Chemical Engineering Journal 358 (2019) 351–361

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Hydrothermal gasification of sorbitol: H_2 optimisation at high carbon gasification efficiencies

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HIGHLIGHTS

- High temperatures reduce H_2 yield due to its consumption in side reactions.
- N_2 stripping enhances H_2 yield without compromising on carbon gasification.
- Developed model provides a good prediction of data in continuous and batch studies.
- Model predicts promising H_2 productivity on an industrial scale.

ARTICLE INFO

Keywords:
Sorbitol
Hydrothermal gasification
Hydrogen
Kinetics
Mass transfer

ABSTRACT

Using both experiments and modelling, hydrothermal gasification of sorbitol (SB) aiming at maximal carbon to gas conversion and H_2 production was investigated over a wide temperature range (270–350 °C). Kinetics were studied in a continuous tubular reactor using a $Pt/\gamma\text{-}Al_2O_3$ catalyst. The addition of N_2, resulting in lower H_2 concentrations in the liquid phase, was found to have a beneficial effect in terms of higher H_2 yield without compromising on the carbon gasification. The highest H_2 yield obtained in this work was 4 mol H_2/mol SB. Existing reaction schemes for sorbitol gasification were used to derive a path-lumped scheme. A multi-phase reactor model including a path-lumped scheme and gas-liquid-solid mass transfer was developed and parameterized based on datasets with varying temperature, space velocity, inlet gas composition (N_2 or H_2) and gas-liquid flow ratio. The developed model was used to provide guidelines for the design of an industrial reactor for the gasification of 10 tons/h of 10 wt% aqueous sorbitol. The effect of N_2 stripping and industrially attainable k_La values were found to boost the H_2 yield from 4 to 12 mol H_2/mol SB making it an attractive process for further consideration.

1. Introduction

Hydrothermal gasification of biomass feeds to valuable chemicals and fuels has received a significant amount of attention in the past few decades. Typically, this type of gasification has been categorised based on temperature ranges of operation. The youngest technology is aqueous phase reforming (APR), developed by Dumesic et al [1]. It requires lower temperatures (200–280 °C) and has been found to be successful in the production of H_2 and alkanes from oxygenates [2]. APR was found to be promising due to its low energy requirements, especially when considering dilute organic streams. Despite many studies in the past decade in the areas of catalyst development and mechanistic studies for model compounds, there is no commercial application yet for relatively complex biomass feeds. Challenges include long operation times (large reactors) due to low kinetic activity at low temperatures and moving from noble metal catalysts towards bi-metallic catalysts to reduce costs while maintaining a good selectivity towards H_2 production [3].

At higher, but still sub-critical temperatures (280–350 °C), shorter residence times are used. Work in this temperature region is limited in comparison to APR and is typically conducted in conjunction with super-critical water gasification (SCWG) [4,5]. SCWG (400–800 °C) has also been extensively studied for complex biomass feedstock. SCWG was found to provide a high reaction rate and selectivity (catalytic) to H_2 at higher temperatures by taking advantage of the thermo-physical properties of water under these conditions, which enable radical based cracking of biomass to small molecules, ending up in the gas phase. However, due to the need for harsh conditions, corrosion of construction material is significant, and considering the limited value of the products, the process is often not economically justified [6,7].

Fig. 1 shows the hydrothermal gasification of C6 sugars and sugar

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https://doi.org/10.1016/j.cej.2018.10.008
Received 13 June 2018; Received in revised form 7 September 2018; Accepted 1 October 2018

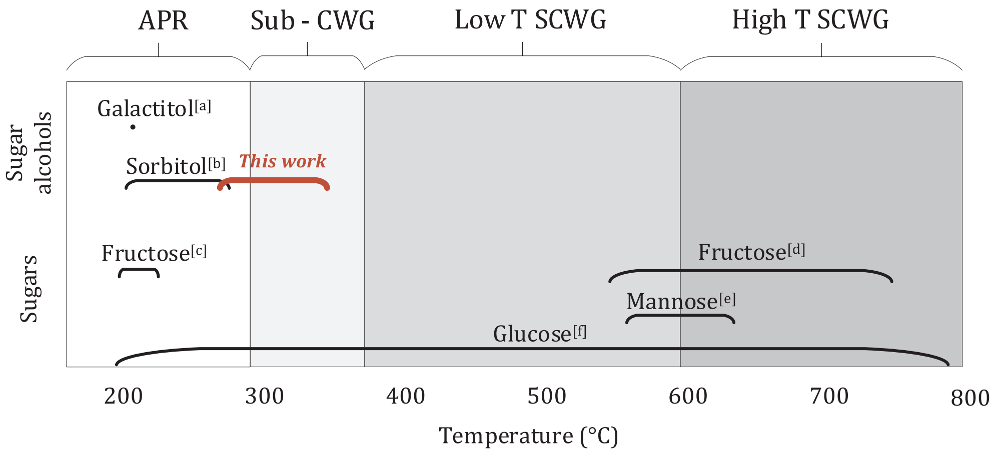

Fig. 1. Studied temperature ranges for hydrothermal gasification of C6 sugars and sugar alcohols. References – a: [8], b: [9], c: [10], d: [11], e: [12], f: [6].

alcohols studied in the entire temperature range, as well as the range considered in this work, indicating the knowledge gap that the current distribution is addressing.

Among biomass-derived materials, sorbitol has been used as a key model oxygenate compound. Sorbitol was found to be more stable under reforming conditions (220–275 °C) in comparison to glucose, it's dehydrogenated counterpart, leading to an increase in H_2 selectivity from 13 to 62% under APR conditions [13]. Sorbitol, therefore, offers a cleaner route towards efficient gas production in comparison to glucose. The treatment of sugars derived from aqueous biomass streams would require a hydrotreating step prior to gasification in order to reduce the coke formation that is associated with the direct gasification of sugars. This is a topic for future studies.

The conversion of sorbitol consists of a complex network of reactions and several studies have been conducted to gain more insight into the reaction mechanism [14–16]. However, all the studies have been conducted within a limited temperature range under APR conditions [9]. With respect to kinetic modelling, Aiouache et al. [17] conducted batch experiments in a temperature range of 220–250 °C using mono and bi-metallic Ni catalysts and developed a path-lumped model for the reforming of sorbitol by using a pseudo-generic intermediate. Kirilin et al. [18] conducted continuous tests in a fixed bed reactor and developed a kinetic model to describe sorbitol reforming at 220 °C using a Pt/γ-Al_2O_3 catalyst. Fig. 2(a) highlights key reactions reported for the hydrothermal gasification of sorbitol.

In this work, the kinetics of the hydrothermal gasification of sorbitol are investigated over a wider temperature range, encompassing both APR and sub-critical conditions (270–350 °C). Experiments are conducted using a commercial 5 wt% Pt/γ-Al_2O_3 catalyst (Sigma-Aldrich) in a continuous up-flow packed bed reactor. It is known that Pt catalysts are expensive and Pt/γ-Al_2O_3 needs improvements with respect to hydrothermal stability [19,20]. However, this work does not focus on catalyst development but on the use of an existing commercially available catalyst in the development of a model that can be used for predictions of H_2 production and carbon gasification on an industrial scale. In this regard, Pt/γ-Al_2O_3 is a benchmark catalyst that was found to be most suitable for the production of H_2 from aqueous biomass streams [9].

The main experimental goal is to determine the optimum H_2 production within the operating window considered. While it is known that higher H_2 selectivity is obtained at lower conversions, feed concentrations and temperatures [21], this study aims to investigate optimum H_2 production rates at higher temperatures and carbon gasification efficiencies. The work presented in this paper is part of an approach that evaluates the feasibility of complete hydrothermal gasification of sorbitol on an industrial scale. To that effect, a reactor model that incorporates both reaction kinetics and mass transfer is developed to enable the design of a reactor for industrial scale purposes.

2. Experimental section

2.1. Catalyst

Experiments were conducted using a commercial 5 wt% Pt/γ-Al_2O_3 catalyst obtained from Sigma-Aldrich. The surface area of the catalyst was measured using a BET analyser and was determined to be 162.5 m^2/g. XRF studies were conducted to confirm the loading of metal on the support and this was found to be 4.65% by weight.

2.2. Experimental setup

The continuous experimental setup is shown in Fig. 3. The vessel for the feed solution stood on a balance that measured its rate of throughput. An additional storage vessel for water was used for purging and cleaning the reactor before and after an experimental run. A 3-way valve that could switch between the two vessels connected to a high-pressure dual head piston HPLC pump (Instrument Solutions LU class), which fed liquid solution continuously within a range of 0.1–3 ml/min. A mass flow controller (Brooks SLA5850) was used to co-feed 10–60 Nml/min of pressurized N_2 into the reactor. Two check valves in series on the gas line were used to ensure that there was no backflow of liquid to the line. The gas and liquid flows were pre-mixed in a T-junction prior to entering the reactor. The reactor was designed as an Inconel tube (ID = 13 mm, L = 20 cm) and was divided into three sections. The entrance of the reactor was filled with inert sand particles. This provided a uniform distribution of gas and liquid in the reactor and also heated up the feed to the desired temperature. The central section was filled with 5 wt% Pt/γ-Al_2O_3 catalyst particles (> 50 μm), homogeneously mixed with inert sand (100 μm). The exit section was also filled with inert sand. This was done in order to reduce the void volume of the reactor by minimising liquid and gas holdup and hence minimising homogeneous decomposition reactions.

For temperature control, three thermocouples (T1, T2 and T3) were attached to the outer wall of the reactor. The reactor temperature was maintained using three electric ovens. The reactor temperature was considered as the average of the three temperatures. The ovens were operated individually such that all three thermocouples of the reactor were at the same temperature (± 3 °C). Cooling water was used to cool the product fluids downstream of the reactor in a co-current tubular heat exchanger. The pressure of the system was controlled via a back-pressure regulator (Dutch Regulators GBT8S). The operating pressure at the set temperature was always at least 20 bars higher than the vapour pressure of water at that temperature. This way, it was ensured that sufficient water was present in the liquid phase.The pressure drop