Process Design and Economic Analysis of Bio-Butanol Process

K. Praveen Kumar

Roll No.: CH12M1003

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Department of Chemical Engineering

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Declaration

I declare that this written submission represents my ideas in my own words, and where others ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the Institute and can also evoke penal action from the sources that have thus not been properly cited, or from whom proper permission has not been taken when needed.

Praveen

(Signature)

(K. Praveen Kumar)

(CH12M1003)

Approval Sheet

This thesis entitled "Process Design and Economic Analysis of Bio-Butanol Process" by Mr. K. Praveen Kumar is approved for the degree of Master of Technology from IIT Hyderabad.

Dr. Saptarshi Majumdar
Department of Chemical Engineering
Indian Institute of Technology Hyderabad

Debaprasad Shee

Dr. Debaprasad Shee
Department of Chemical Engineering
Indian Institute of Technology Hyderabad

Dr. Sunil Kumar Maity
Department of Chemical Engineering
Indian Institute of Technology Hyderabad

Dr. Vinod Janardhanan
Department of Chemical Engineering
Indian Institute of Technology Hyderabad

For Dr. Raja Banerjee, Department of Mechanical Engineering
Indian Institute of Technology Hyderabad
Chairman

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Dedicated to

My Parents

Abstract

Owing to depletion of fossil fuels, increase in crude prices, and large scale environmental pollutions forced to shift current research focus on renewable resources like biomass for production of fuels and chemicals. The bio-butanol is one such alternative fuel for application in existing internal combustion engines that can be produced by fermentation of biomass. The bio-butanol provides an alternative to butanol produced from petrochemical pathways. Thus there is a need to develop the process for large scale production of bio-butanol from biomass in cost effective manner. The objective of the present study is to design processes to produce bio-butanol from various feedstock including sugarcane, corn, and lignocellulosic biomass using aspen plus. The economic estimation of fixed capital investment and production costs has been carried out for a plant capacity of 10,000 tonne per year butanol. The yield of 0.39 g ABE/g glucose with ABE solvents in the ratio 3:6:1 has been considered in entire analysis. It has been found that the fixed capital investment for corn as feedstock was much higher compared to sugarcane and lignocellulosic biomass. This is because of the additional pretreatment required to extract starch from corn and medium preparation. Byproduct credits for gases and chemicals are taken into consideration to calculate the production cost of butanol. For a yield of 0.39 g ABE/g glucose, the bio-butanol production cost was estimated as $1.04, $1.89, $1.42 for sugarcane, corn, and lignocellulosic biomass respectively. These costs are sensitive to changes in feedstock cost which can change the butanol price significantly.

Nomenclature

TPCC	Total Project Capital Cost
IRR	Internal Rate of Return
NPV	Net Present Value
N_{Re}	Reynolds number
$D_{i\ opt}$	Optimum inside pipe diameter
q_f	Fluid flow rate, ft^3/s
ρ	Fluid density, lb/ft^3
FCI	Fixed Capital Investment
TCI	Total Capital Investment
TPC	Total Product Cost

Contents

Chapter 1

Introduction

The diminution of fossil fuels and growing energy demand throughout the world and issues of global warming led researchers to look for alternative renewable resources to deliver energy adequately without significant emission of pollutants and greenhouse gases into earth atmosphere. So, the research has been focused on biomass that can be used as a raw material to produce bio-fuels and chemicals. The biomass could be proved as most promising renewable feedstock if technological advancement results cost-effective production on commercial scale.

1.1 Classification of bio-fuels

Based on the type of feedstock, bio-fuels can be classified into four different categories viz. first, second, third, and fourth generation bio-fuels as shown in Table 1.1. The first generation bio-fuels are made from feedstocks that compete with food crops. Second and third generation bio-fuels (also called the advanced bio-fuels) uses non-edible biomass to produce fuels and chemicals. Second generation bio-fuels use agricultural waste which mostly contain cellulose whereas third generation bio-fuel is made from algae known as algae fuel or oilgae. The fourth generation bio-fuel is based on the transformation of bio-diesel and vegetable oil into biogasoline [M.Fatih Demirbas et al., 2009].

1.2 Production history of bio-fuels

Production of bio-fuels from renewable sources is a traditional method from the past. Ethanol is being produced from sugarcane since 6000 BC and used as an intoxicating ingredient in alcoholic beverages. The ancient Egyptians produced alcohol from vegetable matter by fermentation [M.Fatih Demirbas et al., 2009]. The production of butanol by ABE fermentation was flourished in the early 20th century after Pasteur discovered butanol production from anaerobic cultivation in 1861. This has become the largest industrial fermentation process in the world next to ethanol. But this process declined by 1960 because of competition with petrochemical industry due to rise in feedstock cost. However in Russia and South Africa the process sustained because of low feedstock costs [Sang Yup Lee et al., 2008]. The butanol is used as a solvent in rubber industry and as a fuel. During 1924-1927 new plants for production of butanol from sugarcane molasses were established and the discovery of fermenting strains improved the production by 60%. By 1936 more butanol production plants were built in many countries which include India, Japan, Brazil, South Africa, Australia and USSR. In 1945, the ABE process was considered as the second largest bio-fuel industry next to ethanol as 66% of butanol and 10% of acetone in the world was produced by this process [P. Durre et al., 1998].

Today most of the butanol in the world is produced from petroleum by either oxo or adol processes [Brekke. K. et al., 2007]. During 1980-1990 extensive research was made on the solventogenic clostridia, a strain used in ABE fermentation for further development in fermentation characteristics [Ezeji TC et al., 2004]. Moreover the increasing demand to use renewable feedstock for production of fuels and chemicals along with innovative developments in biotechnology is creating a new interest to produce butanol via fermentation. Recent advances in genetic engineering and its application to solventogenic clostridia produced hyper-butanol producing strain [TC Ezeji et al., 2007]. Computational and experimental studies also improved fermentation techniques which resulted significant yield and recovery.

1.3 Characteristics of n-butanol

Butanol from plant sources is produced by fermentation and is commonly called as bio-butanol. Butanol from fossil fuels is petro-butanol. Butanol obtained from both sources has same chemical properties. Butanol has a wide range of applications in industry as a solvent and has high energy density and low hygroscopic nature than ethanol. Additionally butanol is less corrosive and offers more blending with gasoline compared to ethanol. The vapor pressure of butanol is 7.5 times less than ethanol which makes its transportation easily through existing pipelines. All these considerations make butanol a superior fuel than ethanol [Bohlmann et al., 2007].

Usages of bio-butanol

1. As a solvent in dyes, inks etc.
2. Used as raw material for preparing flotation aids such as butyl xanthate.
3. In pharmaceutical industries as an extractant.
4. As an additive in cleaning agents and in polishes.
5. In the textile industry as a solubilizer.
6. As an additive in engines along with gasoline.

1.4 Butanol as a fuel

Currently, bio-butanol is the most attracting fuel because of its superior fuel properties like low hygroscopic nature, high calorific value, and low vapor pressure compared to other bio-fuels [Manish Kumar et al., 2012]. Table 1.2 shows the comparison of bio-butanol to other fuels. The values of air fuel ratio and energy content of butanol are close to gasoline which allows high blending ratios with gasoline in existing engines. These considerations are making butanol to be used as a fuel more efficiently than ethanol. In contrary, few properties of butanol such as higher viscosity, high toxicity and lower octane rating are disadvantageous when compared to ethanol. Lower octane number fuel is more susceptible to knocking which will ultimately lead to low fuel efficiency and engine damage.

Table 1.1. Classification of bio-fuels.

Generation	Feedstock	Example
First generation bio-fuels	Sugar, starch, vegetable oils, or animal fats	Bioalcohols, vegetable oil, biodiesel, biosyngas, biogas
Second generation bio-fuels	Non-food crops, wheat straw, corn, wood, solid waste, energy crop	Bioalcohols, bio-oil, bio-DMF, biohydrogen, bio-Fischer–Tropsch diesel, wood diesel
Third generation bio-fuels	Algae	Vegetable oil, biodiesel
Fourth generation bio-fuels	Vegetable oil, biodiesel	Biogasoline

Table 1.2. Comparison of bio-butanol to other fuels

Properties	Bio-butanol	Bioethanol	Gasoline
Caloric value (MJ/l)	29.2	21.2	32.5
Air–fuel ratio	11.2	9	14.6
Heat of vaporization (MJ/kg)	0.43	0.92	0.36
Research octane number	96	129	91-99
Motor octane number	78	102	81-99
Solubility in water	Immiscible	Miscible	Immiscible

Chapter 2

Literature Review

2.1 Literature Review

This chapter deals with economic study done by previous researchers for production of bio-butanol from different feedstock. An economic assessment for the production of bio-butanol was made by Manish Kumar et al., 2012. The feedstock considered is both cellulosic and non-cellulosic. The butanol is produced by ABE (acetone-butanol-ethanol) fermentation and its recovery by distillation. The analysis showed that for glucose as feedstock the total fixed capital was 37% less compared to cellulosic feedstock and the production cost of butanol from glucose was four fold higher compared to sugarcane and cellulosic feedstock. Therefore, butanol production from sugarcane and cellulosic feedstock were found to be suitable with the production cost ranging $0.59-0.75 per kg butanol.

Qureshi et al., 2000 made economic assessment for butanol production from corn using clostridium beijerinckii BA101, a hyper butanol producing strain. The process is a batch fermentation followed by the recovery of solvents via distillation with total productivity of 0.38 g $L^{-1}h^{-1}$, ABE solvents. For a plant capacity of 150000 metric ton of ABE per year, the total equipment cost and total operating cost was estimated to be $\$33.2 \times 10^6$ and $\$109.56 \times 10^6$ respectively. Based on ABE yield of 0.42 and corn price of $71 per ton, the final production cost for butanol was estimated to be $0.55 per kg.

Economic comparison was made in Merwe et al., 2013, for three process designs for butanol production from sugarcane molasses. The first one is a batch fermentation followed by the recovery of solvents by steam stripping distillation, the second one utilizes liquid-liquid extraction process in place of distillation and the third process consisted fed batch fermentation and gas stripping with CO_2. According to their study, third process with a total capacity of 118800 ton/annum butanol was the cost effective process among the three designed and had the lowest

TPCC (Total Project Capital Cost) of $ 187 million. For this design the first order estimate of the TPCC was $190 m resulting in 36 % IRR and NPV of $960 million.

Marlatt et al., 1986 made an economic comparison between the fermentation process using corn as feedstock and an advanced petrochemical process known as oxo process which is the hydroformylation of propylene with hydrogen and carbon monoxide in the presence of rhodium as a catalyst. For a plant capacity of 200 MM lb/yr, the analysis revealed that the cost for fermentation was low (by ca. 5.96/1b) but the capital cost were higher compared to petrochemical process. Li et al., 2013 made a study on cocultures of clostridium beijerinckii and Clostridium tyrobutyricum in free-cell and immobilized-cell fermentation modes which enhance butanol production. This was performed in a fibrous-bed bioreactor (FBB) with cassava starch as feed. The butanol production was 6.66 g/L with a yield of 0.18 g/g and productivity of 0.96 g/L.h while the total ABE yield was 0.36 g/g which was the highest among all processes studied, which suggests that this continuous coculture mode may be suitable for industrial ABE production without any need of repeated sterilization and inoculation.

2.2 Objectives

The main objective of the study was to build a conceptual process design for bio-butanol production on a commercial scale from sugarcane, starchy, and lignocellulosic biomass, and its recovery using distillation. Evaluation of cost of production of butanol based conceptual process design for various feedstocks is another objective of the project. The specific objectives of the project are as follows.

- Complete depiction of process designs for production and its recovery of bio-butanol using aspen plus.
- The economics of the plants were calculated using the methods prescribed in standard textbooks.
- Comparing designs on the basis of fixed capital investment, operating costs, and final product cost.

Chapter 3

Methodology

The process parameters was estimated based on simulated process flow diagram using Aspen plus. The design for the whole process for this study was prepared through literature review and economic evaluation was done through the methods prescribed in standard book [Peter MS, Timmerhaus KD et al., 1991]. The overall process design and economic evaluation was carried out considering 10000 tonne per annum bio-butanol from various feedstock. Several costs involved in commercial plants like fixed capital investment, interest, depreciation, and other costs were also covered both qualitatively and quantitatively. Basic cost data were calculated from different cost correlations. The total cost data was expressed in dollars. The following section displays a brief elucidation to estimate the economic parameters. Figure 3.1 depicts process flow diagrams for production of butanol from various feedstocks (sugarcane, corn and lignocellulose).

3.1 Cost calculations

3.1.1 Estimating Equipment Costs by Scaling

When no cost data are available for a particular new piece of equipment its cost can be determined if the new equipment is similar to the existing one for which the cost data available by six-tenths factor rule.

$$\text{Cost of equip. A} = \text{cost of equip. B} * \left(\text{Capacity of equip A} \,|\, \text{Capacity of equip B}\right)^{0.6} \text{ --- [1]}$$

Typical scaling exponents can be obtained from standard reference book Peters and Timmerhaus (1991). As the prices may change with time due to change in economic conditions, the new costs must be updated such that the equivalent cost at the present time can be calculated. This can be done by the use of cost indexes.

Present cost = original cost × [index value at present time/index value at time original cost was obtained]

The Marshall and Swift all-industry and process-industry equipment indexes, the Engineering News-Record construction index, the Nelson-Farrar refinery construction index and the Chemical Engineering plant cost index are some of the indexes commonly used. Table 3.1 lists the index value for previous census.

3.2 Breakup cost Calculations

3.2.1 Size of Equipment

Costs for tanks and storage equipment are calculated based on the capacity vs cost graph given in Figure 3.2 or if the index value and the cost of old equipment is known then the cost can be estimated using eq. (1).

3.2.2 Cost of piping

The cost for piping covers labor, valves, fittings, pipe, supports, and other terms involved in the complete erection of all piping used directly in the process. Since process-plant piping can run as high as 80 percent of purchased-equipment cost or 20 percent of tied-capital investment, it is understandable that accuracy of the entire estimate can be seriously affected by the improper application of estimation techniques to this one component. Table 3.2 presents a rough estimate of the piping costs for various types of chemical processes. The accurate way to predict the piping costs based on flow rates can be calculated based on standard graph (diameter vs purchased cost) given in Figure 3.3. The optimum diameter can be calculated by the formulae for turbulent flow ($N_{Re} > 2100$) in steel pipes.

$$D_{i,\,opt} = 3.9\, q_f^{0.45}\, \rho^{0.13}$$

$D_{i\,opt}$ = optimum inside pipe diameter, in.

q_f = fluid flow rate, ft^3/s

ρ = fluid density, lb/ft^3

3.2.3 Electrical Installations

This costs primarily consists of electrical installation labor and this amounts to about 10-15% of total purchased equipment. This may be as high as 40% for specific process plants. As an overall estimation the electrical installation is taken as 3-10% of total fixed capital investment.

3.2.4 Land

The cost for land and the accompanying surveys and fees depends on the location of the property and may vary by a cost factor per acre as high as thirty to fifty between a rural district and a highly industrialized area. As a rough average, land costs for industrial plants amount to 4 to 8 percent of the purchased-equipment cost or 1 to 2 percent of the total capital investment.

3.2.5 Buildings (including services)

The cost for buildings including services consists of expenses for labor, materials, and supplies involved in the erection of all buildings connected with the plant. Costs for plumbing, heating, lighting, ventilation, and similar building services are included. The cost of buildings, including services for different types of process plants, is shown in Table 3.3 and 3.4 as a percentage of purchased equipment cost and fixed capital investment.

3.2.6 Purchased-Equipment Installation

The installation of equipment include labor costs, construction expenses and miscellaneous costs associated with the erection of the plant. Table 3.5 presents the values of installation cost expressed as percentage of purchased equipment cost for different types of equipment.

Table 3.1. Cost Index values [Peter MS, Timmerhaus KD et al., 1991]

Year	Marshall and Swift installed-equipment indexes, 1926 = 100 All-industry	Process-industry	Eng. News-Record construction index 1913 = 100	1949 = 100	1967 = 100	Nelson-Farrar refinery construction index, 1946 = 100	Chemical engineering plant cost index 1957-1959 = 100
1975	444	452	2412	464	207	576	182
1976	472	479	2401	503	224	616	192
1977	505	514	2576	540	241	653	204
1978	545	552	2776	582	259	701	219
1979	599	607	3003	630	281	757	239
1980	560	675	3237	679	303	823	261
1981	721	745	3535	741	330	904	297
1982	746	774	3825	802	357	977	314
1983	761	786	4066	852	380	1026	317
1984	780	806	4146	869	387	1061	323
1985	790	813	4195	879	392	1074	325
1986	798	817	4295	900	401	1090	318
1987	814	830	4406	924	412	1122	324
1988	852	870	4519	947	422	1165	343
1989	895	914	4606	965	429	1194	355
1990 (Jan.)	904†	924	4673	979	435	1203	356

Table 3.2. Piping costs.

Type of process plant	Percent of purchased-equipment			Percent of fixed-capital investment
	Material	Labor	Total	Total
Solid	9	7	16	4
Solid-fluid	17	14	31	7
fluid	36	30	66	13

Table 3.3. Cost of buildings and services as percentage of purchased-equipment cost.

Type of process plant	Percentage of purchased-equipment cost		
	New plant at new site	New unit at existing site	Expansion at an existing site
Solid	68	25	15
Solid-fluid	47	29	7
fluid	45	5-18	6

Table 3.4. Cost of buildings and services as percentage of fixed capital investment.

Type of process plant	Percentage of fixed capital investment		
	New plant at new site	New unit at existing site	Expansion at an existing site
Solid	18	1	4
Solid-fluid	12	7	2
fluid	10	2-4	2

Table 3.5. Installation cost as percentage of the purchased-equipment cost.

Type of equipment	Installation cost, %
Centrifugal separators	20-60
Compressors	30-60
Dryers	25-60
Evaporators	25-90
Filters	65-80
Heat exchangers	30-60
Mechanical crystallizers	30-60
Metal tanks	30-60
Mixers	20-40
Pumps	25-60
Towers	60-90
Vacuum crystallizers	40-70
Wood tanks	30-60

Figure 3.1. Schematic process flow diagram for production of butanol [Manish Kumar et al., 2012].

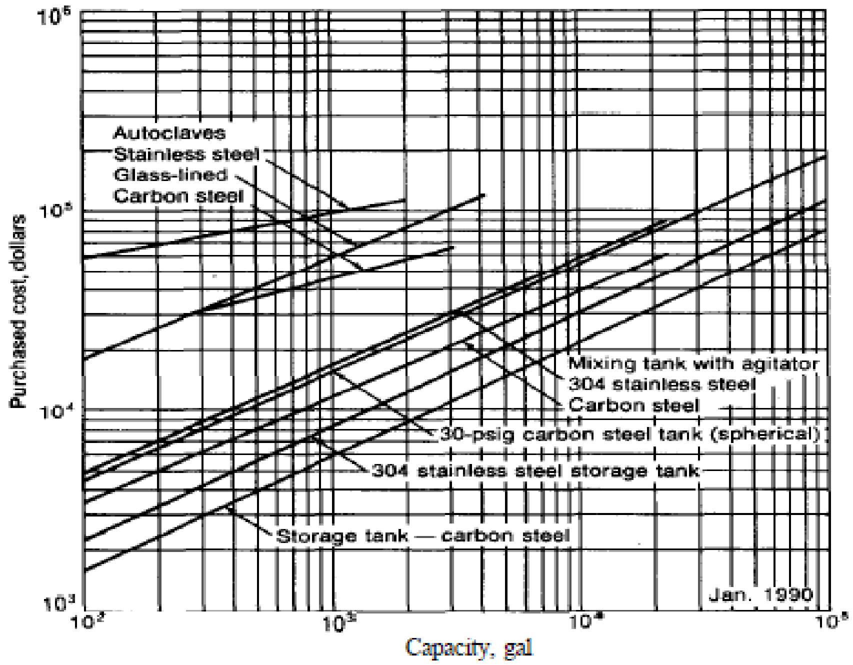


Figure 3.2. Cost vs Capacity graph [Peter MS, Timmerhaus KD et al., 1991].

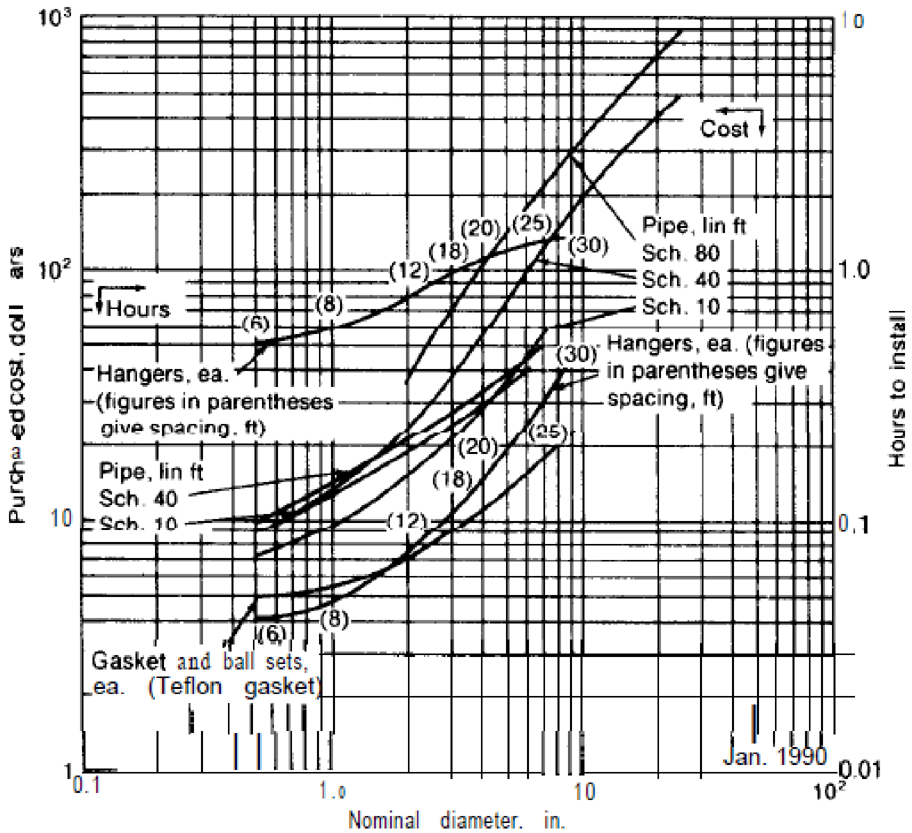


Figure 3.3. Diameter vs Purchased cost ($) [Peter MS, Timmerhaus KD et al., 1991].

Chapter 4

Economic Analysis

4.1 Process Overview

It was depicted as a plant designed to produce 10000 tonne/year of bio-butanol from sugarcane, starch, and lignocellulosic biomass. The cost of raw materials are presented in Table 4.1. The process followed in this study comprise the following steps:

1. Sugar extraction from feedstock
2. Removal of solids from sugar solution
3. Saccharification of sugars to glucose.
4. Fermentation of glucose to ABE (Acetone, Butanol, Ethanol).
5. Separation and purification of the obtained products.

It was assumed that all the facilities are available at the plant site itself and no transportation as well as product storage costs are included in this study. The credits of by-products have been included to enhance the overall production cost. Using the arrangement of the equipment shown in Figure.4.1, Figure.4.2 and Figure.4.3 mass balances for the proposed process design has been calculated in aspen plus.

4.2 Sugarcane to n-butanol

Feedstock Composition**.** The composition of sugarcane varies significantly from place to place and as illustrated in Table 4.2 [Manish Kumar et al., 2012]. It was assumed that composition of sugarcane is fixed and was assumed to contain only sucrose, water and solids for Aspen simulation due to nonexistence of properties in aspen data bank.

Process Description. The following section pronounces in detail the process steps to convert sugarcane extract to butanol. The process was designated as a batch fermentation of sugarcane solution by clostridium species and recovery of products using distillation. The overall design of the process was simulated using aspen plus shown in Figure 4.1 and the summary of material balance is shown in step 3. The following assumptions were made for the process design.

1. Yield of 0.39 g/g ABE was assumed.
2. The plant was assumed to be in operation 300 days per year.
3. The fermentation time (including turnaround) was assumed to be 80 hr.
4. No losses were considered for any type of process.

Step 1-Pretreatment: In this step sugarcane was mechanically crushed using a crusher for extraction of juice and the bagasse which is the byproduct of this step was separated prior sending to the screen filter where intermediate solids are removed. Subsequently the sugar solution was pumped to a mixer where lime is added to maintain the pH of the solution around 6-7 and the precipitate formed during the process is removed as sludge using a centrifuge. The clarified solution containing 15.6 wt% sucrose was sent to hydrolysis tank where water at equivalent moles of sucrose and nutrient at 0.04g/L was added to convert the sugar to glucose. Consequently the resulting glucose solution was pumped to the mixing tank where water was added to make the final glucose concentration to 20 g/L.

Step 2-Fermentation: In this section the diluted glucose solution (60 g/L) was fermented to produce acetone, butanol and ethanol. The process was generally a batch process where clostridium acetobutylicum was used as a biocatalyst and the fermentation time assumed was 72 hr at a temperature of 35^{0}C [N. Qureshi et al., 2001]. The reaction was assumed to take place according to the stoichiometry given below.

$$95C_6H_{12}O_6 \rightarrow 60C_4H_9OH + 30CH_3COCH_3 + 10C_2H_5OH + 220CO_2 + 120H_2 + 30H_2O$$

The fermentation broth containing ABE and water (96.2 wt%) water was sent to a flash column to separate butanol and water prior sending to another distillation. The off gases resulting from fermentation has a mole flow of 1.26 mol H_2/mole glucose and 2.31 mole CO_2/mole glucose and are collected at the top of the flash column which will additionally add economic value to the overall design.

Step 3- Separation of solvents: In this section total seven distillation columns and a flash column was used for the effective recovery of solvents from the fermentation broth (refer to Figure 4.4). The fermentation product from the flash column was sent to the first distillation column (DC1) where most of the water, solids and other impurities are removed. This column operates at 1 atm pressure and has total 29 number of stages of with feed stage at 3, a reflux ratio of 0.2 and distillate to feed ratio (D/F) of 0.02. The top product has a total flow rate of 2.65 tonne/hr with mass fractions 0.431, 0.162, 0.054, 0.353 of butanol, acetone, ethanol and water respectively. The bottom product has a total mass flow rate of 68.82 tonne/hr with almost 98.65 wt % of water removed from feed and only traces of ABE is lost in this column.

The overhead stream from DC1 column was pumped to DC2 column where acetone at 99.9 wt% is recovered as top product along with traces of butanol, ethanol and water. This column operates at 1 atm pressure and has total of 64 number of stages of with feed stage at 53, a reflux ratio of 4.3 and distillate to feed ratio of 0.1035. The top product has a total flow rate of 0.45 tonne/hr with mass fractions 0, 0.942, 0.05, 0.008 of butanol, acetone, ethanol and water respectively. The final acetone stream has a mass flow rate of 0.45 tonne/hr. The bottom product has a total mass flow rate of 2.19 tonne/hr with significant amounts of butanol, ethanol and water.

Subsequently the bottoms from DC2 column (B2) was pumped to DC3 column where the main objective was to separate ethanol and butanol along with water containing in both the distillate as well as bottom stream. This column operates at operates at 1 atm pressure and has a total of 35 stages with feed stage at 3, reflux ratio of 12.9 and distillate to feed ratio of 0.064. The total mass flow rates of distillate and bottom stream are 0.16 and 2.03 tonne/hr respectively.

The distillate from DC3 containing ethanol and water is sent to azeotropic distillation (DC6) where ethylene glycol was used as an entrainer and most of the ethanol was recovered as distillate. The column operates at 1 atm with 15 stages having feed stage at 10 and entrainer stage at 3. Reflux ratio was set at 1.5 with distillate to feed ratio 0.305. Only 38.7 wt% of ethanol produced during fermentation was recovered owing to small amounts of ethanol produced compared to other solvents. The ethanol was recovered as distillate has a total final mass flow rate of 0.055 tonne/hr with 92.8 wt% purity.

The bottom stream from DC6 was sent to another distillation column DC7 with the aim to recover ethylene glycol as bottom product and recycle as entrainer to DC6. The column operates at ambient conditions with total 18 stages having feed stage at 8 and reflux ratio of 0.8. 99.3 wt% of ethylene glycol is recovered.

The bottom stream from DC3 containing butanol and water was sent to a flash column where it operates at ambient conditions to remove excess water. The downstream (SL1) was a mixture of water and butanol which was rich in water was sent to another distillation column DC4 in order to recover maximum possible amount of butanol. The column DC4 operates at 1 atm pressure and has 10 stages with feed stage at 2, a reflux ratio of 0.1 and distillate to feed ratio of 0.8. The distillate stream having total mass flow rate of 0.293 tonne/hr with 0.295 wt% was again fed to the flash column whereas the bottom product was almost water containing traces of butanol.

The intermediate stream from flash (SL1) rich in butanol having 0.829 wt% was pumped to the distillation column DC5 where it operates at 1 atm having 15 stages with feed stage 2, reflux ratio of 0.1 and the final butanol stream was recovered as bottom product with a flow rate of 1.13 tonne/hr with a purity of 99.99 wt%. 99.12 wt% of the butanol produced from fermentation is recovered as the final product. The distillate of column DC5 containing significant amount of butanol with 0.63 wt% was fed back to the flash to recover butanol. Table 4.9 refers to mass flow rate of solvents in each distillation column.

4.3 Corn to n-butanol

Feedstock Composition. The same assumptions are considered as in section 4.2 and it was assumed that the composition of corn is fixed and was assumed to contain starch, oil, fiber and water for aspen simulation. The composition in wt % is illustrated in Table 4.3 [N. Qureshi et al., 2001].

Process description. Corn wet milling process was used in the corn milling section of the plant. In this process the corn was soaked in water at 50^0 C followed by grinding, sieving and centrifugation. The sieving resulted in the removal of fiber while centrifugation in the removal of gluten. Batch fermentation was used in the process. The clarified solution was pumped to the saccharification tank followed by fermentation. The fermentation and separation of solvents was similar as that referred in section 4.2. Medium and fermentation process used by Parekh et al., 1999 was used for butanol production.

Preparation of medium. The glucose/CSW (Corn Steep Water) medium used contained 6% glucose (w/v), 1.6% CSW solids (w/v), 0.1% cysteine hydro-chloride (w/v), and 0.0012% $FeSO_4.7H_2O$ (w/v). CSW contains micro-nutrients such as vitamins and metal salts that may be required for growth of C. beijerinckii strains. For preparation of CSW medium, 10% solids CSW was pretreated as follows.

i. To raw CSW (pH-4.2), cysteine-HCl was added followed by adjustment of pH to 6.8 using NaOH.
ii. The CSW was left overnight at 0^0C and was centrifuged the following day at 27500xg for 60 min at 4^0C.
iii. The clear supernatant obtained after centrifugation was filter-sterilized through a series of filters.
iv. The clear CSW was diluted with distilled water to achieve the desired concentration.
v. The medium was inoculated with 5% (v/v) inoculum and was continuously bubbled with 50 ml/min of N_2.

vi. This was added to the fermentor containing glucose and $FeSO_4.7H_2O$.

4.4 Lignocellulosic biomass to n-butanol

Feed stock composition. The similar assumptions are considered as in section 4.2 and it was presumed that the composition of lignocellulosic biomass was fixed and is assumed to contain only cellulose, hemicellulose and lignin for aspen simulation. The composition in wt % is illustrated in Table 4.4 [Carolina Conde Meijiaa et al., 2012].

Process description. The detailed description of the whole process is elucidated in four steps.

Step 1- LHW (Liquid Hot Water) pretreatment: In this section treating the lignocellulose biomass with hot water was considered which converts most of the hemicellulose to soluble sugars mainly xylan, arabinose, mannose and a small extent of cellulose to glucose. The reactor operates at 190^0C temperature and 14 atm pressure. Because of high temperature of the process some of the lignin was solubilized which bare some portion of cellulose for further hydrolysis. The pretreatment conditions and the reactions are summarized in Table 4.5 and 4.6. Apart from xylose, furfural is formed by degradation of xylan and acetic acid was liberated from hydrolysis of hemicellulose.

Step 2- Saccharification or hydrolysis: In this step the exiting stream from LHW process was cooled to 50^0C and 1 atm where a major portion of the cellulose was converted to glucose and xylan to xylose. Consequently the hydrolysate was sieved to remove solids and the resulting glucose solution was pumped to the mixing tank where water was added to make the final glucose concentration to 20 g/L. The reactions taking place in hydrolysis reactor are summarized in Table 4.7.

Step 3-Fermentation: The fermentation was same as that referred in section 4.2 step 2 and the conditions in the fermentor are given in Table 4.8.

Step 4-Separation of solvents: Refer to section 4.2 step 3.

4.5 Process Economic Analysis

Table 4.10 (a), (b), (c), (d) gives the information pertaining to fixed capital cost ($), operating cost, product cost for a 10,000 tonne per annum butanol plant for varied feedstock.

Sizing and Equipment costs. Sizing of equipment was calculated manually **(section 3)** according to mass balances and the costs have been calculated using methods prescribed in standard textbook [Peter MS, Timmerhaus KD et al., 1991]. The graphs provide information of purchased equipment cost as a function of capacity and it assistances in sizing of the equipment. The equations for predicting the size of the equipment has been discussed in section 3. The material of construction for general equipment is assumed to be made of carbon steel and for tanks involving chemical reactions is assumed to be made of SS. Lang factor of 4.1 has been used to calculate the fixed capital investment and 4.9 for total capital investment [Peter MS, Timmerhaus KD et al., 1991]. This cost takes into consideration all the purchased equipment, its installation as well as piping, instrumentation, electricity etc.

Total production costs. The total Production is a combination of several costs as listed below.

1. Direct Production cost

i. Raw material cost
ii. Operating labor & Supervision
iii. Electricity
iv. Maintenance & Repairs
v. Laboratory charges
vi. Chemicals
vii. Utilities

2. ***Fixed charges***
    i. Depreciation
    ii. Taxes
    iii. Insurance
    iv. Rent
3. ***Plant overhead costs***
    i. Safety and protection
    ii. Storage facilities
4. ***Administrative Expenses***
    i. Executive salaries
    ii. Office Maintenance
    iii. Communications
5. ***Interest***
6. ***Research & Development***

Direct Production cost [Peter MS, Timmerhaus KD et al., 1991**].**

- *Raw material*: This cost has been calculated according to the sugarcane market price @Rs.2500/ton. The required amount of sugarcane needed was calculated as per the material balance.
- *Operating labor:* This cost has been assumed to be 100000$/yr.
- *Electricity:* This cost was assumed to be 3.5% of fixed capital investment.
- *Maintenance & repairs:* This cost was assumed to be 6% of fixed capital investment
- *Laboratory:* This cost was assumed to be 15% of operating labor.
- *Wastewater treatment:* It was assumed that the plant discharges 5000 gal/day of waste water and this cost was depicted from standard textbook.

Fixed charges

- *Depreciation:* This cost was assumed to be 10% of total capital investment.
- *Taxes:* This cost was assumed to be 4% of fixed capital investment.
- *Insurance:* This cost was assumed to be 1% of fixed capital investment.
- *Interest:* This cost was assumed to be 14% of total capital investment

Other Expenses

- *Administrative costs:* This was assumed to be 4% of total product cost
- *Research & Development:* This was assumed to be 5% of total product cost

Net production cost. It was assumed that the byproducts will also add values to the overall economics of the plant. Assumptions made to evaluate the economics of the plant.

1. All the costs are calculated in $ (@ Rs.60/$)
2. Material of construction for all storage tanks are considered to be made of carbon steel.
3. Material of construction for all other tanks and equipment are considered to be made of stainless steel.
4. Raw material cost was assumed to be Rs. 2500/ton as per local market survey.
5. Straight line method has been considered for calculating depreciation.
6. Baggase cost was considered to be Rs. 450/ton as per local market survey.
7. Working volume of fermentor tanks has been considered as 80%.
8. The plant was assumed to be in operation 300 days per year.
9. The fermentation time (including turnaround) has been assumed to be 80 hr.
10. No losses has been considered for any type of process.
11. Lang factor of 4.1 has been assumed for calculating the fixed capital investment (FCI) and 4.9 for Total capital investment (TCI).
12. Generation of 5000 gal/day of waste water has been assumed.
13. Yield of 0.39 g/g ABE was assumed.
14. Mixing was assumed only in lime treatment and mixer tank.
15. ABE recovery from fermentation broth- 98%.
16. Life of the plant was assumed to be 20 years.
17. Table 4.11 gives the costs that has been assumed as percentage of FCI/TCI/Total Product Cost (TPC)

Table 4.1. Raw material cost

Feedstock Price	$/ton
Sugarcane	41.66
Corn	214
Lignocellulose biomass	35

Table 4.2. Sugarcane composition

Composition of Sugarcane	wt. %
Sucrose	13.3
Cellulose	4.77
Hemicellulose	4.53
Lignin	2.62
Water	71.57
Reducing Sugar	0.62
Minerals	0.2
Impurities	1.79
Dirt	0.6
Total	**100**

Table 4.3. Corn composition

Composition of Corn	wt. %
Starch	75
Oil	4.5
Water	13.5
Fiber, Protein, ash	7

Table 4.4. Lignocellulose biomass composition

Composition of lignocellulosic biomass	wt. %
Cellulose	40
Hemicellulose	27
Lignin	23
Others	10

Table 4.5. LHW pretreatment conditions

Pretreatment conditions	
Temperature	190^0C
Pressure	14 atm
Duration	2-3 min

Table 4.6. LHW pretreatment reactions and conversions

Rxn No.	Stoichiometry	% conversion
1.	Cellulose + Water → Glucose	4.1
2.	Xylan + Water → Xylose	61.4
3.	Xylan → Furfural + 2Water	5.1
4.	Xylan +Water→2.5Acetic acid	9.2

Table 4.7. LHW hydrolysis reactions and conversions

Rxn No.	Stoichiometry	% conversion
1.	Cellulose + Water → Glucose	55.8
2.	Xylan + Water → Xylose	40.6

Table 4.8. Fermentation conditions

Temperature	38^0C
Pressure	1atm
Duration	72 hr

Table 4.9. Design specifications of distillation columns.

	DC1	DC2	DC3	DC4	DC5	DC6	DC7
Number of Stages	29	64	35	10	15	15	18
Feed stage	3	53	13	2	2	(6)-10; (8)-3	8
Reflux ratio	0.2	4.3	12.9	0.1	0.1	1.5	0.8
Distillate-to-feed mole ratio	0.02	0.103	0.064	0.8	0.35	0.305	0.13
Feed mass flow rate, kg/h							
A	428.84	428.84	0.42	0	0	0.42	0.002
B	1143.59	1143.59	1143.59	86.65	1770.22	10.67	10.656
E	142.94	142.77	119.96	3.64	11.46	119.67	64.37
W	69759	937.72	934.16	1106.46	352.72	31.06	27.27
EG	0	0	0	0	0	10.86	10.82
Distillate mass flow rate, kg/h							
A	428.84	428.42	0.422	0	0	0.42	0.002
B	1143.59	0	10.67	86.58	637.37	0.014	0.073
E	142.77	22.8	119.67	3.53	11.29	55.29	14.17
W	937.72	3.559	31.06	203.28	352.80	3.79	2
EG	0	0	0	0	0	0.04	0
Bottom mass flow rate, kg/h							
A	0	0.42	0	0	0	0.002	0
B	0	1143.59	1132.92	0	1133.98	10.656	10.58
E	0.175	119.96	0.29	0	0	64.37	50.20
W	68821.29	934.16	903.09	903	0	27.27	25.27
EG	0	0	0	0	0	10.82	10.82

Table 4.10 (a). Fixed capital investment ($)

Feedstock	**Sugarcane**	**Corn**	**Lignocellulose**
Steeping tank	-	2966564	-
Wet Grinding	-	1500000	-
Fermentors (6-each 500 m^3)	121330	121330	121330
Pretreatment tank	-	-	242660
Crusher	25000	-	150000
Filter	15000	10000	20000
Lime Treatment tank (2*500 m^3)	13481.11	-	13481.11
Medium preparation tank	-	2022	-
Centrifuge	63450	120000	95175
Mixing tank (2*500 m^3)	13481.11	-	13481.11
Distillation columns (7)	265405	265405	265405
Boilers (7)	114124	114124	114124
Heat Exchangers	113750	113750	113750
Storage Tanks	12133	12133	12133
Pumps (8)	2022	2022	2022
Pumps for process (5)	305000	305000	305000
Total Equipment Cost ($)	**1064176**	**5487350**	**1455080**

Table 4.10 (b). Total operating costs ($)

Feedstock	**Sugarcane**	**Corn**	**Lignocellulose**
Raw Material	11437536.48	11958687	5212200
Operating labor (assumed/yr)	100000	100000	150000
Executive employee (assumed)	15500	15500	15500
Steam	248000	-	9292608
Electricity (3.5% FCI)	152709.2879	787434	208804
Process water	335385.4063	923100	424876
Waste water Treatment	70000	70000	100000
Maintenance & Repairs (6% FCI)	261787.3507	1349888	357949.7
Operating supply (6% FCI)	261787.3507	1349888	357949.7
laboratory (15% Operating labor)	15000	15000	15000
Chemicals	294480	2100	294480
Enzyme	3359216	3359216	3359216
Total	**16551401.87**	**19930814**	**19788584**
Indirect costs			
Insurance	43631.22	157486	59658.28
Taxes	174524.90	449962	238633.1
Interest	730024.88	1344401	998185
Depreciation	521446.34	274367	71298.3
Total	**1469627.36**	**2226218**	**2009466**
Other Expenses			
Administration	51600	51600	51600
Distribution and selling costs	129000	129000	129000
R & D	64500	64500	64500
Total	**245100**	**245100**	**245100**
Total Operating Cost($)	**18266129**	**22402131**	**22043150**

Table 4.10 (c). Cost of chemicals ($)

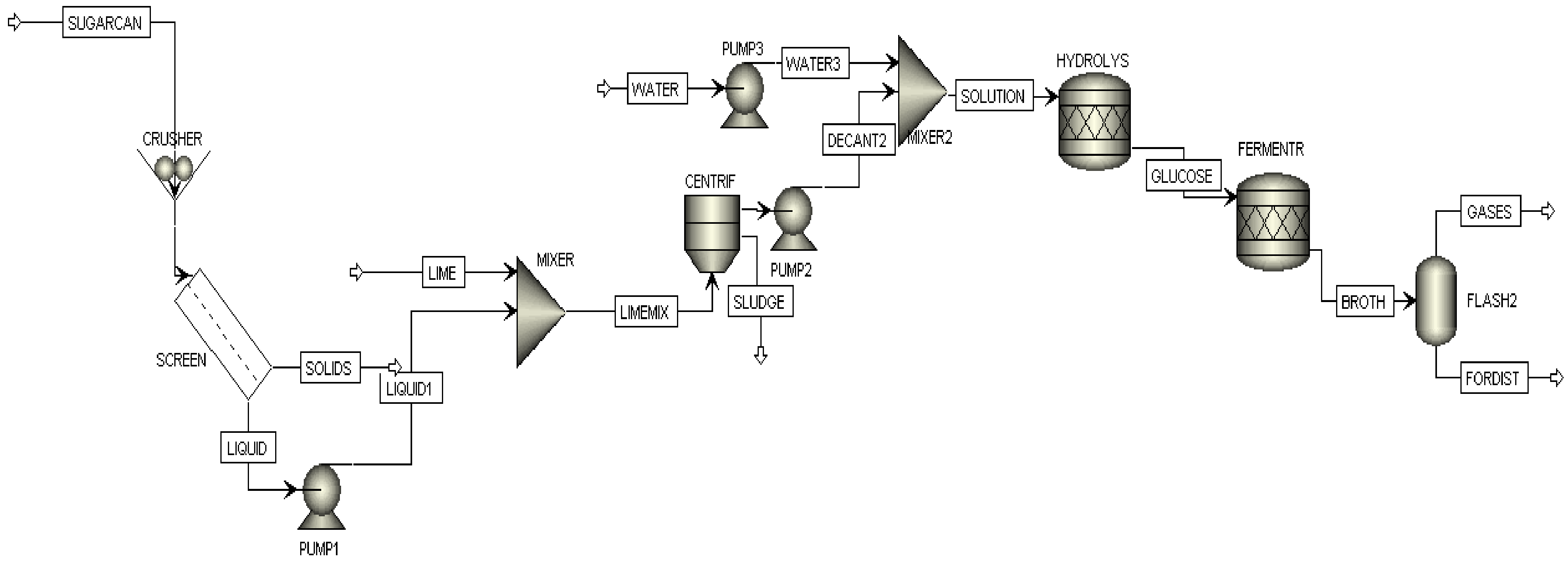
Cost of Chemicals	Price ($)	Basis
Calcium Hydroxide	0.075	kg
Acetone	1.13	kg
Ethanol	1.08	kg
Gas(H_2+CO_2)	0.1	kg
Enzyme	-	
Bagasse	7.5	ton

Table 4.10 (d). Calculated cost of butanol ($)

Feedstock	Byproduct cost	Net production cost	Butanol cost/kg
Sugarcane	7810458	10455671	1.04
Corn	7810458	18145791	1.89
LBM	7810458	1549775	1.42

Table 4.11. Assumed costs as % of FCI/TCI

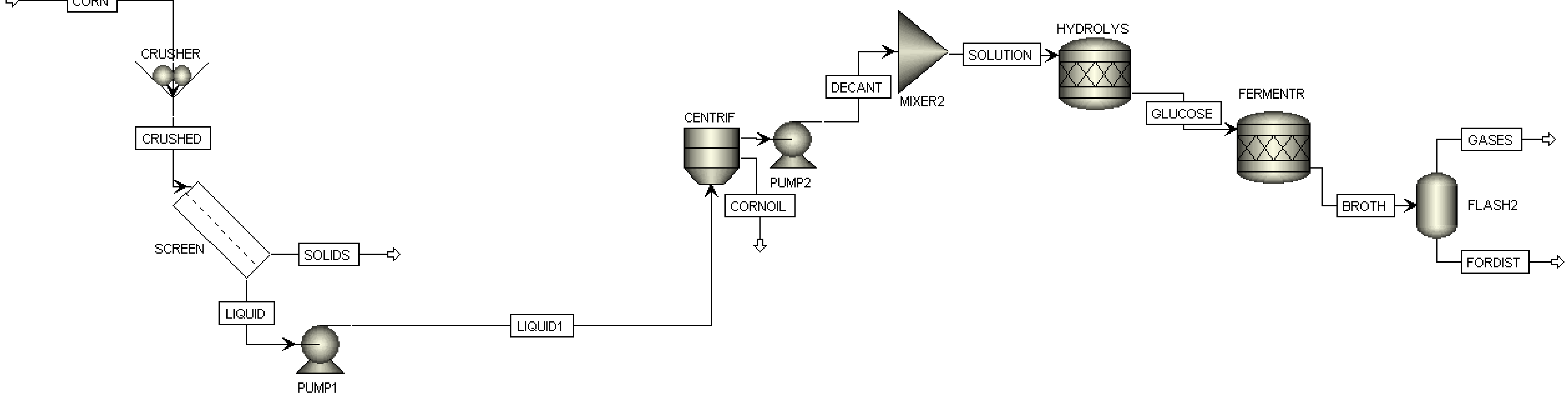
Parameter	% FCI/TCI
Maintenance	6% FCI
Laboratory	15% FCI
Insurance	0.7% FCI
Interest	5% TCI
Administrative costs	4% TPC
R & D	5% TPC
Depreciation	10% TCI



	Broth	Crushed	Liquid	Solids	Liquid1	Lime	Limemix	Decanted	Decant2	Water	Water3	Sludge	Solution	Glucose	Broth	Gases	Fordist
Temperature K	306.1	294.8	294.8		294.9	298	294.9	294.9	295	298	298.1	294.9	297	298	306.1	298	298
Pressure N/sqm	101325	101325	101325	101325	202650	101325	101325	101300	202650	101325	202650	101300	202650	101325	101325	75993.75	75993.75
Vapor Frac	0.017	0	0		0	0	0	0	0	0	0	0	0	0	0.017	1	0
Mole Flow kmol/sec	1.092	0.361	0.361	0	0.361	0	0.361	0.35	0.35	0.715	0.715	0.011	1.066	1.066	1.092	0.019	1.074
Mass Flow kg/sec	20.298	7.64	7.64	0	7.64	0	7.64	7.415	7.415	12.883	12.883	0.225	20.298	20.298	20.298	0.444	19.854
Volume Flow cum/sec	0.481	0.007	0.007	0	0.007	0	0.007	0.007	0.007	0.013	0.013	0	0.02	0.02	0.481	0.609	0.02
Enthalpy MMBtu/hr	-1060.37	-372.927	-372.927		-372.919	0	-372.918	-361.953	-361.945	-697.087	-697.072	-10.965	-1059.016	-1061.28	-1060.37	-13.213	-1049.42
Mass Flow kg/sec																	
Water	19.113	6.443	6.443	0	6.443	0	6.443	6.253	6.253	12.883	12.883	0.189	19.136	19.074	19.113	0.014	19.099

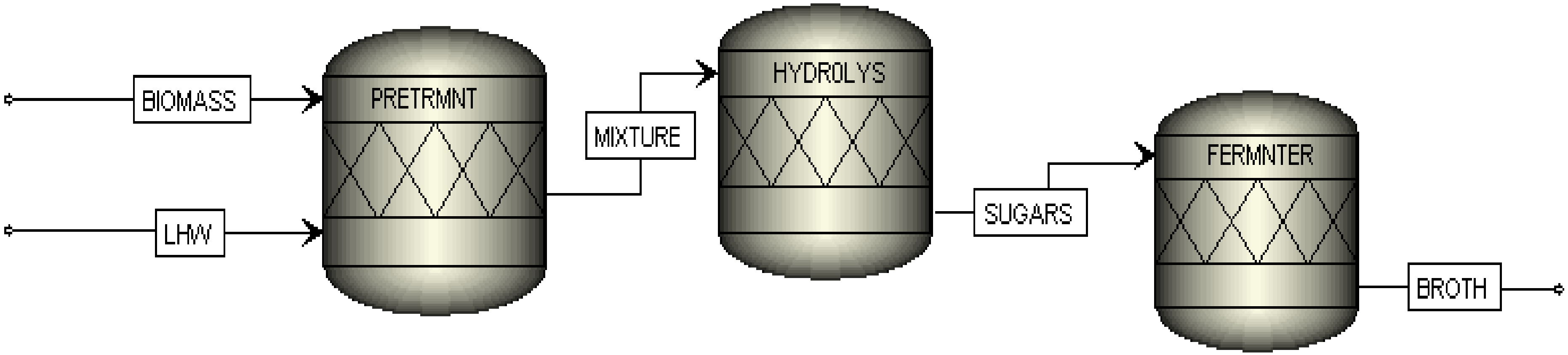
Sucrose	0	1.197	1.197	0	1.197	0	1.197	1.162	1.162	0	0	0.035	1.162	0	0	0	0
Glucose	0	0	0	0	0	0	0	0	0	0	0	0	0	1.223	0	0	0
Acetone	0.125	0	0	0	0	0	0	0	0	0	0	0	0	0	0.125	0.001	0.124
N-But-01	0.318	0	0	0	0	0	0	0	0	0	0	0	0	0	0.318	0	0.318
Ethanol	0.033	0	0	0	0	0	0	0	0	0	0	0	0	0	0.033	0	0.033
CO_2	0.692	0	0	0	0	0	0	0	0	0	0	0	0	0	0.692	0.412	0.28
Hydrogen	0.017	0	0	0	0	0	0	0	0	0	0	0	0	0	0.017	0.017	0

Figure 4.1. Process flow diagram for production of butanol from sugarcane.



	Crushed	Liquid	Solids	Liquid1	Cornoil	Decant	Solution	Glucose	Broth	Gases	Fordist	Solution
Temperature K	298	298		298.2	298.2	298.2	298.2	298	306.1	298	298	298.2
Pressure N/sqm	101325	101325	101325	202650	144247.8	202650	202650	101325	101325	75993.75	75993.75	202650
Vapor Frac	0	0		0	0	0	0	0	0.569	1	0	0
Mole Flow kmol/sec	0.019	0.019	0	0.019	0	0.019	0.019	0.019	0.047	0.026	0.02	0.019
Mass Flow kg/sec	1.772	1.772	0	1.772	0.022	1.75	1.75	1.75	1.75	0.785	0.965	1.75
Volume Flow cum/sec	0.001	0.001	0	0.001	0	0.001	0.001	0.001	0.668	0.859	0.001	0.001
Enthalpy MMBtu/hr	-43.724	-43.724		-43.723	-0.539	-43.183	-43.183	-45.755	-46.806	-22.68	-24.256	-43.183
Mass Flow kg/sec												
Water	0.269	0.269	0	0.269	0.003	0.266	0.266	0.203	0.243	0.012	0.231	0.266
Glucose	0	0	0	0	0	0	0	1.253	0	0	0	0
Acetone	0	0	0	0	0	0	0	0	0.128	0.044	0.084	0
Butanol	0	0	0	0	0	0	0	0	0.326	0.005	0.321	0
Ethanol	0	0	0	0	0	0	0	0	0.034	0.004	0.03	0
Co2	0	0	0	0	0	0	0	0	0.709	0.702	0.006	0
Hydrogen	0	0	0	0	0	0	0	0	0.018	0.018	0	0
Starch	1.418	1.418	0	1.418	0.017	1.4	1.4	0.21	0.21	0	0.21	1.4
Oil	0.085	0.085	0	0.085	0.001	0.084	0.084	0.084	0.084	0	0.084	0.084

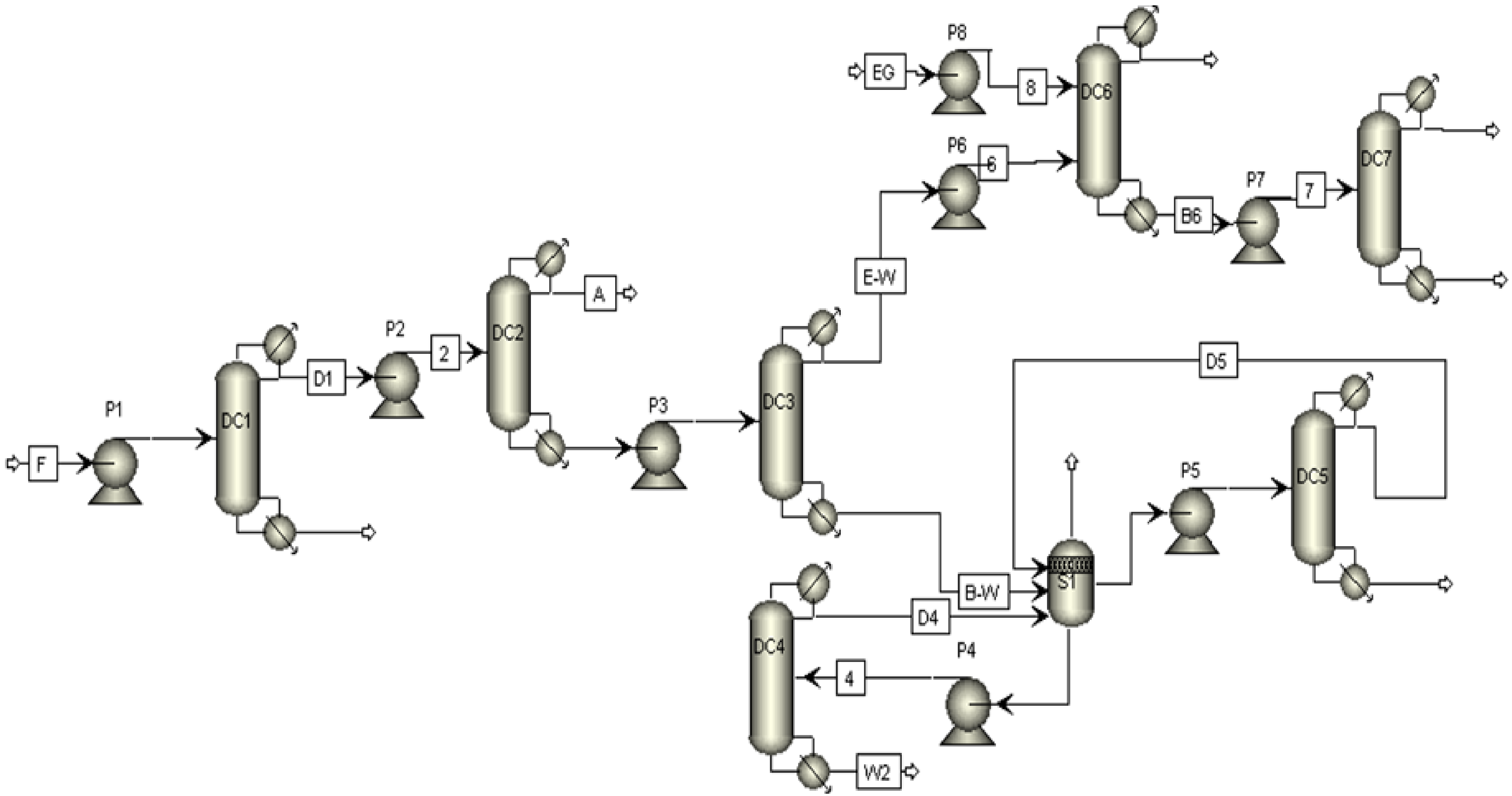
Figure 4.2. Process flow diagram for production of butanol from corn.



	LHW	BIOMASS	MIXTURE	SUGARS	BROTH
Total Flow kmol/sec	1.179554	0.0750168	1.246279	1.238634	1.266471
Total Flow kg/sec	21.25	4.722222	25.9722	25.9722	25.97219
Total Flow cum/sec	3.271142	3.73E-03	0.2411951	0.3549297	0.831236
Temperature K	473.15	298.15	463.15	323.15	306.15
Pressure N/sqm	1.42E+06	1.01E+05	1.42E+06	1.01E+05	1.01E+05
Mass Flow kg/sec					
Water	21.25	0.8772303	21.9428	21.80509	21.84521
Cellulos	0	1.983193	1.899899	0.8397555	0.8397555
Xylose	0	0	1.480947	1.647025	1.647025
Glucose	0	0	0.0925492	1.27049	0
Xylan	0	1.861799	0.2923024	0.1461512	0.1461512
Ethyl-01	0	0	0	0	0
Furfural	0	0	0.0690561	0.0690561	0.0690561
Aceticac	0	0	0.1946406	0.1946406	0.1946406
Zymo	0	0	0	0	0
Lacticac	0	0	0	0	0
Succinic	0	0	0	0	0

Glycerol	0	0	0	0	0
Oxygen	0	0	0	0	0
CO_2	0	0	0	0	0.7187225
Ethanol	0	0	0	0	0.0341978
Butanol	0	0	0	0	0.3301355
Acetone	0	0	0	0	0.1293413
Hydrogen	0	0	0	0	0.017957

Figure 4.3. Process flow diagram for production of butanol from lignocellulosic biomass.


F
P1
DC1
D1
P2
2
DC2
A
P3
DC3
E-W
P6
6
EG
P8
8
DC6
B6
P7
7
DC7
D5
DC5
P5
S1
B-W
D4
DC4
4
P4
W2

	1	D1	W1	2	A	B2	3	E-W	B-W	4	D4	W2	5	D5	B	6	8	E	B6	7	W3	EGR
Temperature C	37	73.5	101.8	73.5	55.8	89.8	90.4	55.8	95.4	78.4	66.3	90.8	78.9	71.8	92.9	56	197.6	55.8	58.8	58.9	55.8	59.3
Pressure bar	2	1	1.139	2	1	1.314	2	1	1.169	2	1	1.045	10	1	1.07	2	2	1	1.07	2	1	1.085
Vapor Frac	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mole Flow kmol/hr	5850.96	117.019	5733.941	117.019	12.111	104.908	104.908	6.714	98.194	61.577	12.685	49.261	135.164	85.862	47.307	6.714	0.175	2.103	4.786	4.786	0.622	4.164
Mass Flow kg/hr	108000	4099.368	103900.6	4099.368	691.145	3408.224	3408.224	380.224	3028	1513.925	494.406	1029.588	5064.333	3055.852	1943.42	380.224	10.862	120.53	270.556	270.556	35.379	235.177
Volume Flow cum/hr	110.765	5.052	113.61	5.053	0.919	4.203	4.207	0.505	3.699	1.767	0.624	1.161	6.317	3.798	2.449	0.505	0.011	0.16	0.355	0.356	0.047	0.308
Enthalpy MMkcal/hr	-398.367	-7.871	-383.477	-7.871	-0.707	-7.113	-7.113	-0.393	-6.728	-4.14	-0.836	-3.325	-9.171	-5.774	-3.31	-0.393	-0.018	-0.123	-0.288	-0.288	-0.036	-0.252
Mass Flow kg/hr																						
B	2268	1611.89	656.11	1611.89	0	1611.89	1611.89	0.001	1611.89	282.069	130.407	159.51	2425.909	965.682	1432.334	0.001	0	0	0.001	0.001	0	0.001
A	1080	1079.903	0.097	1079.903	685.615	394.288	394.288	375.722	18.566	205.106	198.27	0.298	837.898	826.167	0	375.722	0	119.781	255.941	255.941	35.03	220.911
E	216	42.976	173.024	42.976	0.003	42.973	42.973	0.143	42.83	81.463	49.923	34.792	353.092	341.802	11.417	0.143	0	0.013	0.13	0.13	0.008	0.122
W	104436	1364.599	103071.4	1364.599	5.526	1359.073	1359.073	4.359	1354.714	945.287	115.806	834.989	1447.434	922.201	499.668	4.359	0	0.719	3.64	3.64	0.341	3.299
EG	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	10.862	0.017	10.844	10.844	0	10.844
CO_2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hydrogen	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Figure 4.4. A schematic diagram of recovery of products of ABE fermentation through distillation.

Conclusions

In the present study, the process design and economic analysis for production of bio-butanol has been studied on commercial scale (10000 tonne/yr) from various feedstock. The overall process includes three major steps viz. pretreatment and hydrolysis, fermentation, and distillation. The properties of non-data bank compounds in Aspen plus were obtained from NREL database. Of the three feedstock for production of butanol, the sugarcane showed lowest price of $1.04 per kg butanol followed by lignocellulosic biomass ($1.42) and corn ($2.12) respectively. These costs are sensitive to changes in feedstock cost which can change the butanol price markedly. It has been found that raw material cost majorly influences the overall product cost. The cost of final product depends on the type of feedstock and increase in productivity of butanol could decrease the product cost. The recovery of solvents needed seven distillation columns thus increasing the fixed capital investment and particularly this process required recovery of huge amount of water prior to distillation which proved to be adding additional cost significantly.

Future scope

The results produced in this work represents the base case results and further investigations need to be done to estimate the actual process conditions. The major limitations for this process are high toxicity of solvents to enzymes, low solvent yields by bacteria, long fermentation time and high energy requirement for recovery of water prior downstream processing. Huge power requirement for mechanical crushing is also a major concern for this process to be economically viable. Here two steps which have a major impact on the overall economics of the plant are the fermentation and the downstream operations. The possible ways to improve the existing design are

- The physical property methods for non-data bank compounds needs to be updated to get more accurate results.
- Inhibitors are to be considered in the process by incorporating all the side reactions taking place in the reactors.
- If enzymatic kinetic data along with stoichiometry data are to be used it will facilitate to get more accurate results.
- New enzymes which can produce more amount of solvents and have better tolerance to solvents are to be used in fermentation process to increase the productivity as well as the yield. This will further bring down the production cost of butanol to a significant value.
- Also, for downstream processes all possible designs having different configurations have to be compared for efficient recovery of solvents.

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