PREPARATION OF D-ARABINOSE IN A LABORATORY FLUIDIZED BED ELECTRODE CELL

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Received December 23, 1994
Accepted March 15, 1995

Results of experimental work emloying an electrochemical reactor with the fluidized bed electrode to prepare D-arabinose by direct degradative oxidation of sodium D-gluconate without chemical oxidizing agents are presented. The observed yield of D-arabinose exceeded 70% by mass related to the theoretically obtainable amount with the selectivity ranging between 96 and 98.1%. The undesirable product was mainly D-erythrose produced by consecutive reaction from D-arabinose. Typical specific electric power consumption ranged between 7.5 and 14 kWh per kg of D-arabinose.

Only a limited number of monosaccharides can be isolated directly from natural materials. The majority of them are synthesized mostly from natural monosaccharides as starting materials. Natural resources of D-arabinose do not meet existing demand for this monosaccharide with a variety of practical utilizations: In pharmacy for the synthesis of vitamins and other important pharmaceuticals, in biochemistry as a culture medium for cultivation of microorganisms.

Various chemical, electro- and biochemical methods have been used for oxidation of glucose to salts of D-gluconic acid and also oxidative degradation to D-arabinose and, eventually, to lower sugars. An excellent survey of existing methods for the first of these steps has been published by de Wilt[1].

Considerable attention has been devoted to the mechanism and kinetics of chemical oxidation by halogens (bromine), or halogen compounds (hypoiodide or hypochlorite). The course of the reaction has been found to be strongly influenced by pH and steric configuration of the starting material. In acid solution the free halogen or hypohalous acid is the active oxidant, whereas in alkaline media the hypohalous acid or ion plays the major role[2]. With D-glucose as a starting material its β-form reacts much faster than corresponding anomers. In fact, the oxidation rate is controlled by the rate of transformation to the β-form[3–5].

The main disadvantage of the processes involving chemical oxidizing agents (e.g. hypochlorite) is associated with the difficulty of separating the product from the large quantity of salts. This disadvantage is partly overcome by indirect electrochemical

oxidation. The method relies on the oxidation of an aldonic acid while the oxidant is being continuously regenerated electrochemically in the course of the reaction. The reaction yields correspond almost quantitatively to the amount of current passed. This suggests that no undesirable side reactions occur. Procedures involving only small amounts of regenerated oxidant are advantageous compared with the purely chemical methods.

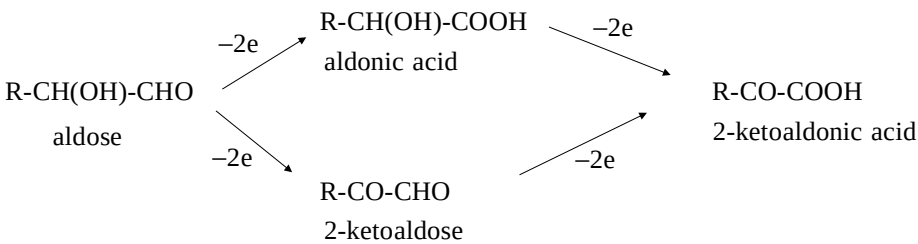
Cerium ions have been also used for indirect electrochemical oxidative degradation of D-gluconic acid to D-arabinose at low pH and in the presence of low alcohols[6,7]. The conversion above 70% and the selectivity nearly 80% are typical for these studies by several authors[8,9]. The major disadvantage is the toxicity of Ce compounds. Their perfect separation from the reaction mixture is costly.

Direct electrooxidation of D-glucose was studied for the first time by Neuberg et al.[10]. A remarkable contribution of this work was the discovery that carbon dioxide can be electrochemically split from aldonic acids with the formation of corresponding lower aldoses. The process is assumed[11] to follow gradual degradation to acid and 2-ketoaldonic acid. The degradation chain may be continued all the way down to carbon dioxide.

These results have been later confirmed by Hay and Smith[12]. Although aldonic acids were not detected in the reaction mixture the authors anticipated their formation as the first intermediate step. They concluded that if such acidic intermediated participate in these reactions the aldoses must be strongly favored in any equilibria involving oxidized compounds, and/or the oxidation must be very slow relative to decarboxylation so that at any instant the concentration of the intermediate is below present levels of detection. The yields of D-arabinose and other monosaccharides have been in semimicro amounts.

A mechanism was proposed[13], although it was impossible to detect the intermediate compounds involving formation of aldonic acid or 2-ketoaldose as the first step of electrooxidation. In the second step these intermediates are oxidized giving an 2-ketoaldonic acid which can decarboxylate to a lower aldose having one carbon atom less:

Thus the two-step electrooxidation



is followed by decarboxylation

$$\underset{\text{2-ketoaldonic acid}}{\text{R–CO–COOH}} \longrightarrow \underset{\text{lower aldose}}{\text{R–CHO}} + CO_2 \quad .$$

The above literature survey shows that direct electrooxidation represents potentially promising method for sequential degradation of sugars and their derivates to lower homologs. Both the reaction mechanism and the existence of optimum reaction conditions providing meaningful yields are yet to be investigated.

The aim of this work is to test utilization of the fluidized bed electrode cell for direct oxidative degradation of sodium D-gluconate to D-arabinose according to the folowing reaction scheme:

$$\underset{\text{sodium D-gluconate}}{HOH_2C–[CH(OH)]_4–COONa} + H_2O - 2\,e \longrightarrow$$

$$\longrightarrow \underset{\text{D-arabinose}}{HOH_2C–[C(OH)]_3–CHO} + NaHCO_3 + 2\,H^+$$

while minimizing the extent of the side anodic reaction:

$$2\,OH^- - 2\,e \longrightarrow H_2O + 1/2\,O_2$$

and possible consecutive degradation of D-arabinose to lower carbohydrates.
The expected main cathodic reaction is:

$$2\,H^+ + 2\,e \longrightarrow 2\,H \longrightarrow H_2 \quad .$$

EXPERIMENTAL

Experimental Setup

The experiments have been carried out in a laboratory experimental setup with a fluidized bed anode. The scheme of the setup operating in the batch mode is shown in Fig. 1.

The central part of the setup is the fluidized bed electrode (FBE) cell 1. The cell is a parallelepiped manufactured from perspex glass slabs 3 mm thick. The external dimensions of the

parallelepiped (thickness × width × height) are 25 × 70 × 400 mm, where thickness is the distance between graphite current feeder 2 and cathode 3.

The interior chamber of the cell is divided by a porous PVC separator 4 made of an 0.8 mm thick sheet into the anode 5 and the cathode 6 compartments. The separator is supported by a rectangular piece of 2 mm thick stainless steel expanded metal sheet 3 to secure its position in the cell. This stainless steel expanded metal sheet functions at the same time as a cathode. A non-permeable stencil is mounted on the separator in order to define the surface area of permeable "active window area" of 84 cm^2 for an accurate evaluation of apparent current densities. Although the separator is sufficiently permeable for the reacting solution it prevents contact of the fluidizing particles in the anode compartment with the cathode.

The anode compartment contains a current feeder 2 manufactured a block of graphite and formed as a 5 mm thick slab with its width and height to fit easily into the cell. The anode itself is a bed 5 of 200 cm^3 irregular graphite particles 400 – 600 μm in diameter kept in fluidizing motion by the flow of the reacting solution. As is apparent the direction of the flow of the reacting solution (electrolyte) is perpendicular to the flow of electric current.

Both electrodes were connected to a DC power supply 13 permitting operation in both the amperostatic and potentiostatic mode. The maximum current available was 20 A.

The reaction solution was stored in a thermostated storage tank 7. From here it was driven by a PTFE-coated centrifugal pump 8 via a bank of rotameters 10 into the two compartments of the fluidized bed cell. The flow rate through the anode and the cathode compartment of the cell could be adjusted and metered independently by the valves 9 in individual branches of the rotameter bank 10.

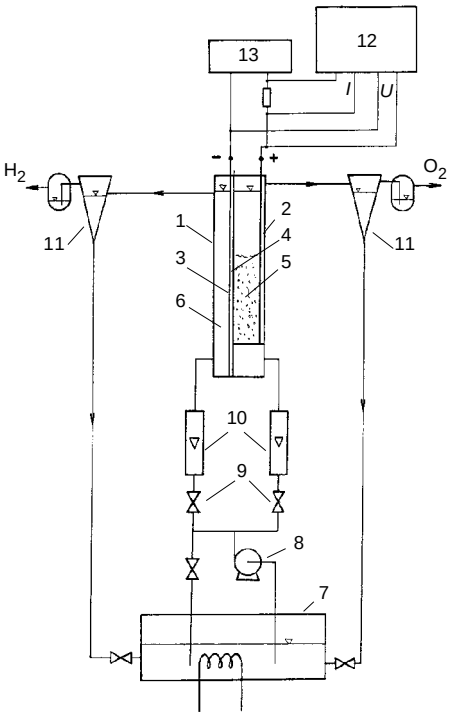


FIG. 1
Scheme of the experimental setup with the fluidized bed electrode (FBE) cell. 1 FBE cell, 2 current feeder, 3 cathode, 4 PVC separator, 5 anode compartment, 6 cathode compartment, 7 thermostated storage tank, 8 centrifugal pump, 9 valves, 10 rotameters, 11 gas separators, 12 recorder, 13 DC power supply

Reacting solution upon leaving the cell returned into the storage tank via a gas/liquid separators 11. The anode and cathode were equipped each with its individual gas/liquid separator to prevent mixing of the evolving oxygen and hydrogen gases that could pose a hazard of explosion.

The voltage applied to the electrodes and the total current were both continuously monitored and recorded 12 throughout the experiment carried out in a batchwise manner.

Experimental Method

The experimental procedure consisted routinely from several steps. Firstly, the tank was filled with the starting solution of sodium D-gluconate of known concentration. The starting solutions were prepared by dissolving crystalline sodium D-gluconate in water to obtain concentrations typical for the product solution of the fermentation oxidation of glucose to sodium D-gluconate (ca 180 g dm^{-3}). The fermentation production of D-gluconate from glucose has been known and well developed for a long time to represent a potentially attractive and inexpensive source of the starting solution. Sodium D-gluconate used in all experiments in this study was prepared by the fermentation oxidation.

The circulation pump was switched on and operated for some time to reach the desired temperature of the circulated solution and the reaction cell.

The flow rate in the anode compartment was set to 180 $dm^3\ h^{-1}$ providing for a twenty per cent fluidized bed expansion. The twenty per cent bed expansion was found optimal on the basis of an extensive set of preliminary experimental runs. The flow rate through the cathode compartment was kept at a lower value amounting usually to 25% of the rate through the fluidized bed anode compartment. The same reacting solution was circulated through the cathode and the anode compartments and so we say that the cell is thus operated in the undivided-cell mode.

After reaching the desired temperature and the flow regime in the cell the power supply was switched on and the solution circulating through the cell was being sampled at regular intervals, typically every 60 min. Drawn samples of the circulated solution were kept in sealed vials for later analysis.

Only amperostatic mode and batch way arrangement of operation of the cell was employed consistently throughout this study. The used DC power supply provided automated control of the voltage applied on the cell to maintain constant-current, amperostatic mode of operation. The set total current was read off by the meter integrated directly in the DC power supply. The transient history of the regime of the cell was recorded on a two-pen chart recorder recording the voltage as well as the total current in dependence on time.

After setting the bed expansion and the total DC current the process remained fairly stable for the whole period of the run (10 – 14 h). Occasional adjustments of the valves had to be made in order to maintain constant flow rate. Only cooling was needed in the storage tank to maintain an isothermal regime in the cell by removing the heat evolving in the circulating solution partly by the ohmic resistance of the electrolyte, partly by the circulation pump.

Analytical Methods

Three analytical methods[14] have been used for analysis of the reaction mixture.

Schoorl's titration method has been used as a fast method for the determination of the total concentration of reducing sugars produced by electrolysis. The method is based on the reduction of Cu^{2+} ions, added to the sample in excess, to Cu^{+} ions by the reducing sugars present in the solution. The remaining Cu^{2+} ions are reduced by the added solution of iodide producing iodine. The amount of iodine is finally titrated by the solution of thiosulfite. Schoorl's titration provided us with a simple and sufficiently accurate on-the-spot means of ascertaining the actual progress of the reaction.

Paper chromatographic analysis on a Whatman No. 2 paper was utilized for a semi-quantitative detection of the stepwise degradation of the parent compound to a mixture of lower aldoses. The elution solvent was a mixture of water, ethanol and butanol in the volume ratio 5 : 1 : 4. The chromatogram was developed after 16 h by the silver nitrate solution. Paper chromatography proved to be a cheap substitute for the full-fledged qualitative and quantitative analysis providing the information about the selectivity of the reaction.

Finally, HPLC has been used for a precise quantitative analysis of the reaction mixture. The employed method was fairly laborious in spite of the fact that a 1090M Hewlett–Packard liquid chromatograph equipped with diode-array and refractometry detectors in series was available. The difficulty and laboriousness of the method rested in the presence of sodium carbonate as a ionic substance in the mixture with sugars. This necessitated use of two-step two-column analysis: 4×250 mm Silasorb SPH amine – 10 μm and 3.3×150 mm CGC Separon NH_2 – 5 μm. Water and acetonitrile used were of "for HPLC" grade.

Data Processing

The bulk of experimental data as the flow rates, total electric currents (given as DC currents from DC power supply applied on the cell), cell voltages, concentrations of the starting solution, temperature of the reaction solution and the analyses of the samples taken were used to obtain the following quantities of interest:

Current efficiency η for D-arabinose as the product, calculated as a ratio of the current spent effectively for the production of D-arabinose in reaction mixture (determined from the results of chemical analyses) to the total current applied to the cell over the time period (charge) of the experimental run.

Specific electric power consumption *P*, defined as the amount of electric power in kWh spent for the production of one kg D-arabinose in reaction mixture.

Apparent current density *j*, calculated as a ratio of the total current applied on the cell related to the active window area of the PVC separator.

Conversion of the reaction *C*, taken as the fraction of sodium D-gluconate reacted in the anode compartment.

Selectivity of the reaction *S*, taken as the percentage of the starting material converted into the desired product – D-arabinose.

Productivity *M*, taken as the weight of D-arabinose produced per unit time.

RESULTS AND DISCUSSION

The experiments carried out in this study were designed primarily to reveal the effect of apparent curent density, temperature and concentration of sodium D-gluconate on the conversion, voltage on the cell, specific electric power consumption and current efficiency.

With the practicability and economy of the future process in mind we have restricted the experiments to using water solution of sodium D-gluconate as a parent compound (starting material). the acidity of the starting solutions prepared was pH 5.6 with no other electrolytes added for pH or conductivity adjustments. The concentrations of the starting solution ranged between 88 g dm^{-3}, at the lower end, and 225 g dm^{-3}, at the

upper end of the concentration range. The concentration of about 175 g dm^{-3} may be regarded as typical for the product solution of the fermentation oxidation process.

The effect of total DC current (after the 6 h experimental run at t = 25 °C) on the productivity M, current efficiency η, cell voltage U and specific electric power consumption P for two different starting concentrations of sodium D-gluconate is shown in Fig. 2. The total current of about 10 A (equivalent to the apparent current density of 119 mA per square centimeter of the active window area of the separator), appears optimal from the standpoint of current efficiency. Higher total currents and apparent current densities, respectively, increase the preference of the undesirable side anodic reaction (oxygen evolution) owing to the increasing cell voltage. The decrease of the current efficiency past the optimum of 10 A is particularly drastic for the lower of the two concentrations of the starting solution employed.

The specific electric power consumption P increases almost exponentially with the increasing total current (apparent current density) and becomes particularly severe for the lower of the two concentrations of the starting solution. The maximum specific

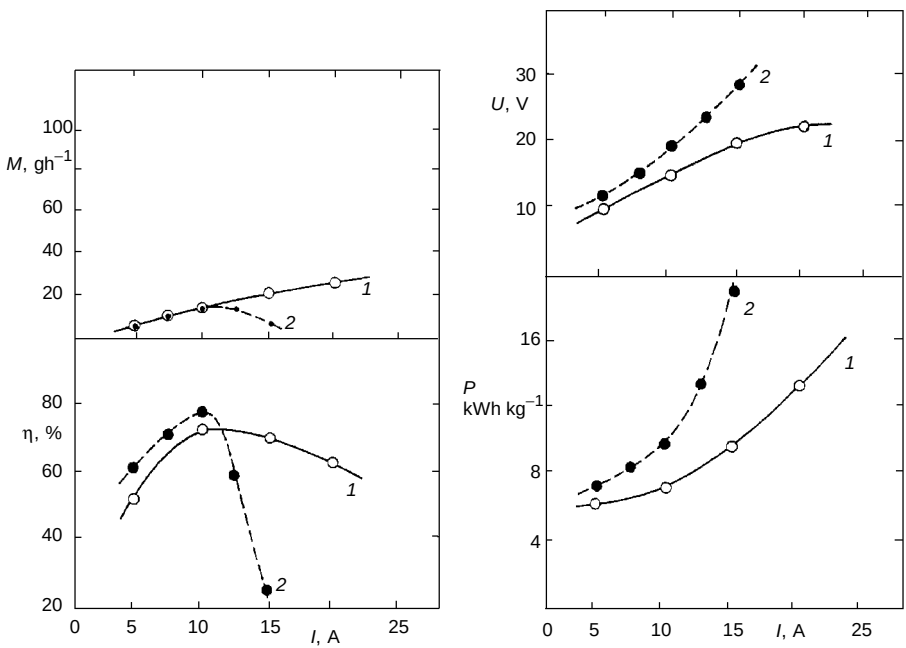


FIG. 2

The effect of total DC current I applied for the period of 6 h to the cell on the productivity M, current efficiency η, cell voltage U and specific electric power consumption P for two concentrations of the starting solution of sodium D-gluconate at t = 25 °C: *1* c_0 = 175 g dm^{-3}, *2* c_0 = 88 g dm^{-3}

electric power consumption of 43 kWh kg^{-1} of D-arabinose was experienced in this study for the starting concentration of the solution of 88 g dm^{-3} and total current 17 A.

Although the productivity of the cell *M* is about the same for both investigated starting concentrations of the sodium D-gluconate, the other characteristics are all more favorable for the higher starting concentration. This difference is clearly attributable to a lesser relative extent of the side anodic reaction (production of oxygen) which results in markedly better current efficiency and lower cell voltage at high apparent current density conditions.

The experimental results in Figs 3 and 4 are presented in the form of time plots of quantities of interest.

The effect of the starting concentration of sodium D-gluconate is better apparent from Fig. 3 plotting the transient development of the conversion, current efficiency and specific electric power consumption for three concentrations of the starting solution of sodium D-gluconate at t = 25 °C.

From this figure it is seen that in the early stages of the electrooxidation the reaction behaves as being lower than first-order because conversion grows slower with time for

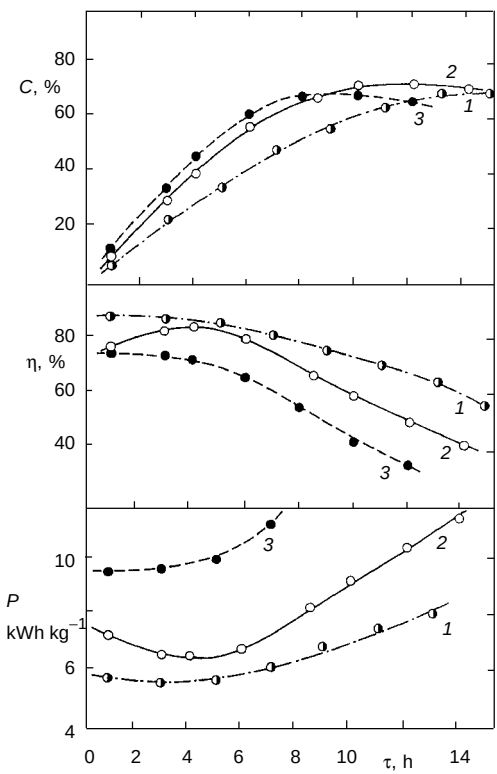


FIG. 3
Transient development of the conversion *C*, current efficiency η and specific electric power consumption *P* for three concentrations of the starting solution of sodium D-gluconate at t = 25 °C: *1* c_0 = 225 g dm^{-3}, *2* c_0 = 155 g dm^{-3}, *3* c_0= 92 g dm^{-3}

increasing concentration of the starting solution. However, as the reaction approaches its maximum conversion, which occurs in our experimental setup after approximately 8 h, the net rate of the reactions leading to the desired product, D-arabinose, rapidly decreases. D-Arabinose is being consumed by consecutive reactions, which becomes manifested in Fig. 3 by decreasing current efficiency and increasing specific electric power consumption. The decrease of the current efficiency with time, on the contrary, is slower for the higher starting concentrations.

The specific electric power consumption has more favorable values for higher starting concentrations of sodium D-gluconate and begins to deteriorate progressively for all three concentrations investigated after about the same period of time, i.e. about 6 h.

In spite of the lower initial growth of the conversion higher starting concentration of sodium D-gluconate appears thus favorable in that the starting compound is converted into the desired product at higher rate, with higher current efficiency and lower specific electric power consumption.

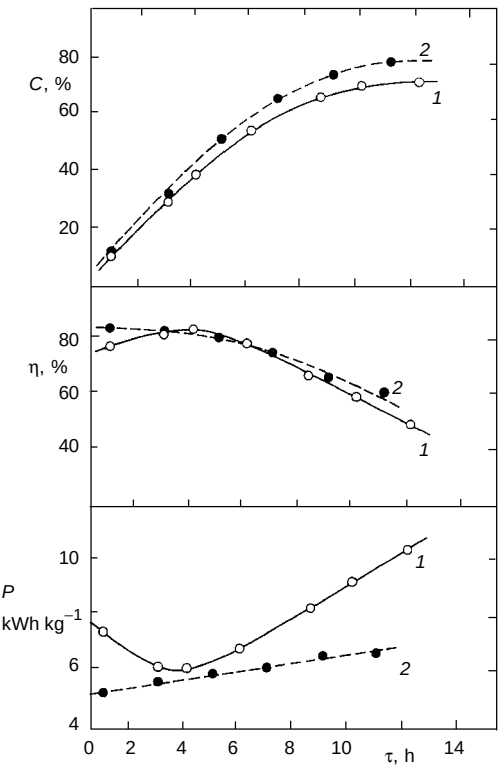


FIG. 4
Transient development of the conversion *C*, current efficiency η and specific electric power consumption *P* for two temperatures of the reaction solution and 175 g dm^{-3} concentration of the starting solution of sodium D-gluconate: *1* t = 25 °C, *2* t = 40 °C

Higher starting concentration of sodium D-gluconate thus contributes to higher productivity of D-arabinose at higher current efficiency and lower specific electric power consumption. Roughly one can say that a 50% increase of the starting concentration of sodium D-gluconate over the average concentration (160 g dm^{-3}) produced by the fermentation oxidation increases the productivity by 32% while maintaining conversion still at 68%. After an 11 h run the current efficiency remains still 70% and the specific electric power consumption 7.5 kWh kg^{-1} of D-arabinose. Higher concentration of sodium D-gluconate significantly increases the economy of the process.

The effect of the reaction temperature in the fluidized bed cell is shown in Fig. 4 plotting the transient development of the conversion, current efficiency and specific electric power consumption for 25 °C and 40 °C. From the figure it is seen that conversion increases faster at higher temperature while the current efficiency do not differ appreciably with the current efficiency at the higher temperature being more often higher. The specific electric power consumption, however, is consistently better for the higher temperature, this difference being increasingly more significant with time, i.e. at higher conversions. Higher temperature thus also has a positive effect on the performance of the fluidized bed cell, similarly as increasing concentration. Roughly it can be said that an increase of temperature from 25 °C to 40 °C is equivalent to an increase of the concentration of sodium D-gluconate in the starting solution by 50%.

Making an analogous comparison to the concentration of starting material, one finds the effect of temperature much stronger. The increase of the temperature of 15 °C represented specific electric power consumption drops to 6.7 kWh kg^{-1} of D-arabinose.

The temperature of 40 °C, however, appears to represent a critical limit. Experimental temperatures over of this value contribute to rapid degradation of D-arabinose to D-erythrose amounting up to 10% at 50 °C, while at temperatures up to 40 °C D-erythrose content remains within 1 – 4%.

Temperature and current density dominate among the factors affecting the selectivity of the reaction. Simultaneous positive effects of temperature and concentration, however, are not additive.

CONCLUSIONS

A new method of production of D-arabinose using a fluidized bed anode has been experimentally tested in a laboratory setup. The new method capitalizes the high effective surface per unit volume of the fluidizing particles and effective introduction of turbulence of the electrolyte through the cell resulting into the high mass transfer rate. The former of these features allows to use high apparent current densities for the reaction to follow the desired scheme without large scale destruction of the starting material.

The experimental results obtained in this study appear that conversions of direct electrochemical oxidation of sodium D-gluconate to D-arabinose in the fluidized bed electrode cell can excess of 70% to the desired product with the selectivity ranging between 98.1 and 96% (1 – 4% of other products in the resulting mixture) and so the method is comparable to competitive chemical methods.

The method is ecologically very soft because the direct electrochemical oxidation in the fluidized bed cell requires no oxidizing agents (the reaction takes place directly on the surface of the electrically charged fluidizing particles) and so there is no need to separate the reduced form of chemical oxidizing agents from the mixture that are later difficult to separate and dispose off. No chemical substances need be added that might later be undesirable even in traces in pharmaceutical products.

The principal undesirable reactions in the anode compartment of the fluidized bed electrode cell are production of gaseous oxygen, as the side reaction, and degradation of D-arabinose to D-erythrose as the consecutive reaction. These reactions cause decreased selectivity and increased specific electric power consumption. Fortunately, the low reaction rate leading to D-erythrose causes only minor decrease of the selectivity under suitable operating conditions.

The experiments in the fluidized bed electrode cell have been carried out with sodium D-gluconate solution at pH 5.6 without addition of any other electrolyte. Although there are some disadvantages of this alternative, such as lower conductivity of the solution and with it associated higher heat evolution and higher specific electric power consumption, the obvious ensuing separation steps are greatly simplified: Only $NaHCO_3$ and the unreacted sodium D-gluconate need be removed from the product mixture. Owing to the low amount of these salts generated, simple ion exchange columns will suffice for this task.

SYMBOLS

c_0	starting concentration of sodium D-gluconate, g dm^{-3}
C	conversion of the reaction, %
I	total DC electric current, A
j	current density, A cm^{-2}
M	productivity, g h^{-1}
P	specific electric power consumption, kWh kg^{-1}
S	selectivity of the reaction, %
t	temperature, °C
U	voltage, V
η	current efficiency, %
τ	time, h

REFERENCES

1. de Wilt H. G. J.: Ind. Eng. Chem., Prod. Res. Dev. *11*, 370, 374 (1972).

2. Green J. W.: *The Carbohydrates* (W. Pigman, Ed.), p. 336. Academic Press, New York 1957.
3. Barker I. R. L., Overend W. G., Rees S. W.: J. Chem. Soc. *1964*, 3254.
4. Isbell H. S., Schaffer R., Sniegoski L. T.: J. Res. Natl. Bur. Stand, A *68*, 145 (1964).
5. Isbell H. S., Frush H. L., Tipson R. S.: Chem. Ind. (London) *1961*, 593.
6. Nakamura Y.: Nogushi Kenkyusho Jiho *25*, 26 (1982); Chem. Abstr. *98*, 126495 (1983).
7. Nakamura Y.: Nippon Kagaku Kaishi *10*, 1727 (1982); Chem. Abstr. *98*, 34860 (1983).
8. Pottenger C. R., Johnson D. C.: J. Polym. Sci., A-1, *8*, 301 (1970).
9. Mehrotra R. N., Amis E. S.: J. Org. Chem. *39*, 1788 (1974).
10. Neuberg C., Scott L., Lachmann S.: Biochem. Z. *24*, 152 (1910).
11. Karabinos J. V.: Euclides *14*, 211 (1954); Chem. Abstr. *49*, 4533 (1955).
12. Hay G. W., Smith F.: Can. J. Chem. *47*, 417 (1969).
13. Baizer M. M., Lund H.: *Organic Electrochemistry*, 2nd ed., p. 510. Dekker, Inc., New York 1983.
14. Jiricny V., Stanek V., Borovcova M.: *Res. Rep. No. 47*. Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic 1989.