**HIGH ACTIVITY CATALYSTS FOR POLYOLS PRODUCTION
FROM C-6 SUGARS [PUBLIC VERSION]**

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FINAL PROJECT REPORT
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Project Summary:

Over the course of this project, many significant discoveries have been made in the process for the conversion of sorbitol to value added products. These results are summarized below.

FY 2000

The objective was developing a process for the production of propylene glycol (PG), ethylene glycol (EG), and glycerol from sorbitol. After an examination of previous work, the process was successfully demonstrated in a 40cc trickle bed reactor with the first generation active metal on carbon catalyst. This testing demonstrated 1) slight increase in catalyst performance during the 1500 hours on stream, 2) successful operation conditions around 200C and 240C, and 3) minimal effects from artificially increasing catalyst wetting. This data was used for the initial economic evaluations that identified the importance of maximizing propylene glycol selectivity.

A carbon supported bimetallic catalyst was also developed to convert glycerol to propylene glycol that serves to increase the yield of the higher value component. This catalyst was also demonstrated in the batch reactor and in the trickle bed reactor with success. Selectivity to PG from glycerol appeared fixed in the trickle bed at about 70% over most of the conditions tested, with performance degrading above 220C.

This bimetallic catalyst was also found to be more active than the first generation catalyst for the sorbitol hydrogenolysis process. This catalyst would allow a single bed to be used for both sorbitol conversion and PG enrichment of the product stream, and is referred to as the Second Generation Catalyst.

FY 2001

It was found that adding additional base (NaOH) to the feedstock for sorbitol hydrogenolysis resulted in an activity increase coupled with more product ending up as sodium lactate. Lowering base concentration reduced the overall selectivity of the hydrogenolysis due to acidic conditions. Limited trickle bed tests where base added in small increments over the course of a reaction (rather than all at once) hinted that there could be a positive effect on the selectivity to PG, but specialized equipment would be needed to demonstrate this conclusively, to ensure more careful and even distribution of the NaOH.

Due to the primary carbon support becoming unavailable, experiments were performed in conjunction with the support manufacturer that identified a replacement support with nearly equivalent performance for this process.

A test matrix of the second generation bimetallic catalyst was performed that demonstrated the overall process performance in respect to the relative concentrations of the metals on carbon. This determined effective operating compositions for this catalyst on the sorbitol and glycerol processes and indicated where the optimal concentrations may be found.

FY 2002

Catalysts with a carbon supports that had been modified in various ways by the manufacturer were evaluated, including treatments such as advanced oxidation, promoters, thermal treatments, and others. Among the supports tested, oxidized supports appeared to show some improvements over the baseline catalyst, while others resulted in little improvement.

While pushing the process to highest conversion of sorbitol and intermediates determined that the process requires more base than originally determined for the highest selectivity to propylene glycol. Subsequent testing was performed at higher base loadings, but this fact may make staged base addition attractive in the future.

The system was demonstrated on a trickle bed with 750ml of the second generation bimetallic catalyst, which represented a 30 times scale up from previous reactor testing. The work demonstrated that the higher wetting found in scale-up system does impact the process negatively, but elevating the bed temperature 15C resulted in restoring much of the performance loss.

Lifetime testing was performed on the second generation bimetallic catalyst demonstrating minimal activity loss over the course of 1700 hours on stream at 210C under conditions for high propylene glycol selectivity. The catalyst used for the flow reactor and lifetime testing was produced by a commercial catalyst manufacturer and can be supplied in exactly this form in batches large enough for industrial operation.

Results from 12th Quarter

Significant progress has been made this quarter in completing the final phase of this project for the examination of the process for catalytically converting sorbitol to value added products. A number of batch tests have been performed, flow reactor product has been shared with our research partner at MSU, a lifetime study of the second generation bimetallic catalyst has been successfully performed, and a commercial catalyst similar to the first generation catalyst has been investigated in the flow reactor.

Results Summary:

1. Batch Reactor Tests of Various Catalysts

A limited number of batch tests were performed this quarter in support of the sorbitol and glycerol conversion processes. These consisted of a set of tests with the second generation bimetallic catalyst around where the optimal metal concentration may exist, inspired by the matrix testing of previous quarters.

As reported in the previous quarter, the matrix predicted the best PG selectivity results by using the bimetallic catalyst with reduced amounts of Metal 2. While the lower boundary of the matrix was set at an artificially selected amount of the second metal, it was decided to extrapolate and examine catalysts between that lower boundary and zero with the sorbitol process. The comparison of those tests is shown in Figure 1 below and reports the results at the 4 hour sampling interval after catalytic hydrogenolysis of sorbitol at 220C with hydrogen pressure.

FIGURE 1

It is apparent that for the limited conditions selected, there is a significant difference in the conversion and product mix which demonstrates much more variability than was demonstrated in the original matrix testing. At the “Lower” concentration of Metal 2 below, it appears that the preference for the C3-C4 bond cleavage of sorbitol is much less than expected for typical catalysts with more Metal 2. In addition, the selectivity to EG, PG, and glycerol is reduced while the selectivity to sodium lactate is actually increased. It is apparent that the optimal range for the second metal is likely to be around the “Low” or “Lower” concentration of Metal 2 tested in this matrix.

This information, combined with the previously observed effects of Metal 1 while coupled with low amounts of the second metal indicates that at much reduced concentrations of Metal 2, the first metal has more of an effect on the activity of the catalyst. This indicates a need for further investigation of this bimetallic catalyst at low concentrations of Metal 2, which may be key in determining the optimal concentrations of both metals on this catalyst for the sorbitol reaction. In addition, currently no attempt has been made to control the metal location on the catalyst particle, such as the use of edge coating techniques. The nature of this process to prefer supports with higher macroporosity indicate that moving to an edge coated type of metals deposition may also improve catalyst performance. It may be important to investigate along both of these phenomena in future work.

Similarly, a few tests were performed with these lower Metal 2 concentration catalysts on an aqueous glycerol feed. The glycerol test data summary is shown in Figure 2.

FIGURE 2

While only two of the low Metal 2 containing catalysts were tested for glycerol, the results are interesting. During matrix testing, the statistical analysis suggested that the bottom end of the matrix would provide the highest selectivity to propylene glycol. This most recent testing demonstrated very consistent selectivity of 80% PG from glycerol.

This is surprising, as during much of the testing of the glycerol conversion process, most permutations of reaction conditions generated a maximum selectivity of 70% with slightly better results at lower temperature and considerably worse selectivity around the high temperatures tested.

This indicates that the selectivity to PG from glycerol can probably be controlled by further optimization of the catalyst composition of the catalyst around and below the low concentration of the second metal. This, combined with examining the temperature and metals location effects, may be the key to nailing down excellent selectivity from this process which to date has been somewhat elusive.

This also represents the significant conclusion that there is a deviation between the expected optimal catalyst loading for the sorbitol and glycerol processes. This may be a handle for understanding the mechanism involved in the two very different processes, the former consisting of C-C hydrogenolysis and the latter primarily C-O bond scission for dehydroxylation. The fact that the bimetallic catalyst with the “Lower” amount of the second metal for glycerol yielded a 2:1 ratio of PG to lactate instead of the 14:1 ratio that was observed with “Low” concentration of the second metal suggests an apparent shift in the reaction mechanism based solely on the metal loading, which may be taken advantage of to generate rational design for improving the propylene glycol selectivity. This phenomenon needs to be examined more completely.

These observations strongly suggest that exceeding the apparent 70% selectivity barrier of PG from glycerol may now be possible by controlling the metal matrix, indicating that propylene glycol yields from sorbitol might also be more easily achieved.

2. Lifetime Study for Second Generation Bimetallic Catalyst

The second generation bimetallic catalyst has shown great promise in the hydrogenolysis of sorbitol to polyols over the original first generation catalyst. Originally, the first generation catalyst was subjected to lifetime testing with good results prior to the discovery of the second generation catalyst. However, prior to this quarter, only a single charge of the second generation catalyst had been run continuously in a flow reactor and for approximately 200 hours. As stated in the previous reporting period, understanding how the performance of a catalyst changes over time is as important as evaluating the best catalyst and conditions for a particular reaction. For this reason, it was decided to undertake a catalyst lifetime study with the second generation bimetallic catalyst that was part of the 2.5 liters of catalyst supplied by a commercial catalyst manufacturer for the large flow reactor tests. The loading conditions of the reactor were reported in the previous quarter, as was the feeds consisting of 75ml/hr of 25% Sorbitol and 2.2% NaOH over a 30cc bed held at 210C and 1800psi of hydrogen at a 5 H₂ : 1 sorbitol ratio.

Every attempt was made to operate the reactor at these specified conditions. However, there were a few process upsets that occurred as a result of the long term testing. The hydrogen feed to the reactor was interrupted in two events lasting approximately 12 and 24 hours each. Additionally, the liquid feed to the reactor was also lost on two occasions.

Over the course of the test, the feed concentration varied only slightly with respect to sorbitol and base, which should not have introduced any unusual effects.

Following each upset where the hydrogen flow to the reactor was lost, the product from the reactor took on a brown coloring, yielded the smell of an ether-like compound, and the pH dropped from around about 9.5 to around 7. When hydrogen supply was restored, the reactor product would slowly regain its normal colorless appearance and pH of about 9.5. The typical odor of the product would also return.

Table 2

Date	Time	HOS	Event
7/3/2002	11:37	0	Run Started
7/7/2002	14:08	99	Feed #2
7/11/2002	18:22	223	Feed #3
7/16/2002	9:34	341	Restarted flow, feed starved for 12 hours
7/20/2002	11:21	432	Feed #4
7/22/2002	13:48	482	H2 restarted, hydrogen starved for 12 to 36 hours
8/2/2002	14:55	747	Feed #5
8/13/2002	8:00	1004	Feed #6
8/22/2002	17:21	1230	Feed #7
8/28/2002	11:15	1367	Restarted Flow, feed starved for 12 to 36 hours
9/5/2002	15:22	1556	H2 restarted, hydrogen starved for 12 to 36 hours
9/10/2002	11:13	1680	Run Halted

A list of major events during the flow reactor test is shown in Table 2, above. In the table, HOS refers to “hours on stream” or cumulative elapsed time of reactor operation.

The conversion and selectivity data for the primary products are shown in Figure 3 and in tabular form in Table 3.

From this data set, there are a number of observations that have been made.

First, it appears that the catalyst is quite stable running at high sorbitol conversion over this period. Overall, there was observed a slight decline in overall selectivity to PG while EG remained stable and glycerol seemed to increase slightly. The slight variations in selectivity may offer a clue to the nature of the hydrogenolysis and the effect of the catalyst on the mechanism for the particular species of 3-carbon material that is formed in the reaction. This also may be a function of the activity of the catalyst changing over time. This cannot be directly inferred from the conversion data, as the reactor conditions were such that the sorbitol conversion was complete for the entire test period except where H2 upsets occurred. The reaction was performed at high sorbitol conversion in order to produce as much propylene glycol as possible from sorbitol, C5 and C4 intermediates, and glycerol normally found in the reactor product.

The amount of material reported as erythritol appears to show little change over the course of the reaction. Ion exchange tests have demonstrated that the material reported as erythritol may in fact be a combination of erythritol and an organic acid that co-elutes

with it. However, the fact that the erythritol amount resultant from the process is stable cannot be used to confirm or deny any apparent activity loss of the catalyst. Finally, the variations in selectivity may be a function of the sensitivity of the process to base loading. Looking at the feed pH data, it appears that towards the end of the test, the final two feed mixtures both were at somewhat lower pH than the earlier feed stocks. It is known that the feed pH has an increased effect on catalyst activity with higher pH, so this may be a possible explanation for the activity change.

This should not detract from the excellent observation, that the stable catalyst performance over the 1700 hrs of testing indicates that the catalyst and process appears to be relatively unaffected by loss of hydrogen or loss of sorbitol feed. This is of particular interest because both active metals are known to be less firmly bound to the carbon support under low pH conditions.

The two hydrogen starvation periods, perhaps lasting for a day or more each had little effect on the steady state catalyst condition. These periods of hydrogen starvation produced a liquid product with a light brown color and a pH around 7.5 and overall low sorbitol conversion and selectivity to desired products. While the hydrogen starvation periods seemed to have no lasting negative impact on the catalyst, the reduced pH would be expected to leach some of the metal from the carbon support and would eventually deactivate the catalyst.

FIGURE 3

Catalyst Lifetime Testing, 30cc Flow Reactor, 2nd Generation catalyst, 75ml/hr, 1800psi, 210C.

Table 3

Sample	F13-1	F13-2	F13-3	F13-4	F13-5	F13-6	F13-7	F13-8	F13-9	F13-10	F13-11	F13-12	F13-13	F13-14	F13-15	F13-16	F13-17	F13-18	F13-19	F13-20	F13-21
hrs on stream	7	22.6	47.8	75.7	98.5	118.5	190.1	222.8	243.5	288.3	341	383.6	431.7	482.2	526.5	575.2	611	652.7	699.3	747.3	793.7
temp (C)	210	210	210	210	210	210	210	210	210	210	210	210	210	210	210	210	210	210	210	210	210
press (psi)	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800
flow (ml/hr)	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75
feed sorb%	22.78	22.78	22.78	22.78	24.83	24.83	24.83	24.69	24.69	24.69	24.69	24.69	25.20	25.20	25.20	25.20	25.20	25.20	25.20	25.20	25.20
contact (hr)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
H2 ratio	5	5	5	5	5	5	5	5	5	5	5	5	5	0	5	5	5	5	5	5	5
base %	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
feed pH	13.04	13.04	13.04	13.04	13.06	13.06	13.06	13.06	13.06	13.06	13.06	13.06	13.02	13.02	13.02	13.02	13.02	13.02	13.02	13.04	13.04
prod pH	9.63	9.62	9.49	9.52	9.52	9.57	9.50	9.52	9.51	9.49	9.55	9.52	9.56	7.38	9.52	9.70	9.73	9.74	9.66	9.66	9.74
Conversion	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.90	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Selectivity (carbon molar)																					
Xylitol	0.0	1.3	1.1	1.2	1.2	1.1	1.1	1.2	1.1	1.1	1.1	1.1	1.0	2.5	1.4	1.4	0.0	1.2	1.3	1.2	1.2
erythritol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.1	0.0	0.0	0.1	0.1	0.0
threitol	4.4	2.9	2.2	2.4	1.9	2.0	1.7	1.8	1.7	1.6	1.6	1.5	1.5	2.1	1.5	1.7	1.7	1.7	1.7	1.7	1.7
lactate	5.6	5.5	4.5	4.1	4.1	4.0	3.8	3.7	3.3	3.5	3.3	3.6	3.3	4.6	3.7	4.1	4.0	3.9	4.3	3.4	3.5
glycerol	7.7	7.4	8.0	8.1	7.1	7.3	7.6	8.0	7.6	7.8	7.7	7.9	7.7	7.7	8.8	9.3	8.1	8.1	8.9	8.5	7.4
1,2,4 BTO	0.0	0.3	0.0	0.0	0.3	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.3	0.3	0.0	0.0	0.2	0.0
EG	13.2	13.7	15.6	15.7	14.2	14.5	16.0	16.0	16.0	16.0	16.5	16.4	15.9	13.1	15.4	16.9	14.9	15.1	16.4	15.3	15.9
PG	43.1	43.1	45.2	46.8	43.3	43.7	43.4	44.9	44.6	44.7	44.0	44.2	44.2	36.1	41.6	46.5	42.3	43.0	45.2	42.7	43.5
1,3 PD	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2,3 BDO	5.0	0.0	4.9	5.2	4.4	4.5	4.6	4.5	4.7	4.6	4.6	4.4	4.2	3.9	4.3	4.9	4.5	4.3	4.2	4.5	4.8
1,3 BDO	3.6	3.6	3.3	3.3	3.2	3.0	2.8	3.0	3.1	3.0	3.0	2.9	2.9	2.8	2.9	3.0	2.9	3.0	2.8	2.9	3.5
MeOH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,2 BDO	3.9	4.2	4.2	4.6	4.0	4.1	3.9	4.3	3.8	3.8	3.6	4.2	3.8	4.0	4.0	4.4	3.6	3.7	4.0	3.7	4.1
1,4 BDO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
EtOH	3.2	3.5	2.6	2.9	2.8	2.7	2.1	2.4	2.3	2.2	2.0	2.1	2.1	2.4	2.0	1.2	2.0	1.6	1.5	2.1	1.9
2-PrOH	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.1	0.1	0.2	0.0	0.2	0.2	0.0	0.1	0.0
1-PrOH	0.6	0.7	0.6	0.5	0.5	0.5	0.6	0.5	0.6	0.5	0.5	0.4	0.4	0.4	0.4	0.2	0.5	0.5	0.3	0.4	0.0
total	90.2	86.2	92.2	95.0	87.2	87.3	87.9	90.2	88.8	88.9	88.2	88.8	87.0	80.0	86.5	94.1	85.2	86.3	90.6	86.9	87.4

Table 3 - continued

Sample	F13-22	F13-23	F13-24	F13-25	F13-26	F13-27	F13-28	F13-29	F13-30	F13-31	F13-32	F13-33	F13-34	F13-40	F13-41	F13-42	F13-43	F13-44	F13-45	F13-46	F13-47
hrs on stream	822.5	837.4	887.1	918.6	963	1013	1060	1088	1132	1181	1230	1274	1316	1373	1394	1422	1465	1512	1584	1641	1680
temp (C)	210	210	210	210	210	210	210	210	210	210	210	210	210	210	210	210	210	210	210	210	210
press (psi)	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800
flow (ml/hr)	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75
feed sorb%	25.20	25.20	25.20	25.20	25.20	25.15	25.15	25.15	25.15	25.15	25.15	25.39	25.39	25.39	25.39	25.39	25.39	25.39	25.39	25.39	25.39
contact (hr)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
H2 ratio	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
base %	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
feed pH	13.04	13.04	13.04	13.04	13.04	12.97	12.97	12.97	12.97	12.97	12.97	12.85	12.85	12.85	12.85	12.85	12.85	12.85	12.85	12.85	12.85
prod pH	9.83	9.86	9.81	9.66	9.59	9.61	9.50	9.50	9.76	9.68	9.46	9.19	9.35	9.87	9.82	9.75	9.68	9.61	9.76	9.75	9.77
Conversion	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Selectivity (carbon molar)																					
Xylitol	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.1	1.1	1.3	1.5	1.2	1.3	1.1	1.2	1.2	1.1	1.5	1.2	1.2
erythritol	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.2	0.4	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0
threitol	1.9	2.1	1.9	1.4	1.3	1.2	1.2	1.6	1.9	1.8	1.4	1.5	1.5	2.6	1.9	1.7	1.4	1.4	1.5	1.3	1.2
lactate	3.8	4.3	4.0	3.3	3.1	2.9	2.7	3.4	3.7	3.7	3.1	3.1	3.3	5.0	4.1	3.7	3.4	3.3	3.9	3.4	3.3
glycerol	7.0	7.6	7.6	9.7	10.0	9.5	10.2	8.1	7.2	7.4	10.7	12.2	9.2	7.1	8.1	8.0	8.3	8.4	9.4	9.1	8.9
1,2,4 BTO	0.0	0.0	0.2	0.6	0.5	0.1	0.2	0.0	0.0	0.0	0.7	0.9	0.5	0.0	0.2	0.2	0.2	0.2	0.4	0.0	0.2
EG	15.2	15.1	15.3	16.7	17.0	17.0	17.0	16.2	15.5	15.5	16.9	16.6	16.5	13.8	14.4	15.8	16.4	16.3	15.2	15.0	14.9
PG	43.4	43.8	43.1	42.7	43.0	42.6	41.7	42.6	43.4	43.1	42.2	39.9	42.6	41.3	42.4	42.8	43.5	43.2	40.2	41.7	41.6
1,3 PD	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2,3 BDO	4.2	4.3	4.3	4.3	4.4	4.2	4.2	4.2	4.3	4.3	4.4	4.3	4.3	4.0	4.4	4.2	4.3	4.3	4.3	4.5	4.4
1,3 BDO	3.2	3.3	3.1	2.9	2.9	2.8	2.7	3.0	3.1	3.1	2.8	2.7	2.9	3.1	2.8	3.0	2.9	3.0	3.0	2.7	2.7
MeOH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,2 BDO	3.7	4.1	3.7	3.7	3.7	3.6	3.5	3.6	3.7	3.7	3.9	3.8	4.0	3.9	3.3	4.0	4.0	4.0	3.7	3.4	3.4
1,4 BDO	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.2	0.1	0.0	0.0	0.0	0.0	0.2	0.0	0.0
EtOH	1.9	2.0	1.9	1.3	1.2	1.0	0.9	1.3	1.7	1.7	1.2	0.9	1.4	2.2	1.4	1.6	1.4	1.4	1.7	1.2	1.1
2-PrOH	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2
1-PrOH	0.0	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.4	0.4	0.6	0.4	0.5	0.4	0.5	0.6	0.5	0.5
total	85.4	88.6	86.1	88.0	88.4	86.2	85.6	85.2	85.7	85.5	89.6	88.4	88.4	85.1	84.9	86.8	87.6	87.3	86.0	84.2	83.6

During the hydrogen starvation periods, the sorbitol conversion was low. In addition, overall selectivity to known HPLC calibrated molecules was low with no large unidentified peaks detectable by refractive index. It is unclear if material is being produced that is soluble yet undetectable with our current analysis or if material is exiting the liquid phase into a solid or gaseous phase. Unfortunately, gas analysis was not performed during one of the hydrogen outages. Most likely, the polymeric material is not being formed, as such materials can often be identified at low molecular weights and unknown peaks were observed in the HPLC trace where these materials tend to elute.

Most importantly, upon reinstating the hydrogen flow, the catalyst appears to return to its original selectivity of the desired products after a short apparent re-equilibration period where the selectivity rebounds slightly over the course of a few days of operation.

Next, the product pH provides some interesting observations. All of the pH data was taken in one campaign on the archived samples following the end of the test. Following a process upset, the product pH appears to oscillate slightly before returning to normal. This recovery period appears to last multiple days before the product pH returns to a more stable value. In addition, there appears to be an effect on the product pH that changes with changing feed pH. The effect also appears to last for a few days when a feedstock is changed to one that has a slightly different base loading. This may represent some equilibrium for the co-catalysts within the catalyst support that may take some time to achieve. Overall, the pH also appears to vary slightly with unknown causes during the course of the run. The sensitivity of the product pH with regards to adjustments within the process conditions may indicate that this metric may be a valuable indicator of subtle operational changes, but currently the data is too variable to generate specific correlations.

It is also encouraging that no upward adjustments in reactor temperature were required to achieve complete sorbitol conversion. This, as much as any other observation, strongly suggests good catalyst stability.

At the conclusion of the study, the catalyst was carefully removed from the reactor and segregated into three portions. Representative samples were then taken from the top, middle, and bottom of the bed portions. These samples were analyzed for metal content and compared to a fresh sample of the unreduced, unused catalyst.

A few observations of significance can be made from this analysis. There are slight differences in the two active metal concentrations between the fresh (unused) catalyst and that recovered from the flow reactor. The concentration of Metal 1 is lower at the top and middle of the reactor, but essentially the same at the bottom of the reactor as in the fresh catalyst sample. This suggests that some of Metal 1 was lost from the reactor over time. This metal may be susceptible to removal from the carbon support in lower pH conditions. It is possible that when the pH dropped during the two periods of hydrogen starvation, Metal 1 began to be removed from the catalyst. Previous work has shown that the process is somewhat insensitive to the amount of Metal 1 present. As long as the initial Metal 1 concentration is high enough to protect the catalyst from severe

deactivation, the Metal 1 concentration may not be highly critical for this particular formulation.

The Metal 2 concentration is lower at the top of the reactor, essentially unchanged in the middle of the reactor, and higher at the bottom of the flow reactor bed. This would suggest that some of the Metal 2 has migrated or chromatographed down the bed over time. As shown in the batch reactor tests discussed in the beginning of this report, Metal 2 demonstrated a selectivity “sweet spot” at lower concentrations. So as Metal 2 is being lost, then the catalyst may actually improve for a while before declining as it approaches very low concentrations. This could be corrected by doping the feed with Metal 2 periodically, or some other way of infusing fresh Metal 2 to the catalyst support. In this lifetime study, the concentrations of Metal 2 never fell to such levels to observe this effect. Of course, movement of Metal 2 in the catalyst bed may also have been a result of pH drop during the hydrogen starvation upsets. Without more definitive data, the actual cause of apparent metals movement is currently unknown.

The sodium concentration of the catalyst taken from the reactor was significantly higher than that in the unused catalyst. This is expected because sodium hydroxide was used for the pH setting of the feedstock. The increased sodium concentration appears to have no effect on the performance of the reaction and in fact may be beneficial.

Another good observation is that the catalyst did not accumulate any significant amounts of corrosion metal such as Fe, Cr, V, or Ni during the 1700 hour life test. This strongly supports conventional 316 stainless steel and not exotic metals as the construction material for commercial operation of this process.

In summary, the lifetime testing for the second generation catalyst appeared to be a success. The catalyst was processed for 1700 hours with only minor loss in activity. The catalyst appeared to be resilient to process upsets and did not require re-reduction following hydrogen starvation. The metals analysis indicated that the catalyst was generally not much affected over the life of the study, but catalysts using lower concentrations of both metals might be more sensitive to process conditions or have reduced life expectancy.

3. Disposition of Flow Reactor Product

The lifetime study for the second generation catalyst provided a large amount of product at a high conversion of sorbitol and over 9% by weight propylene glycol. Nearly 110 liters of usable processed material was produced from this run (approximately 20 more liters was produced in unusable condition during the hydrogen starvation process upsets and the equilibration following them).

The usable product material is desirable for follow-on processing with our partner organization on the project, Michigan State University. Approximately 20 liters of the product was subjected to cation and anion exchange. This 20 liter sample was sent to MSU along with 60 liters of raw product from the reactor. This large volume of realistic

product test material will hopefully assist MSU separations studies in support of this project.

4. Flow Reactor Testing, Industrial Catalyst

A commercially prepared industrial catalyst was examined upon the recommendation of the catalyst manufacturer. In batch testing, this catalyst yielded consistent selectivity to PG from sorbitol that was higher than most of the other catalysts screened to date. Due to these unusual and encouraging results, it was decided to examine this catalyst in the flow reactor to examine the phenomenon more carefully. The catalyst generated higher than expected propylene glycol selectivity (approximately 34% versus around 21% normal for other catalysts). To evaluate this catalyst, it was loaded into the 30cc flow reactor for limited testing.

The results are shown below in Table 5.

Total Conversion and PG Selectivity Comparison													
Sample	F14-10	F14-13*	F14-1	F14-11*	F14-5	F14-12	F14-3	F14-8	F14-9	F14-2	F14-4	F14-7	F14-6
temp (C)	210	210	210	210	190	210	200	180	190	170	190	180	180
press (psi)	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800	1800
flow (ml/hr)	10	10	75	75	20	75	75	20	50	15	75	50	75
feed sorb%	22.845	22.845	22.845	22.845	22.845	22.845	22.845	22.845	22.845	22.845	22.845	22.845	22.845
contact (hr)	3	3	0.4	0.4	1.5	0.4	0.4	1.5	0.6	2	0.4	0.6	0.4
H2 ratio	15	15	5	5	7.7	6.8	5	7.7	7.5	25	5	7.5	5
NaOH %	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
feed pH	12.38	12.38	12.38	12.38	12.38	12.38	12.38	12.38	12.38	12.38	12.38	12.38	12.38
prod pH	12.01	11.81	12.16	12.24	12.07	12.05	12.31	12.04	12.06	12.17	12.12	12.1	12.09
HOS	7	11	4	5	13	3.5	4	15	3.5	17	6	4	22
Conversion	99%	99%	87%	77%	77%	75%	65%	59%	58%	56%	46%	39%	30%
Color	dark	dark	dark	dark	light	dark	light	light	light	light	clear	clear	clear
Selectivity													
Xylitol	2.0	1.8	1.5	0.0	1.5	0.0	0.0	0.0	2.9	0.0	0.0	0.0	0.0
erythritol	0.0	0.0	0.2	0.3	0.4	0.3	0.6	1.6	1.4	2.1	1.3	2.4	2.7
threitol	0.5	0.5	0.5	0.5	0.7	0.5	0.7	1.8	1.3	2.3	1.4	2.3	2.4
lactate	1.9	1.8	1.7	1.4	1.1	1.4	1.3	2.0	1.8	2.4	1.8	2.2	2.4
glycerol	5.1	5.8	6.4	8.7	11.8	8.6	10.5	18.5	15.5	21.0	16.9	22.8	23.9
1,2,4 BTO	0.0	0.0	0.0	0.3	0.4	0.3	0.2	1.5	0.0	1.9	1.2	1.7	1.8
EG	19.1	18.9	18.4	19.4	18.0	19.6	18.8	17.8	19.0	17.0	18.8	18.2	18.7
PG	56.1	55.3	51.4	53.8	52.7	54.6	52.9	50.8	49.6	48.2	53.0	50.3	51.5
1,3 PD	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2,3 BDO	4.3	4.3	5.2	5.4	5.1	5.6	5.2	5.6	5.1	5.3	5.2	4.7	4.8
1,3 BDO	4.0	4.0	4.1	3.9	3.6	4.0	3.6	3.4	2.9	3.3	3.1	2.5	2.3
MeOH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,2 BDO	5.7	5.8	5.5	6.2	6.4	6.3	6.2	6.4	5.4	6.2	6.2	5.9	5.7
1,4 BDO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
EtOH	0.8	0.9	0.6	1.1	0.4	1.0	0.7	0.4	0.0	0.3	0.2	0.0	0.0
2-PrOH	0.1	0.0	0.0	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1-PrOH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
total	99.3	99.0	95.5	101.1	102.2	102.3	100.7	109.9	104.9	110.0	109.1	113.0	116.4
PG+7*Gly	59.6	59.3	55.9	59.9	60.9	60.6	60.3	63.8	60.5	62.9	64.8	66.2	68.3
PG+EG+Gly	80.2	79.9	76.2	81.9	82.4	82.9	82.3	87.1	84.1	86.3	88.7	91.3	94.2
liq recovery	0.96	1.06	1.00	1.04	1.02	1.05	1.05	1.06	1.03	0.99	1.01	1.02	0.99

* = repeat of previous conditions

The data in Table 5 is sorted by conversion of the sorbitol to products, with the run conditions having the highest conversions shown first. The three highlighted rows at the top of the table show the run conditions that were varied from sample to sample. The remaining highlighted rows show key results of the key analytical data. The following observations were made from reviewing this data.

As expected, the highest conversions generally resulted when the process was run at higher temperature. The PG selectivity also seemed to follow this trend while the glycerol production significantly increased when the run conditions were at lower temperatures as has been observed elsewhere. Lactate production also tended to increase at lower temperatures, as has been reported in previous work.

Upon first running the process, the catalyst generated the brown coloring similar to that observed during hydrogen starvation in the reactor, but it is not apparent if the coloring could have been due to material loss from the catalyst. The conditions were 1800psi, 75ml/hr, and 210C with the standard 5:1 ratio of hydrogen to sorbitol. The product resumed its colorless appearance after moving to the next set of conditions at much lower temperature and sorbitol conversion. It was surmised that this catalyst might have been extremely active in the first portion of the bed that the reaction may have been temporarily starved of hydrogen at the catalyst surface. Subsequent testing at other run conditions, however, showed that the brown color tended to increase or decrease with the reaction temperature, with the darkest color appearing at higher temperatures. The color may possibly be an indicator of caramelization, but this was not confirmed by any analysis. In other flow reaction tests, hydrogen starved conditions typically result in a drop in sorbitol conversion to products. In this case, though, the deeper color was observed with higher conversions.

The flow reactor test seemed to confirm the observation of the batch reactor test in demonstrating this catalyst has relatively high propylene glycol selectivity. It is expected that further analysis may be required on this catalyst loading, dispersion, and support characteristics that could be translated to yield even better results with the second generation catalyst.

5. Future work

This report marks the conclusion of the scope of this phase of the project. The project has resulted in many encouraging findings to suggest the practical and commercial viability of catalytic processing of sorbitol to high value products with good selectivity and process control. In addition, we believe there are further improvements that can be realized to significantly advance this process. Recommendations have been prepared and submitted with regards to ways to improve and optimize the catalyst and this process.