CHEMICAL MODIFICATION OF STARCHES IN THE PRESENCE OF SUPERCRITICAL CO2

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Starches are reacted with organic acid anhydrides to produce a variety of starch ester compounds that have both edible and industrial applications. Supercritical carbon dioxide was investigated as a possible alternative reaction medium for the preparation of starch succinate esters. Cornstarch (10 wt% moisture) was combined with equimolar amounts of succinic, 2-octen-1-ylsuccinic, or 2-dodecen-1-ylsuccinic anhydrides in carbon dioxide at 80° C and 54 MPa for two hours with either an acid or base catalyst. The starch was recovered and extracted with 50% (v/v) aqueous ethanol and dried in a vacuum oven. Analysis of the reaction products indicated that the base catalyst, sodium hydroxide, was more effective than the acid catalyst, acetic acid, in the formation of starch esters. Succinic anhydride was substituted onto the starch to a greater extent than either of the other acid anhydrides investigated regardless of catalyst. These results suggest the possibility of using supercritical carbon dioxide in the preparation of starch esters.

INTRODUCTION

Supercritical carbon dioxide was examined as a possible reaction medium for the preparation of starch alkenyl succinates. Starch esters have been prepared previously with organic solvents such as pyridine, pyrrolidone, and dimethylacetamide, in aqueous slurries, or even solventless with a high degree of substitution [1 - 3]. Organic solvents, however, are problematic for the preparation of materials intended for use in the food industry whereas supercritical carbon dioxide is considered nontoxic and suitable for processing edible products. Supercritical carbon dioxide also exhibits lipophilic behavior that may be more advantageous in the formation of hydrophobic derivatives than aqueous systems. The recently reported solventless reaction of starch requires the preliminary formation of the formate ester that subsequently reacts with the desired higher molecular weight acid chloride in the absence of an organic solvent [3]. The possibility of using supercritical carbon dioxide would be most attractive in a single step reaction without pretreatment of the starch or preparation of an intermediate. The relatively low temperature and favorable solubility properties of supercritical carbon dioxide also present ideal conditions to prevent degradation of the starch during reaction and to facilitate product recovery.

The properties of a modified starch are determined by both the chemical nature of the substituent group and the degree of substitution [4, 5]. The introduction of long chain, aliphatic structures through the ester linkage, has remained elusive without using an organic solvent or pretreatment of the starch substrate. Identification of the reaction conditions that could achieve this in a process acceptable to the food industry would be a significant advancement.

MATERIALS AND METHODS

Samples of waxy corn starch (Staley), high amylose corn starch (National Starch), potato starch (Aveloe), and wheat starch (MidWest Grain) were obtained and moisture levels were determined gravimetrically. The starch samples were stored in sealed plastic containers prior to use. Succinic anhydride, (2-dodecen-1-yl) succinic anhydride, (2 octen-1-yl) succinic anhydride, phenolphthalein and citric acid were obtained from Sigma Chemical Co. (St. Louis, MO). Potassium hydroxide and hydrochloric acid were obtained from Fisher Scientific (Pittsburgh, PA). Glacial acetic acid was obtained from EM Science (Gibbstown, NJ). Absolute ethanol was obtained from Aaper Alcohol and Chemical Co. (Shelbyville, KY). Zinc chloride, aluminum acetyl acetonate, and aluminum chloride hexahydrate were obtained from Aldrich

Reactions were performed with an automated supercritical fluid extractor, the ISCO model 3560 SFX (Lincoln, NE), operated in the static extraction mode. Starch, reactant, and catalyst were accurately weighed into tared 10 ml extraction vials and the extractor was programmed to fill the vials with carbon dioxide and maintain a pressure of 54 MPa and a temperature of 50 °C or 80 °C for two hours. After a few preliminary reactions were performed with succinic anhydride a five factor, two level, fractional factorial design was followed to examine the effect of moisture, reactant, starch/reactant ratio, catalyst, and temperature, on the formation of the 2-dodecen-1-yl succinate and 2 octen-1-yl succinate starch esters. Starch, 1.0 g, was placed in a 10 ml stainless steel extraction vial. Deionized water was added to adjust the moisture level to 20 wt% for high moisture treatments and reactants were added at 25 or 50 mol% of anhydrous starch. Glacial acetic acid, 180 meq, was added as the acid catalyst and potassium hydroxide, 8 meq, as the base catalyst. Additional reactions were performed with potato, wheat, waxy and high amylose cornstarch using zinc chloride, aluminum acetyl succinate, or aluminum chloride hexahydrate catalysts.

Following the reaction the contents of the extraction vials were transferred to a glass sample bottle and mixed with 100 ml of 50 % (v/v) ethanol, covered, and allowed to stir for at least 12 hours at ambient temperature on a magnetic stirring plate. Stirring was discontinued to allow the solids to settle and the liquid phase was decanted and replaced with 100 ml of 50 % (v/v) aqueous ethanol. This mixture was acidified to pH 4 – 6 with 0.05 M citric acid and stirred for one hour. The liquid phase was again decanted and replaced with 100 ml of 50 % (v/v) aqueous ethanol. This mixture was allowed to stir for another hour and then the solids were recovered by vacuum filtration. The solids were transferred to aluminum weighing pans and placed in a 70 °C vacuum oven for 1 hour. The dried samples were stored in a dessicator.

Samples of the dried starch reaction products were weighed and mixed with 50 ml of aqueous ethanol (50 % v/v) and 50 ml of 1 N postassium hydroxide standard per gram of starch. The mixtures were covered and stirred for at least 12 hours at ambient temperature on a magnetic stirring plate. A few drops of an ethanolic solution of phenolphthalein was added to each mixture and then back-titrated with 1 N hydrochloric acid standard. Titrations were replicated and the degree of substitution was calculated from the mass of starch and the volume of titrant delivered.

RESULTS

Initial reactions were conducted with a waxy cornstarch, containing 10% moisture, at 80° C and 54 MPa carbon dioxide. When held at these conditions for two hours succinic anhydride reacted with cornstarch without a catalyst, however, the longer chain alkenyl succinic anhydrides exhibited negligible reactivity. Similar results were obtained with the addition of the acid catalyst, glacial acetic acid. However, the addition of the base catalyst, sodium hydroxide, promoted the reaction of the octenyl- and dodecenyl succinic anhydrides with cornstarch. These preliminary results were used to guide a more detailed investigation of the reaction of the longer chain alkenyl succinic anhydrides with cornstarch.

A Plackett-Burman experimental design was used to investigate the effects of moisture, catalyst, temperature, reactant, and reactant ratio on the formation of starch esters. The levels of these factors were selected to maintain carbon dioxide in the supercritical state while providing favorable reaction conditions for the formation of starch esters. Extremely high moisture levels would not be compatible with the supercritical carbon dioxide due to solubility limitations that could result in a phase separation. Elevated temperatures have also been shown to promote the degradation of the starch and were avoided. The degree of substitution (ds) was selected as the response variable. The data were first analyzed for interactions between the factors since fractional factorial designs may exhibit confounding. Analysis of variance was used to test for two and three way interaction effects. These results indicated that the higher order interaction terms were not significant (Table 1). A normal plot of the residuals exhibited an acceptable linear pattern (Fig. 1).

The main effects plot is presented in Fig. 2 and shows the response mean for each factor level compared to the overall mean. The slopes indicate the strength of these effects. The reactant ratio exhibited the largest effect on the degree of substitution and acted in a positive manner. The other main effects included the catalyst type, acid or base, and the reactant, octenyl succinic anhydride or dodecenyl succinic anhydride. Although the slopes appear positive and negative respectively this is an artifact of coding since these are not continuous factors. The response was greater with the base catalyst than with the acid catalyst (Table 2). The octenyl succinic anhydride was also more reactive toward starch than the dodecenyl succinic anhydride. Interestingly, both temperature and moisture exhibited negligible effects on the response variable at these treatment levels.

The highest observed ds values were obtained at 50° C, 20% moisture, with the higher reactant ratio and the potassium hydroxide catalyst. Ds values of 0.25 were obtained for both octenyl and the dodecenyl succinate cornstarch esters at these conditions. Results for the reactions of succinic anhydride with the alternative starch sources and catalysts are presented in Table 3. All of these reactions were performed at 50° C and 54 MPa of carbon dioxide for two hours. These results suggest that zinc chloride may represent a more effective acid catalyst than acetic acid for the reaction of succinic anhydride with waxy cornstarch and potato starch. For comparison a ds of 0.12 was obtained with octenyl succinic anhydride and waxy cornstarch. A disadvantage of using such a catalyst, however, is the more difficult separation and recovery from the product mixture.

These results were obtained in a batch reactor without the benefit of agitation and should be considered qualitative. In the context of a screening experiment, however, the trends observed here are useful and will be incorporated into the design of a more complete examination of supercritical reaction conditions for the modifications of starch.

CONCLUSIONS

These results demonstrated the potential application of supercritical carbon dioxide as a reaction medium to prepare starch esters from alkenyl succinic anhydrides with a base catalyst. The degree of substitution obtained at 50° C and 54 MPa was relatively low, 0.25, compared to the high DS values reported when these materials are reacted in organic solvents, however, further research is planned to explore the use of more effective catalysts and continuous as opposed to batch reactors.

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Table 1: Analysis of variance tables for selected models of ds (coded units)

First order model

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	5	0.1066	0.1066	0.021320	2.29	0.076
Residual Error	26	0.2426	0.2426	0.009330		
Total	31	0.3492				

Second order model

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	5	0.10660	0.10660	0.021320	1.93	0.145
2-Way Interactions	10	0.06605	0.06605	0.006605	0.60	0.793
Residual Error	16	0.17652	0.17652	0.011032		
Total	31	0.34917				

Table 2: Estimated effects and coefficients of ds (coded units)

Term	Effect	Coef	SE Coef	T	P
Constant	0.11858	0.01707	6.94	0.000	
Moisture	-0.00365	-0.00183	0.01707	-0.11	0.916
Catalyst	0.02860	0.01430	0.01707	0.84	0.410
Temperature	0.00452	0.00226	0.01707	0.13	0.896
Reactant	-0.03510	-0.01755	0.01707	-1.03	0.314
Ratio	0.10603	0.05301	0.01707	3.10	0.005

Table 3: DS values obtained for succinic anhydride with alternative catalysts and starches

Starch	Catalyst	DS
Waxy corn	Zinc chloride	1.16
	Aluminum acetyl acetonate	0.82
	Aluminum chloride hexahydrate	0.80
High amylose corn	Zinc chloride	0.93
	Aluminum acetyl acetonate	0.85
	Aluminum chloride hexahydrate	0.91
Potato	Zinc chloride	1.27
	Aluminum acetyl acetonate	0.82
	Aluminum chloride hexahydrate	0.82
Wheat	Zinc chloride	0.74
	Aluminum acetyl acetonate	0.83
	Aluminum chloride hexahydrate	0.70

Figure 1: Probability plot

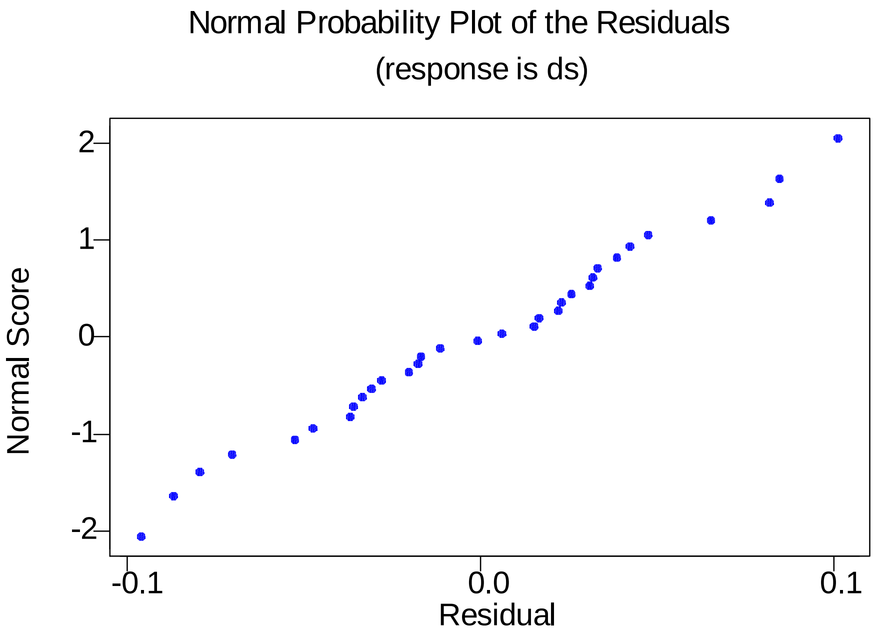

Figure 2: Main effects plot