

DEHYDRATION OF CARBOHYDRATES IN SUPERCRITICAL WATER

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INTRODUCTION

The State of Hawaii is a leading producer of sugarcane and pineapples. The phytomass waste that results from this production is mainly burned to generate electric power. To use lignocellulose materials more effectively some programs are under development. One of the most promising seems to be the conversion of phytomass under pressure and temperature higher or near the critical point of the solvent into chemicals. Near this point the chemical and physical properties of solvent are both liquid- and gas-like and the fluid could be very useful for production of chemicals with higher yields and selectivity obtained using more conventional conditions. The factors affecting supercritical (SC) processing are solvent, catalyst, parameters of the reactor and accesibility of substrate.

The dehydration of cellulose and chitin in supercritical acetone resulted in the formation of anhydrosugars with acceptable yields (1). We used water as a solvent because of its excellent characteristics as a solvent for carbohydrates, its ionic strength, and lower solubility of dehydration products. The reactions which we could suppose to take place under SC conditions in the presence or without inorganic acids or bases are mutarotation, epimerization, dehydration, degradation reaction to levulinic acid, saccharinic acids, as well as, aldol- and retro-aldol reaction. From all the products the most important seems to be 1,6-anhydro- -D-glucopyranose, 5-hydroxymethylfuraldehyde, 2-furaldehyde, and levulinic acid.

Most of the authors who studied production of chemicals from phytomass or its model compounds under SC conditions used batch or semi-continuous reactors (1-6). The negative effect of these reactors on reactions taking place are diminished heat transfer, lower reproducibility, and industrial applicability in comparison to flow reactors. In this paper we discuss the processing of D-glucose using the SC flow reactor under sub- and supercritical conditions.

EXPERIMENTAL

Prior to the initiation of flow, the system is brought up to pressure by an air compressor. Premixed reactant solutions were pumped into the reactor at a controlled flow rate by an HPLC pump. The solution flow through the reactor, pass a 10 port valve dual loop sampling system, and is collected in product accumulator. The flow of products into the accumulator displaces air through a back-pressure regulator which maintains the reactor system at the desired pressure.

The reactant flow is rapidly heated to reaction temperature by the entry heat guard, and maintained at isothermal conditions by a Trans-temp Infrared furnace and an exit heat guard. Samples captured in 5.4 ml sample loops are released into sealed, evacuated test tubes for quantitative analysis by GC, GC-MS, and HPLC instruments within the laboratory. The outer annulus of the reactor is a 4.572 mm ID Hastelloy C-276 tube, and the inner annulus is a 3.175 mm OD sintered alumina tube, giving the reactor an effective hydraulic diameter of 1.4 mm. The alumina tube accommodates a movable type K thermocouple along the reactor's axis, which provides for the measurement of axial temperature gradients along the reactor's functional length. Radial temperature gradients are measured as differences between the centerline temperatures and temperatures measured at 10 fixed positions along the outer wall of the reactor using type K thermocouples. The entire reactor and sampling system is housed in a protective enclosure which can be purged of air (oxygen) during studies involving flammable solvents (such as methanol).

The reactor apparatus can be characterized by the following representative nondimensional numbers: $Re = 420$, $Pr = 1.86$, $Sc = 0.86$, $Pe_h = 776$ (thermal diffusion), $Pe_m = 358$ (species diffusion), and $Da = 0.40$. We have determined from the temperature profile of the reactor during operation that radial temperature gradients within the annular flow reactor are negligible. A computer program, which accurately accounts for the effects of the various fluid (solvent, solvent and solute, air) compressibilities on flow measurements, calculates mass and elemental balances for each experiment.

RESULTS AND DISCUSSION

Results of experiments probing the dehydration chemistry of D-glucose in SC water ($P = 34.5$ MPa) are summarized in Table 1. We began the first experiment at 200°C . As can be seen under this condition no dehydration products were observed and only a small amount of D-glucose was epimerized to D-mannose. At 250°C we observed 5-hydroxymethylfuraldehyde as the only dehydration product. The presence of sulphuric acid or sodium hydroxide increased the conversion of substrate. The acid increased the yield of dehydration product and also 2-furaldehyde occurred as product of pentose dehydration. On the other hand, base decreased the yields of furan derivatives and produced lactic acid as a beta elimination, benzoic acid rearrangement, and retro-aldol reaction product. The decrease of flow rate and omission of catalysts increased the yield of 5-hydroxymethylfuraldehyde, as well as the conversion. A further increase of temperature to 275°C increased the conversion of substrate and yield of dehydration product. The presence of acid decreased yield of furan derivatives. In the presence of sodium hydroxide lactic acid was the predominant product. At 300°C and in absence of catalyst the yield of furan derivatives increased further. These results confirm that water is more selective for dehydration when used without catalyst in the SC flow reactor. In some experiments we were not able to identify some degradation products. This resulted in lower carbon balances than have been reported in our earlier work.

When the reaction was run under supercritical conditions (385°C, residence time of 24 seconds) the yield of furan derivatives decreased dramatically and products of retro-aldol reaction (acetol and formaldehyde) were observed. The levulinic acid was probably destroyed in this way. Under SC conditions gaseous products were also observed. Their presence indicate that decarbonylation, decarboxylation, and other fragmentation reactions were taking place. These were probably due to homolytic reaction processes.

CONCLUSIONS

The reactions of D-glucose at 34.5 MPa and temperature interval from 200 to 385°C in SC flow reactor are epimerization, dehydration, degradation to acids, and retro-aldolization. The experiments confirmed that water when used without catalyst is more selective for dehydration. Further research will follow to increase the yield of selected products.

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TABLE 1

Processing of D-Glucose in SC Flow Reactor at 34.5 MPa

| PRODUCT | YIELD (%) ^a | | | | | | | | | | |
|-----------------------------|------------------------|-----|-----|--------------------------------|------|-----|--------------------------------|------|-----|-----------------|-----|
| | 52 | 24 | 11 | 3 | 20 | 8 | 1 | 1 | 1 | 1 | --- |
| $C_6H_{12}O_6$ ^b | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| $C_6H_{12}O_6$ ^c | --- | 4 | 2 | 2 | 1 | 1 | --- | --- | --- | --- | --- |
| $C_6H_6O_3$ ^d | --- | 23 | 27 | 25 | 5 | 31 | 18 | 5 | 21 | 3 | --- |
| $C_5H_4O_2$ ^e | --- | --- | --- | 9 | --- | 10 | 12 | --- | 13 | 1 | --- |
| $C_3H_6O_3$ ^f | --- | --- | --- | --- | 10 | --- | --- | 81 | --- | --- | --- |
| $C_3H_6O_2$ ^g | --- | --- | --- | --- | --- | --- | --- | --- | --- | 23 | --- |
| $C_2H_4O_2$ ^h | --- | --- | --- | --- | 7 | --- | --- | --- | --- | 10 | --- |
| CH_2O ⁱ | --- | --- | --- | --- | --- | --- | --- | --- | --- | 36 | --- |
| CATALYST ^j | --- | --- | --- | H ₂ SO ₄ | NaOH | --- | H ₂ SO ₄ | NaOH | --- | --- | --- |
| TEMPERATURE ^k | 200 | 250 | 250 | 250 | 250 | 275 | 275 | 275 | 300 | 385 | --- |
| RESIDENCE TIME ^l | 41 | 38 | 76 | 38 | 38 | 35 | 36 | 36 | 49 | 24 | --- |
| CONVERSION (%) | 5 | 38 | 57 | 53 | 89 | 62 | 82 | 97 | 98 | 97 ^m | --- |

^a100 (moles of product/moles of reactant converted). ^bD-Mannose. ^cD-Fructose. ^d5-Hydroxymethylfuraldehyde. ^e2-Furaldehyde. ^fLactic acid. ^gAcetol. ^hGlycerinaldehyde. ⁱFormaldehyde. ^j5 mm of catalyst. ^kDegrees of Centigrade. ^lSeconds. ^mAlso gaseous products: Carbon monoxide (9.3 %), carbon dioxide (55.7 %), hydrogen (34.5 %), methane (0.2 %), ethylene (0.3 %), and ethane (0.1 %).