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A. L. Compere[a]; J. M. Googin[a]; W. L. Griffith[a]
[a] Oak Ridge National Laboratory, Oak Ridge, Tennessee

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Effect of Possible Interferences on the Extraction of 1-Butanol from Aqueous Solution by the Ethyl Esters of Soybean Oil Fatty Acids

A. L. COMPERE, J. M. GOOGIN, and W. L. GRIFFITH

OAK RIDGE NATIONAL LABORATORY
P. O. BOX X
OAK RIDGE, TENNESSEE 37831

ABSTRACT

The methyl, ethyl, propyl and butyl esters of vegetable and tree oils are effective solvent extractants for 1-butanol from aqueous solution. Early applications of this process will probably involve bacterial mixed solvent fermentations of relatively impure waste and low-valued carbohydrates. Two types of materials, salts and solvents, could be expected to affect the extraction of 1-butanol from such industrial fermentation systems. The effect of four salts, three alcohols, and a ketone were evaluated using factorial experiments. Variations in NaCl, Na_2SO_4, Na_2SO_3, and $KHPO_4$ from 0 to 0.15 *M* on the extraction of 0.1 to 4.1% 1-butanol from aqueous solutions at 25, 40, and 55 C gave small changes in distribution coefficient. Mild increases occurred with increasing teperature and increasing NaCl, Na_2SO_4, and KH_2PO_4. Mild decreases in 1-butanol extraction occurred with increasing Na_2SO_3. Variations in acetone, ethanol, and 2-propanol concentrations ranging between 0 and 4% w/v at 25, 40 and 55 C gave small changes in distribution coefficient at 1-butanol concentrations ranging between 0.1 and 4.1% w/v had little effect. A slight increase in 1-butanol extraction was observed with increasing 1-pentanol under similar conditions.

INTRODUCTION

Neutral solvents fermentations, which produce primarily 1-butanol, 2-propanol, acetone, and ethanol, have been used industrially since World War I. These bacterial fermentations are characterized by both the ability to use a wide variety of carbohydrates and by the production of a range of solvents, rather than by the production of a single solvent (1).

The most common industrial fermentations produce around two-thirds 1-butanol, with the balance of solvents including acetone or 2-propanol or ethanol. Occasional cultures produce some 1-pentanol. Total solvents concentration in industrial fermentations is generally 2 or 3% w/v, with laboratory fermentation yields as high as 4 or 5% reported. The fermentation is generally thought to involve the reversible conversion of volatile acids to alcohols, with a substantial fraction of the acid left unconverted at the end of the fermentation. Fermentation offgases include hydrogen, as well as carbon dioxide. These features of bacterial solvent fermentations lend themselves well to product concentration and removal by solvent extraction, and a preliminary process evaluation using the advanced system for process engineering (ASPEN) indicated that a solvent extraction using a vegetable oil monoester, such as the ethyl ester of soy fatty acids, followed by a low temperature vacuum distillation, might provide a favorable energy balance when compared to conventional ethanol processes (2).

Because 1-butanol typically is a major, but not sole, fermentation product, other fermentation-produced materials, such as acetone, ethanol, and 1-propanol, could lower the distribution coefficient, resulting in poor extraction.

In evaluating a fermentation-extraction process, we felt it important to consider the probable feedstock. We felt that, based on quantity, sterility, and availability, wood pulping liquors represented a particularly good choice. The availability of a large excess of low temperature process heat in pulp mills at temperatures near those needed for the vacuum distillation could contribute substantially toward process energy requirements.

Earlier experiments showed the *Clostridia* used for neutral solvents fermentations to have a reasonable tolerance to most of the salts found in wood pulp blowdown streams at concentrations typical of the more common pulping process liquors, such as kraft and weak acid sulfite (3). A southern pine kraft process liquor was estimated to contain the following sodium salts, in m*M*: bisulfite, 87; carbonate, 525; chloride, 3; hydroxide, 85; sulfide, 62; and sulfate, 14 (4). Weak acid sulfite liquor contains around 10 m*M* sulfite. Pulp liquors also contain significant amounts of organic toxicants, an unaddressed problem which could significantly interfere with solvents production (5). Under present conditions, a complete fermentation of pulp liquors might be expected to yield to 5% solvents, with more typical yields expected to be 2 or 3%. Some of the fermented carbohydrate is in the form of volatile acids.

At present, yeast are unable to ferment the carbohydrates in most pulp streams. At low expected product levels, distillation and product separation schemes may well be uneconomic or have a poor energy balance. A neutral solvents fermentation, coupled with a solvent extraction, might be attractive to wood pulp industries because of available excess of low-temperature process heat; reduction of pulp stream viscosity with consequent improvements in evaporative concentration; and use of hydrogen offgas in equipment currently using natural gas. However, this will only be possible if the solvent extraction is not adversely affected by expected process interferences, such as alcohols, ketones, and salts across the expected range of 1-butanol concentration.

EXPERIMENTAL

Soybean oil ethyl ester. Soybean oil fatty acid ethyl ester was prepared according to the method described by Reid and coworkers (6). Six hundred grams of soybean oil was refluxed with 1500 ml of ethanol in the presence of 30 ml of sulfuric acid for at least

20 h. The ester was then washed several times with saturated NaCl solution, neutralized with Na_2CO_3 to the methyl orange end point. The residual alcohol and water was removed by distillation. Yield was comparable to that obtained by Reid and coworkers. Ester was stored at room temperature in a glass stoppered bottle with Na_2SO_4. The soybean oil was a raw production sample from A. E. Staley.

Aqueous—organic solvent extractions. Samples containing 0.2 ml each of aqueous 1-butanol, 0.2 ml alcohol, acetone, or salt stock solution, and 0.4 ml of soy ethyl ester were held at 25, 40, or 55 C for at least 2 h. During the extraction period, samples were vortexed twice to insure good mass transfer. Stock solutions were prepared at double their final concentrations. Phase separation problems in the butanol and pentanol stocks were managed by briskly stirring the stock solution during aliquot removal.

Each sample contained approximately 10^3 dps of ^{14}C 1-butanol. After the phases cleanly separated, 0.200 ml of each phase was removed using a positive displacement micropipette, placed in a scintillation vial, mixed with 20 ml of Packard Insta-Gel scintillation fluid, and counted in a Packard Model 3375 Tri-Carb counter. Distribution coefficients, K_d, were calculated as the ratio of the concentration of 1-butanol %w/v in the organic phase to the concentration of 1-butanol %w/v in the aqueous phase.

RESULTS

Sodium chloride, sulfite, and sulfate were selected as high concentration pulp liquor salts likely to affect 1-butanol solvent extraction. Potassium acid phosphate was also investigated because it is commonly added to weak acid sulfite liquor prior to yeast fermentation. Salt concentrations tested were 0, 50, 100, and 150 m*M*. These values cover the range for pulp stream sodium salts with the exception of carbonate, present at around 0.5 *M*. However, fermentation occurs at pH values ranging between 2.5 and 5, making it reasonable to expect to find carbon dioxide in process offgas and sodium compounds as the salts of black liquor and fermentation produced organic acids.

As shown in Table 1, increasing sodium chloride gives small increases in the extraction of 1-butanol from aqueous solutions. This appears to be most pronounced at higher NaCl concentrations and 25 C. With sodium sulfate, the effect appears to be somewhat more marked. Again, the data indicate statistically significant (>99.9%), but small, differences that might well be overshadowed by changes in vegetable oil ester composition (7).

In contrast, data for sodium sulfite indicates a small, but statistically significant (>99.9%), decrease in 1-butanol extraction with increasing salt concentration. This difference increases somewhat with increasing temperature, and may indicate formation of solvates. Potassium acid phosphate follows the pattern of sodium chloride and sodium sulfate, with a slight, but significant (>99.9%), increase in distribution coefficient with increasing salt concentration.

To put the values obtained in perspective, there appears to be more change in 1-butanol extraction between different esters of the same vegetable oil or different vegetable oil batches than is produced by the concentrations of salts tested (7).

The effect of additions of acetone and ethanol were of most concern. However, as shown in Table 2, these materials did not have a significant effect on 1-butanol extraction, even at forty times the 1-butanol concentration. At most, a very slight decrease in 1-butanol extraction at 55 C and 4% 2-propanol and control samples was shown. Otherwise, no signifi-

Table 1. Effect of Sodium Salts on 1-Butanol Distribution Coefficients

Expected Salts	Temp °C	Salt Conc, *M*	1-Butanol, %w/v				
			0.1	1.1	2.1	3.1	4.1
NaCl	25	0.0	1.3	1.4	1.4	1.5	1.6
		0.05	1.3	1.5	1.6	1.5	1.6
		0.10	1.4	1.5	1.6	1.6	1.7
		0.15	1.5	1.5	1.6	1.6	1.7
	40	0.0	1.8	1.9	2.0	2.0	2.1
		0.05	1.7	1.7	2.0	1.9	2.0
		0.10	2.0	1.9	1.9	2.0	2.0
		0.15	2.0	1.9	2.0	2.0	2.1
	55	0.0	2.4	2.4	2.4	2.5	2.4
		0.05	2.3	2.3	2.3	2.4	2.4
		0.10	2.3	2.4	2.4	2.4	2.4
		0.15	2.3	2.6	2.6	2.5	2.5
Na_2SO_4	25	0.0	1.3	1.4	1.4	1.5	1.6
		0.05	1.4	1.5	1.6	1.6	1.7
		0.10	1.7	1.7	1.9	1.9	1.9
		0.15	1.8	1.7	1.8	1.9	2.2
	40	0.0	1.8	1.9	2.0	2.0	2.1
		0.05	1.6	1.8	2.1	2.2	2.2
		0.10	2.1	2.0	2.2	2.3	2.3
		0.15	2.1	2.2	2.3	2.4	2.5
	55	0.0	2.4	2.4	2.4	2.5	2.6
		0.05	2.5	2.7	2.6	2.5	2.6
		0.10	2.7	2.7	2.6	2.6	2.7
		0.15	2.9	2.8	3.0	3.0	3.0
Na_2SO_3	25	0.0	1.3	1.4	1.4	1.5	1.6
		0.05	1.3	1.3	1.4	1.5	1.6
		0.10	1.1	1.2	1.3	1.6	1.4
		0.15	1.2	1.2	1.3	1.3	1.4
	40	0.0	1.8	1.9	2.0	2.0	2.1
		0.05	1.8	1.8	2.0	2.1	2.1
		0.10	1.5	1.6	1.8	1.8	2.2
		0.15	1.4	1.5	1.6	1.6	
	55	0.0	2.4	2.4	2.4	2.5	2.6
		0.05	2.3	2.3	2.5	2.3	2.3
		0.10	2.2	2.3	2.3	2.1	2.1
		0.15	2.0	2.0	2.0	1.8	1.9
KH_2PO_4	25	0.0	1.3	1.4	1.4	1.5	1.6
		0.05	1.3	1.4	1.5	1.6	1.7
		0.10	1.4	1.5	1.5	1.6	1.7
		0.15	1.5	1.6	1.6	1.6	1.8
	40	0.0	1.8	1.9	2.0	2.0	2.1
		0.05	1.8	2.0	2.0	2.1	2.1
		0.10	1.9	2.0	2.0	2.1	2.2
		0.15	1.8	1.9	2.0	2.1	2.2
	55	0.0	2.4	2.3	2.4	2.5	2.6
		0.05	2.6	2.4	2.5	2.3	2.5
		0.10	2.5	2.6	2.5	2.5	2.5
		0.15	2.5	2.5	2.7	2.6	2.8

Table 2. Effect of Alcohols and Ketones on 1-Butanol Distribution Coefficients

Expected Cosolvents	Temp °C	Additive Conc, %w/v	1-Butanol, %w/v				
			0.1	1.1	2.1	3.1	4.1
Acetone	25	0.0	1.3	1.4	1.4	1.5	1.6
		1.0	1.3	1.4	1.6	1.6	1.7
		2.0	1.3	1.4	1.5	1.6	1.6
		3.0	1.3	1.3	1.5	1.5	1.6
		4.0	1.3	1.3	1.4	1.5	1.6
	40	0.0	1.8	1.9	2.0	2.0	2.1
		1.0	1.7	1.8	2.0	2.0	2.0
		2.0	1.5	1.7	1.9	1.9	2.0
		3.0	1.5	1.7	1.8	1.8	1.9
		4.0	1.5	1.6	1.7	1.6	1.8
	55	0.0	2.4	2.4	2.4	2.5	2.6
		1.0	2.3	2.3	2.4	2.3	2.3
		2.0	2.2	2.2	2.2	2.1	2.3
		3.0	2.0	2.2	2.2	2.1	2.2
		4.0	2.3	2.2	2.2	2.2	2.3
Ethanol	25	0.0	1.3	1.4	1.4	1.5	1.6
		1.0	1.3	1.4	1.4	1.5	1.6
		2.0	1.2	1.3	1.4	1.5	1.5
		3.0	1.3	1.3	1.4	1.5	1.6
		4.0	1.3	1.4	1.5	1.5	1.5
	40	0.0	1.8	1.9	2.0	2.0	2.1
		1.0	1.8	1.8	1.9	2.0	1.9
		2.0	1.8	1.8	1.9	1.9	2.0
		3.0	1.8	1.8	1.9	1.9	2.0
		4.0	1.7	1.8	1.7	1.8	2.0
	55	0.0	2.4	2.4	2.4	2.5	2.6
		1.0	2.2	2.2	2.3	2.4	2.4
		2.0	2.2	2.3	2.4	2.4	2.4
		3.0	2.2	2.3	2.4	2.4	2.4
		4.0	2.2	2.3	2.4	2.3	2.4
2-Propanol	25	0.0	1.3	1.4	1.4	1.5	1.6
		1.0	1.3	1.4	1.6	1.6	1.7
		2.0	1.3	1.4	1.6	1.5	1.6
		3.0	1.2	1.4	1.4	1.5	1.6
		4.0	1.2	1.4	1.4	1.4	1.6
	40	0.0	1.8	1.9	2.0	2.0	2.1
		1.0	1.9	2.0	2.0	2.0	2.2
		2.0	1.8	1.9	1.9	2.0	2.0
		3.0	1.9	1.8	1.9	2.0	2.0
		4.0	1.8	1.7	1.9	1.9	1.9
	55	0.0	2.4	2.4	2.4	2.5	2.6
		1.0	2.1	2.2	2.2	2.4	2.5
		2.0	2.2	2.3	2.3	2.3	2.3
		3.0	2.0	2.1	2.1	2.2	2.3
		4.0	2.0	2.1	2.1	2.2	2.2
1-Pentanol	25	0.0	1.3	1.4	1.4	1.5	1.6
		1.0	1.4	1.5	1.6	1.5	1.6
		2.0	1.5	1.5	1.6	1.5	1.8
		3.0	1.5	1.7	1.8	1.7	1.8
	40	0.0	1.8	1.9	2.0	2.0	2.1
		1.0	2.0	2.0	2.0	2.1	2.1
		2.0	2.0	2.0	2.2	2.1	2.1
		3.0	2.2	2.2	2.3	2.3	2.2
	55	0.0	2.4	2.4	2.4	2.5	2.6
		1.0	2.4	2.6	2.7	2.6	2.6
		2.0	2.5	2.8	2.8	2.6	2.8

cant effect of 2-propanol addition is apparent. However, there is a slight increase in 1-butanol extraction coefficients with increasing 1-pentanol addition. Pentanol concentrations were reported for levels only up to 3% at 25 and 40 C, and 2% at 55 C due to the limited solubility of 1-pentanol in water. Significance levels for the slopes were above 95%, with most data at 40 and 55 C around 99%.

CONCLUSIONS

At concentrations likely in wood pulp streams, sodium chloride, sulfite, and sulfate, and potassium acid phosphate appear to have limited effect on 1-butanol extraction by soybean oil ethyl esters. Several other questions, most notably the effects of organic acids and their sodium salts on the extraction, require resolution prior to more detailed process evaluations.

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