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Ethanol, the Ultimate Feedstock

A Technoeconomic Evaluation of Ethanol Manufacture in Fluidized Bed Bioreactors Operating with Immobilized Cells

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ABSTRACT

Ethanol appears to be a key factor in the "biomass alternative" to fossil feedstocks for producing fuels and chemicals. If produced at a low enough price relative to crude oil, it and its derivates could account for 159 billion pounds, or 50%, of the US production of synthetic organic chemicals, presently valued at $113 billion. This use would consume 4.2 billion bushels, or about 54%, of the corn crop.

This study evaluated the potential savings in ethanol manufacture to be gained by applying advanced process engineering or genetic engineering of improved organisms, centering on the use of fluidized bed bioreactors operating at high cell densities with immobilized cells of either the *Saccharomyces* yeast or the bacterium: *Zymomonas mobilis*.

A new continuous plant could produce at about $1.82/gal based on *Zymomonas* or $1.97/gal based on the *Saccharomyces* yeast. The bacterium has a competitive edge as a result of its lower sensitivity to product inhibition.

There appears to be no inherent design limitation to effect the engineering improvements required for the advanced process. In a longer-term, more difficult research effort, it might be possible to reduce or eliminate product inhibition to reduce cost even further.

Index Entries: Ethanol; technoeconomics; fluidized bioreactor; immobilized cells; renewable biomass.

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INTRODUCTION

Since the Middle East oil crisis of 1973, many people in government, academia, and industry have been concerned about the strategic implications of a loss of a major source of crude oil for American industry. The recent war in the Persian Gulf only accentuated the extent to which the United States is dependent on an uncertain oil supply. Even before this crisis, many market forecasters were predicting an upswing in the price of crude oil (*1–7*). Consequently, over the past decade, a large number of research programs have been directed toward exploring the potential use of abundant renewable materials as basic feedstocks for fuels and chemicals.

Ultimately, ethanol will have to become one of the most important chemical feedstocks, if only because it can provide a technically demonstrated, albeit not yet economical, route to ethylene. Ethylene is the most important feedstock for the chemical industry. US production amounted to 37.5 billion pounds in 1990 (*8*). If ethanol could be produced at a low enough price to serve as the precursor to ethylene and butadiene, it and its derivatives could account for 159 billion pounds, or 50% of the US production of 316 billion pounds of synthetic organic chemicals, presently valued at $113 billion (*9*). This use would consume 4.2 billion bushels or about 54% of the 7930-million-bushel corn crop forecast by the USDA for the 1990/91 crop year (*10*).

Unfortunately, reaction stoichiometry is on the side of the petrochemical routes to ethylene. At a yield of 98%, it requires 1.64 pounds of ethanol to produce a pound of ethylene. As a result, raw material economics is adversely affected. It is enough at the moment to hope that the cost of fermentation ethanol can continue to compete with the cost of producing ethanol from ethylene.

MARKET POSITION

The US now leads among major world producers of ethanol (*11*). Production of synthetic ethanol has declined, whereas fermentation ethanol has increased over the past decade. Annual production in 1989 amounted to:

Million gallons	Synthetic	Fermentation	Total
US	150	600	750
Western Europe	150	350	500
Japan	25	25	50

In the US, synthetic ethanol is produced in the Shell process by the direct hydration of ethylene. At a yield of 97%, it requires 0.63 lb of ethylene/lb of ethanol. Over the decade prior to 1973, the prices of ethylene and synthetic ethanol were relatively stable at $0.035/lb and $0.35/gal,

respectively. However, soaring chemical prices resulting from the energy crisis of 1973 raised the price of ethylene to a peak of $0.26 in 1981. Following this, it dropped back to $0.15/lb before rising to the 2Q91 (i.e., 2nd quarter of 1991) price of $0.24 or $1.00/gal of synthetic ethanol (*12*). This cost is almost as much as the current $1.20 (depressed) price for fermentation ethanol.

FUEL ETHANOL PLANTS OF THE 1970s

The period of the late 1970s marked the heyday of construction of new fuel ethanol plants or retrofitting of former liquor distilleries. A case was developed for such a facility assuming a 60-million-gal yeast-based plant built with a midpoint of construction in 1976. Cell recycle was not included. Thus, the case was an attempt to reconstruct the economics for the plants that constituted the fuel alcohol industry at that time.

Investment in this plant in 1976 dollars amounted to $1.57/annual gal, comprising $1.31 for direct and allocated plant investment and $0.26 for working capital. Of the plant investment, the cost of 12 500,000-gal fermenters accounted for 46%.

The cost of manufacture (mill cost) in 1980 amounted to $1.00/gal at a cost of sales of $1.26. This cost performance leads to a pretax return on investment of 30% for a selling price of $1.79/gal. Raw materials comprise 58% of cost of manufacture and 32% of selling price. Capital-related charges account for 37% of selling price.

This case is compared in Table 1 with several estimates made in about 1980 by various organizations: a task force of the American Institute of Chemical Engineers chaired by I. B. Margiloff of Publicker Industries (*13*); a study commissioned by the Department of Energy (*14*); and a study made by the Katzen organization for a plant with maximum energy recovery (*15–17*). Agreement is generally good considering the diverse viewpoints and bases.

EFFECT OF VENTURE TIMING

If the plants described in the preceding section were to be built today, costs would be substantially higher. Construction costs for a plant with a midpoint of construction of 1986 would be 79% higher than the plant built in 1976. Also, the cost assumed for substrate in 1988 was almost twice that used in the earlier estimate. This point is discussed later. As a net result, the selling price in 1990 would have to be $2.58/gal to yield a 30% pretax return as compared with currently distressed prices of $1.20/gal for fuel alcohol (*18*). This may be one reason why new plants are not being built.

Table 1
Comparison of Estimates
Ethanol Process Economics
Batch Fermentation—No Cell Recycle

Estimate	AIChE	D.O.E.	Katzen	B.E.A.
Capacity—million GPY	40	50	50	60
Midpoint of construction			1981	1976
Investment—$/gal				
Direct and alloc. plant investment			$1.28	$1.31
Working capital			0.12	0.26
Total investment			$1.40	$1.57
		Operating year		
COST—$/gal	1980	1983	1983	1980
Corn	$1.12	$1.20	$1.09	
B.P. credits	(0.50)	(0.60)	(0.47)	
Net corn	$0.62	$0.60	$0.63	$0.59
Other raw materials	0.14	0.07	0.02	0.01
Total raw materials	0.76	0.67	0.65	0.60
Utilities	0.19	0.20	0.11	0.22
Labor-related	0.07	0.08	0.06	0.06
Capital-related	0.43	0.17	0.21	0.15
Cost of manufacture		$1.12	$1.03	$1.03
SE, D, R&D, Adm, & I.C.		0.18	0.18	0.23
Cost of sales	$1.43	$1.30	$1.21	$1.26
Pretax Earnings @30% ROI			0.47	0.53
Selling price			$1.68	$1.79

*Syrup ex wet mill at $0.038/pound equivalent glucose.

The estimate for 1990 operation is compared with that for 1980 in Table 2. The effects of raw material and capital charges are clear. The 1990 estimate serves as the base case in this study for comparison with the estimates made for plants employing more advanced technology.

SCOPE OF THE STUDY

In the current technoeconomic study of the ethanol process, the state of the art for its fermentative manufacture by the yeast *Saccharomyces cerevisiae* was reviewed and compared with expected performance of the newer *Zymomonas mobilis* bacterium operating as immobilized cells in a fluidized bed bioreactor. From this, scenarios for an improved process were developed based on the expectations for adapting either system to reach plausible cell densities and effective concentration levels. The economics of these scenarios was then developed. The sensitivity of the eco-

Table 2
Effect of Venture Timing
66 MM GPY Ethanol Manufacture
Inhibited *Saccharomyces* Yeast
Batch Fermentation—No Cell Recycle

Midpoint of construction	1976	1986
Construction cost index	74	132
Operating year	1980	1990
Substrate cost—$/pound equiv. glucose	$0.038	$0.065
Investment—$ million		
Direct permanent investment	$54.5	$94.0
Allocated power, services & gen.	24.1	26.8
Working capital	15.4	22.3
Total investment	$94.1	$143.1
Cost—$/gal		
Raw materials	$0.57	$0.94
Utilities	0.22	0.15
Labor-related	0.06	0.11
Capital-related	0.14	0.23
Cost of manufacture	$0.99	$1.43
SE, D, R&D, Adm, & I.C.	0.27	0.36
Cost of sales	$1.26	$1.79
Pretax earnings based on 30% ROI	0.52	0.79
Byproduct credits	0.00	0.00
Selling price	$1.78	$2.58

nomics to attaining, exceeding, or falling short of goals for key operating parameters was also determined. It is hoped that the results will provide a strong perspective as to the relative merits for supporting reesarch on any of the alternatives and the direction in which the research should be channeled so as to be economically relevant and improve the technoeconomic position of the process.

BIOPROCESS PROBLEMS

In general, fermentation processes have two major problems: (a) inherently poor yields resulting from the production of byproducts, including high levels of carbon dioxide needed to maintain the electronic balance of the metabolism of the organism, coupled with the current relatively high cost of renewable sugars and starches compared with the presently depressed prices for petroleum; and (b) the inhibition of most organisms by their own products, which causes the fermentation to shut down after reaching only low product concentrations, as a result of which the recovery of product from dilute aqueous solution is accordingly expensive.

YIELD AND RAW MATERIAL ECONOMICS

Raw material economics has always been one of the most important parameters in determining the commercial viability of fermentation processes. In the US, corn is the principal substrate for fermentation ethanol, comprising 77% of the grain used and 68% of all substrates. Substrate cost is determined by the combination of demand and price.

Substrate Demand

Product yield, as determined by fermentation stoichiometry, is obviously an important cost-determining factor (*19–24*). Thus, the theoretical yield of ethanol from glucose amounts to 48 wt% for the yeast system and 50 wt% for the bacterium. In practice, the actual approach to theoretical is 90–95% for the yeast and about 98% for the bacterium because of the consumption of glucose for cell growth and maintenance. The difference arises because *Z. mobilis* consumes only 1 net ATP/glucose whereas *S. cerevisiae* consumes 2. Hence, the cell yield per unit of glucose consumed for cells is twice as high for the bacterium as for the yeast (*25,26*).

Overall, then, even though the organisms are operating close to their biological limit, carbon yields for either system are poor as a result of large losses to carbon dioxide and sundry other byproducts. Actual glucose demands amount to 2.19–2.31 lb/lb of ethanol or 2.27–2.40 gal of absolute alcohol/bushel of corn for the yeast and about 2.03 lb/lb or 2.59 gal/bushel for the bacterium, giving the latter a 7–12% competitive advantage in raw material costs.

Basis for Sugar Price

The cost of the sugar substrate is another very important element of cost, particularly if engineering improvements of the process can be realized. This study was based on the availability of a contract supply of a dilute 45% corn syrup from an adjoining wet mill at a transfer price of $0.065/lb equivalent glucose (*27*). In contrast, the cost of corn net of wet mill byproduct credits has averaged $0.026/lb equivalent glucose over the past 6 yr (*10*). Certainly, the hydrolysis can be done better and cheaper as part of a large wet mill than as the mash operation used in older distilleries. In addition, handling hydrolysis as part of the wet mill rather than in fermentation eliminates tieing up expensive fermenters as slow hydrolyzers.

Substrate Competitiveness

It cannot be expected that the yield of ethanol from sugar can be increased over its present biological limit. Consequently, further competitiveness of corn-based processes will have to depend on increases in the cost of crude oil relative to corn.

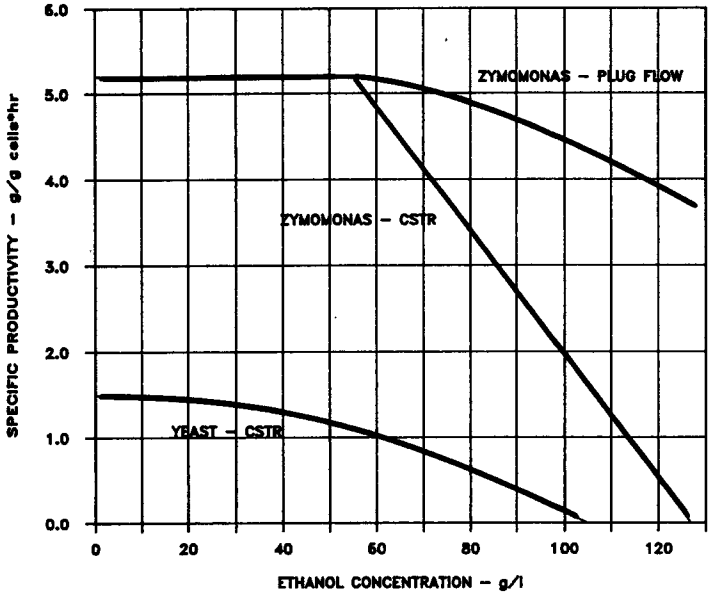


Fig. 1. Effect of ethanol inhibition on specific productivity.

PRODUCT INHIBITION

As with most fermentations, both *Saccharomyces cerevisiae* and *Zymomonas mobilis* are inhibited by their own substrate and products. Fermentation kinetics and process inhibition have been studied by a number of researchers for *Saccharomyces* (*28–34*) and *Zymononas* (*35–45*). Although agreement is not perfect, it appears that the yeast fermentation is totally inhibited by ethanol concentrations of about 105 g/L. The inhibitory cutoff for the bacterium is distinct higher at 127 g/L. Furthermore, as shown in Fig. 1, the decay in specific productivity for *Zymomonas* is flat at 5.2 g product/g cells*L up to a concentration of 55 g/L, after which inhibition begins. For the yeast, the maximum specificity of 1.5 g/(g)(L) drops over the whole range of concentration. Thus, as product concentration increases, specific productivity decreases, as does dilution rate for a fixed ratio of product to cells. This adverse effect has a profound influence on cost, and leads to a tradeoff between maximizing concentration and maximizing dilution rate.

One possible solution to the inhibition problem would be to integrate the fermentation and distillation sections of the process so as to increase productivity while removing the product from the field of fermentation as rapidly as it forms. This is an automatic consequence of converting from a batch to a continuous process in which a proportionate increase in cell density is effected either by immobilizing the cells, as in the Oak Ridge case, to prevent their loss from the fermenter or by filtering the cells from

the beer and recycling them while maintaining product concentration in the fermenter near the threshold of inhibition. The immobilization approach would be preferable, since it would avoid passing cells through a filter and, possibly, a still with possible deactivation of cells by thermal or mechanical attrition with possible plugging of the trays of the still.

Thus, assuming that specific productivity (g product/g cell*h) remains constant at constant (but maximum allowable) product concentration, the higher the cell density, the greater the volumetric productivity (g product/l*h), the shorter the fermentation time and, hence, the smaller the fermenter size and investment required for a desired design capacity, or for an existing fermentation plant, the greater the throughput and production level. It appears then that the development of a continuous fermentation system is a fundamental requirement for improving the economic viability of the ethanol process. Continuous opeation has been demonstrated at less than commercial scale by Bajpai and Margaritis (*37*), Ghose and Tyagi (*29,46*), Wilke (*28,32,47*), Davison and Scott (*48,49*), and others.

Scott and Davison (*50*) are operating a rack-scale 2.5-m fluidized bed bioreactor at the Oak Ridge National Laboratory. The process is based on *Zymomonas mobilis* immobilized within 1.0–1.5 mm K-carrageenen beads at cell loadings of 15–50 g/L beads (6.6–22 g/L fermenter). The fermenter is operated in a continuous mode at 30°C and pH 5.0. It was reported that plug-flow kinetics is achieved. Yield was reported to be 0.49 g ethanol/g glucose converted or 97.5% of the theoretical yield. Glucose spill is below 0.1% at an ethanol concentration of 74 g/L and a volumetric productivity of 60 g/L*h. Volumetric productivity is normally in the range 50–120 g/L*h, but has reached 186 g/L*h with 95% glucose conversion by recycling cells to higher density. This performance is in sharp contrast with the volumetric productivities of 1–2 g/L*h usually reported by conventional yeast-based plants. Alternatively, new organisms might be genetically engineered to be less inhibited by product and/or have a higher specific productivity than the wild strain.

PROCESS SCENARIO FOR THIS STUDY

This study was based on using a fluidized bed bioreactor similar in design to the Oak Ridge approach. Cell density can be increased by either retaining cells in the fermenter or by recycling. For this study, it was assumed that the beer leaving the fermenter train is passed to a filter unit to separate cells from the broth. The cell slurry is recycled except for a purge bleed equal to the amount produced.

A standard distillation train was assumed for the base case. Greater heat economy might be realized by a more elaborate heat recovery scheme (*15,16*). It would be interesting to compare the conventional design with cases based on using the Dartmouth IHOSR (Intermediate Heat Pumps and Optimal Sidestream Return) distillation process (*51*).

In either design, the cell-free broth enters the first (beer) still of the distillation train, wherein the ethanol azeotrope and low boiling impurities are separated from salts, high boiling byproducts, and water. The aqueous tails from the stripping section are sent to waste disposal. No recovery of purged cells as distillers grains was assumed in this model. Fusel oils (amyl alcohols, mainly 3-methyl-1-butanol) are removed as a sidestream drawoff from the beer still. Low boilers are separated overhead in a refiner, and the azeotrope is sent to a dehydration column to recover absolute ethanol.

OPERATING SCENARIO

It was assumed that the plant would be sited in the Midwest adjoining a corn wet mill. Capacity was sized to a 60-million gallons/yr absolute ethanol plant with a midpoint of construction in 1986 and operating in 1990 at 90% utility. The investment estimates include a 30% contingency for undeveloped design, and so on.

ECONOMIC POTENTIAL OF ADVANCED FERMENTER SYSTEMS

An economic model for the advanced fermenter systems was used to explore the potential advantages of operating with cell recycle and/or improved specific productivity for both inhibited and noninhibited systems of either *Saccharomyces cerevisiae* or *Zymomonas mobilis* under either batch or continuous modes. The conversion economics of the ethanol fermentation process can be improved in two ways: (1) by increasing product concentration or (2) by increasing fermentation rate. Of the two, increasing product concentration has the greater effect on cost. At any desired production level, the reciprocal of concentration—L/g—represents the volume of the equipment required for the complete process: media preparation, fermentation, product recovery, and product refining. Hence, concentration has a dominant effect on total process investment.

Fermentation rate affects only fermenter volume and investment. However, since fermenter investment usually accounts for a large part of total investment, the effect of rate on cost can be very large indeed. At a fixed production level and product concentration, fermentation rate can be increased and fermenter volume decreased by increasing cell density, increasing specific productivity, or both.

Increasing cell density by containing the cells in an imobilized state in the fermenter or by recycling involves the appropriate engineering of the system under the constraints of broth viscosity and organism viability. However, increasing specific productivity involves producing a genetic

Table 3
Inhibited Batch System
Effect of Product Concentration

Product conc. g/L	Specific prod'ity g/g*h	Volume prod'ity g/L*h	Dilution rate 1/h	Fermenter investment $ million	Ferm. inv./ tot. plant investment	Capital costs $/gal	Total cost $/gal
Ethanol ex *S. Cerevisiae*							
40	1.28	1.80	0.045	$52	38%	$1.13	$2.78
50	1.17	1.90	0.038	$48	40%	$1.03	$2.62
60	1.04	1.92	0.032	$48	42%	$0.97	$2.53
70	0.84	1.75	0.025	$52	46%	$0.96	$2.51
80	0.63	1.44	0.018	$63	53%	$1.02	$2.56
90	0.38	0.99	0.011	$94	64%	$1.24	$2.82
100	0.13	0.40	0.004	$255	83%	$2.53	$4.29
Ethanol ex *Zymomonas mobilis*							
50	5.2	3.1	0.063	$29	29%	$0.87	$2.37
60	4.8	3.5	0.059	$26	28%	$0.79	$2.25
70	4.1	3.7	0.053	$25	29%	$0.74	$2.18
80	3.4	3.7	0.046	$25	31%	$0.71	$2.13
90	2.7	3.5	0.039	$26	33%	$0.70	$2.11
100	2.0	3.0	0.030	$30	37%	$0.71	$2.12
110	1.2	2.3	0.021	$41	46%	$0.78	$2.19
120	0.5	1.1	0.009	$84	64%	$1.11	$2.57

change in the organism, which may be difficult to achieve in practice. Nevertheless, both approaches have merit and need to be pursued.

Inhibited Batch Systems Without Cell Recyle

Inhibited systems exhibit a minimum in cost as product concentration is increased up to the point of total inhibition. This effect is shown for the batch systems in Table 3 for a situation involving little or no cell cycle. (Cell density was held constant during the calculation of sensitivity, which means the cases at low concentrations had a small cell recycle involved.)

It should be noted that, for the batch system, the term "dilution rate," as used in this study, refers to the reciprocal of the sum of batch time plus turnaround time, i.e., 1/(bt+tt). For the large fermenters used in the models, a turnaround time of 12 h was used for draining, cleaning, sterilizing, refilling, and inoculating the fermenter after each batch run. This loss of time is not incurred in continuous operation, which, as will be seen, has a large effect on cost. It should also be noted that specific productivity as used in this study refers to run time only, whereas volumetric productivity and dilution rate take into account the turnaround time for batch operation.

Table 4
Inhibited Batch System
Effect of Product Concentration and Cell Recycle
on Cost-Plus-Return, $/gal

Product conc.—g/L	Cell density—g/L					
	5	10	20	50	100	150
Ethanol ex *S. cerevisiae*						
40	$2.69	$2.62	$2.58	$2.54	$2.51	$2.49
50	$2.52	$2.45	$2.41	$2.37	$2.34	$2.33
60	$2.42	$2.33	$2.29	$2.26	$2.23	$2.22
70	$2.37	$2.27	$2.21	$2.17	$2.15	$2.14
80	$2.37	$2.24	$2.17	$2.12	$2.09	$2.08
90	$2.51	$2.28	$2.16	$2.09	$2.05	$2.04
100	$3.37	$2.69	$2.35	$2.14	$2.06	$2.03
Ethanol ex *Zymomonas mobilis*						
50	$2.33	$2.31	$2.30	$2.28	$2.26	$2.24
60	$2.21	$2.19	$2.18	$2.16	$2.15	$2.13
70	$2.13	$2.11	$2.10	$2.08	$2.06	$2.05
80	$2.07	$2.05	$2.03	$2.02	$2.00	$1.99
90	$2.04	$2.00	$1.99	$1.97	$1.95	$1.95
100	$2.02	$1.97	$1.95	$1.93	$1.92	$1.91
110	$2.04	$1.97	$1.93	$1.90	$1.89	$1.88
120	$2.21	$2.04	$1.95	$1.90	$1.87	$1.86

For the yeast, specific productivity and dilution rate are decreased 10-fold. However, because of the opposing effects of concentration vs productivity, volumetric productivity is maximized and fermenter investment is minimized at about 55 g/L. Capital charges and total cost are minimized at a higher concentration of about 70 g/L as a result of the effect of concentration on the rest of the plant as well.

The results for *Zymomonas* were similar, except that the costs for the bacterium cases were always lower as a result of higher specific productivities, with a minimum cost of about $2.11/gal compared with a minimum of $2.51 for the yeast. In addition, the bacterium can operate at concentrations higher than the yeast cutoff.

Inhibited Batch Systems With Cell Recycle

Cost is very sensitive to the recycle of cells. As shown in Table 4, cost decreases with increases in cell density at any product concentration. This effect mainly results from a concomitant reduction in fermenter investment. Total flow through a fermenter and specific productivity are fixed, irrespective of cell density, by fixing product concentration and annual production rate. Consequently, as cell density is increased by re-

cycle, fermentation time and volume (investment) can be correspondingly decreased in the design to balance production rate at a constant specific productivity.

For any product concentration, then, it is clearly desirable to operate at as high a cell recycle as possible. For example, Wilke operated at yeast concentrations up to 124 g dry wt/L at a volumetric productivity of 82 g/L*h (*28*), and Rogers reported operating with *Zymomonas* densities of 40 g/L for over 50 h (*40*) at a volumetric productivity of 120 g/L*h. However, cell densities above these may produce unacceptable viscosities and adverse effects on the organism in the fermenter. This is an important point for further research clarification.

As a practical matter, it does not appear from the projections of Table 4 that increasing cell densities much above 50 g/L would have a significant effect on reducing further the cost of the product. At that cell density, the cost of ethanol by the yeast system at a concentration of 90 g/L would be $2.09/gal compared with $1.90 for the bacterium system at 110 g/L of product.

Inhibited Constant Environment

Continuous Systems Without Cell Recycle

The very real advantage of operating in a continuous mode can be seen from the data of Table 5. It can be seen that volumetric productivity and dilution rate have values quite higher at low product concentrations than the respective cases for batch operation. The difference is related to batch turnaround time. At low concentrations, fermenter residence time is low and the relative adverse effect of turnaround is high, thus limiting dilution rates to low values. At high concentrations, fermenter time is very high and the effect of turnaround becomes insignificant, so that dilution rates for batch vs continuous operation approach each other.

Turnaround imposes a strict ceiling on effective dilution rate for batch operation. Thus, even at a fermenter time of zero, dilution rate is held to 0.083 h^{-1} (1/12 h). Continuous operation is not so constrained and can approach effective dilution rates near infinity, at which the cost of fermenters become insignificant relative to total plant investment.

For operation without cell recycle in a constant environment, continuous mode, the yeast exhibits a minimum cost-plus-return price of $2.36/gal at a product concentration of about 65 g/L. The corresponding minimum price for the *Zymomonas* system is $2.00 at 85 g/L.

Inhibited Constant Environment

Continuous Systems With Cell Recycle

The corresponding data for operation with cell recycle in a constant environment continuous system are shown in Fig. 2 for the yeast and Fig. 3 for the bacterium. For these cases, the minimum cost for the yeast at a

Table 5
Inhibited Continuous System
Effect of Product Concentration

Product conc. g/L	Specific prod'ity g/g*h	Volume prod'ity g/L*h	Dilution rate 1/h	Fermenter investment $ million	Ferm. inv./ tot. plant investment	Capital costs $/gal	Total cost $/gal
Ethanol ex *S. Cerevisiae*							
40	1.28	3.88	0.097	$24	22%	$0.91	$2.52
50	1.17	3.54	0.071	$26	26%	$0.85	$2.41
60	1.04	3.15	0.052	$29	31%	$0.82	$2.36
70	0.84	2.53	0.036	$36	37%	$0.83	$2.36
80	0.63	1.89	0.024	$49	46%	$0.90	$2.42
90	0.38	1.14	0.013	$81	60%	$1.14	$2.69
100	0.13	0.38	0.004	$244	83%	$2.42	$4.15
Ethanol ex *Zymomonas mobilis*							
50	5.2	12.7	0.254	$7	9%	$0.69	$2.17
60	4.8	11.8	0.197	$8	11%	$0.64	$2.08
70	4.1	10.1	0.144	$9	13%	$0.61	$2.03
80	3.4	8.3	0.104	$11	16%	$0.60	$2.00
90	2.7	6.5	0.072	$14	21%	$0.60	$2.00
100	2.0	4.8	0.048	$19	28%	$0.62	$2.01
110	1.2	3.0	0.027	$31	39%	$0.70	$2.10
120	0.5	1.2	0.010	$75	61%	$1.04	$2.48

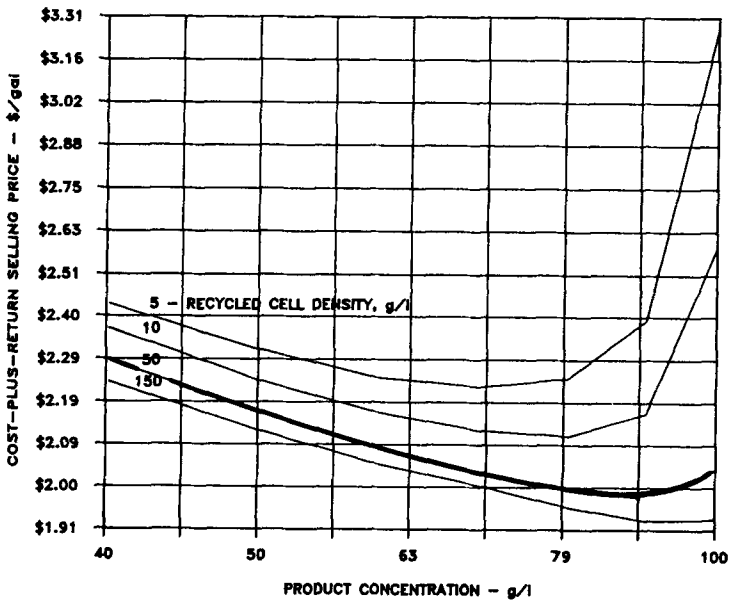


Fig. 2. Ethanol inhibited *Saccharomyces*—continuous constant environment system.

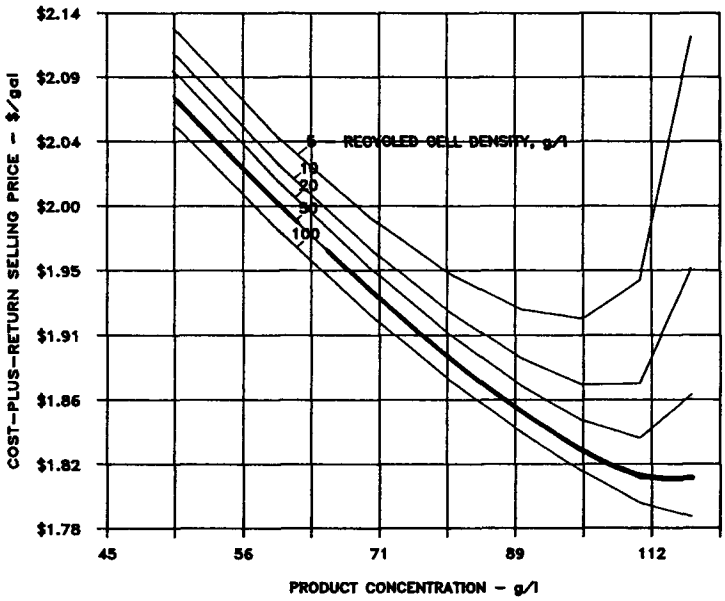


Fig. 3. Ethanol inhibited *Zymomonas*—continuous constant environment system.

cell density of 50 g/L is $1.97/gal at a product density of 90 g/L. For the bacterium, the minimum for a cell density of 50 g/L is $1.81 at 110 g/L. As cell density is increased, the minimum in cost moves toward higher product concentrations.

Inhibited Plug Flow

Continuous Systems With Cell Recycle

It is well known that the kinetics of any first-order reaction system is favored by operating in a plug-flow regime. The effect on specific productivity of *Zymomonas* was shown in Fig. 1. The cost data for plug-flow operation with *Zymomonas* are shown in Fig. 4. In contrast to constant environment operation (Table 5), the decay in volumetric productivity and dilution rate with increases in product concentration is much less severe. Neither are minima exhibited within the field of the data shown. Minima have to exist with any exhibited system, but in this case occur at concentrations very close to total inhibition.

Without cell recycle, the case for using plug flow is very strong. Thus, plug flow at a cell density of 50 g/L and product concentration of 110 g/L exhibits a cost of $1.89/gal compared with a minimum cost of $2.00 for the constant environment case at the same cell density of 50 g/L, but at an optimum product concentration of 85 g/L.

With the preferred cell recycle mode, the advantage of plug flow is lost. At high cell densities, both regimes are approaching an effectively

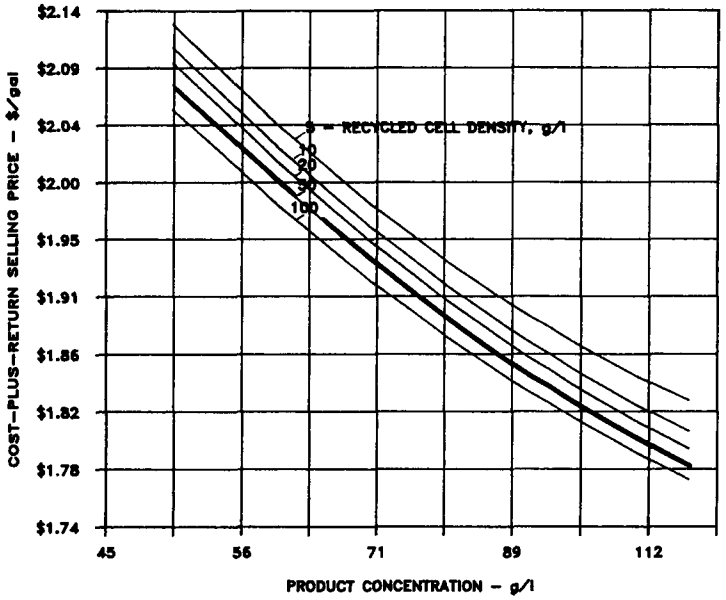


Fig. 4. Ethanol inhibited *Zymomonas*—continuous plug-flow system.

infinite dilution rate even at product concentrations up to 110 g/L, which would otherwise favor plug flow. At high dilution rate, the effect of fermenter investment is minimal. As a result, both regimes exhibit costs of about $1.80/gal at a product concentration of 110 g/L.

Noninhibited Continuous Systems

It would be admittedly difficult to engineer an organism that is not inhibited by product. However, if this could be accomplished with *Zymomonas* or *Saccharomyces cerevisiae,* cost would be reduced further according to the cost projections of Figs. 5 and 6. These depict a continuous system operating at various combinations of product concentration and dilution rates.

Dilution rate can be controlled independently of concentration by constraining or recycling cells to higher cell densities and/or by developing an organism with a higher specific productivity. For dilution rates below 0.083 h^{-1}, the data can also be used to represent batch operation. At high product concentrations, dilution rates above 0.1 h^{-1} converge near an infinite dilution rate.

For a dilution rate of 0.1 h^{-1} at a product concentration of 150 g/L, the cost of ethanol from *Zymomonas* would be reduced to $1.79/gal—a reduction of 30% below the $2.55/gal base case cost for the current commercial state of the art. The corresponding cost for the yeast system would be $1.88—a 26% reduction.

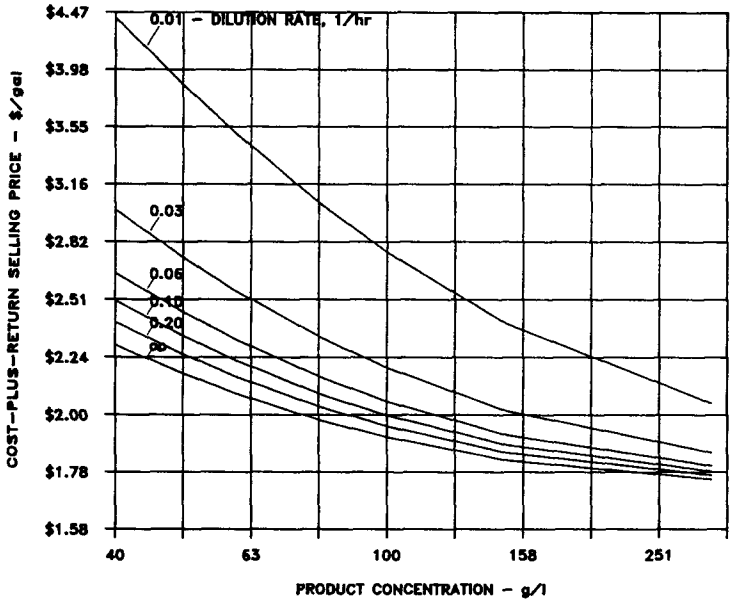


Fig. 5. Ethanol noninhibited *Saccharomyces*—continuous constant environment system.

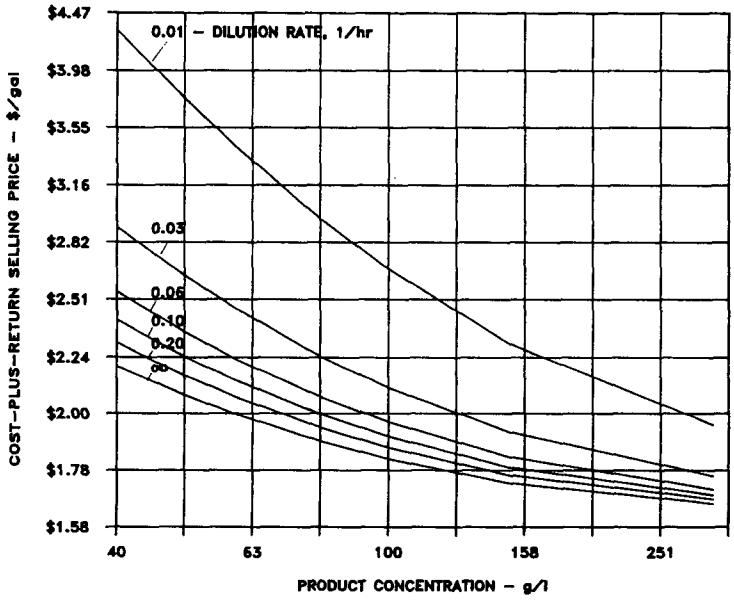


Fig. 6. Ethanol noninhibited *Zymomonas*—continuous system.

Effect of Sugar Price

As noted earlier, the transfer price for glucose in the form of corn syrup is uncertain, but quite important to the overall economics of the product. The sensitivity of cost-plus-return price to changes in the price of equivalent glucose is shown in Fig. 7 for an inhibited *Zymomonas* operating in a continuous constant environment system. At the assumed price of $0.065/

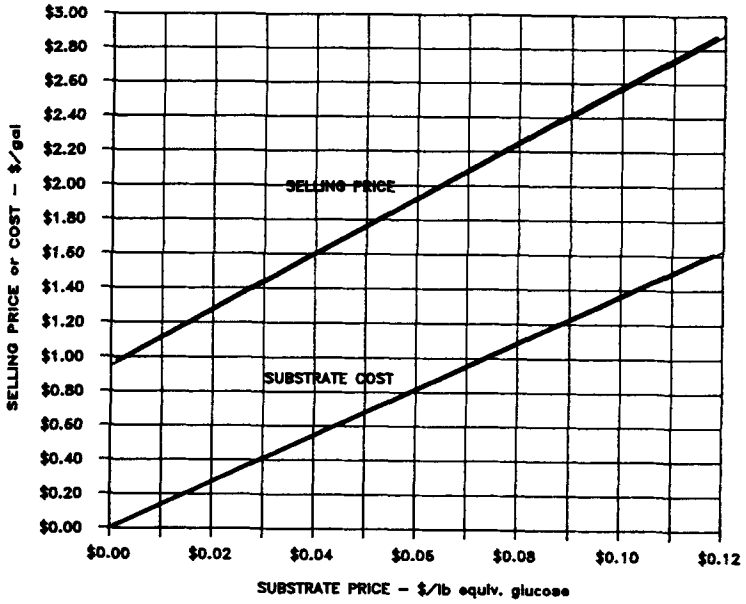


Fig. 7. Ethanol inhibited *Zymomonas mobilis*—continuous constant environment system.

lb, ethanol price would be $2.00/gal, and substrate cost would account for 71% of the cost of manufacture and 44% of selling price. However, at a bare "net corn" price of $0.038/lb of sugar, the alcohol could sell for as little as $1.56/gal. Conversely, at a list price for syrup of $0.12/lb, the ethanol would have to sell for $2.56/gal. Clearly, the leverage of sugar price is very high.

Glycerine Recovery?

With the exception of carbon dioxide, glycerine is formed at the highest concentration of any of the chemical byproducts of the ethanol fermentation process, i.e., at 4.6 wt% for yeast and at 1.1 wt% for *Zymomonas*. A brief study was made of the economic feasibility of recovering glycerine in the distillation train of the yeast system. This requires the addition of a large still and reboiler to separate water and other lower boilers overhead from the glycerine in the tails. A smaller still is also required to remove glycerine overhead from residual salts and acids. It does not appear economical to recover glycerine in this way. Both expense and investment are adversely affected.

STRATEGIES FOR INTRODUCING THE ADVANCED TECHNOLOGY

Obviously, much needs to be done in research at rack scale and pilot plant scale to prove out the projections described in this study. If that can

Table 6
Ethanol ex *Zymomonas mobilis*
Retrofitted Plant*—Inhibited Batch System
Effect of Product Concentration and Cell Recycle
on Cost-Plus-Return, $/gal

Product conc.—g/L	Cell density—g/L				
	5	10	20	50	100
50	$1.96	$1.94	$1.93	$1.92	$1.90
60	$1.88	$1.87	$1.86	$1.85	$1.83
70	$1.83	$1.82	$1.81	$1.80	$1.78
80	$1.79	$1.78	$1.77	$1.76	$1.75
90	$1.76	$1.75	$1.74	$1.73	$1.72
100	$1.73	$1.72	$1.71	$1.70	$1.69
110	$1.71	$1.70	$1.69	$1.69	$1.68
120	$1.70	$1.69	$1.68	$1.67	$1.66
120	$1.70	$1.69	$1.68	$1.67	$1.66

*MPC—1976; operating year—1990; substrate @ 0.065/pound.

be realized, however, a first step toward implementing the new systems might be to retrofit an existing fuel grade ethanol plant.

Retrofitting Existing Plants

It is beyond the scope of this study to evaluate the nuances of retrofitting existing plants. Too much depends on the design of the plant, and the financial aspects of the supporting or ancillary businesses of the operator.

However, as a first approximation, a case was developed based on introducing in 1990 an inhibited *Zymomonas* in a batch plant built around 1976. A sugar transfer price of $0.065 was assumed—the same as for the 1986 base case, but almost twice as high as the sugar price basis used in the 1976 plant of Table 2. The results are shown in Table 6. Product cost would be $1.69 by recycling to a cell density of 50 g/L at a product concentration of 110 g/L. This cost is in fact lower than the 1980 price of $1.79, even though the substrate cost is much higher.

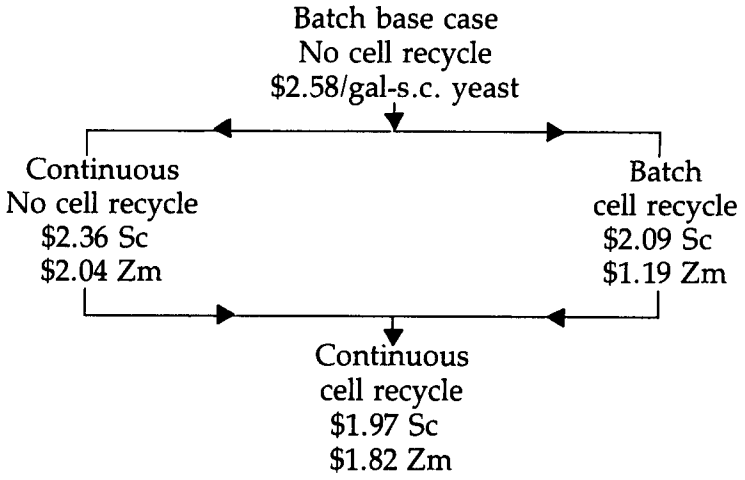
For such a saving to be realistically obtained, the operator would have to exercise one of a couple of options: (1) Transfering the now excess fermenter investment off the ethanol books by: (a) writing down in place and taking the tax saving or (b) applying the excess equipment to another venture, or (2) Expanding the investment base in medium preparation and product recovery and distillation to match the increased fermenter capacity at a higher production rate. None of these options may be of interest to incumbent operators. It is suggested that studies be made pertinent to specific plant cases to develop a better picture of retrofitting possibilities.

Table 7
Optimized Process Conditions 60 MM GPY Ethanol Manufacture
Inhibited *Saccharomyces* Yeast 1986 MPC—1990 Operating Year

	Batch	Batch	Continuous
Mode			
Product concentration—g/L	70	90	90
Cell recycle	No	Yes	Yes
Cell density—g/L	2.6	50	50
Investment—$ million			
Direct permanent investment	$94.0	$47.6	$35.3
Allocated power, services & gen.	26.8	22.1	22.1
Working capital	22.3	19.2	18.5
Total investment	$143.1	$88.9	$75.9
Cost—$/gal			
Raw materials	$0.94	$0.95	$0.95
Utilities	0.15	0.13	0.13
Labor-related	0.11	0.10	0.10
Capital-related	0.23	0.13	0.10
Cost of manufacture	$1.43	$1.30	$1.27
SE, D, R&D, Adm, & I.C.	0.36	0.29	0.28
Cost of sales	$1.79	$1.59	$1.55
Pretax earnings based on 30% ROI	0.79	0.49	0.42
Byproduct credits	0.00	0.00	0.00
Selling price	$2.58	$2.09	$1.97

Design of New Plants

The most advantageous strategy for retrofitting or for the stepwise introduction of the new technology in new plants appears to follow the right-side path of the following alternatives for an inhibited system:



The financial performance of these cases is summarized in Tables 7 and 8.

Table 8
Optimized Process Conditions 60 MM GPY Ethanol Manufacture
Inhibited *Zymomonas* Bacterium 1986 MPC—1990 Operating Year

	Batch	Continuous	Continuous	Batch	Continuous	Continuous
Mode						
Cell recycle	No	No	No	Yes	Yes	Yes
Cell density—g/L	1.8	1.8	1.8	50	50	50
Product concentration—g/L	90	90	90	110	110	110
Kinetics—const. envirm't/plug flow	PF	CE	PF	PF	CE	PF
Investment—$ million						
Direct permanent investment	$61.7	$49.4	$41.3	$39.8	$29.7	$28.7
Allocated power, services & gen'l.	22.7	22.7	22.7	19.6	19.6	19.6
Working capital	19.2	18.5	18.1	17.6	17.1	17.0
Total investment	$103.6	$90.7	$82.1	$77.0	$66.4	$65.3
Cost—$/gal						
Raw materials	$0.89	$0.89	$0.89	$0.89	$0.89	$0.89
Utilities	0.12	0.12	0.12	0.11	0.11	0.11
Labor-related	0.10	0.10	0.10	0.10	0.10	0.10
Capital-related	0.16	0.13	0.11	0.11	0.09	0.08
Cost of manufacture	$1.27	$1.25	$1.23	$1.21	$1.19	$1.18
SE, D, R&D, Adm, & I.C.	0.30	0.29	0.28	0.27	0.26	0.26
Cost of sales	$1.58	$1.54	$1.51	$1.48	$1.45	$1.44
Pretax earnings based on 30% ROI	0.58	0.50	0.46	0.43	0.37	0.36
Byproduct credits	0.00	0.00	0.00	0.00	0.00	0.00
Selling price	$2.15	$2.04	$1.96	$1.91	$1.82	1.81

CONCLUSIONS

It appeared from the results of the study that improvements to either yeast or bacterium processes could be effective in reducing the cost of producing ethanol to commercially acceptable levels. However, the *Zymomonas* process would appear to be the better choice for development.

The use of continuous fermentation in a fluidized bioreactor system coupled with cell mobilization and/or recycle could substantially reduce the cost of ethanol and, generically, other products that are now produced at low concentrations and volumetric productivities as a result of product inhibition. Such an economic breakthrough cannot be realized until the system has been fully demonstrated in a continuous process over an extended period at pilot scale, optimized according to the findings of this study, and scaled up for the specific fermentation process of interest.

There appears to be no inherent design limitation in effecting the engineering improvements required in the process operation.

Such may not be the case in attempting to develop an organism with improved product tolerance and/or higher specific productivity. The goal is sufficiently important, however, to warrant the laboratory effort.

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