

## Experimental investigation and kinetic modeling of the hydrothermal reforming of sorbitol

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### Highlights

- Experimental investigation of temperature effects on the aqueous phase reforming of sorbitol.
- Development of a model to describe gas production over a temperature range (270-350°C).
- Application of the model for optimum H<sub>2</sub> production.

### 1. Introduction

Hydrothermal processing of biomass feeds has received a significant amount of attention in the past 20 years. Among biomass-derived materials, sorbitol has been used as a key model oxygenate compound. Sorbitol was found to be more stable under reforming conditions in comparison to glucose, its dehydrogenated counterpart. The reforming of sorbitol has been found to consist of a complex network of reactions and several studies have been conducted to gain more insight into the reaction mechanism and the influence of catalysts and operating conditions on it [1].

In this work, the kinetics of the reforming of sorbitol over a wide temperature range is investigated, using a benchmark catalyst (5wt% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). A mathematical model is developed to identify reaction paths and to determine the reaction rate parameters. The model, based on the experimental results, is used for the prediction of optimum H<sub>2</sub> production rates and yields on an industrial scale.

### 2. Methods

Experimental setup: A continuous fixed bed reactor setup is used for experimental work. A high pressure dual head piston HPLC pump (Instrument Solutions LU class) is used to feed 10wt% of sorbitol solution continuously within a range of 0.1 – 3ml/min, with and without co-feeding of N<sub>2</sub> into the reactor. The reactor operating pressure is 20 bar above the saturation pressure of water at the set temperature. The reactor consists of an Inconel tube (ID = 13mm, L = 20 cm) and is filled with a 5wt% Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> commercial catalyst homogeneously mixed with inert sand. It is housed centrally in the reactor tube, which is heated by 3 electric ovens placed in series. Cooling water is used to cool the product fluids downstream of the reactor in a co-current tubular heat exchanger. After passing a backpressure regulator, the mixture of liquids and gases is separated in a gas-liquid separator, operated under atmospheric conditions.

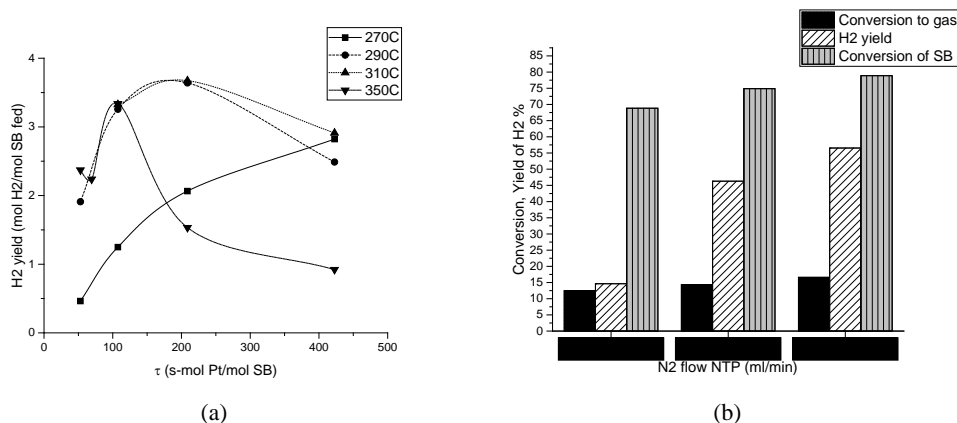
Gaseous products are sent to a gas meter, and a Rapid Refinery Gas Analyser (Varian) is used for separation and quantification of H<sub>2</sub>, CO<sub>2</sub>, CO, N<sub>2</sub>, O<sub>2</sub> and gaseous alkanes (C<sub>1</sub>-C<sub>5</sub>). Liquid products are analysed off-line for their carbon content using a Flash 2000 Elemental Analyser and for residual sorbitol concentrations using a HPLC column (HiPlex H+, RID detector).

Prior to experimental tests, the catalyst was reduced in-situ by flowing 30 ml STP/min H<sub>2</sub> over the catalyst bed for 2 hours at a temperature of 400°C. The setup was then flushed with water and pressurized. A series of catalytic tests was then conducted at varying feed flow rates (0.1-2ml/min), N<sub>2</sub> flow rates (0-60 STP ml/min), and temperatures (270-350°C).

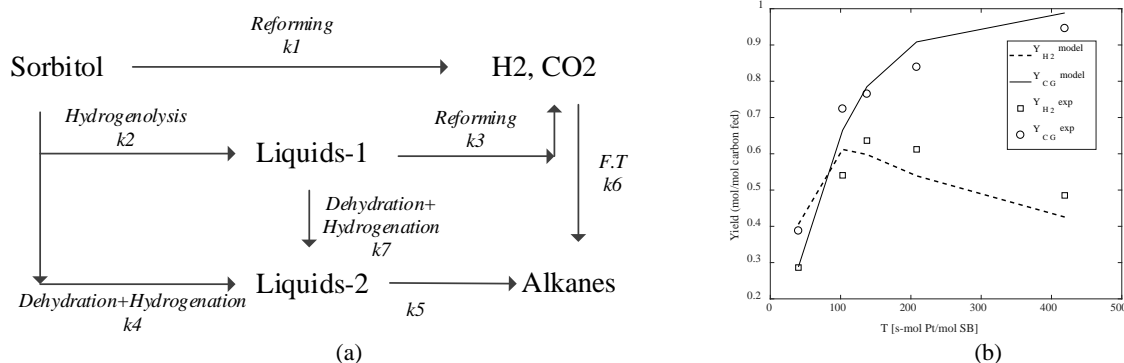
### 3. Results and discussion

Experimental results: The influence of varying residence time on the gasification efficacy was studied at different temperatures in the range of 270 and 350°C. Figure 1(a) shows the results for H<sub>2</sub> yield at all four temperatures studied at varying residence times. At higher temperatures, H<sub>2</sub> goes through an optimum due to its consumption in side reactions. This effect increases as temperature increases. Figure 1(b) shows the

influence of  $N_2$  as a stripping gas and the effect observed is in line with literature findings [2]. A large influence of the  $N_2$  flow is seen on  $H_2$  production, confirming that  $N_2$  strips  $H_2$  out of the reactor before its being consumed in unwanted side reactions.



**Figure 1.** (a) Effect of residence time and temperature on  $H_2$  yield. (b) Effect of  $N_2$  stripping on  $H_2$  yield and conversion  
The path lumped model was developed based on reaction schemes from literature [2] and is shown in Figure 2(a). Sorbitol undergoes reforming to produce  $H_2$  and  $CO_2$ . Produced  $H_2$  is consumed in several side reactions to produce liquid intermediates. Liquids-1 ( $OH/C = 1$ ) represents species that have a similar behavior as sorbitol. Liquids-2 ( $OH/C < 1$ ) represents dehydrated species that produce gaseous alkanes.



**Figure 2.** (a) Path lumped scheme. (b) Data fitting of hydrogen yield and carbon to gas yield at 310°C  
Kinetic parameters were estimated using a least squares minimization method in Matlab. The set of kinetic rate data, including Arrhenius activation energies are reported and successfully used in the adopted lumped path model to describe the experimental results. For illustration, Figure 2(b) shows the model fit of the experimental data at 310°C.

The model was used to size an industrial reactor (capacity: 200 t/h of feed solution) for optimum  $H_2$  production, resulting in a multitubular reactor system with 12 m long tubes. Production rate of  $H_2$  was found to be promising, at 4 mol  $H_2/m^3 \cdot s$  and an annual production of 9500 tons.

#### 4. Conclusions

This work presents the first temperature dependent kinetics and mass transfer model for the hydrothermal reforming of sorbitol. The model approximates the complex reaction mechanism by using a lumping strategy. Kinetic parameters are estimated and this information is further utilized to size an industrial reactor.

#### References

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#### Keywords

Sorbitol; Hydrothermal reforming; Kinetics; Mass transfer; Reactor model.