GLUCOSE HYDROGENATION IN A TRICKLE-BED REACTOR

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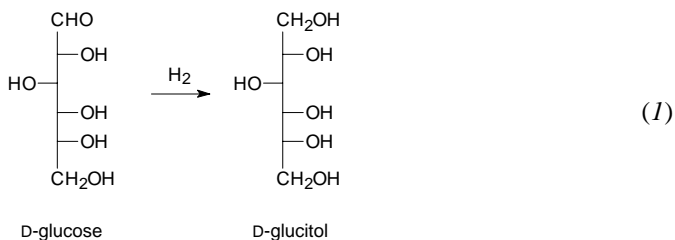
Catalytic hydrogenation of 40% aqueous solutions of D-glucose to D-glucitol was studied in a high-pressure trickle-bed reactor. The reactions were performed on a supported nickel catalyst at temperatures ranging from 115 to 165 °C and in the pressure range 0.5 to 10 MPa. The order of the reaction with respect to hydrogen is 0.65 and apparent activation energy 23.8–48.5 kJ mol^{-1}, the latter depending on initial molar glucose concentration and density and viscosity of the solution. The influence of external diffusion is necessary to take into account for scaling-up the process.
Key words: D-Glucose; Sorbitol; Hydrogenation; Nickel on kieselgur catalyst; Trickle-bed reactor.

D-Glucitol (D-Sorbitol) has a variety of applications in pharmaceutics, cosmetics and textile and pulp industry, from the synthesis of vitamin C to food products. Its esters and derivatives are used in plasticizers, emulsifiers and detergents. Production of sorbitol is mainly based on glucose hydrogenation on Raney nickel[1–3] in batch stirred tank reactors or continuous bubbled towers followed by catalyst separation and ion-exchange purification. Ruthenium appears as a new promising catalyst studied both supported on carrier[4] and in a form of homogeneous phosphine complex[5]. The use[4,6,7] of trickle-bed reactor with supported metal catalyst allows to eliminate catalyst separation and to improve the economy of the process.

The catalytic hydrogenation of glucose to glucitol is an exothermic reaction[6] ($\Delta H^0_{298} = -57.36$ kJ mol^{-1}), which proceeds according to the Eq. (*1*).

$$
\begin{array}{ccc}
\text{CHO} & & \text{CH}_2\text{OH} \\
\text{—OH} & & \text{—OH} \\
\text{HO—} & \xrightarrow{\text{H}_2} \text{HO—} \\
\text{—OH} & & \text{—OH} \\
\text{—OH} & & \text{—OH} \\
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH} \\
\text{D-glucose} & & \text{D-glucitol}
\end{array}
\tag{1}
$$

The back reaction, dehydrogenation of sorbitol, can be neglected due to high hydrogenation equilibrium constant, amounting 470 at 150 °C. Undesirable side and consecu-

tive reactions like isomerization[1] of D-glucose to D-galactose and hydrogenolysis[2] of glucitol to glycerol and propylene glycol play an important role outside of the temperature range used. The kinetics[8–10] of hydrogenation on Raney nickel have been studied in detail. The reaction is first order with respect to glucose and its order with respect to hydrogen ranges from 0.5 to 1.

The aim of the work was to test feasibility of D-glucose hydrogenation on commercial supported nickel catalysts in continuous trickle-bed reactor. The influence of reaction conditions and glucose solution properties on the rate of glucose conversion was investigated.

EXPERIMENTAL

The hydrogenation catalyst used was nickel on kieselgur (12% NiO, 2% Cr_2O_3) Cherox 37-03, Chemopetrol Group, a.s., Litvinov, Czech Republic, its original 8×8 mm pellets were crushed to size 2–3 mm. Two pretreatment methods were used; (i) the reduced and stabilized form of the catalyst was reactivated with hydrogen in the reactor at 175–200 °C for 3 h at space velocity 500 h^{-1} (catalyst a), and (ii) the catalyst was calcined for two hours at 420 °C and after that it was reduced for 12 h at 370 °C and of hydrogen space velocity 500 h^{-1} (catalyst b).

The hydrogenated aqueous solutions of glucose contained 40% D-glucose (I), 40% D-glucose and 15% D-glucitol (II), or 40% D-glucose and 27% D-glucitol (III).

The experiments were carried out in a trickle-bed micropilot reactor which consisted of a 540-mm long stainless steel tube with an inner diameter of 30 mm. The volume of the catalyst bed, which was located in the middle zone of the isothermal region, was 200 ml. The reactor was equipped with a thermocouple probe in the axis of the bed and an electronically controlled heating jacket. Hydrogen was fed from a gas cylinder and depressurized gas flow was set up at 5 l h^{-1}. An aqueous solution of glucose was fed with a high pressure pump (50–400 ml h^{-1}) to a preheater and mixed with hydrogen at the inlet of the reactor. At the outlet of the reactor, liquid and gas flows were cooled and separated in the phase separator.
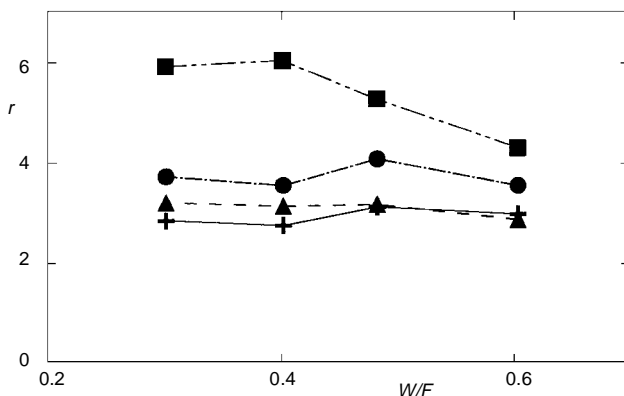

FIG. 1

Mean reaction rate r (mmol g^{-1} h^{-1}) *versus* residence time W/F (h g ml^{-1}) at various temperatures: (✚) 115 °C, (Δ) 130 °C, (●) 145 °C, (■) 165 °C, solution I, catalyst a

Determination of glucose in reaction mixtures was performed by spectrophotometry at 520 nm using an alkaline solution of 3,5-dinitrosalicylic acid. The recommended concentration range is 0.05–0.60 g l^{-1} glucose. The soluble nickel was determined as a red complex with diacetyl dioxime.

RESULTS AND DISCUSSION

In the trickle-bed reactor, kinetic experiments can be influenced by internal and external diffusion, inside and outside the particle of the catalyst. The internal diffusion limitation is generally accepted in reactor packed by pellets of porous catalyst. On the other hand, elimination of influence of external diffusion on kinetic results is necessary. In the kinetic regime, the rate of glucose hydrogenation is independent of the residence time of the liquid in the bed. In Fig. 1 is shown the mean reaction rate *vs* residence time dependence in the catalyst bed for various temperatures. The range of experimental conditions for kinetic measurements was found for space hour velocities of the liquid ranging from 1 to 2, and at temperatures from 115 to 165 °C. Therefore, further evaluation of kinetic parameters was carried out in this region.

The effect of partial pressure of hydrogen on the rate of glucose hydrogenation is presented in Fig. 2. The published[8–10] reaction orders with respect to hydrogen partial

TABLE I
Properties of reaction mixtures

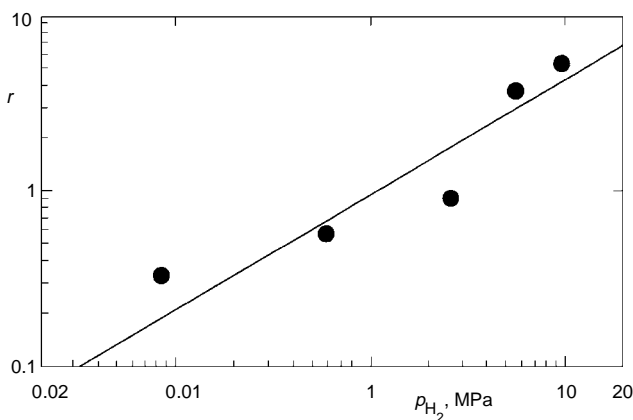| r, mmol g^{-1} h^{-1}	2.46	3.00	5.26	6.32
T, K	388	403	418	438

FIG. 2
Effect of partial pressure of hydrogen p_{H_2} on the hydrogenation rate of glucose r; liquid feed 0.4 l h^{-1}, 145 °C, solution I, catalyst a

pressure range from 0.5 to 1. In the presented experiments the straight line follows the rate order of 0.65. pH value of the resulting reaction mixture was between of 3.9 and 5.1.

From the mean reaction rates measured at 115–165 °C, under 10 MPa of total pressure and the feed of 400 ml h^{-1}, the apparent activation energy was obtained. The values for three glucose solutions and two catalyst pretreatment methods are presented in Table I. The catalyst a with pretreatment according to (i) exhibited higher activity; in addition, the activation energy is almost half of that for the catalyst b pretreated according to (ii). Therefore, the reaction rate was probably influenced by external mass transfer limitations.
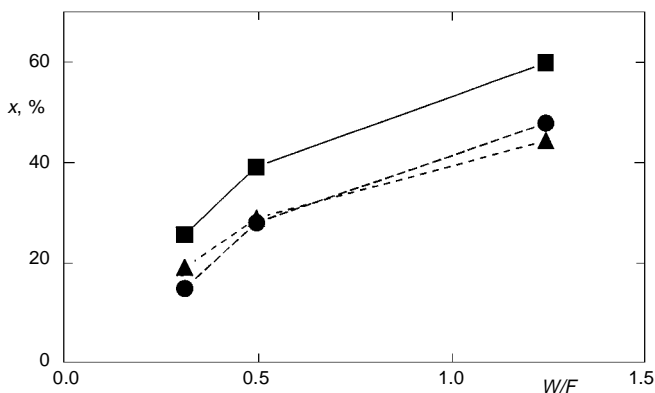

FIG. 3
Conversion x *versus* residence time W/F of various glucose solutions; 145 °C, 6 MPa total pressure, solution: ■ I, ▲ II, ● III, catalyst b
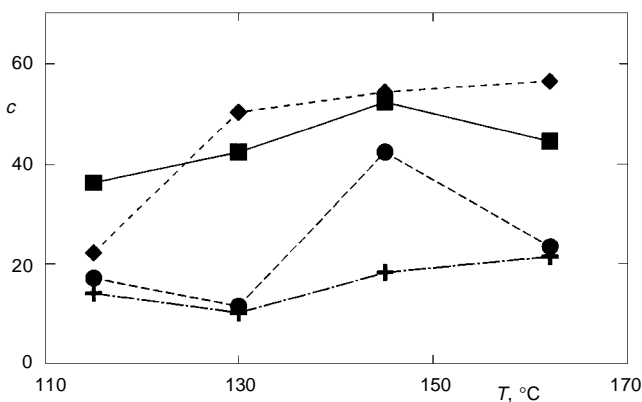

FIG. 4
Nickel leakage at various liquid feeds: ■ 50, ◆ 100, ● 250, ✚ 400 ml h^{-1}, solution I, catalyst b

Thus, external diffusion was responsible for different effects of residence time on glucose conversion for solutions with different water contents (see Fig. 3). The increase in density and especially in viscosity due to the sorbitol content shifted the reaction conditions to the diffusion region. The course of conversion of both sorbitol solutions was hardly to distinguish, so the decrease in activity may have been caused by sorbitol sorption.

The main problem of long-term utilisation of the supported catalyst is the leakage of active metal, which follows in decreasing of catalyst activity. In Fig. 4, the dependence of the nickel content in the reaction mixture on temperature is presented for various liquid feeds. It can be concluded that the metal content depends mainly on the residence time proportional to the reciprocal liquid feed and influence of temperature is not such important.

The commercially stabilized catalyst of the type a exhibited somewhat higher activity in comparison to the laboratory b type, probably due to possible metal sintration during laboratory catalyst reduction; on the other hand, the higher activity shifts the reaction to the diffusion-limited region.

CONCLUSIONS

Hydrogenation of glucose can be performed continually with more than 98% conversion in a trickle-bed reactor with the fixed bed of supported nickel catalyst. The reaction is first order with respect to glucose and of the order of 0.65 with respect to hydrogen. Nevertheless, the kinetic data obtained at conditions unaffected by internal and/or external diffusion can be misleading for scaling up the process. The real glucose hydrogenation proceeds under strong diffusion limitations due to high substrate concentrations, viscosity of solutions, temperature and pressure, and therefore the process must be investigated under these conditions.

SYMBOLS

c	concentration, mg l^{-1}
E_a	activation energy, J mol^{-1}
F	liquid feed, ml h^{-1}
p	pressure, MPa
r	reaction rate, mmol $g_{cat}^{-1}\,h^{-1}$
T	temperature, K
W	weight of catalyst, g
x	glucose conversion, %

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