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A STUDY ON WASTEWATER MINIMIZATION IN INDIRECT ELECTROCHEMICAL SYNTHESIS OF BENZALDEHYDE

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ABSTRACT

Development of methods of pollution prevention is a strategic orientation for environmental protection. This paper describes studies on waste minimization in benzaldehyde production by using indirect electrochemical oxidation of toluene instead of the seriously polluting traditional chemical process. The new technology developed eliminates the discharge of wastewater by recycling the reactive solution and gives a higher yield of benzaldehyde. Copyright © 1996 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Indirect electrochemical synthesis; mediator; Mn(III)/Mn(II); benzaldehyde; recycle of the reactive solution.

INTRODUCTION

Benzaldehyde is an intermediate widely used in the syntheses of fine chemicals (Baizer, 1980). The traditional chemical process for its production has the disadvantages of being lengthy, complicated, having a low yield of - 58%, and discharging large amounts of corrosive gases and organic effluents (see Fig. 1).

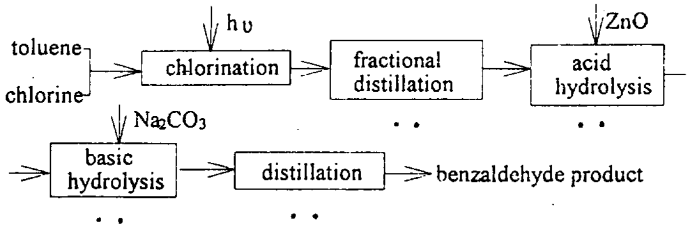


Figure 1. A schematic drawing of the traditional chemical production process for benzaldehyde ".." marks the points of waste discharge.

In recent years much work has been done to reduce the discharge of wastewater and improve the yield of benzaldehyde in electrochemical production processes. Mn(III)/Mn(II) has been used as mediator in the oxidation of toluene to benzaldehyde. Mn(III) is produced from $MnSO_4$ in an electrolytic cell and then added to a reactor where toluene is oxidized to benzaldehyde. The basic chemical equations are

$$\mathrm{Mn(II)} - e \xrightarrow{H_2SO_4} \mathrm{Mn(III)} \tag{1}$$

$$4\mathrm{Mn(III)} + C_6H_5CH_3 + H_2O \xrightarrow{H_2SO_4} 4\mathrm{Mn(II)} + C_6H_5CHO + 4H^+ \tag{2}$$

There have been investigations on homogenous electrolysis, in-cell and ex-cell electrolysis and diaphragmless cell electrolysis to raise the yield of benzaldehyde (Comninellis, 1982, 1991; Boardman, 1983; Kim, 1989). To further improve yield of benzaldehyde, systematic study has been done on heterogeneous electrolysis of $MnSO_4$ (Hu *et al.*, 1994). Reports from our lab and labs abroad have shown that: to obtain high yields of benzaldehyde, it is essential to use a low acidity (40% H_2SO_4) for electrolytic production of Mn(III) and a high acidity (>60% H_2SO_4) for oxidation of toluene to benzaldehyde. This has led to the problem of acid effluent (Fig. 2) in the production process as a result of imbalance in H_2SO_4 concentration.

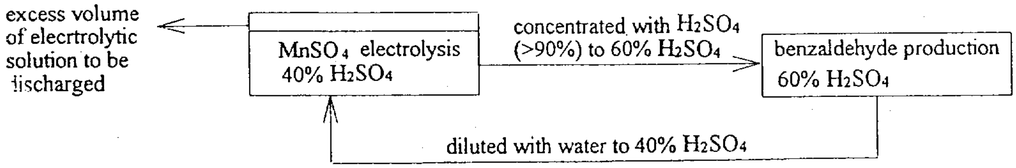


Figure 2. Flow diagram for the low acidity electrolysis-high acidity synthesis process.

As a solution, we have tried to achieve the recycling of the reactive solution through a process involving distillation and concentration (Fig. 3), but it is lengthy, complicated and energy consuming, and hence leads to higher cost.

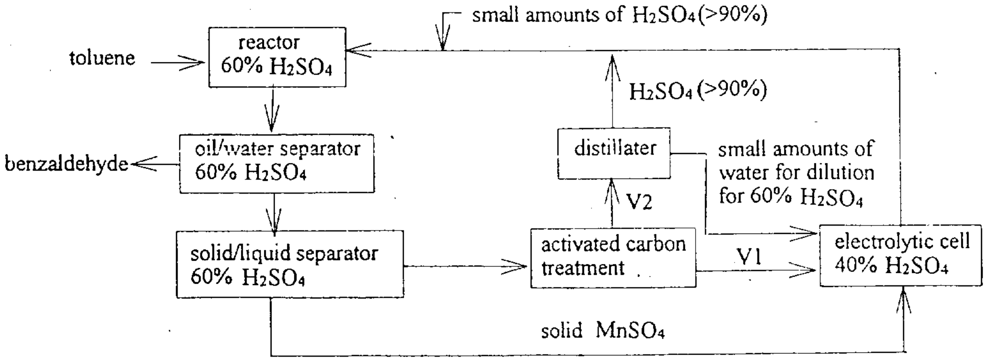


Figure 3. Flow diagram of the process involving recycling of reactive solution. V1: diluted to 40% H_2SO_4 with water. V2: concentrated by distillation to H_2SO_4 (>90%)

Therefore, to realize the wastewater minimization in indirect electrochemical synthesis of benzaldehyde by recycling reactive solution, two main problems must be resolved. First, the sulfuric acid concentration of electrolysis should be in accordance with that of the oxidation of toluene to benzaldehyde by MN(III). And another problem is to resolve the current efficiency losses during the recycling process.

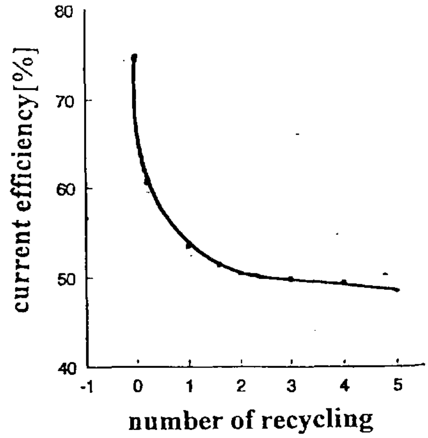


Figure 4. Fall of current efficiency in recycling of reactive solution.

In this paper, we have studied the improvement of current efficiency of electrolytic production of Mn(III) in 60% H_2SO_4, by selecting optimum electrode material, optimization of electrolytic conditions, and removal of organic impurities by activated carbon and recycling of the reactive solution.

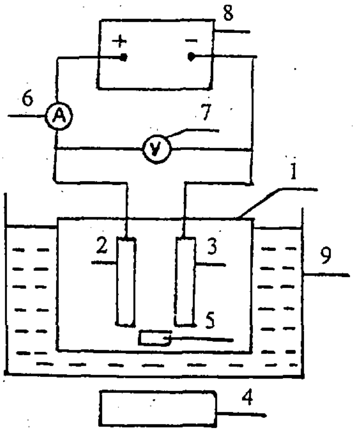
EXPERIMENTAL PART

Materials and instruments.

$MnSO_4{\cdot}H_2O$ AR, concentrated H_2SO_4 (92%) AR, 0.2mol/l standard ferrous ammonium sulfate solution, WYJ-type voltage stabilizer: range 50V, 3A.

Experimental procedures.

Electrochemical oxidation of $MnSO_4$: $MnSO_4$ is oxidized in a diaphragmless electrolytic cell



1. electrolytic cell
2. anode
3. cathode
4. magnetic stirrer
5. magnetic stirring bar
6. amperemeter
7. voltmeter
8. voltage stabilizer
9. water bath

Figure 5. A sketch of electrochemical oxidation of MnSO .

$MnSO_4 \cdot H_20$ and 60% H_2SO_4 are put into the electrolytic cell. Stirring speed, electrolysis temperature and current density are regulated and then electrolysis begins. During electrolysis, small amounts of electrolyte are removed for Mn(III) determination.

Analysis of Mn(III): The concentration of Mn(III) is determined by titration with standard ferrous ammonium sulfate solution. The current efficiency:

$$\eta\% = \frac{[Mn(III)] \cdot V \cdot F}{I \cdot t} \times 100\% \tag{3}$$

η: current efficiency;
[Mn(III)]: conc. of Mn(III), mol/l;
V: Volume of electrolyte, l;
F: Faraday constant;
I: current strength, A;
t: time of electrolysis, hr.

RESULTS AND DISCUSSION

Selection of electrode material

Several electrode materials have been studied in accordance with their effects on current efficiency, resistance to acid corrosion and cost (see Table 1)

Table 1. Effect of electrode materials on current efficiency

Anode	Cathod	Current efficiency %
Ru(Ti)	Ru(Ti)	23
Ti	Graphite	32
Pb	Graphite	65
Pb	Pb	72
Pb—Sb—As	Pb—Sb—As	75

$MnSO_4$: 1mol/l, H_2SO_4: 60%, temperature: 60℃, current density: 60mA/cm^2, time: 1hr

Pb—Sb—As alloy is hard, cheap and highly resistant to corrosion in H_2SO_4 solution. From Table1, we see that current efficiency is highest for Pb—Sb—As. So Pb—Sb—As alloy is decided upon as the best material for anode and cathode.

Optimization of electrolytic conditions

Current efficiency of heterogeneous electrochemical oxidation of Mn(II) is closely related to electrolytic conditions. The effects of major factors such as $MnSO_4$ concentration, current density, temperature and time electrolysis have been studied.

Effect of MnSO4 concentration. Unlike the situation in homogenous electrolysis, $MnSO_4$ concentration is of the utmost importance to current efficiency in heterogeneous electrooxidation of Mn(II) in 60% H_2SO_4

solution. The relationship between concentration of $MnSO_4$ and current efficiency is shown in Figure 6. The $MnSO_4$ conc. is selected as 1 mol/l.

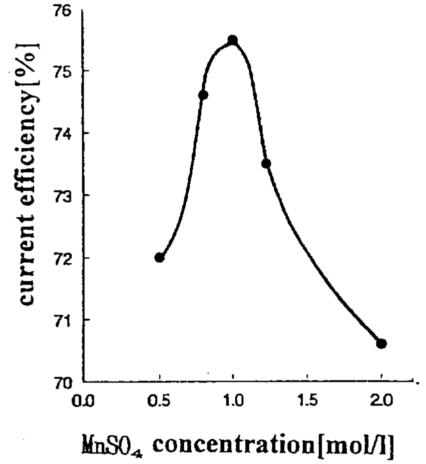


Figure 6. Effect of $MnSO_4$ conc. on current efficiency. Temperature: 60°C; current density: 60mA/cm^2; time: 2 hours.

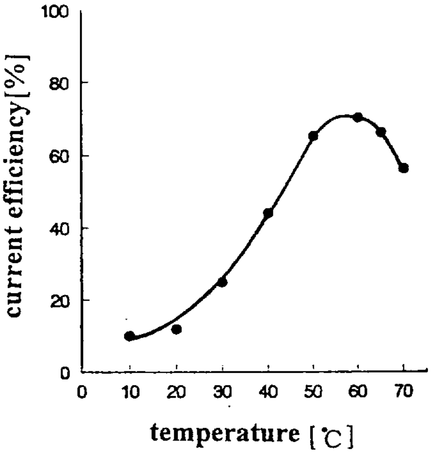


Figure 7. Effect of temperature on current efficiency. $MnSO_4$ conc.: 1 mol/l; current density: 60mA/cm^2; time: 1 hour.

Effect of the temperature of electrolysis: Temperature has a great effect on the current efficiency. Should the temperature be too low, it will lead to low electrolytic reaction velocity and low current efficiency. If temperature is too high, it will lead to higher reaction speed, greater O_2 evolution and lowering in current efficiency. Experimental results show the optimum temperature to be 60°C (see Fig. 7).

Effect of current densisty: Current density has a rather large effect not only on current efficiency, but also on the production of Mn(III). The lower is the current density, the higher will be the current efficiency, while Mn(III) production rate will be lower. When current density increases, the anodic potential and oxygen evolution will increase accordingly, resulting in a fall of the current efficiency. Taking into consideration both the current efficiency and the Mn(III) productivity, we have selected 60mA/cm^2 as the current density (see Fig. 8).

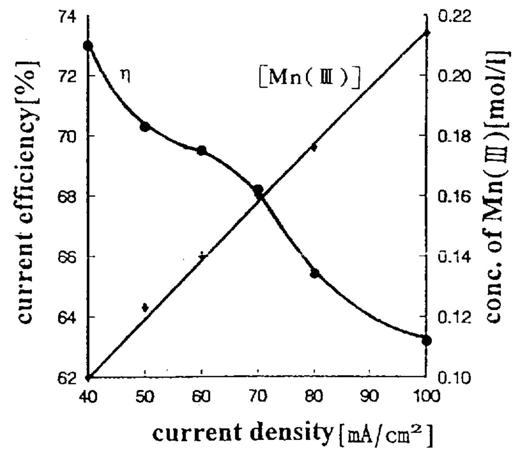


Figure 8. Effect of current density on current efficiency. $MnSO_4$ conc.: 1 mol/l; H_2SO_4 conc.: 60%; temperature 60°C; time: 1 hour.

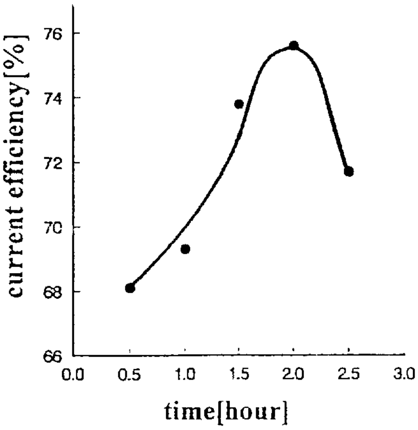


Figure 9. Effect of time of electrolysis on current efficiency. $MnSO_4$ conc.: 1 mol/l; H_2SO_4 conc.: 60%; temperature 60°C; current density: 60mA/cm^2.

Effect of time of electrolysis

From Figure 9, we see that time of electrolysis has a rather large effect on the current efficiency of heterogeneous electrolysis of $MnSO_4$ in 60% H_2SO_4. The optimum time of electrolysis is 2 hours when the current efficiency reaches 75%.

Through the above studies, we obtained the optimum parameters for heterogeous electrolysis of $MnSO_4$ using both Pb-Sb-As alloy anode and cathod; $MnSO_4$ concentration: 1 mol/l; current density: 60mA/cm^2, temperature: 60°C; time: 2 hours. Under the above conditions, a current efficiency up to 75% can be obtained, which is only a little less than the 80% attained in the 40% H_2SO_4 electrolytic solution.

Studies on recycling of the reactive solution

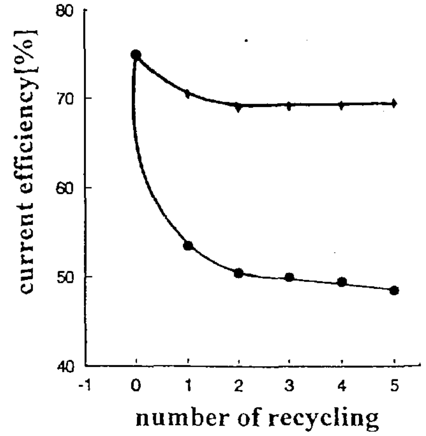


Figure 10. Relationship between the recycling numbers of the reactive solution and current efficiency before (bottom curve) and after (top curve) activated carbon treatment. $MnSO_4$ conc.: 1 mol/l; H_2SO_4 conc.: 60%; current density: 60mA/cm^2; temperature 60°C; time: 2 hours.

The term "reactive solution" here refers to the 60% H_2SO_4 aqeous solution phase separated form the organic phase containing the benzaldehyde product. Successful recycling of the reactive solution will ensure "100%" use of its $MnSO_4$ and H_2SO_4 contents, thus achieving a no-waste discharge and non-polluting process. Experimental results have shown that if the reactive solution is recycled and used as it was obtained from the oil/water separator without purification, current efficiency will fall as the number of recycles increases (See Fig. 10). This is probably due to the small amounts of organic impurities produced in the oxidation of toluene by Mn(III) and remaining in the reactive solution. These impurities either will react on the anode or cathode or will further react with Mn(III) causing a fall in current efficiency. Using activated carbon treatment to remove the organic impurities, the problem of falling current efficiency is solved (Fig. 10). A flow diagram of the simplified process with recycling of the reactive solution is shown in Fig. 11.

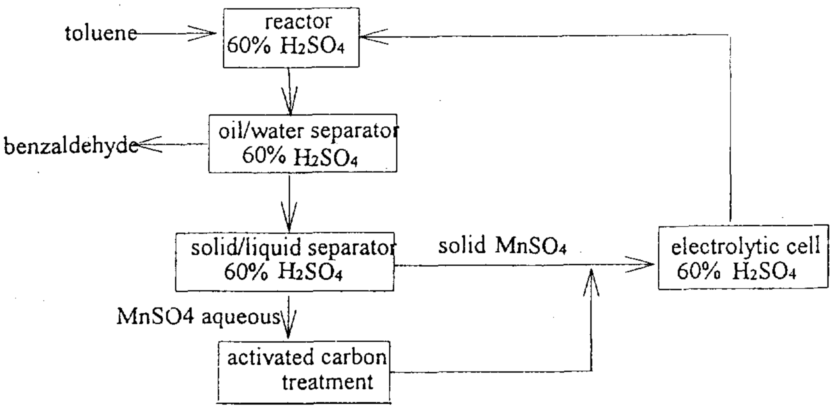


Figure 11. Flow diagram of the processs of heterogeneous indirect electroproduction of benzaldehyde with recycling of the reactive solution.

CONCLUSION

The new technology described is characterized by the recycling of the reactive solution and no wastewater production. This paper has successfully resolved two main important problems in recycling. Firstly, both heterogeneous electrolysis of $MnSO_4$ and synthesis of benzaldehyde by oxidation of Mn(III) can be carried out separately in the same concentration of sulfuric acid (60% H_2SO_4) with high current efficiency and high yield of benzaldehyde respectively. Secondly, the organic impurities in reactive solution causing the fall in current efficiency and diminishing the recycle numbers are removed effectively by activated carbon.

Obviously the development and adoption of such a new process will be highly beneficial to the preservation of the water environment.

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