

The Economics of Acetone-Butanol Fermentation: Theoretical and Market Considerations

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Abstract

Acetone-butanol (AB) fermentation was once run commercially in many countries until these chemicals could be made more cheaply from fossil oil sources. Research into the revitalisation of the process has shown that the process could once again be run economically in niche markets if run in a relatively small industrial scale processing low-grade agricultural products. The following analysis is intended to help identify suitable niche markets.

Theoretical Limits

The main limitations to the economics of the AB-fermentation are dictated by chemical stoichiometry and by the First Law of Thermodynamics (which says that energy can neither be created nor destroyed) which represent the mass and energy balances. In terms of a fermentation process producing bulk chemicals, this means that the fermentation products cannot contain more mass nor more energy in sum than the fermentation substrate. In fact since fermentation processes are exothermic the product will certainly contain less energy than the substrates. The mass and energy yields in turn determine the absolute, theoretical limits to the process economics. These limits can be represented by a graph of minimum product price as a function of substrate price, whereby the substrate price divided by the yield gives the minimum possible product price. Quantification of these theoretical limits depends therefore only on the chemical characteristics of the compounds involved. Table 1 shows the relevant stoichiometric equations (as of yet no bacterium is known which makes only acetone and carbon dioxide from glucose), and Table 2 lists the chemical properties required to quantify both the energy and mass yields. Since the molecular weights of 1-butanol, acetone and ethanol are 74, 58 and 46 g/mol, their energies of combustion are 2.7, 1.8 and 1.4 kJ/mol, the energy of combustion of glucose is 2.8 kJ/mol and of hydrogen 0.29 kJ/mol then it is easy to estimate that a 6:3:1:0.4 product mix of 1-butanol:acetone:ethanol: hydrogen has a theoretical mass yield of 37% and a theoretical energy yield of 94 %. A more rigorous calculation of the energy yields based on the Gibbs Free Energy rather than the

combustion energies has been prepared by the author (Gapes, unpublished results).

Investment and Production Costs

In reality, the costs of production and of capital expenditure (as a component of production costs and as a hurdle for investors) must also be considered. Investment costs enter into the economic assessment of AB-fermentation in three ways. Firstly, a large capital investment before production starts will greatly reduce the number of possible investors and effectively exclude financially weak consortia, a position which is worsened by the increased risk associated with new and innovative processes. This is a major problem for the niche markets identified below. Secondly, investment costs directly increase production costs both as depreciation and for financing (interest and repayments). For these three reasons major reductions in investment costs and/or staggering and delaying investments especially until after productions starts will all help improve process economics. Table 3 shows two estimates for investment requirements estimated by the author. The first plant (Gapes, 1982) was designed using the same technology as used industrially in the first half of this century *i.e.* batch fermentation followed by distillation. The second plant (Gapes, 1993) was designed as a continuous plant with on-line product separation using membrane technology. Both these budget estimates were generated as described by Peters and Timmerhaus (1980) and by Perry and Chilton (1973). Direct costs were calculated by listing and then pricing each major item of equipment and then factors were applied to estimate other costs. The effect of errors and inaccuracies is discussed below and the permissibility of comparing estimates for different countries and dates is handled similarly.

The investment estimates show that although large sterilisable pressure vessels for use as fermenter is expensive, other factors have equal influence on the investment costs - for example capital costs for product separation are of a comparable magnitude. Also, although it is often argued that batch operation is less economic than continuous production and although continuous operation may indeed increase fermenter productivity, there are extra costs involved not only to install dedicated sterilisation equipment but also to install piping, valves and other fixtures capable of reliably supporting absolute sterility at all times. From the point of view of investment costs

Table 1. Stoichiometric Equations

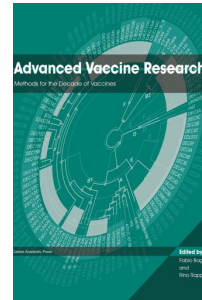
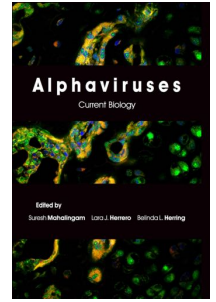
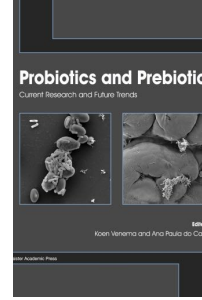
Product	Stoichiometric Equation			
acetone	$C_6H_{12}O_6 + H_2O$	\rightarrow	$CH_3COCH_3 + 3CO_2$	$+ 4H_2$
1-butanol	$C_6H_{12}O_6 + H_2O$	\rightarrow	$C_4H_9OH + 2CO_2$	$+ H_2O$
ethanol	$C_6H_{12}O_6 + 2H_2O$	$\rightarrow 2$	$C_2H_5OH + 2CO_2$	
acetate	$C_6H_{12}O_6 + 4H_2O$	$\rightarrow 2$	$CH_3COOH + 2CO_2$	$+ 4H_2$
butyrate	$C_6H_{12}O_6 + 2H_2O$	\rightarrow	$C_3H_7COOH + 2CO_2$	$+ 2H_2$

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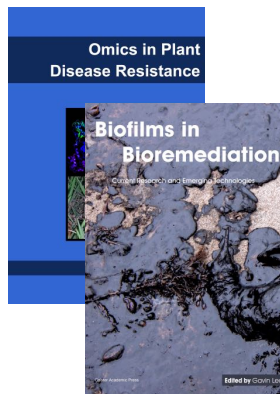
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Table 2. Table of Compound Properties

Component / Reaction	s.g ¹	Mr ² (g/mol)	Comb ³ (J/g)	Comb ³ (kJ/mol)
Glucose		180.16	15,544	2,800
Xylose		150.13	15,564	2,337
Acetic Acid	1.04	60.05	14,550	874
Ethanol	0.78	46.07	29,685	1,368
Acetone	0.79	58.08	30,797	1,789
1-Butanol	0.81	74.12	36,066	2,673
Butyric Acid	0.94	88.10	24,761	2,181
Hydrogen		2.02	141,375	286
A:B:E 3:6:1		66.50	33,847	2,277

¹ Specific gravity (Chem. Eng. Handbook 1973)

² Molecular weight (Chem. Eng. Handbook 1973)

³ Comb. = Heat of combustion (Weast 1977)

alone it is unlikely that continuous operation is of great advantage as the requirement for sterility is of dominating importance and governs investment in the fermentation plant. The choice of product separation technology for removal of product from the beer is also not of deciding importance with respect to investment costs. Traditional distillation columns incur investments of roughly similar magnitude to gas-stripping, extraction or even membrane evaporating equipment. Use of low flux, highly selective pervaporation membranes might even incur higher investment costs due not only to large membrane areas required, but due to operational problems such as possible capillary blockages and the possible compromising of sterility if the membrane becomes perforated.

Production costs for the two examples in Table 3 are presented in Table 4. These budget estimates were generated as described by Peters and Timmerhaus (1980) and by Perry and Chilton (1973) using factors to estimate indirect and other costs. Substrate costs were excluded from these calculations and will be considered later. Energy costs were also found to be low since energy balances show that combustion of the hydrogen and methane from a biogas plant covers most of the process's heat requirements. Energy imports to the plant are, however, necessary for plant start-up and for contingency purposes.

The cost of financing is the largest single production cost after substrate and energy costs and includes both

depreciation and interest payments on capital borrowed. Although good design and construction practices do much to avoid an unnecessary inflation of costs, a plant designed for sterile fermentation is significantly and unavoidably more expensive than non-sterile designs, such as used in ethanol distilleries. This means that compromising on the quality of equipment for an acetone-butanol plant will leave the process susceptible to contamination by competing micro-organisms and phages (*i.e.* viruses). The effect on process reliability can be catastrophic - the ramifications for the process economics is discussed in more detail below. Jones (2000) illustrated this very clearly in his account of the effects of viruses on reliability in the industrial plants during the first half of this century.

The direct and indirect costs associated with personnel in both production and in administration can to some extent be reduced by automation and out-sourcing. The examples calculated in Table 4 are based on the assumption of four shifts of two persons and a further two persons in administration. Analogous to many small European ethanol distilleries, however, it is probable that personnel be reduced to under half this level once the process is running acceptably. Long-term out-sourcing of strain development activities both to improve fermentation yields and performance and as a strategy against phage infestation will most likely be necessary due to the skills and equipment involved. Further, costs for sales and marketing and also research and development (additional to strain development) are necessary but probably lower than other cost factors.

In order to establish both impartiality and accuracy in the two economic analyses presented in Table 4, the data were compared with analyses published by other authors. (Gapes, unpublished results). The estimates in Table 4 along with those in the literature agree that production costs are in the order of 2 to 3 EUR/kg for a grass roots plant of capacity above approx. 20,000 t/a of fermentable carbohydrate. If capital and other costs can be markedly reduced, by for example extensive use of existing facilities, then the price may drop by up to a half.

The Product Market

The world market prices of acetone and of 1-butanol in Rotterdam are shown in Figure 1. The price can be seen

Table 3. Table of Investment Costs

Batch Plant (4,500 t/a)(mill EUR, 1980)			Continu. Plant (30,000 t/a)(mill EUR, 1987)		
Item	Amount	%	Item	Amount	
Equipment	0.40	26%	Equipment	2.93	64%
Installation	0.04	3%	Civil & Installation	(incl.above)	
Piping	0.08	5%	Piping	0.30	7%
Instruments	0.06	4%	Measurement & Control	0.22	5%
Electrical	0.04	2%	Electrical	(incl.above)	
Civil	0.04	3%	Building & Services	0.08	2%
Buildings	0.03	2%	Lagging	(incl.above)	
Lagging	0.02	1%	Yard Improvements	0.04	1%
Services, Yard	0.20	13%	Startup Costs	0.21	5%
Land	0.02	2%	DIRECT COSTS	3.77	83%
DIRECT COSTS	0.94	60%	Engineering & Supervision	(incl. above)	
Engineer. & Superv.	0.19	12%	Construction expenses	(incl. above)	
Construc. exp. & contr.	0.19	12%	Contingency	0.33	7%
Contingency	0.09	6%	INDIRECT COSTS	0.33	7%
INDIRECT COSTS	0.47	30%	FIXED CAPITAL INV.	4.10	90%
FIXED CAPITAL INV.	1.41	90%	Working Capital	0.46	10%
Working Capital	0.16	10%	TOTAL CAPITAL INV.	4.6	100%
TOTAL CAPITAL INV.	1.6	100%			

Table 4. Table of Production Costs

Batch Plant (4,500 t/a)(mill EUR, 1980)			Cont. Plant (30,000 t/a)(mill EUR, 1987)		
Item	Amount	%	Item	Amount	%
Raw Materials	0.00	0%	Raw Materials	0.00	0%
Operating Labour	0.09	11%	Operating Labour	0.48	27%
Utilities	0.05	6%	Utilities	0.04	2%
Maintenance & Repairs	0.07	9%	Maintenance & Repairs	0.09	5%
Operating Supplies	0.01	1%	Operating Supplies	0.01	1%
Laboratory charges	0.03	4%	Laboratory charges	0.10	5%
DIRECT PROD. COST	0.25	31%	DIRECT PROD. COST	0.71	40%
Depreciation	0.09	12%	Depreciation	0.35	20%
Insurance and Taxes	0.07	9%	Insurance and Taxes	0.08	5%
Overheads	0.05	7%	Overheads	0.07	4%
FIXED CHARGES	0.22	28%	FIXED CHARGES	0.50	28%
Administration	0.05	6%	Administration	0.05	3%
Distribution	0.08	10%	Distribution	0.13	7%
Research & Devel	0.04	5%	Research & Devel	0.07	4%
Financing	0.16	20%	Financing	0.33	18%
GENERAL EXPENSES	0.32	41%	GENERAL EXPENSES	0.57	32%
PRODUCTIONCOST	0.8	100%	PRODUCTIONCOST	1.8	100%

to fluctuate widely from year to year dependent to a large extent on the price of crude oil. Average prices over the last five years are $0.45 \pm 30\%$ EUR/kg for acetone and $0.61 \pm 29\%$ EUR/kg for 1-butanol. The quantities used in Europe are very large and data describing demand quantitatively and submitted voluntarily to the relevant customs and duties departments of Denmark, Finland, France, Italy, Spain and Austria show that more than 640,000 t/a of acetone and 63,000 t/a of butanol cross the border of these countries alone, whereby neither internal flows in these countries nor data for Germany and some other EU countries are included in this figure. Estimates for the whole of the EU based on these figures suggest that at least 12 mill t/a and 1.2 mill t/a of acetone and butanol respectively crosses the national borders (excluding internal production and use).

Ethanol is, however, in contrast to both acetone and butanol, produced internally predominantly for internal consumption - the bulk of the ethanol produced therefore does not therefore appear in import/export statistics. Nor does installed production capacity give a good indication as the majority of small facilities only run for several months per year. European trade in ethanol shows that more ethanol crosses the national boundaries than butanol and

approximately 1/3 of the acetone quantity demonstrating once again that the market is much larger than any amount produced by a single AB-facility (the process produces only about 10 % the weight of butanol and acetone as ethanol). On the other hand the market for ethanol is, however, still grossly oversupplied and controlled by government monopolies in much of Europe, although these regulations are currently being revised or dismantled. For example the removal of most of the regulations supporting the Austrian ethanol monopoly over the last 5 years has resulted in the closure of all but 3 of the 36 small agricultural distilleries in operation at the beginning of the 1990's. This deregulation, the gross over-capacity in Europe and the current enormous production capacity currently installed in North America have driven European ethanol prices down to 0.42 EUR/kg and still dropping. Hence, although the market for ethanol is large its contribution to income is low.

Although these estimates for European trade are imprecise it is clear that one or even several fermentation plants selling into these markets will not effect market prices nor market structure significantly and as such these estimates are sufficient to show that the market is large enough to absorb the products of a small acetone-butanol industry.

Combining Theory with Market Information

The discussion above can be summarised in a single graph made up of a straight line with a slope equal to the inverse of the yield and which intersects the vertical axis as defined by the production costs (refer Figure 2). An area has been used instead of a simple line to reflect the uncertainty in the estimate for production costs. Two separate lines for production costs have been drawn showing the much lower production costs if an existing plant can be easily modified as opposed to a new (*i.e.* "grass-roots") plant. A horizontal line has been used to represent the average market price for product, whereby fluctuations of approx. 30 % were assumed. Product ratios of 6:3:1 were assumed to calculate this average price. It should be noted that the acetone and 1-butanol prices are strongly correlated hence the product mix cannot be relied upon to reduce income uncertainties.

The graph shows clearly that the break-even price of substrate lies between 0.05 and 0.09 EUR/kg for a grass

International Product Prices

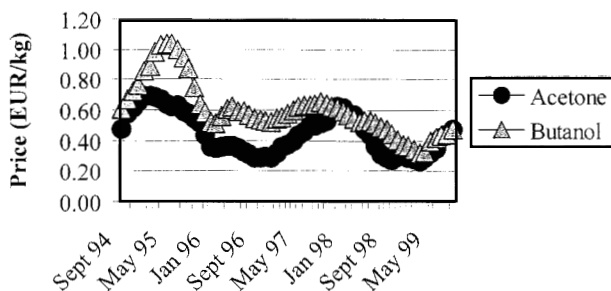


Figure 1. International Product Prices (Rotterdam Market)

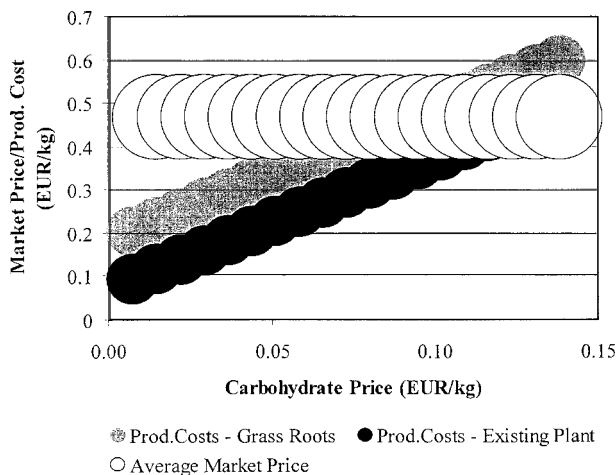


Figure 2. Market Prices vs. Production Costs for the Acetone-Butanol Products

roots plant or between 0.09 and 0.13 EUR/kg if an existing plant can be modified at low cost. The exact break-even price depends on both the predominant price achieved for the product and on the exact substrate costs. Above a substrate price of approx. 0.09 EUR/kg for a grass-roots or 0.13 EUR/kg for an existing plant the AB-process cannot be economic unless subsidies or other support measures are available. Obviously if the prices achieved for the products are higher then a higher substrate price can be paid.

The sale of by-products is at present unlikely to change this conclusion under current market conditions. One can imagine that both the hydrogen and the methane produced from the slops or even the slops themselves might be sold, however, this would have to be weighed up against the cost of importing energy. The feasibility calculations presented have assumed that the hydrogen is used to generate energy and that the CO₂ is vented to atmosphere. Indeed the sale of the slops as animal feed provided an important income for the previous world-wide AB-production earlier this century, however, at present the animal feed market is not considered to be a reliable market and as such this possible income has been ignored in the calculations presented. It is also possible that the carbon dioxide be cleaned and sold at a profit. This consideration

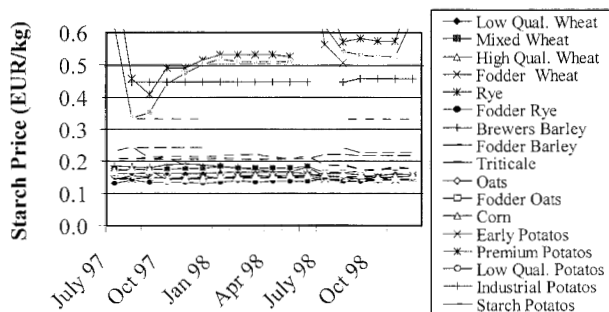


Figure 3. Starch Prices in Austria

was not included as a source of income in the economic analyses as the CO₂ market is said to be less than installed production capacity and that the possible profit is too small to make a major impact on AB-economics.

The Substrate Market

In order to reduce substrate costs which contribute over 60% of total production costs in typical bulk-chemical fermentation processes (e.g. Lenz and Moreira 1980), an acetone-butanol fermentation plant must be able to use a variety of substrates including those of low grade substrate such as frozen potato, corn contaminated by mycotoxins and sugar beet surpluses. In this context fermentation plants should be small and located de-centrally in order to meet the specific needs of the local, preferably rural regions (e.g. Lovitt *et al.* 1988). The substrate prices quoted in this article refer to the price of fermentable carbohydrate per kilogram, hence 0.07 EUR/kg as a break-even price refers to the price of a kilogram of sugar or starch. Current market prices for the cheapest starch products (grains) in bulk sales of agricultural crops are, however, in the range of 0.14 to 0.21 EUR/kg. Figure 3 shows the price development in Austria since mid 1997. Non of the crops considered are capable of providing carbohydrate at a price below 0.09 EUR/kg, hence the AB-process does not appear to be economic for purpose grown crops at these prices under the assumptions used as a basis for this economic analysis.

The niche market for the process using present technology can therefore be specified as the conversion of cheap, low grade substrates selling into the chemical market - indeed ethanol distilleries have already shown this to be possible for a bulk-chemical fermentation process for many decades. This is a similar conclusion to that of Marlatt and Datta (1986), who stated that a fermentative AB-process probably had higher capital costs but lower production costs than acetone and butanol production by the petrochemical industry. Further research and development might well be able to extend the substrate range to include the cheapest purpose-grown crops, however, these technologies are still research goals and not proven. Perhaps the most exciting research goal is the activation of possible endogenous cellulase enzymes identified in the recently completed genome study for *Clostridium acetobutylicum* (Soucaille, P. personal communication). It is thought that these genes can be easily reactivated and as a result these bacteria may then be able to metabolise cellulose directly. This might significantly impact on the economic feasibility of this process, depending of course on the level of activity achieved.

Sensitivity Analysis

A sensitivity analysis has been performed on the models to ascertain both the effect of errors and uncertainties in the estimates made and to determine how research and development efforts can be targeted to make the AB-process economic. Hence price fluctuations in the product market have been presented graphically in Figure 2 not by a horizontal line but by as an area represented by elongated cloud. The uncertainties present in estimates for the production costs have similarly been indicated by an elongated cloud of slope equal to the inverse of the yield. Two such parallel areas represent the production cost

estimates for a grass roots plant and for the case where extensive capital expenditure is not required. The width of the elongated clouds in Figure 2 approximates in all three cases the amount of uncertainty. Figure 2 also includes the sensitivity analysis for substrate prices - the reader can look at the graph and determine the economic feasibility for any substrate price.

Implicit in the economic analyses and in Figure 2, however, are two assumptions: firstly that energy requirements are largely generated internally from combustion of hydrogen and methane and secondly that the yield is defined and invariable. Energy balances based on final engineering designs for a plant can be used to consolidate the assumption that energy requirements can indeed be covered by internal generation, as is presently thought likely. Since energy costs themselves contribute only a fraction of the total production costs they do not on their own make the process uneconomic if energy must be imported - which would only be the case if hydrogen and methane were to be otherwise sold thereby also contributing to plant income. Fuel costs for imported energy amount typically to between 10 % and 20 % of production costs if neither hydrogen nor methane is available.

The second assumption, that the yield is defined and invariable, requires much closer attention. Although the chemical stoichiometry and the First Law of Thermodynamics precisely define the maximum energy and mass yields, both yields can drop well below these limits. The yield used in Figure 2 is the mass yield of solvent defined as the weight of acetone, butanol and ethanol per unit fermented carbohydrate. Figure 2 was drawn assuming a mass yield of 33 %, which is typical of both laboratory data and of the industrial yields achieved throughout the world earlier this century. Yields of up to 40 % can be achieved both theoretically and have also been reported in the literature, however, well run fermentations seldom sustain yield averages better than 37 %. If average yields above 33 % can be sustained then the economics of the AB-fermentation will improve slightly, however, it must be noted that even if yields reach their theoretical maximum this alone will not make the process economic. Other factors such as substrate and production costs are much more important. The question of yield does, however, remain very important since if yields fall to 25 % or even lower, which is also reported for laboratory fermentations and from industry earlier this century, then the fermentation feasibility fails. It will therefore be imperative that AB-fermentation plants are supported by laboratories conducting strain improvement and protection strategies against phage infestation.

Economic Optimisation

Once a market niche has been identified then economic optimisation of the process is necessary to enable the maximum to be paid for substrate, or to provide the highest return on investment or even just to compete successfully in an open market. Further optimisation might include the use of continuous fermentation, whereby significant improvements in volumetric productivity can be achieved. Although the problems of fermentation stability and reliability under continuous conditions are of particular concern with an AB-fermentation process and although the continuous operation in general is not preferred by

fermentation technologists because of contamination problems, experiences from Dokshukino Plant in former USSR (Hospodka, 1966) and from Austrian Pilot Plant (Nimcevic and Gapes, 2000) have shown that both fermentation stability can be achieved and that contamination problems can be avoided. It appears that continuous runs of 4 weeks or more are sufficiently long for the economic advantages to be noticeable.

The low final solvent concentrations reached due to product toxicity means that the AB-fermentation is a recovery cost-intensive process, similar in this respect to the biochemical production of proteins, vitamins, antibiotics etc. Another class of biochemical products are the conversion cost-intensive processes, where the volumetric productivity is of a paramount importance (*e.g.* production of baker's yeast, ethanol, lactic acid; Cooney, 1983). As a result the acetone-butanol fermentation is both a conversion and a recovery cost-intensive process and its economy feasibility appears to be far away from any chance of profitability. However, Marlatt and Data (1986) have shown that if an improved strain which tolerates slightly higher butanol concentrations is used and when the volumetric productivity is increased by about 50%, the production costs for fermentation butanol would be similar to the production costs for synthetic butanol. Moreover, Woods (1995) stated that if the final solvent concentration can be increased by approximately one-third (*i.e.* to the levels of 22-28 g/litre) and if the fermentation time of the batch fermentation of 40-60 hours can be maintained, the acetone-butanol fermentation should be industrially viable. As can be seen, in the first case reductions in both conversion cost-intensity and in recovery cost-intensity were required in order to reach economy feasibility. In the second case recovery costs appear to be more significant. Nevertheless, according to the numbers of reports both solvent productivity and final solvent concentration can be increased at least under laboratory conditions and this can improve the economic feasibility.

The process economics can be further increased when on-line product removal is used, whereby a number of advantages contributing fermentation reliability are achieved, including reduced product inhibition and enhanced culture stability. Among the on-line product removal techniques membrane techniques including pervaporation are thought to have potential for the AB-fermentation (Ennis *et al.*, 1986). A number of drawbacks must, however, be taken into account before industrial scale operation is attempted, including high investment costs, membrane fouling, salt accumulation in the fermentation medium, blockage of narrow capillaries and contamination risks on perforation. Furthermore, pervaporation and membrane evaporation include a phase change as the liquids vaporise and it is well-known that this is very energy intensive and the energy of the phase change cannot be recovered and it is ultimately lost.

Further considerations regarding process optimisation in continuous operation and also the inclusion of on-line product removal have been included in the contribution of Nimcevic and Gapes (2000).

Conclusions

AB-fermentation appears to be economic if processing cheap low-grade substrates into the chemical market.

Ethanol fermentation facilities have shown this to be possible for a bulk-chemical fermentation process for many decades.

Acknowledgements

The author wishes to thank both Hans Baumgartner and Dragan Nimcevic for their help in collating data.

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