Adsorption 11: 917–920, 2005

Selective Adsorption of a Substance Derived from Saccharides onto Synthetic Resin Particles

HIDEO HATTORI* AND KIYOHIKO TAJIMA
Research & Development Section, Genesis Research Institute, Nagoya, Japan
hattori@tcp-ip.or.jp

H. TED CHANG
Global Pharmaceutical Operations, Abbott Laboratories, North Chicago, U.S.A.

TAKASHI MURAYAMA AND EIJI FURUYA
Department of Industrial Chemistry, Meiji University, Kawasaki, Japan

Abstract. Most, if not all, of the chemicals and chemical products are made using crude oils as the feedstock. However, this feedstock is decreasing and the utilization of it is causing global climate change. An alternative feedstock must be developed to alleviate these problems. Saccharides (sugars) meet these requirements partly because many useful intermediates and products can be obtained in the presence of an acid. In the case when D-fructose reacts with concentrate hydrochloric acid, 5-hydroxymethyl-furfural (HMF) is formed as the primary product. HMF is well known as one of many useful chemicals from biomass. However, it reacts further to form a HMF dimmer, and it also decomposes to smaller molecules such as levulinic acid. This kind of complex reaction is difficult to control through process variables including temperature, time, pressure, and solvent, in order to obtain selectively a specific product. In this study, a method of direct reaction control using adsorption in the same vessel. The results show that HMF dimmer can be selectively adsorbed onto synthetic resin particles. The results are almost the same as those obtained from a phenolics-carbonaceous adsorbent system.

Keywords: saccharides, decomposition, synthetic resin, adsorption, HMF dimmer

1. Introduction

In the last three decades, a huge number of synthetic chemical and products were produced to improve the standard of living of human beings. Almost all these products are derived from petroleum-based feedstock. The conversion and manufacturing of these chemical products are producing greenhouse gaseous. Furthermore, the petroleum resources are limited and can be consumed in the foreseeable future. Chemical industry using carbohydrate-based feedstock can avoid these problems.

Saccharides can be converted into many chemicals in the presence of an acid. The conversion take place successively and hence give many intermediates and products. In the case shown in Fig. 1, 1,5-hydroxymethyl-furfural(2) is obtained as the primary product from D-fructose(1) reaction in concentrate hydrochloric acid (Shaw et al., 1967). This primary product, HMF, is not stable under the reaction conditions and it reacts further to give HMF dimmer(3), or decomposes to compounds such as levulinic acid(6) and formic acid(7) and others. The decomposition proceeds via the dehydrated tautomer(5) of the hexadienal derivative(4) derived from compound 2 by hydrolysis reaction. It is possible that further tautomerization of

---

*To whom correspondence should be addressed.

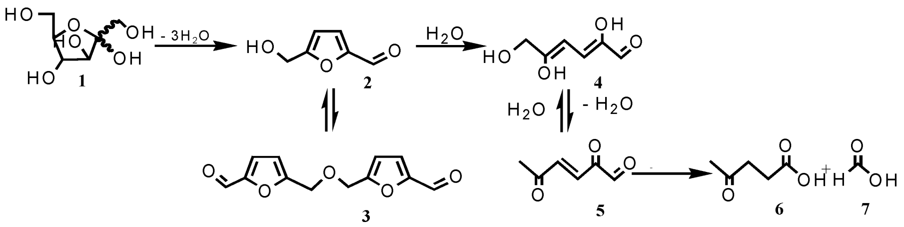

Figure 1. Reaction of D-fructose under acidic condition.

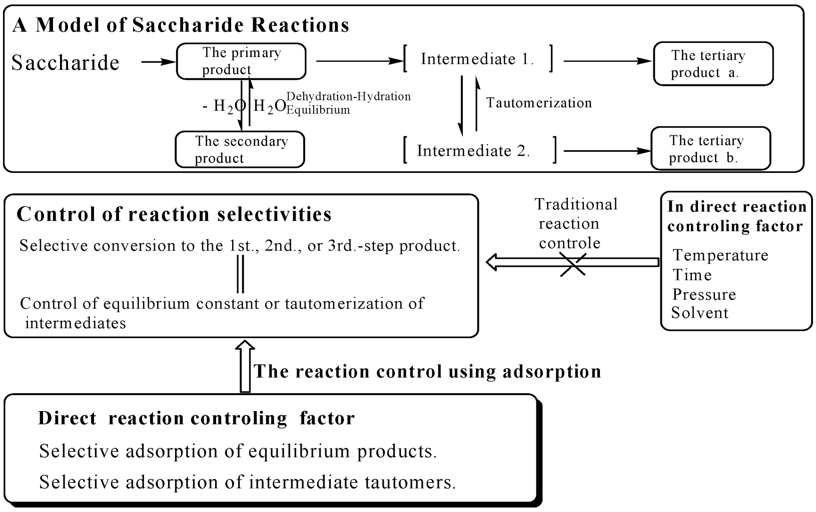

Figure 2. Flow diagram for adsorption-controlled saccharide reaction.

compound can give many more tautomers. The overall reaction scheme is very complicated as shown in Fig. 2. It is very difficult to control such a complex saccharides reactions using indirect reaction control variables such as temperature, time, pressure, solvent, and others, in order to obtain selectively one specific product.

In this study we evaluated the control of D-fructose degradation reaction using an adsorption technology. In this “adsorption-controlled” method, one or more compounds (e.g., equilibrium product and/or intermediate tautomer) are adsorbed selectively and thus separated from the other compounds. In the subsequent step(s) the compounds adsorbed can be desorbed and further reactions can be carried out simultaneously. This technology means a direct control of complex reactions, unstable equilibrium products and intermediate tautomers. The technology is more efficient than the traditional indirect-control methods.

This paper focuses on the adsorptive separation of specific substance(s) from a chemical reaction milieu. It was clear from experimental results obtained by the reaction of D-fructose in concentrated hydrochloric acid that synthetic resin particles adsorb HMF dimmer, and not 1,5-hydroxymethyl-furfural (i.e., HMF). The dimmer can be hydrolyzed later easily to give HMF monomer. The monomer is an important raw material for chemical synthesis in biomass industry.

2. Experimental Procedure

2.1. Materials

Synthetic XAD-2000 resin used in this study is a stylene-divinylbenzene type polymer manufactured by Rohm and Haas, Japan. The resin was pretreated by successive washing with iso-propanol, methanol and distilled water. The resin was then stored in sealed bottles at about 278°K. Key physical properties for the resin are listed in Table 1.

Extra pure grade D-Fructose manufactured by Kokusan Chemical Works Co., Ltd. was used as the test material for chemical decomposition. The sugar was not pretreated. Hydrochloric acid manufactured by Junsei Chemical Co., Ltd. was used as received, without any pretreatment.

Table 1. Physical properties of XAD-2000.

Average particle radius*	1.3×10^{-4} m
Porosity of particles**	0.434
Surface area**	6.2×10^{5} m^2/kg
Average pore diameter**	4.5×10^{-9} m

*Wet resin.

**Dry resin, supplied by the manufacturer (Organo, 1985).

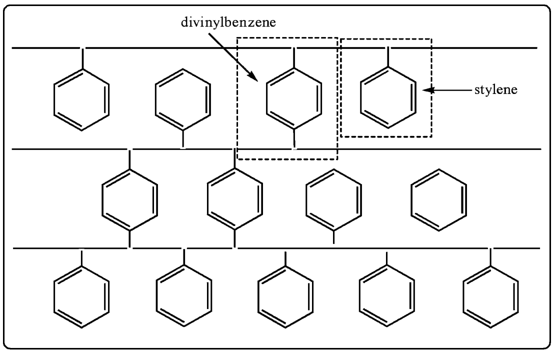

Figure 3. Structural model for XAD-2000 resin.

2.2. Methods

Experiments were carried out in 50 ml magnetic stirred batch reactor at room temperature. Before the chemical reaction, resin particles (0.5 g) were immersed in hydrochloric acid (11 N, 10 ml) and the mixture was ultrasonicated for 10 min. Subsequently, 0.18 g of D-Fructose was dosed into the resin-acid mixture and stirred for 20 hours.

After the reaction, the resin particles were filtered from the mixture. The resin was desorbed by adding iso-propanol to determine the compounds captured by the resin. After the liquid mixture was concentrated by distillation under vacuum, adsorbate(s) were separated using thin chromatographic and identified by NMR. After the desorption, the resin particles were dried and weighed.

Compounds dissolved in liquid phase were extracted using iso-propanol. The extract was concentrated by distillation under vacuum. The resulting oily liquid was diluted by acetone and the constituent component was separated by thin layer chromatography (TLC). Each TLC-separated compound was analyzed by NMR. When D-Fructose is present in the oily mateiral, the sugar was removed by successive extraction with ethylacetate (EtOAc). The extract was then concentrated by distillation under vacuum. The compounds in the exract were separated by TLC and analyzed by NMR, as described previously.

3. Results and Discussions

For comparison, a traditional liquid-phase "control" reaction of D-fructose in hydrochloric acid was performed. The resulting solution contained many compounds as expected (see Fig. 1)—namely HMF, HMF dimmer, levulinic acid and formic acid. The same reaction was then performed in the presence of XAD-2000 resin. While the same type of compounds were identified in the liquid phase, the results show that

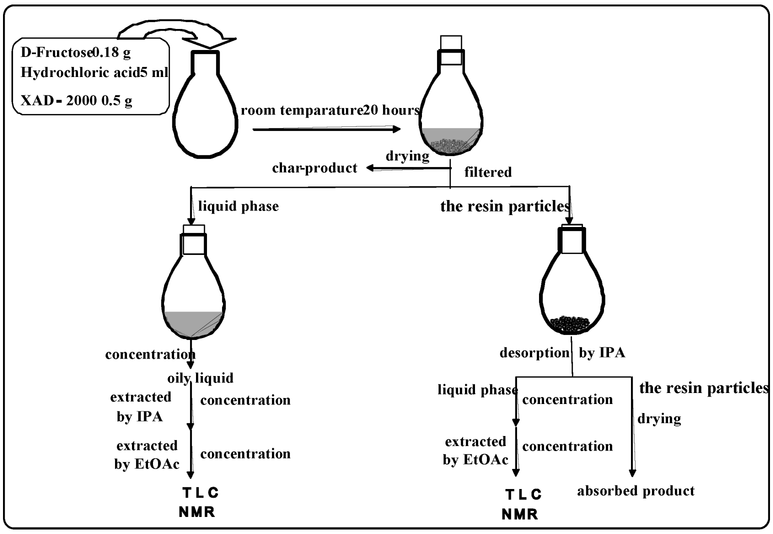

Figure 4. Flow diagram for experimental procedures.

HMF dimmer was adsorbed preferentially up to 60% (w/w) by XAD-2000. The results further show that the amount of HMF dimmer adsorbed is dependent upon the content of divinylbenzene groups in the resin (see Fig. 3). This result suggests strongly that the crosslink structures of divinylbenzene are essential to facilitae and enhance the adsorption of HMF dimmer.

In a recent study, Otake et al. (2003) evaluated the relationship between the highest occupied molecular orbital (HOMO) of adsorbate carbon and the Freundlich exponent (1/n). They used a system consisted of phenolic adsorbates and carbonaceous adsorbent. They found that 1/n was a function of adsorbate molecule's total electron density in the HOMO (see Figs. 3 and 4). This result suggests that a molecule with more π electrons can be adsorbed more abundantly than those molecules with a fewer π electrons.

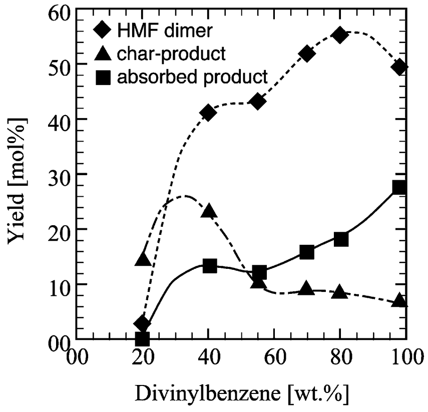

Figure 5. Dependency of HMF dimmer yield on divinyl-benzene content in resin.

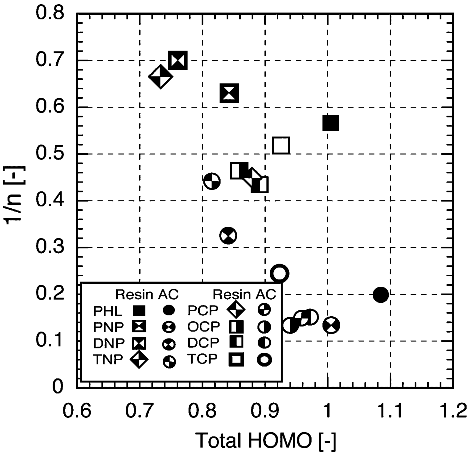

Figure 6. Dependency of $1/n$ on electron density.

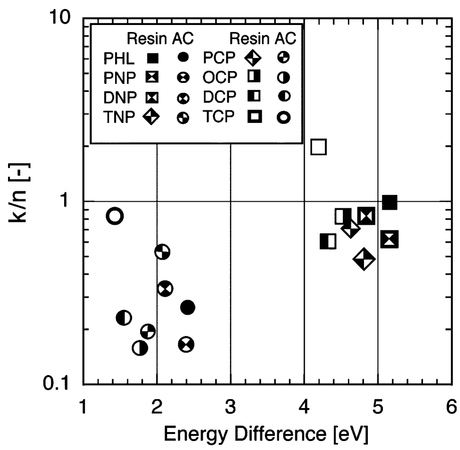

Figure 7. Dependency of k/n on energy difference.

The finding by Otake et al. was applied in this study in the adsorption of desired products in the complex D-Fructose reaction (Fig. 1). Since HMF dimmer has the greatest number of π electrons among the compounds in the reaction milieu, it is expected to be adsorbed the highest amount per the findings of Otake et al. The results of this study suggests that resin adsorption can be used in the same reactor with the hydrolysis of sugar to remove undesirable by-products. This process essentially combines reaction and separation into one efficient and cost-effective step.

4. Conclusion

This study developed an efficient and cost-effective technology that combines wet reaction with adsorption, in the same reactor, for the acidic hydrolysis of D-Fructose. The results show that resin adsorption can remove preferentially an undesirable by-product—1,5-hydroxy-methylfurfural dimmer, and leave the main product HMF in the liquid phase. The adsorbed HMF dimmer can be later desorbed and react further to obtain extra product HMF, thus maximizing the reaction yield. The preferential adsorption of HMF dimmer can be explained successfully using the HOMO π electron density of adsorbate.

References

Otake, Y., N. Khalili, T. Chang, and E. Furuya, "Relationship between Freundlich-Type Equation Constants and Molecular Orbital Properties," *Separation and Purification Technology*, in press.

Shaw, P.E., J.H. Tatum, and R.E. Berry, "Acid-Catalyzed Degradation of D-Fructose," *Carbohyd. Res.*, **5**, 266–273 (1967).