JOURNAL OF APPLIED ELECTROCHEMISTRY 24 (1994) 930–935

Production of D-arabinose in a pilot plant fluidized bed electrochemical reactor

V. JIŘIČNÝ, V. STANĚK

Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague 6, Suchdol 2, Czech Republic

Received 19 July 1993; revised 2 February 1994

This paper presents results of experimental work on the development of a pilot plant fluidized bed reactor for production of D-arabinose using liquor from the fermentation oxidation of D-glucose to D-gluconic acid as starting material. Two electrochemical reactors with a fluidized bed anode of production capacity 0.065 kg h^{-1} and 0.325 kg h^{-1}, respectively, have been developed. These figures represent five and twenty-five times the production capacity of the original laboratory FBE cell. The performance of these reactors compares satisfactorily with the laboratory scale cell, reported in an earlier paper [1]. The average conversion of 68–72% is slightly lower in comparison with the 75% of the laboratory cell. The specific electric energy consumption of 9–14 kWh kg^{-1} of D-arabinose is slightly higher than the 7.5–11 kWh kg^{-1}, typical of the laboratory cell.

1. Introduction

An earlier experimental study [1] has shown that preparation of D-arabinose by direct electrochemical oxidation of aqueous solution of salts of D-gluconic acid in a laboratory fluidized bed electrode (FBE) cell is potentially attractive for large scale production. The competitiveness compared to existing, largely chemical, methods of production rests in the good conversion, high selectivity and yield and low specific energy consumption. The principal advantage, however, is that direct electrochemical oxidation simplifies subsequent separation of D-arabinose from the reaction mixture with essentially no undesirable byproducts which are difficult to dispose of. This feature makes the new method particularly promising from the standpoint of minimizing the separation and purification costs and the burden on the environment.

Aldonic acids, their lactones or salts are the initial products of a number of chemical, biochemical and electrochemical oxidations of aldoses [1, 2]. D-gluconic acid is a metabolic intermediate present in animals, plants and micro-organisms. Many electrochemical studies have been conducted to establish the mechanism and conditions of its oxidation [3–6]. Prevailing methods of its industrial production are electrochemical [7] or chemical and biochemical procedures [2, 8], both being very effective from the economic point of view.

Oxidative methods have also been used for degradation of the salts or derivatives of D-gluconic acid to D-arabinose or to lower sugars. By far the most widely used method for large scale industrial production of D-arabinose is chemical oxidation of sodium D-gluconate by sodium hypochlorite. As a consequence, a large amount of sodium chloride has to be removed from the reaction mixture in subsequent separation steps by multiple crystallization and/or electrodialysis [8].

1.1. *Electrochemical oxidation to D-arabinose*

Previous results [1] of direct degradative oxidation of sodium D-gluconate to D-arabinose in an electrochemical cell with a fluidized bed anode, according to the following reaction scheme, proved to be very promising.

$$NaOOC - (HCOH)_4 - CH_2OH + H_2O - 2e^- \longrightarrow HOC - (HCOH)_3 - CH_2OH + NaHCO_3 + 2H^+$$

The process does not require that any oxidation agent be added to the reaction mixture. Oxidation takes place on the surface of fluidized particles by direct electron exchange between the particles and the substrate. There is no need for regeneration of the oxidizing agent. The aim is to minimize the extent of undesirable anodic reaction according to the following scheme

$$2OH^- - 2e^- \longrightarrow H_2O + \tfrac{1}{2}O_2$$

and also the extent of eventual consecutive degradation of D-arabinose to lower carbohydrates. The cathodic reaction is hydrogen evolution.

$$2H^+ + 2e^- \longrightarrow 2H \longrightarrow H_2$$

Laboratory tests [1] have shown conversion and selectivity comparable to the other methods used for D-arabinose production. Due to the absence

0021-891X

Table 1. Survey of methods of D-arabinose production

Method	*Reference*
Isolation from natural materials	[13–16]
Chemical oxidation by hypochlorite	[8]
Chemical oxidation by hydrogen peroxide	[17]
Direct/indirect electrochemical oxidation	[18, 19]
Electrochemical reduction	[20]

of spent oxidizing agent and the low amount of side products (< 4%), subsequent separation and purification processes to isolate high purity (> 99%) crystalline D-arabinose were easy and simple. The whole production process is thereby ecologically soft. A review of various methods leading to D-arabinose is given in Table 1.

1.2. *Fluidized bed electrodes, FBE*

Three dimensional packed, fluidized or porous electrodes are essentially beds of conducting particles functioning as an electrode; the current being fed via a feeder electrode. The bed of particles is situated in a flow channel so that the electrolyte passes between the particles. Packed and fluidized bed electrodes are particularly well suited as they provide large specific surface and thus alleviate the limitations posed by the requirement of low current density in organic synthesis. Typical values of the specific surface reach as much as $150\,cm^{-1}$.

For the design and use of these electrodes the following must be taken into account [10]:

(i) if the potential difference between the desired reaction, on the one hand, and a parallel or consecutive reaction, on the other hand, is not large, a greater current efficiency and reaction selectivity can be achieved with the FBE than with the packed bed electrodes thanks to the more uniform distribution of the potential in the FBE;
(ii) a higher voltage is required to attain the same current density with the FBE than with the packed bed electrode; and
(iii) the design of the FBE must ensure that no inactive zone appears inside the bed, as this adversely affects the space-time yield.

The first and the last item on this list are of special importance in this work as the parallel reaction involved is liberation of a gaseous component and the consecutive reactions are oxidative degradations of the main product.

Practical applications of the FBE cell systems to date have been primarily in the extraction of metals from low grade ores, leaching liquors, conventional waste electrolytes and recovery of metals from effluents [22, 23]. Applications in organic electrochemistry are scarce [24, 25].

1.3. *Scale up problems in electrochemical processes*

One of the most important features of an industrial cell is the need for a large electrode area. Since capital costs are often proportional to the electrode area of the reactor, the increase of the electrode surface area becomes expensive unless it is achieved through an increase in the specific surface of the electrode. This problem becomes particularly severe in the case of organic electrode reactions where current densities may be small [9].

In this respect application of the fluidized bed or packed bed electrode cell is very effective. The high specific production capacity of the cell contributes significantly to the compactness of the design and hence lower investment costs. A previous study [1] showed that the use of a packed bed electrode for D-arabinose production is hampered due to the evolution of oxygen as a parallel reaction and with it the associated problem of gas being held in the bed over an extended period of time. For this reason work with fluidized bed electrode reactors was undertaken.

Prediction of the performance of an industrial size cell based solely on data from a laboratory cell is difficult [11] and an investigation of the behaviour of an intermediate size cell is indispensable. Because the earlier experiments [1] were carried out in a laboratory size cell only, the aim was to develop a FBE reactor capable of sustaining a commercial level of production. The target annual production capacity was set at one metric ton of high purity crystalline D-arabinose. The scale up work has been split in two steps. Each of these steps represented scale up by a factor of five with the result amounting to a twenty-five times bigger FBE reactor in comparison to the laboratory FBE cell [1].

This paper presents results of the scale up of the electrochemical fluidized bed anode reactor, processing directly as the starting material the liquor from the fermentation oxidation of D-glucose, as an alternative method for D-arabinose production. A major objective is the maintenance at high selectivity of the reaction and high conversion while, at the same time, minimizing the specific electric energy consumption.

2. Experimental apparatus

2.1. *Design and construction of the FBE reactors*

A battery type arrangement was chosen. The reactor was constructed as a multiple cell unit in which cathodes, current feeders and diaphragms were assembled alternately as in a filter press.

The principal attraction of the battery type arrangement is that it is only the width of the anode compartment with the fluidized bed that is being enlarged (in our case from 0.07 m of the laboratory cell to 0.175 m) while the distance between the current feeder and the cathode (0.02 m) and the height of the fluidized bed (0.2 m at 25% bed expansion)

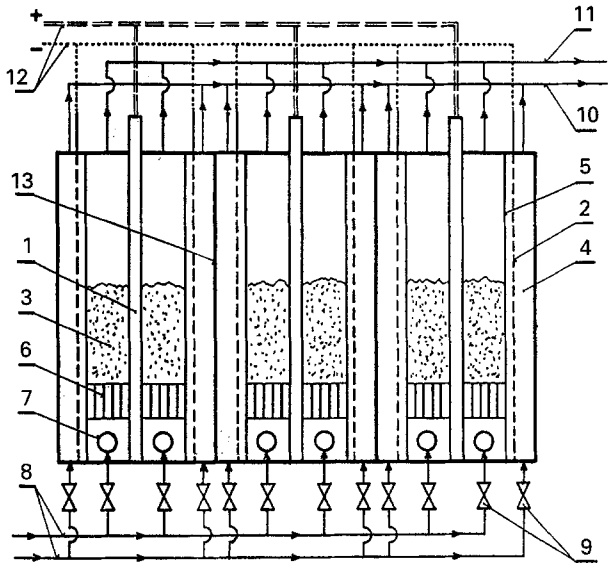

Fig. 1. Sketch of the battery type FBE reactor (showing three cells). Key: (1) graphite current feeder; (2) stainless steel expanded metal sheet (cathode); (3) anode compartment with the fluidized layer; (4) cathode compartment; (5) PVC diaphragm, (6) slots of the liquid feed distributor; (7) tubes of the liquid predistributor; (8) electrolyte feed; (9) control valves; (10) catholyte outlet; (11) anolyte outlet; (12) power lines; (13) nonconducting separating barrier.

remain unchanged. The battery type arrangement is particularly helpful in overcoming the difficulties associated with scale up over more than an order of magnitude.

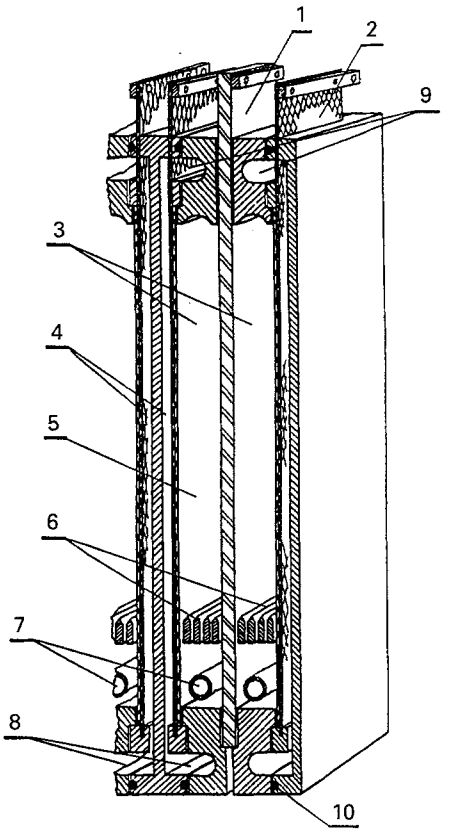

Fig. 2. 3D scheme of the battery type FBE reactor (showing one cell). Key: (1) graphite current feeder; (2) stainless steel expanded metal sheet (cathode); (3) anode compartments; (4) cathode compartments; (5) PVC diaphragm; (6) slots of the liquid feed distributor; (7) tubes of the liquid predistributor; (8) electrolyte inlets; (9) electrolyte outlets; (10) sealing.

The arrangement and construction of the first FBE reactor is seen in Figs 1 and 2. This reactor is referred to as the battery type pilot reactor (BTPR). A single cell of this reactor (the scale up factor of 5, Fig. 2) consists of two anode (3) and two cathode compartments (4). It has an external mounting frame fixing the compartments together, while the compartments are fed individually (7,8) by electrolyte. This arrangement enabled operation of the BTPR both in the divided and undivided mode.

Further scale up with this construction arrangement, was simple; the production capacity was further enhanced by increasing the number of cells (five cells for the scale up factor of 25).

Because it was permissible to operate the FBE reactor in the undivided cell mode, the next reactor was designed as a single common tank housing alternating anode and cathode compartments. The reactor was sized for one metric ton annual production capacity. The new design eliminated the problem of leakage and simplified the maintenance and service of the reactor. This second reactor is referred to as the tank type pilot reactor (TTPR).

The TTPR reactor had a common electrolyte feed to all the cathodic and anodic compartments. Interconnection of all anode chambers provided for the same bed expansion in all compartments and prevented entrainment and flushing of the particles from the reactor. The design of the TTPR made replacement of individual current feeders and cathodes easy, the construction simpler and manufacture cheaper than with the BTPR. These improvements, however, were accomplished at the expense of loss of modularity of the reactor; the TTPR can only be operated as an undivided cell.

The BTPR and TTPR reactors employed a bed of fluidized 400–600 μm diameter graphite particles functioning as anode. Twenty-five percent bed expansion was used in all runs. Graphite plates were used as current feeders. The anode and the cathode compartments were separated by a porous PVC diaphragm to prevent direct contact of fluidized particles with the cathode. The diaphragm allowed limited bulk flow between anode and cathode compartments. The cathode was a stainless steel expanded-metal sheet. The bodies of the BTPR and TTPR were manufactured from Perspex.

All materials used in the construction of the reactors, i.e. graphite, stainless steel, PVC and Perspex, are nontoxic, thus avoiding product contamination.

The electrodes of the BTPR and TTPR reactors were connected in a monopolar arrangement to a d.c. power supply and a recorder monitoring the voltage and the current applied to the cell. The galvanostatic mode was employed. The flow of the electrolyte was perpendicular to the flow of electric current.

Both the BTPR and TTPR were designed as airtight reactors.

The external size of the TTPR reactor for production of one metric ton of D-arabinose was 0.24 m × 0.6 m × 0.6 m.

2.2. *Experimental procedure*

The experimental procedure to test the designed units was the same as that employed earlier in the study of the laboratory cell [1].

The reaction mixture was circulated by a centrifugal pump from a temperature controlled storage tank through the reactors and back to the storage tank. Fermentation liquor containing sodium D-gluconate from the fermentation oxidation of glucose was used as starting material. The typical mean concentration of sodium D-gluconate in the liquor was 160 g dm^{-3}. (The efficiency of the fermentation oxidation is high and exceeds 99%.) This solution was used after filtration through kieselguhr to remove residual biomaterials.

The current, voltage and temperature were continuously monitored throughout each run. The average time for a single run was approximately 11 h. Both reactors, the BTPR and TTPR, were operated as undivided cells and in the galvanostatic mode only.

The level of the electrolyte in the reactors was continuously monitored and controlled as a precaution against accidental draining, emptying and overheating of the Perspex glass body of the reactors. The reaction mixture at the outlet of the reactors was maintained at 35 ± 1 °C. For this purpose the storage tanks of both reactors were equipped with coolers to remove heat evolved in the reactor. Temperatures in excess of 40 °C caused thermal degradation of the product and considerable decrease of selectivity. The flow rate of the reaction mixture, set at 80 dm^3 min^{-1}, determined the 25% bed expansion.

Temperature exceeding a pre-set limit or a decrease of the liquid in the reactor below a certain level actuated a switch disconnecting the reactor from the d.c. source and, in the latter case, also a switch shutting off the circulation pump. Both states were also signalled visually and acoustically. After setting the bed expansion and d.c.-current the process remained stable for the whole run.

The off gases produced by the cathodic (hydrogen) and side parasite anodic (oxygen) reactions were carefully vented via an auxiliary pipe to atmosphere by a pressurized air ejector.

Current efficiency for D-arabinose production was calculated as a ratio of the current spent to produce D-arabinose (determined analytically) to the total current for the given period of time.

Three analytical methods were used for analysis of the reaction mixture: Schoorl's titration method was used in the final 2 h of each experimental run for fast quantitative determination of the overall amount of reducing sugars produced by electrolysis. Paper chromatographic analysis was utilized for a qualitative detection of the stepwise degradation of the parent compound to a mixture of lower aldoses. Finally HPLC was used for a precise quantitative analysis of the reaction mixture. The conditions of all analytical methods used are detailed elsewhere [21].

3. Results and discussion

The liquor from the fermentation oxidation of glucose proved to be a good starting material. The electrical conductivity of the solution of sodium D-gluconate from the fermentation oxidation was sufficient to sustain electrochemical oxidation. The initial voltage did not exceed 21 V and decreased to 11–14 V in the course of the reaction due to the generation of sodium hydroxide, or carbonate in the mixture.

The fact that the feed solution, initially containing practically only sodium D-gluconate at a concentration of about 160 g dm^{-3}, did not require addition of electrolytes to adjust the conductivity was beneficial. This feature, together with the sufficiently high conversion (> 70%) and selectivity (> 96%), was a prerequisite for minimization of the requirements on subsequent separation and raffination of crystalline D-arabinose from the reaction mixture.

The experiments showed that good uniformity of fluidization of the bed of BTPR and TTPR depended on good venting of the anode chambers of the oxygen generated by the anode side reaction. Sufficiently high volume flow rate of the reaction mixture through the anode chambers prevented oxygen bubbles from coalescence into larger bubbles inside the fluidized layer or formation of bubble clusters causing undesirable nonhomogeneities of the bed and, in turn, disturbances of the potential.

Venting of hydrogen, generated in much larger quantities on the surface of the expanded metal sheet cathode, was facilitated by the design of the cathode chamber itself. The narrow width of this chamber provided for high liquid velocities in the cathode space and easy entrainment of gas bubbles.

The uniformity of distribution of liquid among individual anode chambers was found to be an important factor. Flow non-uniformities distinctly affected the ohmic resistance of individual chambers and, hence, the current distribution, as the anodes were connected to the d.c. power source in parallel. The uniformity of the current distribution among individual chambers directly affected the reaction conversion and selectivity. Under optimum (from the standpoint of conversion) current density the absolute current amounted to 45–50 A in the case of the BTPR reactor, or 225–250 A for the TTPR reactor. The optimum current density amounted in both cases to 119 mA cm^{-2}.

Conditions for the separation and raffination of the product for industrial purposes have been developed in the Research Institute for Pharmacy

Table 2. A comparison of the laboratory FBE cell with a single cell of the BTPR

Parameter	*Laboratory FBE cell*	*BTPR (single cell)*
Effective surface of membrane/m^2	0.0084	0.042
Volume of particles of FBE/m^3	1.8×10^{-4}	9.25×10^{-4}
Current density/A m^{-2}	1190	1190
Absolute current/A	10	50
Cell voltage/V	13–18	13–18
Rate of production of D-arabinose/kg h^{-1}	app. 0.013	app. 0.065
Maximum annual production/kg y^{-1}	39.9	199.5
External cell dimensions height × width × length/m	0.4 × 0.05 × 0.07	0.4 × 0.19 × 0.09
Flow rate of electrolyte/dm^3 min^{-1}	app. 3–3.5	app. 15–17.5

and Biochemistry, Prague. These processes provided the product, after the first crystallization, of minimum purity 97% D-arabinose. The purity after the second crystallization reached 99.5%. The unreacted sodium D-gluconate was recycled.

A comparison of the construction and operating parameters of a single cell (compartment) of the BTPR reactor with the laboratory FBE cell is shown in Table 2. Extensive quantities such as production capacity clearly reflect the scale up factor of 5.

An extreme case of operation of the BTPR and TTPR reactors was the use of a packed bed anode. This situation occurred accidentally following partial plugging of the electrolyte distributor and in turn a drop in flow rate. The conversion under these conditions decreased but remained above 50%, while selectivity dropped to about 90% or 85% depending on whether this situation was accompanied by an excessive temperature rise. After installation of the flow rate monitoring and control this situation did not occur further.

An undesirable situation also occurred following flushing of some of the fluidizing particles out of one or more anode chambers. The loss of particles from the fluidized bed decreased the interfacial surface of the anode, increased the current density, which, in turn, severely reduced conversion, selectivity and reactor productivity. To avoid this situation the anode chambers were equipped at the top electrolyte outlet with sieves functioning as particle filters. Also the intake of the storage tank was equipped with sieves which prevented plugging of the distributor by the flushed particles.

In the course of the reaction the surface of the current feeder, as well as the surface of the particles, was eroded. Long term observation of the operation of the TTPR reactor showed, however, that the durability of individual construction components was good. The life span of the current feeder was determined to be about six months under continuous three-shift operation. Although the current feeder remained fully functional even after this period, its surface became pitted. Further erosion was locally accelerated, which could bring about serious problems in the overall performance of the TTPR. Replacement of the current feeder after six months thus appears advisable.

The life span of the separating diaphragms of the TTPR was found to depend on the adherence to optimum operating conditions, particularly the current density and temperature. Marked excursion above the optimum operating temperature led to the deformation of the diaphragm and increased ohmic resistance of the chamber. Adherence to the optimum regime also positively affected the life span of the graphite parts of the TTPR reactor.

Carbon fines released into the reaction mixture by erosion of the graphite parts of the TTPR had to be removed by filtration from the product solution prior to crystallization and raffination of D-arabinose. The graphite particles, consumed by erosion (attrition), were replenished regularly. The loss of the graphite granulate was determined to be about 2 dm^3 (bulk) per annum. In order to prevent accumulation of the carbon fines the reactor was rinsed after 4–5 runs.

The performance of the BTPR and TTPR reactors is compared with the laboratory cell in Table 3. TTPR performance is given for two different concentrations of the starting material. The table shows the conversion of the BTPR and TTPR reactors for comparable concentrations of the starting material (about 160 g dm^{-3}) to be by 3–5% lower. This decrease, is attributable to nonuniformity of distribution of the electrolyte among individual

Table 3. A comparison of the laboratory FBE cell with the BTPR and TTPR

Reactor	*Laboratory FBE cell*	*BTPR*	*TTPR*	*TTPR*
Volume of reaction mixture/dm^3	2	6	35	35
Concentration of sodium gluconate/g dm^{-3}	158	160	158	186
Conversion/%	74.6	71.7	69.5	75.1
Specific power consumption/kWh kg^{-1}	10.5	12.8	14	13
Temperature/°C	36	36	36	36
Current/A	10	45	225	225
Voltage/V	13–18	14–21	14–21	13–18

chambers and to the entrainment of carbon particles. However, at the higher concentration of the starting solution (186 g dm^{-3}) the conversion in TTPR reaches essentially the same level as in the laboratory FBE cell. Use of increased concentration of gluconate, violates the restriction of using fermentation liquor directly as a starting solution.

4. Conclusions

A new method has been developed for the production of D-arabinose by direct electrochemical oxidation in an electrochemical tank type pilot plant reactor with the fluidized bed anode with an annual capacity of 1 metric ton of D-arabinose.

The conversion of the reactor can be maintained around 70% and selectivity above 90%. Although these values are less than those achieved with the hypochlorite method the new method has the following advantages:

(i) The starting material is the reaction mixture from the fermentation oxidation of D-glucose to sodium D-gluconate without addition of auxiliary electrolytes.
(ii) The apparatus is constructed from nontoxic materials satisfying criteria for a pharmaceutical production.
(iii) Subsequent separation of the product from the reaction mixture is simple and unreacted gluconate is recycled.
(iv) The amount of salts generated in the process is by several orders of magnitude less in comparison with the hypochlorite method.
(v) The associated investment costs are low compared to plate–plate electrolysers, while the operation and maintenance is simple.
(iv) The process has been covered by several international patents [12].

References

[1] V. Jiřičný and V. Staněk, *J. Appl. Electrochem.*, in press.
[2] H. G. J. de Wilt, *Ind. Eng. Chem. Prod. Res. Develop.* **11**(4), (1972) 370 and **11**(4), (1972) 374.
[3] Yu. B. Vassilyev, O. A. Khazova and N. N. Nikolajeva, *J. Electroanal. Chem.* **196** (1985) 105.
[4] M. J. Fioshin, I. A. Avrutskaja, T. A. Malachova and T. E. Mulina, *Elektrochimija* **10** (1974) 796.
[5] P. N. Pintauro, D. K. Johnson, K. Park, M. M. Baizer and K. Nobe, *J. Appl. Electrochem.* **14** (1984) 209.
[6] K. Park, P. N. Pintauro, M. M. Baizer and K. Nobe, *J. Electrochem. Soc.* **132**(8), (1985) 1850.
[7] A. Mehta, D. N. Purohit and R. A. Misr, *Orient. J. Chem.* **5**(4), (1989) 304.
[8] R. Wolf, Merck GmbH, *German Patents 2 923 267* (1980), *2 923 268* (1980) *Eur. Pat. Appl. 20 959* (1981).
[9] F. Goodridge, *Chem. Proc. Eng.* **49** (1968) 93.
[10] G. Kreysa and E. Heitz, 'Principles of Electrochemical Engineering', Dechema (1986).
[11] F. Goodridge, *J. Chem. Tech. Biotechnol.* **38** (1987) 127.
[12] V. Jiřičný, V. Staněk and M. Borovcová, *Czechoslovak. Patent 271 428* (1990), *US Patent 4 950 3600* (1990), *Swiss Patent 675 726* (1990), *German Patent Appl. 3 840 541* (1991).
[13] J. Kubala and H. Kraus, *Czechoslovak Patent 225 576* (1982).
[14] B. Tschiersch, K. Schwate and J. Stokon, *German (GDR) Patent 143 261* (1980).
[15] N. N. Golyseva, N. V. Plekhanova and G. P. Fedorchenko, *USSR Patent 1 017 337* (1983).
[16] N. N. Golyseva, N. V. Pekhanova, K. B. Grozbarev and G. P. Fedorchenko, *USSR Patent 1 009 470 A* (1983).
[17] V. Bilik, *Czechoslovak Patent 6749-83*(1983).
[18] G. W. Hay and F. Smith, *Can. J. Chem.* **47** (1969) 417.
[19] J. Kubala, Š. Kučár and K. Linek, *Czechoslovak Patent 22 576* (1982).
[20] A. Schytil., 'Preparation of Pure D-arabinose by Electrochemical Reduction', (in Czech) Institute of Chemical Technology, Prague (1987).
[21] V. Jiřičný, V. Staněk and M. Borovcová, Research report 43/87, (in Czech) Institute of Chemical Process Fundamentals, Czech. Acad. Sci., Prague (1987).
[22] C. L. Lopez–Cacicedo, *Trans. Inst. Met. Finish.* **53** (1975) 74.
[23] F. Coeuret, *J. Appl. Electrochem.* **10**(6), (1980) 687.
[24] W. Meissner and G. Härtel, **7/8** (1992) 17.
[25] N. L. Weinberg, 'Technique of Electroorganic Synthesis', Techniques of Chemistry, Vol. 5, John Wiley & Sons., New York (1974).