©Copyright 1992 by The Humana Press Inc.
All rights of any nature whatsoever reserved.
0273-2289/92/3435—0515$02.40

Conversion of Bioprocess Ethanol to Industrial Chemical Products

Applications of Process Models for Energy-Economic Assessments

NARESH K. ROHATGI AND JOHN D. INGHAM*

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA

ABSTRACT

Ethanol is commercially produced by bioconversion and by hydration of ethylene. Bioconversion has the significant advantage that utilization of nonrenewable petroleum resources is minimized. Advanced bioprocesses for aqueous ethanol can also be integrated with downstream systems for energy-efficient conversion to added-value chemicals, such as esters or other ethylene or ethanol derivatives. Since the energy-intensive step involving azeotrope dehydration is eliminated, net process energy requirements can be less than for production of anhydrous ethanol. Energy-economic assessments of a potential esterification process are described, where ethanol vapor in the presence of water from a bioreactor is catalytically converted to ethyl acetate. A commercial ASPEN process simulation program was used, and results were compared with an assessment based on a JPL computer model. Detailed evaluations of the sensitivity of cost of production to factors, such as material costs and annual production rates, were also completed.

Index Entries: ASPEN; process integration; computer-aided design; ethyl acetate.

*Author to whom all correspondence and reprint requests should be addressed.

INTRODUCTION

At the present time, the most important bioprocess for large-scale production of commodity chemicals is fermentation to ethanol. In general, the economics of most bioprocesses for chemicals will not be favorable relative to petrochemical processes until petroleum resources are less readily available, more costly, or the bioprocess technologies are more economically competitive with conventional chemical processes. However, the use of renewable biomass as a primary feedstock has significant advantages with respect to decreased dependence on petroleum imports, higher energy conservation, and minimization of adverse environmental effects. An important future energy advantage is the increase in potential utilization of renewable resources for production of chemicals other than ethanol if bioprocess ethanol is used as the raw material for various integrated processes. In addition to ethanol, several other industrial chemicals can be made biochemically, including *n*-butanol, acetic, and lactic acids, and 2,3-butanediol, but the rates of production are relatively low (which may lead to large reactors and prohibitively high capital investment costs). Isolation of these products is generally energy and capital intensive, because most are less volatile than water, which has to be separated, usually in relatively large amounts.

Many of the most important petrochemicals made from ethylene could be produced from ethanol, either directly or after dehydration to ethylene. The cost to convert 1 kg-mol of ethanol to 1 kg-mol of ethylene has been estimated to result in a required selling price for ethylene that is 1.35 times the price of ethanol. On a mass basis, the factor is 2.22 because the mol wt of ethanol (46.07) is higher than ethylene (28.03) and the maximum possible yield is only .608 kg ethylene/kg ethanol. (The dehydration cost estimate is based on a process proposed by Tsao and Reilly [*1*] in 1978). The cost of ethanol currently exceeds that for ethylene, and the cost of production of ethanol would have to be lower than ethylene before it would be an acceptable ethylene substitute. The purpose of the assessments described here is to demonstrate the use of new methods for process synthesis and evaluation, primarily as a means of determining where research should be directed to provide more general and more competitive biochemical-chemical processes for large-scale production of industrial chemicals. Currently, there are relatively few good assessment methods available to evaluate bioprocesses accurately. This report provides an initial approach to meet the need for reliable preliminary assessments.

METHODS

Computer Models

Software used for process assessments was ASPEN PLUS (ASPEN Technology, Inc., Cambridge, MA). It requires a 386 computer with 16

megabytes of expanded memory. Information provided by the ASPEN simulations is extremely detailed. Each report shows complete mass and energy balances, conditions, stream compositions, flow rates, and economic predictions. Because of numerous loops and iterations, each simulation run time is 30–60 min using a 386 microcomputer running at 33 mHz and equipped with a math coprocessor. A computer model under development at JPL was also used to estimate fermentation costs and for comparison with ASPEN PLUS results. It consists of a series of process reaction types (e.g., hydrogenation, dehydration, esterification) for selection from menu lists, and the selected type is modified as appropriate for an assessment. For a specific reaction of each type, default values for numerous parameters, such as stoichiometric factors, rates, concentrations, materials costs, and economic values, are displayed and can be changed during the run, or in the program, to create a new assessment. Mass and energy balances are provided, and costs are computed on the basis of a factored estimate. A large number of known processes will be included and verified to ensure that cost estimate protocols are reliable. Additional assessments (where numerous process variations can be incorporated) may be completed within a few minutes. Since only the subprograms for each specific assessment are put into the computer memory as needed (and are automatically deleted before each subsequent run), there is no need for expanded memory or other special computer capabilities. The current version consists of a series of interactive menu-driven subprograms that run consecutively. The completed program will include a user-accessible library of equipment lists that are automatically scaled according to process flow rates, with appropriate cost factors for materials, year of construction, and specific process requirements. Procedures will be provided to incorporate alternative feedstock and conversion options, and to link and integrate a series of conversion steps that can be selected from the library. The purpose of the model is to provide rapid, reliable assessments of process concepts rather than specific equipment or detailed design capabilities.

Assessment Approach

Estimates of a range of prices for ethanol (plus water) made by the vacuferm process (2,3) were calculated using the JPL program, followed by detailed sensitivity assessments with ASPEN. Table 1 shows some of the elements of the basis for process assessments. The differences between some factors (e.g., mid-year of construction period, depreciation rate, and labor rate) are the result of independent program assumptions. The discount rate is not used in the current version of the JPL model, where the rate of return entered was 25% of the total capital investment before taxes. An improved method for profitability evaluation will be defined. The ASPEN program provides calculations for discounted cash flow, annual present value, and net present worth for the service life and dis-

Table 1
Cost Element Basis: ASPEN and JPL Process Models

Element or cost factor	ASPEN simulator	JPL model
Total production, 10^6kg/y[a]	27	27
Production capacity, %	100	100
Operating d/yr	328	333
Year of construc (mid)	1988	1986
Year of operation	1990	1990
Discount rate, %	15	Not used
Return on investment, %	15	25
Depreciation, %/yr	6.67	10
Construction labor, $/h	29	Not used
Operating labor, $/h	25	22.25
Fuel cost, $/$10^6$ kJ	4.22	4.74[b]
Water, 10^{-4} $/kg	2.65	–[b]
Acetic acid, $/kg[a]	.64	.64
Glucose (from cornstarch), $/kg[a]	.15	.15

[a]Base case.
[b]Average, as steam equivalent for all process energy (includes a nominal allowance for water cost).

count rate selected. The assumed plant life was 30 yr, and the return was 15% of total capital investment after taxes.

RESULTS AND DISCUSSION

Process Description

The process evaluated is shown in Fig. 1, which shows the streams used in the simulation, as AM, S10, S01, and so forth, for ethyl acetate, and includes some of the heat exchanger paths proposed for heat transfer and recovery. In the integrated ethyl acetate process (Fig. 1), ethanol is produced as a 6 wt% solution, from which ethanol-water vapor at an equilibrium ethanol concentration of approx 42 wt% is removed with a vacuum pump. It is assumed that a concentraton of 6 wt% is appropriate for a vacuferm process. For most continuous ethanol processes, the concentration is lower than for operational batch or semicontinuous processes, to minimize rate inhibition by the product formed. The mass balance calculated by the JPL program is shown in Table 2. This product stream (ethanol-water) is fractionated to produce 87 wt% ethanol vapor, which is then mixed with acetic acid and passed through a catalytic reactor to convert it to ethyl acetate, which is recovered by distillation. The mass balance for esterification (from the ASPEN simulation) is shown in Table 3. Esterification rates and equilibrium relationships were estimated from results by Hoerig et al. (*4*). Earlier calculations indicated that less energy is needed if

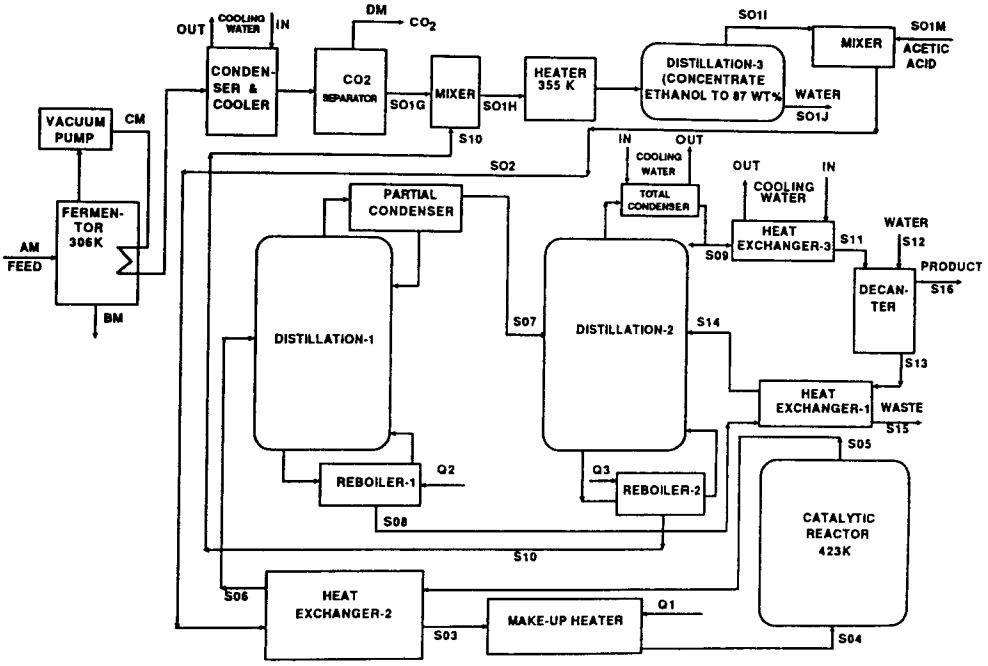

Fig. 1. ASPEN-simulated process flowsheet for conversion of bioprocess ethanol to ethyl acetate.

Table 2
Mass Balance for Ethanol-Water for Production of 55×10^6 kg/yr of Ethyl Acetate[a]

Component	AM	BM	CM	DM	EM
Glucose	3723	64			
Ethanol		153	1609		1609
Carbon dioxide			1813	1813	
Water	4302	2100	2202		2202
Miscellaneous	148	101			
Cells		131			
Total	8173	2549	5624	1813	3811

[a]Process stream flow rates, kg/h.

Process streams: AM = feed; BM = fermenter bleed; CM = vapor from fermentor; DM = carbon dioxide; EM = ethanol-water (intermediate for ethyl acetate production. EM = S01G, Table 2). Mass balance: Total in = AM = 8173; total out = BM + DM + EM = 8173.

the alcohol is purified to 87 wt%, but not all of the process characteristics have been optimized. For example, an alternative ethanol process could result in lower energy consumption or costs. Excess acetic acid in stream S15 could be recovered, which would decrease materials costs by as much as $.035/kg of ethyl acetate. A second possible alternative would be to adjust the amount of acetic acid in the feed and shift the reaction equilibrium in the product recovery column (by removing ester as it is formed)

Table 3
Mass Balance for Production of 55×10^6 kg/yr of Ethyl Acetate[a]

Component	EM, SO1G	SO1H	SO1I	SO1J	SO2, SO3, SO4	SO5, SO6	SO7
Process stream flow rates, kg/h:							
Ethanol	1609	3387	3384	3	3384	1842	1842
Acetic acid		26		26	2207	199	26
Ethyl acetate		4	4		4	2951	2951
Water	2202	4283	487	3797	487	1090	508
Total	3811	7700	3875	3826	6082	6082	5327

Component	SO8, S15	S10	SO9, S11	S12	S13, S14	S16
Ethanol		1778	1619		1555	64
Acetic acid	173	26				
Ethyl acetate		4	3909		962	2947
Water	581	2081	297	1730	1870	157
Total	754	3889	5825	1730	4387	3168

[a]Process energy consumption: 4480 kJ/kg ethyl acetate and 8820 kJ/kg of ethanol converted (including energy for fermentation). An ASPEN simulation for a process to produce 93 wt% (95 vol%) ethanol from 6 wt% ethanol in the fermentor indicated that 9336 kJ/kg ethanol would be consumed.

to increase the ester yield. A third alternative is to increase the ethanol–acetic acid ratio. The excess ethanol could be recycled (and recovered) more easily than acetic acid.

Process Energy Consumption

Process energy consumption is 4480 kJ/kg (1928 BTU/lb) of ethyl acetate (Table 3) or 8820 kJ/kg of ethanol converted to ester, which can be compared to 9336 kJ/kg estimated for production of 95 vol% ethanol by a separate ASPEN simulation. There are energy and cost differences for anhydrous ethyl acetate relative to anhydrous ethanol; the current added cost for anhydrous products is \$.066/kg of ester and \$.265/kg of ethanol. The added increment is comparatively high for alcohol, because it is more energy and capital intensive to remove water from ethanol than from ethyl acetate.

Process Economics

Economic assessment results are shown for a 27.8 10^6 kg/yr plant in Fig. 2, where the ASPEN and JPL model programs were used. The capital investments (1–3) are shown as ratios of costs to annual production. All costs that contribute to the selling price are shown as 4 to 10, and it can be

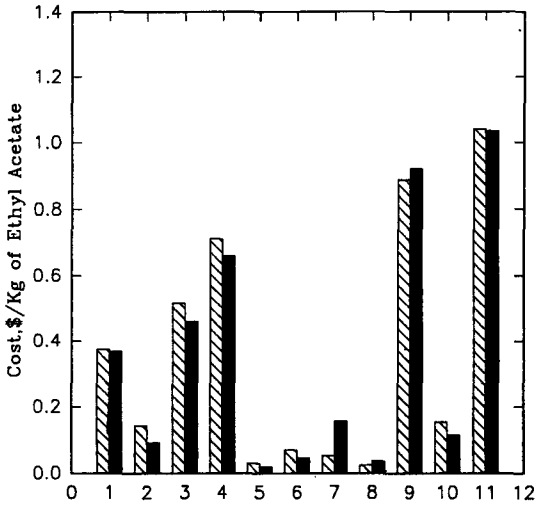

Fig. 2. Distribution of costs for production of ethyl acetate: comparison of estimates by an ASPEN process simulator and a JPL computer program. Ethyl acetate production = 27.82×10^6 kg/yr. ▨ ASPEN, ■ JPL $. (1) Fixed capital investment, ($)(yr)/kg, (2) working and start-up capital, ($)(yr)/kg, (3) total capital investment, ($)(yr)/kg, (4) raw materials, (5) utilities, (6) labor, (7) general and operating expenses, (8) depreciation, (9) cost of production, (10) return on investment, (11) selling price.

seen that the cost of raw materials is >70% of the cost of production. This high cost distorts the turnover (100×[gross sales]/total investment, or 100×[selling price]/[total capital investment/total annual production], %). In this assessment, the turnover is about 210%, yet the average for the chemical industry is approx 122% (*5*). As correctly pointed out by one referee, high turnover is usually the result of capital cost estimates that are too low; however, when the calculation was repeated using the JPL program, with the only change consisting of a reduction in raw material costs to one-third of the original estimate, the turnover was 118% (100×[selling price], $.55/kg, divided by capital cost, $.465/kg). In the case of interest, it appears that high turnover is caused primarily by a high ratio of raw material costs to selling price, which suggests that useful alternatives to turnover can be derived by including modifications that normalize the effects of other unusual cost factors. The JPL program is based on established principles for process synthesis and evaluation (*6–9*), but is not as detailed as ASPEN and is in an early development stage. It gave higher general and operating expenses and lower capital costs, with the result that total costs and selling price are nearly the same for both assessments. The two programs were run completely independently, and then the results were compared. The JPL program is being developed as a user-friendly, interactive menu program for conceptual process synthesis and preliminary evaluations.

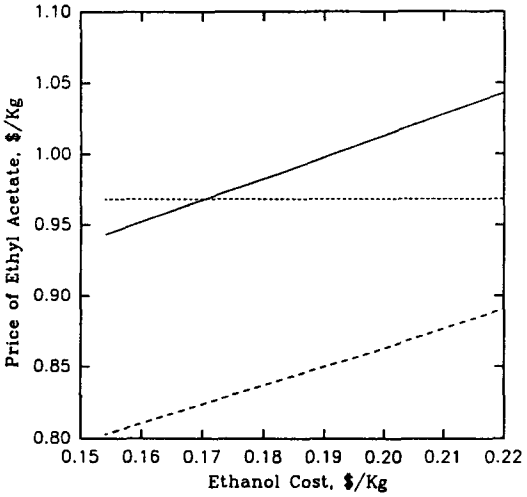

Fig. 3. Sensitivity of ethyl acetate cost of production and selling price to cost of 42.2 wt% ethanol-water. Ethyl acetate production = 55×10^6 kg/yr, acetate acid price = \$0.638/kg, —— projected selling price, ---- manufacturing price, ---- estimated market price.

Effect of Ethanol and Substrate Costs on Selling Price

When fermentation processes are considered for industrial chemicals production, it is invariably found that the cost of production is greatly affected by the feedstock cost, mainly because the oxygen content of carbohydrates is much higher than is found in most useful chemicals. As a result, carbon dioxide or water is produced, which results in low mass yields. For example, if lactic acid (which can be produced in high mass yield from sugar) is converted to another product, such as acetaldehyde or an ester, at least 1 mol of water and carbon dioxide is formed. It is difficult to assign a reasonable raw material price to sugar, partly because market prices are subject to such large fluctuations. In this work, it was estimated that at a sugar cost of \$.15/kg, the transfer price for 42.2 wt% ethanol vapor would be about \$.44/kg of ethanol, or \$.19/kg as ethanol-water. Then the price was varied in a series of ASPEN simulations to estimate the sensitivity of ethyl acetate selling price to ethanol and, indirectly, to sugar costs. The results are shown in Fig. 3. The selling price of ethyl acetate is proportional to ethanol cost, shown in the figure as \$/kg of 42.2% ethanol (which is divided by .422 to obtain the cost/kg of ethanol). For the base case, the price of acetic acid was \$.64/kg, which was an actual price when ethyl acetate was \$.90/kg, according to the Chemical Marketing Reporter, CMR, (*10*) during the second quarter of 1990.

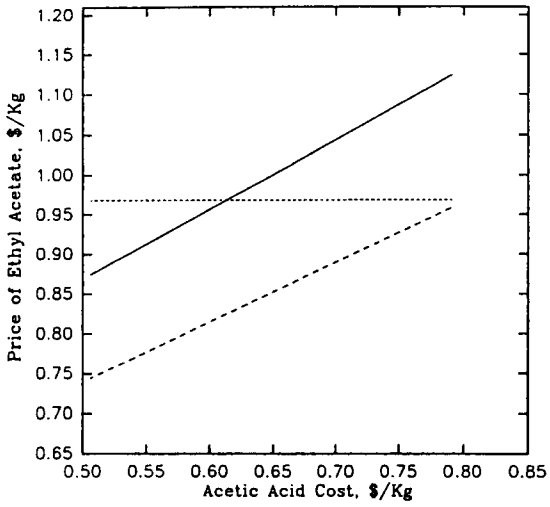

Fig. 4. Sensitivity of ethyl acetate cost of production and selling price to cost of acetic acid. Ethyl acetate production = 55×10^6 kg/yr, ethanol price = \$0.185/kg, —— projected selling price, ---- manufacturing price, ---- estimated market price.

Effect of Acetic Acid Cost

The actual price that would apply to acetic acid for the process is also not known, but sensitivity of the ester price is shown in Fig. 4. Eventually it may be competitive to make acetic acid by oxidation of bioprocess ethanol. In that case, chemical oxidation would probably be more economical than fermentation (of ethanol to acid) because of the difficulties inherent in the separation of water from acetic acid. If the actual costs for ethanol and acetic acid are as high as \$.48 and \$.79/kg (a first quarter, 1991 price for acetic acid [*10*]), the selling price for ethyl acetate would need to exceed its current price significantly, on the basis of results in Figs. 3 and 4. It would also be necessary to ensure that increased capacity would not be expected to saturate available markets.

Plant Capacity and Materials of Construction

The effects of specific plant capacity are shown in Fig. 5. The capital investment escalates rapidly for plants at < 27 million kg/y capacity. The comparison in Fig. 6 shows the effects on costs when stainless steel (304) for critical process equipment is substituted with carbon steel. The differences in cost of production and selling price are .028 and \$.035/kg, which are relatively small values compared to most other increments.

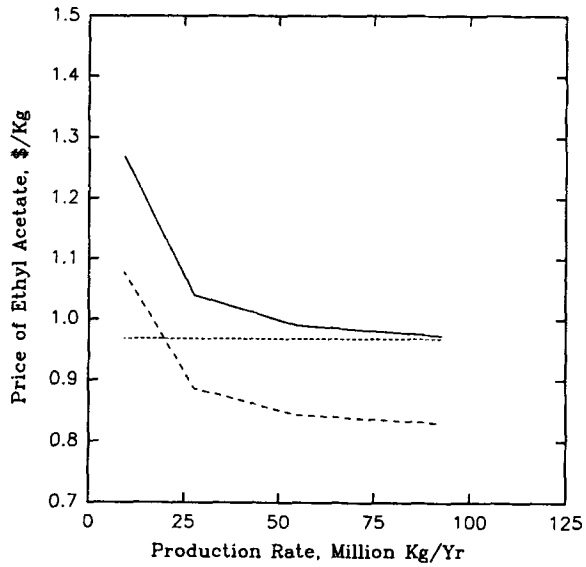

Fig. 5. Sensitivity of ethyl acetate selling price to plant capacity as annual production rate of ethyl acetate. Ethyl acetate production = 55×10^6 kg/yr, acetic acid price = \$0.638/kg, ethanol price = \$0.185/kg, —— projected selling price, ---- manufacturing price, ---- estimated market price.

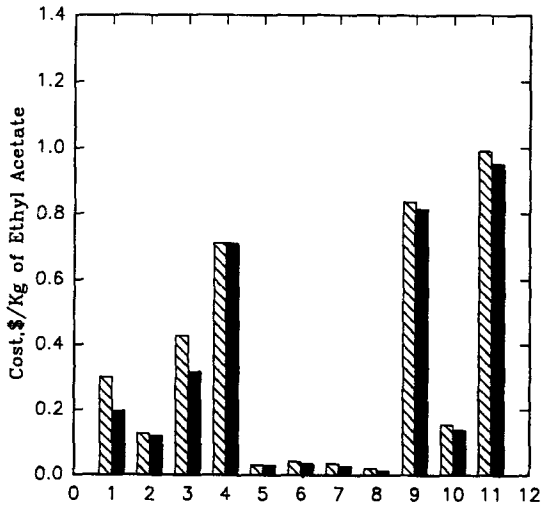

Fig. 6. Effect of process equipment materials (stainless steel, 304 and carbon steel) on capital and production costs, and selling price of ethyl acetate. Ethyl acetate production = 55×10^6 kg/yr. ▨ stainless steel, ■ carbon steel. (1) Fixed capital investment, (\$)(yr)/kg, (2) working and start-up capital, (\$)(yr)/kg, (3) total capital investment, (\$)(yr)/kg, (4) raw materials, (5) utilities, (6) labor, (7) general and operating expenses, (8) depreciation, (9) cost of production, (10) return on investment, (11) selling price.

SUMMARY

Bioprocesses can be employed to minimize the consumption of nonrenewable petroleum resources. Advanced bioprocesses for aqueous ethanol can be integrated with downstream systems for energy-efficient conversion to added-value chemicals, such as esters or other ethylene (or ethanol) derivatives. Since the energy-intensive step involving azeotrope dehydration is eliminated, net process energy requirements can be less than for production of anhydrous ethanol. Detailed energy-economic assessments of a potential esterification process, where ethanol vapor in the presence of water from a bioreactor is catalytically converted to ethyl acetate, have shown that such processes are likely to become more competitive as the cost of substrates decreases relative to petroleum costs. A commercial ASPEN process simulation provided a reasonably consistent comparison with energy economics calculated using JPL developed software. Evaluation of the sensitivity of cost of production to factors, such as material costs and annual production capacity, have shown that the largest effects on costs are caused by low mass yields and relatively high feedstock costs. Further research and development should be directed toward improvements in process yields and development of efficient processes for hydrolytic conversion of cellulosic materials to produce economically glucose for use as a substrate for industrial bioprocesses (*9,11*). At the present time, it would not be economically attractive to produce ethyl acetate by the described process. Similar processes may be appropriate for other ethyl esters where the added value is higher (e.g., ethyl butyrate, which was $3.30–3.75/kg when butyric acid was $1.05/kg in March 1991 [*10*]); however, supplies could easily exceed the demand for such relatively high-cost esters.

ACKNOWLEDGMENT

This article was prepared by the Jet Propulsion Laboratory, California Institute of Technology, for the US Department of Energy through an agreement with the National Aeronautics and Space Administration.

REFERENCES

1. Tsao, U. and Reilly, J. W. (1978), *Hydrocarb. Proc* **Feb,** 133.
2. Cysewski, G. R. and Wilke, C. R. (1977), *Biotechnol. & Bioeng.* **19,** 1125.
3. Maiorella, B. and Wilke, C. R. (1980), *Biotechnol & Bioeng.* **22,** 1749.
4. Hoerig, H. F., Hanson, D., and Kowalke, O. L. (1943), *Ind. Eng. & Chem.* **35,** 575.

5. *Facts and Figures for the Chemical Industry* (1990), *Chem. and Eng. News,* **June 18,** pp. 34–83.
6. Rudd, D. F., Fathi-Afshar, S., Trevino, A. A., and Stadherr, M. A. (1981), *Petrochemical Technology Assessment,* John Wiley, New York.
7. Peters, M. S. and Timmerhaus, K. D. (1980), *Plant Design and Economics for Chemical Engineers,* McGraw-Hill, New York.
8. Douglas, J. M. (1988), *Conceptual Design of Chemical Processes,* McGraw-Hill, New York.
9. Hacking, A. J. (1988), *Economic Aspects of Biotechnology,* Cambridge University Press, Cambridge, UK.
10. *Chemical Marketing Reporter,* (1990) May 7 and (1991) March 13, New York.
11. Goldstein, I. S. (1981), *Organic Chemicals from Biomass,* CRC Press, Boca Raton, FL.