# American Institute
# of
# Chemical Engineers

## NATIONAL STUDENT DESIGN COMPETITION

## 1992

345 East 47 Street • New York, New York 10017

# AIChE NATIONAL STUDENT DESIGN COMPETITION

# 1992

# Alternative Fermentation Processes for Ethanol Production

## DEADLINE FOR MAILING

Solutions must be postmarked not later than **Midnight, June 26, 1992.**

## RULES OF THE CONTEST

Solutions will be graded on (a) substantial correctness of results and soundness of conclusions, (b) ingenuity and logic employed, (c) accuracy of computations, and (d) form of presentation. Accuracy of computations is intended to mean primarily freedom from mistakes; extreme precision is not necessary.

It is to be assumed that the statement of the problem contains all the pertinent data except for those readily available in handbooks and similar reference works. The use of textbooks, handbooks, journal articles, and lecture notes is permitted, and use of the supporting data provided by AIChE for this case study is strongly encouraged.

Students may use any available commercial or library computer programs in preparing their solutions. Students are warned, however, that physical property data built into such programs may differ from data given in the problem statement. In such cases, as with data from other literature sources, values given in the problem statement are most applicable. Students using commercial or library computer programs or other solution aids should so state in their reports and include proper references and documentation. Students are further advised that the problem can be solved without the use of sophisticated computer programs. Judging is based on the overall suitability of the solution, not on skills in manipulating computer programs.

The Student Contest Problem is designed to be solved by individual chemical engineering students working entirely alone, and it is judged on that basis. There are, however, other academically sound approaches to using the problem. The following confidentiality rules therefore apply:

1. ***For students whose solutions may be considered for the contest:***
   The problem may not be discussed with anyone (students, faculty, or others, in or out of class) before or during the period allowed for solution. Discussion with faculty and students at that school is permitted only after complete final reports have been submitted to the chapter counselor.

2. ***For students whose solutions are not intended for the contest:***
   Discussion with faculty and with other students at that school who are not participating in the contest is permitted.

3. ***For all students:***
   The problem may not be discussed with students or faculty from other schools, or with individuals in the same school who are still working on the problem for the contest, until after June 26, 1992. This is particularly important in cases where neighboring institutions may be using different schedules.

Submission of a solution for the competition implies strict adherence to these conditions.

A period of not more than thirty days is allowed for completion of the solution. This period may be selected at the discretion of the individual counselor, but in order to be eligible for an award a solution must be postmarked not later that midnight, June 26, 1992. ONLY SOLUTIONS SUBMITTED BY NATIONAL STUDENT MEMBERS OF AIChE WILL BE CONSIDERED FOR AWARDS.

THE FINISHED REPORT SHOULD BE SUBMITTED TO THE CHAPTER COUNSELOR WITHIN THE 30–DAY PERIOD. There should not be any variation in form of content between the solution submitted to the chapter counselor and that sent to the AIChE office. The body of the report must be suitable for reproduction, that is, typewritten or computer–generated. Tables may be written in ink. Supporting calculations and other appendix material may be in pencil. Each counselor should select the best solution or solutions, not to exceed two, from his or her chapter and send these by registered mail to the Institute.

Two copies of the solution(s) must be accompanied by a letter of transmittal giving only the contestant's name, school address, home address, home telephone number, and student chapter, lightly attached to the report. This letter will be retained for identification by the executive director of the Institute. The solution itself must bear no reference to the student's name or institution by which it might be identified. In this connection, graph paper bearing the name of the institution should be avoided. Original manuscript(s) must remain in the possession of the student chapter counselor, or faculty member, sponsoring the student(s).

As soon as the winners have been notified, original manuscripts for first, second, third and honorable mention categories must be forwarded to the office of the executive director as soon as possible.

Richard E. Emmert
Executive Director
American Institute of Chemical Engineers
345 East Forty–seventh Street
New York, New York 10017

If there are any questions about the design problem,
student chapter counselors and
design course instructors are asked to contact:

Dr. Davis W. Hubbard
Michigan Technological University
Department of Chemical Engineering
Houghton, Michigan 49931

• Telephone number 906-487-2140

• Fax number 906-487-2061

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BEFORE SUBMITTING A SOLUTION TO AIChE.

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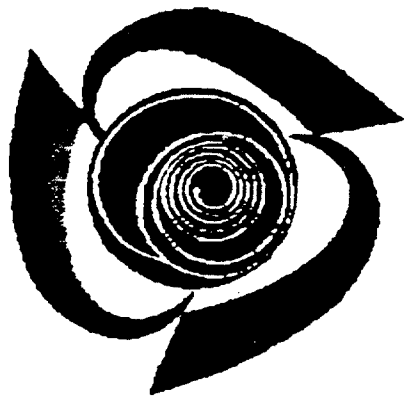

Note: this section can be removed and given to the student as the problem statement. The instructor has the option of providing the students with the flowsheet and process description so that they all begin the design using the same basis or the bracketed sentence can be covered with correction tape and the students left to develop the flowsheet on their own.

**GW Chemicals**
**New Orleans , Louisiana**

UT Consultants
Toledo, Ohio

Subject: Preliminary Design and Evaluation of an Ethanol Production Facility Utilizing Sugar Cane Molasses

This is to confirm the verbal discussions we had last week regarding our intention to build an ethanol production plant in the New Orleans area which will utilize sugar cane molasses imported from the Caribbean. We would like you to provide us with a preliminary technical and economic evaluation of producing ethanol in such a facility. Consider the use of either conventional fermentors (batch, CSTR, CSTR w/recycle) or a new fermentor we are developing, the Hollow Fiber Extractive Fermentor (HFEF). You will receive the performance-cost characteristics of the HFEF as soon as our research group finalizes them.

[ Attached to this letter is a general flowsheet and process description of such a facility.]

The facility is to produce 50 million liters/year of 95 wt % azeotropic ethanol. The plant is to be on-line 330 days per year, 24 hours per day. Waste water generated by this process can be treated at no cost at an adjacent GW plant. Based on company guidelines we require that you base your calculations on a 10 or 15 year service life with MACRS depreciation and zero salvage value. Set the price of the products to achieve a 15% discounted cash flow rate of return. Additional economic factors are attached to this letter.

When preparing your report we request that you consider the following:

1. determine the "best" process alternative
2. provide the rationale for the elimination or selection of any process alternative
3. prepare detailed material and energy balances for the selected process
4. size and estimate the purchase cost of all major pieces of equipment for the selected process
5. estimate the fixed capital investment
6. determine the final ethanol cost in cents/liter
7. optimize the process as you see fit to minimize the cost of the ethanol

Sincerely,

Mr. Sweet
President
GW Chemicals

## ECONOMICS INFORMATION

**1987 Cost Data**

| | |
|---|---|
| Molasses ( @50 wt % SUGAR ) | $69.61/short ton FOB New Orleans |
| Nutrients | $0.0095/liter ethanol |
| Operating Labor | $19/man-hour |
| Yeast Market Value | $0.12 /Kg of 50 wt % dried yeast product |
| Low Pressure Steam (50 psig) | $12.20 /1000 Kg |
| High Pressure Steam (600 psig) | $17.30 /1000 Kg |
| Exhaust Heat | $1.29/1000 MJ (credit for 1 atm steam) |
| Cooling Water : | |
| 20 °C | $0.04 / 1000 Kg |
| 30 °C | $0.02 / 1000 Kg |
| Electricity | $0.074 / K Watt-hour |
| Natural Gas | $4.00 / 1000 MJ |

MJ = million Joules

* Use Lang Factors for determination of capital investment.
* For depreciation, use MACRS and zero salvage value.
* For final product price calculation, set the prices of the products to provide 15% discounted cash flow rate or return with a 10 or 15 year project life.

**TECHNICAL INFORMATION**

* The temperature of the process feed must reach 120°C in the sterilizer.

## Description of General Flowsheet for Ethanol Production

The attached flowsheet (Figure 1) and the following description apply to a process which would utilize a batch fermentor or a CSTR fermentor with the possibility of yeast recycle.

A molasses feed, 50 wt % sugar, is mixed with nutrients and water then sterilized by direct steam injection. This stream is fed into the fermentation system which, in the case of batch, is assumed to operate by staggering the harvest times for batch reactors to provide a continuous product flow. Air is sparged into the fermentation system to maintain the optimum oxygen concentration. An absorber is used to scrub ethanol from the resulting carbon dioxide and air stream leaving the fermentor. The fermentation beer is centrifuged and part of the concentrated yeast cream is recycled back to the fermentor in the CSTR with recycle case. Cell recycle will increase the productivity of the fermentor by increasing the cell density and thus has the potential to decrease fermentor costs. However, the cost of centrifuging a more concentrated fermentor product stream may offset the savings. The remaining yeast in this case and all the yeast cream in the case of a batch or CSTR without recycle fermentor is otherwise fed to a rotary dryer which produces a 50 wt % dried yeast that will be credited as a cattle feed product. The centrifuge supernatant is sent to a stripper for concentration and then to a vacuum distillation column to obtain the 95 wt % ethanol product.

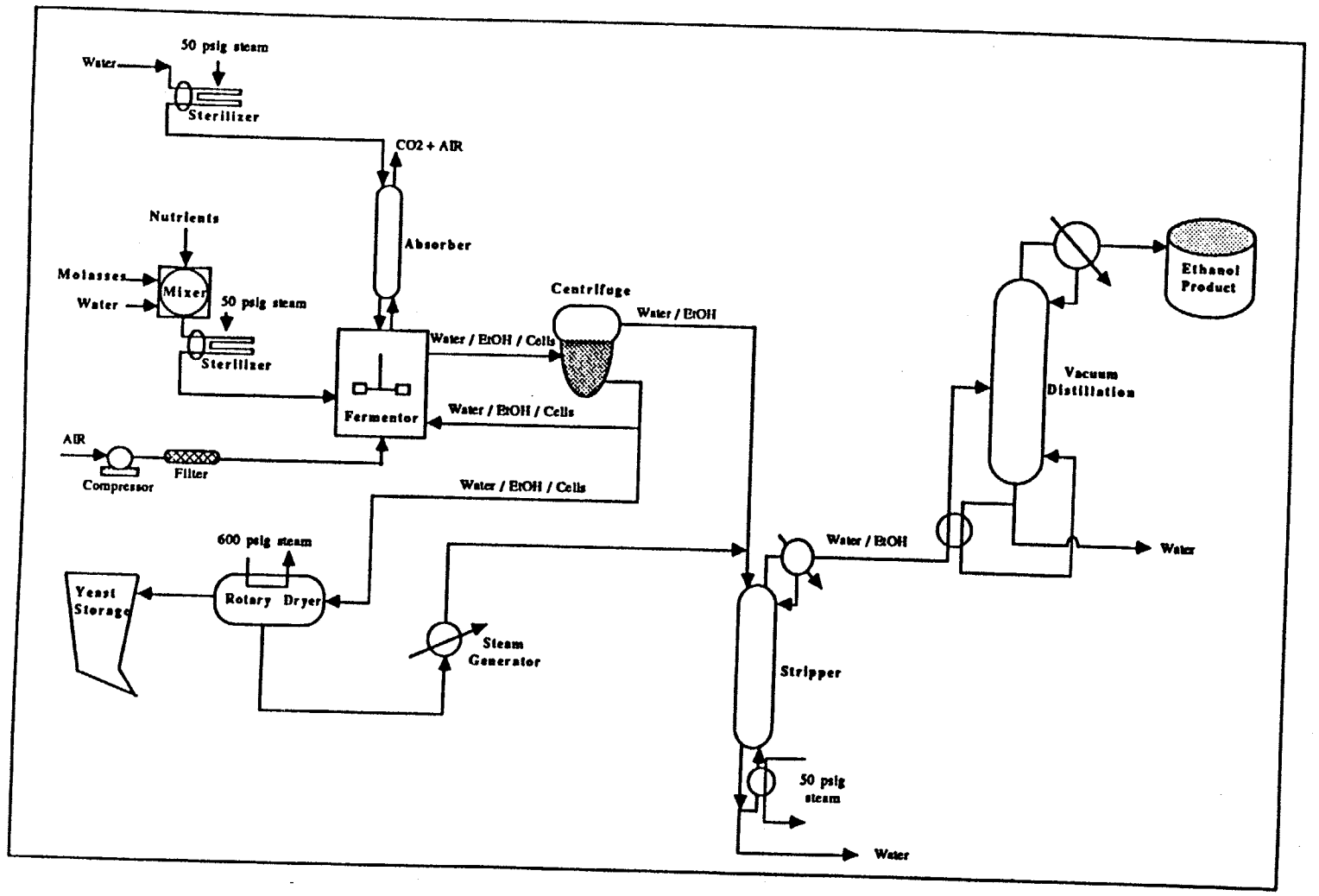


Figure 1. General flow sheet for a process that would employ a batch , simple CSTR , or CSTR with recycle fermentor to produce ethanol .

**Instructor Note:** Memo to be given to the students concerning the HFEF. Once again the bracketed sentence at end of the HFEF report can be covered with correction tape and the students left to develop the flowsheet on their own.

**GW Chemicals**
**New Orleans , Louisiana**

UT Consultants
Toledo,Ohio

Subject : Additional Information Regarding the Proposed Ethanol Production Process .

Our research team has finished their report summarizing their findings regarding the expected performance of the HFEF . A copy of the report is attached . We look forward to receiving your report concerning the evaluation of the ethanol production plant .

Sincerely
President
GW Chemicals

Att: HFEF Report .

Report on the Investigation of a Hollow Fiber Extractive Fermentor (HFEF) for the Production of Ethanol

**Introduction :**

The economics of a fermentation process can be improved by reducing end product inhibition and increasing fermentor cell density . Several fermentation systems have been proposed and some investigated , which take advantage of this . Removal of ethanol by dialysis , vacuum , flash , extractive and membrane extractive fermentation have been reported as well as increased cell density by use of an APV tower , hollow fiber immobilized cells , gel entrapment of cells , etc. [I.1].

In an extractive fermentor , ethanol is removed from the fermentation beer by either direct contacting with a suitable extractant in the fermentor [I.2] or by a separate vessel where the aqueous phase is recycled back to the fermentor [I.3] .

A suitable extractant should have the following properties :

1- nontoxic to yeast cells since toxicity would reduce the efficiency of the cell mass or completely destroy the cells .

2- thermally stable , which means it can be sterilized , product distilled and extractant recycled repeatedly .

3- insoluble or has a low solubility in water to prevent its loss through the aqueous phase and thus the added cost of wastewater treatment and extractant replenishment .

4- high selectivity for ethanol and fermentation by-products ,

expressed as a high distribution coefficient for ethanol and a low distribution coefficient for nutrients .

5- can be easily separated from the aqueous phase, requiring that it has a considerable density difference and does not form a stable emulsion with water .

6- ethanol can be easily separated from it which requires a low volatility compared to ethanol .

7- commercially available and inexpensive .

The literature contains several studies to identify suitable solvents . Matsumura and Markl [I.4] screened solvents based on their selectivity for ethanol over water and confirmed Roddy's [I.5] results that the best extractants are alcohols and esters . Their best solvents in terms of selectivity were found to be 2-ethyl-1-butanol and tri-n-butylphosphate (TBP) respectively . Roddy reached the same conclusion but pointed out that 2-ethyl-1-butanol has a relatively high solubility in water ( 8.5 grams per liter ) and its extraction properties for trace minerals are not well understood which reduces its attractiveness . On the other hand , TBP has a very low solubility in water ( 0.42 grams per liter ) and it is a well documented chemical . Thus Roddy concluded that TBP is better suited in spite of the fact that its selectivity is lower than that for 2-ethyl-1-butanol . Table I.1 summarizes the physical properties of TBP .

In these studies and others , however , the most promising solvents in terms of selectivity were often found to be toxic to the yeast cells , the mechanism of toxicity , though , was not investigated . Cho and Shuler [I.8] investigated a multimembrane fermentor that uses TBP as the extractant and found that it is not toxic to the yeast in dissolved form . Instead , the

| Property | Value |
|---|---|
| Molecular Weight | 266.31 |
| Boiling Point | |
| at 760 torr | 289ºC |
| at 27 torr | 177-178ºC |
| at 10 torr | 150ºC |
| Freezing Point | <-80 ºC |
| Density at 25ºC | 0.973 |
| Viscosity at 25ºC | 3.41 centipoise |
| Specific Heat | 0.41 cal/g ºC |
| Latent Heat of Vaporization | 55.1 cal/g |
| Flash Point , Cleveland Open Cup | 295ºF |
| Solubility in Water at 25 ºC | 0.42 g/lit |
| Solubility of Water in TBP at 25ºC | 64 g/lit |
| Cost in 1986 [I.7] | 3.74 $/Kg |

Table I.1. Physical Properties of tri-n-butylphosphate (TBP) (from Ref. I.6) .

toxic effect observed by other researchers may be due to the "... interaction of TBP emulsions with yeast cells which results in weakening the cell envelope and/or blocking transport of nutrients . This toxic effect could be termed as physical toxicity ..." .

Thus a possible solution to the dilemma of a toxic but suitable extractant lies in introducing a physical barrier which would allow limited contact between the extractant and fermentation broth . Matsumura and Markl [I.9] used an artificial kidney hollow fiber module in series with a fermentor containing immobilized cells in gel beads and successfully fermented a 500 g/liter glucose feed .

A further disadvantage of direct contact between the extracting solvent and fermentation broth was pointed out by Fournier [I.11] who presented and investigated a mathematical model of the in-situ extractive fermentation of ethanol . When the ratio of solvent to aqueous feed flow was increased , the volumetric productivity decreased . This was attributed to the additional reactor volume needed to both , maintain the required residence time and accommodate the increased solvent phase volume

Hollow fibers which are made of tubular microporous membranes with diameters on the order of a hundred microns , can be used to circumvent this problem . By providing a large surface area - up to 40 square centimeters per cubic centimeter - [I.12] hollow fibers can increase the contact area between a solvent and the fermentation aqueous phase with a much lower reactor volume taken up by the solvent than that required in direct contact . Problems of loading , flooding and channeling encountered in conventional extraction equipment are also avoided .

Hollow fibers are already in use in artificial kidney devices . More recently , the use of hollow fiber modules has been investigated in the

synthesis of protein [I.13] , in the extraction of phenol and phenolic compounds from waste generated by various industries [I.14] , in antibiotic extraction and acetic acid recovery [I.15] , and in the culture and growth of mammalian cells [I.16] which are used to produce medically important biochemicals such monoclonal antibodies [I.17] , vaccines , interferons and hormones .

The use of hollow fibers in extractive fermentation could offer the following additional advantages over conventional extractive fermentation :

1- high membrane surface area per unit equipment volume eliminates the need to disperse the solvent .

2- the possibility of emulsion formation is eliminated , thus downstream separation problems and physical toxicity of the solvent to the yeast are avoided .

3- independent variation of solvent and aqueous feed rates is possible because of the separation of the two phases by the hollow fiber membrane with the result that loading , flooding and channeling are not a problem .

**Description of an HFEF :**

A schematic of the HFEF proposed by Fournier [I.18] for the production of ethanol appears in Figure 1 . The fermentation broth enters the HFEF shell and flows upwards as it ferments . Evolved carbon dioxide gas leaves the fermentor at the top . The extracting solvent also enters at the bottom and flows upward through a grid of vertical hollow fiber tubes assumed to be uniformly distributed across the shell space . As ethanol is produced from fermenting sugar it diffuses through the pores of the hollow fibers into the solvent .The continuous removal of ethanol from the aqueous phase into the solvent phase prevents end product inhibition and increases

volumetric productivity . Both solvent and aqueous phases leave at the top of the fermentor .

Flow of the aqueous and solvent phases is cocurrent since the highest sugar concentration and thus ethanol production rate is at the inlet of the fermentation broth . To prevent end product inhibition and thus reduced productivity , the extraction rate at the aqueous phase inlet must be maximized . This is achieved by introducing the solvent feed with zero ethanol concentration at the bottom to provide the maximum concentration driving force for the efficient removal of ethanol .

Figure 2 shows a closer look at the vicinity of the hollow fiber wall . The hollow fiber used in this study is manufactured by Celanese Corporation under the commercial name Celgard X-20 [I.19] . It has a porosity of 40 % with an average pore size of 0.03 microns and an outer diameter of 450 microns and a wall thickness of 25 microns. It is made from polypropylene and is resistant to acids , bases and most chemicals . The membrane is hydrophobic , thus water does not easily enter its pores while the solvent wets the membrane and can flow through its pores. A nominal higher pressure on the aqueous side will prevent the solvent from leaking to the aqueous phase and provide an interface within the hollow fibers where mass transfer can occur . A schematic of the proposed commercial scale HFEF design is shown in Figure 3.

**Results of Investigation :**

The correlations described below were obtained as a result of our investigation of the HFEF . We found that volumetric productivity is significantly influenced by fermentor yeast cell density while feed sugar concentration had a negligible effect . The solvent we used was TBP . We investigated the effect of using different TBP flowrates on volumetric

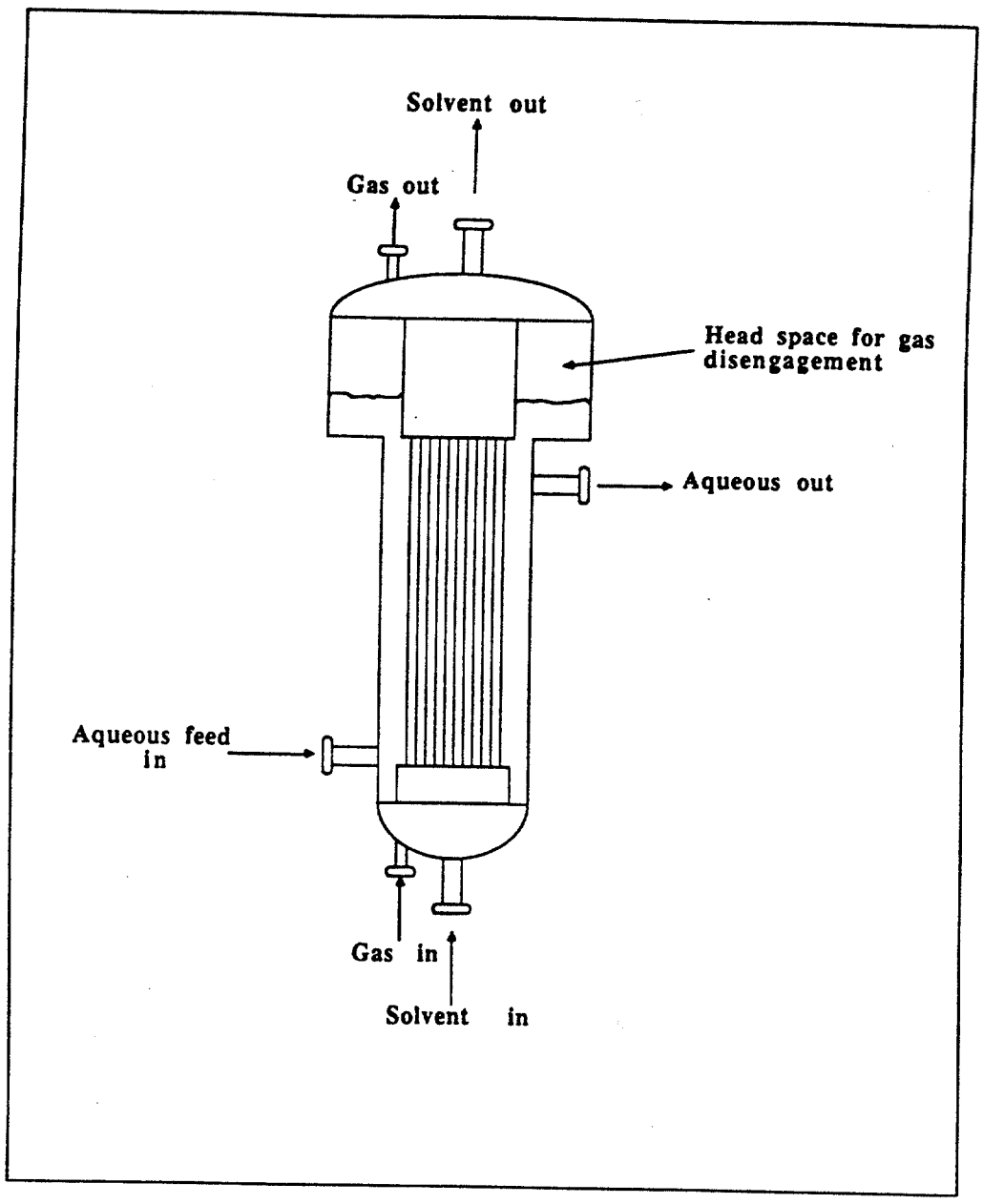


Figure 1. Illustration of a Hollow Fiber Extractive Fermentor . (CF.Ref.I.18)

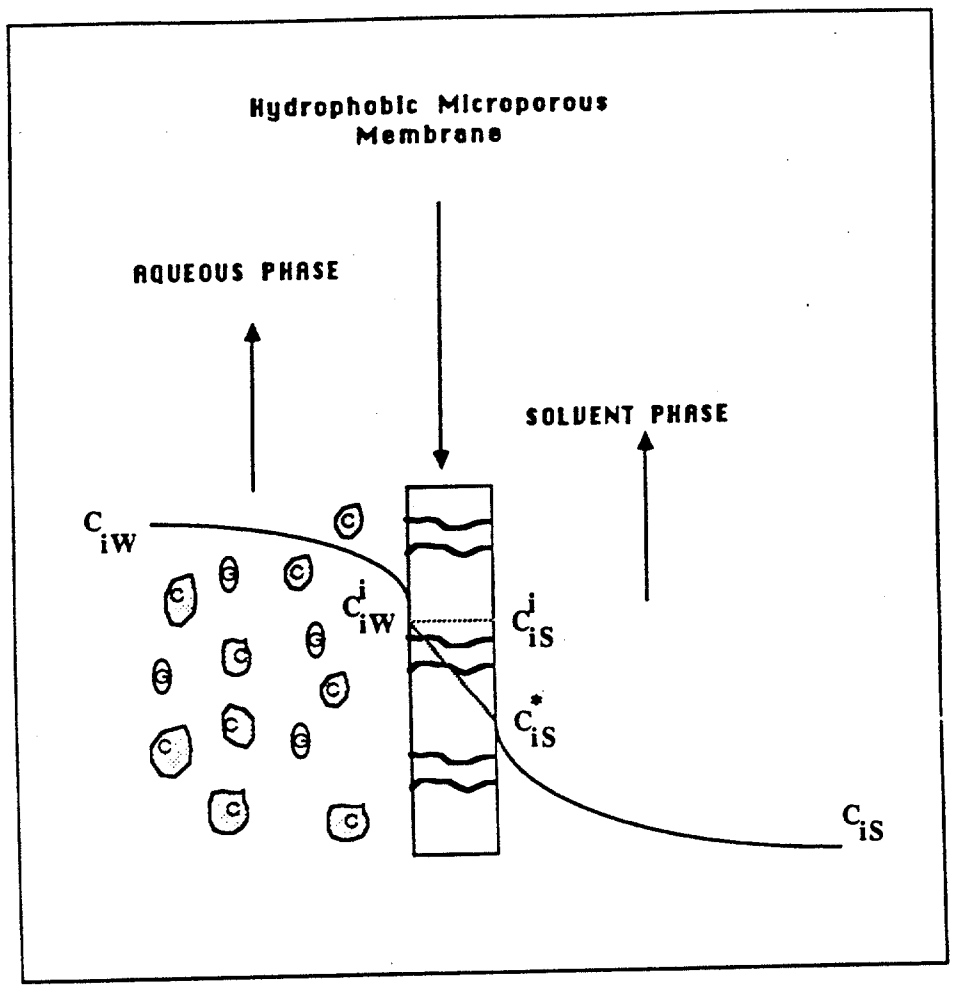


Figure 2 . Schematic of the solute concentration profiles in the vicinity of the hollow fiber membrane wall . G = gas , C = cells . (CF.Ref. I.18)

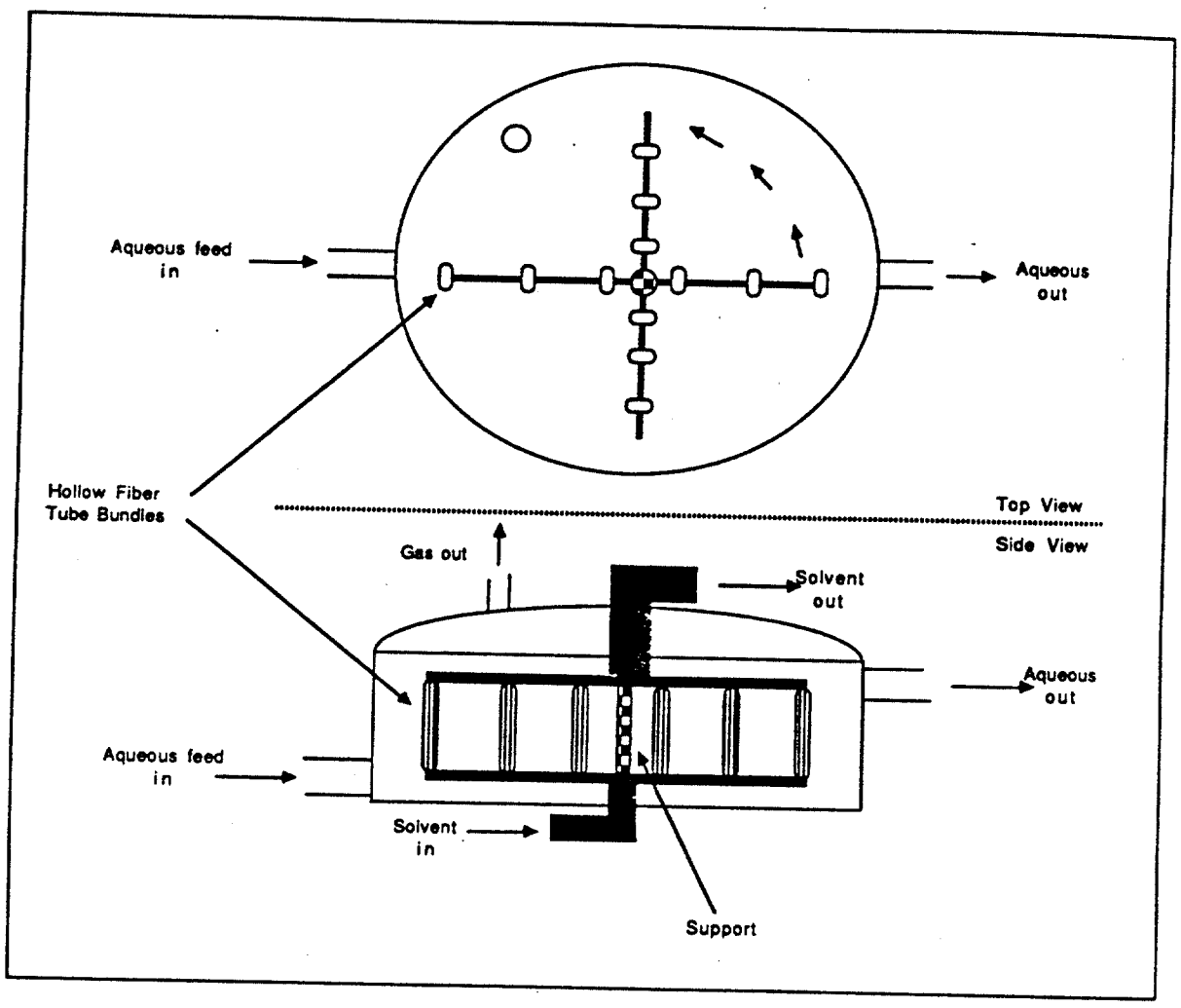


Figure 3. Schematic of the Proposed Commercial Scale HFEF Design .

productivity and found that increasing the ratio of solvent to aqueous feed flow improved productivity . However, we feel that this increase , though , is not significant enough to warrant use of high solvent flow rates and the resulting increase in costs associated with handling a larger TBP flow . The results presented here , therefore , are for a TBP flowrate that we feel will be the most economical to use for the production capacity of the proposed ethanol production facility . The equations presented below are valid at 30°C and atmospheric pressure.

TBP flowrate : 165000 Lb / hr

$Pe = 19.5 + 1.28\,X$

$Ces = 0.016 - 2.3 \times 10^{-5} X + 8.1 \times 10^{-4} Ws$

$Cws = 0.0266 - 0.5 \times 10^{-5} X - 0.52 \times 10^{-4} Ws$

$Cew = 0.0183 + 5.7 \times 10^{-5} X + 1.21 \times 10^{-3} Ws$

Where :

| | |
|---|---|
| X | Fermentor inlet yeast cell density [gram (dry weight) cells per liter] . |
| Ws | Weight percent sugar in feed to fermentor. |
| Pe | Fermentor volumetric productivity [grams ethanol produced per liter total fermentor volume ( shell and fibers )per hour] . |
| Ces | Exit concentration of ethanol in solvent phase [ Kg per liter] . |

Cws Exit concentration of water in solvent phase [ Kg per liter] .

Cew Exit concentration of ethanol in water phase [ Kg per liter] .

The following formula , which is based on the current hollow fiber cost of $4 per square foot of external fiber surface area can be used to estimate the total fiber cost for a given HFEF reactor volume :

$$C_f = 0.8\ V_r/R$$

Where :

$C_f$ total fiber cost [$] .

$V_r$ reactor volume in [$ft^3$] .

R hollow fiber outer radius [ft] .

The above discussion presents GW Chemicals current findings on the performance of HFEF contactors. We hope this information will prove useful in the economic evaluation of the proposed processes. [Figure 4 represents our thoughts on what the HFEF ethanol production plant might look like.]

Instructor Note: The following description may be removed if it is desired that the students develop the HFEF flowsheet on their own.

*Description of the HFEF Flowsheet*

Molasses is fed to the HFEF process as was the case for the CSTR fermentor process . This is mixed with recycled yeast cream and fed to the shell-side of the HFEF at a temperature of 30 °C . Recycled solvent also at 30 °C is passed through the fibers of the HFEF . Fermentation takes place and the ethanol and water laden solvent leaves the HFEF and is preheated in a heat integration exchanger , the solvent pre-heater cooler . The solvent is then fed to the solvent recovery tower where ethanol and water are separated from the solvent . The tower reboiler uses a DOWTHERM fluid heater system to achieve the high boiling point of the solvent . Relatively pure solvent (99.999 wt % ) at 289 °C is cooled down in the solvent pre-heater cooler to approximately 150 °C . The solvent cooler brings the temperature of the recycled solvent back to 30 °C where solvent loss is replenished and the solvent fed back to the HFEF .

Gas leaving the fermentor , mainly carbon dioxide with a small amount of air that is sparged into the fermentor to provide oxygen for the yeast cells , is assumed to leave in equilibrium with the aqueous phase thus providing an estimate of ethanol stripped by the gas . This ethanol is recovered from the gas by contact with water in an absorber . The aqueous phase leaving the HFEF is centrifuged and the supernatant is fed to the stripper for ethanol concentration . Part of the yeast cream from the centrifuge is recycled back as discussed above and the remaining part is dried to 50 wt % yeast product in a rotary dryer and stored . The superheated vapors from the dryer are used to generate steam and are then mixed with the centrifuge supernatant going to the stripper . The ethanol

water vapor leaving the stripper is combined with that leaving the solvent recovery tower and the resulting stream is fed to the vacuum distillation column where a 95 wt % azeotropic ethanol product is easily obtained.

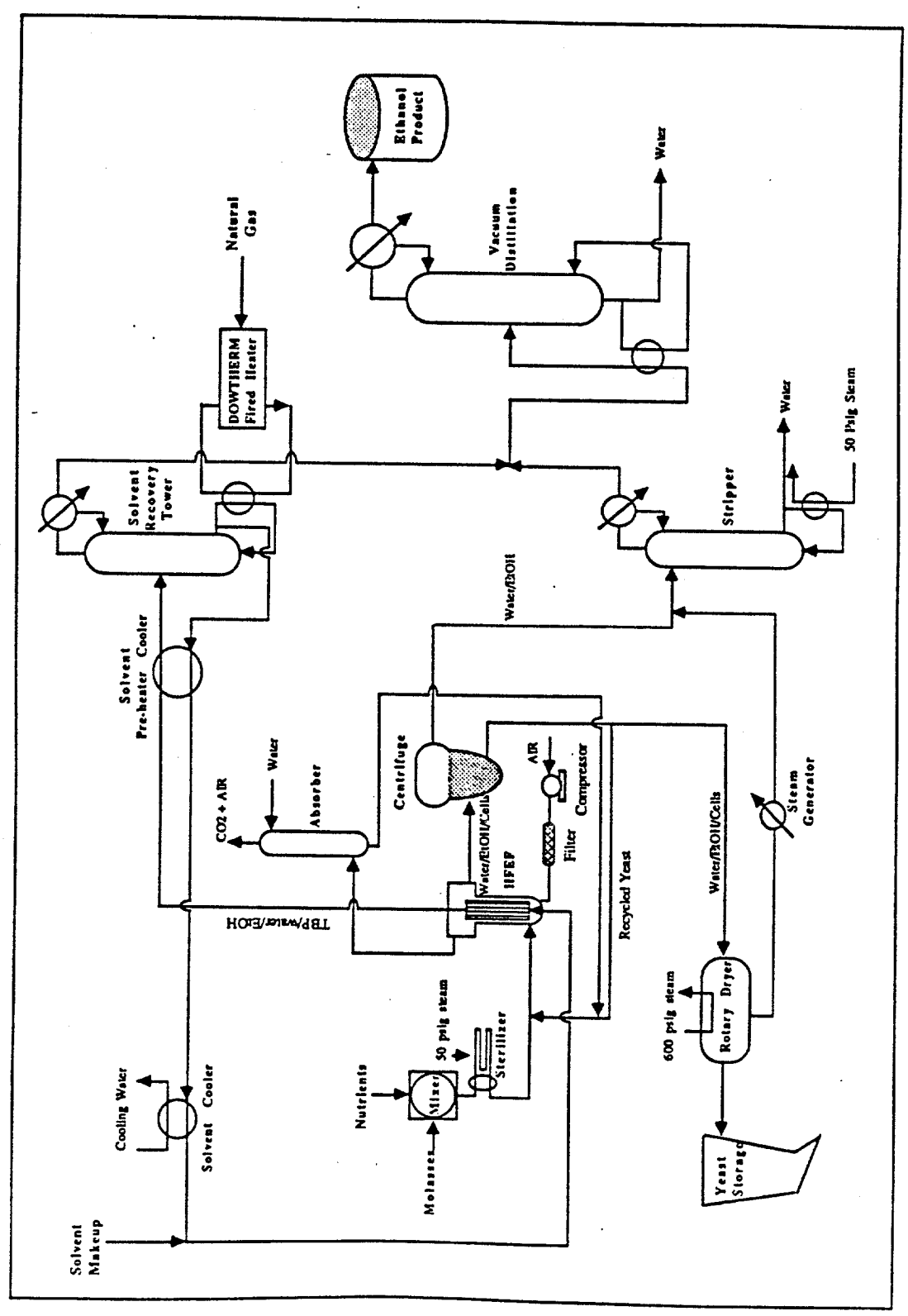


Figure 4. Flowsheet of the Process Using a HFEF to Produce Ethanol .

# SECTION II

# TEACHING AIDS

Note - This section contains material which is essential to the successful completion of the design. The instructor should decide how this material is to be presented or if the students should research it for themselves, given the necessary references.

## Generation of Preliminary Processes

The following factors can be used to stimulate discussion in class or within the groups on what must be considered in developing the process flowsheet.

The first step of the design process is to generate flowsheet alternatives. The major decision that must be made is whether to use a batch, CSTR, CSTR w/cell recycle, or HFEF fermentor. Fermentation costs can be a significant portion of the overall cost of the ethanol product. Other factors that should be considered or included in the flowsheet are the following:

1. dilution of the molasses feedstock with water to result in a SUGAR feed concentration that will not result in significant product inhibition and hence reduce fermentor productivity. Achieving optimal productivity of batch and CSTR fermentors typically require SUGAR Feed concentrations in the range of 10-16 wt %; because of ethanol removal, an extractive fermentor such as the HFEF, can handle feeds with A SUGAR concentration as high as 50 wt %. The students should investigate the effect of entering SUGAR concentration and cell density on the volumetric productivity and SUGAR conversion. The enclosed CSTR fermentor program and the discussion on ethanol production kinetics can be used to perform these calculations.

2. The feed to the fermentor must be sterile. This can easily be achieved by direct injection of 50 psig steam raising the feed temperature to 120°C followed by cooling to the fermentation temperature which is 30°C.

3. Oxygen must be supplied to the fermentor at a concentration less than saturation. The air is required to supply oxygen for certain metabolic processes not related to the anaerobic production of ethanol. This air must also be filtered to remove contamination.

4. The fermentation reaction generates a significant volume of carbon dioxide which will strip ethanol from the fermentor. The ethanol that is removed should be considered for recovery. This can easily be attained using a absorber with sterile water as the absorbent.

5. The product stream from the fermentor contains a significant quantity of

Note - This section contains material which is essential to the successful completion of the design. The instructor should decide how this material is to be presented or if the students should research it for themselves, given the necessary references.

yeast cells produced as part of the fermentation. These cells must be separated prior to the downstream concentration of the ethanol product. One approach is to use centrifuges (see attached brochures). All of the yeast cream from the centrifuge can be concentrated (consider the use of a steam heated rotary dryer) and dried to produce a by-product cattle feed or a portion of the yeast cream can be recycled to the fermentor to boost the fermentor cell density resulting in an increased fermentor volumetric productivity.

6. The supernatant from the centrifuge is a rather dilute solution of ethanol and water. The process water (steam) generated by the rotary dryer used to concentrate the yeast cream may also contain residual amounts of ethanol. This stream and the supernatant stream may be combined prior to ethanol concentration. One may want to consider the possibility of using a steam heated stripper to concentrate the ethanol prior to distillation.

7. Final concentration of ethanol to the azeotropic concentration of 95 wt% can be performed by distillation. The major design consideration at this point is whether to operate at atmospheric pressure or at reduced pressure. Since the azeotrope occurs at 95 wt % (89.43 mole % ethanol) at atmospheric pressure the choice is either an extractive distillation using a solvent such as benzene or operate at a pressure which is low enough that the azeotrope disappears. As the pressure is reduced, the relative volatility of ethanol increases and consequently, the ethanol azeotropic composition increases until, at some critical pressure, the azeotrope disappears. Vacuum operation allows one to produce a product of the normal atmospheric azeotropic composition in a single distillation step. The advantage of vacuum operation in this case is that the reflux may be reduced (due to the higher volatility) with a corresponding savings in energy.

This critical pressure can be found by a "straightforward back of the envelope calculation" which would be a good homework problem for the student. Given that the infinite dilution activity coefficient for water in ethanol is about 2.48 [II.12] it can be shown that the azeotrope just disappears at a pressure of 80 mm Hg and a temperature of 303°K.

*Solution:*

- at an azeotrope, $\alpha_{ew} = 1 = \gamma_e P^s_e / \gamma_w P^s_w$ , assuming an ideal gas

- let the critical pressure be defined where $X_e \rightarrow 1$, then $\gamma_e \rightarrow 1$ and $\gamma_w \rightarrow \gamma_w^\infty$

Note - This section contains material which is essential to the successful completion of the design. The instructor should decide how this material is to be presented or if the students should research it for themselves, given the necessary references.

• we then have the result that $\ln \gamma_w^{\infty} = \ln (P^s_e / P^s_w)$ which allows the temperature to be determined given the vapor pressure data

• knowing the temperature, we can then show that $P = P^s_e(T)$

8. For the process employing the HFEF and tri-n-butylphosphate (TBP) as the extraction solvent the following additional points must be considered. The solvent leaving the HFEF will contain at a low concentration (several wt %) the bulk of the ethanol produced in the HFEF. The ethanol can easily be separated from the TBP by distillation. The column energy usage can be significantly reduced by preheating the column feed with the nearly pure solvent product from the column bottoms. The column bottoms (TBP) can then be recycled to the HFEF for reuse. One might want to consider additional heat integration of this stream, for example, generating low pressure steam or operating reboilers for the distillation steps. The aqueous stream leaving the HFEF will once again go to a centrifuge and can be processed as discussed for the conventional cases.

Note - This section contains material which is essential to the successful completion of the design. The instructor should decide how this material is to be presented or if the students should research it for themselves, given the necessary references.

## Constants for the Modelling of Activity Coefficients

Design of the separation systems will require knowledge of the nonideal solution behavior of the streams containing 1-water, 2-ethanol, and 3-TBP. The NRTL Flowtran parameters for the possible binary interactions are:

| binary | $a_{ij}$ | $a_{ji}$ | $b_{ij}$ | $b_{ji}$ | $c_{ij} = c_{ji}$ |
|---|---|---|---|---|---|
| 1 & 2 | 0 | 0 | 783.67 | -111.93 | 0.286 |
| 1 & 3 | 0 | 0 | 2857.26 | 79.28 | 0.3 |

The constants for water and ethanol were obtained from Gmehling et. al.[II.12] whereas the constants for water and TBP are based on mutual solubility data. The ethanol and TBP binary were assumed to form a regular solution in the NRTL option of FLOWTRAN.

The corresponding Flowtran pair statements are as follows:

For TBP and Water.....PAIR 6 1 5 0 0 79.28 2857.26 0.3 0

For Ethanol and Water.....PAIR 2 1 5 0 0 -111.93 783.67 0.286 0

where the Flowtran component list is :

1- water
2- ethanol
3- carbon dioxide
4- yeast
5- sugar
6- TBP

Note - This section contains material which is essential to the successful completion of the design. The instructor should decide how this material is to be presented or if the students should research it for themselves, given the necessary references.

## The Kinetics of Ethanol Production by Fermentation

Conversion of sugars to ethanol is an anaerobic biological reaction catalyzed by yeast cells . Many commercially used yeasts are chemoheterotrophs , whose energy and carbon needs are satisfied by monosaccharides ( simple sugars ) such as glucose [II.1] (references are located at the end of the report). Disaccharides such as sucrose can also be utilized after hydrolysis by the yeast to a glucose and fructose mixture (invert sugar ) . A consequence of this hydrolysis is that the resulting fermentable solids are 105.26 % of the original sucrose solids [II.2] .

The fermentation reaction is as follows :

$$\text{GLUCOSE} + \text{NUTRIENTS} \xrightarrow{\text{CELLS}} \text{ETHANOL} + \text{CARBON DIOXIDE} + \text{CELLS} + \text{BY-PRODUCTS} + \text{ENERGY} \qquad (1)$$

Trace amounts of oxygen are also needed since it is one of the constituents of the cell mass produced. Nutrients refers to the other constituents of the cell mass , namely : nitrogen , phosphorus , sulfur , potassium , magnesium and trace minerals . Also required are the organic growth factors , for yeast these are mainly vitamins in addition to amino acids , purines and pyrimidines . By-products of the fermentation reaction are [II.3] glycerol , acetaldehyde , 2,3-butanediol , and acetic , butryic , formic , lactic and succinic acids . Table II.1 provides an example

| Product | mM product / 100 mM glucose |
|---|---|
| Ethanol | 177 |
| Carbon dioxide | 180.8 |
| 2-3-Butanediol | 0.48 |
| Glycerol | 6.6 |
| Acetic acid | 0.69 |
| Butryic acid | 0.32 |
| Formic acid | 0.42 |
| Lactic acid | 0.38 |
| Succinic acid | 0.26 |
| Acetaldehyde | 5.0 |

Table II.1. Products of the Alcoholic Fermentation of Glucose by Saccharomyces cerevisiae from Synthetic Media . (data from Ref. II.3)

Note - This section contains material which is essential to the successful completion of the design. The instructor should decide how this material is to be presented or if the students should research it for themselves, given the necessary references.

of typical yields of fermentation products .

Maiorella et al [II.4] present the following expression for the specific production rate of ethanol in grams per gram cell (dry basis) per hour . The constants are based on data obtained by Bazua and Wilke [II.5] @ 30°C for the yeast Saccharomyces cerevisiae (ATCC No. 4126) :

$$\nu = \nu_{max} \left[ \frac{C_{GW}}{C_m + C_{GW}} \right] \left[ 1 - \frac{C_{EW}}{C_{EWmax}} \right]^N \qquad (2)$$

Equation (2) is a generalization proposed by Levenspiel [II.6] of the Monod [II.7] equation . The first bracketed term is the standard Monod form representing the effect of the limiting substrate concentration , glucose in this case , on the production rate . The Monod constant , $C_m$ , is equal to 0.315 grams per liter . The maximum specific ethanol production rate ($\nu_{max}$) for Bazua's data is 1.85 grams ethanol per gram cell per hour . The second term represents the inhibitory effect of ethanol . $C_{EWmax}$ , the limiting ethanol concentration at which the specific ethanol production rate approaches zero , and N the the toxic power constant are both calculated quantities found using the procedure suggested by Levenspiel . For Bazua's data , $C_{EWmax}$ and N were calculated to be 87.5 gram per liter and 0.36 respectively . The experimental data from Bazua along with the correlation presented in equation (2) are shown in Figure II.1 . The production rate of ethanol rapidly approaches zero as $C_{EW}$ approaches $C_{EWmax}$ .

The cell growth rate , gram cells formed per gram cells per hour , is related to the specific ethanol production rate by the following :

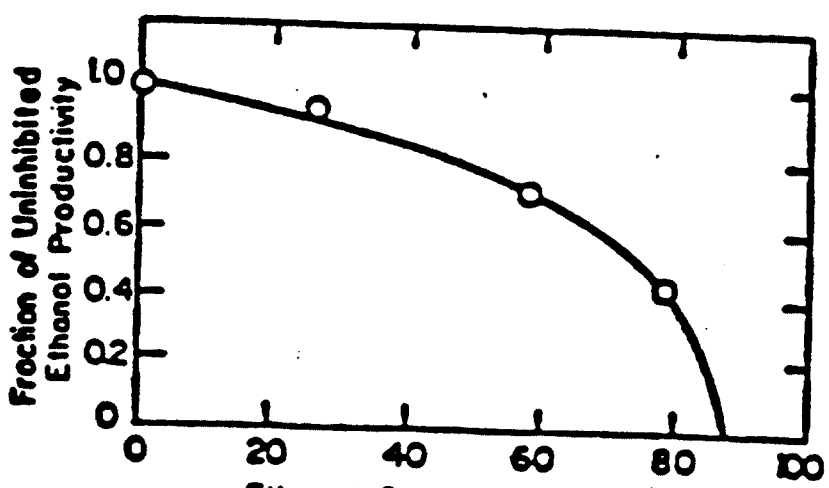


Figure II.1 Inhibitory Effect of Ethanol on Specific Ethanol Productivity by Saccharomyces cerevisiae.

Note - This section contains material which is essential to the successful completion of the design. The instructor should decide how this material is to be presented or if the students should research it for themselves, given the necessary references.

$$\mu = E\,\nu \qquad (3)$$

Where E is the efficiency of sugar utilization for cell production and is equal to 0.249 for Bazua's data.

The theoretical yield for the conversion of glucose to ethanol is given by :

1 gram glucose -----> 0.51 gram ethanol + 0.49 gram carbon dioxide (4)

The actual yield , however , is lower because some of the glucose is utilized in cell mass and by-product formation . The actual yield for ethanol is 0.434 gram ethanol per gram of glucose consumed . The yields for carbon dioxide and cell mass ( dry basis ) are 0.415 and 0.108 respectively .

The effect of by-products on fermentation kinetics was investigated by Maiorella et al [II.3] and the toxic concentrations for several of them were determined . The results show that for by-products such as formic and acetic acids , in concentrations below the toxic level , an increase in ethanol production and a decrease in cell production is observed . They suggest that this effect is due to interference with cell membrane phosphate transport requiring the cells to increase their metabolism to provide more energy in the form of ATP , and thus produce more ethanol . By-product inhibition is not normally observed unless the concentration of these products becomes appreciable due to the fermentation system used . In vacuum fermentation , for example , by-product inhibition is a problem because these products remain in the fermentation broth since they are less volatile than ethanol and water [II.8] .

Note - This section contains material which is essential to the successful completion of the design. The instructor should decide how this material is to be presented or if the students should research it for themselves, given the necessary references.

A similar effect to that of fermentation by-products was observed by Maiorella et al [II.9] for various salts (e.g. sodium chloride , potassium chloride , potassium phosphate , etc. ) present in commercial fermentation feeds such as molasses . Their effect would be pronounced only if the fermentation scheme used increases their concentration sufficiently as in vacuum fermentation or fermentation with water recycle .

In a preliminary study , only the effect of sugar substrate concentration and ethanol inhibition as given by equation (2) would be considered in modeling ethanol fermentation kinetics . By-product and sugar feed component effects can be neglected.

The kinetic expression presented earlier allows one to develop mathematical models of fermentor alternatives. Figures II.2-4 [II.4] summarize the expected performance of batch and continuous stirred tank fermentors (CSTF).

Figure II.2 illustrates for a batch fermentor the effect of feed glucose concentration on residence time and volumetric productivity (grams ethanol produced/fermentor volume/time). The fermentation was carried out to a residual glucose concentration of 2.8 g/L. Increasing the feed glucose concentration increases the fermentor cell density as well as the fermentor ethanol concentration. The increase in cell density initially balances the reduction in the specific productivity (grams ethanol/grams of cells/time) as a result of increased product inhibition at higher fermentor ethanol concentrations. Thus the volumetric productivity continues to increase with increasing inlet glucose concentration. However, at some critical glucose feed concentration, ethanol inhibition becomes much more pronounced and volumetric productivity starts to fall off until the ethanol

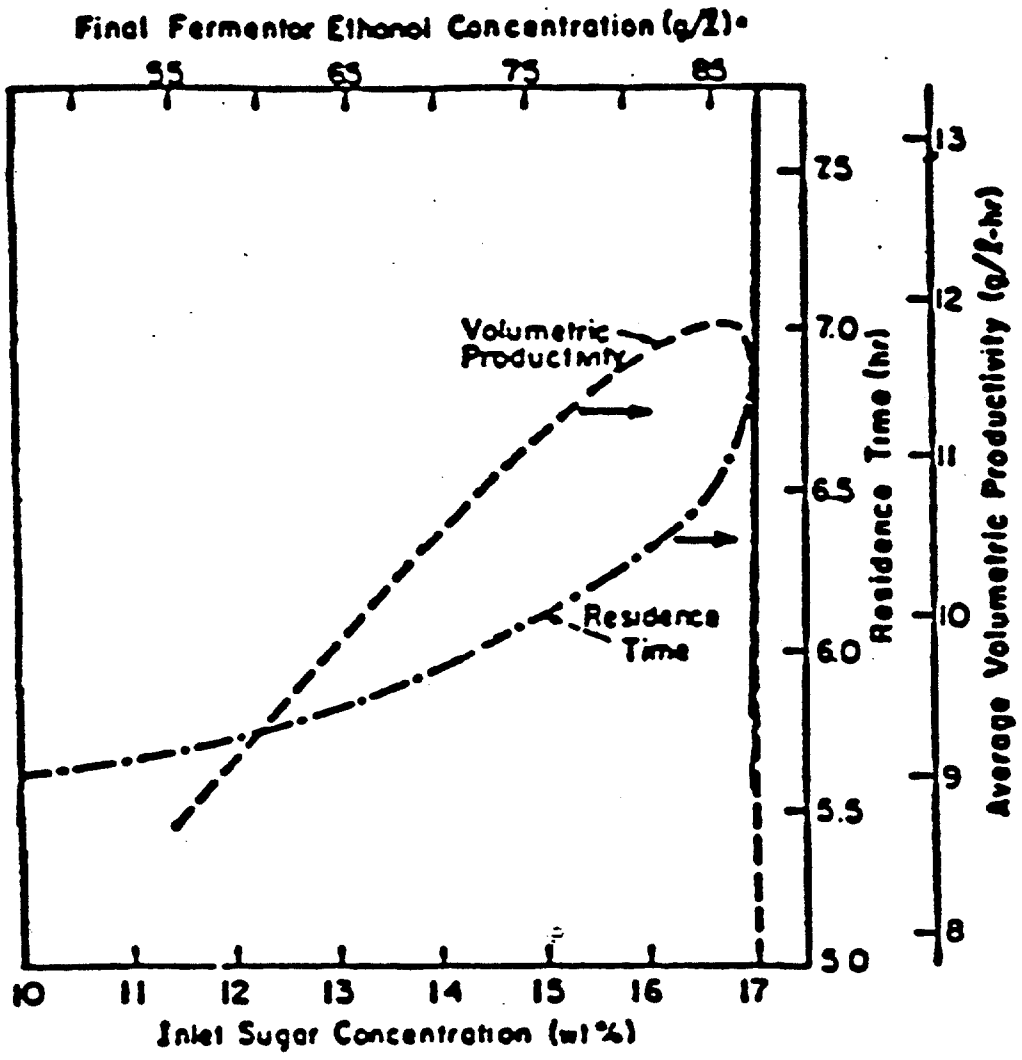


Figure II.2 Batch Fermentation Volumetric Productivity vs. Ethanol Product Concentration (reported in gEtOH/L water).

Note - This section contains material which is essential to the successful completion of the design. The instructor should decide how this material is to be presented or if the students should research it for themselves, given the necessary references.

concentration reaches 87.5 g/L where inhibition halts the fermentation. For the batch fermentor the maximum volumetric productivity is for a 16.7 wt % glucose feed for which the average volumetric productivity is nearly 12 g/L/hr. A 6.54 hour residence time is required to perform the batch fermentation under these conditions. This is illustrated in Figure II.3. An inoculum providing an initial cell density of 2.1 g/L and a initial ethanol concentration of 8.6 g/L was assumed.

Figure II.4 shows the effect of glucose feed concentration on the volumetric productivity of a continuous stirred tank fermentor. Once again the residual glucose concentration in the fermentor was 2.8 g/L. As in the batch fermentation there is an optimum volumetric productivity due to the tradeoff between higher cell densities at higher glucose feed concentrations and increased ethanol inhibition. The maximum volumetric productivity is about 16.5 g/L/hr at a feed glucose concentration of 13 wt %.

The effect of cell recycle on volumetric productivity for the CSTF can be investigated using the CSTF computer program which is described in the next section. Since higher cell densities can be maintained within the fermentor for a given feed glucose concentration the volumetric productivity will be increased in comparison to the case with no cell recycle. However, the increased volumetric productivity and resulting decrease in fermentor size and cost will be partially offset by the additional downstream cell separation and recycle costs.

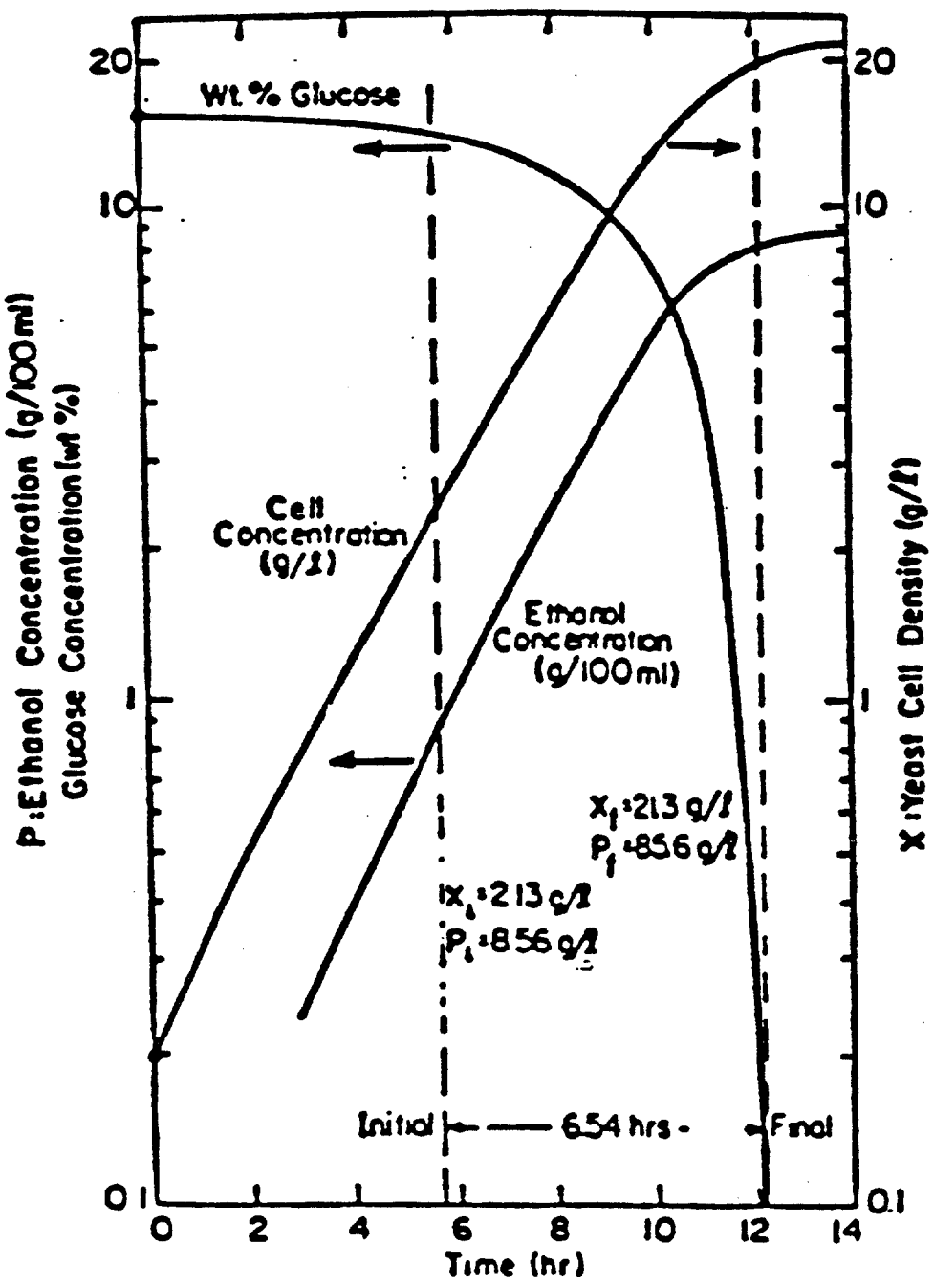


Figure II.3 Batch Fermentation Curve for Saccharomyces cerevisiae var. anamensis. 16.7 wt% Glucose Feed Concentration.

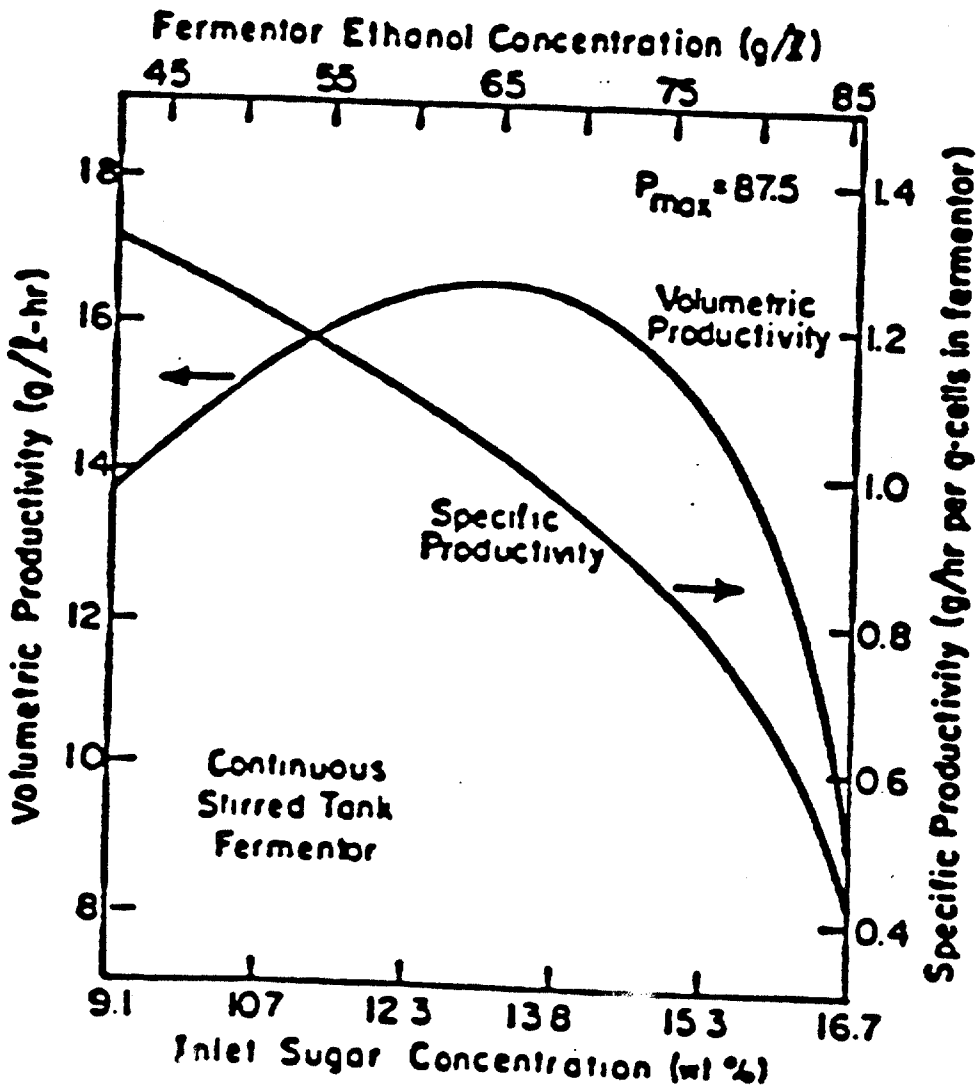


Figure II.4 Effect of Ethanol Product Concentration on Specific and Total Volumetric Productivity of a CSTF.

Instructor Note: For reactor sizing calculations, a BASIC program can be prepared to perform the work. The students should be able to develop a program of ths nature on their own.

## CSTR Fermentor Model

This development is taken from Bailey and Ollis [II.1] , page 382 . The computer program developed based on this can handle a feed with any cell density , sugar concentration and ethanol concentration . It will detect ethanol inhibition if it occurs . The program reads flowrates of various components , performs the fermentation reaction based on the kinetic model presented earlier and outputs fermentor size , volumetric productivity , dilution rate and product concentrations .

The following quantities are defined :

$X_0$ = inlet fermentor yeast cell density .

X = fermentor and exit yeast cell density .

F = volumetric flowrate through fermentor .

V = fermentor volume .

$\mu$ = Specific cell growth rate (kinetics constants valid at 30°C, 1atm).

D= F/V = dilution rate .

Using a mass balance on cells over the fermentor volume we have :

$$D X_0 = (D - \mu) X$$

from which :

$$D = F/V = \mu X / (X - X_0)$$

(1) by assuming a given sugar conversion , $\mu$ can be calculated from the kinetic expression for the fermentation reaction .

(2) final product yields and concentrations (including X) can be calculated from the known yield factors for the fermentation reaction .

(3) by calculating D and for a given volumetric flowrate, the fermentor volume can be calculated .

(4) from the mass of ethanol produced per time and the fermentor volume obtained the volumetric productivity is easily calculated .

A listing of the BASIC program written to simulate a CSTR fermentor appears on the following page. A disk is also provided with this Case Study.

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