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Kinetics of glucose hydrogenation in a trickle-bed reactor

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Abstract

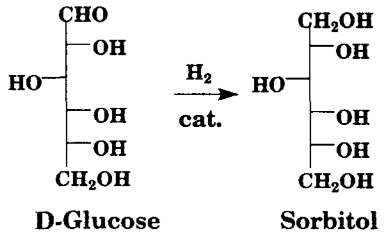
The kinetics of the catalytic hydrogenation of aqueous solutions of D-glucose to produce sorbitol was studied in a high pressure trickle-bed reactor with cocurrent downflow mode. The hydrogenation reactions were performed on a supported nickel catalyst in the temperature range 343 to 403 K and in the pressure range 4 to 12 MPa. Reaction rates were measured on the catalyst extrudates as such or after crushing and sieving them. The kinetic data obtained from measurements of the initial reaction rates as a function of temperature, pressure and mass of catalyst were interpreted with a Langmuir–Hinshelwood rate law where the reaction between adsorbed glucose and hydrogen is the rate-determining step.

1. Introduction

Sorbitol is a useful chemical which is used industrially in a variety of physical and chemical processes. It is the starting chemical for the synthesis of vitamin C, and is also widely used as a softener and as a humectant in various food products. Its esters and derivatives are used in protecting coatings, plasticizers, emulsifiers and detergents.

Sorbitol is still mainly produced by glucose hydrogenation on Raney-nickel catalysts in stirred tank reactors operating in batch mode. Continuous hydrogenation in fixed-bed, catalytic reactors would be better suited to cope with the increasingly high demand for this valuable intermediate obtained from renewable sources. In this study, glucose hydrogenation was conducted in a trickle-bed reactor filled with extrudates of supported nickel catalyst and kinetic data modelling was carried out.

The catalytic hydrogenation of glucose to sorbitol is a thermodynamically spontaneous, exothermic reaction ($K_{423\,K} = 473$, $\Delta H^{\circ}_{298\,K} = -58.5$ $kJ \cdot mol^{-1}$), which proceeds according to the following equation:



A number of papers have been devoted to the study of glucose hydrogenation kinetics [1–9]. However, these previous investigations were conducted in batch reactors. This work is, to our knowledge, the first attempt to perform kinetic data modelling in a trickle-bed reactor.

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2. Experimental

2.1. Catalyst

Silica–alumina supported nickel catalysts of composition 48.4% Ni; 5.15% Al; 8.46% Si; 0.27% Mg; 0.34% Na; 0.47% Fe were purchased from Harshaw (Ni-3266E 1/16 in.). They were available in the form of cylindrical extrudates (average particle length 6.3 mm and diameter 1.6 mm). These attrition resistant catalysts (side crushing strength of 48 N) had a relatively low surface area (140 $m^2 \cdot g^{-1}$), a total pore volume of ca. 0.48 $cm^3 \cdot g^{-1}$ and an apparent bulk density of 0.80 $g \cdot cm^{-3}$. They were in a reduced form, stabilized against pyrophorocity.

Catalysts were pretreated in the reactor under 2 MPa H_2-pressure (hydrogen flow: 20 $Nl \cdot h^{-1}$) with a temperature ramp of 40 $K \cdot h^{-1}$ until 413 K. After cooling at room temperature, the reactor was pressurized at 4–12 MPa with a continuous flow of hydrogen. Degassed, high purity water was pumped at 300 $ml \cdot h^{-1}$ and the temperature was increased from room temperature to the working temperature (343–403 K). Then, the water flow was replaced by a water solution of glucose (1–40 wt.-%).

2.2. Reactor and operating conditions

Experiments were carried out in a trickle-bed micropilot reactor (LCT 570 VINCI) given in Fig. 1. Hydrogen from a gas cylinder was depressurized to 4–12 MPa and its flow rate was monitored by a mass flow controller (Brooks 5850 TR) to obtain a constant flow of 10 to 100 $Nl \cdot h^{-1}$. Aqueous solutions of glucose fed with a high pressure pump (30–800 $ml \cdot h^{-1}$), were mixed with hydrogen at the inlet of the reactor which consisted of a stainless steel (316) tube (length 330 mm, internal diameter 18.6 mm, and internal volume 60 cm^3). A cocurrent down-flow of hydrogen and degassed aqueous solution of glucose were passed through the catalyst bed which was located in an isothermal zone obtained by controlling the temperature of two clam-shell type ovens. At the reactor outlet, liquid and gas flows were cooled and recovered in a separator where the liquid was recovered at the bottom and the gas was depres-

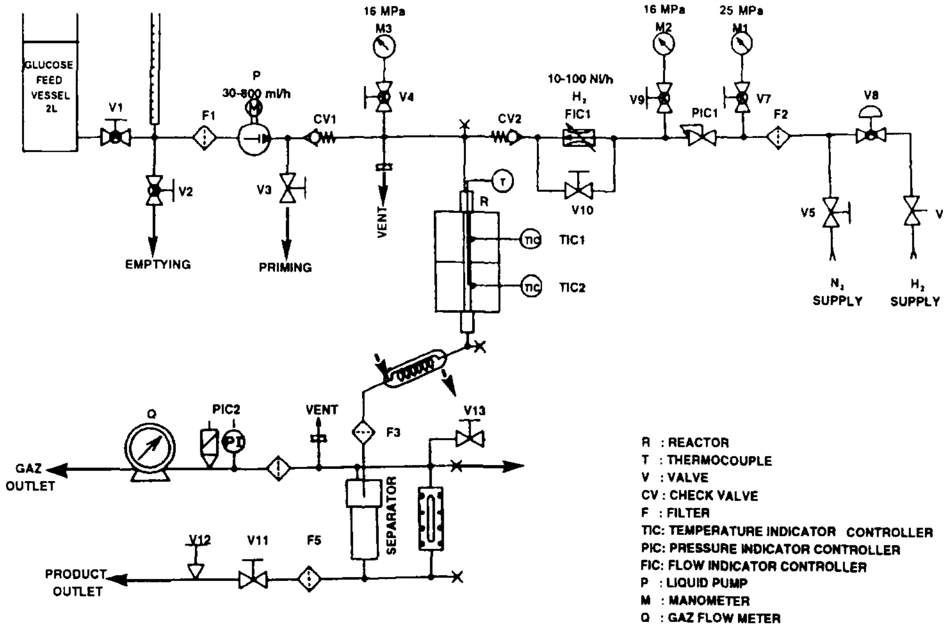

Fig. 1. Laboratory micropilot VINCI LCT 570.

surized to the atmospheric pressure by the backpressure regulator (Brooks 5835P).

The conversion and product distribution were followed by HPLC analysis of the solution taken from the gas–liquid separator at regular time intervals. A selectivity to sorbitol higher than 98% was always obtained and the stability of the catalysts was monitored during several days on stream.

3. Results and discussion

3.1. Influence of external and internal diffusion

In the kinetic regime, the rate of glucose hydrogenation expressed in mmol · h^{-1} should be proportional to the mass of catalyst and independent of the size of catalyst pellets. To verify these points, a 40 wt.-% aqueous solution of glucose (2.61 mol · l^{-1}) was hydrogenated under 8 MPa H_2-pressure at 403 K with different masses of catalyst (5 g and 15 g) and with different sizes of catalyst particles. Measurements were carried out on the 6–1.6 mm extrudates and on the crushed extrudates sieved into 0.5–0.8 mm particles. The liquid flow rate was fixed at 500 ml · h^{-1} to maintain a glucose conversion smaller than 20% in order to obtain accurate initial reaction rates. The reaction data for the extrudates and crushed extrudates are given in Table 1.

For both catalysts, a three-fold increase in the catalyst mass produces only a two-fold increase in the initial rate of glucose formation which indicates that the hydrogenation of glucose is partly limited by external diffusion. Moreover, for the same catalyst loading, the crushing of pellets strongly increases the rate of glucose hydrogenation which implies that the reaction rate on the extrudates is limited by internal diffusion.

Table 1
Influence of the catalyst mass

	Ni-3266E extrudated		Ni-3266E crushed	
Catalyst mass (g)	5	15	5	15
Nickel mass (g_{Ni})	2.5	7.5	2.5	7.5
Glucose conversion (%)	5.5	11	10.5	19
Reaction rate (mmol h^{-1})	72	143	136	248

Temperature: 403 K; pressure: 8 MPa; glucose concentration: 2.61 mol · l^{-1}; liquid flow-rate: 500 ml · h^{-1}; gas flow-rate: 20 Nl · h^{-1}.

To obtain a better insight on the influence of internal diffusion, glucose conversion was measured as a function of the residence time which was adjusted either by changing the liquid flow rate (36–500 ml · h^{-1}) or the catalyst mass (5–15 g).

Figs. 2a and 2b give the conversion of a 40 wt.-% aqueous solution of glucose as a function of residence time on the catalyst extrudates and on the crushed extrudates, respectively. In the latter case, the conversion at 0.2 g_{Ni} · h · ml^{-1} residence time reached 99.8% (12.5 mmol · h^{-1} · g_{Ni}^{-1}) whereas on the non-crushed extrudates the conversion was only 44% (5.5 mmol · h^{-1} · g_{Ni}^{-1}). Clearly, the reaction rate is severely limited by internal diffusion in the extrudates. In the case of crushed extrudates, it can be concluded that internal diffusion limitation is weak since an effectiveness factor $\eta = 0.9$ was obtained with the approach

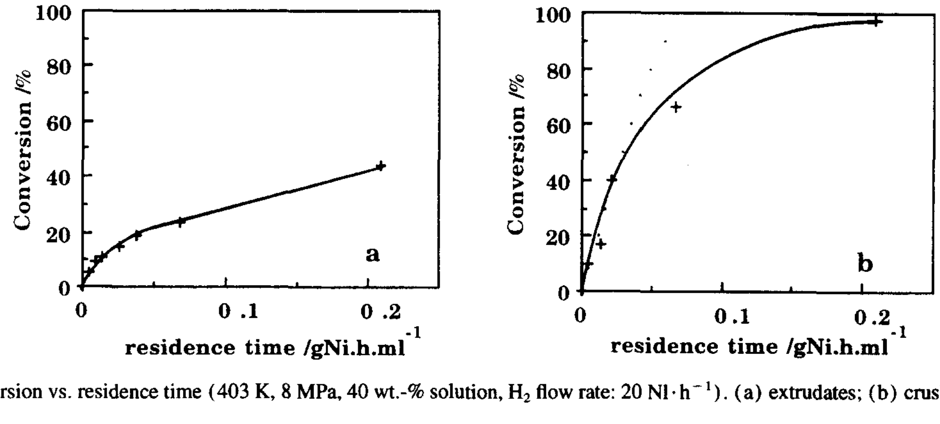

Fig. 2. Conversion vs. residence time (403 K, 8 MPa, 40 wt.-% solution, H_2 flow rate: 20 Nl · h^{-1}). (a) extrudates; (b) crushed extrudates.

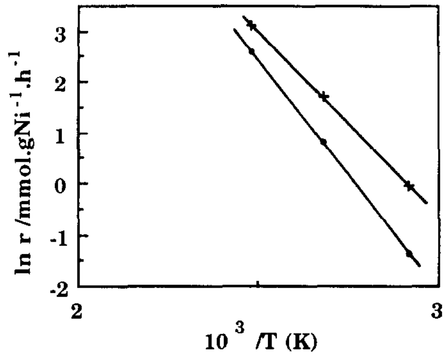

Fig. 3. Arrhenius plot on extrudates (+ 40 wt.-% solution; ● 10 wt.-% solution).

used by Weisz and Hicks [10]. Subsequent experiments were conducted on the crushed catalyst.

3.2. Kinetic studies

Kinetics studies were performed on the crushed catalysts with a low loading (5 g) and a high liquid flow rate (500 ml $\cdot$ h^{-1}) to minimize the effect of external diffusion. Under these conditions, the reactor works in the differential mode and the initial rates were measured more accurately. Preliminary experiments have been done to check that the sorbitol concentration has no effect on the glucose conversion.

From the Arrhenius plot of the initial rates measured in the range 343 K and 403 K under 8 MPa H_2 pressure (Fig. 3), an activation energy of about 67 kJ $\cdot$ mol^{-1} was obtained whatever the glucose concentration (10–40 wt.-%). This value, much larger than the activation energy of diffusion in liquids (12–21 kJ $\cdot$ mol^{-1}), indicates that the reaction rate is controlled by the kinetics on the metal surface.

Table 2 gives the initial specific rates at 403 K on the crushed catalysts as a function of glucose concentration ($C_g = 0.056$; 0.58; 2.6 mol $\cdot$ l^{-1} corresponding respectively to 1, 10 and 40 wt.-% aqueous solutions of glucose) and of the hydrogen pressure ($P_{H_2} = 4$, 8 and 12 MPa).

We have tried to account for these data with different rate laws corresponding to different rate controlling steps. The Langmuir–Hinshelwood rate law, assuming the desorption of sorbitol as the rate-determining step as previously proposed by Brahme and Doraiswamy [8], could not account satisfactorily for the reaction data. Only, the following rate law

$$r = k \cdot (K_g C_g \cdot K_{H_2} P_{H_2} / (1 + K_g C_g + K_{H_2} P_{H_2})^2) \qquad (1)$$

corresponding to a rate control by surface reaction between adsorbed glucose and adsorbed hydrogen, can be used to model the reaction kinetics as shown hereafter. Note that the term, $K_s C_s$, corresponding to the fraction of the surface occupied by adsorbed sorbitol, has been omitted because different amounts of sorbitol added to the reaction medium have no effect on glucose hydrogenation rates which indicates that sorbitol adsorption on nickel is weak, therefore $K_s C_s$ is negligible compared to others terms in Eq. (1).

From Eq. (1), two linear transforms, (2) and (3), can be written:

$$(P_{H_2}/r)^{1/2} = (K_{H_2}/k \cdot K_g C_g)^{1/2} P_{H_2} + (1 + K_g C_g)/(k \cdot K_{H_2} K_g C_g)^{1/2} \qquad (2)$$

$$(C_g/r)^{1/2} = (K_g/k \cdot K_{H_2} P_{H_2})^{1/2} C_g + (1 + K_{H_2} P_{H_2})/(k \cdot K_g K_{H_2} P_{H_2})^{1/2} \qquad (3)$$

The plots of $(P_{H_2}/r)^{1/2}$ as a function of P_{H_2} obtained from the rate measurements at three different glucose concentrations, give straight lines (Fig. 4a). Similarly, the plots of $(C_g/r)^{1/2}$ as a function of C_g from rate measurements at three

Table 2
Initial rates of the glucose hydrogenation at 403 K on crushed catalysts vs. glucose concentration and H_2 pressure

C_g (mol $\cdot$ l^{-1})	PH_2 (MPa)	r (mmol/h $\cdot$ g_{Ni})
0.056	4	5.2
	8	5.9
	12	6.4
0.58	4	22
	8	33.8
	12	38
2.61	4	37.5
	8	53.1
	12	53.1

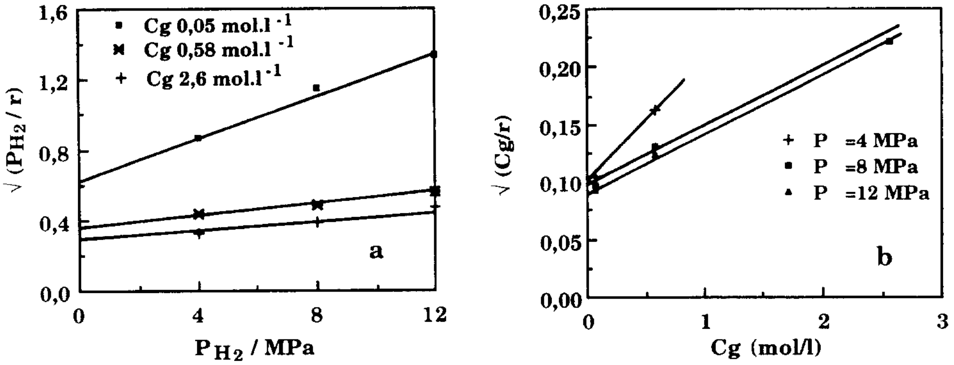

Fig. 4. Linear transform of Langmuir–Hinshelwood rate law. (a) $(P_{H_2}/r)^{1/2}$ vs. P_{H_2}; (b) $(C_g/r)^{1/2}$ vs. C_g.

hydrogen pressures, give straight lines (Fig. 4b). From the values of the slopes and of the ordinate intercepts of these linear transforms, it is possible to deduce the rate constant k, and the adsorption equilibrium constants K_g and K_{H_2} of glucose and hydrogen, respectively.

For example, with $C_g = 0.58$ mol·l^{-1}, (5a), the transform $(P_{H_2}/r)^{1/2}$ vs. P_{H_2}, gives:

$$(K_{H_2}/k \cdot K_g \cdot 0.58)^{1/2} = 1.71 \cdot 10^{-2} \text{ and}$$

$$(1 + K_g \cdot 0.58)/(k \cdot K_{H_2} K_g \cdot 0.58)^{1/2} = 0.354$$

Similarly, with $P_{H_2} = 8$ MPa, (5b), the transform $(C_g/r)^{1/2}$ vs. C_g, leads to:

$$(K_g/k \cdot K_{H_2} \cdot 8)^{1/2} = 0.051 \text{ and}$$

$$(1 + K_{H_2} \cdot 8)/(k \cdot K_g K_{H_2} \cdot 8)^{1/2} = 0.093$$

Thus, we obtain a system of four equations with three unknowns. Since three different values of C_g and P_{H_2}, respectively, have been considered, twelve equations are available from which the best agreement is obtained with: $k = 497$ mmol·h^{-1}·g$_{Ni}^{-1}$, $K_g = 0.8654$ l·mol^{-1} and $P_{H_2} = 0.0723$ MPa^{-1}.

With these values the rate equation becomes:

$$r\,(\text{mmol} \cdot \text{h}^{-1} \cdot \text{g}_{Ni}^{-1}) = 497 \times \frac{0.8654 C_g \times 0.0723 P_{H_2}}{(1 + 0.8654 C_g + 0.0723 P_{H_2})^2} \quad (4)$$

Taking in account the activation energy calculated earlier (67 kJ·mol^{-1}), the general rate equation is:

$$r\,(\text{mmol} \cdot \text{h}^{-1} \cdot \text{g}_{Ni}^{-1}) = \frac{1.3 \times 10^{10} C_g P_{H_2}}{(1 + 0.8654 C_g + 0.0723 P_{H_2})^2} e^{-(8000/T)} \quad (5)$$

This rate equation has been checked in two different ways. Firstly, we have verified that this equation accounts for the experimental curve 2b, giving conversion as a function of residence time. Since $r = -\mathrm{d}C_g/\mathrm{d}\delta$, it becomes

$$-\frac{\mathrm{d}C_g}{\mathrm{d}\delta} = \frac{249 \times C_g}{(1.578 + 0.8654 C_g)^2} \quad (6)$$

Since $C_g = C_{g0}\,(1 - \tau)$:

$$\frac{\mathrm{d}\tau}{\mathrm{d}\delta} = \frac{249(1 - \tau)}{(1.578 + 0.8654 C_{g0}(1 - \tau))^2} \quad (7)$$

The integration of Eq. (7) gives a relation between the conversion of glucose and the residence time at different values of C_{g0}:

$$\delta = -0.01 \ln(1 - \tau) + 0.011 C_{g0} \times \tau - 0.0015 C_{g0}^2 (1 - \tau)^2 + 0.0015 C_{g0}^2 \quad (8)$$

In the case of a 40 wt.-% solution ($C_{g0} = 2.61$ mol·l^{-1}), Eq. (8) becomes:

$$\delta = -0.01 \ln(1 - \tau) + 0.0287 \times \tau - 0.01(1 - \tau)^2 + 0.01 \quad (9)$$

The plot of this model equation is given on Fig. 2b as a dotted line. There is good agreement with the experimental curve for residence times lower than 0.04 g$_{Ni}$·h·ml^{-1} i.e. for conversions up to

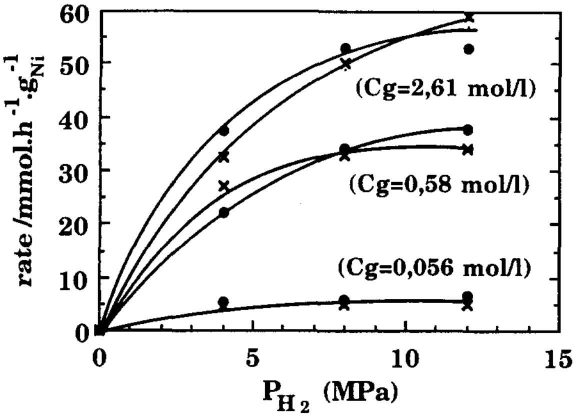

Fig. 5. Experimental (●) and calculated (×) initial rates of reaction as a function of hydrogen pressure and glucose concentration.

50%. The deviation at higher conversion is probably due to the influence of external diffusion.

Secondly, we have checked that the rate equation accounts for the reaction data given in Table 2. Indeed, Fig. 5 shows that there is good agreement between the calculated and experimental initial rates as a function of the hydrogen pressure and glucose concentration.

4. Conclusion

Glucose hydrogenation can be conducted at 100% conversion in a trickle-bed reactor with a fixed-bed of supported nickel catalyst. Kinetic data modelling was satisfactorily achieved with a Langmuir–Hinshelwood rate law where the reaction between glucose and hydrogen, both adsorbed on the nickel surface, is rate-determining. The constants for the rate law have been established from a set of experiments conducted with different glucose concentrations and hydrogen pressures. It was shown that the calculated rates match the experimental rates measured at low conversion. Furthermore, the calculated curve giving the conversion as a function of residence time is in good agreement with the experimental curve, at least at low conversion when the external diffusion does not perturb the kinetics.

Acknowledgements

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Appendix 1

τ	conversion of glucose
δ	residence time, defined as m_{Ni}/F where m_{Ni} is the nickel mass and F the flow of aqueous solution of glucose ($g_{Ni}\cdot h\cdot ml^{-1}$)
r	rate of glucose hydrogenation (mmol glucose$\cdot h^{-1}\cdot g_{Ni}$)
C_g	glucose concentration ($mol\cdot l^{-1}$)
P_{H2}	hydrogen pressure (MPa)
k	rate constant ($mmol\cdot h^{-1}\cdot g_{Ni}^{-1}$)
K_g	adsorption equilibrium constant for glucose ($l\cdot mol^{-1}$)
P_{H2}	adsorption equilibrium constant for hydrogen (MPa^{-1})
0 in subscript	initial condition

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