Solvent Extraction of Ethanol from Aqueous Solutions Using Biobased Oils, Alcohols, and Esters

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ABSTRACT: Distribution coefficients and separation factors were determined for the partitioning of ethanol and water from aqueous mixtures into several vegetable oils and their fatty alcohol and fatty ester derivatives. Castor oil, ricinoleyl alcohol, and methyl ricinoleate all show higher ethanol distribution coefficients, and similar or reduced separation factors, relative to other oils and derivatives studied here or reported by others. Of particular interest, ricinoleyl alcohol has an ethanol distribution coefficient 50% higher than that of oleyl alcohol, a commonly studied solvent for ethanol extraction from fermentation broths.

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KEY WORDS: Ethanol, fatty alcohols, fatty esters, solvent extraction, vegetable oils.

Interest is growing rapidly in the biorefining of ethanol, butanol, diols, and other products derived from fermentation of renewable substrates. Fuel ethanol is primarily derived from grains; as of January 2006, U.S. plant capacity was approximately 16.4×10^9 L/yr (4,336 MM gal/yr), with another 6.6×10^9 L/yr (1,746 MM gal/yr) capacity under construction (1). Much effort has been devoted to laboratory-scale fermentation for butanol (2). DuPont is pursuing 1,3-propanediol (3). A common critical problem for these water-soluble products is their recovery from dilute aqueous solutions. Though distillation is a standard method for recovering low-boiling products such as ethanol, the energy requirements for the separation can be high by this method, especially when the concentration of the product in the feed is very low. At high product concentrations, azeotropes also are a common problem in distillation and require additional processing *via* azeotropic or extractive distillation, adsorption, or pervaporation to yield a dry product.

Liquid–liquid solvent extraction is an attractive alternative separation process for ethanol and higher alcohols. Continuous removal of the product during fermentation is possible. This can be important, as generally these products are inhibitory to the microorganisms producing them, hence continuous removal of these products can increase fermentor productivity and substrate yield. As an alternative to distillation for ethanol, solvent extraction has the potential to be more energy efficient (4,5).

Criteria that must be considered when choosing an extraction solvent include extraction performance, chemical stability, solubility in the aqueous feed, immiscibility of phases, emulsion or foam formation, economic separation of the solvent and product, biocompatibility with the fermentation organisms, safety hazards to plant workers, and environmental risk *via* air or water emissions. No single solvent performs well in all these criteria; hence a compromise must be made. In terms of extraction performance for ethanol, Munson and King (6) rank classes of solvents by increasing ethanol distribution coefficients: hydrocarbons < ethers < ketones < amines < esters < alcohols < carboxylic acids. Alcohols, esters, and ketones are attractive because of their lower reactivity relative to carboxylic acids and amines and their generally higher distribution coefficients relative to ethers and hydrocarbons.

Toxicity of extraction solvents to the fermentation microorganisms has been a key issue, eliminating most solvents of interest in the lower M.W. range. Vegetable oils and their derivatives have been investigated for use as extractants in fermentations. For ethanol recovery from fermentation broths, many have studied the use of oleyl alcohol as an extractant because it satisfies many of the criteria described above. Generally, oleyl alcohol is nontoxic to the fermentation microorganisms. However, its ethanol extraction performance is inadequate for commercial application. Mehta and Fraser (7) suggested the use of higher M.W. hydrocarbons and vegetable oils that form conjugate solution pairs with ethanol. They considered hexadecane, cottonseed oil, and white light paraffin oil, and presented extraction data for the paraffin oil. The extraction is carried out at an elevated temperature, and the ethanol is recovered from the solvent *via* a drop in temperature that results in phase separation. Rahman *et al.* (8) considered the use of olive, coconut, or soybean oil as extraction solvents in a similar process but used only soybean oil in the experimentation. They found that extraction of ethanol from feed solutions containing less than 30% ethanol was low and did not become significant until above 60%; in addition, solvent-to-feed ratios were quite high. Honda *et al*. (9) determined partition coefficients, emulsion behavior, and yeast toxicity for several solvent classes, including substituted phenolics, several vegetable oils (castor, olive, and others), alcohols (decanol, lauryl, oleyl, and others), and carboxylic acids but did not report separation factors. Based on the results, they used castor oil in immobilized yeast gel beads as a protectant for phenolic extraction solvents. For butanol extraction, Groot *et al*. (10) examined 36 solvents, including several vegetable oils (castor oil, soybean oil, and others), fatty esters (methyl and ethyl oleates, and others), paraffinic hydrocarbons, and several primary alcohols (up to C_{12}). They

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TABLE 1
Extractant Solvents, Sources, and Characterization

Extractant	Predominant FA species	Grade	Source[a]	Characterization[b]
Coconut oil	Lauric [C12:0]	Refined, 76°F	Alnor Oil	44–52% lauric, <10% unsat., FFA <0.05%, SV 250–264, IV 6–12
Olive oil	Oleic [C18:1]	Edible, NF	Welch, Holme & Clark	72.6% oleic, FFA 0.12 wt%, IV 83.1, SV 194.3
Castor oil	Ricinoleic [12-hydroxy C18:1]	Neutralized	Alnor Oil	87.1% ricinoleic, FFA 0.33%, IV 85.1, SV 178.7, HV 161.6
Safflower oil	Linoleic [C18:2]	Edible, high-linoleic acid	Alnor Oil	75% linoleic, FFA 0.04%
Methyl laurate	Lauric		Aldrich	99.9%
Methyl oleate	Oleic		Aldrich	99.8%
Ethyl oleate	Oleic		Aldrich	99.6%
Butyl oleate	Oleic		Spectrum	65%
Methyl ricinoleate	Ricinoleic		Spectrum	99.5%
Methyl linoleate	Linoleic		Sigma	99.5%
Lauryl alcohol	Lauric	ACS reagent	Aldrich	98.52%
Oleyl alcohol	Oleic	Jarcol 95BJ	Jarchem	93% oleyl, SV 0.15, HV 207, IV 91.3
Ricinoleyl alcohol	Ricinoleic		MP Biomedicals	89.1% ricinoleyl

[a]Alnor Oil, Valley Stream, NY; Welch, Holme & Clark, Newark, NJ; Sigma-Aldrich, St. Louis, MO; Spectrum Chemicals and Laboratory Products, Gardena, CA; Jarchem, Newark, NJ; MP Biomedicals, Aurora, OH.
[b]Characterization definitions: FFA = free fatty acids, expressed as oleic acid; IV = iodine value; SV = saponification value; HV = hydroxyl value.

noted a higher distribution coefficient for castor oil vs. other oils tested, and higher distribution coefficients for fatty esters vs. their parent TG.

Previously (11), we studied the ethanol-extractive performance of a wide variety of C_6–C_{12} alcohol solvents to determine the effects of M.W., position of the hydroxyl group, and branching. Here, we examine the ethanol extraction performance of several vegetable oils and their derivative fatty esters and fatty alcohols. Oils and derivatives with functional groups that can form associations with ethanol and water were of particular interest for increasing the ethanol distribution coefficient. Castor oil TG are composed primarily (87–89%) of ricinoleic acid (12), which has a 12-hydroxyl group. The hydroxyl group, by providing additional hydrogen bonding sites, should increase ethanol capacity compared with oils that do not contain such groups. This effect should also manifest in the derivative esters and alcohols.

Oils selected had TG that were formed primarily from the fatty moiety of interest in each category: saturated, single unsaturated, double unsaturated, and hydroxyl-containing. The four oils chosen were coconut (saturated, lauric), olive (single unsaturated, oleic), safflower (double unsaturated, linoleic), and castor (hydroxyl-containing, single unsaturated, ricinoleic). The derivative esters chosen for comparison were methyl laurate, methyl oleate, methyl linoleate, and methyl ricinoleate. Additionally, methyl oleate was compared with ethyl and butyl oleate. The derivative alcohols chosen were lauryl (1-dodecanol), oleyl, and ricinoleyl.

For the purpose of limiting the set of potential solvents, extraction performance is a convenient and relatively fast initial screening exercise, where a single set of operating conditions (temperature, aqueous phase concentration) is chosen for comparison of the solvents. Final selection and suitability of a solvent would depend on follow-up studies investigating toxicity to fermentation microorganisms, phase separation (emulsion and foam generation), and the other criteria noted above. Full phase diagram data, with tie lines, also should be generated to define the performance of the solvent in the full operating space that will be encountered.

EXPERIMENTAL PROCEDURES

A solvent screening technique was used that measured the partition of ethanol and water between an aqueous phase, initially 5 wt% ethanol, and the solvent phase. The extractions were at 33°C with an aqueous-to-organic phase volume ratio of 2:1 and a total liquid volume of 7.5 mL. The mixtures were emulsified multiple times to ensure equilibrium was reached, then phase-separated by centrifugation at the extraction temperature. Each phase was then analyzed by GC using an internal standard method to determine its ethanol and water concentrations. Additional details can be found in Offeman *et al*. (13).

Extraction performance comparisons of solvents at a particular operating point can be conveniently represented by two characteristics: distribution coefficient K_{DE} and separation factor α. The distribution coefficient indexes the solvent's capacity for the extracted component, while the separation factor is the solvent's selectivity for one component over another. The equilibrium distribution coefficient for ethanol is defined as $K_{DE} = [EtOH]_{org}/[EtOH]_{aq}$, the ratio of the weight percentage of ethanol in the organic phase to the weight percentage of ethanol in the aqueous phase. The equilibrium distribution coefficient for water is defined similarly as $K_{DW} = [H_2O]_{org}/[H_2O]_{aq}$. The separation factor, $\alpha = K_{DE}/K_{DW}$, is the ratio of ethanol to water in the organic phase divided by the ratio in the aqueous phase.

Sources and characterization of the extraction solvents are shown in Table 1. Ethanol was 200 proof anhydrous grade,

from Aaper Alcohol and Chemical Co. (Shelbyville, KY). The organic-phase diluent was 1-pentanol (99.73%; Aldrich, Milwaukee, WI), the aqueous phase internal standard was 1-butanol (99.95%; Aldrich), and the organic-phase internal standard was 1-hexanol (99.49%; Aldrich). Distilled water was used in all solutions. The oils, esters, and alcohols were used as received.

RESULTS AND DISCUSSION

Vegetable oils are not single compound materials, but are mixtures of TG, with generally less than 2% nonglyceride components for refined oils (14). The TG are glycerol esters of FA; therefore, each TG molecule can be formed from three FA that may all be the same, or may be different. Although we associate relatively pure ester and alcohol derivatives with certain vegetable oils, it is important to realize that the oils are mixtures and that the oil FA component to which we associate the derivatives is only the dominant FA in the oil. Also, FFA present in vegetable oils can create phase separation difficulties (emulsions, foam generation) in industrial-scale liquid–liquid extraction operations. In this work, longer centrifugation times were required to attain clarity of the phases for the vegetable oils in comparison with the esters and alcohols studied.

The results of the solvent extraction screening method are shown in Table 2. Multiple runs were carried out for each solvent; the average values are shown. Previously reported literature K_{DE} values and separation factors are shown for comparison.

The ethanol distribution coefficients and separation factors in this work compare reasonably well with those in the literature. Differences between the present data and literature values may be explained by differences in experimental conditions, solvent purity, and extraction and analytical methodology. For example, K_{DE} increases with increasing extraction temperature and increasing aqueous-phase ethanol concentration (13,19). Large differences in results for a single alcohol solvent often can be found between different literature sources, even at similar temperature and ethanol concentration conditions.

Groupings and trends are revealed when the separation factor α is plotted against the ethanol distribution coefficient K_{DE} (Fig. 1) for the oil, ester, and alcohol data sets. Olive, safflower, and coconut oil form a group with K_{DE} near 0.05 and α near 23. The methyl esters of the dominant FA of these oils show slight improvement in K_{DE} and α. Performance of the esters would be expected to be near that of the parent TG, which are, of course, also esters. Interestingly, the ethyl and *n*-butyl esters of oleic acid show considerably higher α values than that of the methyl ester (32.0, 32.3, and 21.4, respectively). We have seen a similar effect in previous studies on C_8 branched alcohols: the change in branch length from methyl to ethyl increased α much more than the ethyl-to-propyl or ethyl-to-butyl cases (11). This effect may be due to a combination of increased steric shielding of the ester oxygens and increased dispersion forces between the alkyl group and ethanol. In the case of butyl oleate, however, it should be noted that the purity of this solvent was only 65%; impurities may well be affecting its performance relative to pure butyl oleate. In general, mixtures of solvents behave in an additive manner.

Oleyl and lauryl alcohol both show much higher K_{DE} and lower α values relative to the parent oils, olive and coconut, respectively. The increased affinity for both ethanol and water of the hydroxyl group relative to the ester is evident. It can be seen that lauryl alcohol has a higher K_{DE} than oleyl alcohol. This is due to the lower M.W. of lauryl alcohol. The concentration of hydroxyl groups (and therefore number of sites associating with ethanol or water) in a given mass of each solvent decreases linearly as M.W. increases. This effect has been noted by Murphy *et al*. (15) and Offeman *et al*. (11). The M.W. of lauryl alcohol

TABLE 2
Extraction Results at 33°C and $[EtOH]_{Aq}^{0}$ = 5 wt%, and Comparison with Literature Data

	This study		Literature		
Extractant	α	K_{DE}	α	K_{DE}	T (°C)/$[EtOH]_{Aq}$ (ref)[a]
Coconut oil (prim. lauric)	23.4	0.0557			
Olive oil (prim. oleic)	21.6	0.0458		0.04	30/9.1% (9)
Castor oil (prim. ricinoleic)	15.9	0.193		0.08	30/9.1% (9)
Safflower oil (prim. linoleic)	24.0	0.0451			
Methyl laurate	28.5	0.0962			
Methyl oleate	21.4	0.0739			
Ethyl oleate	32.0	0.0652			
Butyl oleate	32.3	0.0621			
Methyl ricinoleate	17.2	0.294			
Methyl linoleate	28.0	0.0708			
Lauryl alcohol	12.2	0.448	10	0.35	23/7.4% (15)
				0.37	30/9.1% (9)
			9.2	0.59	35/14.6% (16)
Oleyl alcohol	16.1	0.306	22.8	0.21	25/4.3% (17)
				0.24	30/9.1% (9)
				0.34	65/n.r.% (18)
Ricinoleyl alcohol	15.1	0.461			

[a]n.r., purity not recorded.

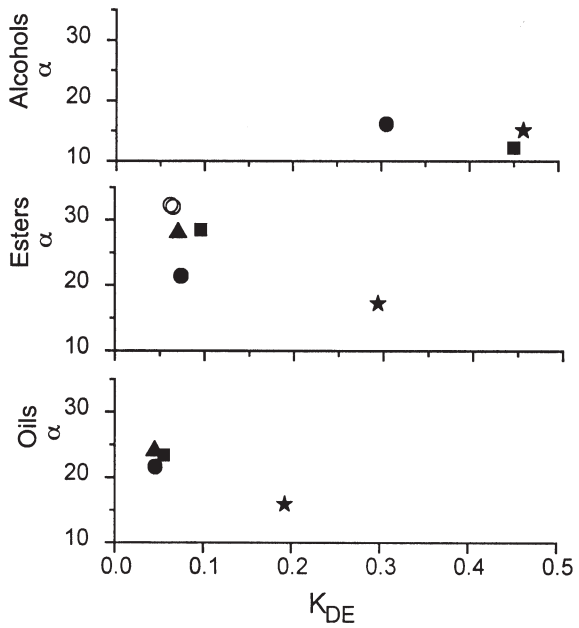

FIG. 1. Ethanol-extractive performance of oils and derivatives. C18:1 compounds: (●) olive oil, methyl oleate, oleyl alcohol, (○) ethyl oleate and butyl oleate; C18:1-OH compounds: (★) castor oil, methyl ricinoleate, ricinoleyl alcohol; C18:2 compounds: (▲) safflower oil, methyl linoleate; C12:0 compounds: (■) coconut oil, methyl laurate, lauryl alcohol.

(C_{12}) is lower than oleyl alcohol (C_{18}) by a factor of 1.44, hence the concentration of its hydroxyl groups is higher than that of oleyl alcohol by the same factor. This closely matches the observed difference in K_{DE} of a factor of 1.42.

In comparison with the other oils studied, the K_{DE} for castor oil is markedly higher by a factor of 3.9 (0.193 vs. 0.05). A decrease in α by a factor of 0.7 (16 vs. 23) also occurs. This is attributable to the 12-hydroxy group in the ricinoleyl component, which greatly increases the affinity for ethanol and for water. The K_{DE} for methyl ricinoleate is greater than that of castor oil by a factor of 1.5, and nearly the same factor is seen for methyl oleate relative to olive oil. A slight increase in α is observed for methyl ricinoleate vs. castor oil. As with the oils, methyl ricinoleate is higher by a factor of 4 in K_{DE} compared with the other esters, and α is 20% lower.

Similarly, ricinoleyl alcohol shows another large increase in K_{DE} over methyl ricinoleate, though not proportionately as high as those seen for oleyl and lauryl alcohols when compared with their methyl esters. The effect of adding a second hydroxyl seems to be less than adding the first hydroxyl. Nonetheless, ricinoleyl alcohol is seen to have the largest K_{DE} of the alcohols studied. Lauryl alcohol (1-dodecanol) has been studied in fermentation systems. It seems to have both a higher toxicity to microorganisms and a higher solubility in the aqueous phase than oleyl alcohol, which is unfortunate since its extraction performance is almost as good as ricinoleyl alcohol. Oleyl alcohol has been the solvent of choice in most research on extractive fermentation systems. Ricinoleyl alcohol performs with a similar separation factor, but with a 50% higher ethanol distribution coefficient.

Thus, compared with base oils, ester groups increase α and K_{DE} modestly, with the more hydrophobic ethyl and butyl esters increasing α more than methyl, whereas the hydrophilic hydroxyl group of the alcohols greatly increases K_{DE} and modestly decreases α.

The high ethanol distribution coefficients for castor oil compared with other vegetable oils studied, and for ricinoleyl alcohol compared with oleyl alcohol and, to a lesser extent, lauryl alcohol, merits further study of their use in extraction of alcohols from fermentation broths. By comparison with similar high-M.W. solvents, castor oil and ricinoleyl alcohol/esters would not be expected to be toxic to fermentation organisms, unlike alcohol solvents at or below 12 carbons in chain length. However, it would be important to verify toxicity against the specific microorganisms to be used in any fermentation system using solvent extraction for recovery of alcohols.

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