrogen chloride on its conversion.

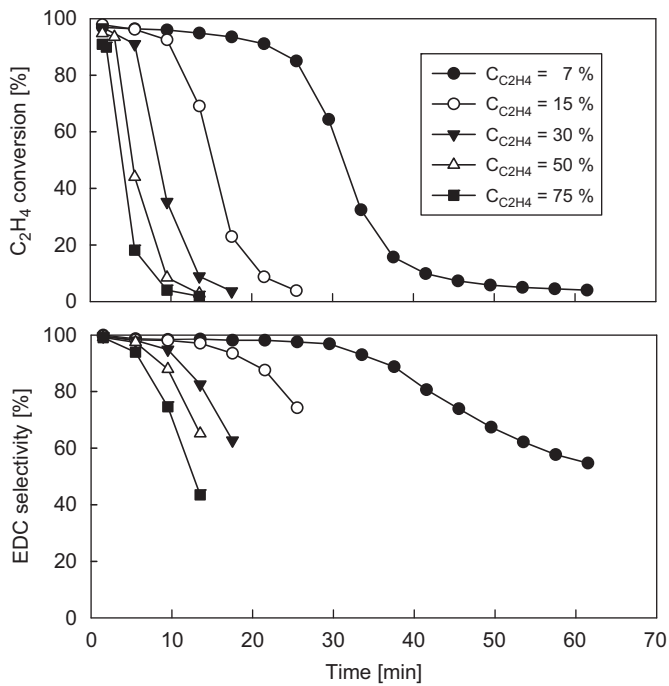


Fig. 6. Effect of ethylene concentration on ethylene conversion and EDC selectivity.

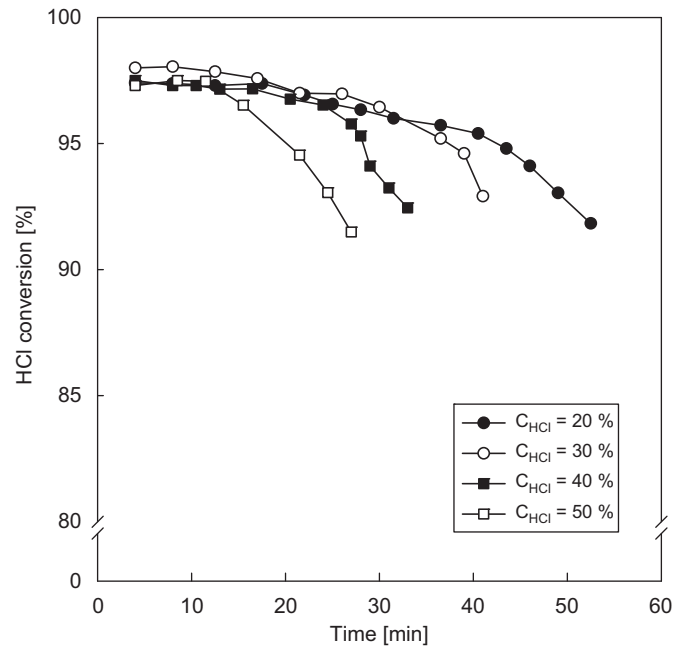


Fig. 8. Effect of hydrogen chloride concentration on its conversion.

As can be seen, the hydrogen chloride conversion increases approximately 95% conversion over 20 s with increasing gas residence time. Comparing with the reduction data, contacting time between the gas and solids in the oxidation reaction is twice longer. Therefore, the oxidation reaction rate is relatively slow than that of the reduction reaction. The effect of hydrogen chloride concentration on its conversion at a gas residence time of 20 s is shown in Fig. 8. The maximum conversion of hydrogen chloride is found to be 97–98% regardless of the feeding concentration but the reaction rate increases with increasing feeding concentration at the given reaction condition.

3.4. Solid inventory ratio of the two-step oxychlorination for the continuous system

Based on the obtained data, the solid inventory ratio was determined for the continuous two-step oxychlorination process. The solid inventory ratio is defined as the ratio of solid mass weight (W_{ox}/W_{red}) needed for maintaining the mass balance of oxidation and reduction for the continuous process and this is a function of solid residence time in the reaction. Based on the average ethylene conversion of 94% ($R_{red,gas} = 10$ s, $C_{C_2H_4} = 50\%$) with EDC selectivity of 97–98% and the average hydrogen chloride conversion of 97.4%

($R_{\text{ox,gas}} = 20$ s, $C_{\text{HCl}} = 50\%$ at $O_2/HCl = 0.5$) from Figs. 6 and 8, the solid inventory ratio can be determined to be 3.3. It can be also interpreted by the solid reactant conversion defined by

$$X_s = M_r/M_{tr} \quad (5)$$

where X_s is solid reactant conversion, M_r mole of copper reacted, and M_{tr} mole of copper to react. As a result, solid reactant conversion is found to be 54% at the optimum operating condition. Although Wachi and Asai (1994) reported in their kinetic study of the reduction that the solid conversion of 64% was obtained at the optimum performance, this difference from this study is a reasonable one since contacting efficiency between gas and solid phases in the fluidized bed reactor is relatively lower than in an ideal reactor for the kinetic study. Meanwhile, there was no observation of catalyst sublimation due to the heat of reaction and the particle attrition during the fluidization operation was insignificant for the reaction.

In view of designing the present process, two interconnecting bubbling fluidized bed reactors with the solid inventory ratio of 3.3 can be selected as a continuous two-step oxychlorination system based on the obtained results of the gas and solid reactant residence times. In this respect, the concept of double-loop (i.e. with two driving forces) solids circulation system involving two gas streams (Kunii and Levenspiel, 1991) is a desirable one. In addition, a pneumatic transfer line for upward solid transport and non-mechanical valves for the control of solid flow are also needed for the continuous reaction system.

4. Conclusion

The two-step oxychlorination process of oxidation and reduction reactions were carried out in the fluidized bed reactor and the optimum operating conditions for each reaction was determined to provide the basic design data for the continuous fluidized bed process. For the fluidization stability, stable fluidization condition was maintained in the reduction stage but in the oxidation stage, the inert gas of 60% in the total flow rate was needed into the bed to maintain the stable fluidization state in the present system. Also, the particle agglomeration can be prevented at the O_2/HCl molar ratio over 0.5. Based on the average ethylene conversion of 94% with EDC selectivity of 97–98% and the average hydrogen chloride conversion of 97.4%, the solid inventory ratio is determined to be 3.3 and the solid conversion is found to be about 54% at the optimum operating conditions.

Notation

$C_{C_2H_4}$	concentration of ethylene, %
C_{HCl}	concentration of hydrogen chloride, %
F	volumetric flow rate, m^3/s

ΔH_r^0	enthalpy of reaction, kJ/mol
M_r	mole of copper reacted, mol
M_{tr}	mole of copper to react, mol
ΔP	pressure drop, Pa
ΔP_0	the pressure drop by bed weight, Pa
Q	fluidization stability
$R_{\text{ox,gas}}$	gas residence time in oxidation, s
$R_{\text{red,gas}}$	gas residence time in reduction, s
U_{mf}	minimum fluidizing gas velocity, m/s
V	volume of solid particle in the bed, m^3
W_{ox}	solid mass weight in oxidation, kg
W_{red}	solid mass weight in reduction, kg
X_s	conversion of solid reactant, %

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