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APPENDICES

APPENDIX A

A. Experimental Designs (32)

Factorial designs are most efficient for the study of the effects or two or more factors in relatively few experiments as compared to the one-factor-at-a-time technique. The one-factor-at-a-time technique, varying one factor while keeping the other factors at a constant level, is tedious when a large number of factors have to be investigated, whereas statistically based experimental designs are more efficient approach to deal with a large number of variables. Moreover, if there are statistical interaction between factors, that is where the effect of one factor is dependent on the value of another factor, then this formation will not be obtained using the one-factor-at-a-time technique.

Factorial designs allow one to study a large number of variables simultaneously, while a large amount of information is obtained with a reduced experimental effort. The 3^k design is completely randomized. It provides the smallest number of runs which k factors can be studied in a complete factorial design. Consequently, these designs are widely used in factor screening experiments.

APPENDIX B

B. Calculation of Degree of Substitution by ^{1}H-NMR Method

With ^{1}H-NMR spectroscopy, the DS was calculated using the integrated intensities of the signals at δ 0.9-1.1 ppm from methyl protons in the hydroxypropyl groups and the integrated intensities of the signals at δ 5.1-5.5 ppm from the equatorial protons of the anhydroglucose unit of starch (Fig. B.1). The DS can be calculated directly from the equation B.1.

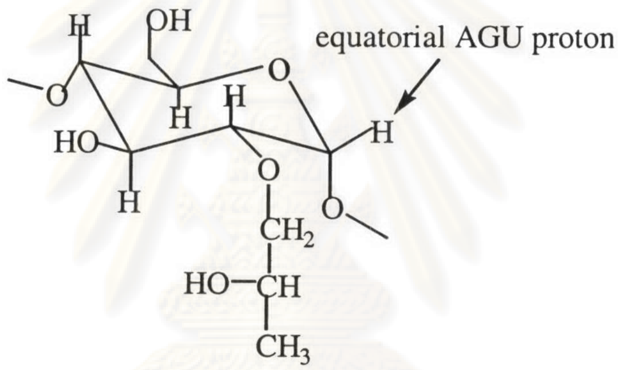

Figure B.1 Hydroxypropylated starch

$$DS = \frac{I_{HP}}{3I_{AGU}} \qquad (B.1)$$

In which I_{HP} = The area of the NMR peak from the hydroxypropyl group of the starch

I_{AGU} = The area of the NMR peak from the equatorial proton of the anhydroglucose unit of starch. This peak area is multiplied by 3 due to the fact that three reactive sites are present at one anhydroglucose unit.

APPENDIX C

C. Calculation of Reaction Efficiency

The reaction efficiency (RE) was calculated by dividing the experimental DS by the theoretical DS. The theoretical DS, DS_t is the maximal DS obtained for complete conversion of the limiting reactant, either propylene oxide or sodium hydroxide, assuming that no side reaction occurs. The reaction efficiency (RE) between zero and unity and is given by

$$RE\,[\%] = \frac{DS}{DS_t} \times 100 \qquad (C.1)$$

With

$$DS_t = \frac{n_{PO,0}}{n_{AGU,0}}$$

$n_{PO,0}$ = the initial amount of moles of propylene oxide

$n_{AGU,0}$ = the initial amount of moles of starch

APPDENDIX D

D. Effect of Sodium Sulfate on Degree of Substitution and Reaction Efficiency

Table D.1 Effect of sodium sulfate on degree of substitution and reaction efficiency

Batch	Na_2SO_4 (%dry starch)	Weight (g)	No.	DS	Average DS	Average RE
1	0	0.0099	1	0.0356	0.0358 ± 0.0045	16.03
			2	0.0393		
			3	0.0401		
2	0	0.0100	1	0.0344		
			2	0.0322		
			3	0.0299		
3	0	0.0100	1	0.0420		
			2	0.0386		
			3	0.0301		
1	10	0.0097	1	0.0856	0.0806 ± 0.0068	36.08
			2	0.0759		
			3	0.0731		
2	10	0.0098	1	0.0799		
			2	0.0810		
			3	0.0692		
3	10	0.0098	1	0.0854		
			2	0.0898		
			3	0.0858		
1	15	0.0100	1	0.0766	0.0827 ± 0.0083	37.02
			2	0.0823		
			3	0.0841		
2	15	0.0101	1	0.0770		
			2	0.0811		
			3	0.0879		
3	15	0.0102	1	0.0831		
			2	0.0713		
			3	0.1006		

Batch	Na_2SO_4 (%dry starch)	Weight (g)	No.	DS	Average DS	Average RE
1	20	0.0097	1	0.1044	0.1004 ± 0.0078	44.94
			2	0.1102		
			3	0.1058		
2	20	0.0099	1	0.0987		
			2	0.1011		
			3	0.0840		
3	20	0.0099	1	0.1009		
			2	0.0923		
			3	0.1038		
1	25	0.0100	1	0.1122	0.1095 ± 0.0068	49.02
			2	0.1061		
			3	0.1281		
2	25	0.0101	1	0.0998		
			2	0.1095		
			3	0.0997		
3	25	0.0102	1	0.1265		
			2	0.1134		
			3	0.0902		

APPDENDIX E

E. Effect of Sodium Hydroxide on Degree of Substitution and Reaction Efficiency

Table E.1 Effect of sodium hydroxide on degree of substitution and reaction efficiency

Batch	NaOH (%dry starch)	Weight (g)	No.	DS	Average DS	Average RE
1	0.5	0.0100	1	0.0496	0.0503 ± 0.0072	22.50
			2	0.0489		
			3	0.0516		
2	0.5	0.0102	1	0.0632		
			2	0.0499		
			3	0.0533		
3	0.5	0.0101	1	0.0521		
			2	0.0488		
			3	0.0353		
1	1.0	0.0099	1	0.0856	0.0806 ± 0.0068	36.08
			2	0.0759		
			3	0.0731		
2	1.0	0.0098	1	0.0799		
			2	0.0810		
			3	0.0692		
3	1.0	0.0100	1	0.0854		
			2	0.0898		
			3	0.0858		
1	1.5	0.0098	1	0.1011	0.0975 ± 0.0085	43.64
			2	0.0856		
			3	0.0863		
2	1.5	0.0102	1	0.0944		
			2	0.1005		
			3	0.0928		
3	15	0.0101	1	0.1068		
			2	0.0997		
			3	0.1106		

Batch	NaOH (%dry starch)	Weight (g)	No.	DS	Average DS	Average RE
1	2.0	0.0100	1	0.1026	0.1025 ± 0.0084	45.88
			2	0.0973		
			3	0.1142		
2	2.0	0.0101	1	0.0999		
			2	0.1044		
			3	0.0981		
3	2.0	0.0102	1	0.1123		
			2	0.0997		
			3	0.0960		

APPDENDIX F

F. Effect of Propylene Oxide on Degree of Substitution and Reaction Efficiency

Table F.1 Effect of propylene oxide on degree of substitution and reaction efficiency

Batch	Propylene oxide (%dry starch)	Weight (g)	No.	DS	Average DS	Average RE
			1	0.0452		
1	5	0.0099	2	0.0411		
			3	0.0399		
			1	0.0540		
2	5	0.0100	2	0.0388	0.0443 ± 0.0057	31.70
			3	0.0436		
			1	0.0423		
3	5	0.0100	2	0.0502		
			3	0.0436		
			1	0.0856		
1	8	0.0096	2	0.0759		
			3	0.0731		
			1	0.0799		
2	8	0.0098	2	0.0810	0.0806 ± 0.0068	36.08
			3	0.0692		
			1	0.0854		
3	8	0.0099	2	0.0898		
			3	0.0858		
1			1	0.1465		
	12	0.0100	2	0.1248		
			3	0.1392		
			1	0.1461		
2	12	0.0100	2	0.1482	0.1365 ± 0.0093	40.70
			3	0.1263		
			1	0.1344		
3	12	0.0100	2	0.1499		
			3	0.1131		

Batch	Propylene oxide (%dry starch)	Weight (g)	No.	DS	Average DS	Average RE
1	14	0.0099	1	0.1698	0.1668 ± 0.0084	42.66
			2	0.1819		
			3	0.1685		
2	14	0.0098	1	0.1668		
			2	0.1743		
			3	0.1551		
3	14	0.0098	1	0.1669		
			2	0.1583		
			3	0.1596		
1	20	0.0097	1	0.2565	0.2565 ± 0.0085	45.92
			2	0.2593		
			3	0.2568		
2	20	0.0098	1	0.2465		
			2	0.2533		
			3	0.2419		
3	20	0.0099	1	0.2688		
			2	0.2665		
			3	0.2589		

APPDENDIX G

G. Effect of Reaction time on Degree of Substitution and Reaction Efficiency

Table G.1 Effect of reaction time on degree of substitution and reaction efficiency

Batch	Reaction time (hours)	Weight (g)	No.	DS	Average DS	Average RE
1	3	0.0099	1	0.0811	0.0825 ± 0.0071	21.10
			2	0.0798		
			3	0.0829		
2	3	0.0102	1	0.0955		
			2	0.0831		
			3	0.0699		
3	3	0.0101	1	0.0815		
			2	0.0786		
			3	0.0901		
1	6	0.0098	1	0.1365	0.1398 ± 0.0057	35.75
			2	0.1299		
			3	0.1269		
2	6	0.0099	1	0.1286		
			2	0.1336		
			3	0.1246		
3	6	0.0097	1	0.1202		
			2	0.1296		
			3	0.1383		
1	14	0.0101	1	0.2396	0.2318 ± 0.0043	59.28
			2	0.2365		
			3	0.2298		
2	14	0.0100	1	0.2309		
			2	0.2310		
			3	0.2265		
3	14	0.0100	1	0.2315		
			2	0.2265		
			3	0.2339		

Batch	Reaction time (hours)	Weight (g)	No.	DS	Average DS	Average RE
1	18	0.0099	1	0.2499	0.2565 ± 0.0064	65.60
			2	0.2465		
			3	0.2615		
2	18	0.0100	1	0.2533		
			2	0.2547		
			3	0.2612		
3	18	0.0098	1	0.2596		
			2	0.2546		
			3	0.2672		
1	21	0.0100	1	0.2669	0.2693 ± 0..0052	68.87
			2	0.2656		
			3	0.2709		
2	21	0.0100	1	0.2711		
			2	0.2676		
			3	0.2747		
3	21	0.0100	1	0.2734		
			2	0.2746		
			3	0.2586		
1	24	0.0097	1	0.2861	0.2725 ± 0.0096	69.69
			2	0.2733		
			3	0.2659		
2	24	0.0099	1	0.2598		
			2	0.2672		
			3	0.2746		
3	24	0.0099	1	0.2646		
			2	0.2722		
			3	0.2883		

APPENDIX H

H. High Degree of Substitution and Reaction Efficiency of Hydroxypropylated Tapioca Starch

Table H.1 Degree of substitution and reaction efficiency of high hydroxypropylated tapioca starch

Batch	Weight (g)	No.	DS	Average DS	Average RE
1	0.0099	1	0.2754	0.2797 ± 0.0049	71.53
		2	0.2819		
		3	0.2880		
2	0.0100	1	0.2768		
		2	0.2754		
		3	0.2718		
3	0.0100	1	0.2819		
		2	0.2768		
		3	0.2848		

APPENDIX I

I. Characteristic of Hydroxypropylated Tapioca Starch in Water

Experiment no.	NaOH (%v/w)	PO (%v/w)	Na_2SO_4 (%v/w)	Temperature (°C)	Time (hrs)	DS	RE (%)	Moisture (%)
Native tapioca	-	-	-	-	-	-	-	13.17
1	1.0	8	10	40	24	0.0806	36.3	13.80
2	1.0	14	10	40	24	0.1668	42.7	13.05
3	1.0	20	10	40	24	0.2565	45.9	12.90
4	1.5	8	10	40	24	0.0975	43.7	13.78
5	1.5	14	10	40	24	0.2093	53.5	13.49
6	1.5	20	10	40	24	-	-	-
7	2.0	8	10	40	24	0.1025	45.9	14.52
8	2.0	14	10	40	24	-	-	-
9	2.0	20	10	40	24	-	-	-
10	1.0	8	15	40	24	0.0827	37.0	14.66
11	1.0	14	15	40	24	0.1871	47.8	14.04
12	1.0	20	15	40	24	0.2598	46.5	13.39
13	1.5	8	15	40	24	0.1062	47.5	13.99
14	1.5	14	15	40	24	0.2112	54.0	13.76
15	1.5	20	15	40	24	-	-	-
16	2.0	8	15	40	24	0.1175	53.7	13.93
17	2.0	14	15	40	24	-	-	-
18	2.0	20	15	40	24	-	-	-
19	1.0	8	20	40	24	0.1004	45.0	14.52
20	1.0	14	20	40	24	0.1906	48.7	13.94
21	1.0	20	20	40	24	0.2614	46.8	13.79
22	1.5	8	20	40	24	0.1144	51.2	14.62
23	1.5	14	20	40	24	0.2260	57.8	13.22
24	1.5	20	20	40	24	-	-	-
25	2.0	8	20	40	24	0.1212	54.3	13.60
26	2.0	14	20	40	24	0.2725	69.7	10.99
27	2.0	20	20	40	24	-	-	-

APPENDIX J

J. Characteristic of Hydroxypropylated Tapioca Starch in Aqueous Ethanol

Experiment no.	NaOH (%v/w)	PO (%v/w)	Ethanol : H_2O	Temperature (^oC)	Time (hrs)	DS	RE (%)	Moisture (%)
Native tapioca	-	-	-	-	-	-	-	13.71
28	1.0	8	30:70	40	24	0.0426	19.1	14.53
29	1.0	14	30:70	40	24	0.1013	25.9	13.36
30	1.0	20	30:70	40	24	0.1482	26.5	14.13
31	1.5	8	30:70	40	24	0.0667	29.8	13.05
32	1.5	14	30:70	40	24	0.1289	33.0	13.81
33	1.5	20	30:70	40	24	-	-	-
34	2.0	8	30:70	40	24	0.0694	31.1	13.91
35	2.0	14	30:70	40	24	-	-	-
36	2.0	20	30:70	40	24	-	-	-
37	1.0	8	50:50	40	24	0.0397	17.8	11.78
38	1.0	14	50:50	40	24	0.0842	21.5	11.82
39	1.0	20	50:50	40	24	0.1156	20.7	13.03
40	1.5	8	50:50	40	24	0.0532	23.8	13.79
41	1.5	14	50:50	40	24	0.0975	24.9	11.99
42	1.5	20	50:50	40	24	0.1568	28.1	13.54
43	2.0	8	50:50	40	24	0.0580	26.0	12.42
44	2.0	14	50:50	40	24	0.1203	30.1	13.35
45	2.0	20	50:50	40	24	0.1899	34.0	12.44
46	1.0	8	70:30	40	24	0.0374	16.7	12.14
47	1.0	14	70:30	40	24	0.0566	14.5	13.76
48	1.0	20	70:30	40	24	0.0935	16.7	13.28
49	1.5	8	70:30	40	24	0.0422	18.9	11.77
50	1.5	14	70:30	40	24	0.0773	19.8	13.76
51	1.5	20	70:30	40	24	0.1323	23.7	12.03
52	2.0	8	70:30	40	24	0.0510	22.8	11.96
53	2.0	14	70:30	40	24	0.1037	26.5	11.16
54	2.0	20	70:30	40	24	0.1603	28.7	13.18

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