

ISSN 2334-9883



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PROCEEDINGS
CONFERENCE OF AGRONOMY
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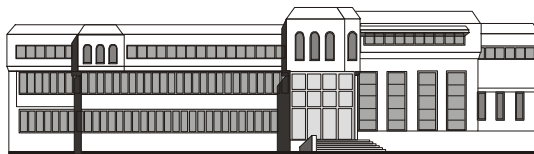


Vol. 9, Issue 9, 2015
Čačak, 26-28 August 2015

CONFERENCE OF AGRONOMY STUDENTS

ORGANISER AND PUBLISHER

Faculty of Agronomy – Čačak
Cara Dušana 34, 32000 Čačak
e-mail: afdekanat@kg.ac.rs
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Cover page: Dr. Snežana Tanasković

Supported by: Ministry of Education, Science and Technological Development,
Republic of Serbia and City of Čačak

Printed and bound by: “Studio za dizajn“, Vukašina Ignjatovića br. 12, Čačak

Number of copies: 80

IX CONFERENCE OF AGRONOMY STUDENTS
26 - 28 August 2015 - Faculty of Agronomy – Čačak, Serbia

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Effect of process parameters on the electrolysis of benzaldehyde

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Abstract: Simultaneous electrochemical production of benzyl alcohol and benzoic acid from benzaldehyde precursor was investigated. Reduction reactions were investigated on amalgamated and non-amalgamated zinc electrode. Overpotential for evolution of hydrogen on amalgamated zinc electrode was higher than that of non-amalgamated zinc electrode which resulted in a small current efficiency for hydrogen evolution on amalgamated zinc electrode. The presence of benzaldehyde in electrolyte solution inhibited hydrogen evolution. The hydrogen evolution decreased with an increase of benzaldehyde concentration. The cathodic yield for production of benzylalcohol was high over a very broad current density interval. On the other side, hypobromous acid which was produced by hydrolysis of bromine was used for oxidation of benzaldehyde into benzoic acid. According to these experimental results, it can be concluded that amalgamated zinc electrode can be used for industrial electrolysis of benzaldehyde.

Key words: electrolysis, electroreduction, amalgamated zinc, benzaldehyde, benzyl alcohol, benzoic acid

Introduction

Food additives are extremely important for food production and processing because they are used to prevent food spoilage. Benzaldehyde, benzyl alcohol and benzoic acid are one of the most common additives. These additives can be synthesized in various ways. Benzaldehyde is generally produced by chlorination or oxygenation of toluene (Brühne and Wright, 2002). Benzaldehyde (C_6H_5CHO) is colorless nontoxic aromatic liquid found in

essential oils (peach kernels, almond) and it is used in food technology as flavoring agent, in pharmaceutical industry and it is generally recognized as a safe. It is also present in food, e.g. alcoholic drinks, milk products, meat, tea, relishes, etc. (CoE, 1992). High concentration of this organic compound can damage chromosomes of mammals, although carcinogenic effects haven't been proofed yet (Feron et al., 1991).

Benzyl alcohol is synthesized by hydrolysis of benzyl chloride with sodium hydroxide (Brühne and Wright, 2007). In food technology benzyl alcohol is used as flavoring agent, chemical preservative and solvent (Burdock, 1995). Electrochemical synthesis of benzyl alcohol is the most effective synthesis method. It is agreed that the products of the cathodic reduction of aldehydes and ketons is a mixture of the alcohol and the pinacol. Therefore, the products of the cathodic reduction of benzaldehyde are pinacol and benzyl alcohol. Pinacol (hydrobenzoin) was synthesized by dimerisation of two radical intermediate formed by addition of $1\text{H}^+ + 1\text{e}^-$ on the carbonyl group of benzaldehyde (Guená and Pletcher, 1998). On the other side, benzyl alcohol is the result of addition of $2\text{H}^+ + 2\text{e}^-$ on the carbonyl group of benzaldehyde.

Guená and Pletcher (1998) have studied the reduction of benzaldehyde in acidic water-methanol mixture. Rotating Pb disc electrode was used in these experiments, which confirmed that the shape of the voltammograms was independent of the concentration of benzaldehyde, solvent composition, choice of inert electrolyte and temperature. The magnitude of the currents was proportional to benzaldehyde concentration and decreased slightly with increasing methanol content and temperature increase.

The results demonstrated that the potential of cathodic reduction of benzaldehyde influenced on the ratio of hydrobenzoin to benzyl alcohol. Parameters such as reactant concentration, temperature and mass transport have little influence on the product distribution. However, an increase of cathode potential resulted in increased benzyl alcohol concentration and decreased pinacol concentration.

Material and methods

Electroreduction was run at an amalgamated and non-amalgamated zinc cathode, which was located on the bottom of the cell with a surface area of 4.5 cm^2 . Dimensionally stable electrode based on $\text{RuO}_2/\text{TiO}_2$ was used as an anode. The cathode was made of copper substrate which was previously cleaned by immersing in saturated solution of NaOH in absolute ethanol for 10 minutes; then it was immersed in boiling solution containing 20 mas.% HCl for 10 s and finally washed with plenty distilled water. Electrodeposition of zinc on copper substrate was performed from sulphate bath containing $31.122\text{ g/dm}^3\text{ ZnSO}_4$, 4

g/dm^3 PbSO_4 and 1.5 g/dm^3 $(\text{NH}_4)_2\text{SO}_4$ at temperature of 25°C and $\text{pH}=10$; electrodeposition current density was 60 mA/cm^2 . Amalgamated electrode was obtained by simple dipping of previously obtained zinc electrode into 0.1 mol dm^{-3} HgCl_2 for a short time (60 s) at 25°C .

Aqueous electrolyte solution contained 0.8 mol dm^{-3} KBr and 50 vol.% ethanol. Cathodic current efficiencies for hydrogen evolution were investigated as a function of current density in the absence and presence of benzaldehyde (benzaldehyde concentration range was $0.4 - 1.2 \text{ mol dm}^{-3}$) at 25°C .

Current efficiencies for hydrogen evolution were measured by monitoring the volume of produced hydrogen. Graduated burette was put above cathode. Time necessary to release specified volume of hydrogen was measured.

Standard potentiostat (Model 173 Potentiostat/Galvanostat, EG&G Princeton Applied Research, Princeton, USA) and digital voltmeter (MS 8209 Digital Multimeter, Mastech) were used for detecting polarization curves. Saturated calomel electrode was used as a referent electrode.

Results and discussion

Cathodic polarization curve for the electrodeposition of Zn^{2+} ions on copper substrate is shown in Fig. 1. Since deposition current was 60 mA/cm^2 , it can be seen from Figure 1 that deposition potential of Zn^{2+} ions was about -1.38 V versus saturated calomel electrode at 25°C and $\text{pH}=10$.

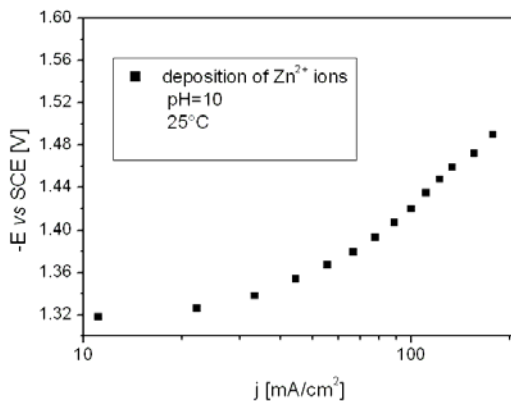
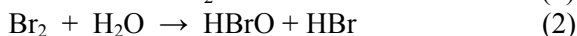


Figure 1. Cathodic polarization curve for zinc electrodeposition on copper substrate from the sulphate bath (31.12 g/dm^3 ZnSO_4 , 1.5 g/dm^3 $(\text{NH}_4)_2\text{SO}_4$, 25°C and $\text{pH}=10$)

On the titanium anodes activated by solid solutions of rutile structure ($\text{RuO}_2/\text{TiO}_2$), the bromide ions were oxidized in elementary bromine (reaction

1) which hydrolyzes into hypobromous acid and hydrobromic acid: (reaction 2) (Spasojević et al., 2003):



On the other side, the hydrogen ions and hypobromous acid are reduced on zinc cathode in the following reactions:



The polarization curves for electroreductions on zinc and amalgamated zinc electrodes are shown in Fig. 2. There is a similarity in the shape of the polarization curves on both electrode materials. However, the overpotential of the hydrogen evolution on amalgamated zinc electrode is higher than that for zinc electrode. This is possible because the adsorption of hydrogen ions on amalgamated zinc electrode surface is much weaker than at the non-amalgamated zinc electrode surface.

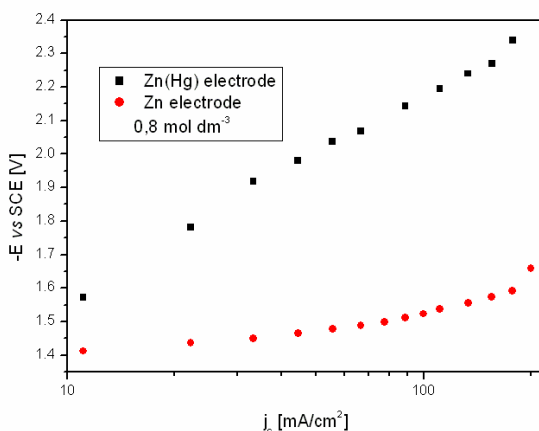


Figure 2. Cathodic polarization curves for hydrogen evolution on zinc (●) and amalgamated zinc (■) electrodes obtained from electrolyte solution ($0,8 \text{ mol/dm}^3$ KBr , 50 vol % $\text{C}_2\text{H}_5\text{OH}$; $t= 25^\circ\text{C}$ and $\text{pH}=2$).

High overpotential for electroreduction of hydrogen ions on amalgamated zinc electrode resulted in smaller cathodic current efficiency of hydrogen evolution on the amalgamated zinc electrode than that of the non-amalgamated

zinc electrode (Figure 3). On the other side, the presence of benzaldehyde in electrolyte solutions inhibited the evolution of hydrogen on amalgamated zinc electrode which resulted in even lower hydrogen yields.

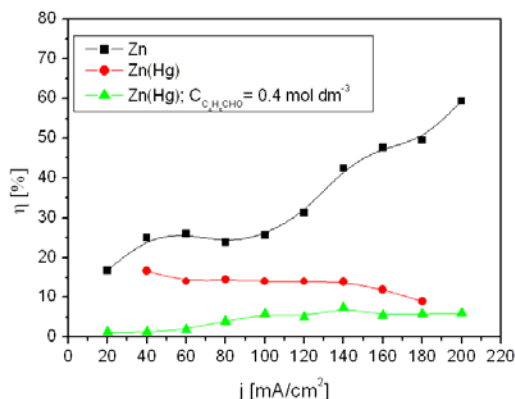


Figure 3. Cathodic current efficiency of hydrogen plotted as a function of current density obtained from electrolyte solution ($0,8 \text{ mol/dm}^3 \text{ KBr}$, $50 \text{ vol } \% \text{ C}_2\text{H}_5\text{OH}$; $t = 25^\circ\text{C}$) in the absence of benzaldehyde: non-amalgamated zinc electrode (■) and amalgamated zinc electrode (●); cathodic current efficiency of hydrogen evolution obtained on the amalgamated zinc electrode immersed in basic electrolyte solution in the presence of benzaldehyde (concentration of benzaldehyde = 0.4 mol dm^{-3}) (▲).

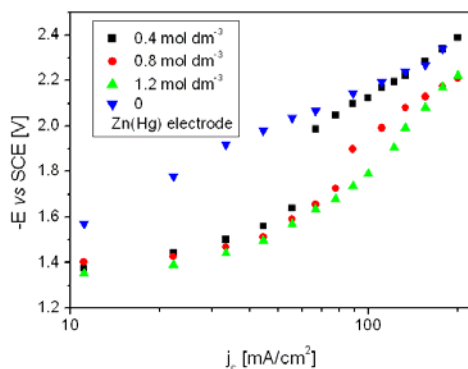
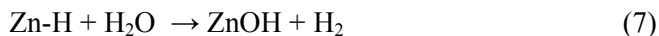
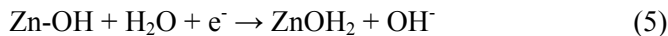


Figure 4. Cathodic polarization curves of the amalgamated zinc electrode obtained from electrolyte solution ($0,8 \text{ mol/dm}^3 \text{ KBr}$, $50 \text{ vol } \% \text{ C}_2\text{H}_5\text{OH}$, $t = 25^\circ\text{C}$) in the absence (▼) and presence of benzaldehyde (■ - 0.4 mol/dm^3 benzaldehyde; ● - 0.8 mol/dm^3 benzaldehyde; ▲ - 1.2 mol/dm^3 benzaldehyde)

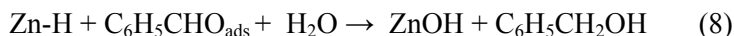
Cathodic polarization curves of the amalgamated zinc electrode obtained from electrolyte solution in the absence and the presence of benzaldehyde are shown in Figure 4. It can be seen that overpotential decreases with an increase of benzaldehyde concentration. Within the potential range between -1.4 V and -2.2 V, the reduction currents in the presence of benzaldehyde are considerably higher than those in the absence of benzaldehyde. There is a Tafel dependence with the slope of 120 mV/dec in the presence of benzaldehyde within the potential range between -1.3 V and -1.45 V. However, in potential range between -1.45 and -2.1 V there is cathodic limiting current which increases with an increase of benzaldehyde concentration.

The analysis of polarization curves of hydrogen evolution and faraday impedance measurements suggest that Zn-atoms were covered with oxy-species and pure metallic Zn-atoms exist on the amalgamated zinc cathode within the potential range of -0.6 to -2.4 (Trišović et al. 2001). At lower overpotentials, hydrogen is evolved on the surface Zn-atoms covered with oxy-species. The proposed hydrogen evolution mechanism is as follows:



The reaction mechanism consists of three consecutive elementary steps, i.e., two electrochemical steps (reactions 5 and 6) and one chemical step (reaction 7) (Trišović et al. 2001). In the third step (chemical step), intermediary species, Zn-H, reacts with an H₂O molecule to evolve H₂ and forms the metal hydroxide again. The limiting currents shown in Fig. 4 are dependent on the heterogeneous chemical reaction (7).

In the presence of benzaldehyde, adsorbed hydrogen atom obtained after two electrochemical steps (reactions 1 and 2) reacts with an adsorbed benzaldehyde molecule to form benzyl alcohol (reactions 8).



However, in anode part, obtained hypobromite oxidizes the carbonyl group of benzaldehyde into carboxyl group which resulted in formation of benzoic acid:

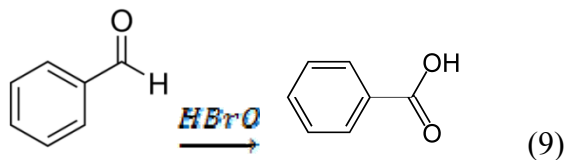


Figure 5 shows that there are low current efficiencies of hydrogen evolution on amalgamated zinc electrode at different benzaldehyde concentration over a very broad current density interval. It can be assumed that the dominant cathodic reaction is the electroreduction of benzaldehyde into benzyl alcohol since most of hypobromous acid was probably used to convert benzaldehyde into benzoic acid.

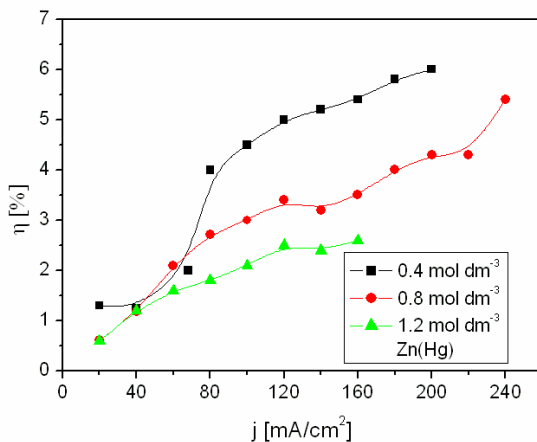


Figure 5. Cathodic current efficiency for hydrogen evolution on the amalgamated zinc electrode plotted as a function of current densities and benzaldehyde concentrations

Conclusions

Mechanically stable and adherent zinc coating was prepared by electrodeposition of zinc ions from sulphate bath onto the surface of copper substrate. Zinc coating was immersed in a HgCl_2 solution which resulted in formation of amalgamated zinc coating. Overpotential of hydrogen evolution on amalgamated zinc electrode was higher than that on non-amalgamated electrode. It was found that the current efficiency for hydrogen evolution on amalgamated zinc electrode was very low during the electrolysis of electrolyte solution which

contains benzaldehyde. The cathode limiting currents which are strongly dependent on the heterogeneous chemical reaction between adsorbed hydrogen atom and benzaldehyde molecule increased with increasing of benzaldehyde concentration. On the other side, cathodic overpotential and the current efficiency for hydrogen evolution on amalgamated zinc electrode decreased with increasing of benzaldehyde concentration. Benzaldehyde was also oxydised by hypobromus acid into benzoic acid. According to these experimental results, it can be concluded that amalgamated zinc electrode can be used for industrial electrolysis of benzaldehyde.

Acknowledgements

This work has been supported by the Ministry of Education and Science of the Republic of Serbia through Project No. 17205.

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CIP - Каталогизacija y publikaciji
Народна библиотека Србије, Београд

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PROCEEDINGS conference of agronomy students with international participation / for the publisher VladetaStevović. - Vol. 8, issue 8 (2013)-
. - Čačak : Faculty of Agronomy, 2013- (Čačak : Studio za dizajn). - 24 cm

Naslovpouzetsakoričnoglista. - Je nastavak: Smotra naučnih radova
Studenata agronomije = ISSN 1450-7323
ISSN 2334-9883 = Proceedings conference of agronomy students
COBISS.SR-ID 204397836