Paired Electrolysis of Acetone to Produce Diacetone Alcohol in a Divided Cell

蔡明瞭 (Ming-Liao Tsai)

Abstract

Paired electrolysis of acetone in a divided cell was carried out in this study. Protone H^+ and OH^- anion were simultaneously generated at anode and cathode, respectively, by paired electrolysis. Acetone was catalytically condensed to form diacetone alcohol (daa). The factors which affected both anodic and cathodic reactions were explored. The results indicate that interrupt electrolysis is better than that of continuous electrolysis. The reaction rate of aldol condensation at cathode is faster than that at anode. The yield of daa increase from 100 to 800 g/F with increasing concentration of acetone from 2 to 8 M. The selectivity of daa almost reaches 100% and the yeild of daa was 120 g/F during 120 coul electricity passed.

摘 要

本實驗乃在一隔離槽中進行，以陰陽極組對同時電解產生氫質子及氫氧根離子，進而催化丙酮形成二丙酮醇，探討各種影響組對電解丙酮反應的因素。結果證明，間斷式電解法較連續式佳，且陰極槽中之反應速率較陽極槽中之縮合反應快。當丙酮濃度由2M增加至8M時，二丙酮醇的產率由 $100gF^{-1}$ 增加至 $800gF^{-1}$，溫度爲30℃時8M的丙酮及0.2M NaCl濃度下，最佳產率爲 $1300gF^{-1}$。

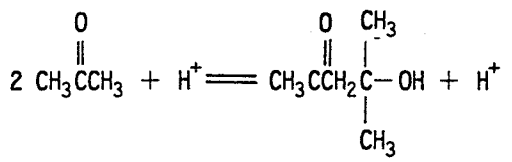
Introduction

Many special chemicals can be produced by aldol condensation [1-6]. However, few reports concerned the synthesis of chemicals by electrochemical aldol condensation [7]. In general, only one working electrode was used in the electrolysis system. However, in some cases, both cathode and anode were simultaneously used as the working electrodes i.e. Paired electrolysis. There are many advantages by paired electrolysis of the paired electrolysis of organic compounds[8-11]. Unfortunately, few or no reports concerned the simultaneously generation of catalyst at both anode and cathode for in situ synthesizing organic compounds by electrolysis. In this study, aldol condensation of acetone were simultaneously catalyzed at both athode and anode by paired electrolysis. It is an electrochemical reaction process, and the major product diacetone alcohol was obtained. The reaction was shown as following :

Cathode: $2H_2O + 2e^- \rightleftharpoons 2OH^- + H_2$ (1)

$$2\ CH_3\overset{\overset{O}{\|}}{C}CH_3 + OH^- \rightleftharpoons CH_3\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \quad (2)$$

Anode: $2H_2O \rightleftharpoons 2H^+ + 1/2\ O_2 + 2e^-$ (3)



(4)

Experimental

The paired electrosynthesis of diacetone alcohol was performed in divided cell using platinum plates as anode and cathode, respectively. The anolyte and catholyte were divided by a porous glass as shown in Fig 1. The electrolyte was prepared by mixing desired amounds of sodium chloride and acetone in a fixed volume of distillated water. At the beginning of a run, the temperature of the cells was controlled at a desired value by water bath. When the system was at steady state, the current was supplied at a desired value from the power supply. During a run, both catholyte and anolyte were sampled periodically and analyzed by a gas chromatography.

Rseults and discussion

Product composition

Fig.2 shows a typical product compositions of catholyte anolyte and the total product. In general, the product daa in catholyte is higher than that in anolyte. The conentration of total daa reaches $24*10^{-3}$ M. The selectivity of daa is 100% and almost no by product is found.

Effect of amount of electricity passed

Increasing the amount of electricity passed from 120 to 480 coul decreases the yield of daa from 120 to 60 g/F as shown in Fig.3. By paired eletrolysis, both OH^- and H^+ could be regenerated as catalysts for aldol ondensation. When 80 coul of electricity supplied, the pH values of both catholyte and anolyte were significiantly changed from 7 to 12 and 7 to 3, respectively, as shown in Fig.4.

Effect of operating tyes on paired eletrolysis

Only one product, daa, could be obtained by interrupt paired electrolysis during 120 coul charge passed. Both daa and mesity oxide were obtained in situ in anolyte and only daa appeared in catholyte by continuous electrolysis as shown in Fig.5. The selectivity of daa by continuous and interrupt electrolysis methode was 70% and 100%. As shown in Fig.6, diacetone alcohol may be reoxidized by anode in acid condition[12]. The yield of daa by interrupt electrolysis is higher than that of continuous electrolysis. as shown in Fig 7. Since continuous electrolysis may get more reoxidized of the product.

Effect of concentration of acetone

Increasing the concentration of acetone from 2 to 8 M increase the daa formation rate in catholyte and anolyte from $3.7*10^{-3}$ to $1.58*10^{-2}$ mole/l-hr and from $1.2*10^{-3}$ to $5.5*10^{-3}$ $^{-3}$ mole/l-hr, respectively as shown in Figs. 8 and 9. The yield of daa increased when the concentration of acetone increased as shown in Fig.10.

Effect of current density

The yield of daa measured by paired e.ectrolysis by increasing the current density from 40 to 10 mA/cm^2 is shown in Fig.11. The yield of daa did not change for further increasing the current density.

Effect of concentration of electrolyte

The effect of concentration of sodium chloride on the formation rate of daa is shown in Figs.12 and 13. The formation rate of daa in both catholyte and anolyte increase when the concentration of sodium chloride decreases, as shown in Fig.14.

Effect of temperature

The effect of temperature on the reaction rate, equilibrium concentration and the yield of daa are shown in Figs 15 to 17, respectively. The reaction rate of aldol reaction in both catholyte and anolyte increased from $40*10^{-3}$ to $59*10^{-3}$ M-hr^{-1} and from $9.5*10^{-3}$ to $18*10^{-3}$ M-hr^{-1} respectively, when the temperature increased from 25 to 31℃. But the equilibrium concentration of daa was lower in catholyte. Since aldol condensation is reversible and exothermic reaction[13]. When temperature increases, the equilibrium of daa formatiom is not found in anolyte.

Conclusions

The diacetone alcohol from aldol condensation of acetone by paired electrolysis was obtained. The yield of daa by interrupt paired electrolysis was better then that of continuous. The reaction rate of aldol condensation in catholyte was faster than that in anolyte. The selectivity of daa was almost 100% and no by-product was found. The yield of daa by paired electrolysis significantly increased with the concentration of acetone. On the other hand, the yield of daa significantly decreased with concentration of sodium shloride. The results also revealed that the formation rate of daa in both catholyte and anolyte increased with temperature significantly. The best yield of daa is 1300 gF^{-1} at 8M acetone, 0.2M NaCl and 31℃.

Reference

1. Y. Tencer, M. Michman and I. Goldenfeld, J. Organomet. Chem., 412, 203-14, 1991.
2. T. Mukaiyama, H. Uchirs, and S. Kobayashi, Chem. Lett., 1757-60, 1989.
3. S. Kobayashi, H. Uchirs, Y. Fujishita, I. Shiina and T. Mukaiyama, J. Am. Chem. Soc., 113, 4247-52, 1991.
4. G. Zhang, H. Hattori and K. Tanafe, Bull. Chem. Soc. Jpn., 62, 2070-72, 1989.
5. H. Watanabe, J. Seto, Bull. Chem. sOC. jPN., 64, 2411-15, 1991.
6. N. Sisul, N. Cikouic, J. Jelencic and N. Wolf, React. Kinet. Catal., 40, 227-233, 1989.
7. A. J. Fry, M. Susla, J. Am. Chem. Soc., lll, 3225-29, 1989.
8. M. M. Baizer, Proc. Symp. Elect. Chem. Process. Plet Des., 9, 31, 1989.
9. P. N. Pintanro, D. K. Johnson, K. Park, M. M. Baizer and K. Kofe, J. appl. Electro. Chem., 14, 209, 1984.
10. H. L. Chum and M. M. Baizer, ACS Monograph 183, ACS Washington D. C. 1985.
11. T. C. Chou, S. J. Liaw and B. J. Hwang, J. Chinese Chem. Soc., 34(2), 141-7, 1987.
12. T. C. Chou. J. S. Do, B. J. Hwang and J. J. Jow, J. Chem. Eng. Commum., 43, 47-62, 1987.
13. T. C. Chou, J. S. Do., B. J. Hwang and J. J. Jow, J. ChICHe., 19, 1-7, 1988.
14. J. J. Jow and T. C. Chou, J. Appl. Electrochem., 18, 298-303, 1988.
15. A. A. Frost, R. G. Pearson, Kinetics and Mechanism, p.335, John Willery, Toppan C., Let, Tokyo, 1961.

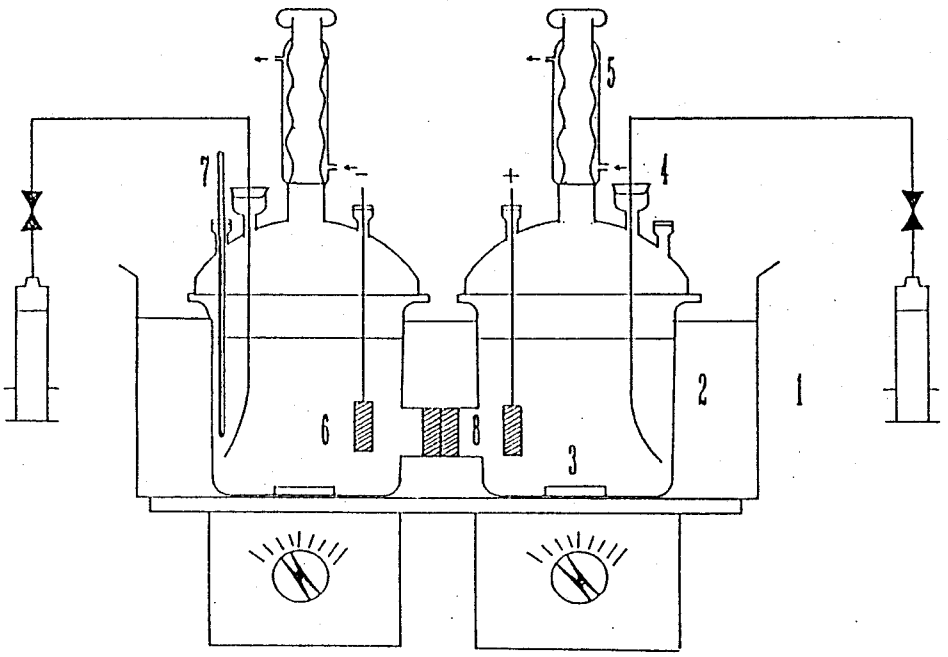


Fig.1 Paired electrolysis of acetoe.
1. Pair Slirrer Thermoslate
2. Reactor
3. Magnetic Stirrer
4. Sampling trap
5. Reflux Condenser
6. Electrode
7. Thermometer
8. Porous Pyrex Glass

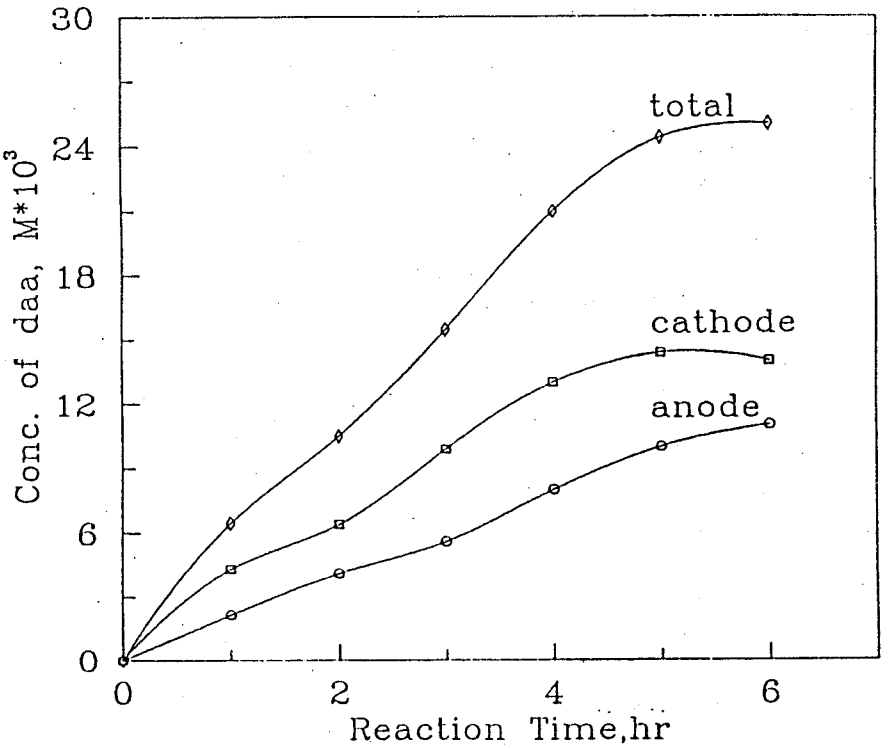


Fig.2 Product compositions of Paired electrolysis of acetone.
Cathode: Pt Anode: Pt Electricity: 240 coul
Electrolyte: 2M NaCl current density: 25 mA/CM^2
Acetone: 2M Temperature: 25℃

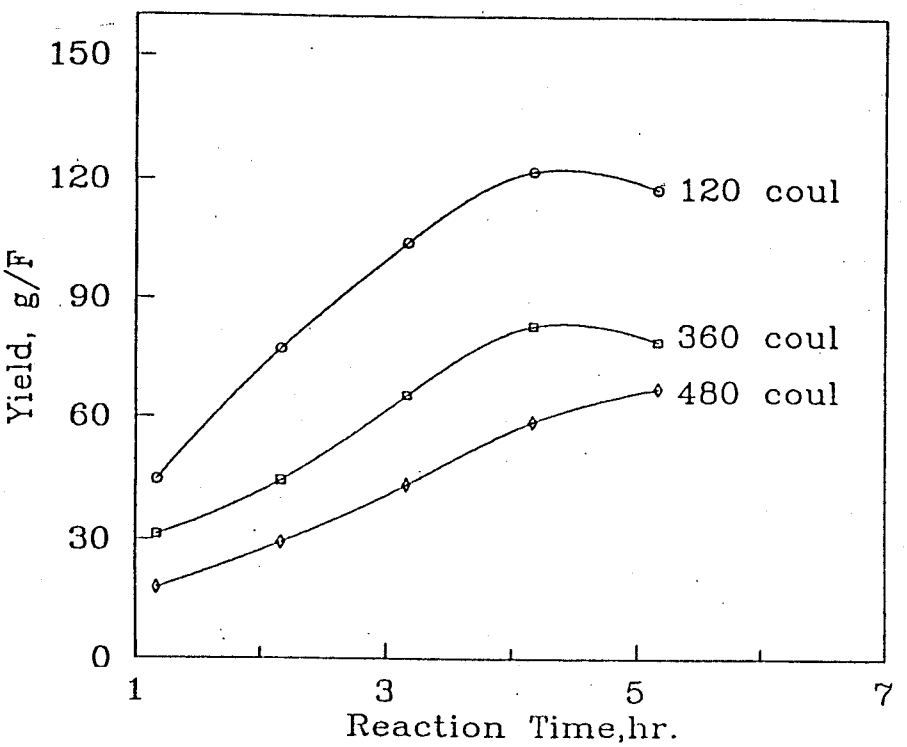


Fig.3 Effect of amount electricity passed on the reaction rate of daa at anode.
Cathode: Pt Anode: Pt Electrolyte: 2M NaCl
Acetone: 2M current density: 25 mA/cm^2
Temperature: 25℃

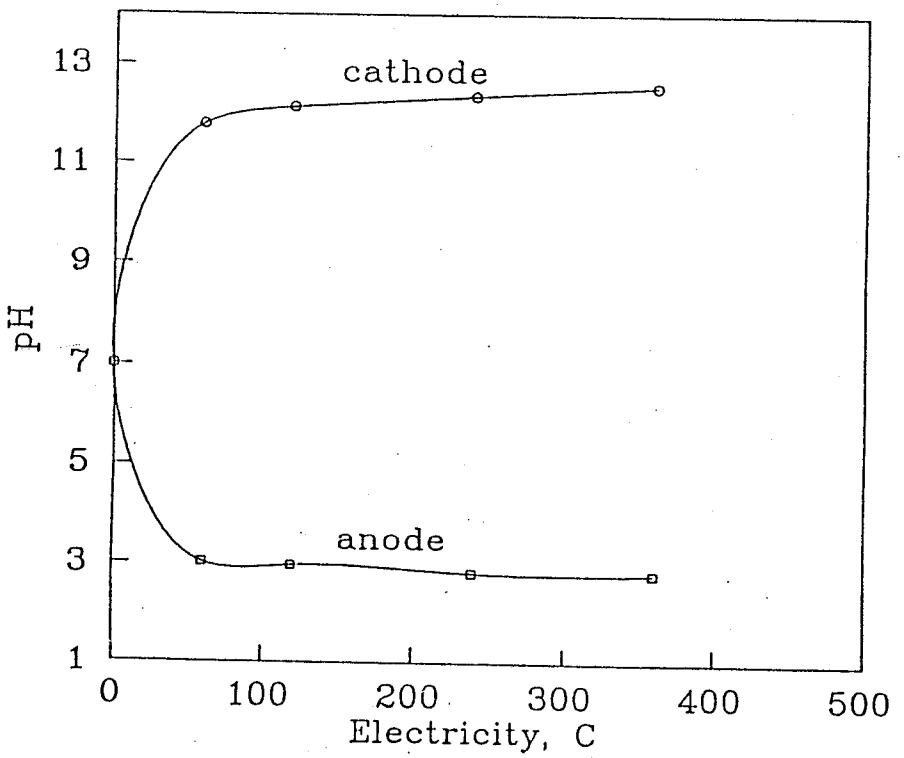


Fig.4 pH value v.s electricity passed.

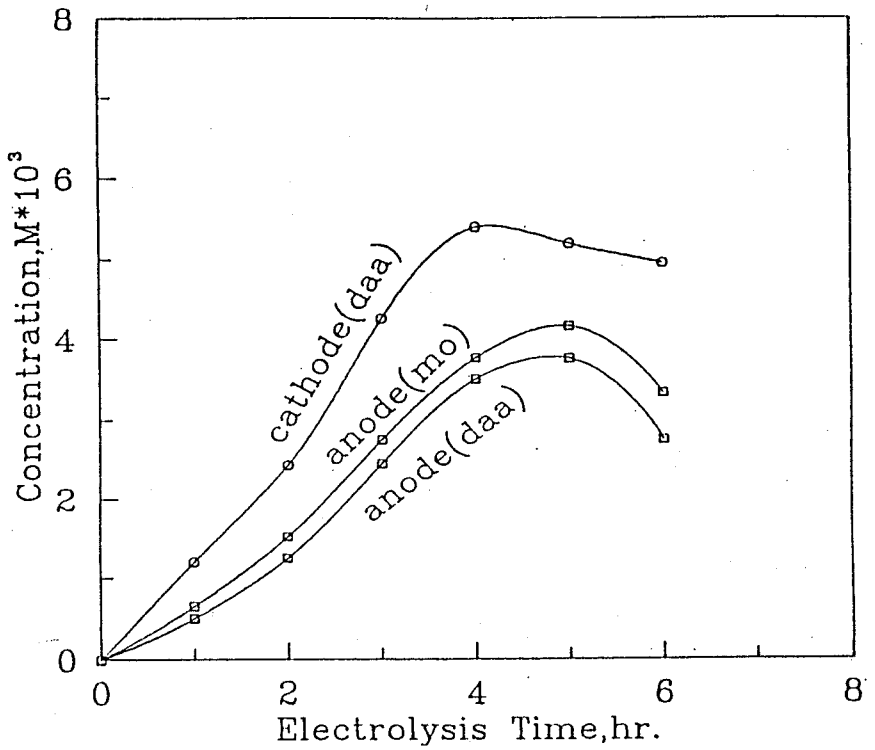


Fig.5 Product compositions of paired electrolysis of acetone.
Cathode: Pt anode: Pt Electrolyte: 2M NaCl
Acetone: 2M Current density: mA/cm^2
Temperature: 25℃

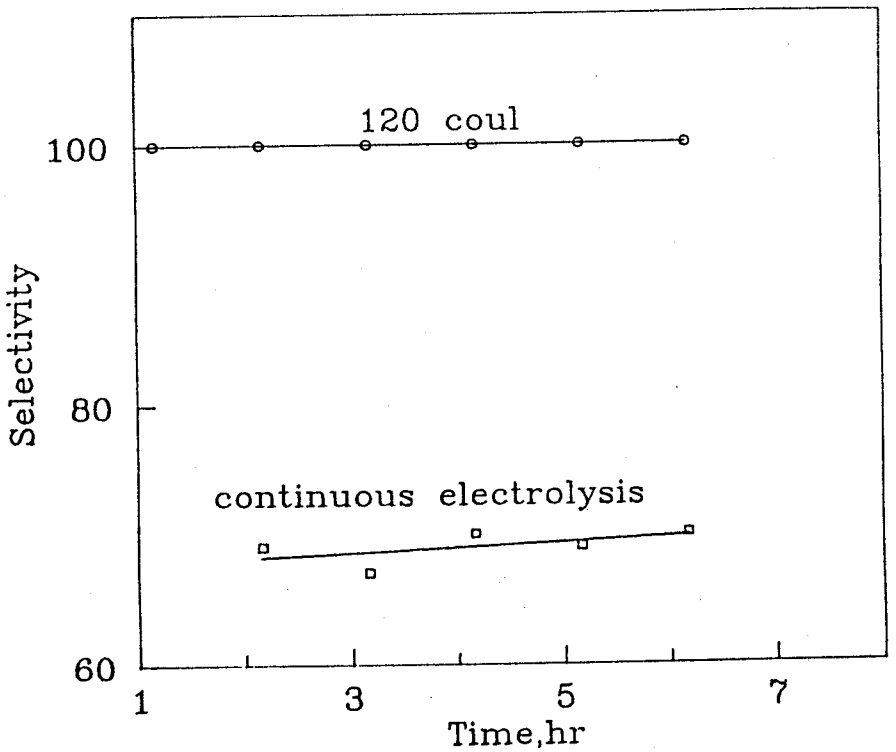


Fig.6 Comparison of the selectivity of interrupt and continous paired electrolysis of aldol reaction.
Cathode: Pt Anode: Pt Electrolyte: 2M NaCl
Acetone: 2M Current density: mA/cm^2
Temperature: 25°

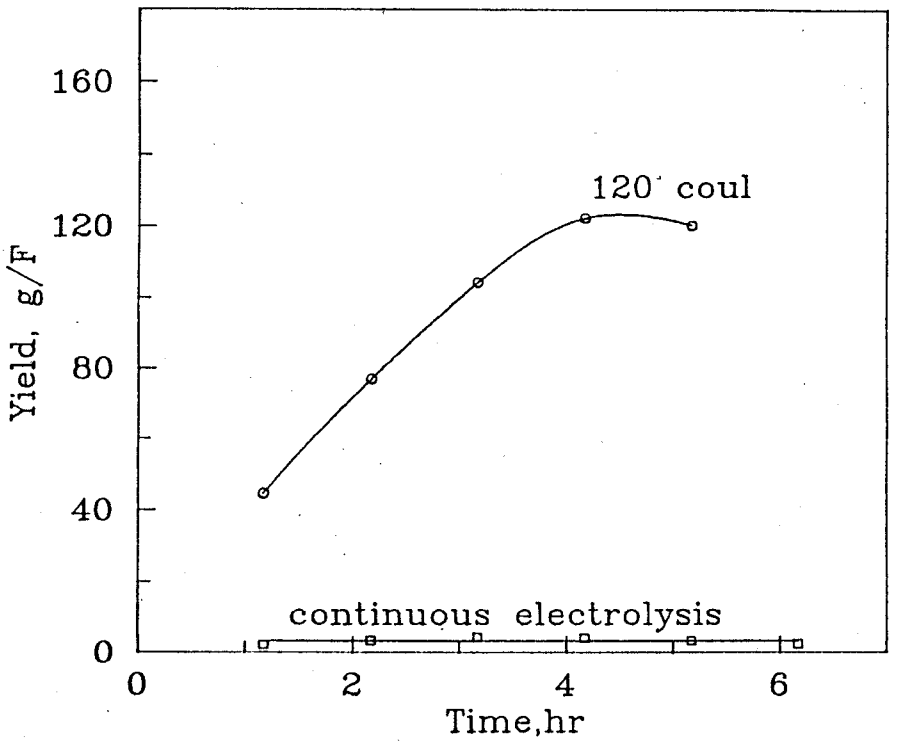


Fig.7 Comparison of the hield of interrupt and continours paired electrolysis of aldol reaction.
Cathode: Pt Anode: Pt Electrolyte: 2M NaCl
Acetone: 2M Current density: ma/cm^2
Temperature: 25 °

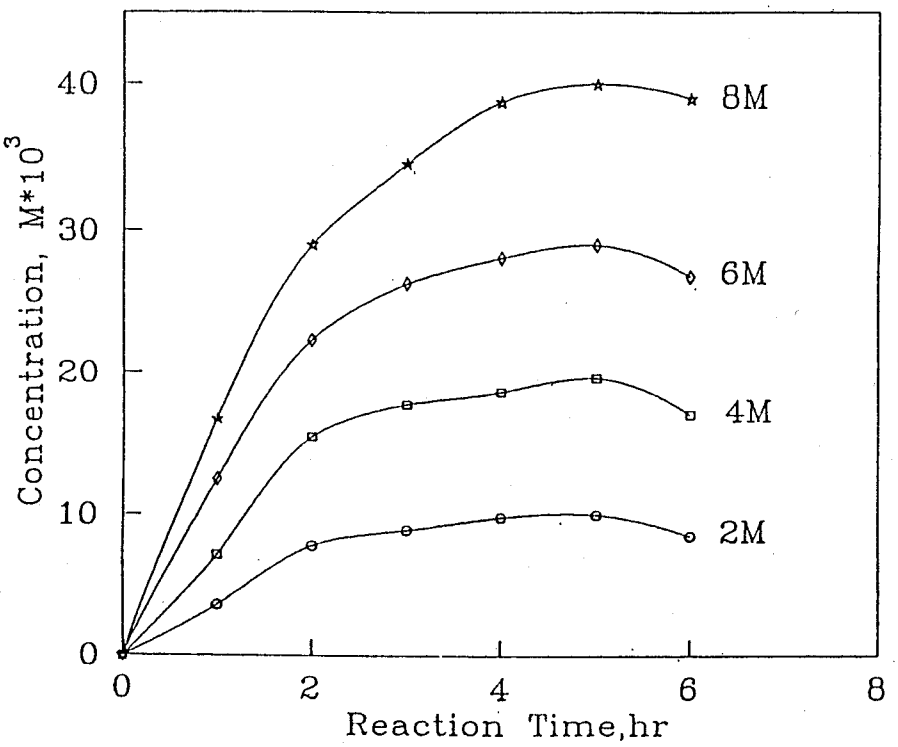


Fig.8 Effect of concentration of acetone on reaction rate at cathode.
Cathode: Pt Anode: Pt Current density: 25 mA/cm^2
Electrolyte: 2M NaCl Electricity: 120 coul
Temperature: 298K

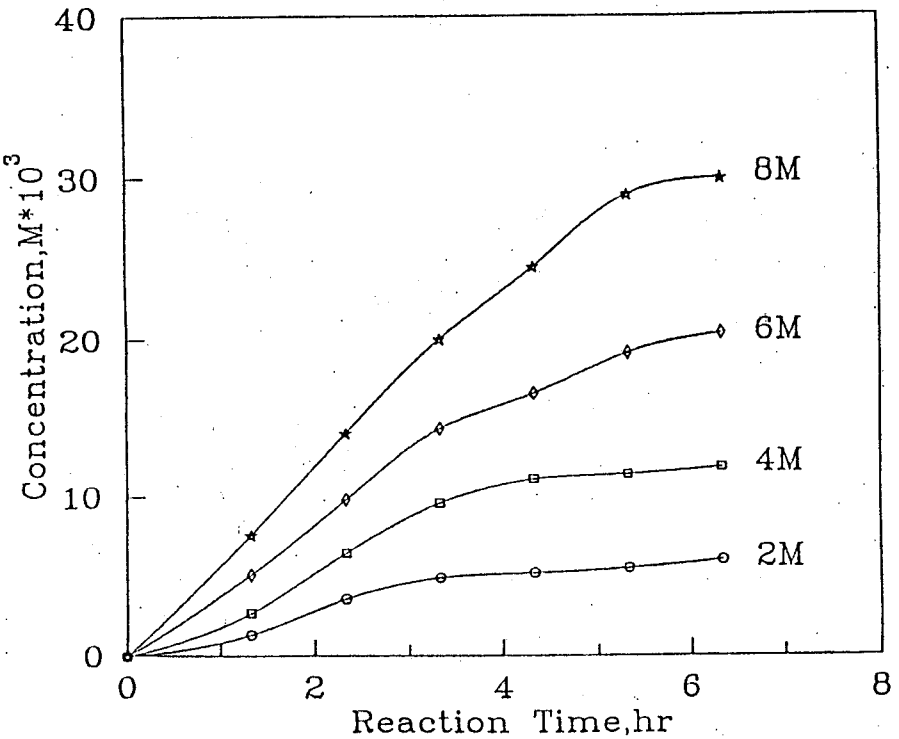


Fig.9 Effect of concentration of acetone on reaction rate at anode.
Cathode: Pt Anode: Pt Current density: 25mA/cm^2
electrolyte: 2M NaCl Electricity: 120 coul
Temperature: 298K

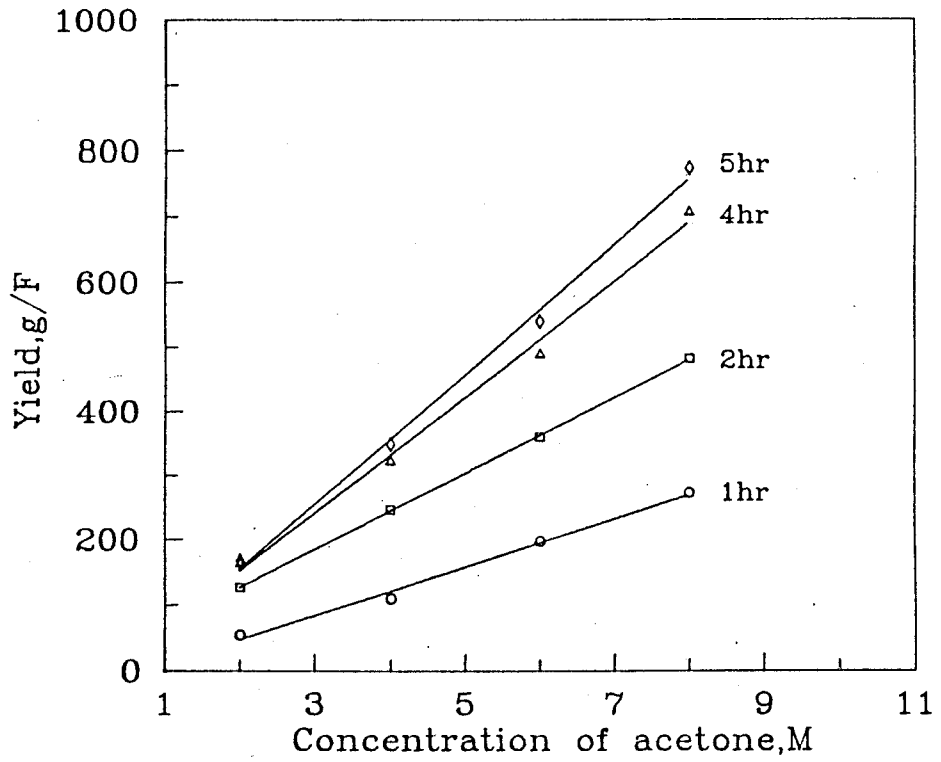


Fig.10 Effect of concentration of acetone on yield

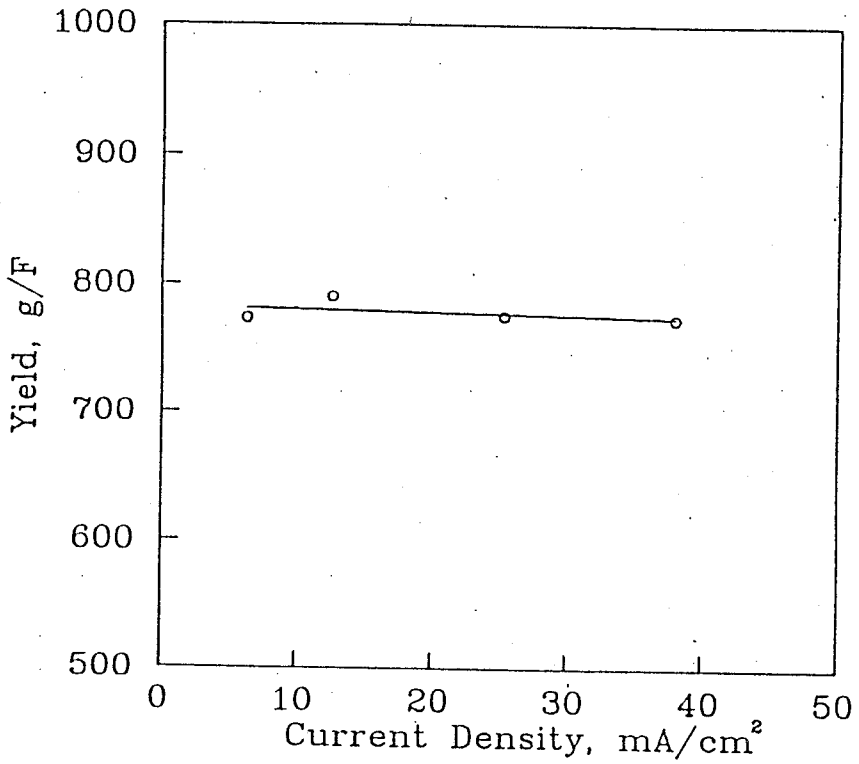


Fig.11 Effect of current density on the yield of pairk electrolysis.
Cathode: Pt Anode: Pt Electrolyte: 2M NaCl
Electricity: 120 coul Acetone: 8M
Temperature: 25℃

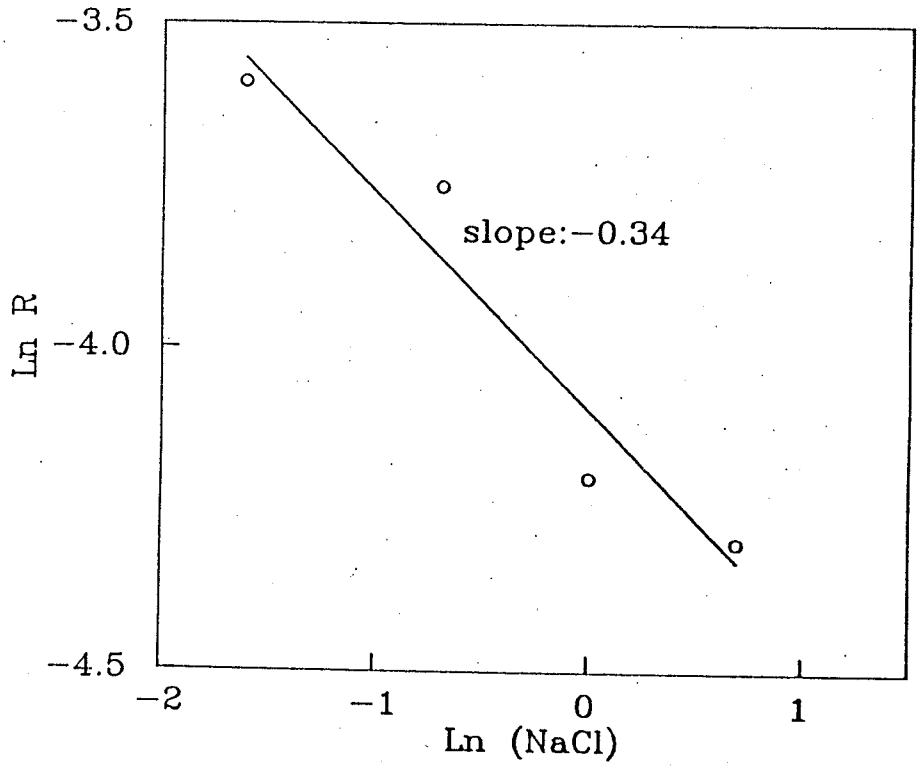


Fig.12 Ln R v.s Ln [NaCl]
Cathode: Pt Anode: Pt Acetone: 8M
Electricity: 120 coul Current density: mA/cm²
Temperature: 25℃

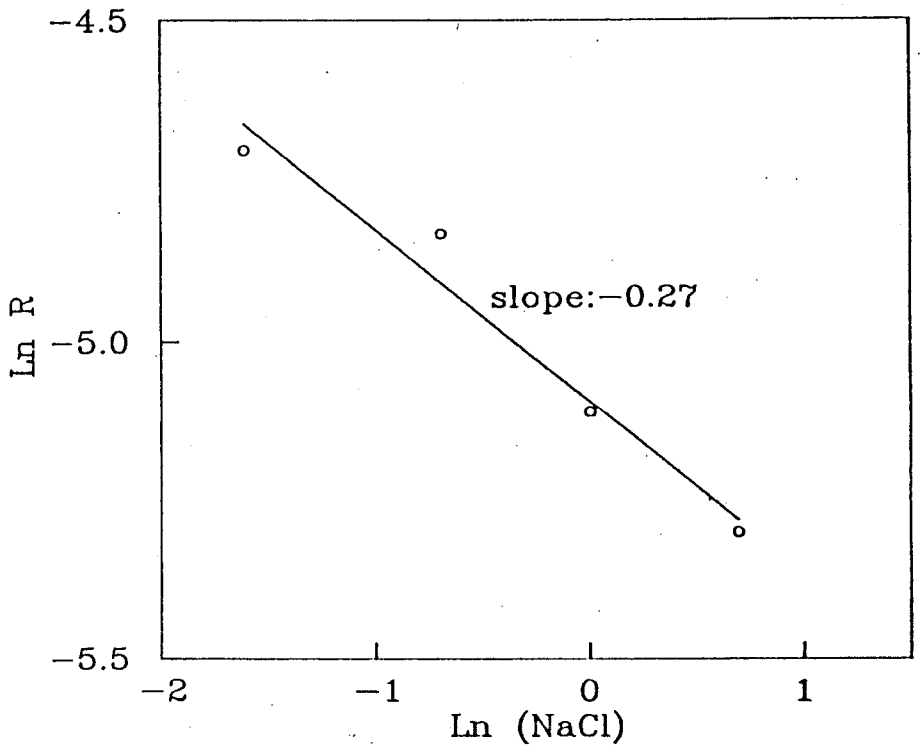


Fig.13 Ln R v.s Ln [NaCl]
Cathode: Pt Anode: Pt Acetone: 8M
Electricity: 120 coul Current density: mA/cm^2
Temperature: 25℃

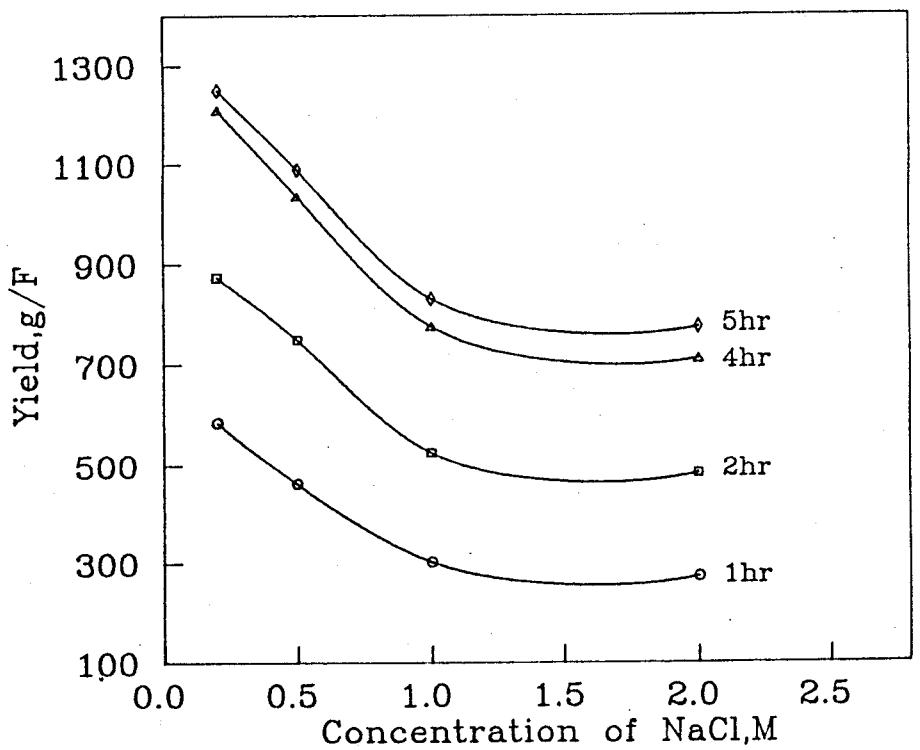


Fig.14 Effect of concentration of sodium chloride on the yield of daa.
Cathode: Pt Anode: Pt Acetone: 8M
Electricity: 120 coul Current density: mA/cm^2
Temperature: 25℃
Electrolyte: 0.2M NaCl

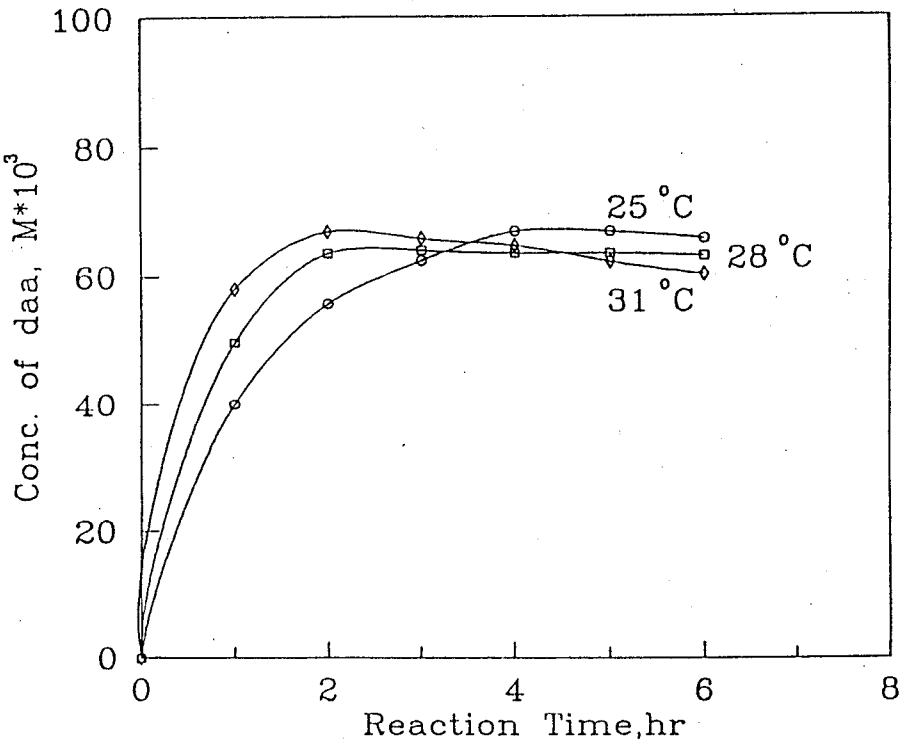


Fig.15 Effect of temperature on the formation rate of daa at cathode.
Cathode: Pt Anode: Pt Current density: 25mA/cm^2
Electrolyte: 2M NaCl Acetone: 2M

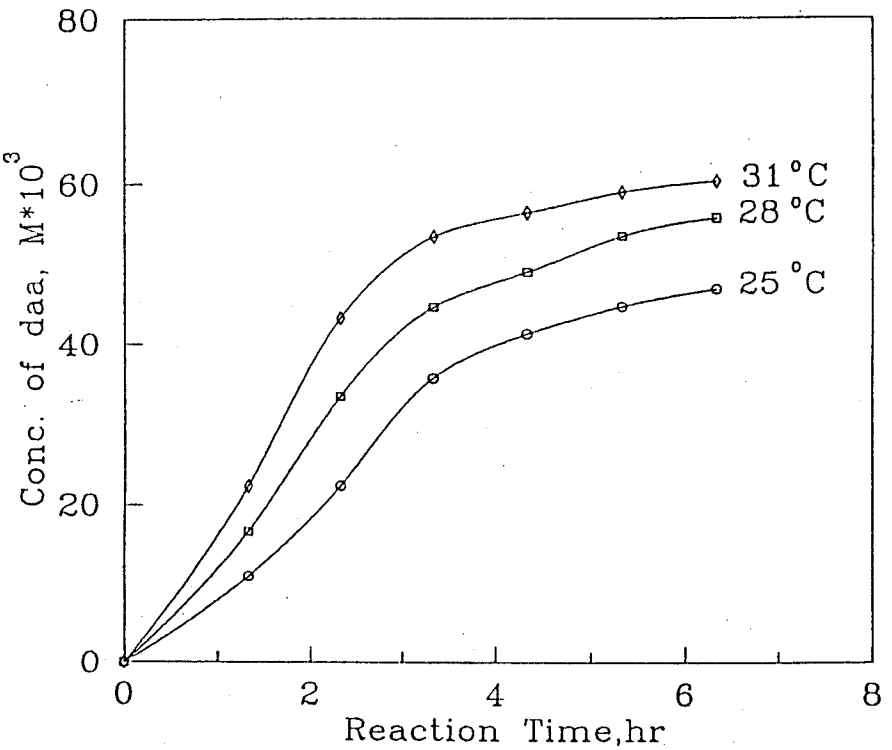


Fig.16 Effect of temperature on the formation rate of daa at anode.
Cathode: Pt Anode: Pt Current density: wt mA/cm^2
Electrolyte: 2M NaCl Acetone: 2M

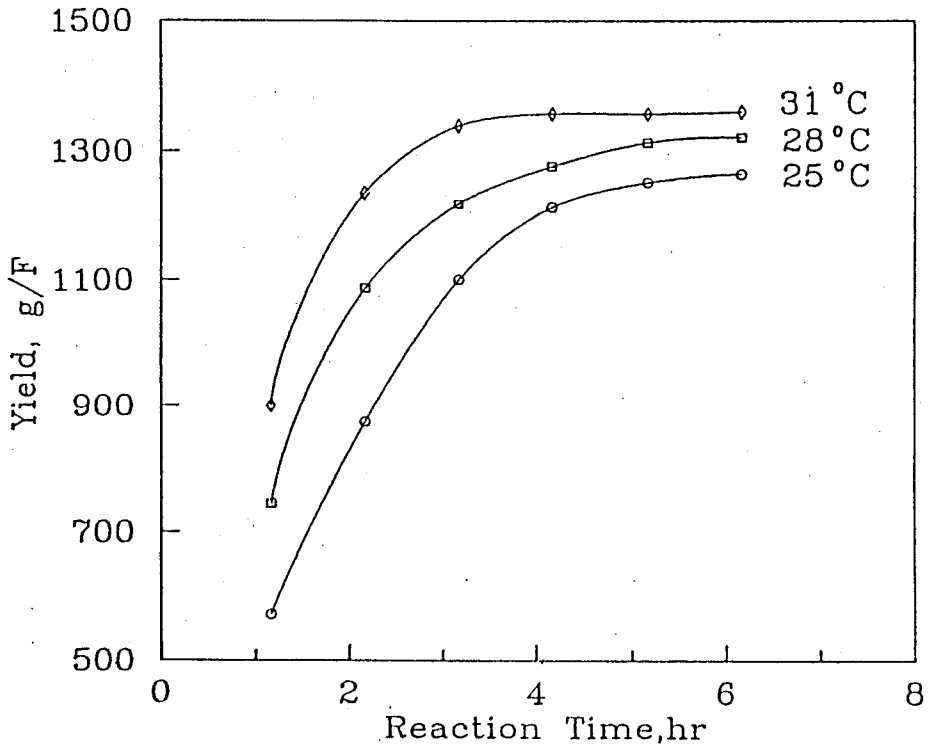


Fig.17 Effect of temperature on the yield of daa.
Cathode: Pt Anode: Pt Acetone: 2M
Electricity: 120 coul Current density: mA/cm^2
Electrolyte: 0.2M NaCl