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Extractive Fermentation of Acetone and Butanol: Process Design and Economic Evaluation

The economics of producing butanol by extractive fermentation were examined. Capital cost and energy requirements were significantly reduced by the use of extractive fermentation.

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Introduction

Although a wide range of chemicals can be produced by fermentation, the accumulation of toxic products in the fermentation broth often inhibits further product formation. Reactor productivities are low and the products are obtained in dilute form. Fermentation processes are thus typically capital-intensive since large reactors and downstream processing equipment are required to handle the large volumes of water introduced into the process. Large amounts of energy must also be expended to recover the dilute products from the broth.

The effects of end-product inhibition can be reduced by removing toxic fermentation products from the broth *in situ*. Several methods of *in situ* product recovery have been developed. Volatile fermentation products, such as ethanol, can be removed from the broth by creating a vacuum in the fermentor so that inhibitory product distill from the broth as they form [*1–4*]. Volatile inhibitory products have also been removed *in situ* by stripping them from the broth into a gas stream. The gas stream can be passed directly through the fermentor [*5, 6*] or can be confined to one side of a semipermeable membrane [*7, 8*].

A number of the methods have been devised to remove nonvolatile inhibitory products from fermentation broth *in situ*. Inhibitory products have been adsorbed onto ion exchange resin [*9–12*], activated carbon [*13–16*] and polymeric resins [*17–20*]. Liquid-liquid extraction has also been used for the *in situ* removal of inhibitory products from fermentation broth. Aqueous phases formed by the addition of polymers to the broth [*21–27*] and organic solvents [*28–34*] have both been used to extract inhibitory products as they form. Perstraction, in which the organic solvent is separated from the fermentation broth by a semipermeable membrane [*35, 36*], has also been employed.

The underlying purpose of all methods of *in situ* product recovery is to decrease the cost of producing chemicals by fermentation. Maiorella, *et al.* [*37*] have evaluated the cost of producing ethanol in flash fermentation and Schoutens and Groot [*38*] have recently estimated the cost of producing iso-propanol/butanol/ethanol in a novel fermentation process employing pervaporation to remove the alcohols *in situ*. Other than these studies, however, few economic evaluations of *in situ* product recovery fermentations have been made.

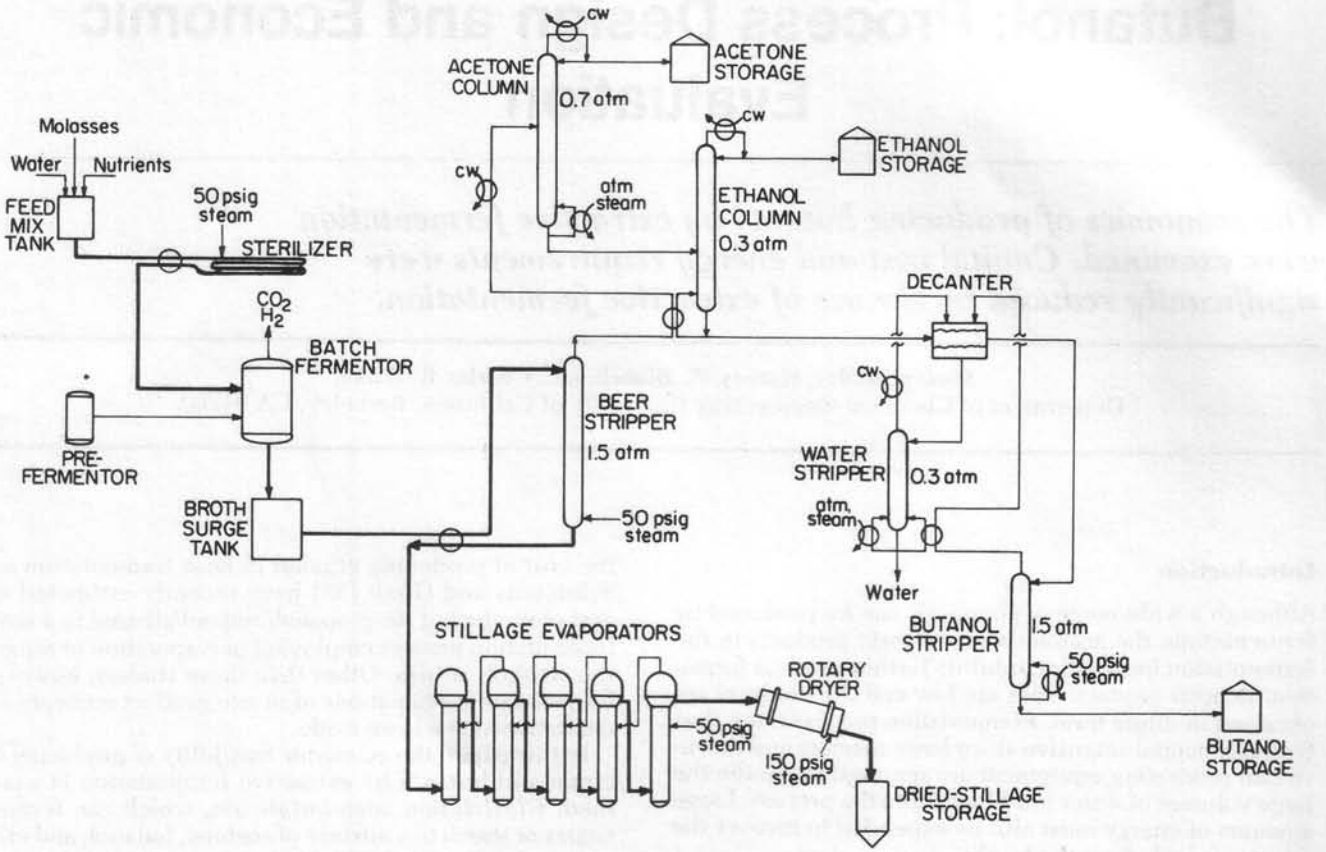
In this paper, the economic feasibility of producing acetone and butanol by extractive fermentation is examined. *Clostridium acetobutylicum*, which can ferment sugars or starch to a mixture of acetone, butanol, and ethanol, is totally inhibited by butanol concentrations of 10–15 g/L [*39, 40, 41*]. Removal of butanol during fermentation has been shown to reduce the effect of butanol inhibition and increase volumetric butanol productivity in batch [*33*] and fed-batch [*34*] culture. The feasibility of using continuous processing steps in extractive fermentation has also been demonstrated in a bench scale-process in which fermentation broth was continuously cycled to an extraction column [*42*]. Results of these studies are used to design an extractive fermentation plant with annual butanol production of 200 million pounds. The cost of producing butanol by extractive fermentation is estimated and compared to the conventional batch fermentation process.

The Conventional Butanol Fermentation Process

Fermentation products are conventionally produced in batch fermentation. A plant using batch fermentation to produce butanol was designed to act as a benchmark for comparison with the extractive fermentation process. The batch process design relies heavily on descriptions of commercial butanol fermentation facilities [*43, 44*], and on a prior economic analysis of the conventional butanol fermentation of molasses [*45*].

Figure 1 shows a schematic of the batch fermentation process. Molasses, containing 55 wt% fermentable sugars and 30 wt% nonfermentable solids, is diluted to 60 g/L sugar and mixed with nutrients in the feed mix tank. Butanol inhibition prevents the use of higher sugar con-

FIGURE 1. Process flow diagram of a batch fermentation for production of butanol, ethanol, and acetone.



centrations in the fermentor. The diluted feed is continuously sterilized by direct steam injection and charged into batch fermentors. Fermentors are inoculated with actively growing cells of a strain of *Clostridium acetobuytlicum* produced in smaller seed fermentors. After 30 hours of fermentation, the broth, containing (in g/L): 13.7 butanol, 5.4 acetone, 1.5 ethanol, 0.2 butyric acid, 0.3 acetic acid, and 3.0 cells, is discharged to the broth surge tank. The batch fermentors are operated on a staggered schedule so that downstream processing is continuous.

Butanol, acetone, and ethanol are stripped from the broth with 50 psig steam in the beer stripper after being heated to 100°C by heat exchange with the stripper-bottoms product. The stripped broth, containing acetic and butyric acids, cells, proteins and nonfermentable molasses solids, is evaporated to 50 wt% solids in the multiple-effect stillage evaporators and then dried to 85 wt% solids in a rotary dryer to give a dried stillage product that can be used as an animal feed supplement [43]. The overhead vapor from the beer stripper, containing approximately 70 wt% water and 30 wt% acetone, butanol, and ethanol, is separated in a series of four distillation columns. 99.5 wt% acetone is taken overhead from the first column. This column is operated at 0.7 atm so that low pressure steam from the last effect of the stillage evaporators can be used in the reboiler. The bottoms product from the acetone column is fed to the ethanol column, which operates at 0.3 atm pressure.

Vacuum operation reduces the reflux needed to produce the 95 wt% ethanol overhead product and allows the total reboiler duty to be met by condensing the overhead vapors from the beer stripper in the ethanol column reboiler. The bottoms product from the ethanol still and the overhead streams from the water and butanol strippers are fed to a decanter where an aqueous-rich phase is allowed to separate from a butanol rich phase. The water-rich phase, containing approximately 9.5 wt% butanol, is refluxed to the water stripper, which produces water containing less than 0.01 wt% butanol. The butanol-rich phase, containing about 23 wt% water, is refluxed to the butanol stripper, which produces a 99.7 wt% butanol product. The operating pressures of the stripping columns are set such that about half of the heat duty in the water stripper reboiler is met by condensing the overhead vapors from the butanol stripper.

Design of the Conventional Fermentation Process

A batch fermentation process was designed to produce 200 million pounds of butanol annually. The plant is operated 24 hours a day with a stream factor of 0.95. The batch fermentors were assumed to operate at a butanol productivity of 0.58 g/L-hr, which is the productivity of *Clostridium acetobutylicum* (ATCC 824) grown in batch culture on glucose [33]; this same strain of *Clostridium* was used in extractive fermentation experiments [*34*, *42*]. The yields of products in batch culture were the values reported by Marlatt and Datta [*46*] in their economic evaluation of the fermentation of corn to butanol.

UNIFAC, a group-contribution method of estimating activity coefficients in nonideal liquid mixtures [*47*], was used to model vapor-liquid equilibrium in the recovery section of the process. Distillation columns were designed using modified computer programs developed by Fredenslund *et al.* [*48*].

Stainless steel construction was specified for equipment in direct contact with fermentation broth because of the presence of acetic and butyric acids. Carbon steel construction was used for other equipment.

Economic Evaluation of the Conventional Fermentation Process

The costs of major equipment in the batch fermentation process are listed in Table 1. Costs were estimated from information given by Peters and Timmerhaus [*49*], Bartholomew and Reisman [*50*], Baasel [*51*] and from vendor's quotations [52], updated to a late 1986 basis (MSI = 800). The fermentation and stillage processing sections each account for about 40% of the total purchased equipment cost of the conventional batch process. Distillation and product storage each account for only about 10% of equipment cost.

Fixed capital and total capital investments for the batch fermentation plant are shown in Table 2. The batch process is capital intensive, requiring a total investment of $154 million. Table 3 shows the manufacturing costs for the batch fermentation process. The costs of the coproducts, acetone and ethanol, were taken from the Chemical Marketing Reporter [53]. The value of dried stillage is updated from Maiorella *et al.* [*54*]. A conservative credit of $0.10/lb hydrogen is used because gas separation equipment is not included in this estimate. In addition, a credit of $0.85/1000 lbs low pressure steam generated in the last effect of the stillage evaporators is taken [55]. No credit is taken for carbon dioxide.

The rational price of butanol for an 18% discounted cash flow rate of return on investment is 61.7 cents/lb. The purchase of molasses accounts for 67% of the final cost of butanol. Stillage processing also represents a major component of the cost of producing butanol by batch fermentation. The large amounts of steam required in the stillage evaporators could be reduced by pre-concentrating the stillage by precipitation or filtration. Soluble nutrients, however, are lost in these operations. In addition, large volumes of spent broth would have to be treated to reduce its high BOD level before discharge. Molasses stillage has a BOD of 15 to 55 Kg O_2/m^3 [*54*, *56*]. At a BOD of 25 Kg O_2/m^3, the fermentation process requires the removal of 1.7×10^8 kg O_2/yr. At a treatment cost of $98.4/1000 lb BOD [*46*], waste treatment would add over 18 cents/lb to the cost of butanol. Thus, although the cost of evaporating the dilute stillage is high, pre-concentration of molasses stillage does not appear attractive.

The estimated cost of producing butanol by batch fermentation in this study is about twice the cost estimated by Marlatt and Datta [*46*] for the fermentation of butanol from corn. The difference in butanol cost is due to different assumptions used in the evaluations. First, Marlatt and Datta assumed a volumetric butanol productivity about three times higher than the productivity used in this study, thus fewer fermentors were required in their design. Second, Marlatt and Datta assumed steam was produced by coal combustion, with a credit for cogeneration and a credit for the heating value of fermentor offgases. This resulted in a net steam cost of $0.49/1000 lb 150 psig steam. The 150 psig steam was charged at $4.00/1000 lb in this study. Finally, a credit of 25.2 cents/lb of butanol for corn based co-products was taken for a net raw material cost of 13.9 cents/lb butanol. In this study, a co-product credit of 9.5 cents/lb butanol is taken, giving a net raw material cost of 32.7 ¢/lb butanol. If the butanol productivity, steam cost, and net raw materials cost used by Marlatt and Datta are used in this study, the rational cost of butanol is 28 ¢/lb, within 5% of the butanol cost estimated by them.

The butanol productivity, steam cost, and net raw material cost used in here are believed to be appropriate for the batch fermentation of butanol from molasses. Productivities ranging from 0.16 to 0.51 g/L hr have been reported for *Clostridium acetobutylicum* growing in batch culture on glucose or whey [*25*, *31*, *41*, 57]. The butanol productivity used in this study, 0.58 g/L hr, is the productivity of the strain of *Clostridium acetobutylicum* (ATCC 824) used in extractive fermentation studies [*34*, *42*] when grown in batch culture [33]. The 150 psig steam was charged at $4.00/1000 lb because the feasibility of providing steam at $0.49/1000 lb by burning the fermentor off-gas, which contains large amounts of carbon dioxide, has not been demonstrated.

Extractive Fermentation of Butanol

In extractive fermentation, end-product inhibition is reduced by extracting toxic fermentation products out of the broth into an organic solvent. The selection of the organic solvent to be used in extractive fermentation is an important process decision. The most severe constraint in the selection of a solvent is that it must be biocompatable with the fermenting microorganisms. Moreover, traces of solvent remaining in the broth should not affect the value of stillage byproducts. The extraction solvent should have a high capacity for the fermentation products in order to minimize solvent inventory and product recovery costs. If the extracted products are recovered by distillation, the solvent should be less volatile than the products so that large amounts of solvent will not have to be vaporized in the distillation column. The extraction solvent should not, however, be so nonvolatile that expensive high pressure steam is required in the reboiler of the solvent regeneration column. Finally, the solvent should be only sparingly soluble in water in order to minimize solvent losses.

Oleyl alcohol, diluted to 50 wt% in decane, was chosen as the extraction solvent in the extractive fermentation

TABLE 1. PURCHASED EQUIPMENT COSTS FOR BATCH FERMENTATION OF BUTANOL.

Item	Size	Units	Cost (10^3%)
STORAGE (2 weeks)			
Molasses	3.3×10^6 gal (c.s.)	2	860
Butanol	1.3×10^6 gal (c.s.)	1	210
Acetone	5.4×10^5 gal (c.s.)	1	107
Ethanol	1.5×10^5 gal (c.s.)	1	40
Dried stillage	1.0×10^5 gal (c.s.)	30	1,811
			3,028
FERMENTATION			
Fermentor	1.3×10^5 gal (s.s.)	62	10,780
Prefermentor	1.1×10^4 gal (s.s.)	31	1,380
Sterilizer	insulated tubing (c.s.)	8	138
Sterilizer heat recovery exchanger	7000 ft² (c.s.)	32	1,940
Feed mix tank	2.6×10^4 gal (s.s.)	8	224
Feed mix tank agitator	130 HP (s.s.)	8	165
Broth surge tank	1.32×10^5 gal (s.s.)	4	759
			15,386
PRODUCT RECOVERY			
Steam stripper	8.25 ft dia, 25 plates (s.s.)	4	1,364
Stripper preheater	7000 ft² (s.s.)	9	872
Intercolumn heat exchanger	1430 ft² (c.s.)	1	25
Acetone column feed cooler	3290 ft² (c.s.)	1	40
Acetone column	8.8 ft dia, 50 trays (c.s.)	1	243
Acetone column condenser	2190 ft² (c.s.)	1	37
Acetone column reboiler	1870 ft² (c.s.)	1	29
Ethanol column	8.5 ft dia, 58 trays (c.s.)	2	540
Ethanol column condenser	5500 ft² (c.s.)	1	53
Water stripper	7.5 ft dia, 20 plates (c.s.)	2	193
Water stripper condenser	1280 ft² (c.s.)	1	24
Water stripper intercolumn reboiler	1500 ft² (c.s.)	1	34
Water stripper reboiler	1330 ft² (c.s.)	1	24
Butanol stripper	7.9 ft dia, 20 plates (c.s.)	1	105
Butanol stripper reboiler	2400 ft² (c.s.)	1	34
			3,617
STILLAGE HANDLING			
Stillage evaportor	16,000 ft² per effect, 5 effects	4	12,354
Rotary dryer	7740 ft², 29.4 HP	5	2,840
Heat recovery exchanger	50 ft² (s.s.)	5	55
			15,249
	Total Purchased Equipment Costs:		$37,280

process. Oleyl alcohol, a commercially available mixture of C-16 to C-18 unsaturated primary alcohols, with C-18 predominating, is a liquid at room temperature with a density of 0.84 g/cm³. Oleyl alcohol has a high capacity for butanol with a distribution coefficient (g/L butanol in solvent/g/L butanol in broth) of 4.3 [*34*]. Bench-scale extractive fermentations using oleyl alcohol as the extraction solvent have been demonstrated in batch [*31*, *33*], fed-batch [*34*], and continuous extraction [*42*] systems. Volumetric butanol productivity was increased from 0.58 g/L hr in batch culture to 1.5 g/L hr in fed-batch extractive fermentation using oleyl alcohol [*34*]. Glucose solutions up to 500 g/L could be fermented and final waste water volume was decreased about fourfold. In a bench-scale extractive fermentation system in which butanol was continuously extracted from fed-batch culture, rapid fermentation was maintained for 55 hours at an overall butanol productivity about twice that obtainable in regular batch or fed-batch culture [*42*].

Oleyl alcohol may be diluted with decane to improve

TABLE 2. CAPITAL INVESTMENT FOR BATCH FERMENTATION OF BUTANOL.

		$MM
1.	Direct Costs	
	purchased equipment	37.28
	equipment installation	14.91
	instrumentation and controls	5.59
	piping	16.78
	electrical	3.73
	buildings	5.97
	yard improvements	2.98
	service facilities	22.37
	land	2.24
	Total Direct Costs	111.85
2.	Indirect Costs	
	engineering and contractor's fee	17.89
	construction expenses	11.93
		29.82
3.	Working Capital	
	feedstocks	1.70
	finished products	1.79
	accounts receivable	6.80
	cash	0.58
	spare parts	1.52
		12.39
	Total Capital Investment:	154.06

the physical properties of the extraction solvent. Because oleyl alcohol is viscous, mass transfer and phase separation are slow when undiluted oleyl alcohol is used as the extraction solvent. At 37°C, oleyl alcohol has a viscosity of 17 cp, while a 50/50 wt% mixture of oleyl alcohol and decane has a viscosity of only 3.1 cp. In addition, oleyl alcohol is nonvolatile with a boiling range of 282–349°C; expensive high-pressure steam is required to regenerate undiluted oleyl alcohol. Dilution of oleyl alcohol with decane lowers the boiling point of the solvent mixture so that cheaper, low-pressure steam can be used in the reboiler. It has been assumed that oleyl alcohol distilled without denaturation; limited experimental studies support this assumption [*42*].

Figure 2 shows the flow sheet for an extractive fermentation process using a 50 wt% mixture of oleyl alcohol in decane as the solvent. Fed-batch operation of the fermentors is used to prevent substrate inhibition of the cells by high concentrations of sugar in the fermentor. The fermentors are charged with molasses diluted to 100 g/L sugar, inoculated with cells grown in the seed fermentor, and operated as batch fermentors until the sugar concentration decreases to about 15 g/L, at which time fed-batch operation is initiated. Molasses, at an equivalent of 500 g/L sugar, is fed to the fermentors as needed to maintain the residual sugar level at 12–15 g/L. A concentrated feed is used to minimize the amount of water introduced into the process. Whole broth is circulated from the fermentor to the extraction column where inhibitory fermentation products are extracted into the oleyl alcohol/decane solvent. Extracted broth is recycled to the fermentor while loaded solvent, containing an average of 21 g/L butanol, 3.5 g/L acetone, and 0.4 g/L ethanol, is sent to the solvent-regeneration column where butanol, acetone, and ethanol are distilled from the solvent. The solvent-regeneration column operates under vacuum so that the bottoms temperature is low enough to use 150 psig steam in the reboiler. Butanol is maintained below severely inhibitory levels in the fermentor and the fed-batch fermentation is carried out for 75 hours. The flow of sugar to the fermentor is stopped near the end of the fermentation in order to allow residual sugar to be consumed.

At the end of fermentation, products remaining in the broth are recovered in the same way as in the batch fermentation process. Residual butanol, acetone, and ethanol are stripped from the broth in the beer stripper and separated in a series of four distillation columns. Stillage is dried to 85 wt% solids and stored for sale. Products recovered from the extraction solvent are purified in a separate series of columns. The overhead vapor from the solvent-regeneration column is first condensed in the solvent-side ethanol column reboiler to provide the heat duty for that column and then fed to the solvent-side butanol column. Because little water is extracted into the decane/oleyl alcohol solvent, butanol can be recovered directly as the bottoms product of the first distillation column. The overhead product is sent to the solvent-side ethanol column where 95 wt% ethanol is recovered as the bottoms product. The remaining water and acetone in the overhead product is sent to the broth side acetone column for further rectification.

Design of the Extractive Fermentation Process

The time-dependent concentrations of products in the fermentor and extraction solvent during fed-batch extractive fermentation were estimated by numerical simulation of the fermentation process. The volumetric production rates of butanol, acetone, ethanol, acetic and butyric acids, cells, hydrogen, and carbon dioxide over the course of extractive fermentation were estimated from a model of the acetone-butanol fermentation developed by Votruba, Volesky and Yerushalmi [*58*], modified to fit data of fed-batch extractive fermentation. The time-dependent concentrations of products in the broth and solvent phases exiting the extraction column were also estimated. The design assume that a Karr reciprocating-plate extraction column is used to contact broth and extraction solvent. A Karr column was used in the design because it has been successfully used to remove butanol *in-situ* from a bench-scale fed-batch fermentation [*42*]. Operation of the Karr column is described elsewhere [*59*, *60*]. The phase hold-ups and mass-transfer coefficients in the column were estimated from a model developed by Hafez, Baird, and Nirdosh [*61*, *62*].

The estimation of the product concentrations in the extractor outlet streams, however, was complicated by the presence of backmixing in the column and by the continued formation of products by viable cells inside the extraction column during extractive fermentation. Equations were thus derived to predict the outlet concentrations from a differential contactor when product forma-

TABLE 3. MANUFACTURING COSTS FOR BATCH FERMENTATION OF BUTANOL.

Item	Basis	¢/lb butanol
Raw Materials		
nutrients	¢/lb BuOH	1.0
water	$1.10/1000 gal	0.8
molasses	$100/ton, 55% sugar	41.2
Utilities		
power	$0.08/kwh	0.6
cooling water	$0.25/1000 gal	0.4
atm steam	$0.85/1000 lb	0.2
50 psig steam	$3.50/1000 lb	11.0
150 psig steam	$4.00/1000 lb	0.8
Co-products		
acetone	$0.27/lb	(10.6)
ethanol	$0.26/lb	(2.8)
hydrogen	$0.10/lb	(0.7)
dried stillage	$60/ton, 85% solid	(9.5)
atm steam	$0.85/1000 lb	(1.3)
Total Variable Cost		31.1
operating labor	$12/man hr, 42 operators	2.1
supervision	15% operating labor	0.3
maintenance	4% fixed capital cost	2.8
operating supplies	15% maintenance	0.4
laboratory charges	15% operating labor	0.3
taxes & insurance	1.5% fixed capital cost	1.0
plant overhead	22 people, $80,000/year	0.9
Total fixed cost		7.8
Capital charges (30% of total capital cost)		22.8
Rational Price (variable + fixed cost + capital charges)		61.7

tion occurs in one of the phases and there is some degree of backmixing in both phases [63].

Product formation rates inside the extractor were assumed to be the same as those inside the fermentor at any given time. The degree of backmixing in the extraction column was estimated using effective axial dispersion coefficients measured in a 7.6 cm dia column [64] and 5 cm dia column [65]. The effect of column diameter on the degree of backmixing was estimated from equations given by Karr for column scale-up [66]. A simulation of the fed-batch extractive fermentation process operating at the conditions listed in Table 4 gave an overall butanol productivity of 0.89 g/L hr. This is a conservative estimate, since productivities as high as 1.5 g/L hr have been measured in laboratory scale fed-batch extractive fermentations [34]. Distillation columns were designed as previously described.

Economic Evaluation of the Extractive Fermentation Process

Equipment costs for a plant using extractive fermentation to produce 200×10^6 lb butanol annually are listed in Table 5. The total purchased equipment cost for the extractive fermentation process is $29.7 million, 20% less than the equipment cost of the conventional batch fermentation process. The lower cost reflects the higher productivity and reduced volume of broth that must be treated in extractive fermentation; fewer fermentors and stillage evaporators are required in the extraction process. The extractive fermentation process requires a total capital investment of $125 million.

Table 6 shows a breakdown of the manufacturing costs associated with extractive fermentation. Byproduct credits and raw materials costs were the same as those used in the batch fermentation process evaluation. In addition, the cost of oleyl alcohol was taken to be $1.35/lb [67] and the cost of decane was estimated to be $0.75/gal [53]. Manufacturing costs are decreased from 38.9 cents/lb butanol in batch fermentation to 30.4 cents/lb in extractive fermentation, primarily because less steam is required to produce a dried stillage product. The rational price of butanol produced by extractive fermentation is 48.9 cents/lb, 20% lower than the 61.7 cents/lb cost of butanol produced by the batch fermentation of molasses.

The savings obtained by using extractive fermentation to produce butanol may be even greater in actual practice. A conservative value of butanol productivity was

FIGURE 2. Process flow diagram of a fed-batch fermentation employing Oleyl alcohol-decane as extractant.

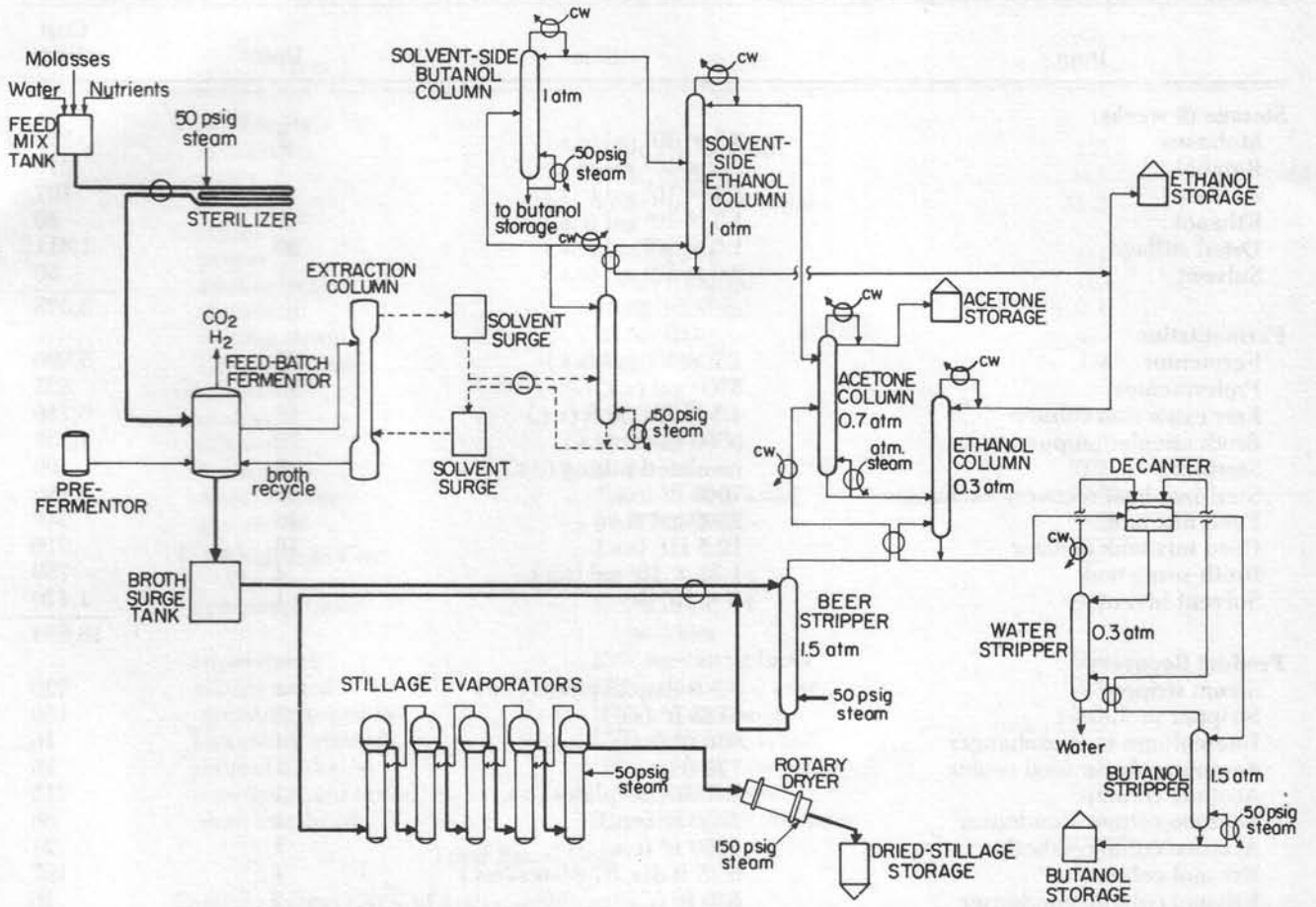


TABLE 4. Operating Conditions Used in Fed-Batch Extractive Fermentation Simulations.

Parameter	Value
Broth flowrate to extractor	50,000 L/hr
Solvent flowrate to extractor	28,800 L/hr
Extractor height	50 ft
Height of an ideal (plug-flow) butanol transfer unit	2.4 ft
Butanol distribution coefficient	2.6
Acetone distribution coefficient	0.3
Ethanol distribution coefficient	0.1
Water solubility in extractive solvent	50 ppm
Solvent solubility in broth 100 ppm	100 ppm
Sugar concentration in feed 500 g/L	500 g/L
Length of fermentation cycle 75 hours	75 hours

used in the exractive fermentation design. Higher productivities, similar to those measured in laboratory experiments, would reduce the number of fermentors required in the plant. More importantly, the yield of butanol was assumed to be the same in batch fermentation and fed-batch extractive fermentation. Butanol yield, however, is increased by the use of extractive fermentation [*34*], probably due to greater conversion of coproduct acids to butanol. Since butanol cost is roughly inversely proportional to butanol yield, the savings obtained from the use of extractive fermentation should be greater than indicated. Also, any increase in the length of fermentation time would result in a higher concentration of solids and cells at the end of fermentation; stillage processing costs would be further reduced. Finally, the product recovery process could be simplified if a strain of *Clostridium acetobutylicum* was used that did not produce ethanol. By extracting all the butanol into the organic solvent, acetone and butanol can be readily recovered. This recovery process eliminates four distillation columns from the extractive fermentation design.

TABLE 5. PURCHASED EQUIPMENT COSTS FOR FED-BATCH EXTRACTIVE FERMENTATION OF BUTANOL.

Item	Size	Units	Cost ($10^3$$)
Storage (2 weeks)			
Molasses	3.3×10^6 gal (c.s.)	2	860
Butanol	1.3×10^6 gal (c.s.)	1	210
Acetone	5.4×10^5 gal (c.s.)	1	107
Ethanol	1.5×10^5 gal (c.s.)	1	40
Dried stillage	1.0×10^5 gal (c.s.)	30	1,811
Solvent	2.0×10^5 gal (c.s.)	1	50
			3,078
Fermentation			
Fermentor	1.2×10^5 gal (s.s.)	36	5,990
Prefermentor	5300 gal (s.s.)	18	535
Karr extraction column	4.5 ft dia, 50 ft (s.s.)	18	5,716
Broth circulation pump	6600 gal/hr (s.s.)	72	1,138
Sterilizer	insulated tubing (c.s.)	18	199
Sterilizer heat recovery exchanger	7000 ft² (c.s.)	36	2,182
Feed mix tank	2500 gal (s.s.)	18	349
Feed mix tank agitator	12.5 HP (s.s.)	18	316
Broth surge tank	1.32×10^5 gal (s.s.)	4	759
Solvent inventory	2×10^6 lb	1	1,470
			18,654
Product Recovery			
Steam stripper	5.5 ft dia, 25 plates (s.s.)	1	220
Stripper preheater	6125 ft² (s.s.)	2	180
Intercolumn heat exchanger	650 ft² (c.s.)	1	16
Acetone column feed cooler	775 ft² (c.s.)	1	18
Acetone column	8 ft dia, 50 plates (c.s.)	1	215
Acetone column condenser	2950 ft² (c.s.)	1	38
Acetone column reboiler	1050 ft² (c.s.)	1	21
Ethanol column	6.75 ft dia, 57 plates (c.s.)	1	197
Ethanol column condenser	650 ft² (c.s.)	1	16
Water stripper	4.8 ft dia, 20 plates (c.s.)	1	53
Water stripper condenser	550 ft² (c.s.)	1	15
Water stripper reboiler	145 ft² (c.s.)	1	7
Butanol stripper	3.5 ft dia, 20 plates, (c.s.)	1	37
Butanol stripper reboiler	495 ft² (c.s.)	1	14
Butanol stripper condenser	325 ft² (c.s.)	1	11
Solvent heat recovery exchanger	7000 ft² (c.s.)	13	788
Extract surge tank	1.32×10^5 gal (c.s.)	2	100
Regenerated solvent surge tank	1.32×10^5 gal (c.s.)	2	100
Solvent regeneration column	7.25 ft dia, 30 plates (c.s.)	3	373
Solvent regeneration reboiler	2890 ft² (c.s.)	1	37
Intercolumn reboiler	730 ft² (c.s.)	1	18
Solvent regeneration condenser	615 ft² (c.s.)	1	16
Butanol column	3 ft dia, 35 plates (c.s.)	1	53
Butanol column reboiler	180 ft² (c.s.)	1	8
Butanol column condenser	225 ft² (c.s.)	1	9
Ethanol column	4.8 ft dia, 38 plates (c.s.)	1	90
Ethanol column condenser	1255 ft² (c.s.)	1	24
			2,674
Stillage Treatment			
Stillage evaporator	11,000 ft² per effect, 5 effects	1	2,483
Rotary dryer	7740 ft², 29.4 HP	5	2,840
Heat recovery exchanger	50 ft² (s.s.)	5	55
			5,378
	Total Purchased Equipment		**$29,784**

TABLE 6. MANUFACTURING COSTS FOR FED-BATCH EXTRACTIVE FERMENTATION OF BUTANOL.

Item	Basis	c/lb butanol
Raw Materials		
nutrients	1 cent/lb Butanol	1.0
water	\$1.10/1000 gal	0.1
molasses	\$100/ton, 55% sugar	41.2
Utilities		
power	\$0.08/kwH	0.9
cooling water	\$0.25/1000 gal	0.3
atm steam	\$0.85/1000 gal	0.1
50 psig steam	\$3.50/1000 lb	1.6
150 psig steam	\$4.00/1000 lb	1.9
Co-products		
acetone	\$0.27/lb	(10.6)
ethanol	\$0.26/lb	(2.8)
hydrogen	\$0.10/lb	(0.7)
dried stillage	\$60/ton, 85% solid	(9.5)
atm steam	\$0.85/1000 lb	(0.2)
Total Variable Cost		23.3
operating labor	\$12/man hr, 44 operators	2.2
supervision	15% operating labor	0.3
maintenance	4% fixed capital cost	2.2
operating supplies	15% maintenance	0.3
laboratory charges	15% operating labor	0.3
solvent make-up	15% solvent inventory	0.1
insurance and taxes	1.5% fixed capital	0.8
plant overhead	22 people, \$80,000/year	0.9
Total Fixed Cost		7.1
Capital charges (30% of total capital cost)		18.5
Rational Price of Butanol		48.9

Other fermentations may also benefit from the use of extractive fermentation. The productivity of iso-propanol and butanol fermentation using *Clostridium beyerinckii* has been shown to be increased by the *in situ* removal of these alcohols during fermentation [7, 8]. Extractive fermentation of iso-propanol and butanol using oleyl alcohol as the extraction solvent may also increase fermentor productivity and allow concentrated substrates to be fermented. Product separation may also be simplified in an extractive fermentation process. Iso-propanol, like ethanol, forms an azeotrope with water; pure iso-propanol cannot be obtained by distilling a dilute solution of iso-propanol in water. In extractive fermentation, however, little water is extracted into the alkane/oleyl alcohol solvent and pure iso-propanol can be produced directly.

Some of the advantages of extractive fermentation will be lost if a dilute substrate is used. The capability of fed-batch extractive fermentation to utilize concentrated feed-stocks is a major advantage over conventional fermentation. If dilute feed-stocks are used, however, the need to preconcentrate the feed reduces the savings achieved in the stillage handling section of the plant.

Conclusions

Butanol can be produced from molasses for about 20% less by extractive fermentation than by conventional batch fermentation. Product inhibition is reduced during extractive fermentation by the *in situ* removal of butanol. Butanol productivity is increased and fewer fermentors are required in the extractive fermentation process. Concentrated feed-stocks can be fermented and stillage treatment costs are significantly reduced. Capital costs for a fed-batch extractive fermentation plant producing 200×10^6 lb of butanol annually are estimated to be about 20% lower than the capital costs of a conventional batch-fermentation plant. Energy requirements of the extraction process are also reduced.

Extractive fermentation can most benefit fermentations that are strongly inhibited by the accumulation of toxic products in the broth, which require the treatment of large volumes of stillage, and that can use the sugars present in concentrated feedstocks. However, potential loss of solvent in the broth and carry over of solvent in stillage are problems to be addressed in any actual process. The

effect of carry over of trace amounts of the solvent employed in the present analysis on the saleability of the stillage for animal feed is beyond the scope of the present analysis, but would be common to all extractive fermentations.

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