HYDROGENATION OF FURFURAL WITH ALKALI-METAL AMALGAMS

V. A. Smirnov, V. A. Tushnalobova, and D. P. Semchenko

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The possibility of reducing furfural to furyl alcohol with potassium and sodium amalgams under the conditions of neutralizing the alkali formed with carbon dioxide has been investigated. The reduction of furfural can be directed to the predominant formation of furyl alcohol by regulating the rate of feed of furfural into the reaction vessel.

Furyl alcohol is widely used in the production of synthetic resins, plastics, and chemically-resistant cements and in a whole series of other industries [1].

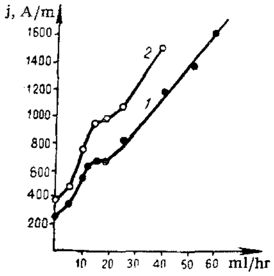


Fig. 1. Influence of the rate of feed of furfural into the reaction vessel on the rate of decomposition of sodium amalgam (1) and potassium amalgam (2).

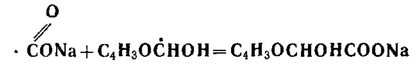
At the present time it is produced from furfural (by the Cannizzaro oxidation-reduction reaction [2], by the Meerwein-Ponndorf reaction [3], or by catalytic reduction with hydrogen under pressure [4,5]). Attempts have also been described to reduce furfural to furyl alcohol electrochemically [6, 7].

Taking the availability of sodium amalgam into account [8], it appeared desirable to use it for the reduction of furfural to furyl alcohol. However, earlier investigations of the amalgam reduction of furfural [9] did not give satisfactory results.

The present communication gives the results of a study of the reduction of furfural with alkali-metal amalgams. The experiments carried out with sodium amalgam showed that furfural is intensively reduced; the rate of decomposition of the amalgam, expressed in electrical units, reaches 10 000 A/m^2 of surface of the amalgam. In this process, the solution in the electrode layer becomes highly alkaline, which favors the occurrence of the Cannizzaro reaction and also the condensation and polymerization of the furfural. In order to eliminate the production of alkaline solution, a detailed study has been made of the reduction of furfural with sodium and potassium amalgams with the neutralization of the alkali formed by carbon dioxide. The possibility was taken into account of the production of formates of the alkali metals by the reaction.

$$2CO_2 + H_2O + 2Na(Hg) = HCOONa + NaHCO_3 + 2Hg \qquad (1)$$

In addition, the intermediate radicals ·COONa formed in the reduction of the carbon dioxide may react with the intermediate radicals $C_4H_3O\dot{C}HOH$ formed in the reduction of the furfural, with the production of furylglycolic acid:



$$\cdot\overset{O}{\overset{/\!/}{C}}ONa + C_4H_3O\dot{C}HOH = C_4H_3OCHOHCOONa \qquad (2)$$

It was found that the neutralization of the reaction mixture with carbon dioxide by the usual procedure is relatively ineffective because of the high rate of the reduction of the furfural and the relatively low rate of the reaction of the carbon dioxide with the alkali formed in the reaction. In view of this, the influence of controlling the rate of feed of furfural in carbon dioxide into the reaction vessel on the direction of the reduction process was studied.

Figure 1 shows the rates of decomposition of sodim and potassium amalgams as functions of the rate of feed of furfural to the reaction vessel with the continuous bubbling of carbon dioxide through the solution at the rate of 15 l/hr. In the absence of a feed of furfural, the rate of decomposition of the amalgam corresponds to the rate of reduction of the carbon dioxide [10, 11]. When furfural was added to the reaction vessel, the rate of decomposition of the amalgam rose approximately in proportion to the rate of feed of the furfural.

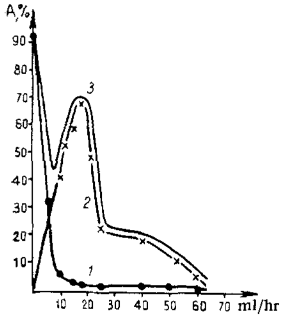
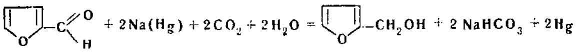


Fig. 2. Influence of the rate of feed of furfural to the reaction vessel on the direction of the reduction process for sodium amalgam: 1) yield of sodium formate; 2) yield of furyl alcohol; 3) total yield of sodium formate and furyl alcohol.

Data on the yield of reduction products as a function of the rate of feed of furfural to the reaction vessel are given in Figs. 2 and 3. It follows from these that at rates of feed of furfural less than 10 ml/hr the fraction of the current consumed in the reduction of the furfural and in the formation of the alkali-metal bicarbonate in accordance with Eq. (3) is low:


(3)

Simultaneously with this reaction the production of the formate and bicarbonate of the alkali metal (Eq. 1) takes place at a fairly high rate. At lower rates of furfural, this reaction becomes the main one. An increase in the rate of feed of furfural raises the yield of furyl alcohol and lowers the yield of sodium formate to 2–3%. The yield of furyl alcohol reaches 65–70%. At high rates of feed of furfural, hydrodimerization, leading to the formation of hydrofuroins becomes the main reaction.

In the reduction of furfural with potassium amalgam, the same dependence of the yield of furyl alcohol on the rate of furfural is obtained, but in this case the maximum yield of furyl alcohol does not exceed 35–38% (Fig. 3).

In order to investigate the possibility of increasing the yield of furyl alcohol at the expense of the hydrofuroins, we carried out experiments with the addition of 0.3–0.5 g/*l* of iron sulfate to the solution [12]. However, the results obtained showed that in this case iron salts do not substantially affect the course of the reductive process. The addition of substances preventing the polymerization and condensation of the furfural and the furyl alcohol, such as urea and triethanolamine, did not lead to the desired results, either. Carrying out the reductive process with the alkali formed being neutralized by sulfur dioxide caused the formation of only a viscous light yellow mass.

Thus, the study of the reduction of furfural to furyl alcohol with potassium and sodium amalgams that we have performed has shown that the conditions of the reaction and the nature of the amalgam exert a fundamental influence on the direction of the reductive process. By using sodium amalgam it is possible to direct the reductive process predominantly to the formation of furyl alcohol and by using potassium amalgam to hydrofuroins.

EXPERIMENTAL

A thermostated reaction vessel fitted with a bubbler, mechanical stirrer and thermometer was charged with 300 ml of sodium amalgam containing 1.5 g-eg of sodium per *l* of mercury (0.25 wt.-% of sodium). Then with constant stirring and the vigorous bubbling of carbon dioxide at the rate of 15 *l*/hr, 500 ml of a 6–8% solution of furfural in water was added from a burette at a predetermined rate. The reaction was carried out at 20°–25° C. After the decomposition of the amalgam, the solution was separated from it and extracted with ether. The ether was evaporated off and the residue was distilled under vacuum. First unchanged furfural distilled over and then furyl alcohol containing a small amount of furfural. The latter was eliminated by binding it as the bisulfite derivative.

The characteristics of the furyl alcohol obtained were: bp 74°–76° C (15 mm), n_D^{20} 1.4852, d_4^{20} 1.1330.

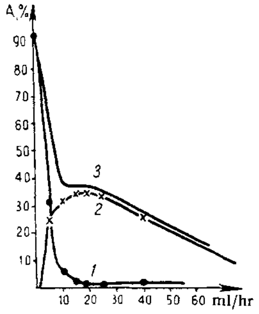


Fig. 3. Influence of the rate of feed of furfural to the reaction vessel on the direction of the reductive process for potassium amalgam: 1) yield of potassium formate; 2) yield of furyl alcohol; 3) total yield of potassium formate and furyl alcohol.

The remaining mass, consisting of a light yellow viscous liquid, distilled at 140°–148° C (2–3 mm) and had characteristics close to those of the hydrofuroins [7]. It apparently consisted of hydrofuroins contaminated with the products of their resinification [7] together with condensation products of furyl alcohol [1].

The aqueous extract was neutralized with dilute sulfuric acid, and the formic acid was distilled from it, its amount being determined by permanganatometric titration [13].

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Novocherkassk Polytechnic Institute