0273-2289/91/2829—0605$03.40

Extractive Fermentation of Acetic Acid

Economic Tradeoff Between Yield of *Clostridium* and Concentration of *Acetobacter*

ROBERT M. BUSCHE

Bio En-Gene-Er Associates, Inc., Wilmington, DE

ABSTRACT

In this technoeconomic evaluation of the manufacture of acetic acid by fermentation, the use of the bacterium: *Acetobacter suboxydans* from the old vinegar process was compared with expected performance of the newer *Clostridium thermoaceticum* bacterium. Both systems were projected to operate as immobilized cells in a continuous, fluidized bed bioreactor, using solvent extraction to recover the product.

Acetobacter metabolizes ethanol aerobically to produce acid at 100 g/L in a low pH medium. This ensures that the product is in the form of a concentrated extractable free acid, rather than as an unextractable salt. Unfortunately, yields from glucose by way of the ethanol fermentation are poor, but near the biological limits of the organisms involved.

Conversely, *C. thermoaceticum* is a thermophilic anaerobe that operates at high fermentation rates on glucose at neutral pH to produce acetate salts directly in substantially quantitative yields. However, it is severely inhibited by product, which restricts concentration to a dilute 20 g/L.

An improved *Acetobacter* system operating with recycled cells at 50 g/L appears capable of producing acid at $0.38/lb, as compared with a $0.29/lb price for synthetic acid. However, this sytem has only a limited margin for process improvement.

The present *Clostridium* system cannot compete, since the required selling price would be $0.42/lb. However, if the organism could be adapted to tolerate higher product concentrations at acid pH, selling price could be reduced to $0.22/lb, or about 80% of the price of synthetic acid.

Index Entries: Acetic acid; extractive fermentation; economics; bioprocessing; thermophilic anaerobes.

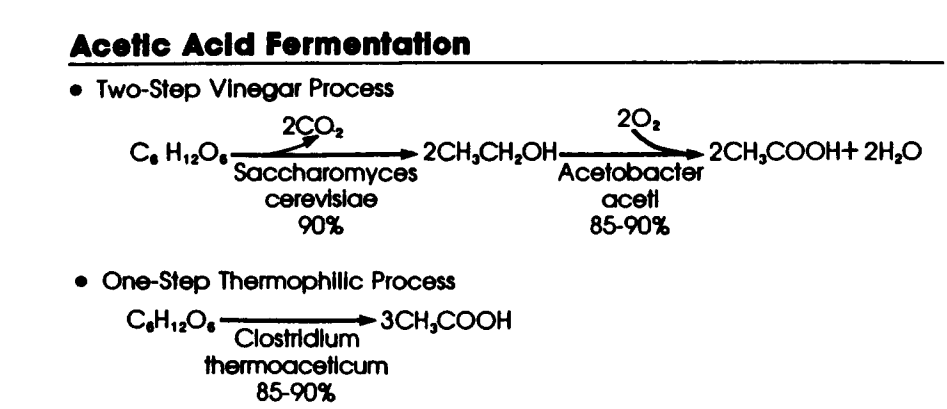


Fig. 1.

INTRODUCTION

Since the Middle East oil crisis of 1973, many people in government, academia, and industry have been concerned about the strategic implications of the potential loss of a major source of petrochemical feedstocks for the American chemical industry. Acetic acid is one example of a basic organic chemical that could be produced from renewable resources rather than fossil feedstocks. Presently, almost all acetic acid is produced synthetically: 62% by the carbonylation of methanol and the rest by the liquid phase oxidation on *n*-butane (*1*). Production in 1989 amounted to 3.8 billion pounds in the US and 8.0 billion pounds worldwide (*2,3*). If corn were to become the sole source of acetic acid, about 160 million bushels or 2% of the corn crop would be consumed for US needs.

FERMENTATION ALTERNATIVES

Industrial acetic acid could be produced by either of two fermentation processes: (1) from corn hydrolysates in a two-step process by way of ethanol using *Acetobacter suboxydans* in an updated version of the old vinegar process, or (2) directly from corn syrup in a new process based on the thermophilic organism, *Clostridium thermoaceticum*. The stoichiometry of these fermentations is shown in Fig. 1.

The *Acetobacter* process can operate at high (10 wt%) product concentrations and low pH, but is limited to a maximum theoretical yield of 2 mol of acetic acid/mol of glucose consumed as a result of the corresponding yield of ethanol from glucose. The *Clostridium* process produces acid at high rates accompanying elevated temperature operation and at yields near the theoretical 3 mol/mol of sugar. In spite of these rate and yield advantages, it is difficult to recover the product from the dilute beer. At the

neutral pH required for satisfactory viability of the organism, the product occurs in dilute 20 g/L salt form. Acidification is required to recover the product by conventional recovery operations.

These process differences represent an economic trade-off between raw material costs and product recovery costs. The purpose of this study is to evaluate the trade-off from the point of view of determining the potential of either process for commercial development and guiding research in this area along economically relevant pathways.

Two-Step *Acetobacter* Process

In the vinegar process, ethanol is produced in the first step at 30°C using conventionally the anaerobic yeast *Saccharomyces cerevisiae* at a yield of about 90%. In the second stage, the aerobic bacterium *Acetobacter aceti* is used to convert the ethanol to acetic acid at a yield of about 85%.

In the early "quick" vinegar process, the dilute alcohol, usually mixed with vinegar, was trickled down tall, wooden tanks packed with beechwood shavings or coke, on which the bacteria lodged as "mother of vinegar" (*4,5*). In later versions of the process, agitated baffled fermenters, similar ot those used for penicillin, were used with cooling coils to control the exothermic reaction at 30°C (*6,7*).

More recently, D. I. C. Wang using *Acetobacter suboxydans* was able to reach a maximum volumetric productivity in continuous culture of 11.5 g acetic acid/L·h at a steady-state acid concentration of 55 g/L, with cell recycle to a cell density of 7 g/L and at a dilution ratio of 0.21/L·h (*8*). This level was in contrast to typical productivities of commercial vinegar production of 0.5 g/L·h (*9*). At a pH of 2.8, substantially all the product was produced in free acid rather than salt form. Yield was 90–95%. Wang's study formed the basis for the two-step model evaluated in this study.

One-Step Thermophilic Process

In contrast to the vinegar process, *Clostridium thermoaceticum* converts glucose almost quantitatively to acetic acid. Hence, at an actual yield of 85–90%, it has the potential for reducing significantly the raw material costs to two-thirds of those for the vinegar process. The organism is a thermophilic anaerobe that ferments glucose, xylose, or other sugars at 58°C (*10*).

A basic problem, however, is that the organism prefers a neutral pH. As a result, the product is in the form of an acetate salt, rather than in the free acid form required to distill or extract the product from the fermenter broth. Schwartz and Keller of Union Carbide (*11*) approached this problem by attempting to adapt the organism to acid pH, thereby converting part of the salt in the broth to free acid. These results are compared in Table 1 with the data Wang obtained (*12*) while operating at neutral pH. As pH was reduced, productivity and product concentration dropped to unacceptable levels.

Table 1
Fermentation Performance

	Clostridium thermoaceticum					Acetobacter suboxidans
	Wang		Yates	Schwartz & Keller		Wang
Fermenter	Batch	Continuous	Continuous	Batch		Continuous
pH	6.8	6.8	6.0	5.5	4.5	2-8
Acetate – g/l (as acid)	45.	25.	18.	16.	4.	55-120
Productivity – g/l-hr	0.8*	8.0**	5.0	0.6	0.06	5.0
Yield – %	85-90	85-90	85-90	77.	85.	90-95
Minimum Glucose – g/gHAc	1.0	1.0	1.0	1.0	1.0	1.5
Temperature °C	60°	60°	58°	58°	58°	30°

*Free cells
**Immobilized Cells (2 if Free Cells)

In a similar study, Yates of Dupont (*13*) operated an 8-L fermenter in a continuous mode without interruption for over 26,000 h, although conditions were varied over this period as part of the experimental program. Acetate was produced at yields above 85%, but at dilute concentrations of 0.25–0.30*M* (15–18 g/L acid) similar to the results reported by Wang and Schwartz and Keller. Yates used a strain of *Clostridium thermoaceticum* obtained from L. G. Ljungdahl at the University of Georgia (*14*). Both Yates and Schwartz and Keller used fermenter media that were too rich to be acceptable in commercial use. Clearly, further work is needed to adapt the organism to a cheaper acid medium without adverse trade-off in other important operating parameters. All three laboratories were making some progress in this regard when the projects were abandoned as a result of softening in oil prices.

PRODUCT RECOVERY

Solvent extraction was used in this study for recovering the product in acid form. The use of distillation for recovering products like acetic acid that boil above water would be prohibitively expensive as a result of an excessive thermal load for boiling water away from the product (*15–20*).

Extraction with High-Boiling Solvent

There is a great deal of information in the literature dealing with the extraction of acetic acid from aqueous solution (*21–25*). King suggested that, since acetic acid is a strong Lewis acid, a strong Lewis base should be ideal as a complexing solvent (*26*). Trioctyl phosphine oxide (TOPO) at 50% in high-boiling ketones like 2-heptanone (150°C) gave a distribution coefficient (K) of 2.5, and solubility in water was only 1 ppm. TOPO was used as the model solvent for this study.

In the extraction process, the distribution coefficient has a determining effect on the number of stages and, hence, on extractor investment,

while the solvent to feed ratio, S/W, determines the cost of recovering the product from the solvent extract. A value of $K \cdot (S/W) = 1.25$ was used in this study as an optimum economic balance between number of stages and volumetric flow.

Solvent Inhibition of the Organism

Although a lot of data exist on the extraction of acetic acid, little is available on the effects of such systems on the viability of the organism. For example, Wang (*27*) reported that sodium acetate had a strong inhibiting effect on the growth of *Clostridium thermoaceticum*, with complete inhibition of cell growth, although not acid production, at 48 g/L. Bar and Gainer (*28*) made a distinction between toxicity arising from solvent dissolved in the broth and that arising from presence of a separate solvent phase, as in *in situ* extraction within the fermenter. They found that cells of *L. delbrueckii* were not inhibited in an *n*-dodecanol-saturated broth, but were inhibited in a two-phase system. Immobilizing the cells in carrageenan beads successfully protected the cells in the latter solution. These effects need further study.

PROCESS SCENARIO USED FOR THIS STUDY

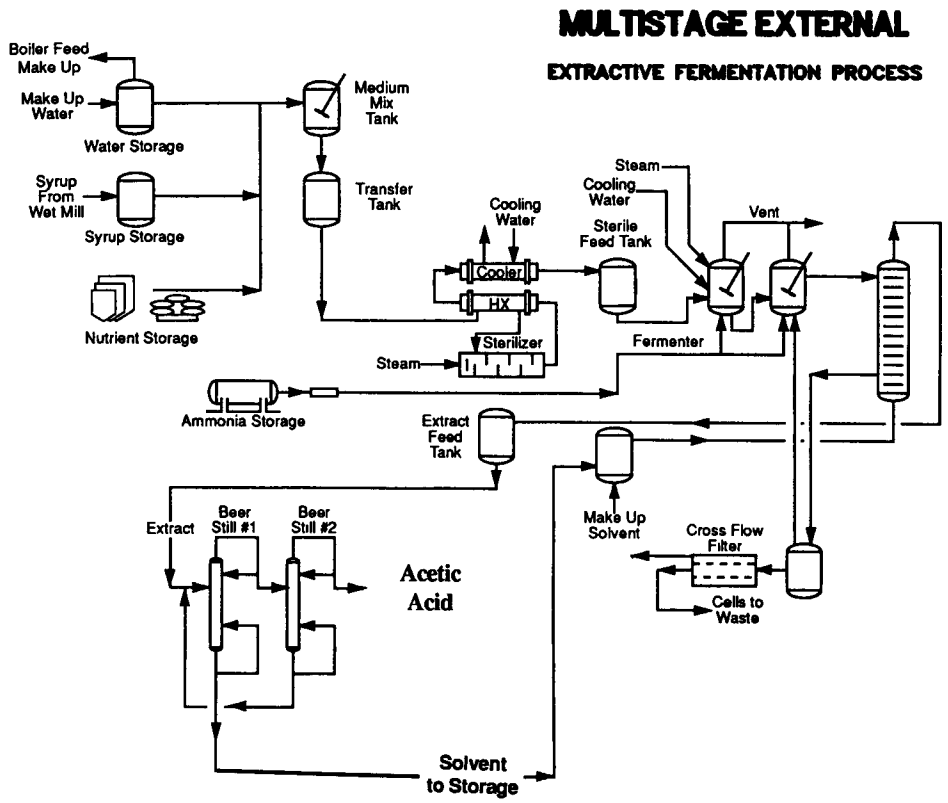
Process Description

From the preceding considerations, it was decided to base the design of the technoeconomic model on the production of acid in fluidized bed bioreactors operating in a continuous mode with either *Clostridium thermoaceticum* on a glucose (corn syrup) substrate or *Acetobacter suboxydans* on ethanol. Four cases were evaluated: (1A) *Acetobacter* at low pH; (1C) *Clostridium* with salt to waste; (2C) *Clostridium* with salt recovered and sold; and (3C) *Clostridium* adapted to operate at low pH.

High cell densities were developed in the fermenters by immobilization to prevent cell escape from the fermenter or by recycling after external filtration. Cells were purged in the amount grown.

The ethanol was similarly prepared in a fluidized bed bioreactor operated with the bacterium *Zymomonas mobilis* on a glucose substrate. The unconcentrated ethanol beer, after removing cells, was sent to the *Acetobacter* fermenters. The acid broth after filtration did not need acidification and was passed directly to the extractors.

For the *Clostridium* fermentation, pH was controlled at 6.0 by ammonia that was added as a nutrient. For a case where ammonium sulfate was recovered and sold as a fertilizer, the acetate filtrate leaving the filters was evaporated to a 40% acetate concentration before feeding to the acidifier. Placing the evaporator in this position reduced the volume of aqueous medium handled in subsequent process steps.



Process Model Used in Economic Study

Fig. 2.

Filtered and, in one case, evaporated *Clostridium* broth was acidified with sulfuric acid to yield free acetic acid and ammonium sulfate as the feed to the extractors.

For any of these process options, the treated broth was extracted in a continuous countercurrent multistage extractor using a high-boiling solvent like TOPO in a suitable carrier. The extract was then treated in a distillation column to separate solvent from acid product. Solvent was recycled while product was sent to storage. A general flow chart for the process is shown in Fig. 2.

The salt solution appearing as the extractor raffinate was sold as such without further purification or concentration, and with a minimum of storage (*29*). If the salt had no commercial value and had to be purged as waste, no evaporation was used. A soluble salt, like ammonium sulfate, had to be disposed of by deep well flooding to prevent contamination of potable water aquifers. An insoluble salt, like calcium sulfate, could have been disposed of in landfills.

Table 2
Extractive Fermentation of Acetic Acid Basecase Conditions

BACTERIUM	Acetobacter suboxydans	Clostridium thermoaceticum
SUBSTRATE	Ethanol	Glucose
Yield	92.5%	87.5%
Demand, g/g acetic acid	0.83*	1.14
FERMENTATION		
pH	2.8	6.0
Temperature C	30	58
Product Concentration, g/l	100	20
Cell Density - formed, g/l	4.2	1.4
- recycled**, g/l	50	50
Specific Productivity, g/g*hr	5.0	3.6
Dilution Rate, 1/hr	2.5	8.9
Volumetric Productivity, g/L*hr	250	179
Fermentation Volume, gal	22,000	30,000
* Equivalent to a glucose demand of 1.68 g/g		
** By immobilizing or recycling		
EXTRACTION		
Solvent	50% TOPO in high boiling solvent	
Distribution Coefficient	2.5	2.5
Solvent/Aqueous Feed	0.5	0.5
Yield to Extract	97%	97%
Extractors		
Units	2	4***
Stages	10	10
Diameter, ft	8.8	11.6****
*** One for Case 2C with evaporated feed		
**** 5.6 ft " " " " "		

Operating Conditions

The assumed basecase operating conditions for the plant are shown in Table 2. The data for the fermentations were based on the work of Wang and Yates. Similarly, the data for the extraction were based on the literature cited. For all cases, it was assumed that cells could be built up to a density of 50 g/L without adverse effects. This goal appears quite reasonable in view of past successes with similar systems. For example, Scott (*30–32*) operates currently with immobilized *Zymomonas* at 22 g/L, and Rogers with free *Zymomonas* at 40 g/L (*33–35*). Wilke operated the *Saccharomyces* yeast at cell densities up to 124 g/L with cell recycle (*36*). It must be strongly stated, however, that none of the data represent more than small-scale research findings, and that considerable research and development will be necessary to validate the conclusions of the study. Hopefully, the results will channel such research toward economically significant goals.

Site Scenario

It was assumed that the plant would be sited in the Midwest adjoining a corn wet mill with dilute, not-evaporated, 45% syrup supplied over the fence by pipeline. Capacity was sized to a 250-million pound/yr glacial

Table 3
Optimized Process Conditions
250 Million PPY Acetic Acid Clostridium vs Acetobacter
1984 MPC – 1988 Operating Year

CASE	1A	3C	2C	1C
MODE				
Bacterium	A. s.	C. ta.	C. ta.	C. ta.
Scenario	Low pH No Salts	Low pH No Salts	Sulfate Recovered	Sulfate To Waste
Substrate	Ethanol	Glucose	Glucose	Glucose
Product Concentration - g/l	100	20	20	20
Cell Recycle - g/g formed	12:1	36:1	36:1	36:1
Cell Density - g/l	50	50	50	50
INVESTMENT-$Million				
Direct Permanent Investment	$39.2	$55.8	$77.5	$57.1
Allocated Power, Services & Gen.	$8.1	$17.8	$19.0	$17.8
Working Capital	$14.6	$11.0	$15.7	$41.3
Total Investment	$61.8	$84.6	$112.2	$116.2
COST-$/lb				
Raw Materials	$0.19	$0.08	$0.13	$0.13
Utilities	$0.01	$0.02	$0.05	$0.51
Labor-Related	$0.02	$0.02	$0.02	$0.02
Capital-Related	$0.02	$0.03	$0.05	$0.03
Cost of Manufacture	$0.24	$0.16	$0.25	$0.70
SE, D, R&D, Adm, & I.C.	$0.05	$0.05	$0.06	$0.12
Cost of Sales	$0.30	$0.21	$0.31	$0.82
Pretax Earnings Based on 30% ROI	$0.08	$0.11	$0.15	$0.15
By-product Credits	$0.00	$0.00	($0.04)	$0.00
Selling Price	$0.38	$0.32	$0.42	$0.98

acetic acid plant with a midpoint of construction (MPC) in 1984 and operating in 1988 at 90% utility. The investment estimates include a 30% contingency for undeveloped design, and so forth. This uncertainty level is on the high side for designs based on reaming out existing facilities and on the low side for designs scaled up from semiworks data. The process and economic models were based on proprietary spreadsheet programs developed by Bio En-Gene-Er Associates, Inc. using generalized cost data from an actual plant.

CLOSTRIDIUM ADAPTED TO LOW pH

Of the cases studied, only Case 3C, *Clostridium* adapted to low pH, appears competitive at current oil prices with synthetic acetic acid (Table 3). Its costs, including a 30% pretax return on investment, would be $0.32/lb compared with the 1990 published price for synthetic acetic acid of $0.29–0.31/lb (*29*). This case assumes that a *Clostridium* mutant organism can be adapted to operate without loss of efficiency at acid pH. This goal will probably be difficult to attain considering the only partial success of Yates and Schwartz and Keller in accomplishing it. However, the leverage on reducing cost would be very great and worth the research effort.

Table 4
Clostridium Fermentation
Sensitivity of Acid Cost, $/lb
To Product Concentration

PRODUCT CONC, g/l	CASE 2C LOW pH	CASE 3C SULFATE RECOVERED
20	$0.31	$0.42
40	$0.26	$0.32
60	$0.24	$0.28
100	$0.22	$0.25
150	$0.22	$0.23

For 3.57 g product/g cells*hr
50 g/l Cell Density

It will also be very important to operate at high cell densities to overcome the adverse effect of low concentration on fermenter investment. Operating without recycle or confinement of cells would increase cost to $0.36/lb or 14% above the basecase at 50 g/L. However, at 50 g/L and above, volumetric productivity is so high (e.g., above 180 g/L·h) that further decreases in fermenter investment have little effect on cost.

In addition to the important goal of adapting to acid conditions, it would be very rewarding to develop an organism that is not inhibited by product. For example, at a cell density of 50 g/L, a *Clostridium* that could operate at 100 g product/L, as does *Acetobacter*, would provide a reduction in cost to $0.22/lb (Table 4). This selling price would be 30% below the basecase and $0.07–0.90/lb below the current price of $0.29–0.31/lb for synthetic acid.

ACETOBACTER AT LOW pH

Case 1A, *Acetobacter* operating at its customary acid pH, shows a slight edge over Case 2C, *Clostridium* at neutral pH with recovery of ammonium sulfate as a byproduct. At $0.38 and $0.42/lb, respectively, neither could compete with the synthetic product at current prices for petrochemical feedstocks.

Raw Material Requirements

The greatest economic obstacle of the two-step process is high substrate demand. At the average overall yield, the process required 2.0 g glucose/g ethanol and 0.83 g ethanol/g acetic acid for an overall sugar demand of 1.68 g glucose/g acetic acid. The *Zymomonas mobilis* bacterial system was selected over the yeast *Saccharomyces cerevisiae* for producing ethanol because of the better yield of the former (*37,38*). Since these yields are near the theoretical maxima for the organisms involved, eco-

Table 5
Ethanol For Acetic Acid
30 MM GPY Ex Immobilized Zymomonas Mobilis
Fluidized Bioreactor – Plug Flow – Cell Recycle

BASIS		
Mid-point of Construction		1984
Operating Year		1988
Substrate - $/lb Equivalent Glucose		$0.065
INVESTMENT - $Million		
Direct Permanent Investment		$9.4
Allocated Power, Services & General		$0.8
Working Capital		$2.2
Total Investment		$12.3
COST - $/Unit	$/gal Ethanol	$/lb Acetic Acid
Raw Materials	$0.88	$0.117
Utilities	$0.01	$0.002
Labor-Related	$0.16	$0.021
Capital-Related	$0.04	$0.005
Cost of Manufacture	$1.09	$0.144
SE, D, R&D, Adm, & I.C.	$0.21	$0.028
Cost of Transfers	$1.30	$0.172
Pretax Earnings Based on 30% ROI	$0.12	$0.016
By-product Credits	$0.00	$0.000
Transfer Price	$1.42	$0.188

nomic improvements to raw material costs will have to depend on cost advantages for corn compared with fossil feedstocks rather than on process improvements.

Because of the overall poor yield for this system, the effectiveness of the ethanol fermentation has a determining effect on overall cost for the acid. The cost of the sugar substrate at $0.065/lb accounts for 62% of the transfer price for the dilute ethanol beer, and the ethanol transfer price accounts for 50% of the $0.38/lb cost-plus-return price for the acid (Table 5). If the sugar price increased to $0.100/lb, the price of acid would increase to $0.46/lb, clearly out of contention with synthetic acid.

Ethanol Fermentation

Because of the heavy burden of raw materials, the conversion process must be on the cutting edge of fermentation technology to compete. For this case, process operating conditions appeared optimized at a product concentration of 100–110 g/L. As shown in Table 6, this point represents the optimum cost balance at a fixed 50 g/L cell density, although cost is relatively flat between 80–120 g/L.

Increasing product concentration decreases total plant investment. However, the attendant drop in specific productivity, resulting from increased product inhibition, decreases dilution rate and volumetric pro-

Table 6
Ethanol Ex Zymomonas Mobilis
Inhibited Continuous System – Constant Environment
Effect of Product Concentration

PRODUCT CONCENT. g/l	SPECIFIC PROD'ITY g/g*hr	VOLUME PROD'ITY g/l*hr	DILUTION RATE l/hr	TOTAL ETHANOL COST $/gal Ethanol	$/lb Acetic Acd	CAPITAL COSTS $/gal	FERMENTER INVEST'MT $million
50	5.2	260	5.2	$1.53	$0.202	$0.25	$0.26
60	4.8	242	4.0	$1.50	$0.198	$0.23	$0.28
70	4.1	206	2.9	$1.48	$0.196	$0.21	$0.33
80	3.4	170	2.1	$1.46	$0.193	$0.20	$0.40
90	2.7	134	1.5	$1.45	$0.192	$0.19	$0.51
100	2.0	98	1.0	$1.44	$0.190	$0.18	$0.69
110	1.2	61	0.6	$1.44	$0.190	$0.18	$1.10
120	0.5	25	0.2	$1.46	$0.192	$0.19	$2.68

@ 50 g/l cell density

ductivity, and increases fermenter investment. Even close to the point of total inhibition at 127 g/L, volumetric productivity is high and fermenter investment relatively low. In this case, it matters little whether the fermenter is operated with constant environment kinetics ($1.44/gal) or with the usually preferred plug flow kinetics ($1.43/gal).

At a plant capacity of 250 million annual pounds of acid consuming 33 million gallons of ethanol, the economics are not particularly scale sensitive. The data indicate that a plant designed for 400 million pounds would only save $0.08/gal out of $1.43 in ethanol cost, which is equivalent to only $0.01/lb of acetic acid.

Acetobacter Fermentation

As with the other cases, a recycle of cells to 50 g/L was assumed for this case. However, cost is not very sensitive to this parameter. Restricting cell density to 4 g/L would only mean an increase in $0.014/lb in cost. Again, the reason for this insensitivity is that volumetric productivities are already above 20 g/L·h, and the influence of fermenter investment on total cost is very low.

Similarly, since *Acetobacter* already operates at a very high 100 g/L product concentration, increasing concentration further would not be a particularly rewarding research goal. For example, at a 50 g/L cell density, an increase in product concentration to 200 g/L would only reduce price to $0.364/lb, corresponding to a $0.014/lb reduction in cost.

Extraction

Total cost increases with increasing solvent/feed ratio over the entire range studied, rising from $0.38/lb at a ratio of 0.5 to $0.45/lb at 6.0. Curiously enough, the investment in extractors is minimized at a ratio of 2.5. It appears that, in order to maintain a constant yield of acid to extract

of 97%, this ratio represents a balance between the effect of decreasing the number of stages required and increasing extractor diameter, as ratio and, hence, combined flow rate rises at a fixed feed flow. The effect is overwhelmed, however, by the increase in investment in distillation equipment to handle the solvent extract.

Provided the solvent does not inhibit the organism, it is very important to identify a solvent for acetic acid with as high a distribution coefficient and selectively as possible. Even so, increasing the coefficient beyond the basecase assumption of 2.5 for TOPO does not appear particularly rewarding.

CLOSTRIDIUM AT NEUTRAL pH WITH SALT RECOVERY

In this "state-of-the-art" Case 2C for the *Clostridium* fermentation, the better yield of *Clostridium*, which amounts to a saving in raw materials of $0.06/lb over the *Acetobacter* case, is not sufficient to make up for its low product concentration and higher plant investment (by $50 million), even at the faster fermentation rate that accompanies operating at elevated temperatures. Salts in neutral *Clostridium* broths would have to be acidified to recover free acetic acid. It was assumed for this case that ammonia would be used for both fermenter pH control and cell growth, and that ammonium acetate in the broth would be acidified with sulfuric acid to form free acetic acid and ammonium sulfate. Ammonium sulfate is highly soluble in water (706 g/1000 g). For Case 2C, it was assumed that it would be recovered as a 40% solution for sale as a fertilizer. There is considerable precedent for doing this. Since 1960, a major source of ammonium sulfate has been as a byproduct in manufacturing caprolactam for nylon 6. The salt is usually used as a 40% solution (*25*).

However, even with the sale of byproduct salt, the very high cost penalty of having to operate the *Clostridium* fermentation at neutral pH can be readily seen by comparing the economics for Cases 3C and 2C in Table 3. Selling price is increased $0.10/lb, or 30% over the extrapolated case at low pH. A $0.040/lb acetic acid credit for ammonium sulfate does not even cover the $0.052/lb increase in raw materials cost created by the need for additional ammonia and sulfuric acid. In addition, higher steam and electrical demands for evaporation and other processing increase utility costs by $0.033/lb. Similarly, a large increase in plant investment of $22.9 million or 31% increases capital charges by $0.052/lb. The most expensive section becomes the addition of evaporators (falling film type with vapor recompression) (*39–41*) and acidification equipment amounting to $28.3 million or 29% of total plant investment.

Sulfate selling price does not have a major effect on acid cost. A basecase price for ammonium sulfate of $70/ton was selected to be on the low side of the published range of $60–120/ton (*29*). If the salt were given away, cost would rise about $0.045/lb acid or 11%.

Most of the additional cost for the sulfate basecase relates to handling and evaporating large quantities of water from a dilute 20 g/L solution. If allowable product concentration were increased to 100 g/L, the cost for acetic acid would be cut nearly in half to $0.025/lb, i.e., substantially under the price for synthetic acid and only $0.01/lb higher than the price of the product from the low pH *Clostridium* case at 100 g/L (Table 4). *Accordingly, eliminating product inhibition so as to increase concentration would be a very rewarding research goal, even for an organism that requires a neutral environment.*

The data show that it would be less rewarding to work on increasing cell density, optimizing solvent/beer ratio, or increasing distribution coefficient as long as plant investment is dominated by equipment related to salt recovery. Although sugar-to-acid yield is good for this case, sugar price does have a large effect.

CLOSTRIDIUM AT NEUTRAL pH WITH SALT TO WASTE

Case 1C, in which dilute sulfate solutions are disposed of by deep welling, is completely out of the picture as a result of the extraordinary charges for waste disposal. The case shown is for ammonium sulfate, a soluble salt. Since it is very difficult to dispose of soluble salts, this represents a "worse case" scenario. For this case, it was assumed that the ammonium sulfate solution would be pumped down a deep well into brackish strata below aquifers of potable water. According to studies made by the Environmental Protection Agency, this type of disposal costs about $20/ton of *total* solution (*42*). For a dilute 20 g/L sulfate solution, this cost amounts to $0.49/lb acetic acid and results in a total acid cost of $0.96/lb. Obviously, this disposal method cannot be used for dilute solutions.

A cheaper alternative to deep welling would be land filling of an insoluble salt. The cost of land filling is independent of the concentration of product and amounts to about $80/dry ton. In contrast, a soluble salt for deep welling would have to be at a concentration above 25 wt% before it could compete. A land fill alternative could be based on using lime to control pH in the *Clostridium* fermentation. During acidification, waste gypsum (calcium sulfate) would be formed at a rate of over a pound for every pound of acetic acid produced. The cost of land filling would be $0.047/lb acetic acid, or a saving of $0.442/lb acid over deep well disposal

costs. This savings would drop the cost of acetic acid of $0.54/lb—still a very high cost compared with other options.

PROCESS DEVELOPMENT STRATEGY

Product Inhibition

Although *Acetobacter* and *Zymomonas* can tolerate product concentrations up to at least 100 g/L, *Clostridium thermoaceticum* is highly inhibited and limited to acetate concentrations of about 20 g/L. Hopefully, an organism that is not inhibited by product and can tolerate low pH might be genetically engineered. Although these goals may be very difficult to attain, the expected benefits are sufficiently important to warrant the laboratory effort.

Cell Immobilization/Recycle

Short of this, the best fermentation strategy appears to be to control product concentration at the optimum level *vis-a-vis* product inhibition, while operating at as high a cell density as is physically and/or biologically possible. Assuming a constant specific productivity at an optimum product concentration, this operating strategy fixes dilution rate at a maximum level, and minimizes fermenter size and investment. An attempt was made in this study to define the optima within the limitations of published data.

Continuous Mode

It also appears that the development of a continuous fermentation system is a fundamental requirement for improving the economic viability of the acetic acid process. As noted previously, Yates operated a small laboratory fermenter for thousands of hours with *Clostridium thermoaceticum* without problems. Scott and Davison (*43*) are operating a rack-scale 2.5-m fluidized bed bioreactor in a continuous mode at the Oak Ridge National Laboratory on various organisms, including *Clostridia* and *Zymomonas mobilis*.

THE COMPETITIVE ENVIRONMENT

Commercial acceptance of the enhanced fermentation process will ultimately depend on the direction taken by crude oil prices. The market is still soft at about $17–20/barrel. However, James McNabb of Conoco (*44*) has pointed out that OPEC operated at only 60% of capacity over the late 1980s. By the early 1990s, production is expected to reach 80%; and market power will shift back from the buyer to the seller, with a corollary increase in oil prices. At that time, it is expected that the US will be im-

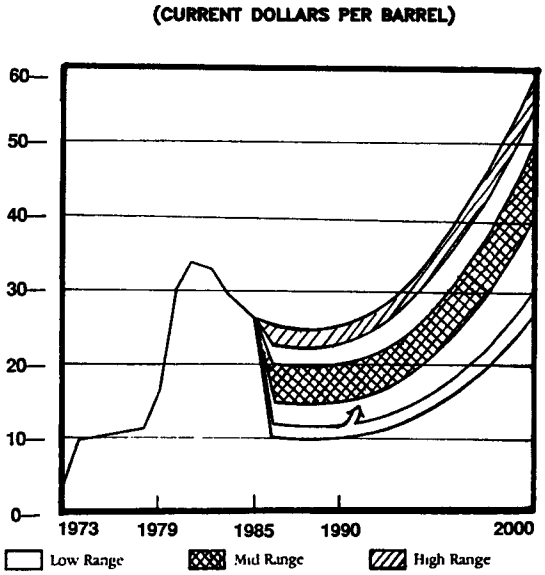


Fig. 3. Courtesy Conoco Inc.

porting half of its oil supply instead of the 7% it imported at the time of the 1973 oil crisis. As a result, he forecasts that oil prices will reach the mid $30s by 1995 and $59/barrel by the year 2000 (Fig. 3). Other market watchers are also foretelling the start of the turnaround in oil prices in the near future (*45–50*). Thus, a doubling in the price for synthetic acetic acid over the next decade is not out of the question.

ACKNOWLEDGMENT

This work was jointly sponsored by the Energy Conversion and Utilization Technologies (ECUT) program of the US Department of Energy and the National Corn Growers Association. Their support is gratefully acknowledged.

REFERENCES

1. Forster, D. (1976), *J. Am. Chem. Soc.* **98(3),** 846.
2. Busche, R. M., "Acetic Acid—Industrial Market Volume and Potential," Bio En-Gene-Er Associates, Inc, May 28, 1987.
3. Reisch, M. S., "Top 50 Chemicals Production Slowed Markedly Last Year," C&E News, 11–15, Apr. 9, 1990.
4. Herrick, H. T. and May, O. E. (1935), *Chem. & Metallurg. Eng.* **42,** 142.

5. Lai, M. N. and Wang, I. H., "A Rapid Process of Manufacturing Vinegar," U.S./R.O.C. Symposium on Fermentation Engineering Fundamentals, University of Pennsylvania, May 30–June 1,1978.
6. Owens, C. H. (1937), US Patent 2,089,412.
7. Hansen, A. E. (1935), *Food Inc.* **7,** 277.
8. Wang, D. I. C., Felipe, V., and Tyo, M. A., "Production of Food Grade Acetic Acid by Fermentation," U.S./R.O.C. Symposium on Fermentation Engineering Fundamentals, University of Pennsylvania, May 30–June 1, 1978.
9. Nickol, G. B. (1979), "Vinegar," *Microbial Technology* 2d ed., Peppler, H. J. and Perlman, D., eds., Academic Press, New York, pp. 155–172.
10. Andreesen, J. R., Schaupp, A., Neuranter, C., Brown, A., and Ljungdahl, L. G. (1973), *J. Bacteriol.* **114(2),** 743–751.
11. Schwartz, R. D. and Keller, F. A. Jr. (1982), *Appl. Environ. Microbiol.* **43,** 117.
12. Wang, D. I. C. (1982), Massachusetts Institute of Technology, private communication.
13. Yates, R. A. (1981), US Patent 4,282,323.
14. Ljungdahl, L. G. (1976), *Trans. Ind. Biol. Soc.* 63, 64.
15. Busche, R. M. (1983), *Biotech. & Bioeng. Symp.* **13,** 597–615.
16. Busche, R. M., Shimshick, E. J., and Yates, R. A. (1982), *Biotech. & Bioeng. Symp.* **12,** 249–262.
17. Busche, R. M. (1985), *Biotechnology—Applications & Research,* Cheremisinoff, P. N. and Ouellette, R. P., eds., Technomic Publishing Co, Lancaster, PA.
18. Null, H. R. (1980), *Chem. Eng. Prog.* **76,** 42.
19. Perry, R. H., Chilton, C. H., and Kirkpatrick, S. D. (1963), *Perry's Chemical Engineer's Handbook,* 4th ed., McGraw-Hill Book Co, New York, pp. 3–113.
20. Mongan, E. L. Jr., Engineering Department, E. I. Dupont de Nemours & Co, Inc., private communication, June 9, 1981.
21. Green, D. W. (1984), *Perry's Chemical Engineers' Handbook,* 6th ed., McGraw-Hill Book Co, New York, pp. 15–10.
22. King, C. J. (1983), *Handbook of Solvent Extraction,* Lo, T. C., Baird, M. H. I., and Hanson, C., eds., John Wiley, New York, pp. 567–573.
23. Brown, W. V. (1963), *Chem. Eng. Prog.* **59,** 65.
24. Yates, R. A., Central Research & Development Dept, E. I. Dupont de Nemours & Co, Inc., private communication, Dec. 1977.
25. *Kirk-Othmer Encyclopedia of Chemical Techology* (1978), 3rd ed., Grayson, M., ed., vol. 2, John Wiley, New York, pp. 533–535.
26. King, C. J. (1987), *Handbook of Separation Process Technology,* Rocisseau, R. W., ed., John Wiley, New York, pp. 760–774.
27. Wang, D. I. C., Fleischchaker, R. J., and Wang, G. Y. (1978), *Biochemical Engineering: Renewable Sources of Energy and Chemical Feedstocks,* Nystrom, J. M. and Barnett, S. M., eds., AIChE Symp. **74,** 181.
28. Bar, R. and Gainer, J. L. (1987), *Biotech. Prog.* **3,** 109–114.
29. *Chem. Mkt. Reporter,* April 27, 1990.
30. Davison, B. H. and Scott, C. D. (1986), *Biotech. & Bioeng. Symp.* **17,** 629–632.
31. Davison, B. H. and Scott, C. D. (1988), *Appl. Biochem. Biotech.* **18,** 19–34.
32. Scott, C. D. (1983), *Biotech. & Bioeng. Symp.* **13,** 237–238.
33. Rogers, P. I., Lee, K. J., Skotnicki, M. L., and Tribe, D. E. (1982), *Adv. Biochem. Eng.* **23,** 37–84.

34. Rogers, P. I., Lee, K. J., and Tribe, D. E., "High Productivity Ethanol Fermentations with *Zymomonas mobilis*," Process Biochem. U. New South Wales, Sydney, Australia, Aug./Sept. 1980.
35. Rogers, P. I., Lee, K. J., Skotnicki, M. L., and Tribe, D. E. (1981), *Advances in Biotechnology*, vol. 2, Young, M. M. and Robinson, C. W., eds., Pergamon Press, pp. 189–194.
36. Cysewski, G. R. and Wilke, C. R. (1977), *Biotech & Bioeng.* **19,** 1125–1143.
37. Montenecourt, B. S. (1985), *Biology of Industrial Microorganisms*, Dumain, A. L. and Solomon, N., eds., Ben Cummings, pp. 261–289.
38. Swings, J. and Deley, J. (1977), *Bacterial Rev.* **41,** 1–46.
39. Fosberg, T. M. and Claussen, H. L. (1982), *TAPPI* **65,** 63.
40. Beesley, A. H. and Rhinesmith, R. D. (1980), *Chem. Eng. Prog.* **76,** 37.
41. Macek, S., Dedert Corp, Olympic Fields, IL, private communication, Apr. 25, 1989.
42. Super, J., Engineering Dept, E. I. Dupont de Nemours & Co. Inc, private communication, Apr. 30, 1989.
43. Davison, B. H., Oak Ridge National Laboratory, private communication, Dec. 13, 1988.
44. McNabb, J. E., "World Energy Outlook Through 2000," Conoco Inc, Wilmington, DE, Sept. 1986.
45. Lynch, M. C. (1988), *Chem. Eng. Prog.* **20.**
46. McCartney, S., "Surge in Price of Oil Foreseen in Next Decade," *News Journal*, Wilmington, DE, p. B10, Dec. 12, 1988.
47. Gupte, P., "Price Surge Ahead," *Forbes*, p. 55, Dec. 12, 1988.
48. Anon, "Oil Futures Prices Jump," *News Journal*, Wilmington, DE, p. 86, Jan. 17, 1898.
49. Layman, P. L., "Middle East Chemical Industry Eyes New Products, Markets," *C & E News*, p. 20, Mar. 6, 1989.
50. Jasper, S. "Oil Service Stocks Are Ready to Soar," *News Journal*, Wilmington, DE, p. B10, Mar. 13, 1989.