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ECUT
ENERGY CONVERSION AND UTILIZATION TECHNOLOGIES PROGRAM

Biocatalyzed Processes for Production of Commodity Chemicals: Assessment of Future Research Advances for N-Butanol Production

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J.D. Ingham

July 1, 1984

Sponsored by:
U.S. Department of Energy
Battelle Pacific Northwest Laboratories
Richland, Washington

Through an Agreement with
National Aeronautics and Space Administration

Prepared by:
ECUT Biocatalysis Project
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91109

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The Biocatalysis Project is managed by the Jet Propulsion Laboratory, California Institute of Technology, for the United States Department of Energy through an agreement with the National Aeronautics and Space Administration. (This report was sponsored by Battelle Pacific Northwest Laboratory, Interagency Order No. B-F6809-A-Z; NASA Task Order RE-152, Amendment 392.)

The Biocatalysis Project focuses on resolving the major technical barriers that impede the potential use of biologically-facilitated continuous chemical production processes.

ABSTRACT

This report is a summary of assessments by Chem Systems Inc. and a further evaluation of the impacts of research advances on energy efficiency and the potential for future industrial production of acetone-butanol-ethanol (ABE) solvents and other products by biocatalyzed processes. Brief discussions of each of the assessments made by CSI, followed by estimates of minimum projected energy consumption and costs for production of solvents by ABE biocatalyzed processes are included. These assessments and further advances discussed in this report show that substantial decreases in energy consumption and costs are possible on the basis of specific research advances; therefore, it appears that a biocatalyzed process for ABE can be developed that will be competitive with conventional petrochemical processes for production of n-butanol and acetone. (In this work, the ABE process was selected and utilized only as an example for methodology development; other possible bioprocesses for production of commodity chemicals are not intended to be excluded.) It has been estimated that process energy consumption can be decreased by >50%, with a corresponding cost reduction of 15-30% (in comparison with a conventional petrochemical process) by increasing microorganism tolerance to n-butanol and efficient recovery of product solvents from the vapor phase.

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EXECUTIVE SUMMARY

The Biocatalysis Project at JPL is a component of the Energy Conversion and Utilization Technologies (ECUT) Program sponsored by the Office of Energy Systems Research, U. S. Department of Energy (DOE). This Project supports applied research and development to assist in providing the technology base required for competitive biocatalyzed processes.

One component of this effort is an economic-energy assessment performed by Chem Systems Inc. (CSI) (Refs. 1 and 2). The purpose of this report is to summarize this assessment and to evaluate the impacts of research advances on energy efficiency and the potential for future industrial production of acetone-butanol-ethanol (ABE) solvents by biocatalyzed processes. Brief discussions of each of the assessments made by CSI are included, followed by estimates of minimum projected energy consumption and costs for production of solvents by ABE biocatalyzed processes, as well as a preliminary evaluation of one approach for estimating potential annual production of commodity chemicals by biocatalyzed processes. The purpose of the work by Chem Systems Inc. was to initiate development of a methodology for making future research and development decisions for the ECUT Biocatalysis Project, i.e., to develop the capability for assessing the impacts of potential research advances on increasing energy efficiency in biocatalyzed processes for producing commodity chemicals. Then the most promising research approaches can be implemented to provide a technology base for eventual commercialization of biocatalyzed processes. Although the acetone-butanol-ethanol (ABE) process was selected and assessed, and the implications of these assessments are discussed and evaluated further in this report, the ABE process has been investigated only as a representative biocatalyzed process for the purpose of methodology development.

These assessments have shown that substantial decreases in energy consumption and costs are possible on the basis of specific research advances; therefore, it appears that a biocatalyzed process for ABE can be developed that will be competitive with conventional petrochemical processes for production of n-butanol and acetone. The conventional process selected for butanol production is carbonylation of propylene (rhodium catalyst) to the aldehyde, followed by hydrogenation (nickel catalyst) to the alcohol. For acetone, propylene is hydrated to isopropanol, followed by dehydrogenation to acetone (Refs. 1 and 2).

The research advances with the greatest impact were increased microorganism tolerance to n-butanol and the improved prehydrolysis-dual enzyme system. However, none of the proposed advanced concepts are necessarily eliminated without further analyses because relatively small modifications in the assumed advance may have large effects on energy and costs. The results suggest that feedstock uniformity, cost, and availability will be major factors in determining the viability of very large-scale biocatalyzed processes.

Potential lower limits for energy and costs for a more advanced conceptual ABE bioprocess have been estimated in this report, and the relationships between energy and product concentration and between costs and product concentration have been defined. This conceptual process is based on a microorganism concentration tolerance of 1.8 wt % and removal of products from the vapor phase at a concentration of ~20 wt %, which corresponds to the vapor concentration for first-stage evaporation of the n-butanol-water azeotrope at a liquid concentration of 1.8%. It has been estimated that energy can be decreased by more than 50%, with a product selling price of ABE solvents of $0.22/lb ±25% by separation of n-butanol from the vapor phase at increased tolerance of the microorganism to n-butanol; the price of ABE solvents by the conventional petrochemical process is $0.33/lb. These assessments indicate that with these research advances all n-butanol would be produced eventually by a biocatalyzed process. However, a preliminary evaluation, based on a model for estimating annual production on the basis of costs, suggests that total production may not be increased much beyond current levels to produce n-butanol to be used as a feedstock to make other commodity chemicals.

SECTION I

INTRODUCTION

One component of the Biocatalysis Project is an economic-energy assessment performed by Chem Systems Inc. (CSI) (Refs. 1 and 2). The purpose of this report is to summarize this assessment and to evaluate the impacts of research advances on energy efficiency and the potential for future industrial production of acetone-butanol-ethanol (ABE) solvents by biocatalyzed processes. Although ABE processes are evaluated as an example in this work, other biocatalytic processes are also discussed.

Before the development of the petrochemical industry beginning in the 1920's, most commodity chemicals were produced from coal or by fermentation processes. The acetone-butanol-ethanol (ABE) process was first developed as a commercial process by Chaim Weizmann in England to produce butanol for artificial rubber. Later, acetone, which was used for the manufacture of explosive cordite during World War I, was the desired product. After the war, n-butanol again became the product of interest, primarily for use as an intermediate for esters to be used as solvents for automobile lacquers. By the early 1950's, petrochemical processes for commodity chemicals began to dominate, and interest in fermentation processes rapidly declined.

A patent was issued in 1932 for a process for continuous ABE fermentation (Ref. 3); even in 1958, research on continuous fermentation was in progress (Refs. 4 and 5). There were also attempts to solve some of the problems associated with large-scale fermentation, such as control of n-butanol-acetone ratios (Ref. 6), virus and phage infection (Ref. 7), and tolerance of microorganisms to higher n-butanol concentrations (Ref. 8). Metabolic inhibition and bacterial strain selection were also investigated and used to develop appropriate process modifications.

There has been renewed interest in ABE fermentation and other processes for biocatalytically producing commodity chemicals because of recent petroleum shortages. At the present time, this interest has tended to subside somewhat because of increased availability of petroleum and because of under-utilized plant capacity for petrochemical processing. However, the relative cost of energy has permanently increased, and further periodic cost increases may still be expected. Therefore, within the next few decades, biocatalyzed processes should become much more important, especially if energy efficiency for such processes can be substantially improved.

This report includes brief discussions of each of the assessments made by CSI, followed by estimates of minimum projected energy consumption and costs for production of solvents by ABE biocatalyzed processes, and a preliminary evaluation by one approach for estimating potential annual production of commodity chemicals by biocatalyzed processes.

SECTION II

POTENTIAL RESEARCH ADVANCES

A. CHEM SYSTEMS ASSESSMENTS

Several potential research advances and applications to ABE processing have been analyzed (Ref. 2). A summary of the results obtained are shown in Table 2-1 for separate process options. In these assessments, process economics were based on a hypothetical Gulf Coast plant designed to produce 50 million gallons of solvents per year in mid-1982. Calculations were made using utilities costs estimated by CSI and by DOE. The latter were about 15 % lower. Those shown in Table 2-1 were based on CSI utilities cost estimates to reflect a slightly more conservative approach because long-term future increases are expected. The total investment costs are about twice the investment for a conventional plant and would tend to further decrease incentives to construct new bioprocess plants, especially when existing conventional plant capacity utilization is much less than 100%.

Assumptions for the base-case included: solvent yield of 27.54% based on total sugar produced by enzymatic hydrolysis of aspen wood, solvent concentration of 1.44 wt % (0.89 wt % n-butanol), and an initial sugar concentration of 5 wt %. Net process energy consumption was 5.37 x 10^9 MBtu for an annual production of 50 x 10^6 gallons of solvents, or 107.4 MBtu/gal (=16.0 MBtu/lb). In these analyses, there was no net energy required for hydrolysis or for fermentation because lignin and unconverted cellulose were burned as fuel; therefore, total net energy consumption (16.0 MBtu/lb) was used for product purification. The greatest disadvantage of the base-case bioprocess is this large amount of energy needed for product separation from water, where most of it is consumed only to increase the water temperature to the distillation temperature.

At n-butanol concentration of 1.1 wt % (solvent concentration ~1.9 wt %) the alcohol normally tends to completely inhibit the biocatalyzed process. For the best case analyzed (improved n-butanol concentration tolerance to allow 2.1 wt % total solvents in the fermenter), energy consumption was decreased to 13.45 MBtu/lb.

Continuous fermentation showed neither a cost or energy advantage. The process analyzed was nearly the same as the batch base-case, except that the fermenters were operated continuously. Although decreased fermentation time favored decreased capital and energy costs, the yield was decreased, which offset any advantages. However, this analysis does not rule out potential advantages of continuous ABE processing on the basis of alternative process assumptions or advanced process design.

Table 2-1. Summary of Individual Research Advances on ABE Economics and Energy Requirements (Ref. 2)

	Base-Case	Continuous Fermentation	Lignol	Baelene	Dual Enzyme	Improved n-Butanol Tolerance (2.1 wt % solvents)	Conventional (from Propylene)
Total Investment, $MM	190.1	187.3	237.9	191.7	178.5	159.3	96.3
Cost of Production, cents/gal:							
Raw Material	86.59	90.13	92.68	86.59	84.57	66.99	150.24
Utilities	43.37	43.79	46.99	39.09	43.39	35.08	5.13
Operating Costs	15.16	13.70	20.15	16.31	14.36	13.10	9.45
Overhead Expenditures	17.37	15.91	22.05	18.16	16.50	15.10	9.98
Credit (By-products)	(23.20)	(22.85)	(71.58)	(23.20)	(23.20)	(22.20)	(21.24)
Cash COP[a]	139.28	140.67	110.29	136.95	135.61	108.07	153.56
Depreciation	56.58	55.16	78.46	58.82	52.92	46.98	31.50
Net COP[a]	195.85	195.82	184.75	195.76	188.53	155.05	185.05
Selling Price at 10% DCF[b]	259.8	259.5	255.5	258.0	249.3	208.5	221.0
Percent Decrease in Price	0	0	1.66	0.69	4.04	19.75	14.9
Percent Decrease (Increase) in Energy	0	0	12	6	2	16	(39)[c]

[a] COP = Cost of production.
[b] DCF = Discounted cash flow.
[c] Reference 1.

The Lignol process (Hydrocarbon Research, Inc.) involves hydrocracking and hydrodealkylation of lignin to phenol, benzene, and fuel oil instead of using lignin as a fuel (as was assumed in the base-case). The decrease in energy consumption of 12% results from energy credits for the products (phenol, etc.). In these assessments, energy (as heat of combustion) of higher value products such as phenol or propylene (in the petroleum-based process) are included as energy debits or credits, but heat energy of low-value, renewable resources (e.g., aspen feedstock) is not included as a debit. Because of significantly increased capital costs and the small effect on price, it appears that this advance would probably not be implemented unless there was an urgent need for the by-products.

Baelene solvent extraction (Baeol, Inc.) involves product purification by solvent extraction. Although Baeol, Inc., has indicated they have a new solvent that extracts essentially all of the n-butanol, acetone, and ethanol, the identity of the solvent is not available; therefore, this analysis was based on utilization of a solvent mentioned in a patent (Ref. 9), F-21 or monofluorodichloromethane. Because the solvent is relatively expensive and slightly soluble in water (0.95 wt % at 25°C and one atmosphere), it must be recovered. The recovery system assumed in this analysis involves heating the dilute solution to distil and separate the solvent. Because this requires about 10 MBtu/lb of solvents produced, total energy consumption is nearly as much as for the base-case. This analysis is valid on the basis of this assumption; however, energy consumption could be significantly decreased (e.g., by vapor compression recovery or, possibly, use of a different solvent). Therefore, solvent extraction as a potentially energy-efficient separation process for ABE products is not necessarily excluded.

In the dual enzyme option, a second enzyme (β-glucosidase) is included in small amounts to catalyze the conversion of cellobiose to glucose and prevent its accumulation, which normally depresses glucose yield. (This enzyme is produced by Aspergillus phoenicis and complements cellulase produced by T.reesei.) Also, prehydrolysis conditions were modified to increase enzyme accessibility. The effect is to increase glucose yield from 90 to 100%; however, no decrease in steam consumption is realized because the unconverted glucose was previously burned with lignin. (At 100% conversion, no glucose is available as part of the solid waste to be burned as fuel.) However, the selling price is decreased about $0.10/gal because of a small decrease in raw materials costs and a larger decrease in capital-related expenses (because of the decreased volume of material being processed). Although this option represents a relatively modest improvement in comparison with the base-case, it could be implemented with a minimum of process modifications and would have a positive impact in the important area of feedstock utilization. On this basis, this option is a significant technological advancement.

The mechanism of product inhibition in the microorganism (Clostridium acetobutylicum) is not well understood, but appears to be associated with the hydrophobicity of n-butanol. It is believed that higher concentrations of alcohol increase fluidity of the lipid regions of cell membranes and cause alterations of membrane-bound enzyme activity, which decrease the transport of carbohydrates. There is a resulting decrease in cell growth rate, cell death, and corresponding decreases in fermentation activity (Ref. 10). This mechanism is based on experiments that have shown membrane-bound ATPase was inhibited by 50% in the presence of either 21 wt % ethyl alcohol, 3 wt % n-butanol, 1 wt % pentanol, 0.1 wt % heptanol or 0.04 wt % octanol (Ref. 11). It was also found that carbohydrate transport was decreased at n-butanol concentrations that are toxic to producing Clostridium (Ref. 10), and that n-butanol caused direct fluidization of the lipids, based on electron-spin resonance-spin label measurements.

Linden, et al, (Ref. 2) found that the presence of carboxylic acids, such as elaidic acid, resulted in increased tolerance of the microorganism to n-butanol. However, it has not yet been unequivocally demonstrated that n-butanol concentrations can be increased during fermentation. Therefore, the concentrations assumed in the CSI analysis were considered to be speculative (i.e., it has not yet been demonstrated that solvent concentrations of 2.1 or 2.9 wt % at industrially acceptable yields and residence times are possible). However, these results [and earlier work (Refs. 13 and 14)] show that without adding fatty acid, higher concentrations and yields may be obtained than were assumed in the base-case; for example, 1.1 wt % n-butanol (1.9 wt % solvents), 99.3% sugar conversion, and 32.5% yield on total sugar in 39 hours was obtained in a control fermentation (Ref 2). Therefore, although it may not be possible to obtain a solvent concentration of 2.9 wt %, 2.1 wt % concentration appears to be feasible.

The results shown in Table 2-1 are for 2.1 wt % total solvents, 100% sugar conversion, 42 hours fermentation, and a total yield of 31.4%. When DOE utilities costs were assumed, the selling price (10% DCF) was decreased to $2.03/gal.

A similar analysis, where the concentration was assumed to be 1.7 wt n-butanol (2.9 wt % solvents), resulted in an estimated price of $1.95/g (CSI utilities costs) and a decrease in energy consumption relative to t base-case of ~ 33% to 10.67 MBtu/lb of products.

Assessments were also made for two cumulative cases. In the first, continuous fermentation, Lignol, and dual enzyme hydrolysis were simultaneously incorporated into the process. The selling price was decreased by 5.8% and energy consumption by 35% relative to the base-case. In the second, these options were included with addition of the n-butanol toxicity limit of 2.9 wt % solvents to give a price decrease of 29% (to $1.84/gal) and a 68% decrease in energy (compared to the base-case). This also represents a 16.7% price advantage over the conventional synthetic method.

In the CSI analyses, propylene (conventional route) and Lignol products were included in calculating energy consumption, whereas energy in aspen feedstock was not. Because of this, for example, energy consumption as utilities was decreased by about 31% compared to the total of 68% for the best case where Lignol products were included as an energy credit. Actual process energy is not decreased when the Lignol process is included; it is increased by about 8%. The high increase in energy consumption for the conventional petroleum-based process compared with the base-case is partly because of the debited feedstock energy. An alternative suggested here is to compare only total process energies, including the process energy required to produce the feedstocks, e.g., synthesis gas and propylene. On this basis, the petrochemical process would require about 12 MBtu/lb (75% of the base-case) to make butanol : acetone at a product wt ratio of 2:1. CSI has also performed assessments of eucalyptus and corn stover as alternative feedstocks for ABE production. For eucalyptus, energy was slightly higher and the price was $2.82/gal because of the lower sugar availability of eucalyptus in comparison with aspen. Corn stover appears more promising, with an estimated price of $2.35/gal because of its lower moisture content (~ 30% for field dried versus ~ 50% for green wood) and its higher sugar content. However, because it contains free sucrose sugar, storage would be expected to be a problem that may increase costs.

B. DISCUSSION OF ASSESSMENT LIMITATIONS

In analyses of this type, the absolute values of costs and energy are subject to relatively large errors or anomalies. It is believed that energy values given are within 20% of actual values; however, actual realized costs may be subject to greater differences, especially if such factors as negligible plant depreciation for an existing plant compared to high depreciation for a new plant are considered. But the relative costs and energy requirements are likely to be reliable to about ± 20% of the <u>differences</u> between the base-case and the cases where advances are included.

These analyses are still very useful for comparisons of potential research advancements and their impacts, but are only relevant to comparisons with the petroleum-based process under special circumstances. These include (1) long-term (>10 year) projections (where all projections become relatively obscure and the availability of petroleum is not known) or (2) when cost or process energy advantages are large and are comparable to those for energy-efficient ethanol biocatalyzed processes, which are currently competitive with the conventional process.

Two cases are very significant as overall conceptual process designs: (1) 2.9 wt % solvent concentration tolerance and (2) the combined options best case, including continuous fermentation, Lignol, dual enzyme, and 2.9 wt % solvents in one bioprocess. Because biocatalyzed processes are relatively independent of petroleum resources, there is an inherent significant long-term energy advantage; however, at the present time the absence of information on future availability of uniform feedstocks is a disadvantage.

With regard to costs, for 2.9 wt % solvents concentration the estimated price is $1.95/gal and for the best case it is $1.84/gal. Nearly all of this difference of $0.11 is because of the incorporation of the dual enzyme system. Because these are about 12 and 17% lower, respectively, than the cost by the conventional process, they should be competitive; however, as indicated above, absolute errors may be relatively large. A reasonable perspective is that progress in the energy-economic analysis is comparable to progress in conceptual process development, and energy efficiency can be significantly improved provided appropriate technological advances can be realized.

C. ANALYSIS OF AN ALTERNATIVE PROCESS: CITRIC ACID

To demonstrate the generality of the methodology developed for analyzing the ABE system, an alternative biocatalyzed process for production of citric acid and furfural (by-product) from aspen was analyzed and compared to the conventional fermentation process for citric acid (Ref. 2). The analysis showed that the price for citric acid would be $0.74/lb compared with 0.675/lb for citric acid by the conventional process. The conventional method is also a fermentation process in this case, with molasses as the feedstock. The price for furfural by-product in this comparison was assumed to be $0.20/lb. The current list prices of citric acid and furfural are about $1.00 and $0.66/lb. If it is assumed that the production price for furfural should be about 66% of the price for citric acid, the furfural by-product price would be higher than $0.20/lb. At a production price for citric acid of $0.67/lb, the selling price for furfural would then be $0.44/lb. Because the CSI analysis also shows that the production prices for citric acid by either the wood or molasses-based processes are equal at a furfural price of $0.475/lb, it can be concluded that production costs by either process are nearly equal. However, these price levels are too high to suggest that large future markets for either product are likely. But if this (and other) lignocellulose-based biocatalyzed processes can be improved through new research advances to the extent that they are competitive at a by-product furfural production price near $0.20/lb, new markets may be expected for furfural. Furfural can be used as an intermediate to produce other chemicals such as tetrahydrofuran, adipic acid, hexamethylenediamine and 1,4-butanediol.

SECTION III

FUTURE IMPACTS OF BIOCATALYSIS RESEARCH

A. POTENTIAL INCREASES IN EFFICIENCY FOR ABE PROCESSES

Although the CSI assessments indicate that production of solvents by biocatalyzed ABE processes could result in decreases in energy requirements and costs of about 30% (not including the energy credit for Lignol products), it can be shown that the lower limits for energy and costs have not yet been estimated. For example, if corn stover was used as the feedstock, there would be further decreases in energy and costs. To a first approximation, additional cost decreases of 30% based on potential research advances discussed above could result in a price of \$1.60 to \$1.65/gal because the production price using corn stover is \$2.35/gal or \$2.30/gal (CSI or DOE utilities costs, respectively). (This estimate reflects a 30% reduction from \$2.30 to \$2.36/gal rather than from \$2.60 and, therefore, may be conservative.) Furthermore, other options that may result in higher energy efficiency have not yet been assessed.

The most promising of these options appears to be energy-efficient separation of solvents during fermentation as a basis for a continuous process where the biocatalyzed reaction would not be inhibited by n-butanol. The reaction rate would be increased, leading to lower capital costs and greatly decreased energy consumption.

To determine the potential lower limit of energy required, relationships between process energy needed and product concentration have been established, as shown in Figure 3-1. Curve B was derived from process energy required (Ref. 1) for the original base-cases [points (●) at 1 and 1.5 wt % solvents]. Because these analyses assumed little heat recovery, B represents the relation between product concentration and energy required for relatively inefficient distillation processes. Curve A was calculated in the same way, based on energy required for purification of ethanol (points ◒) where high heat recovery was assumed (Ref. 15), and therefore represents energy-efficient purification.

Curves A and B are not simple extrapolations of the base data. The difference in energy for the two concentrations (e.g.,●) was obtained by subtraction and confirmed by detailed energy balance calculations to correspond to the difference in steam required for heating the aqueous product solutions to the distillation temperatures at the two concentrations. These values were then adjusted to reflect the amounts of water to be heated at each concentration to calculate a series of points that define the curves. The curves level off at higher concentrations because of the rapid decrease in the water-product ratio, e.g., 99 at 1 wt % and 19 at 5 wt %, etc.

It can be seen that the results are in good agreement with other data in the literature for efficient (Refs. 16 and 17) processes and one inefficient

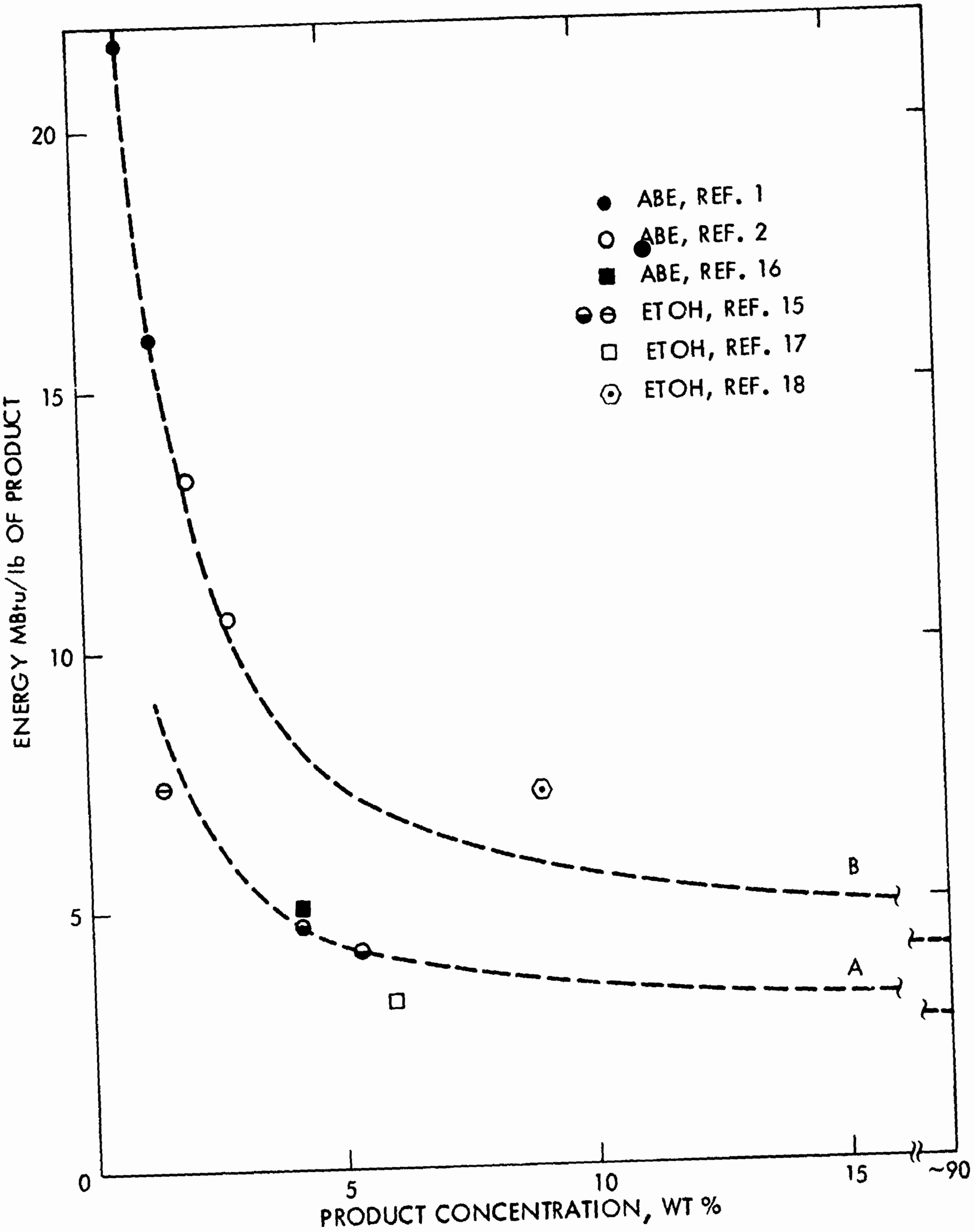

Figure 3-1. Concentration-Energy for Biocatalyzed Processes

(Ref. 18) process. It is even more significant that the points (O) (Ref. 2) that were calculated after the relationship was defined are within less than 3% of the predicted values. Therefore, for estimates of energy consumption at higher concentrations, errors should be well within the ranges normally accepted for most energy analyses and should be within 1 MBtu/lb of product. However, these relationships depend on the initial assumptions and may be shifted to lower energy values for more efficient processes where the total separation energy can be less than energy required for heating the product stream and volatilizing components calculated from heat contents (e.g., for processes such as membrane separation, vapor compression, or multiple-effect distillation with heat recovery).

G.D. Mehta (Ref. 17) has shown that purification of ethanol by a combined distillation-membrane process could provide a lower cost and about the same energy as efficient distillation alone. The energy problem with available membrane systems is that although they are highly efficient for separating water from solute to obtain pure water, as in desalination, high energy efficiency for most purification processes requires selective transport of the solute through the membrane. For example, if a solution of 2 wt % is purified, transport of 80 lb of water through the membrane is required to obtain a 10 wt % solution on the high pressure side (18 lb water, 2 lb product). But a solute-selective membrane would require passage of only 2 lb of solute and 18 lb water. The situation is somewhat analogous to purification by single-effect distillation of water to remove it from a non-volatile product as compared to product distillation (of volatile substances) from water, where vaporization energy is much less. Therefore, a viable membrane system should be designed for selective permeation of the products. Pervaporation membranes are being investigated, but because of the need to volatilize products across a pressure gradient, this type of system can be viewed as a form of distillation where product selectivity may be increased by the membrane.

However, it may not be necessary to increase selectivity because a condensate can be obtained that is enriched from about 1 wt % n-butanol to >7 wt % by flash distillation (Ref. 19) near the fermentation temperature, i.e., by vacuum fermentation. Furthermore, if n-butanol concentration tolerance can be increased to ~1.8 wt % or 3 wt % of total solvents, the enrichment would be even greater, to ~20 wt %. Although measurements and further calculations are being made to obtain more definitive results, inspection of Figure 3-1 shows that under these conditions the energy required would be no more than about 4.8 MBtu/lb of product. If 2.0 MBtu/lb is allowed for vapor compression (which is believed to be substantially more than would be needed), the total is 6.8 MBtu/lb of product. With this research advance, total energy consumption could be reduced by about 57%.

Vacuum fermentation is only one alternative because the vapor is enriched relative to the liquid phase at all pressures up to and including atmospheric pressure. In fact, enrichment is slightly greater at higher pressures (Ref. 20). Therefore, other potentially energy-efficient methods of vapor removal and condensation are likely to include absorption in a liquid or adsorption on a solid and, possibly, vapor compression at a somewhat higher pressure. Another possible approach is conversion of butanol vapor to another product, such as the corresponding acid, aldehyde, or alkenes. But preliminary evaluations indicate that the acid could be produced more efficiently by an alternative biocatalyzed process. Because the aldehyde and butylenes also would be converted to other products, it appears that total process energy would be relatively high.

Preliminary experiments at JPL have shown that vapor condensation from a liquid at 33°C (1 wt %) of n-butanol results in two phases, a butanol and a water-rich phase, confirming that substantial enrichment is obtained. Furthermore, an adsorption experiment (on carbon) showed that even greater enrichment was obtained, and water adsorption would be expected to be much less if the initial solvents concentration was increased to reflect a potential concentration tolerance of 3 wt % solvents. The adsorbent selected for preliminary evaluation was activated carbon, RC 1200-1, 4-12 mesh, supplied by VWR Scientific, San Francisco, California. To simulate a bioreactor, a synthetic mixture (125 ml) containing 0.78 wt % n-butanol and 0.22 wt % acetone was placed in a 100 by 180 mm cylindrical pyrex dish. A smaller petri dish ([illegible]) by 140 mm) containing 20 g of RC 1200-1 carbon was placed on aluminum supports about 3 cm above the bottom and inside the solution container. Therefore, the simulation consisted of a stirred, dilute aqueous product solution with a fixed carbon bed supported above and within the "reactor," so the carbon was accessible only to the vapor phase. The aqueous mixture was magnetically stirred for 16 hours at room temperature after sealing the top with aluminum foil. It was left without stirring for an additional 24 hours, when a sample of the solution was withdrawn for analysis, along with a control containing the inital concentration of n-butanol and acetone. Typical gas chromatograms are shown in Figure 3-2, and the quantitative results are tabulated in Table 3-1. Because the retention times for acetone and n-butanol agreed with numerous other chromatographic determinations made before and after these experiments were completed, peaks corresponding to the two components have been positively identified.

The n-butanol concentration had been decreased from 0.78 to 0.105 wt % and the acetone from 0.22 to 0.062 wt %. Under these conditions 86% (0.83 g) of the alcohol and 72% (0.19 g) of the acetone were adsorbed in 40 hours. At the same time, about 5.5 ml of water was adsorbed (measured from the total increase in weight of the carbon minus the weight of acetone-butanol).

Although most of the heat evolved during adsorption probably could be recovered, possible energy-efficient methods for separation of the product from carbon have not yet been investigated. One possibility is solvent extraction, e.g., with volatile hydrocarbons, because solvent extraction is used effectively for analytical methods applied to atmospheric pollutants adsorbed on carbon. However, additional work is required to determine the most energy-efficient system for solvent adsorption and recovery, including determination of the amount and type of adsorbent required, kinetics of adsorption and desorption, applicable extraction solvents, and further downstream purification requirements. It is already known that activated carbon will selectively remove organic products from vapor streams containing water and carbon dioxide (Ref. 21), which suggests that a carbon column system should be more effective than the carbon bed used in the preliminary experiment. Previous industrial experience has shown that no more than one pound of carbon is needed to purify

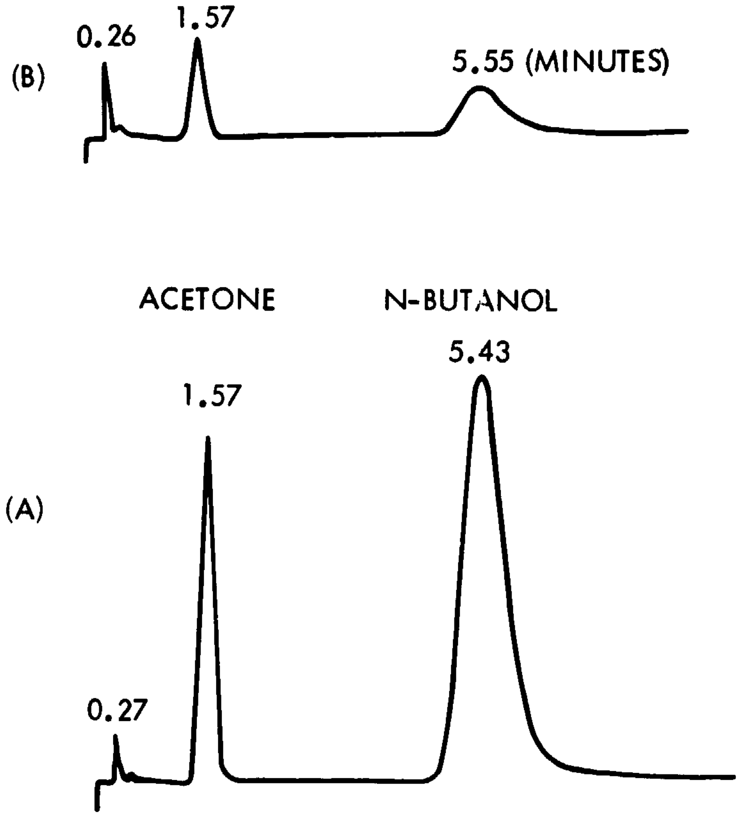

Figure 3-2. Gas Chromatography of Acetone-Butanol Solutions: (A) Before Solvent Removal; (B) After Solvent Adsorption on Activated Carbon

Table 3-1. Gas Chromatography of Acetone-Butanol Solutions Before and After Solvent Adsorption on Activated Carbon[a]

Before Adsorption of Solvents[b]		After Adsorption on Carbon		
Solvent	Peak Area, Arbitrary Units	Peak Area, Arbitrary Units	Solvent in Water, %[c]	Solvent Adsorbed on Carbon, %[c]
Acetone	3,454	982	28.4	71.6
	3,492	975	27.9	72.1
Butanol	12,975	1,794	13.8	86.2
	14,277	1,887	13.2	86.8
Total	16,429	2,776	16.9	83.1
	17,769	2,862	16.1	83.9

[a] Conditions:

(1) Column - Poropak Q
(2) Detector - Flame Ionization
(3) Detector Temperature: 175°C
(4) Column Temperature: 165°C
(5) Injector Temperature: 125°C

[b] Peak areas correspond to 100% of the initial concentrations for each solvent in water; initial concentrations in water were acetone (0.22 wt %), butanol (0.78 wt %), for a total of 1.0 wt %.

[c] As % of the initial concentrations in water. Final concentrations were acetone (0.062 wt %), butanol (0.105 wt %), for a total of 0.167 wt %.

more than forty pounds of carbon dioxide produced during fermentation. Also, the carbon should be developed, if needed, on the basis of maximum capacity, efficiency, and selectivity because carbon characteristics such as volume of hydrophilic micropores (which will adsorb water) will have a pronounced effect on water adsorption relative to solvent adsorption (Ref. 22).

It appears that adsorption for separation of products may be less efficient than alternatives such as vacuum fermentation; therefore, no further work on adsorption processes is currently planned.

B. COST RELATIONSHIPS

Although energy conservation is a primary goal of the ECUT Project, it is secondary to costs in the current industrial environment because corporate decisions (e.g., for plant construction and marketing strategies) are nearly always made on the basis of profitability. Therefore, it is essential to relate energy efficiency to costs. Approximate decreases in costs have been estimated from previous results (Ref. 2) and are shown in Figure 3-3. Beyond 3.5 wt % product concentration, decreases were estimated from Figure 3-1 on the basis of energy consumption and costs. However, because related changes in capital costs are unknown, they are not included. Decreases are expressed as percentages and can be applied with reasonable accuracy to cost of production or to production prices at 10% DCF. The maximum cost decrease is about 36%, based on research advances equivalent to an effective product concentration of ~ 7 wt %, which appears technically feasible on the basis of a total energy consumption of 6.8 MBtu/lb, as estimated previously.

Use of a feedstock such as corn stover results in a production price of $0.22/lb of solvents (compared to $0.25/lb when aspen is used). This price ($0.22/lb) would be well within the costs required for increased production by biocatalyzed processes. This value is believed to be conservatively optimistic, primarily because capital costs would be less for lower reactor volumes associated with continuous processing at up to 30% sugar concentration, and these decreases have not yet been included.

If the production cost is assumed to be subject to errors of ±25%, the range would be $0.17 to $0.28/lb, and the maximum is still about 15% less than the production cost of solvents by conventional processes from propylene However, relatively uniform feedstock availability at reasonable cost appears to be a serious potential problem that must be solved before many large-scale biocatalyzed processes can be implemented.

C. POTENTIAL BIOCATALYZED PRODUCTION OF N-BUTANOL

At the present time, the average production rate of each of the fifteen top organic chemicals produced in the U.S. is about 10 billion lb/yr, and the rate for n-butanol is approximately 700 million lb/yr. Therefore, n-butanol would have to be used as an intermediate or feedstock for additional chemicals to rank among the very high-volume commodity chemicals.

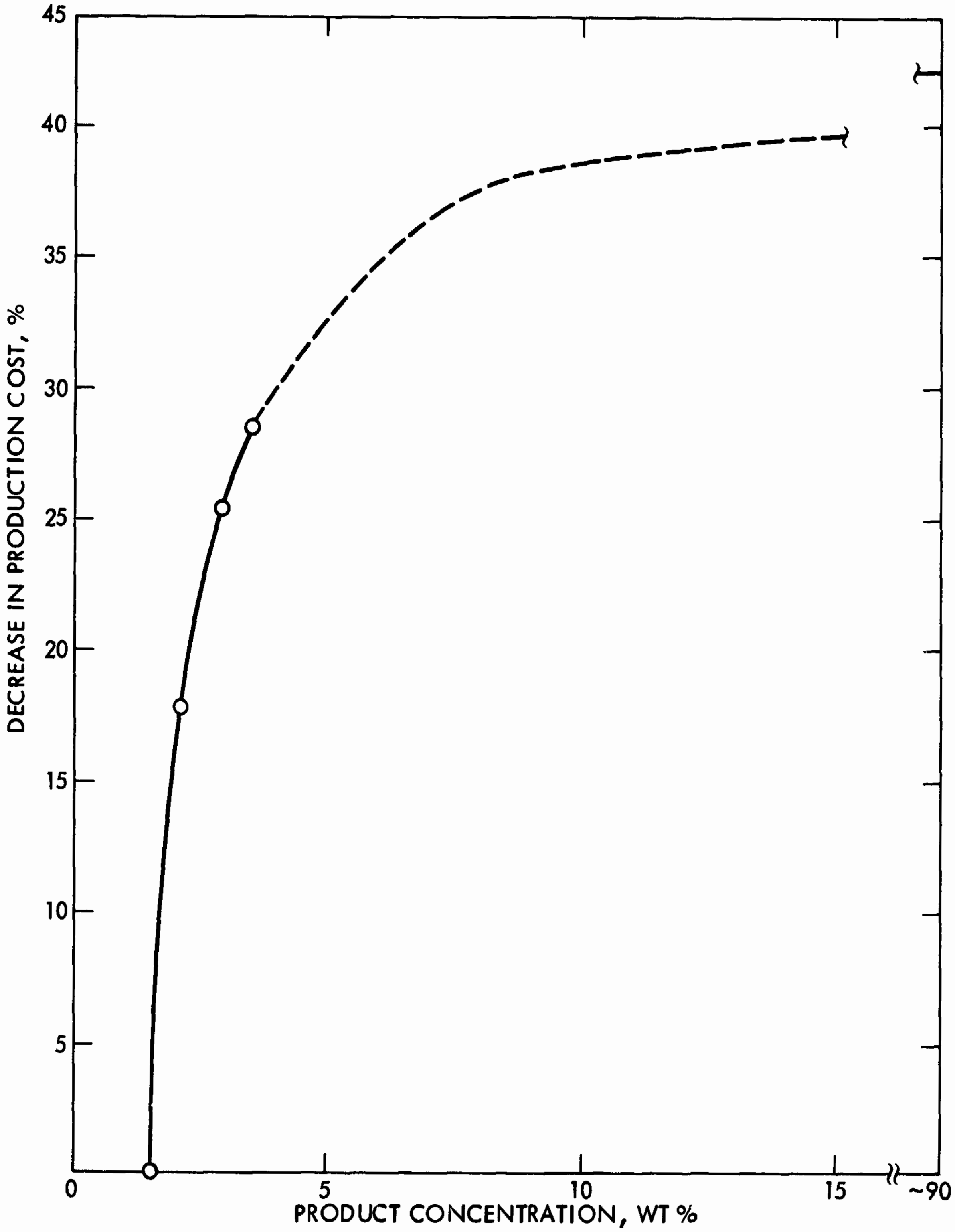

Figure 3-3. Concentration-Production Cost Decrease for ABE Biocatalyzed Processes

An economic model has been developed by D.F. Rudd, et al, (Ref. 23) which has been used to estimate increases in production and utilization of proposed fermentation products if their prices are decreased relative to prices for production by petrochemical processes (Ref. 24). The fermentation products ethanol, isopropanol, n-butanol and 2,3-butanediol were suggested as a possible basis for a major fraction of the U.S. chemical industry to provide a smooth transition toward the advantageous utilization of renewable feedstocks. However, the model indicated that to make these bioprocessed products attractive as feedstocks or intermediates in the production of other chemicals (e.g., to make styrene, where current production is about 7.5 billion lb/yr) would require a significant decrease in the price ratio, f, for 2,3-butanediol, where f is the price of the fermentation product divided by the projected price of the same product produced from petroleum in 1985.

It was estimated that n-butanol would not be produced for use as a feedstock at $f > 0.17$, but isopropanol would be used at $f = 0.6$. To increase utilization to a large scale, it was estimated that f values of 0.2 to 0.4 would be required for most fermentation products. However, this model includes the assumption that current technology would be utilized for feedstock processing. Therefore, if new conversion processes are developed, somewhat higher f values may result in higher utilization of fermentation products as chemical feedstocks than is predicted by the model.

It can be concluded that significant decreases in production costs by biocatalyzed processes are required for significant utilization of the products as feedstocks, and, therefore, further advances in biotechnology and downstream chemical processing are required to maximize the advantages of future utilization of renewable resources.

Although it appears technically feasible to increase energy efficiency (and decrease costs) to the extent that biocatalyzed processes will be used within the next few decades to produce ABE solvents in place of conventional petrochemical processes, large improvements probably would be required to allow utilization of n-butanol as a chemical feedstock--but the required improvements would be less for use of fermentation isopropanol. Because the latter can be produced by bioprocesses that are similar to those for n-butanol (and result in the simultaneous production of n-butanol), most process advances will apply to both n-butanol and isopropanol.

D. DISCUSSION OF PREDICTIVE CAPABILITY

In the application of the model discussed above, a computer program is used to select the technologies that satisfy economic demands for specific products on the basis of about 300 current petrochemical processes. The program also includes consideration of annual production of each chemical needed for a balanced chemical industry, where each product will have a place as a feedstock or commodity. Prices are projected on the basis of 1977 production costs using assumed increases in cost elements for future years.

The model calculations depend on expected, orderly economic conditions and existing technology. As a consequence, changes in availability of specific resources, environmental constraints, and technological advances in chemical or biocatalyzed process technology will affect the predictions.

For example, if there was a significant decrease in the availability of propylene, n-butenes or butane from petroleum, biocatalyzed production of isopropanol, 2,3-butanediol, and n-butanol as feedstocks should become more competitive to make such products as acetone, butadiene,and maleic anhydride. Consideration of these specific products also shows that petrochemical processes are not necessarily energy-efficient. Total petrochemical processing energies for acetone, butadiene, and maleic anhydride are about 17, 33, and 11 MBtu/lb, respectively, including process energy to produce the required feedstocks.

Although it is clear that the model is an extremely useful analytical tool that has been widely accepted and utilized by the petrochemical industry for process assessments, its predictive capabilities are limited by necessary assumptions that may not be consistent with actual future events. Because there are so many uncertainties involved, the total future production of bioprocess products cannot be predicted, but could be many billions of pounds per year depending on many factors, including future research advances and subsequent applications to biochemical engineering of biocatalyzed processes.

SECTION IV

CONCLUSIONS

Economic-energy assessments of the effects of research advances on the biocatalyzed ABE process have been completed (Refs. 1 and 2) to assist in providing a potential technology base required for implementation of competitive biocatalyzed processes. These assessments have shown that substantial decreases in energy consumption and costs are possible on the basis of specific research advances. Therefore, it appears that a biocatalyzed process for ABE can be developed that will be competitive with conventional petrochemical processes for production of n-butanol and acetone.

The research advances with the greatest impact are increased microorganism tolerance to n-butanol and the improved prehydrolysis-dual enzyme system. However, none of the proposed research advances are necessarily totally eliminated without further analyses because relatively small modifications in the assumed advance may have large effects on energy and costs.

The results suggest that feedstock uniformity, cost, and availability will be major factors in determining the viability of very large-scale biocatalyzed processes.

Potential lower limits for energy and costs for a more advanced conceptual ABE bioprocess have been estimated in this report, and the relationship between energy and product concentration and between costs and product concentration have been defined. This conceptual process is based on a microorganism concentration tolerance of 1.8 wt % and removal of products from the vapor phase at a concentration of ~20 wt %, which corresponds to the vapor concentration for first-stage evaporation of the n-butanol-water azeotrope at a liquid concentration of 1.8%. It has been estimated that energy can be decreased by more than 50%, with a product selling price of ABE solvents of \$0.17 to \$0.28/lb by separation of n-butanol from the vapor phase and increased tolerance of the microorganism to n-butanol; the price of ABE solvents by the conventional petrochemical process is \$0.33/lb.

Although various acceptable approaches and assumptions have been used in energy comparisons, for future assessments of energy benefits of new process advancements, it is suggested that total process energy (with the advance) should be compared with total process energy for base-case or operational petrochemical processes. For each process, utilities energy required to produce the feedstocks would be included in the total.

Preliminary evaluations utilizing a model for estimating the expected annual production of products on the basis of costs suggests that n-butanol may not be produced by biocatalyzed processes at costs that indicate it would be used as a feedstock for other chemicals. The total annual future production of commodity chemicals and intermediates by biocatalyzed processes will depend on research advances required to increase energy efficiency and decrease costs in comparison with petrochemical processes. However, it does not appear feasible to project annual production rates on the basis of existing information. Information required includes estimates of future petroleum costs and availability, projections of new developments in feedstock production and conversion, and future market and cost factors.

SECTION V

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