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THE PRODUCTION OF FUEL-GRADE BIOETHANOL FROM CASSAVA STARCH: A CONCEPTUAL PROCESS DESIGN

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ABSTRACT: This project proposes a conceptual process design for the production of bioethanol to produce an alternative fuel that can supplement the gasoline products at a very reasonable price and produces less carbon dioxide emissions which is mandated under section 5 of RA 9367, the Biofuels Law of 2006 which states that all gasoline products will have 10 percent blend bioethanol by 2011. Due to high demand, the project proposes a process design of 10,000 metric tons bioethanol per year using fed-batch fermentation process with *Saccharomyces cerevisiae* CBS 8066 as microorganism. The plant produces 99.80%(w/w) anhydrous alcohol based on the current ASTM specification and operates continuously with an annual production time of 7,200 hours. In order to optimize the overall process, a novel separation technique is considered in this study with respect to process design and economics by integrating pervaporation and ultrafiltration system. For dehydration and recovery of ethanol, hybrid distillation-pervaporation consists of a distillation column and an externally connected pervaporation module is used to overcome the azeotropic composition from the liquid mixtures of water and ethanol. The result is an integrated system of continuously producing bioethanol in purity up to 99.8%(w/w).

KEYWORDS: Biofuels, fermentation, ethanol yield, biomass, *Saccharomyces cerevisiae*.

INTRODUCTION

The Consultative Group on International Agricultural Research (CGIAR) envisions that by 2020 roots and tubers will be integrated into emerging markets through the efficient and environmentally sound production of a diverse range of high-quality, competitive food, feed, and industrial products. Like, for instance, the production of bioethanol from root crops which has been used as one of the fuel options for internal combustion engines.

Bioethanol has been promoted as a solution for a variety of complex problems related to energy and the environment. Compared to fossil fuels, bioethanol has the advantages of being renewable, providing cleaner burning and producing no green-house gases [Altintas *et al*., 2001].

The real debut of bioethanol was in early 1970's when Brazil started the ethanol program to produce ethanol as fuel additive to decrease the amount of petroleum they imported. Since then, Brazil is the major fuel bioethanol producer in the world with current ethanol production capacity of 14 million cubic meter per annum. Throughout the world, there have been many nations incorporating ethanol into the fuel market [Efe *et. al*., 2005].

The current worldwide interest in bioethanol production is not only due to economical reasons but the exhaustion of the fossil fuel and the increasing greenhouse effect due to the high carbon dioxide emissions which urged the nations to search for alternative fuels that can supplement with gasoline products and compatible with petroleum in price.

The Organization for Economic Co-operation and Development (OECD) and UN FAO food agency, projected that global ethanol production, would double between 2007-2017 reaching 125 billion liters. It is expected to grow rapidly over the next decade, mainly with exports from Brazil to the US and EU. As a result, it increases the global demand for ethanol that would be able to sufficiently address the world's growing energy requirements.

Moreover, the Philippine's Biofuels Act of section 5 RA 9367, states that all liquid fuels for motors and engines shall contain locally-sourced biofuels components. The law mandates that all gasoline products will have 10 percent blend bioethanol by 2011 and the marketed fuel-grade ethanol shall meet all industry standards, including specifications for E-grade denatured fuel ethanol.

Today, the Green Future Innovations Inc. (GFII) will build a P6-billion bioethanol plant in Isabela that will produce 54 million liters and generate 19 megawatts annually starting 2012 and contributes to the domestic supply of green energy pursuant to the Biofuels and Renewable Energy Laws.

The GFI's annual production shall be displacing 54 million liters of imported fossil fuel and with world crude prices averaging $ 81 per barrel in which, the foreign exchange savings is estimated at $ 27.5 million per year. Apart from the economic benefits of the project, GFII iterates the socio-economic impact to the farmers and creates more than 15,000 Filipinos will be employed by this project.

DESIGN OBJECTIVE AND REQUIREMENTS

This project aims to design a large-scale process of bioethanol with annual production of 10,000 MT in order to contribute the current global demand of ethanol at 14.5 million tons per annum [Dominy, 2003].

Thus, specific requirements are considered for the design procedure in order to obtain an effective and efficient production plant. These requirements include: the process concepts chosen, mode of operation, the operating conditions, the raw materials used and others. Likewise, it is important that the process design should incorporate features to meet current ASTM standards.

CONCEPTUAL FRAMEWORK

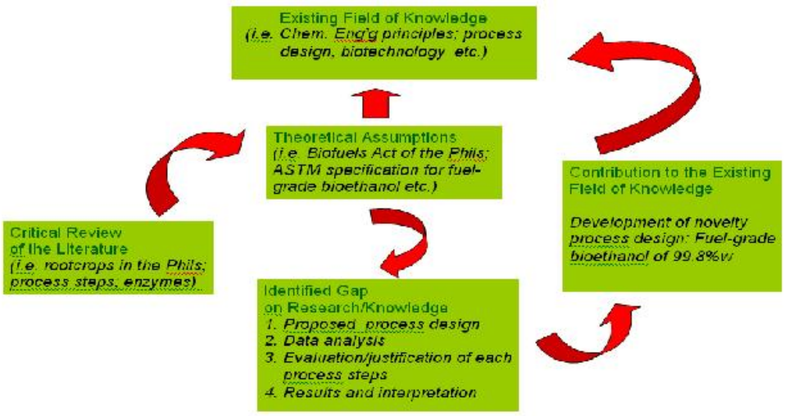


Fig. 1.1 A conceptual framework in production of a fuel-grade bioethanol from cassava starch

METHODOLOGY

In order to attain the objectives of the study, the following shall be utilized as strategies in which necessary data and relevant information will be obtained.

a. A critical review of literatures on the cassava as rootcrops and various designs processes in production of bioethanol.
b. Prepare a conceptual process design based on the proposed project.
c. Present technical and financial studies for the completion of the pilot-scale bioethanol plant.
d. Submit a technical paper to the review committee and apply to the different funding institutions for the realization of this project

Different ethanol grades are available in the market depending on its application. The current ASTM specification for water in fuel ethanol is a maximum of 1.0% (1.3 wt%). Other countries and governments have established lower allowed concentrations of water. But, the European Union standard is 0.3 wt% (standard EN 15376).

Due to the demand, the ethanol production from cassava starch must undergo several processes which include the pre-treatment process, fermentation process and downstream processing in order to meet the required ASTM specifications. This chapter provides us discussion on the different process options. Figure 1.2 depicts the overview for the process steps involved.

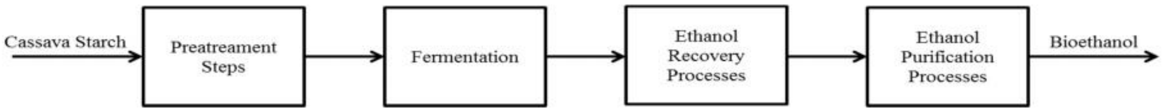


Figure. 1.2 Overview of Process Steps in Bioethanol Production

Process options are evaluated carefully using the criteria for choice. The selection of the process is done based on points system from the most important (5) to the least important (1) criteria as described below.

Table 1.1 Process Option Criteria

Criteria	General Description	Points
Product yield and purity	High product yields that contain less amounts of impurities	5
Economics	Less production cost and products at competitive prices	4
Impact on Environment	Have minimal outputs of by-products and wastes	3
Ease of Operation	Must not be hazardous and operate within safe conditions	2
Process conditions	Must be up-to-date and employ a relatively advanced process	1

Feed Preparation. Cassava starch is used as feedstock in the production of ethanol. From the Bureau of Agricultural Research [2009], the moisture content of the cassava is reduced to 14% by drying at a temperature of 60^0C and is carried out 24 hours per day before readily be available for the fermentation process.

Hydrolysis. The cassava starch undergoes enzymatic hydrolysis to convert starch into glucose. Prior to enzymatic treatment, the starch slurry undergoes gelatinization in a jet cooker. Gelatinization conditions are set at pH of 6.5 and a temperature of 105^0C for 5 minutes. The product of gelatinization is a viscous starch paste. The resulting gelatinized starch undergoes the firs enzymatic step known as liquefaction or dextrinization. The liquefaction process involves the contact of the gelatinized starch with *A-amylase* at a temperature of 95^0C for 2 hours. In this process, the viscosity of the mixture abruptly decreases due to the disruption of the granular structure of the starch into shorter dextrins. The liquefied cassava starch is then subjected to a subsequent saccharification step with the employment of *amyloglucosidase* in order to convert the dextrins into glucose. The saccharification step is done at a pH of 4.5 and a temperature of 60^0C for another 25 hours [Pandey *et al*., 2006, van der Maarel *et al*., 2002].

Yeast Preparation. Ethanol fermentations are carried out with the baker's yeast strain *Saccharomyces cerevisiae* CBS 8066. The yeast is kept on slants of GPY-(glucose/peptone/yeast extract) agar. The inocula for the fermentations are prepared in a shake flask with a medium of 10 kg/m^3 glucose and 10 kg/m^3 yeast extract paste. The fermentation media contained 150-300 kg/m^3 glucose, 7.5 kg/m^3 yeast extract paste, 5 kg/m^3 NH_4CL, 1.0 kg/m^3 KH_2PO_4, 0.25 kg/m^3 $MgSO_4.7H_2O$ and 0.20 kg/m^3 $CaCl_2.2H_2O$ in demineralized water. The solution containing glucose and $CaCl_2.2H_2O$ and the solution containing the rest of the ingredients are sterilized apart at 110^0C [Groot *et al*., 1993]

Fermentation. Fed-batch fermentation is used in this process. A feedstock containing 6% (w/w) fermentable sugar, 2 g/L of yeast and a nutrient solution is continually fed into the fermenter [IATA and McGill University, 2009]. The nutrient solution is composed of $(NH_4)_2SO_4$, 3 g/L KH_2PO_4, and 0.5 g/L $MgSO_4.7H_2O$. The fermentation is done in aerobic conditions with an optimum pH value of 4 to 5, the temperature of 30^0C to 35^0C and the fermentation period take about 3 days. Without yeast, fermentation could require more than 10 days.

In all fermentations the pH was controlled at pH 5.0, by adding 4 N NaOH. The antifoam agent polypropylene glycol was added at regular intervals to the broth (average flow rate about 0.1 ml/h). Air was sparged into the broth at a rate of 0.1 m^3/m^3/min based on total fermentation volume. The temperature of the condenser, where carbon dioxide leaves the system, was kept constant at 4^0C [Groot *et al*., 1993].

During the fermentation, sugar is converted to ethanol with 0.98 of the theoretical yield which corresponds to 0.46-0.50 g ethanol / g sugar. The remaining substrate is utilized by the microorganisms for maintenance, cell growth and production of by-products such as acetic acid, higher alcohols and acetaldehyde. The continuous feed is started after initial glucose has been utilized during the rapid growth phase. The rate of addition of glucose is determined by the need to prevent autolysis, and by the oxygen demand rate.

The fermentation liquid is mixed with turbine impellers. Some air is sparged in the broth to supply a trace amount of oxygen to support growth of yeast. The operating variables for the fed-batch process are given in Table 1.2.

Table 1.2 Fed-batch operating variables [Jackson, 1990]

Volume	150-200 m^3
Power input	3-4 kW/m^3
Air flowrate	0.5-1.0 (v/v)min
Pressure	0.3-0.7 atm
Temperature	22.22-32.22^{0}C
pH	4.0-5.0
Fermentation time	72 hours

The fermentation is carried out in vessels to maintain a continuous operation and to prevent requirement of extra storage tanks for broth and recycle biomass. The biomass is recycled to maintain high cell concentrations in the fermenters.

The fermenter should be of steel with sloping bottoms and closed taps. They are provided with vets to conduct away the carbon dioxide, and frequently with cooling coils to regulate and limit fermenting temperatures. The fermenter is inoculated with three to four percent of yeast mash and the fermentation is carried out in 72 hours (3 days duration) during which time the temperature rises from approximately 73^{0}F to 90^{0}F (22.22-32.22^{0}C) because the reaction is exothermic.

Downstream Processing. For high ethanol productivity, an ultrafiltration module is coupled to the fermenter for cell retention. The broth is recirculated over the ultrafiltration module and part of the liquid permeates through the membrane, as result of a pressure difference over the membrane. A bleed is used to prevent an undesirable build-up of yeast cells. The ultrafiltration is carried out with a 0.1 m^2 hydrophilic hollow fiber membrane module (X-Flow, Hengelo, The Netherlands) [Groot *et al*., 1993].

A novel separation technique is used by pervaporation, in which an ethanol/water mixture is recovered from the broth by evaporation via a selective membrane. For this design, an integrated ethanol production process with biomass retention by an ultrafiltration and in situ ethanol recovery by pervaporation. The mass transfer in pervaporation membranes is based on the solution-diffusion mechanism. A homogenous, nonporous membrane is used through which the compound diffuses only when it dissolves to a certain extent in the membrane. At the downstream side of the membrane, the compound is evaporated in a vacuum and the vapor is trapped in a condenser. The components of a liquid mixture can be separated based on their difference is solubility and diffusivity in the membrane. Microorganism, proteins, salts and the like are rejected by the membrane while volatile byproducts in the fermentations such as the higher alcohols and ester will also be recovered.

Pervaporation is carried out with nitrogen gas as the sweep gas. The gas is circulated by a compressor (15 l gas/min), and the vapors are condensed using a condenser at 0^{0}C and a cold trap at -60^{0}C. Plate and frame modules (5 liters/m^2-h at 30^{0}C, SEMPAS, Horb, FRG) are used, since these modules will be less sensitive to fouling by particulate matter in the broth and ease for cleaning than hollow fiber modules. The sterilization of the plate-and-frame module is disinfected by circulating a 70 wt.% mixture of ethanol in water at about 55^{0}C for 5 h and flushing with 10 L of sterile water [Groot *et al*., 1993].

A hybrid process for integrating distillation with pervaporation is used to produce 95 wt% ethanol from a feed of 50 wt% ethanol. The feed is sent to a distillation column operating at near ambient pressure, where a bottoms product of nearly pure water and an ethanol-rich distillate of 95 wt% are produced. The distillate purity is limited because of the 95.6 wt% ethanol in water azeotrope. The distillate is sent a pervaporation step where permeate of 20 wt% alcohol and a retentate of 99.8 wt% ethanol is produced. The permeate vapor is condense under vacuum and recycled to the distillation column. It requires a total condenser after the distillation tower and a liquid pump to increase the pressure of the column top stream.

The stillage of the distillation process will be processed to concentrate and recover suspended materials or dissolved materials as by-products. While the pervaporator has membrane-based process in which a liquid feed stream from the distillation is brought into contact with one side of a non-porous or molecularly porous membrane [Fleming and Slater, 2007].

RESULTS AND DISCUSSION

The input-output diagram for the production of 10,000 metric tons of ethanol per year using the fed-batch production scheme is shown in Figure 1.3. The quantities of each component are evaluated such that the total input is equal to the total output. The t/h is referred to as ton/ hour.

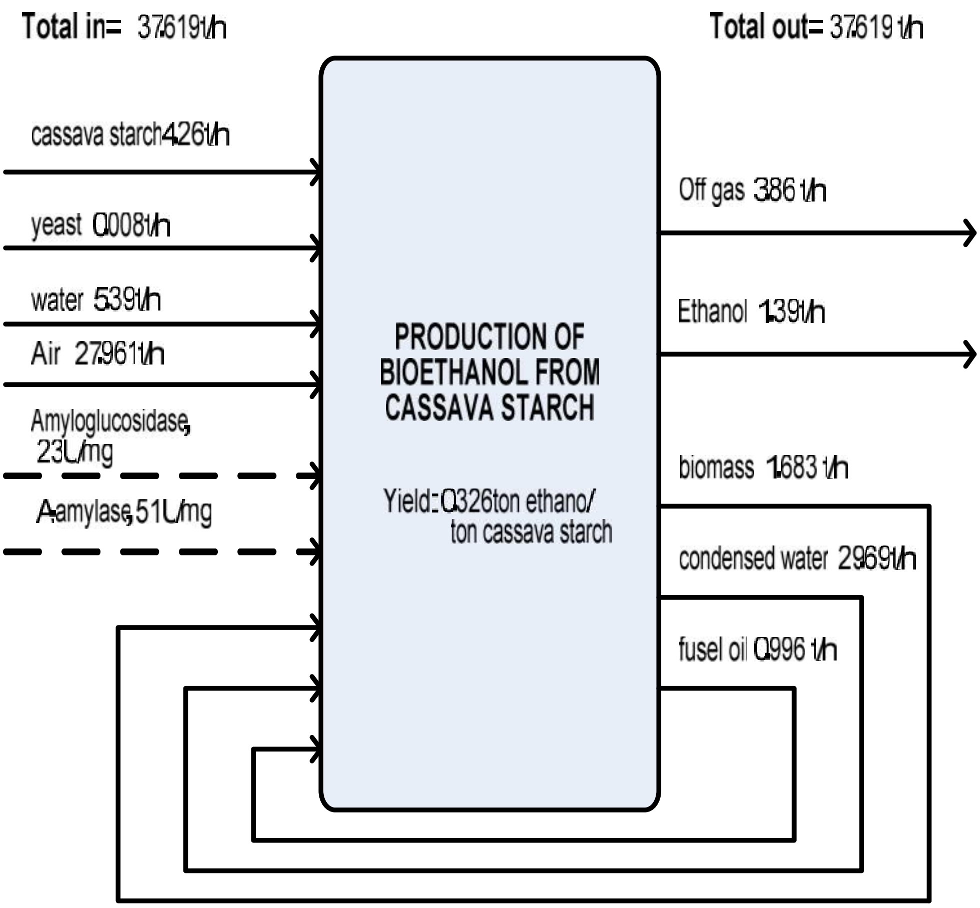


Fig. 1.3 Input-Output diagram for Bioethanol Production from Cassava Starch

BLOCK SCHEME DIAGRAM

** values in parenthesis refer to production in ton per annum*

The composition and the amounts of the components, process conditions, phases, yields and conversions are incorporated in all major streams of the process. The details of the mass balance calculation are given in the Appendixes.

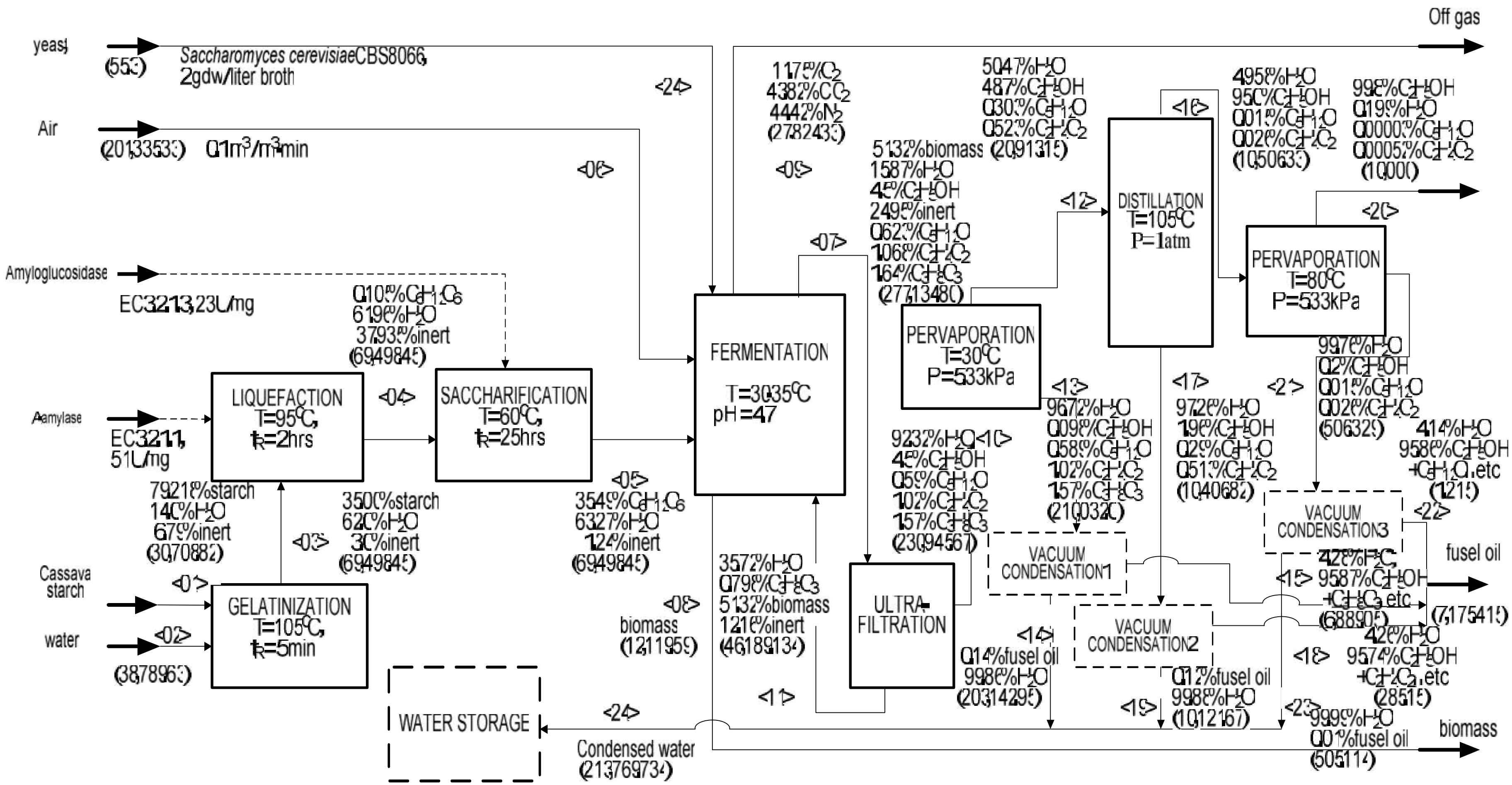
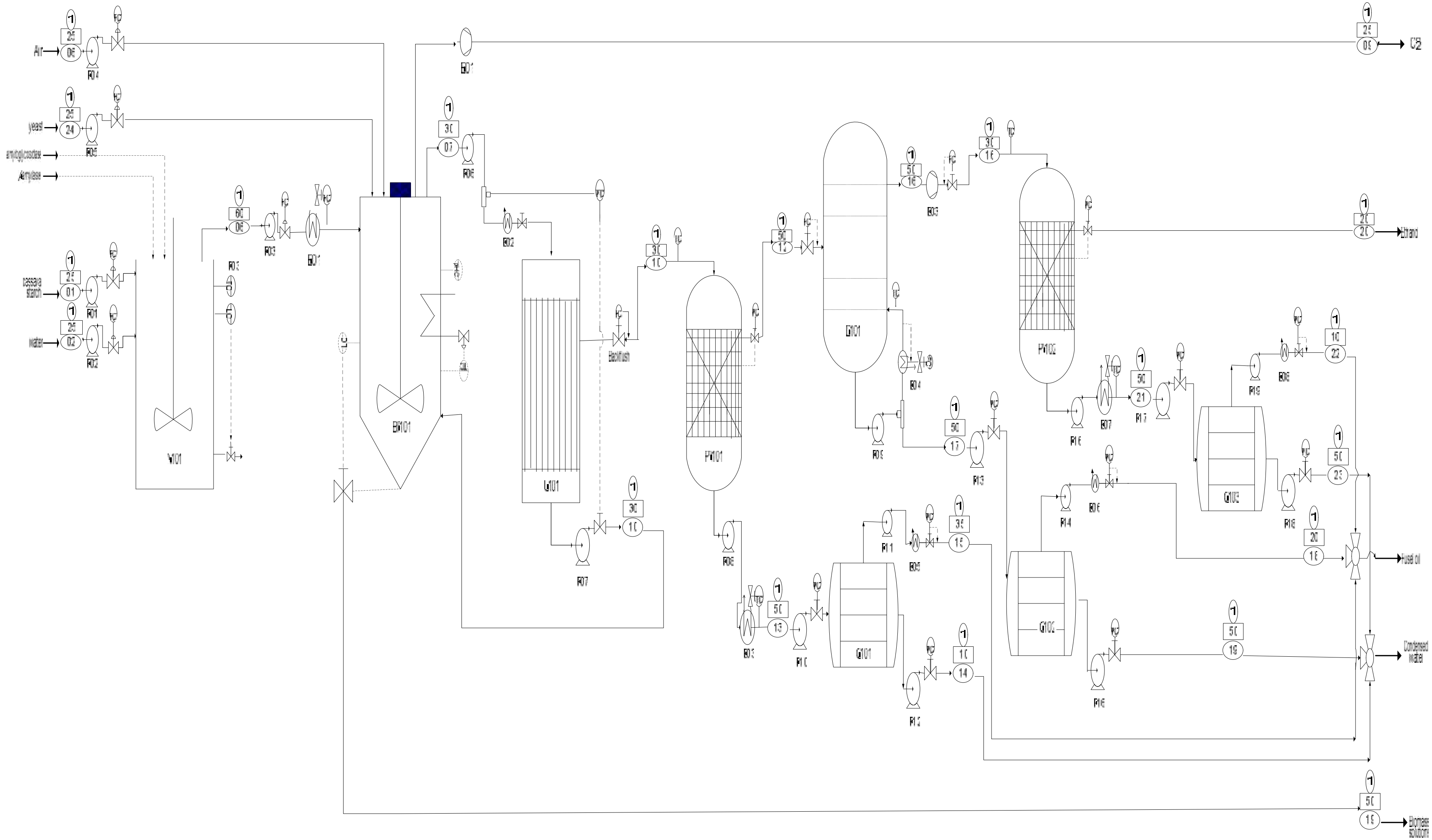


Fig. 1.4 Simplified block scheme diagram of ethanol production with a basis of 10,000 t/a ethanol produced



PROCESS EQUIPMENT SUMMARY			
B-01 : CO_2 blower	P-01/10/13/ : Feed pumps	P-07 : Reciprocating pump	PV-101/102 : Pervaporator
BR-101 : Fermenter	P-02 : water pump	P-8/9/15: Water solution pump	U-101 : Ultrafilter
C-101/102/103: Condensers	P-03 : Slurry feed pump	P-12/16/18 : Condensed water pump	V-101 : Hydrolysis reactor
E-01-08 : Heat exchangers	P-04 : Air pump	P-11/14/19 : Vapor solution pump	
D-101 : Distiller	P-06 : broth circulation pump	P-05: Yeast feed pump	

PROJECT NAME	Fig. 1.5 PROCESS FLOW SCHEME			
DESIGNER	DATE	BIOETHANOL PRODUCTION FROM CASSAVA STARCH		
Neil L. Egloso	8-Sep-13	Stream Number	Temperature (^{0}C)	Pressure (atm)

CASH FLOW ANALYSIS

The construction of the plant is assumed to be 2 years. It is assumed that the first year expense is the engineering, construction and contingency cost. The payment of the fixed capital investment is paid in second year. The working capital and start-up costs are discounted from the first operating year (third year of investment) income. During construction, the line slopes downward from the zero line to indicate increasing negative cash position. As income starts, the line heads up, gradually reducing the investment to zero and this crossing of the zero line represents payout time of 3.06 years. As cash continues to come in, the slope continues upward into positive cash position (profit) area. In the region the cumulative cash flow is positive; the project is earning a return on the investment.

Data for calculation for the annual cumulative cash flow is shown in Appendixes. The summary of cash flow analysis is shown in Fig. 1.6.

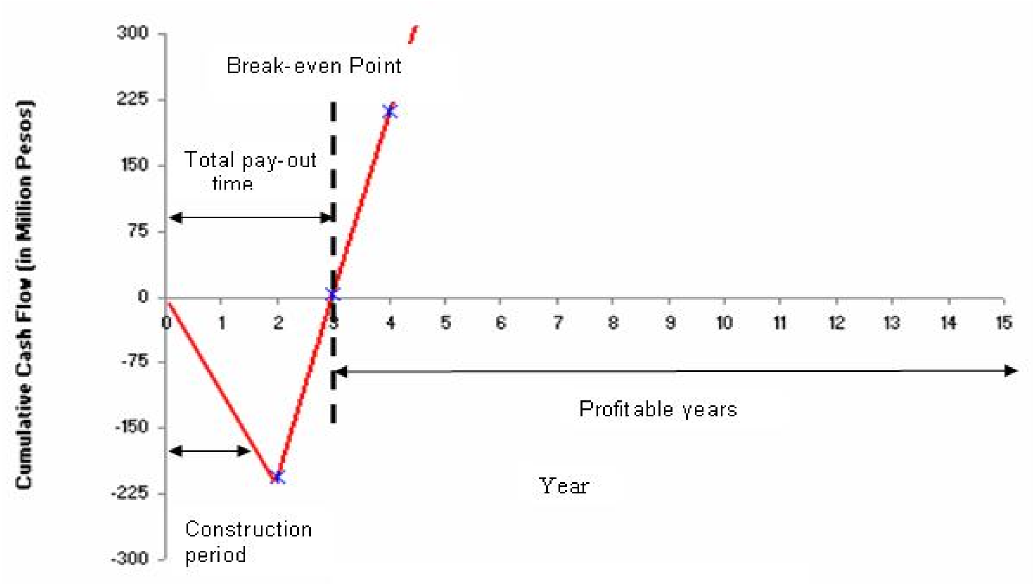


Fig. 1.6 The cash flow diagram

SENSITIVITIES

Sensitivity to economic criteria with respect to product cost, raw material cost and maintenance cost is determined. This anticipates variability of these factors and is taken into consideration. Variance of +50% and -30% are used for product cost, raw material cost, and maintenance cost. Table 1.3 shows the sensitivities of applied variance to economic criteria and Fig. 1.7, sensitivity analysis for cumulative cash flow.

Table 1.3 Sensitivities of Economic Criteria

Economic Criteria		Maintenance cost		Raw material cost		Product cost	
		- 30%	+ 50%	-30%	+ 50%	-30%	+ 50%
ROR	**32.68%**	36.28%	26.68%	43.49%	10.62%	3.99%	80.51%
POT	**3.06**	2.76	3.75	2.30	9.41	25.06	1.24
Average Net Profit	**189.20**	211.78	151.55	256.98	50.81	9.20	489.20
Average Cash flow (with dep.)	**205.03**	227.62	167.39	272.82	66.65	25.03	505.03

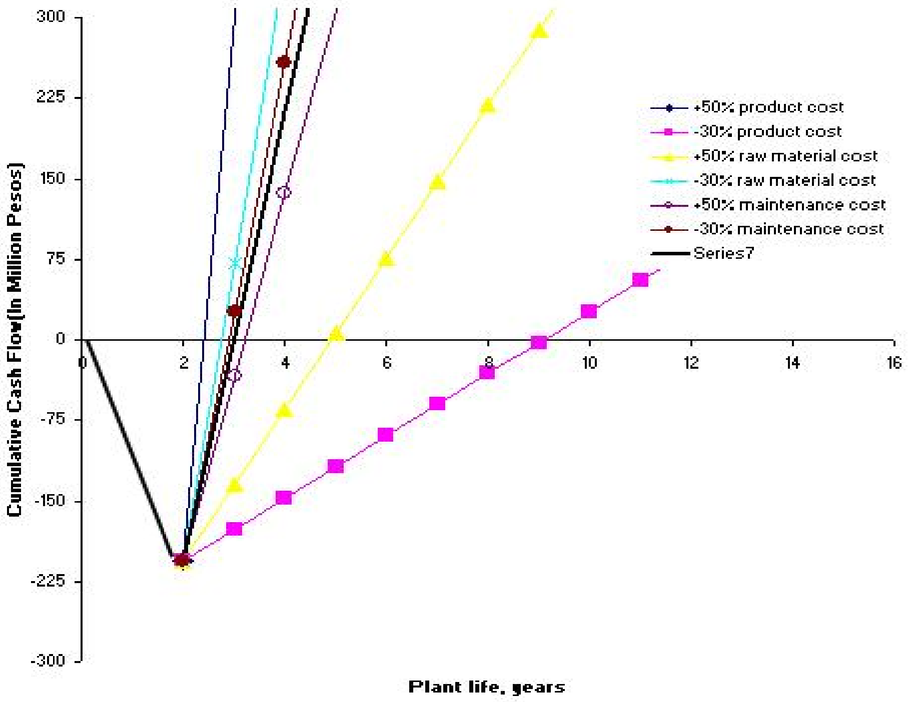


Fig. 1.7 Sensitivity analysis for cumulative cash flow

Sensitivity analysis as shown in Fig. 1.7 describes that it gives no detrimental effect in a raw material cost because the raw materials used are relatively inexpensive except if it would increase by 50%. However, product cost and maintenance cost plays the major role in giving life to the operation of the plant. As observed, variance of -30% in product cost and +50% maintenance costs give a low value of ROR. So, it is necessary to impose strict regulations in the company in case of utilizing resources and utilities of the plant such as manpower, water, and electricity. The company can help minimize operating cost by adopting new technologies that is more efficient and cost-effective. A +50% increased on product price and -30% reduction on maintenance cost would give the higher ROR based on the sensitivity analysis. Hence, annual net cash flow or the earning power may even go higher than what was estimated and would eventually boost the economy of the plant.

CONCLUSIONS

Careful consideration and a specific criterion were used in order to determine which processes were best suited for the design in order to optimize productivity and produce high quality products. This design incorporates the technological advancements and developments by updating the process and makes it relevant to the industry.

A novel separation technique used by integrating pervaporation and ultrafiltration is considered in this study with respect to process design and economics. It increases in productivity and substrate conversion which lead to reduction of the production costs of ethanol, in comparison with traditional processes like batch and continuous fermentation with ethanol recovery by distillation.

Cassava is chosen prior to other crops capable of producing alcohol due to its availability throughout the country. Aside from these, it can obtain several quantity of alcohol as three times rather than sweet potatoes and sugar cane [Combis *et al*, 1995]. It is cheap and is indigenous which costs about 30% from total production cost.

Economic analysis of the plant had shown that the design is economically viable with a rate of return of 32.68% and a pay out time of 3.06 years is expected for the production plant. It is also shown that the product cost and maintenance cost are the most sensitive among other criteria justified. However, the process can be made more profitable and economically appealing by optimizing the operations in order to increase operational efficiency.

Thus, the design calculations proved that ethanol production from cassava starch are technically and economically feasible to invest on.

RECOMMENDATIONS

1. It's highly recommended due to potential benefits of bioethanol in the community in terms of:

    1.1 Health impacts- Replaces bad gasoline additives (MTBE and lead), which are sources of surface and ground water contamination, and dangerous to human health;

    1.2 Political impacts- It potentially replaces crude oil, which is a finite, non-renewable resource; It can be domestically produced, thus reducing *dependence* on oil imports; It can potentially cut oil *import costs*.

    1.3 Socio-economic Impacts- Bioethanol uses agri-products as a feed-stock; It is a renewable source of energy, which can replace fossil fuel in the future; It increases value added and price of agri-products, which increases net farm income; It creates more jobs in the rural sector;

    1.4 Environmental Impacts- Ethanol, richer in octane, promotes more complete combustion of gasoline thus reducing exhaust emissions.

2. In a pilot-scale design, the product bioethanol can be used as an IGP in the Institution and technological-transfer program for research and extension.

3. It serves an *education campaign* to inform consumers of the purpose and benefits of bioethanol**.**

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