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Hydrogenation of D-fructose over activated charcoal supported platinum catalyst

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ABSTRACT

Hydrogenation of D-fructose in the presence of activated charcoal supported platinum as a catalyst was employed for the preparation of D-mannitol. The effects of the reaction time (10–120 min), reaction temperature (283–333 K), and catalyst to D-fructose ratio (1–6%) on the yield of D-mannitol were studied. 45% D-mannitol yield, 41% D-sorbitol yield, and 95% D-fructose conversion were obtained at the conditions of 120 min reaction time, 333 K reaction temperature and 6% catalyst to D-fructose ratio. The reaction kinetic was also studied and the data were modeled by zero-, first- and second-order reaction equations. In the operating regimes studied, the results show that the hydrogenation reaction is of a first order with respect to D-fructose concentration. Also the activation energy of the reaction was determined, and found to be 11 kJ/gmole.

1. Introduction

The hydrogenation of D-fructose to D-mannitol is of great industrial importance, principally because D-mannitol is an important additive in cosmetics, food industry and drugs. An important use of D-mannitol is for the preparation of mannitol hexanitrate which is a well known vasodilator used in the treatment of hypertension (Ghoreishi and Shahrestani, 2009).

D-Mannitol can be extracted from many plant raw materials such as manna, seaweed, and algae. However, the extraction of D-mannitol from these raw materials is not a good commercial source. Both fermentation and catalytic hydrogenation processes are used. The catalytic hydrogenation process has been widely used for the commercial production of D-mannitol (Qjamo *et al.*, 2000).

Nowadays, D-mannitol is usually obtained industrially by catalytic hydrogenation of fructose, sucrose or high fructose syrups. An equal portion of mixture of both D-mannitol and D-sorbitol, the second product of hydrogenation, is obtained by the hydrogenation of D-fructose. Hydrolysis of sucrose produces a mixture of glucose and fructose, from which fructose can be separated by chromatography. Higher yields of D-mannitol are obtained when syrups with high fructose-contents are used (Hoffer *et al.*, 2003).

The fine chemical industries require very clean processes which must prevent any part of the catalyst to end up in the final products. Many studies have been published in the past concerning this catalytic reaction, using noble metals as catalysts (Heinen *et al.*, 2001), showing the high activity of nickel and ruthenium. These metals have been supported using many supports such as alumina and micro-porous carbon. However, noble metals leaching as well as long term stability have been reported to be important issues during the catalytic hydrogenation of D-fructose to D-mannitol. Activated charcoal is charcoal that has been treated with oxygen to open up millions of tiny pores between the carbon atoms. This activated charcoal is widely used because it is cheap, has a high surface area and is resistant to both strongly acidic and strongly basic media. Another advantage is the easy recovery of the precious metal from the catalyst by burning off the charcoal support (Mukherjee *et al.*, 2009). Platinum and ruthenium are the most active catalysts in carbohydrate hydrogenations, both in homogeneous and in heterogeneous catalysis (Crezee *et al.*, 2003).

The catalytic hydrogenation process was used by different researchers to prepare D-mannitol from different feedstocks using different catalysts. Makkee *et al.* (1985) prepared D-mannitol by catalytic hydrogenation of D-glucose over a copper on silica catalyst. Barbosa *et al.* (1999) used NaY zeolite supported ruthenium catalyst for the preparation of D-mannitol by hydrolysis and hydrogenation of sucrose. Heinen *et al.* (2000) prepared D-mannitol by catalytic hydrogenation of fructose over Ru/C catalyst. Also, Kuusisto *et al.* (2005) used CuO–ZnO catalyst for the preparation of D-mannitol by catalytic hydrogenation of D-fructose.

This paper describes a study on the catalytic hydrogenation of D-fructose using platinum on activated charcoal catalysts, besides

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Nomenclature

A	frequency factor
C	initial concentration of D-fructose solution (wt%)
$(C_6H_{12}O_6)_0$	initial concentration of D-fructose in reaction solution (gmole/l)
$(C_6H_{12}O_6)$	final concentration of D-fructose in reaction solution (gmole/l)
E	activation energy (kJ/gmole)
k_0	zero-order reaction rate constant (gmole/liter/min)
k_1	first-order reaction rate constant (/min)
k_2	second-order reaction constant (l/gmole/min)
Q_H	volumetric flow rate of hydrogen (l/min)
R	gas constant (8.314 J/gmole/K)
t	time (min)
T	temperature (K)
V	volume of reaction solution (ml)
W_{fi}	weight of D-fructose in the feed (g)
W_{fo}	weight of D-fructose in the product (g)
W_m	weight of D-mannitol in the product (g)
W_s	weight of D-sorbitol in the product (g)

the kinetics of this reaction and an investigation of the effect of reaction time, reaction temperature, and catalyst ratio on the yield of D-mannitol.

2. Experimental work

2.1. Materials

2.1.1. D-Fructose

D-Fructose (supplied by Hopkins and Williams, Searle Company) of purity 99% was used for the preparation of D-mannitol.

2.1.2. Hydrogen

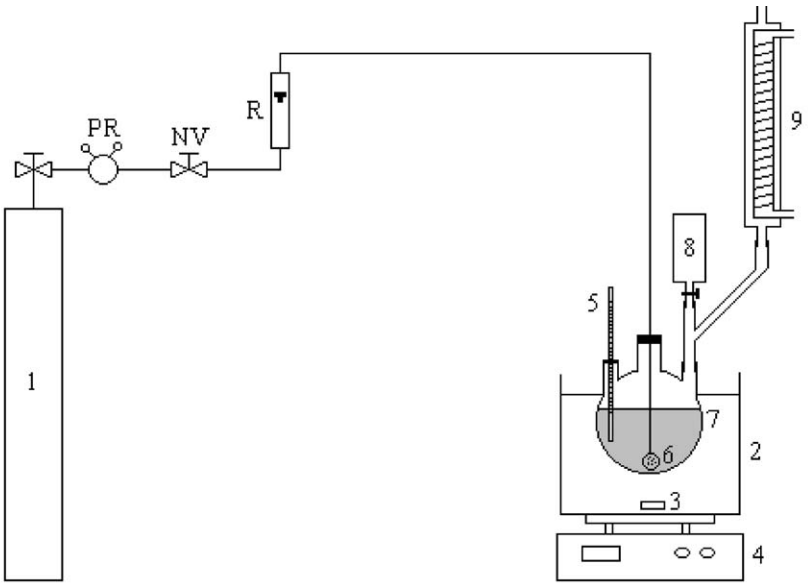
Hydrogen (supplied by Mox-Liade Gases Sdx. Bhd. Factory) of purity 99.9% was used for D-fructose hydrogenation.

2.1.3. Catalyst

Platinum on activated charcoal (supplied by Sigma–Aldrich Company) of a loading 5 wt% Pt, an average pore size 3.7 μm, and surface area 1000 m^2/g was used for the hydrogenation of D-fructose.

2.2. Apparatus

A schematic diagram of laboratory experimental unit used for the hydrogenation of D-fructose is shown in Fig. 1. This unit consists of a reaction flask which was a pyrex three-necked 250 ml glass flask. The feed was charged to the reaction flask through a glass dropping funnel with a capacity of 100 ml, and the hydrogen gas was fed to the reaction flask by means of a special perforated bulb tube (Sparser) in order to keep the solution in considerable agitation and to prevent settling of the catalyst. The loss of vapor from the reaction flask was prevented by using a pyrex double pipe glass condenser with an inner pipe of spiral shape. The reaction flask temperature was measured by a glass thermometer range from 0 to 100 °C, and maintained at the desired value by the use of a water bath. The hydrogen gas flow rate was controlled by a needle valve (Micro Hooke mite) and measured by a rotameter (GEC-Elliott). The composition of product was measured by a Shimadzu HPLC system (Shimadzu, Kyoto, Japan) on a Supelcosil LC-NH_2 column (4.6 mm × 250 mm, 5 μm aminopropyl-bonded silica) with acetonitrile: water (85:15) as the mobile phase. The column was run at 298 K at a flow rate of 1 ml/min. Sugars and sugar alcohols were detected using a refractive index (RI) detector (RID-6A; Shimadzu). Standards were run separately to determine the elution profile and a mixture of standards (such as D-fructose, D-mannitol and D-sorbitol) was also run to determine the chromatographic resolution.



1 Hydrogen cylinder 4 Magnetic stirrer hot plate 7 Reaction flask PR Pressure regulator
2 Water bath 5 Thermometer 8 Dropping funnel NV Needle valve
3 Stir bar 6 Sparser 9 Condenser R Rotameter

Fig. 1. Schematic diagram of D-fructose hydrogenation unit.