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Sugar hydrogenation in continuous reactors: From catalyst particles towards structured catalysts

Víctor A. Sifontes Herrera[a], Daniel E. Rivero Mendoza[a], Anne-Riikka Leino[b], Jyri-Pekka Mikkola[a,c], Aleksey Zolotukhin[d], Kari Eränen[a], Tapio Salmi[a,*]

[a] Laboratory of Industrial Chemistry and Reaction Engineering, Process Chemistry Centre, Åbo Akademi University, FI-20500 Turku/Åbo, Finland
[b] Microelectronics and Materials Physics Laboratories, University of Oulu, FI 90570 Oulu, Finland
[c] Chemistry Department, Chemical and Biochemical Centre, Umeå University, SE 90187 Umeå, Sweden
[d] Department of Physics and Mathematics, University of Eastern Finland, FI 80101 Joensuu, Finland

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ABSTRACT

The density, viscosity and hydrogen solubility of selected sugars (L-arabinose, D-galactose, D-maltose and L-rhamnose) were determined at different temperatures (generally 60, 90 and 130 °C). The role of internal diffusion resistance in porous catalyst layers for sugar hydrogenation was confirmed by numerical simulations based on kinetic data and physical properties. The simulations suggested the use of small catalyst particles or structured catalysts in continuous hydrogenation of the sugars to sugar alcohols. Continuous hydrogenation of L-arabinose was carried out in a laboratory-scale fixed bed reactor with ruthenium catalysts on three different supports (active carbon clothes, carbon nanotubes on sponge-like metallic structures, conventional active carbon catalyst particles). It was proved that continuous hydrogenation is a feasible alternative to batch technology for sugar hydrogenation over conventional catalyst particles and structured catalysts: L-arabinose was converted to arabitol with a very high selectivity.

1. Introduction

Selective catalytic hydrogenation of naturally appearing sugar molecules such as glucose, fructose, xylose, and lactose to the corresponding sugar alcohols is an environmentally benign route to the production of alternative sweeteners based on renewable sources. The preparation of sugar alcohols is based on the following principle: heterogeneous solid, metal-based catalysts, such as sponge nickel and supported ruthenium are used in an aqueous environment and the hydrogen addition is materialized through molecular hydrogen. Thus the use of stoichiometric reducing agents, such as sodium borohydride, is avoided and the hydrogenation process produces no inorganic salts as waste material.

The conventional production technology of sugar alcohols is based on the use of batchwise operating slurry reactors: finely dispersed, supported or sponge metal catalyst (catalyst particles smaller than 0.1 mm) are immersed in a batch of an aqueous sugar solution, to which hydrogen is continuously added so that the pressure is kept constant. Among the reported operating conditions, it can be found that hydrogen pressure is typically kept at 30–180 bar and the temperature ranges from 80 °C to 150 °C [1,2]. The batchwise production technology is well-established, but as the production volumes of sugar alcohols are expected to increase, continuous production technology should be regarded as a serious option.

Continuous reactor technology is a well-established process for the production of bulk chemicals as well as components in fossil and renewable fuels. The most common continuous reactor in catalytic processes is fixed bed, its main benefit being that it is a proven technology and modeling of two-phase fixed beds (gas or liquid + a solid catalyst) is principally well known. However, as a third phase enters the scene, the picture is essentially complicated but, in general, three-phase fixed beds are reliable and sustainable. Furthermore, the catalyst activities can easily be monitored, since the decline in the activity is directly revealed and both the pressure drop and the retarding effect of internal diffusion are illustrated by carrying out experiments with different particle sizes.

* Corresponding author.
E-mail address: tapio.salmi@abo.fi (T. Salmi).

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In recent years, the continuous operation in sugar hydrogenation has been demonstrated, for instance, for glucose hydrogenation in fixed beds, in monoliths and on activated carbon cloths [1,3,4]. Furthermore, it is possible to carry out sugar hydrogenation in loop reactors, where the liquid, containing the catalyst, is recirculated through an external loop system [1]. Since the sugar molecules are large and the solubility of hydrogen is limited, the diffusion limitation inside the porous catalyst layer becomes severe in porous catalyst layers, as has been demonstrated experimentally and by numerical simulations [5,6]. Therefore, egg-shell catalyst pellets and structured catalysts can be considered as feasible alternatives to slurry technology.

The basis of any kind of technology development is the intrinsic reaction kinetics, which has been measured experimentally and modeled mathematically for several sugars [7]. However, as incursion into more complex production technologies progresses, the need to measure physical properties arises. Density, viscosity and hydrogen solubility data is of high importance when dealing with systems prone to internal and external mass transfer limitations (such as conventional fixed bed reactors).

2. Experimental section

2.1. Density measurements

Density measurements for aqueous sugar solutions (l-arabinose, D-galactose, D-maltose, L-rhamnose) were carried out in an Anton-Paar DMA-512P oscillating U-tube density meter equipment (±0.0001 g/cm^3), operating at a pressure range of 1–20 bar and between 60 and 130 °C. A Grant GP-200 (±0.1 °C) thermostatic bath with oil as heating fluid was used to control the temperature within the measuring cell. To recognize inaccuracies in the temperature, due to heat loss, a thermocouple (±1 °C) was inserted directly into the measuring chamber to monitor the temperature. The system was pressurized with nitrogen (AGA 99.999%) at 5 bar to prevent evaporation of the solutions fed at high temperatures. The density values were obtained directly from the device.

Sugar solutions of 25 and 50 wt.% were prepared for each sugar sample. Before feeding the samples into the equipment, the measuring cell was cleaned several times with hot water and ethanol to wash out any impurity that could compromise the reliability of the measurement. The cell was flushed with nitrogen (AGA 99.999%) to dry it. The solution was fed in excess to evacuate gas bubbles using sterilized syringes. At this instant, all the valves were closed, the system was pressurized and it was considered to be the starting point of the measurement. Once the density values were recorded, the system was purged with water and ethanol several times.

2.2. Viscosity measurements

The viscosities of the different aqueous sugar solutions were measured by using an Ostwald glass capillary viscometer, operating between 60 and 90 °C and at atmospheric pressure. Solutions of 25 and 50 wt.% were prepared for each of the studied sugars (L-arabinose, D-galactose, D-maltose, L-rhamnose).

The Ostwald viscometer was filled with the different solutions and placed vertically in a Heidolph Ekt 3001 water thermostatic bath with a ±1 °C precision. Once the thermal equilibrium was reached, the efflux times of the liquids were recorded with a digital stopwatch with a precision of ±0.01 s. The measurements were performed in quintuplets at the different conditions of temperature and composition to minimize the experimental error.

The viscosity determination by using Ostwald viscometers is an indirect technique, i.e. the measured variable is not the viscosity itself but the efflux time of the liquid through the capillary in the viscometer. Once the efflux times are determined, the kinematic viscosity is obtained from $\nu_1 = \left(\frac{t_1}{t_0}\right) \cdot \nu 0$, where ν_0 [m^2/s] is the kinematic viscosity of a known fluid; t_0 [s] is the efflux time of the known liquid through the viscometer; t_1 [s] is the efflux time of the sample through the viscometer and ν_1 [m^2/s] is the kinematic viscosity of the sample. The dynamic viscosity (μ) of the sample is then obtained with the aid of the previously determined kinematic viscosity and the density of the solution: $\mu = \nu\rho$. The reference fluid was de-ionized water and its viscosity values were obtained from the literature [8]. This calibration of the viscometer with pure water was carried out for all the studied temperatures.

To verify that the test solutions remained at their nominal concentrations within reasonable limits, solution samples were withdrawn before and after the determinations and analyzed by high-performance liquid chromatography (HPLC). No significant changes in the concentrations were observed.

2.3. Hydrogen solubility measurements

The hydrogen solubility of different aqueous solutions of sugars were measured in-situ with a Fugatron HYD-100 equipped with a polymeric perfluoro-alkoxy copolymer (FPA) hydrogen-permeating probe, operating between 90 and 130 °C and 10–60 bar. Table 1 shows the different sugar solutions used for the hydrogen solubility measurements.

The Fugatron probe was attached to a pressurized batch reactor (Parr 4561, 300 mL) equipped with baffles, a gas entrainment impeller, a heating jacket, a temperature and stirring rate controller (Parr 4843), a Brooks Instruments pressure controller and microprocessor (Brooks 5866 and Brooks 0154 respectively), and a bubbling chamber for the sugar solution pre-treatment.

After feeding the different sugar solutions to the system, the reactor was purged with nitrogen for 15 min to evacuate oxygen. The gas inlet was switched to hydrogen and the Fugatron instrument was switched on. Subsequently, pressurizing with hydrogen and heating were carried out simultaneously until the desired operating conditions were reached. The stirring speed was set to 1000 rpm to suppress external mass transfer limitations in the system [9]. At the given temperature, pressure and stirring conditions, the system was left to stabilize during 15 min to guarantee that the solution was saturated with hydrogen and then the values of the hydrogen concentration were recorded.

Calibration of Fugatron HYD-100 is an essential part of the measurement. The Fugatron HYD-100 instrument gives information about the concentration (in ppm) of the permeated hydrogen from the problem solution into the carrier gas. Hence, a calibration of the equipment needs to be done before each measurement to estimate the calibration constant (f), which correlates to the concentration of hydrogen in the liquid bulk via the following equation,

$$C_{L,H2} = f.x \quad (1)$$

where f is the equipment calibration constant; $C_{L,H2}$ [mol/L] is the concentration of hydrogen in the bulk; and x [ppm H_2] is the concentration of hydrogen permeated in the carrier gas.

Table 1
Sugar solutions for hydrogen solubility measurements.

Sample	Concentration [wt.%]
L-arabinose	10
L-rhamnose	10
D-maltose	10
D-galactose	4