Wolkite University

COLLEGE OF ENGINEERING AND TECHNOLOGY

DEPARTMENT OF CHEMICAL ENGINEERING

ETHANOL PRODUCTION FROM SELECTED FRUIT PEEL WASTE (ORANGE, MANGO AND BANANA)

BY

NAME	FATHER NAME	ID№
JILALU	MISBA	ENGR 484/08/
DEMEKE	BALGO	ENGR 256/08/
KINFE	KIDANE MARIAM	ENGR 523/08/
HENOK	HANJALA	ENGR 456/08/
MELESE	GUNTA	ENGR 594/08/

A THESIS SUBMITTED TO THE SCHOOL OF UNDERGRADUATE STUDIES OF WOLKITE UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF BATCHELER OF SCINCES IN ENVIRONMENTAL ENGINEERING.

ADVISOR: - ZEYNU SHAMIL

DECEMBER, 28,2020EC

WOLKITE

ETHIOPIA

DECLARATION

We hereby declare that the thesis is based on our original work except for flotation's and citations which have been duly acknowledged. We also declare that it has not been previously or currently submitted for any other department at Wolkite University or other institute.

BY	SIGNATURE
JILALU MISBA	
DEMEKE BALGO	
KINFE KIDANEMARIAM	
HENOK HANJALA	
MELESE GUNTA	

DATE,

DECEMBER, 28,2020EC

TABLE OF CONTENTS

LIST OF TABLE

LIST OF FIGURE

LIST OF ACRONYMS

ANOVA	Analysis of Variance
CO	Carbon monoxide
CO2	Carbon dioxide
DC	Direct Cost
ESDA	Ethiopia Sugar Development Agency
FCI	Fixed Capital Investment
IDC	Indirect Cost
IRR	Internal Rate of Return
PH	power of Hydrogen
SDA	Sugar Development Agency
TCI	Total Capital Investment
TDC	Total Direct Cost
TPDC	Total Plant Direct Cost
VLE	Vapor Liquid Equilibrium
WC	Working Capital
PHBCE	perry hand book of chemical engineering

Acknowledgement

In the name of God, the Most Gracious and the Most Merciful.

All praises to God and His blessing for the completion of this thesis. We thank Him for him selected us to free from the world pandemic called COVID-19 and he make us alive. Also we thank God for all the opportunities, trials and strength that have been showered on us to finish writing the thesis. We experienced so much during this process, not only from the academic aspect but also from the aspect of personality.

This thesis would never have been possible without the support and guidance of various people at the University of Wolkite, therefore would like to express our special gratitude to them.

We would like to acknowledge our advisor ZEYNU SHAMILL for his efforts, comments, fruit full advice, proper supervision of the thesis and reading the manuscript through oor thesis. His knowledge and hands on experience in chemical engineering discipline has added greatly to the depth of information provided by this thesis.

We also would like to express our gratitude to the laboratory technicians of the chemical engineering department YOHANESS and MESERET in particular for their time and help during our experimental work.

Further we would like to give special thanks to biotechnology, and a food processing laboratory assistance by helping us by supporting in both experimental equipment and its installation. Thank them for their hospitality every time we came to their laboratory, as well as for volunteering to help with cleaning the equipment and its installation.

Finally, we would like to express our sincere gratitude to our mother for their r patience and continued support in the last six years.

ABSTRACT

Waste disposal has become one of the major concerns for our country. Fruit peels are the major solid by-product. The dried fruit peels have a content of cellulose and hemicelluloses, which make it suitable as fermentation substrate when hydrolyzed. This thesis aims at utilizing fruit (Banana, Mango and Orange) peels for the production of bio-ethanol by using the yeast *Saccharomyces cerevisiae*, thus, producing a valuable product from the fruit peel wastes. The fruit peels were crushed in to 1-2 cm sizes for easy drying and grinding. Sample drying was carried out in oven (60^0C for 24hr) to obtain easily crushable material. After drying, each of the samples was milled separately. The maximum particle sizes of the ground mixed sample were 1-2 mm. Laboratory experiments of 4 run were conducted to produce bio-ethanol from those fruit peel wastes. The mill samples of 100gm (33.3gm from each sample) were taken and mixed, then passed through steam pretreatment, hydrolysis, and fermentation and distillation process respectively to produce bio-ethanol. The ethanol concentrations of the samples collected every 3 hours intervals by rotary evaporator of fermented solution were measured. The effects of acid concentration, temperature and time on dilute acid hydrolysis were investigated. The Design expert® 7 software were used and significance of the result was set from analysis of variance (ANOVA). The optimum results were obtained at 0.75%v/v acid concentration, 1320C temperature, and 25minute retention time. Under these condition 40% of bio-ethanol were obtained.

Investigation on the technical and economic feasibility of the work for ethanol production was performed. Results from the feasibility study indicated that the proposed work was feasible with rate of return (RR) 25.6% and the payback period of the project is estimated to be 2years.

CHAPTER ONE

1. Introduction

1.1. Background

The production of ethanol from lignocellulose biomass has received considerable attention because of the potential of producing large quantities of ethanol for use as a transportation fuel. Hemicellulose and cellulosic components of lignocellulose biomass are hydrolyzed to their component sugars for subsequent conversion to ethanol by a fermentative process. Hemicellulose and cellulose are usually hydrolyzed with a chemical process (acid) or biological (enzyme) attack. The economic success of ethanol production will depend on efficient conversion of cellulose and hemicellulose to their monomeric sugars and the efficiency of fermenting those sugars to ethanol, while also reducing capital and operating costs (Schell et al., 1992). Over the last few decades, the negative impacts of fossil fuel on the environment and consequent global warming, progressive demand for energy. The alternative fuels are expected to satisfy several requirements including substantial reduction of greenhouse gas emission, worldwide availability of raw materials, and capability of being produced from renewable feedstocks (Hahn-Hagerdal et al., 2006). Production of fuel ethanol from biomass seems to be an interesting alternative to traditional fossil fuel, which can be utilized as a sole fuel in cars with dedicated engines or in fuel blends. Ethanol is currently produced from sugars, starches and cellulosic materials. Cellulosic materials obtained from wood and agricultural residuals, municipal solid wastes and energy crops represent the most abundant global source of biomass. These facts have motivated extensive research toward making an efficient conversion of lignocelluloses into sugar monomers for further fermentation to ethanol (Lin and Tanaka, 2006). Unlike simple sugars which can be directly converted to ethanol, other biomasses such as starches, lignocelluloses and citrus waste need to be pretreated to make sugars available for the subsequent fermentation step. Pretreatment and hydrolysis release a mixture of fermentable sugars as well as potential inhibitory compounds present in the structure of biomass – for instance, phenolic constituents from extractive in wood and limonene from orange peel. Hydrolysis using appropriate enzymes represents the most effective method to liberate simple sugars from cellulosic materials; however, improvement of process rates and lower cost of enzyme production are required. Dilute acid hydrolysis is a fast and economically feasible approach that is widely used (Taherzadeh and Karimi, 2007). Wherever there is human habituation, organic waste is produced, which consist of mainly household food waste, hotel waste, juice house waste, and agricultural waste, human and animal waste. For each year the amount of produced organic waste is increasing dramatically, source separation, composting, anaerobic digestion and anaerobic fermentation with related production is increasingly being considered as a substitute for waste management strategies as land-filling and incineration of municipal solid waste (D. Elango et al, 2007). The citrus fruits and its production have increased since the 1980s. Its production is predicted to approach 67.728 million tons by 2012, representing a 14% increase within 12 years (Plessas, S et al., 2007). Part of this waste is dried to be used as animal feed, but the drying process is costly due to the high moisture content of peels, and therefore a large proportion of waste has to be disposed of. This may result in many problems from both economic and environmental points of view including high transport costs, lack of disposal sites and high organic content (Tripodo, M.M et al., 2004). Citrus processing residues contain both soluble and insoluble carbohydrates. The latter are present in the cell walls of the peels, particularly in the form of pectin, cellulose and hemicellulose. These polymers can be hydrolyzed enzymatically by cellulase, β-glucosidase and pectinase to their corresponding soluble carbohydrates (Wilkins, M.R et al. 2007.; Grohmann, K et al., 1992).

1.2. Significance of the Study

Waste from the food is a challenge to the environment all over the globe, hence these need to be recycled. Fruit and vegetable are a resource of renewable energy with significant fuel source potential for electricity and steam. Bioethanol derived from biomass contribute 10-14% of the total world energy supply and solved the world crisis such as global warming and depletion of fossil fuel. Therefore the significant of studding bioethanol production from biomass used to reduce global pollution, energy consumption, and solid waste management system. Because the combined ill effect of air, soil, and water pollution impending exhaustion of fossil fuel, our world desperately require biofuel replacement for oil in the future. This study was designed to utilize the rotten fruits for the production of biofuel and waste management purposes. The ethanol production from rotten fruits was compared with the data regarding fermentation of, mango, banana and orange for ethanol production. Rotten fruits were used to produce bioethanol by fermentation process.Energy is one of the most fundamental parts of our universe. Energy is used as powers our vehicles, trains, planes and rockets.

1.3. The Statement of the Problem

Inadequate municipal and industrial solid waste collection and disposal creates a range of environmental problems in our country. A considerable amount of waste ends up in open dumps or drainage system, threatening both surface water and ground water quality and causing flooding, which provides a breeding ground for diseases-carrying pests. Open air burning of waste, spontaneous combustion in landfills and incinerating plants that lack effective treatment for gas emissions are causing air pollution. Lack of the most basic solid waste services in crowded, low-income neighbors are a major contributor to the high morbidity and mortality among the urban poor. The adverse effects of inadequate solid waste service on productivity and economic development of the city are significant. Solid waste such as fruit peels largely obtained as a byproduct from hotels, restaurants and juice processing houses in our country. These wastes can entail serious environmental problems unless they change or convert in to some useful products or disposed properly. The aim of this thesis was to investigate the possibility of using and transforming fruit peel waste to something valuable product, namely ethanol there by contributing towards alternative energy supply as well as creating an employment opportunity.

1.4. Objective

1.4.1. General objective

The general objective of these research is to produce Ethanol from selected fruit peels (Mango, banana, and orange).

1.4.2. Specific objective

- To develop and optimize the critical parameters by conducting experimental analysis of the conversion of cellulose, hemicellulose and lignin structures molecule of solid fruit peel waste to ethanol using different series subsequent steps i.e pretreatment (stem explosion), hydrolysis (dilute acid hydrolysis), fermentation (Saccharomyces cerevisiae) and distillation method.
- To determine the bioethanol percentage from fruit peel waste produced through a fermentation process using yeast.
- To determine the optimal acid concentration, temperature and time that give the highest possible efficiency of converting solid fruit peel waste mixture (equal proportion feed stock) to ethanol.

CHAPTER TWO

2.1. Literature Review

2.2. Bio-fuels

Are alcohols, ethers, esters and other chemicals made from cellulose-based Biomass? This includes herbaceous and woody plant, agricultural and forestry residues and a large portion of municipal and industrial waste materials (http://www.ott.doc.gov/biofuels).Bio-fuels are renewable since they are produced from biomass—organic matter, such as plants. They generate about the same amount of carbon dioxide (a greenhouse gas) from the tailpipe as fossil fuels, but the plants that are grown to produce the bio-fuels actually remove carbon dioxide from the atmosphere. Therefore, the net emission of carbon dioxide will be close to zero (Rainner J and Dominik R, 2007).

The bio-fuels industry has evolved from using first generation feedstock (typically food crops) to using second and third generation feedstocks, for both ethanol and biodiesel. While the term biofuels denote any fuel made from biological sources, for most practical uses, the term refers to either ethanol or biodiesel. The last few years have seen tremendous growth in biofuels (Cellulosic Ethanol, 2010).

2.2.1. Alcohol

The word alcohol derives from Arabic al-kuhul, which denotes a fine powder of antimony produced by distilling antimony and used as an eye makeup. Alcohol originally referred to any fine powder, but medieval alchemists later applied the term to the refined products of distillation, and this led to the current usage (http://www.ethanol.org/). Ethanol, the most widely used bio-fuel, is made in a process similar to brewing beer.

The ethanol in the end is blended with gasoline to improve vehicle performance and reduce air pollution (http://www.nrel.gov/lab/pao/biomass_energy.html).

2.2.2. Ethanol

Is a clean-burning, high-octane fuel that is produced from renewable sources? Ethanol is beginning to be used all around the world as a transportation fuel, and it has some distinct advantages. Fuels that burn too quickly make the engine "knock", a characteristic rattling sound. The higher the octane rating, the slower the fuel burns, and the less likely the engine will knock. When ethanol is blended with gasoline, the octane rating of the petrol goes up by three full points, without using harmful additives.

2.3. Bio-ethanol and Its Application as a Fuel

Ethanol, also known as ethyl alcohol with the chemical formula C2H5

Times: “The fuel of the future is going to come from fruit like that sumac out by the road, or from apples, weeds, sawdust – almost anything. There is fuel in every bit of vegetable matter that can be fermented. There's enough alcohol in one year's yield of an acre of potatoes to drive the machinery necessary to cultivate the fields for a hundred years.” However, fossil fuels were predominantly used for automobile transportation throughout the last century, obviously due to their lower production cost. As an automotive fuel, hydrous ethanol can be used as a substitute OH, is a flammable, clear, colorless and slightly toxic chemical compound with acceptable odor. It can be produced either from petrochemical feedstock by the acid-catalyzed hydration of ethene, or from biomass feedstock through fermentation. The fuel of the future is going to come from fruit like that sumac out by the road, or from apples, weeds, sawdust – almost anything. There is fuel in every bit of vegetable matter that can be fermented. Fossil fuels were predominantly used for automobile transportation throughout the last century, obviously due to their lower production cost. As an automotive fuel, hydrous ethanol can be used as a substitute for gasoline in dedicated engines. Anhydrous ethanol, on the other hand, is an effective octane booster when mixed in blends of 5% to 30% with no engine modification requirement (Licht, 2006).

2.4. Current Ethanol Production in Ethiopia

Ethanol is manufactured from microbial conversion of biomass material through fermentation. The production process consists of conversion of biomass to fermentable sugars, fermentation of sugar to ethanol and the separation and purification of ethanol. Fermentation initially produces ethanol containing a substantial amount of water. Then this solution is distilled using distillation column the majority of water to yield up to 95 percent purity ethanol, the balance being water.

The worldwide recent awareness for the use of ethanol to replace petroleum and generation of power along with sugar mill plants should have led to setting up of number of ethanol plants and co-generations. Ethiopia has several sugar real estate (Fincha, Metehara and Wonji Shoa) industries which are run and administered by Sugar Development Agency. Among molasses derived products ethanol takes the largest part, but its utilization must attract the attention of the government policy makers in order to utilize as a bioethanol. Bioethanol or biofuel is ethanol based products that can process into liquid fuels for transport purposes (ESDA, 2005)

Table 1Table 2. 2 summary of sugar and ethanol factory production plan in Ethiopia.

Sugar factories

Year	Description	Unit	wonji	Metahara	Fincha	Tendabo	New	Total
2012	Annual sugar production	Millions Ton	0.075	0.137	0.11	-	-	0.322
	Annual ethanol production	M^3	-	12500	800	-	-	18000
	Annual Grid production	MW	-	-	-	-	-	0
	Annual sugar production	Millions Ton	0.174	0.137	0.27	0.62	1.046	2.25
2015	Annual ethanol production	M^3	10299	25500	20000	55400	70405	181604
	Annual Grid production	MW	17	11	-	73		101
	Annual sugar production	Millions Ton	0.174	0.137	0.27	0.62	3.067	4.268

2020	Annual ethanol production	M^3	10299	25500	20000	55400	278942	390141
	Annual Grid production	MW	17	11	-	91	-	119

Source: Ethiopian Sugar Corporation, 2013

2.4.1. Fruit in Ethiopia

Various kinds of fruit crops grow in different regions of Ethiopia yielding varying quantities of fruits within the private peasant holdings in the traditional way. There are also a few fruit farms that are run by enterprises in the modern way. The volume of fruit production obtained from the peasant farms is small signaling the absence of development in fruit farming (CSAE, 2003). As the data obtained, less than half a million hectares of land is under permanent crops in Ethiopia. Fruit crops constituted more than 8% of the permanent crop area yielding more than 2 million quintals of fruits. Bananas, mangoes, papayas shared 59.65%, 10.85% , 8.11%   and 5.08% of the land under fruit crop and 61.01%, 10.42% and 12.09% of the fruit production, in that order (CSAE, 2003).

SNNPR and Oromia Regions shared about 17 thousand (46.07%) and 15 thousand (40.80%) hectares of the country’s total area under fruit crops, respectively. More than one million quintals (50.00%) and 826 thousand quintals (40.00%) of the country’s total fruit production went for SNNPR and Oromia Regions, in that order. It is also indicated that more than 700 thousand (57%) and 500 thousand (38%) quintals of the country’s total bananas was produced in SNNPR and Oromia regions, respectively and orange 154,624.72 quintals from both (CSAE, 2003).

2.5. Feedstock for Ethanol Production

Almost any plant- based material can be an ethanol feedstock. All plants contain sugars, and these sugars can be fermented to make ethanol in a process called biochemical conversion. Plant material also can be converted to ethanol using heat and chemicals in a process called thermo chemical conversion. Some plants are easier to process into ethanol than others. Some require few resources to grow, while others need intensive care. Some are used for food as well as fuel, while others are cultivated exclusively for ethanol; even plant-based wastes can become ethanol. The following are different type’s feedstocks for ethanol production (Cellulosic Ethanol, 2010).

2.5.1. Sugar

Fermentation involves microorganisms that use the fermentable sugars for food and in the process produces ethanol and other byproducts. These microorganisms can typically use the 6 carbon sugars, one of the most common being glucose. Therefore, biomass materials containing high levels of glucose or precursors to glucose are the easiest to convert to ethanol. Although fungi, bacteria, and yeast microorganisms can be used for fermentation, specific yeast (Saccharomyces cerevisiae also known as Bakers’ yeast, since it is commonly used in the baking industry) is frequently used to ferment glucose to ethanol. Theoretically, 100 grams of glucose will produce 51.4 g of ethanol and 48.8 g of carbon dioxide. However, in practice, the microorganisms use some of the glucose for growth and the actual yield is less than 100%.

Other biomass feedstocks rich in sugars include sugar beet, sweet sorghum, and various fruits. However, these materials are all in the human food chain and, except for some processing residues are generally too expensive to use for fuel ethanol production (J. Janick and P.C. Badger, 2002).

2.5.2. Cellulosic

Like sugar materials, starchy materials are also in the human food chain and are thus expensive. Fortunately, another alternative exists that is cellulosic material. Examples of cellulosic materials are paper, cardboard, wood, and other fibrous plant material. Cellulosic resources are in general very widespread and abundant. For example, forests comprise about 80% of the world’s biomass.

The second generation ethanol feedstock primarily comprises feedstock called cellulosic feedstock. In the case of these feedstocks, ethanol is derived not from the starch component, but from the lignocellulosic component of the feedstock. A large number of non-food wild plants that grow in non-cultivated and non-arable lands, and even plant waste, contain lignocellulose; as a result, the second generation ethanol feedstocks (P.C. Badger, 2002).

Cellulose: is a linear polymer of D-glucose units linked by β-1, 4-linked glucose. Cellulose molecules are completely linear and have a strong tendency to form intra and intermolecular hydrogen bonds. Bundles of cellulose molecules are thus aggregated together in the form of micro-fibrils, in which highly ordered (crystalline) regions alternate with less ordered (amorphous) regions. The basic repeating unit of cellulose is cellobiose. Under normal conditions, cellulose is extremely insoluble in water, which is of course necessary for it to function properly as the structural framework in plant cell walls (O'Sullivan, 1997).

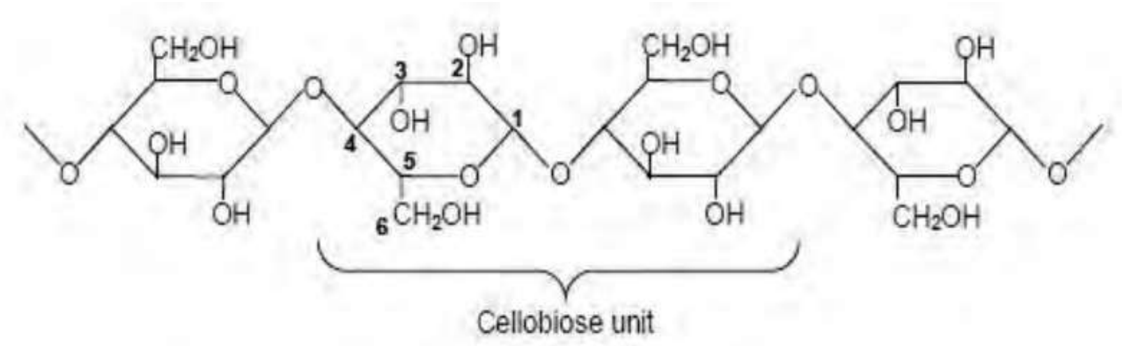


Figure 1 Schematic illustration of the cellulose chain

Hemicelluloses: were originally believed to be intermediates in the biosynthesis of cellulose.

Hemicelluloses are heterogeneous polymers of pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose), and sugar acids. They are generally cataloged according to the main sugar residue in the backbone, e.g., xylans, mannans, and glucans, with xylans and mannans being the most common. Hemicelluloses, because of its branched, amorphous nature, are relatively easy to hydrolyze.

Lignin: is a complex, hydrophobic, cross-linked, three-dimensional aromatic polymer of phenyl propane building blocks. The mechanical strength properties of plants are mainly due to incorporation of lignin into their cell walls, whereby huge plants such as trees can remain upright. P-coumaryl alcohol (I), coniferyl alcohol (II) and sinapyl alcohol (III) are the primary precursors and building units of all lignins. Lignin is one of the most complicated natural polymers with respect to its structure and heterogeneity, which make it extremely resistant to chemical and biological degradation (Lee, 1997).

2.5.3. Fruit peels:

Citrus fruits comprise an important group of fruit crops manufactured worldwide. In the fruit processing industry large amounts of waste materials are produced, in the form of peel, pulp, seeds, etc (Dhillon S. S et al., 2004). The waste materials present significant disposal difficulties and when not used in any way it cause odor and soil pollution (Dhillon S. S et al., 2004 and Ma E., 1993). In the citrus processing industry citrus peels is the major solid by-product and comprises around 50% of the fresh fruit weight. The citrus waste can be used as raw material for extraction of ethanol or in pelletized form for animal feeding. However, the citrus waste has to be dried first, and none of these processes has been found to be very profitable (Mamma D et al., 2008). New techniques are developed and being proposed to An alternative way to utilize citrus processing waste is to produce ethanol or other valuable products by fermenting the sugars in peel hydrolysate.

2.5.4. Starch

Another potential ethanol feedstock is starch. Starch molecules are made up of long chains of glucose molecules. Thus, starchy materials can also be fermented after breaking starch molecules into simple glucose molecules. Examples of starchy materials commonly used around the world for ethanol production include cereal grains, potato, sweet potato, and cassava. Starchy materials require a reaction of starch with water (hydrolysis) to break down the starch into fermentable sugars (saccharification). Typically, hydrolysis is performed by mixing the starch with water to form slurry which is then stirred and heated to rupture the cell walls. Specific enzymes that will break the chemical bonds are added at various times during the heating cycle (J. Janick and P.C. Badger, 2002).

2.6. Overview of Ethanol Process

Ethanol can be produced in two different ways. Either chemically, by hydration of ethylene, which is derived from crude oil or natural gas, or by fermentation of sugar containing feeds, starchy feed materials or lignocellulosic materials. About 5% - 10% of the ethanol produced in the world is a petroleum product. Petroleum ethanol product is made by the catalytic hydration of ethylene with sulfuric acid as the catalyst.The two primary ways of producing fuel ethanol from cellulosic feedstock are: Biochemical conversion process and Thermo chemical conversion process (Cellulosic ethanol, 2010).

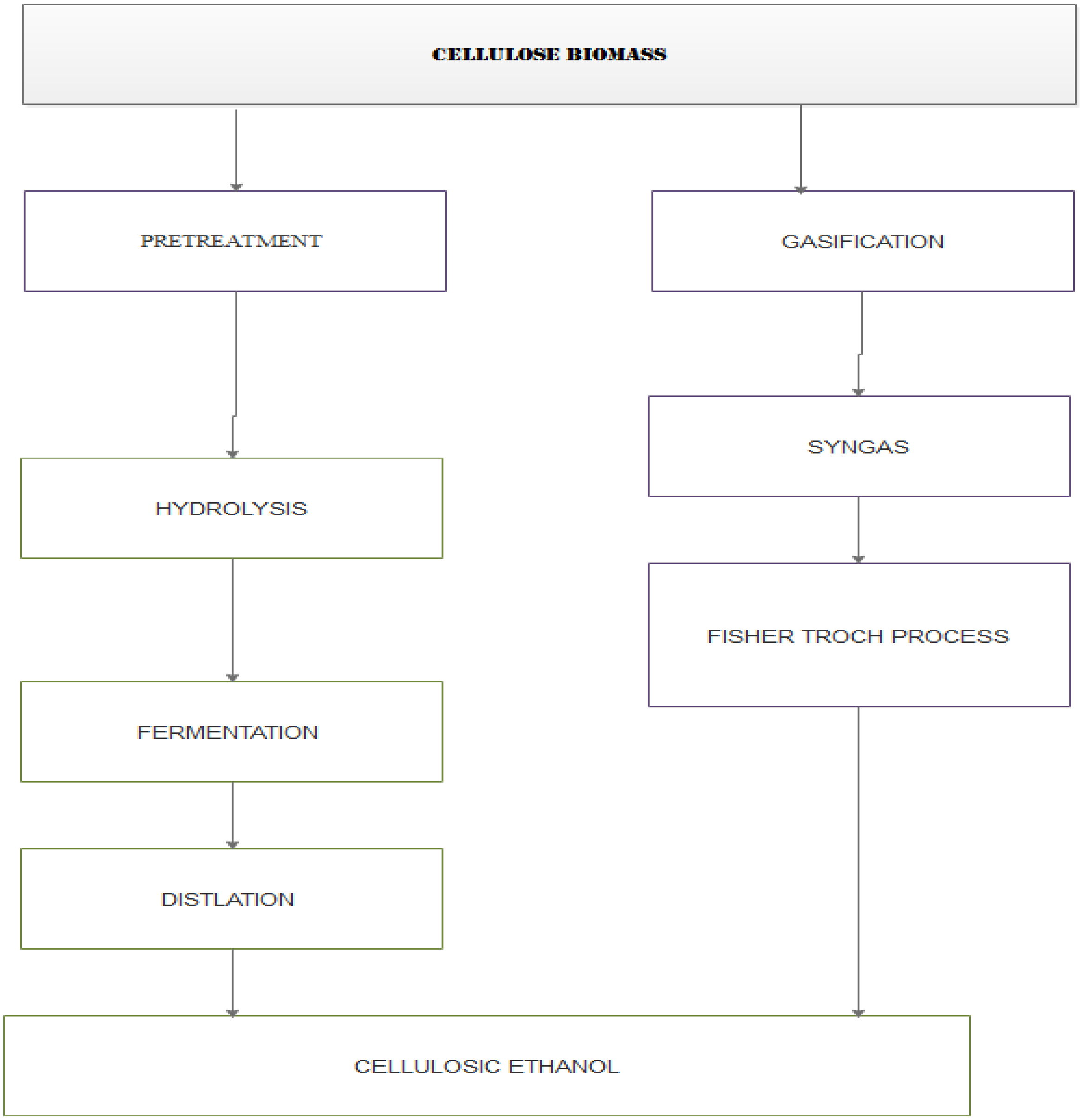


Figure 2 Schematic diagram of cellulosic ethanol production

2.6.1. Biochemical Conversion Process

The technology of ethanol production from biomass feedstocks consists of several steps, and varies depending on the type of raw materials used. It becomes more sophisticated as the raw materials turn from sugars to starches and cellulosic materials. Unlike starch, the specific structure of cellulose favors the ordering of the polymer chains into tightly packed, highly crystalline structures those are water-insoluble and resistant to depolymerization. For production of ethanol from cellulosic feedstocks, four major unit operations are required: pretreatment, hydrolysis, fermentation, and separation purification (Solomon et al., 2007; Taherzadeh and Karimi, 2007. Mosier et al, 2005).

2.6.2. Pretreatment

Pretreatment of biomass is technically challenging and forms a large part of the process cost and therefore will need to be optimized prior to commercialization. Due to the different types of carbohydrates contained in biomass, a package of enzymes/microbes will be required for hydrolysis and fermentation; this package is a significant process cost and requires optimization (Cellulosic ethanol, 2010).

The purpose of the pretreatment is to remove lignin, reduce cellulose crystalline and increase the porosity of the materials. Pretreatment must meet the following requirements: Improve the formation of sugars or the ability to subsequently form sugars by acidic or enzymatic hydrolysis;avoid the degradation or loss of carbohydrate; avoid the formation of byproducts inhibitory to the subsequent hydrolysis and fermentation processes. Physical, chemical, physico-chemical, and biological processes have been used for pretreatment of lignocellulosic materials (Nirbhay Gupta, 2008).

2.6.3. Physical Pretreatment

Mechanical Comminution: Waste materials can be comminuted by a combination of chipping, grinding and milling to reduce cellulose crystallinity. The size of the materials is usually 10–30 mm after chipping and 0.2–2 mm after milling or grinding.

2.6.4. Chemical Pretreatment

Dilute acid has been successfully developed for pretreatment of lignocellulosic materials. The dilute sulfuric acid pretreatment can achieve high reaction rates and significantly improve cellulose hydrolysis (Nirbhay Gupta, 2008). At moderate temperature, direct saccharification suffered from low yields because of sugar decomposition. High temperature in dilute acid treatment is favorable for cellulose hydrolysis. There are primarily two types of dilute acid pretreatment processes: high temperature (greater than 160°C), continuous-flow process for low solids loading (5–10% (weight of substrate/weight of reaction mixture)), and low temperature (less than 160 °C), batch process for high solids loading (10–40%). Although dilute acid pretreatment can significantly improve the cellulose hydrolysis, its cost is usually higher than some Physico-chemical pretreatment processes. A neutralization of pH is necessary for the downstream acidic or enzymatic hydrolysis or fermentation processes (Nirbhay Gupta, 2008).

Alkaline Pretreatment: Some bases can also be used for pretreatment of lignocellulosic materials and the effect of alkaline pretreatment depends on the lignin content of the materials. The mechanism of alkaline hydrolysis is believed to be saponification of intermolecular ester bonds cross linking xylan hemicelluloses and other components, for example, lignin and other hemicellulose. The porosity of the lignocellulosic materials increases with the removal of the crosslinks. Dilute NaOH treatment of lignocellulosic materials caused swelling, leading to an increase in internal surface area, a decrease in the degree of polymerization, a decrease in crystallinity, separation of structural linkages between lignin and carbohydrates, and disruption of the lignin structure.

Steam Explosion (Auto hydrolysis): Steam explosion is the most commonly used method for the pretreatment of lignocellulosic materials. In this method, chipped biomass is treated with high-pressure saturated steam and then pressure is swiftly reduced, which makes the materials undergo an explosive decompression. Steam explosion is typically initiated at a temperature of 90 - 160 ºC for several minutes to a few hours the material is exposed to atmospheric pressure. The process causes hemicellulose degradation and lignin transformation due to high temperature,

thus increasing the potential of cellulose hydrolysis and steam treatment with dilute acid of 0.5 to

1%, temperature of 90 to $140^0{}_C$.The white-rot fungus P. chrysosporium produces lignin-degrading enzymes, lignin peroxidases and manganese-dependent peroxidases, during secondary metabolism in response to carbon or nitrogen limitation. Both enzymes have been found in the extracellular filtrates of many whiterot fungi for the degradation of wood cell walls. Other enzymes including polyphenol oxidases, laccases, HC and residence time of 10 to 40 minutes gives highest yield of ethanol (Solomon, 2007).

2.6.5. Biological Pretreatment

In biological pretreatment processes, microorganisms such as brown, white and soft-rot fungi are used to degrade lignin and some hemicellulose in waste materials. Brown rots mainly attack cellulose, while white and soft rots attack both cellulose and lignin. White-rot fungi are the most effective basidiomycetes for biological pretreatment of lignocellulosic materials. Similar conversion was obtained in the pretreatment by Phanerochaete sordida and Pycnoporus cinnabarinus in four weeks (Nirbhay Gupta, 2008).

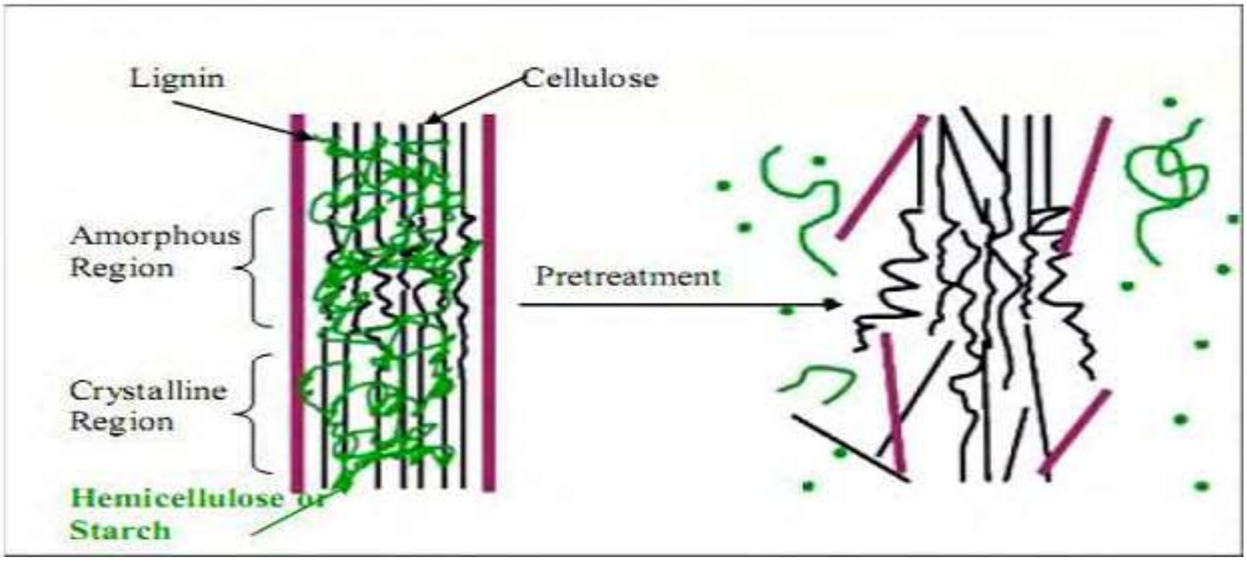


Figure 3 Schematic Representation on Biomass Pre-Treatment (Mosier et al, 2004)

2.7. Hydrolysis

In the hydrolysis reaction, the complex chains of sugars that make up the hemicllulose are broken, releasing simple sugars. The complex hemi-cellulose sugars are converted to a mix of soluble five-carbon sugars, xylose and arabinose, and soluble six-carbon sugars, mannose and galactose. By the action of acids and/or enzymes, the glucose yields of cellulose hydrolysis often exceed 90%, but hydrolysis without preceding pretreatment yields typically less than 20% only. The pretreated feedstock can be hydrolyzed by two methods (Cellulosic Ethanol, 2010).

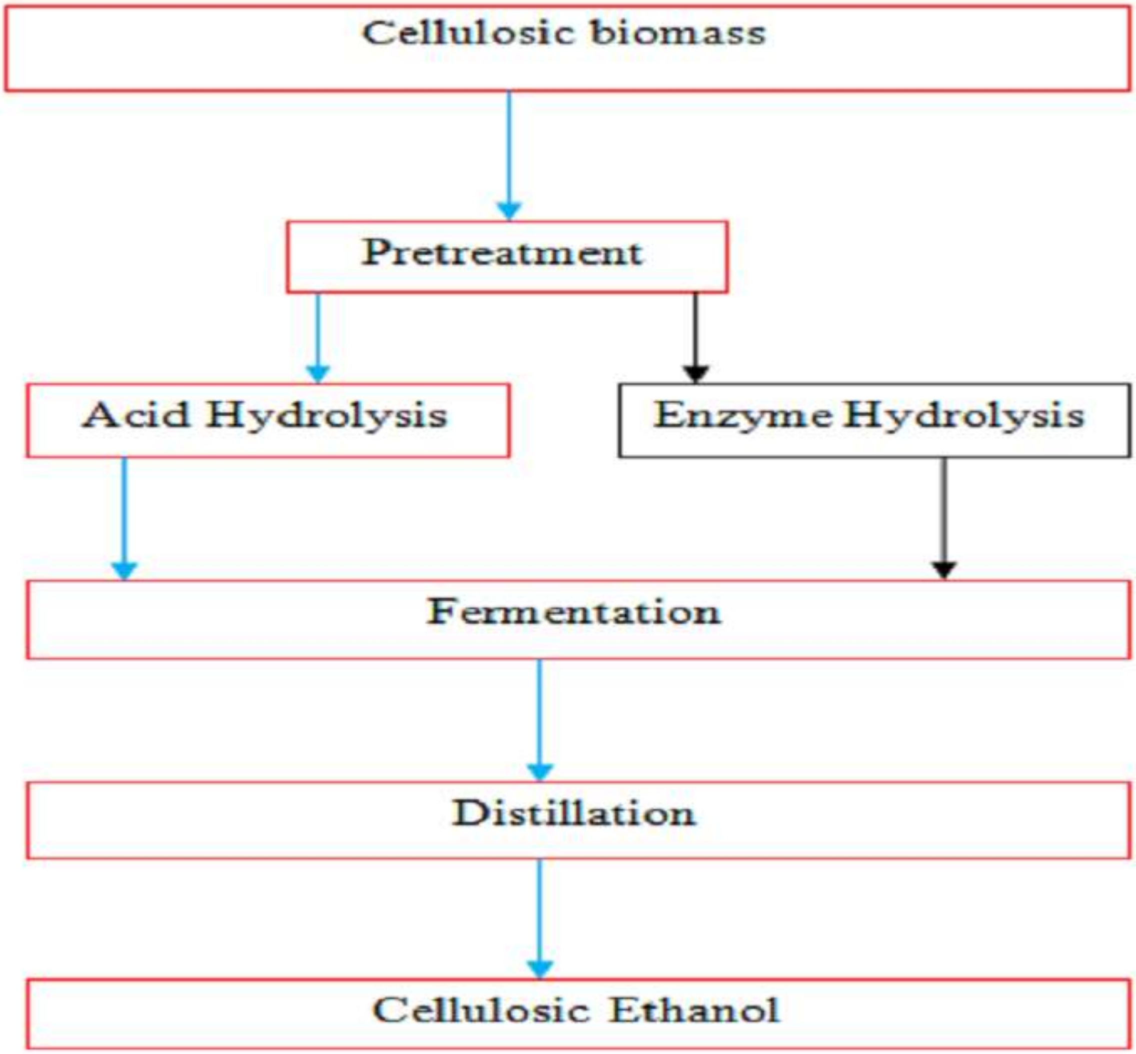


Figure 4 Hydrolyzed methods for cellulosic feedstocks

2.7.1. Acid hydrolysis

Acids have been used to catalyze (speed up) the hydrolysis of starch in “starch cookers “operating at temperatures of 50 to 150°C, a process referred to as acid hydrolysis. There are two basic types of acid processes: dilute acid and concentrated acid, each with variations. Dilute acid processes are conducted under high temperature and pressure, and have reaction times in the range of seconds or minutes while concentrated acid process conducted under low temperatures and pressures employed allow the use of relatively low cost materials, such as fiberglass tanks and piping (Zhu et al., 2008).

2.7.1.1. Dilute Acid Processes:

Most dilute acid processes are limited to a sugar recovery efficiency of around 60 to 75%. The reason for this is that at least two reactions are part of this process. The first reaction converts the cellulosic materials to sugar and the second reaction converts the sugars to other chemicals. Unfortunately, the conditions that cause the first reaction to occur also are the right conditions for the second to occur. Thus, once the cellulosic molecules are broken apart, the reaction proceeds rapidly to break down the sugars into other products most notably furfural, a chemical used in the plastics industry. The biggest advantage of dilute acid processes is their fast rate of reaction, which facilitates continuous processing. The biggest disadvantage is their low sugar yield. For rapid continuous processes, in order to allow adequate acid penetration, feedstocks must also be reduced in size so that the maximum particle dimension is in the range of a few millimeters.

2.7.1.2. Concentrated Acid Process

Concentrated acid process uses relatively mild temperatures and the only pressures involved are usually only those created by pumping materials from vessel to vessel. In the TVA concentrated acid process, corn Stover is mixed with dilute (10%) sulfuric acid, and heated to 100ºC for 2 to 6 hours in the first (or hemicellulose) hydrolysis reactor.

The low temperatures and pressures minimize the degradation of sugars. To recover the sugars, the hydrolyzed material in the first reactor is soaked in water and drained several times. The solid residue from the first stage is then dewatered and soaked in a 30% to 40% concentration of sulfuric acid for 1 to 4 hr. as a precellulose hydrolysis step (Cellulosic Ethanol, 2010). The primary advantage of the concentrated process is the high sugar recovery efficiency, which can be on the order of over 90% of both hemicellulose and cellulose sugars. The low temperatures and pressures employed allow the use of relatively low cost materials such as fiberglass tanks and piping. Unfortunately, it is a relatively slow process and cost effective acid recovery systems have been difficult to develop.

2.7.2. Enzyme hydrolysis

Enzymatic hydrolysis is a method in which cellulases are utilized for the hydrolysis. This is a quite new approach compared to concentrated-acid and dilute-acid hydrolysis. The organism responsible for producing the cellulolytic enzymes was Trichoderma reesei, which today is used in the enzyme industry for producing a wide range of commercial enzymes (Sheehan and Himmel, 1999). The cellulases involved in the hydrolysis of lignocellulose include endoglucanases, which attack low-crystallinity regions of the cellulose fiber and generate free chain-ends, and exoglucanases, which remove cellobiose from the free chain ends. Pretreatment of the lignocellulose prior to the enzymatic hydrolysis is necessary to achieve feasible reaction rates. The aim of the pretreatment is to make the cellulose more accessible to enzymatic attack due to weakening of the protecting lignin and hemicellulose matrix or due to alteration of the pores in the material. Advantages of enzymatic hydrolysis are high yields, due to the highly specific cellulose conversion, and that the reaction is performed at moderate temperatures. Furthermore, the byproduct formation is low. The disadvantages are the slow reaction rate of the enzymes and the high enzyme cost (Lynd et al., 2005). Ethanol production by enzymatic hydrolysis can be performed in a Separate Hydrolysis and Fermentation (SHF) mode or in a Simultaneous Saccharification and Fermentation (SSF) mode. In the SHF process, hydrolysis is performed separately from fermentation, which means that the optimal temperatures for both the enzymatic hydrolysis and fermentation can be applied. A drawback with SHF is that the generated cellobiose functions as cellulase inhibitor (Mandels and Reese, 1963).

2.8. Fermentation

The fermenting of the biomass is conducted under standard fermenting conditions and will utilize all the major biomass. Yeast is the most commonly used microorganism in fermentation processes. The yeasts used are typically brewers' yeasts. Examples of yeast capable of fermenting the decaying biomass include, but are not limited to, Saccharomyces cerevisiae and Saccharomyces uvarum. Non-Sacharomyces yeasts, also known as non-conventional yeasts, are also used to make a number of commercial products.

Microorganisms other than yeast can also be useful in making fermentation products. For example, cellulosic ethanol production also utilizes fungi and bacteria. Examples of these cellulolytic fungi include Trichoderma reesei and Trichoderma viride. One example of a bacteria used in cellulosic ethanol production is Clostridium Ijungdahlii. Mid- to long-term technology under development are expected to improve the fermentation efficiency of the organism, producing higher yields in less time, and an organism requiring less detoxification of the hydrolyzate (Cellulosic Ethanol, 2010).

$$3C_5H_{10}O_5 \xrightarrow{yeast} 5C_2H_5OH + 5CO_2 \qquad \Delta H = -74.986 \ \text{kJ/mol}$$

$$C_6H_{12}O_6 \xrightarrow{yeast} 2C_2H_5OH + 2CO_2 \qquad \Delta H = -84.394 \ \text{kJ/mol}$$

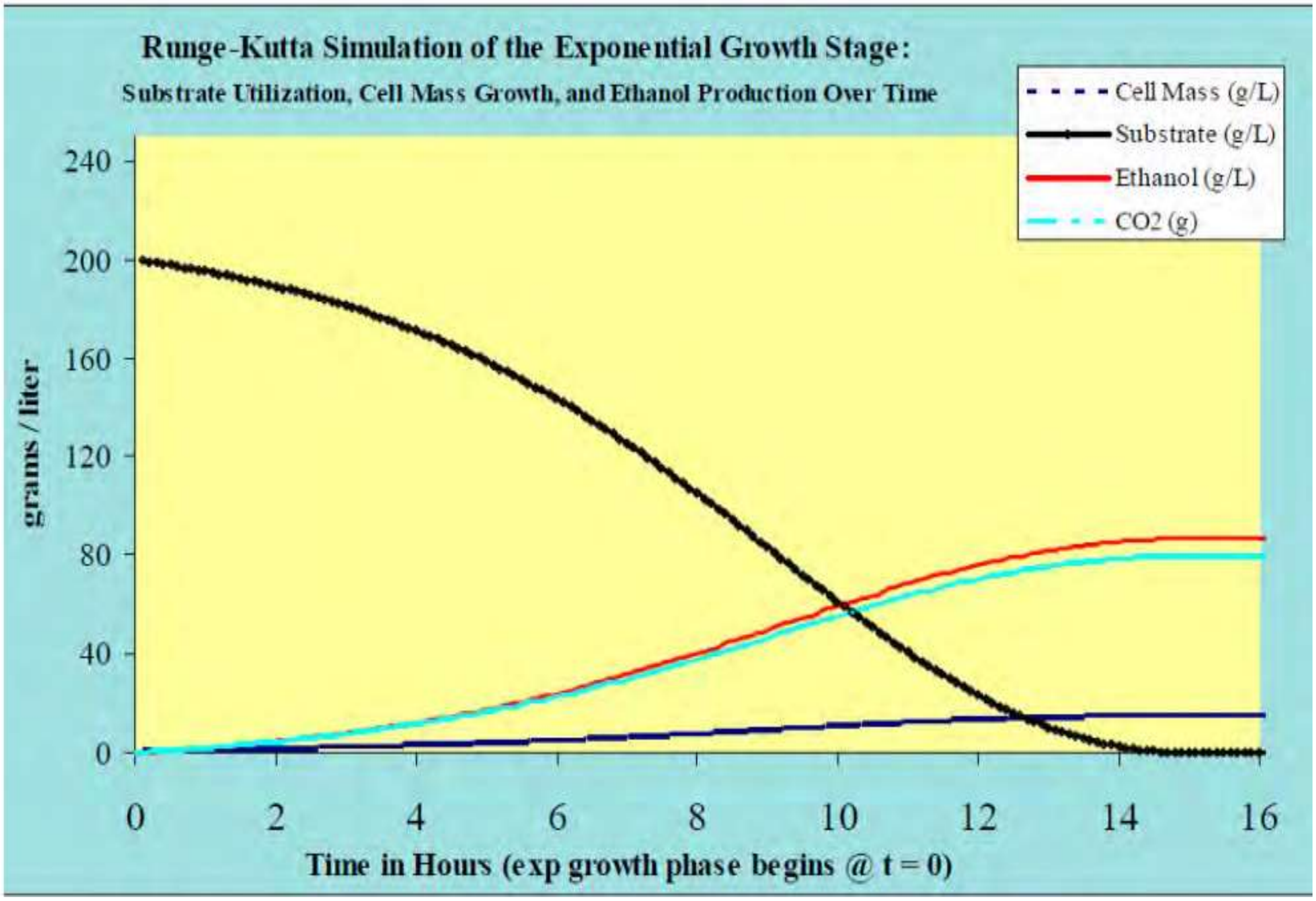


Figure 5 Glucose, Alcohol, CO2, Cell Mass Levels during Fermentation (Source: N. Mosier and M. Ladisch).

2.9. Distillation

Distillation is one of the steps of the purifications. Distillation is the method used to separate two liquid based on their different boiling points. However, to achieve high purification, several distillations are required. This is because all materials have intermolecular interactions with each other, and two materials will co-distill during distillation. This means that proportion between two materials, in this case ethanol and water can be changed, and still, there are two materials in layers, the liquid and the vapor layers (Onuki, 2005). Whatever method of preparation is used, the ethanol is initially obtained in a mixture with water. The ethanol is then extracted from this solution by fractional distillation. Although the boiling point of ethanol, 78.3^0C, is significantly lower than the boiling point of water, 100^0C, these materials cannot be separated completely by distillation. Instead, an azeotrope mixture (i.e. a mixture of 95% ethanol and 5% water) is obtained, and the boiling point of the azeotrope is 78.15^0C. In a distillation, the most volatile material (i.e. the material that has the lowest boiling point) is the first material to distill from the distillation flask, and this material is the azeotrope of 95% ethanol which has the lowest boiling point. If an efficient fractionating column is used, 95% alcohol could be obtained first and then a small intermediate fraction of lower concentration, and then water. But no matter how efficient the fractionating column used, 95% alcohol cannot be further concentrated by distillation because the vapor has exactly the same composition as the liquid; towards distillation, then, 95% alcohol behaves exactly like a pure compound (Jackman, 1987).

2.10. Dehydration

After distillation, about 5% of water remains in ethanol. Especially, this water is a big problem for fuel ethanol because the presence of this amount of water enhances the molecular polarity of ethanol when it is mixed with gasoline. Consequently, they separate into two phases, ethanol phase and gasoline phase. It is easy to imagine that this inhomogeneous fuel is not acceptable. Thus, dehydration can be another issue (Onuki, 2005). For the ethanol to be usable as a fuel, water must be removed. Most of the water is removed by distillation, but the purity is limited to 95-96% due to the formation of a low boiling water ethanol azeotrope. For blending with gasoline, purity of 99.5 to 99.9% is required, depending on temperature, to avoid separation. Currently, the most widely used purification method is a physical absorption process using molecular sieves and another method is azeotropic distillation.

Molecular sieves: There is a lower bound on the fraction of ethanol entering the molecular sieve (0.8). Adsorption takes place at 95 °C. Heat exchanger heats the inlet stream from the mixer up to 95 °C. The molecular sieve is a bed of zeolite that operates in semi-continuous mode. The bed is saturated with water after a period of time and is then regenerated. Hence, there are usually two sieves being operated in parallel – one being saturated with water while the other is being regenerated (or dehydrated) using air under vacuum. Heat exchanger heats air with an assumed relative humidity of 70% at 20 °C to 95 °C. The air at the outlet of the dehydrating molecular sieve is cooled down to 25 °C in heat exchanger and this stream leaves this exchanger saturated with water at 25 °C (Mariano Martín and Ignacio E. Grossmann, Carnegie Mellon University).

2.11. Thermo-chemical Conversion Process

This process route includes production of syngas using gasification of the biomass, and fermentation or catalytic synthesis of the syngas to produce ethanol. The process begins with biomass gasification where, under a controlled oxygen supply, cellulose, hemicellulose, and lignin are converted to synthesis gas (syngas), primarily CO, CO_2 and H_2. This syngas can be converted into ethanol either through catalytic synthesis; biomass gasification offers an attractive alternative system for producing cellulosic ethanol. Although gasification reactions can take many forms, these processes are defined by cranking up the temperature to between 650 and $1{,}400^0$C.

CHAPTER THREE

3. MATERIAL AND METHODS

The experiments of production of ethanol from fruit peel were carried out in the laboratory of Chemical Engineering Department at Wolkite University College of Engineering and Technology.

3.1. Materials Use for the Experiments

3.1.1. Equipments

- Plastic bags: - to collect and transport samples to the laboratory.
- Knife: - for cutting the fruit wastes in to pieces.
- Digital and non-digital driers or ovens: - to dry the sample.
- Crushers: - to crush the dried sample.
- Sieves: - to sieve the crushed sample to the particle size of 2mm.
- Balances: - to weigh samples and yeast.
- Digital pH meter: - to measure the pH of the hydrolysate before fermentation.
- Thermostats: - to control temperature of the sample under experiment (fermentation and distillation) isothermally at the set point.
- Vessels: - to hold samples and additives for hydrolysis, fermentation and distillation experiments.
- Centrifuge: - to separate the soluble liquid from non-soluble part.
- Graduated cylinders of different volumes: - for volume measurement.
- Autoclave: - for sterilization and hydrolysis.
- Pycnometer and Hydrometer: - for density measurement.
- Shaker:-to shake sample and its additives after hydrolysis and before fermentation.
- Fermentation and distillation set ups: - to ferment and distill respectively.

3.1.2. Chemicals

- Dilute Sulfuric Acid (H_2SO_4)
- Sodium Hydroxide (NaOH):- used to adjust the PH of soluble cellulose and hemicelluloses before fermentation.):- used as a pretreatment and hydrolysis fruit peel.
- Yeast extracts (Agar):- used as media preparation.
- Urea: - used as media preparation.
- Dextrose sugar: - used as media preparation.
- $Mg\ SO_4.7\ H_2$
- Yeast (Saccharomyces cerevisiae).

3.2. Procedure of Experiment

The stud y was aimed at optimization of acid hydrolysis in the production of ethanol from fruit peel. Fruit peels were collected from juice house in Gubre town. They were collected in plastic bags and transported to Wolkite university chemical engineering lab for ethanol analysis. The following methods were followed. This section describes about the methodologies and approaches of how experiments were done in this research; it included all steps and procedures of the experiments.

The followings were basic steps for the production of ethanol alcohol, these processes were:-

- Sample collection.
- A pre- treatment phase (size reduction) to make fruit peel agreeable to hydrolysis.
- Hydrolysis to break down the molecules of cellulose and hemicelluloses into simple sugars.
- Yeast fermentation of the resulting (sugar) solution.
- Distillation to produce alcohol.

3.2.1. Sample Preparation

The sample that was acquired had to be prepared and conditioned for pretreatment, hydrolyze, fermentation and distillation. Sample preparation process include: manual size reduction (Knife cutting), drying, grinding and sieving after the samples were collected. Waste peel of orange, mango and banana, each 1.5kg was used for the sample preparation. They were cut by knife into pieces of about 1-2 cm length for drying and grinding. Sample drying was carried out in ove

3.2.2. Pre -Treatment of Fruit Peel Powder

The purpose of the pretreatment was to remove lignin, reduce cellulose crystallinity and increase the porosity of the materials. Pretreatment must meet the following requirements: improve the formation of sugar, avoid the degradation or loss of carbohydrate, avoid the formation of byproduct inhibitors and must be cost effective. Steam Pretreatment: The powders of fruit peel were treated inside autoclave; every different sample was treated separately. Steam pretreatment uses steam at 121oC temperatures. Flow through processes steam at temperature of 121oC through the hemicelluloses and cellulosic material. First, the fruit peel powders were treated and it feed as batches, every batch contains 100 g (equal proportion, 33.3g) of screened fruit peel powder with 10:1(v/w) ratio of water to the sample. The temperature was applied at 121°C; then released the pressure until the pressure 0 bar. The retention time for every batch was15min. Finally the samples was kept in autoclave for the given pretreatment time and temperature and allowed to cool.

(A) (B) (C)

Figure 6 (A) Banana peel, (B) Mango peel and (C) Orange peel sample

3.2.2.1. Procedures in Steam Pretreatments

Add 100 g of grinded fruit peel in to 2000 ml conical flasks. Add 1000ml of distilled water. The conical flasks capped with the help of rubber plugs. Autoclave at a temperature of 121^{0}C. After finishing the given pretreatment time and temperature the sample in autoclave and allowed to cool and separate soluble from the non-soluble portion. The non-soluble portion is hydrolyzed in the next steps and put the soluble solution in another 2000ml conical flask.

(a) (b)

Figure 7(a) Steam Pretreatment of fruit peels powder in autoclave (b) Sample ready for pretreatment.

3.2.3. Acid Hydrolysis

The cellulose molecules which are composed of long chains are broken down to simple sugar, before it is fermented for alcohol production. Even though there are many types of hydrolysis types, dilute acid hydrolysis is an easy and productive process and the amount of alcohol produced in case of acid hydrolysis is more than that of alkaline hydrolysis. Each sample had to pass through five primary experiments that were in series to get the final result ethanol, that is: size reduction, pretreatment, hydrolysis, fermentation and distillation. The three -parameter were applied to hydrolysis step of the experimentation. The hydrolysis experiments for ethanol production and optimization were conducted in a completely randomized design using Design expert® 7 software. 100g of grinded fruit peels were used for each experiment and the factors for hydrolysis were time (5 to 45 minutes), hydrolysis temperature (100 to132^{0}C), and acid concentration (0.5 to1%).

Table 2 Minimum and Maximum values of parameters

Factors	Minimum	Maximum
Hydrolysis time(minutes)	5	30
Hydrolysis temperature^{0}C	100	132

Acid concentration (% by volume of distilled water)	0.5	1

Table 3 Experimental design formulated for hydrolysis stage

S. Number	Actual Value		
	Acid con.	Temp (^{0}C).	Time(Min)
1	0.50	100	10
2	0.75	120	15
3	1	132	30

Figure 8 Sample ready for hydrolysis

3.2.3.1. Procedures for Acid Hydrolysis

Add 1 liter of 0.5% to 1% (v/v) diluted sulfuric acid to the non-soluble component from pretreatment steps in the order of experimental design for all experiment and soak for 24hr. The fruit peels were then hydrolyze in the reactor between 100 and132^{o}C. After hydrolysis, neutralize with 10 M NaOH until the pH became around 7. For 5 to 25min. Separate the solid particles from the liquid in the hydrolyzate by centrifugation (to remove the non-fermentable lignin portion). After separate the solid part, wash the solid part with distilled water two times. The washing was performed in order to extract all soluble sugars from the solid fruit peel material. To obtain the original sugar concentration in the hydrolyzate, the liquid parts were boiled until the liquid weight become 1.0 kg. Then solid and liquid parts placed in the freezer until used. Then mix the soluble component with the previously filter solution from the pretreatment step for the next procedure.

(a) (b)

Figure 9 (a) Sample ready for centrifugal separation (b) Centrifuge Machine

3.2.3.2. PH Adjustment

Before addition of any micro-organism to the above prepared samples, pH of these samples has to be adjusted. Otherwise the micro-organism will die in hyper acidic or basic state. A pH of around 5.0 -5.5 is maintained.

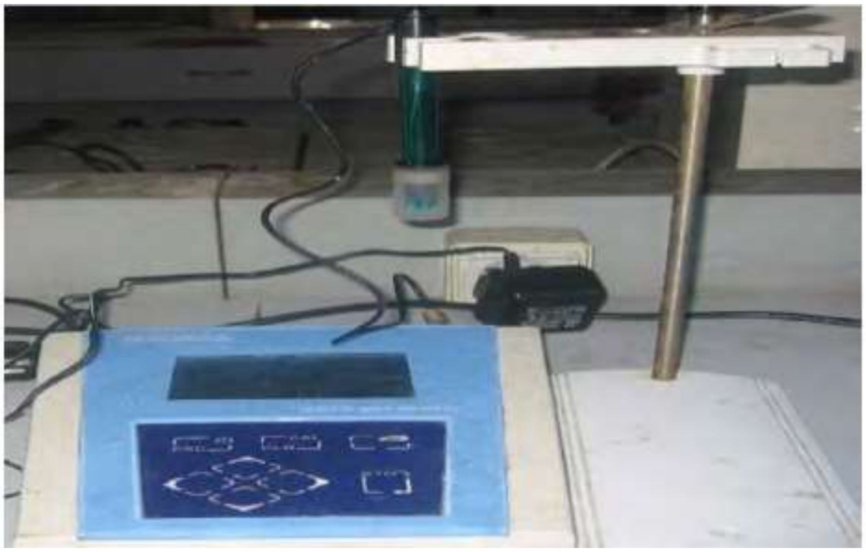


Figure 10 pH meter

3.2.3.2.1. Procedures in pH adjustment

Mix pretreated and hydrolyzed solution, filtered, shaken substrate primarily checked for pH using a digital pH meter. The pH then adjusted to 5.0-5.5. Mix samples (pretreated and hydrolyzed) were acid hydrolyzed, so it needs highly basic solution to bring the pH in the range of 5.0-5.5. Sodium hydroxide solution was added drop wise to the other flask with constant stirring until the pH reaches to a range of 5.0-5.5. If suppose the pH goes beyond 5.0-5.5, concentrated sulfuric or hydrochloric acid was added drop wise to maintain the pH in the range.

3.2.4. Sterilization

The reactor and all the equipment's that were used for fermentation purposes were sterilized (autoclaved). The sterilization was carried out at a temperature of 121^0C for 15 minutes.

Figure *11 Sterilization equipment*

3.2.5. Fermentation

The aim of the experiment was to measure the ethanol production by the fungus (Saccharomyces cerevisiae) using fruit peel hydrolyzate as energy and carbon source. The clear solutions then go to fermentation. The fermentation was carried out under anaerobic condition at a temperature of 30^{O}C for preparing 100 ml media, we add, pH 5.5 with 200 rpm stirring condition for 3 days. Before conducting fermentation, we had preparation of media for the yeast. In order to prepare the media, we had the favorable condition for yeast growth or to supply the required amount of nutrients. Mix the following nutrients in their proportion.

3.2.5.1. Media Preparation

- For preparing 100 ml media, we add
- Sugar (Dextrose) = 10 gm
- Yeast extract = 0.2 gm
- Urea = 1.0gm
- Make up water = 100 ml
- Mg SO4.7 H2O = 1.0g

Procedures in Media Preparation

To the above 100 ml media, 0.5 gm of yeast, Saccharomyces cerevisiae (instant premium) was added in a 250 ml conical flask. The conical flasks were properly covered with aluminum foil. The conical flask was placed in a shaking incubator for 24hrs, a temperature of 30^{O}C and 200rpm.

(a) (b)

Figure 12(a) Shaker incubator (b) media after 24hr incubation

The Procedure for Fermentation

The sample was conditioned to temperature of 30^{0}C 30C before fermentation step was started. This was the temperature at which all fermentation experiments were carried out. The adapted media with the proportion of 1:10 to the soluble sample mix then placed in the shaking incubator at a temperature of 30^{0}C, 1 hour and 120 rpm. Set autoclavable reactor at 30^{0}C and 200 rpm and then mix the prepared sample with the media prepared into the autoclavable reactor using sterilized funnel. The parameters of fermentation i.e. fermentation time, yeast concentration (yeast proportion) and fermentation temperature were set to be at 72 hour, 10% (with the proportion of 1:10 that is the prepared media and sample respectively) and 30^{0}C respectively. And after 72 hours of fermentation, the samples were taken out and distilled. Base (2 M NaOH) added automatically by a pump into the bioreactor every time to drop PH below 5.5.

3.2.6. Distillation

Distillation was the last step in the production of ethanol from fruit peel experiments. It is the purifications steps. Distillation is the method used to separate two liquid based on their different boiling points. However, to achieve high purification, several distillations are required. In this experiment separation were used by rotary evaporator at a temperature of 85^0C for 3hrs.

Components of experimental setup

- Distillation vessel
- Special top-fit of distillation vessel
- Condenser
- 90^0C diverting glass that fits at the end of condenser and the top of harvesting vessel.
- Condenser tubing
- Harvesting vessel.
- Stands and fixing screws.
- Beaker.
- Thermostat.
- The thermostat supporting flat metal bar.

All distillation experiments were carried out at a temperature of 85^0C and a distillation time of 3 hours.

Figure 13 Distillations (Rotary Evaporator))

3.2.7. Density Measurements

The ethanol concentrations of the samples collected every 3 hours intervals by rotary evaporator of fermented solution were measured by the following the procedure of Geirwyr (1995). The specific gravity of the produced alcohol was determined and alcohol concentration was got from the relationship between the specific gravity and the proportion of ethanol in alcohol solution at 20^0C and a distillation time of 3 hours. Weigh the pycnometer (specific gravity bottle) with stopper after cleaning, drying and note the weight as X1 at 20^oC. Filled the pycnometer with distilled water and take the weight of the water at 20^oC and note as X3. Make the pycnometer empty, clean, dry and then filled with sample (alcohol) of the experimental result. Determine the weight of the sample at 20^oC and note as X2. Calculate the net weight in grams of the alcoholic liquid in the pycnometer by subtracting the weight of the empty specific gravity bottle or pycnometer. Calculate specific gravity of sample according to the formula given.

Specific gravity of sample = (X2-X1)/(X3-X1), where: X1- weight (g) of empty pycnometer

X2- weight (g) of pycnometer + sample

X3- weight (g) of pycnometer + water

CHAPTER FOUR

4. RESULT AND DISCUSSION

4.1. Statistical Analysis of the Experimental Results

The process consists of four parts: pretreatment to remove lignin, reduce cellulose crystallinity, sterilize the fruit peel and increase the porosity of the materials, dilute acid hydrolysis and fermentation to produce ethanol, distillation to remove the ethanol. After following the above series of procedure, the experimental outcomes of those particular results are measured for their moisture content using electronic balance and to know the mass of fruit peel after drying. The results are indicated below, table 4.1 (using electronic) and 4.2 (using Pycnometer). Experimental, design expert® 7 software, gives a great tool to study the outcome (effect) of different variables in any process so that it also use this tool to discuss the result obtained from the experiment.

Table 4 result obtained from the preparation

Fruit peel	Mass before drying(Gm)	Mass after drying (gm)	Moisture content
Mango	492	165.0	327
Banana	422	95.5	326
Orange	469	122.7	346.3

From the experimental procedure we have investigate that mass orange has higher moisture content than the rest other fruit peel to these lead to higher energy consumption to dry. The moisture content of each fruit peel is calculated as follow

$$MC = MBD - MAD$$

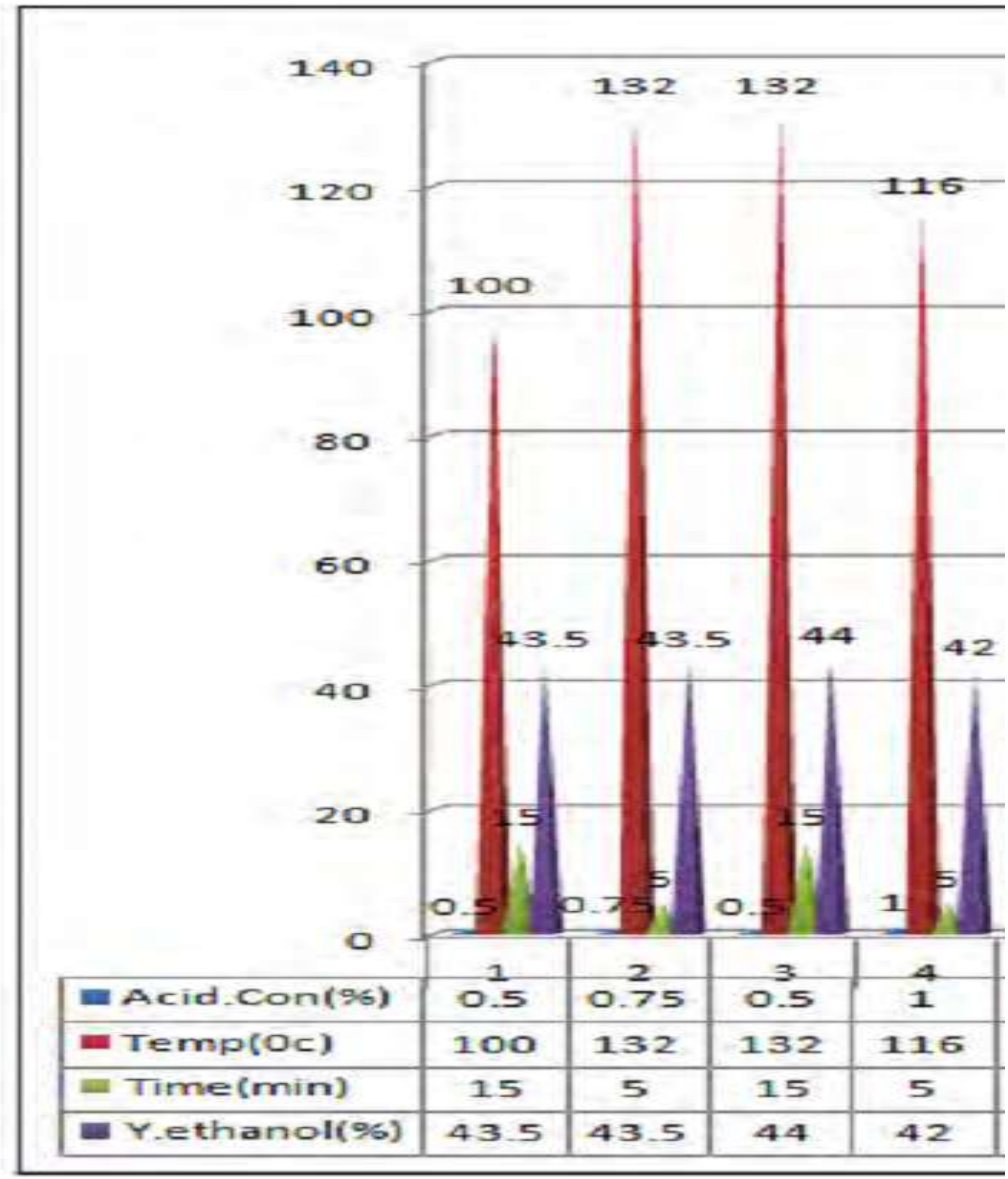
Where, MC is mass of moisture content

MBD mass before drying, MAD, mass after drying

Table 5 yield of ethanol

Run No	Densities(g/ml^3)	Yield of ethanol (%)
1	0.90	40
2	0.90	40
3	0.90	40
4	0.93	38

As shown on the above two table (table 4.2) the yield of ethanol concentration (%) are different since hydrometer are read two digits after point where as the pycnometer are measured, the variation of the yield of ethanol production is due the factor that is applied on it the measuring equipment accuracy. Hydro meter is the seldom measuring equipment. But the pycnometer result were read exactly from Perry Chemical Engineering Handbook. The discussion will be on measuring equipment the availability of laboratory appartures. From the experiment the max yield of ethanol is 1, 2, and 3, run. The accuracy of the measuring pycnometer is the same as PHCE as shown below.



	1	2	3	4
🟦 Acid.Con(%)	0.5	0.75	0.5	1
🟥 Temp(0c)	100	132	132	116
🟩 Time(min)	15	5	15	5
🟪 Y.ethanol(%)	43.5	43.5	44	42

Source PHCE

Figure 14 Ethanol yield and parameters condition

As we see from the above figure 4.1 high yield of ethanol were observed at 0.75% acid concentration, at 132^{0}C temperature and at the time of 15min. In this study experimental design techniques were used to determine the effects of the acid concentration, hydrolysis time and temperature on the efficiency of ethanol yield. A total of 4 experiments were carried out for optimization purpose where the effect of each factor was analyzed by using lower and higher values from optimized conditions. The ethanol yields obtained from experiments were used as a response parameter for optimization and table 4.3 show respective yields of each run with the factor.

Table 6 optimization table

Run No	Acid conc.(% by weight)	Temperature (^{0}C)	Time (min)	Yield of Ethanol (%)
1	0.5	100	10	40
2	0.75	132	25	40
3	1	132	15	40
4	0.5	116	30	38

4.2. Effects of Experimental Variables on Hydrolysis

Ethanol production can be affected by many parameters starting from sample preparation to distillation, the hydrolysis steps has a complex connection with independent variables. The best way of showing the effects of this parameter for the yield of ethanol are to generate response surface plots of the equation. The three dimensional i.e. interactions, contours and response surfaces effect were plotted in figures (4.2), (4.3) and (4.4) below as a function of the interactions of any two of the variables by holding the other value of the variable at middle. For the interaction figures, black and red line indicates low and high level of parameters respectively. For the interaction figures, black and red line indicates low and high level of parameters respectively.

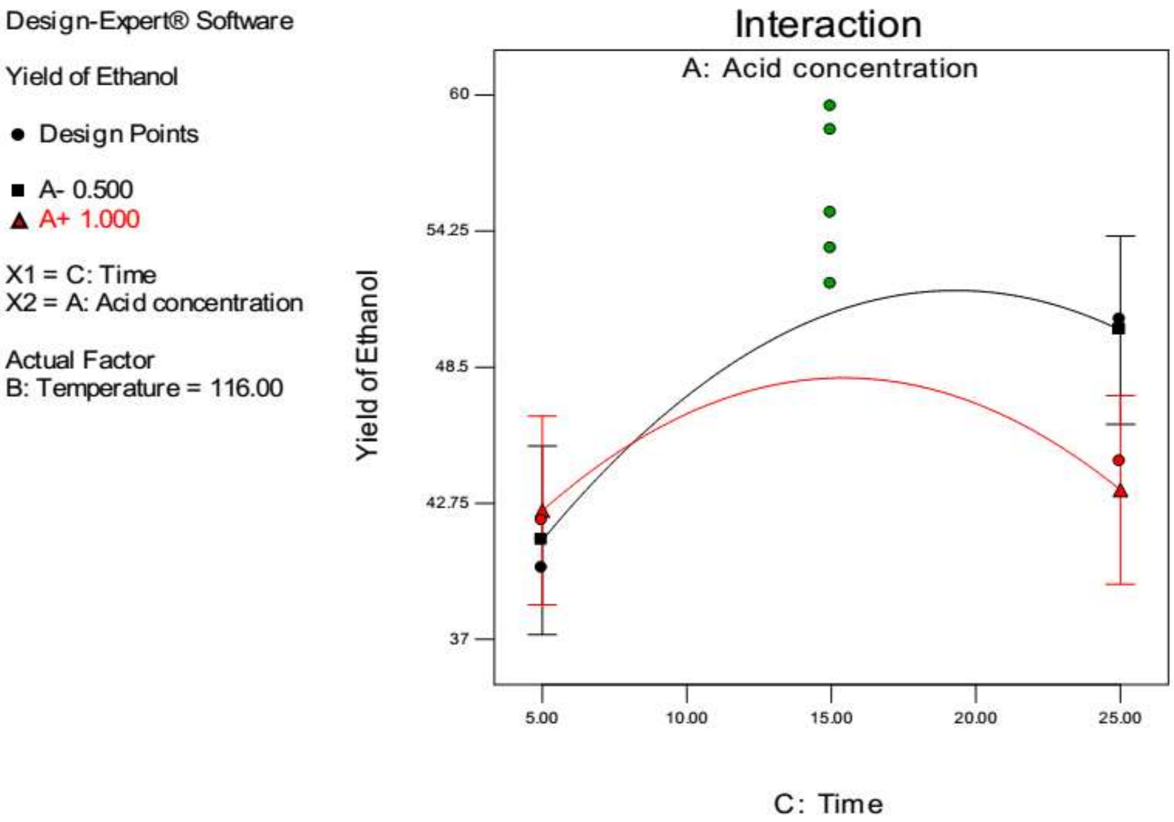


Figure 4.2. The effects of time and acid concentration.

(a)The effects of time and acid concentration (fixed) on the yield of ethanol, when the temperature was at the center point.

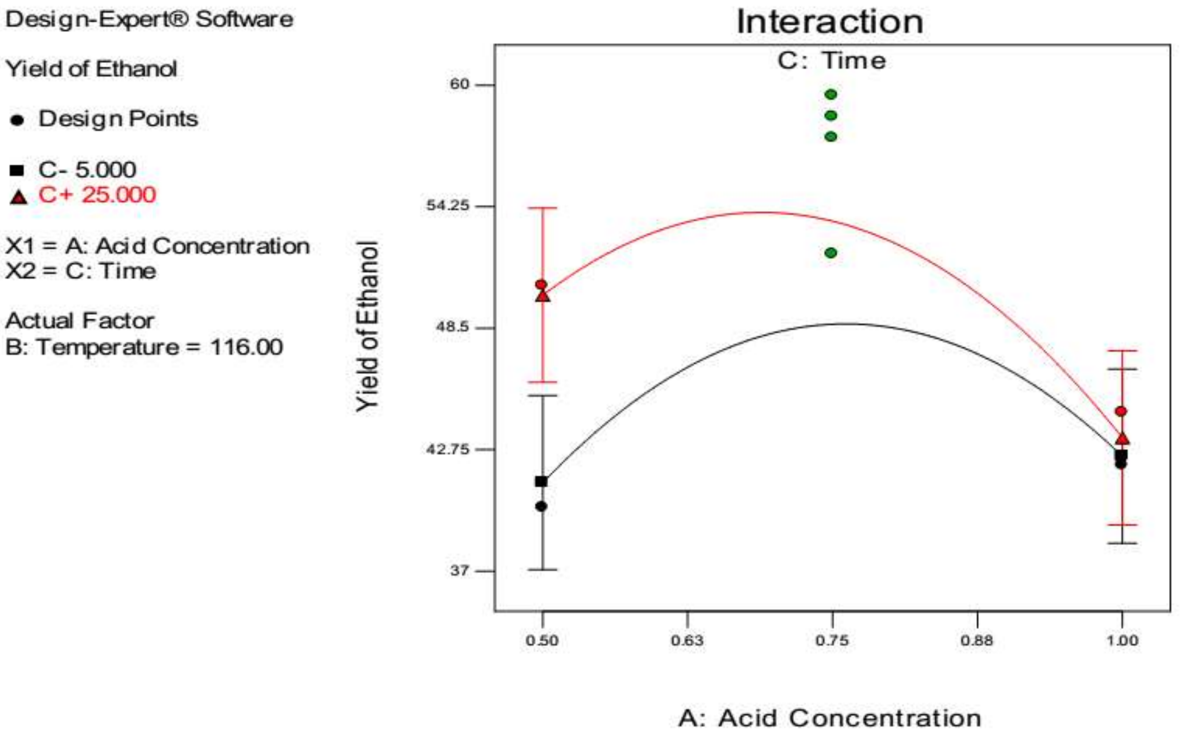


Figure 4.3 the effects of time (fixed) and acid concentration

On the yield of ethanol, when the temperature was at the center point

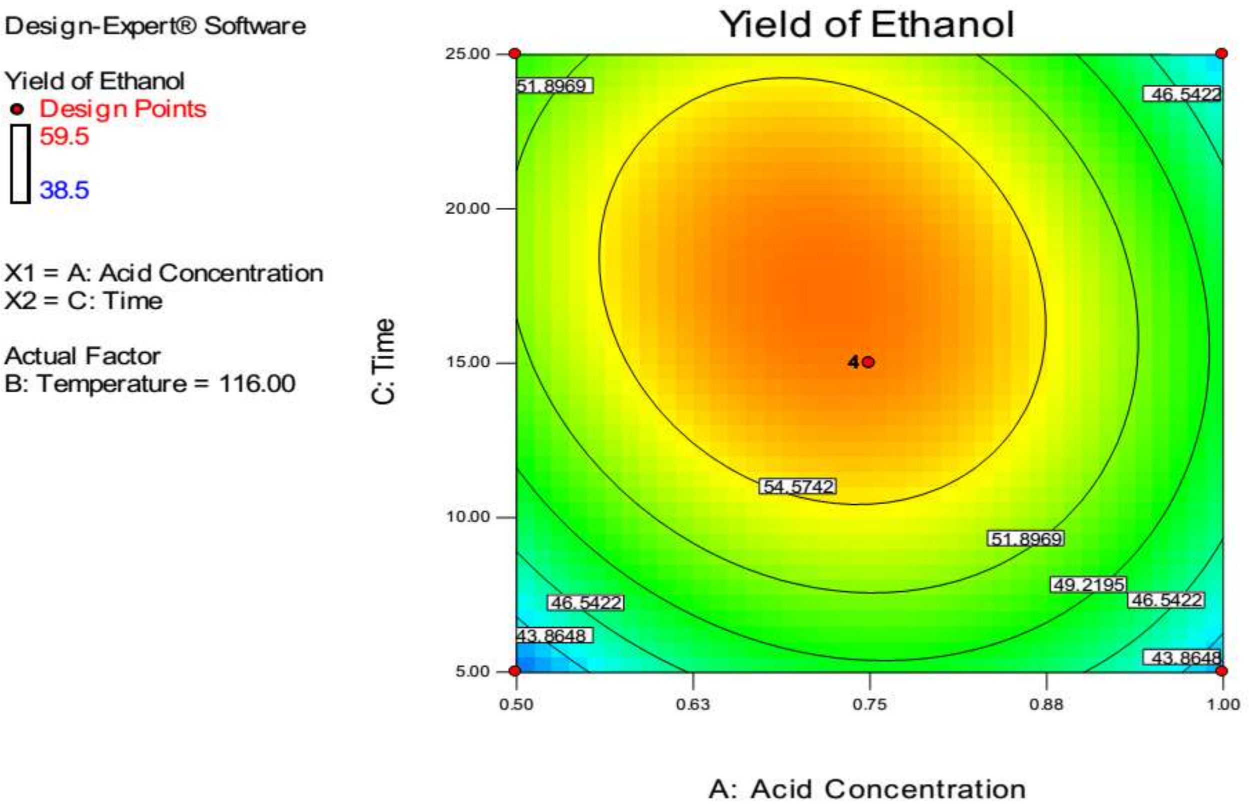


Figure 15 Contour plots of the effects of acid concentration and time on ethanol yield.

The effects of acid concentration and time on the yield of ethanol, temperature was selected at the center point, are shown in figure 4.4 (a) & (b). At the lower and higher levels of acid concentration and time, the production of ethanol yield level decrease since it has effect of the hydrolysis treatment. At lower acid concentration and time the cellulose might not hydrolysis to simple glucose and at higher acid concentration and time the cellulose might convert to other molecules which might not be fermentable. Hence both acid concentration and time have strong relationship for the yield of ethanol production.

4.3. Optimizations

The optimization of hydrolysis criteria for ethanol production from fruit peel using dilute acid treatment are summarized as follows:

Table 7 optimization of hydrolysis criteria for ethanol production from fruit peel using dilute acid

Parameters	Purpose	Minimum value	Maximum value
Acid concentration (%)		0.5	1
Temperature(^{0}C)		100	116
Time (min)		10	25
Yield of Ethanol (%)		40	40

CHAPTER FIVE

5. Material and Energy Balance

Material and energy balances are very important in an industry. Material balances are fundamental to the control of processing, particularly in the control of yields of the products. The first material balances are determined in the exploratory stages of a new process, improved during pilot plant experiments when the process is being planned and tested, checked out when the plant is commissioned and then refined and maintained as a control instrument as production continues. When any changes occur in the process the material balances need to be determined again. The increasing cost of energy has caused the industries to examine means of reducing energy consumption in processing. Energy balances are used in the examination of the various stages of a process, over the whole process and even extending over the total production system from the raw material to the finished product.

The energy balance determinations are also made to determine the energy requirements of the process, the heating, cooling and power required. In this plant operation it is thought that an energy balance (energy audit) on the plant will show the pattern of energy usage and suggest areas for conservation and savings.

5.1. Material Balance

Basis: one operation day/24hr ,

Production: $3*10^6$lit/year of ethanol (99.9%) with plant operation of 300 calendar days per year.

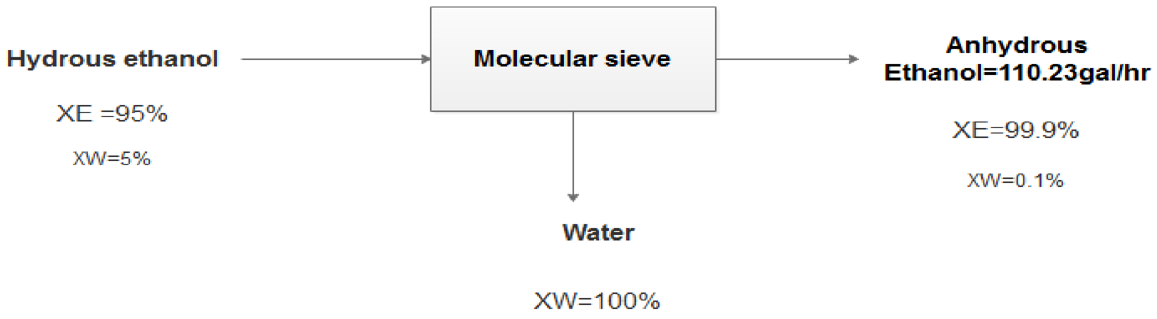
Anhydrous ethanol (lit/hr) = $\frac{\boldsymbol{total\ capacity}}{\boldsymbol{24*300}} = 416.67\ lit/hr$**,** = 110.23gal/hr

$$\varrho = \frac{m}{v}\text{ , m} = \varrho\, v\text{ , where } \varrho = \text{density of ethanol}$$

$$= 6.61\frac{Ib}{gal}*110.23\frac{gal}{hr} = 728.6203\frac{Ib}{hr}$$

$$= 728.6203\frac{Ib}{hr}*\frac{1kg}{2.20462\ Ib}$$

$$m = 330.5\ \frac{kg}{hr}\ = 2379.6\frac{ton}{yr}$$



Where XE= Percentage of Ethanol

XW= Percentage of water

Hydrous ethanol (gal/hr.) enter into sieve = $\frac{\boldsymbol{anhydrous\ \ Ethanol}}{\boldsymbol{1-hydrous\ Ethanol\ fraction}}$ = $\frac{110.23\text{gal/hr./}}{(1-0.05)}$= 347.4kg/hr.= **2504.88ton/yr.**

The water that is trapped by the molecular sieve is

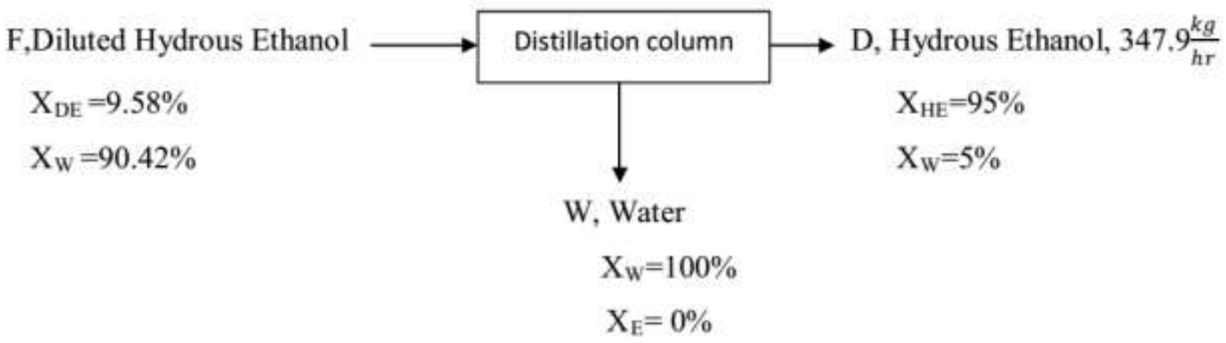
Mass flow rate of hydrous ethanol = Mass flow rate of water leave sieve + Mass flow rate of anhydrous ethanol leave the sieve

MHE = MW + MAE

MW = MHE - MAE= 347.9-330.5 = 17.4$\frac{Kg}{hr.}$ = 125.28$\frac{ton}{year}$

5.1.1. Material balance for distillation

It is the equipment used for the purification of ethanol from water-ethanol mixture. The mixture from fermentation enter in to the distillation with the mixture of 9.58% ethanol and the rest water, then with two series distillation column the purification of ethanol come to 95%.



Where XDE = fraction of diluted hydrous ethanol

XW = fraction of dilute hydrous ethanol and hydrous ethanol

XHE = fraction of hydrous ethanol

MB, W = F-D, F = W + D

From ethanol component balance, we have

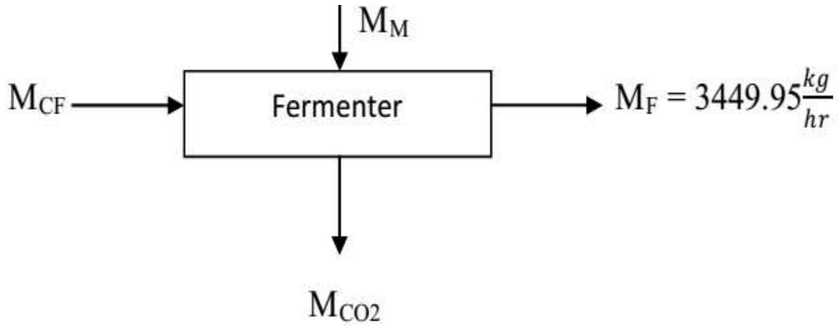
$$F*XF = W*XE + D*XHE$$

$$F = \frac{W*XE+DXHE}{XF}$$

From these, W = F-D, $= 3449.95 - 347.9 = 3102.05\frac{kg}{hr} = 22334.76\,\frac{ton}{year}$

5.1.2. Material Balance for Fermentation

Total material balance in the fermenter



Where MCF = mass of centrifuge (filter) mash

MM =mass of media

MCO2 = mass of co2 release

M_F = mass of fermented mash.

From the reaction of fermentation

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$$

$$180\ gm/mol \longrightarrow 92gm/mol\ ethanol + 88\ gm/mol\ CO_2 for\ 100\%\ conversion.$$

But 1 – 3% of glucose not changed from literature and we have to take the value i.e. 97% efficiency.

$\frac{MGF}{180} = \frac{347.9}{2*46}$, $M_{GF} = \frac{347.9*180}{88} * 0.97 = 660.25\frac{kg}{hr.} = 4753.8\frac{ton}{yr}$

And the amount of carbon dioxide produced is

$\frac{660.25}{180} = \frac{MCO2}{88}$ - M_{CO2} = =2324.09$\frac{ton}{yr}$ of CO_2 produced

Mass of the media is 10% of the mass of filter mash, hence from the total mass balance

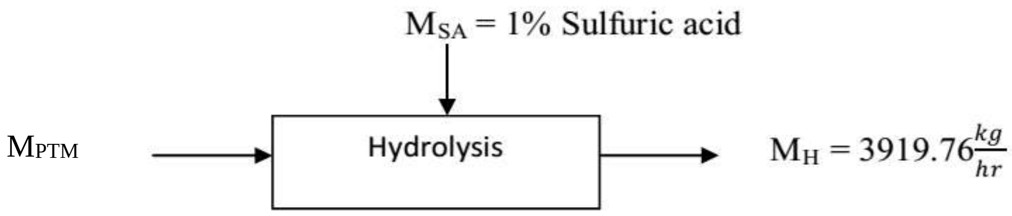
$M_{CF} + M_M = M_F + M_{CO2}$

$M_{CF} + 0.1\ M_{CF} = 3449.95\frac{kg}{hr} + 322.79\frac{kg}{hr} = 1.1M_{CF} = 3772.74\frac{kg}{hr}$

M_{CF} = 3429.76kg/hr., M_M, = 342.98kg/hr. = 24369.48ton/yr.

5.1.3. Mass balance for dilute acid treatment (Hydrolysis)

The pretreated sample is soaked and treated with 1% sulfuric acid to convert cellulose to glucose and serve as catalyst meaning it has no any reaction with cellulose.



Where M_{PTM} = Mass flow rate of pretreated mixture

$M_{SA,}$ = mass of diluted sulfuric acid

Reaction

$$C_6H_{10}O_5 + H_2O \longrightarrow C_6H_{12}O_6$$

1 mole of cellulose ⟶ 1 mole of glucose for 100% conversion.

But not complete conversion and assume that 95% of cellulose converts to glucose.

$$\frac{MPTM}{162} = \frac{3919.79}{180}$$

M_{PTM} = $3351.39\frac{kg}{hr}$ = 24130ton/yr.

Applying total mass balance

$M_{PTM} + M_{SA} = M_H$

$M_{SA} = M_H - M_{PTM}$

= 3919.76 – 3351.39

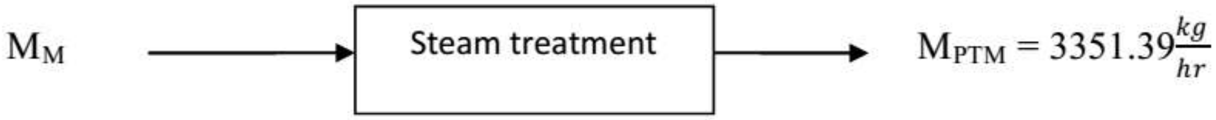
= 568.37 kg/hr. = 4092.26 ton/yr. of 1% dilute sulfuric acid.

From this component of mass of sulfuric acid,

= 0.01*568.37 = = 5.6837kg/hr. = 40.92ton/yr. of sulfuric acid

5.1.4. Mass balance for steam treatment

It is the method to prepare the sample for dilute acid treatment.



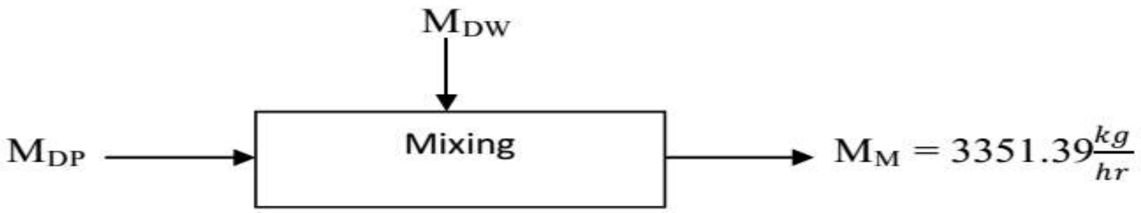
Where MM =Mass flow rate of mixture

$M_M = M_{PTM}$

M_M= 3351.39 kg/hr. = 24130ton/yr.

5.1.5. Material balance for Mixing

It is the equipment used to make homogenous suspension of distilled water and dry fruit peel powder.



Where M_{DP} = Mass flow rate of dry fruit peel powder

M_{DW} = Mass flow rate of distilled water

$M_{in} = M_{out}$

$M_{DP} + M_{DW} = M_M$

$M_{DP} + 10M_{DP}$= 3351.39kg/hr. = 11MDP = 3351.39kg/hr.

M_{DP} = 304.67kg/hr. = 2193.6ton/yr.

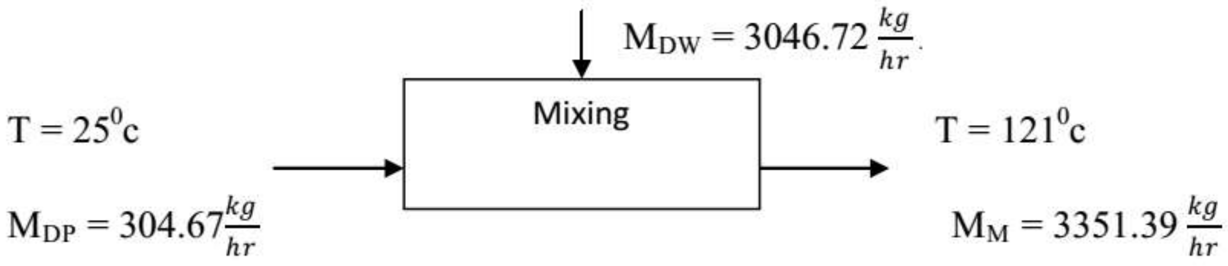
M_{DW} = 10*304.67kg/hr. = 3046.72kg/hr. = 21936.38ton/year

5.2. Energy Balance

Energy is an important and costly input in the production process of ethanol. After feedstock costs, it is the most expensive variable cost. This energy is utilized in two forms, thermal (steam) and electrical. Electrical energy is used to run machinery with moving parts or motors such as pumps, centrifuges, and mills.

5.2.1. Energy Balance for Mixing

It is the energy used for mix the grind fruit peel powder and distilled water to make suspension.



$$C_{PM} = \frac{304.67*3.90+3046.72*4.18}{304.67+3046.72} = 4.155\frac{kJ}{kg.k}$$

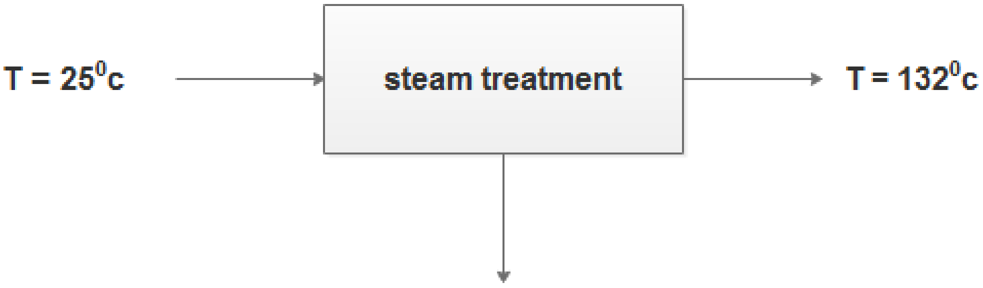
The heat required for mixing is, $Q = M_{WCP}\ \Delta T$

$$= 3351.39*4.155*(25 - 20)$$

$$= 69625.117 KJ/Kg$$

5.2.2. Energy balance on steam treatment

It is the energy used for pretreatment



The heat required for steam pretreatment is, $Q = M\ C_p\ \Delta T=$

Where m = mass of fruit peel

C_P = specific heat of wetted fruit peel

$\Delta T = T_f - T_i$ $Q = m\ C_p\ \Delta T$

$$= 3351.39 kg/hr. \times\ 4.124 * (132 - 25)^o k$$

$$= 1478861.707\frac{KJ}{hr.}$$

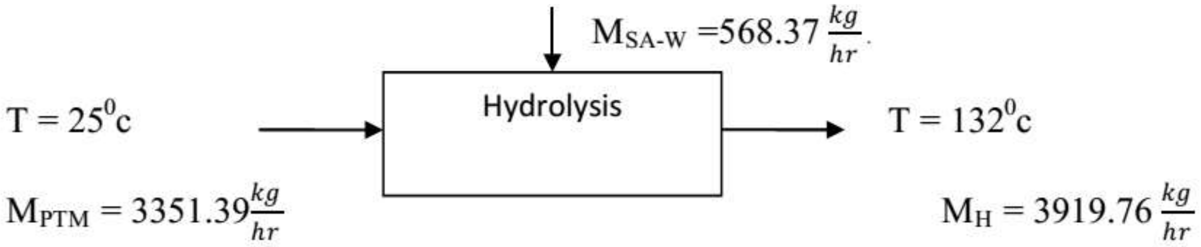
Steam consumption

$$Q = M_S \, Cp \, \Delta T + hlw$$

$$M_S = \frac{Q}{Cp\Delta t + HFW} = \frac{1478861.7}{4.16*107+2256.7} = 500.16kg$$

5.2.3. Energy balance for Hydrolysis

It is the energy used for hydrolyses cellulose to glucose



$$C_{PM} = \frac{3351.39*3.90+568.37*4.18}{3351.39+568.37} = 4.13\frac{kJ}{kg.k}$$

The heat required for hydrolysis is

$Q = M_H CP\Delta T$

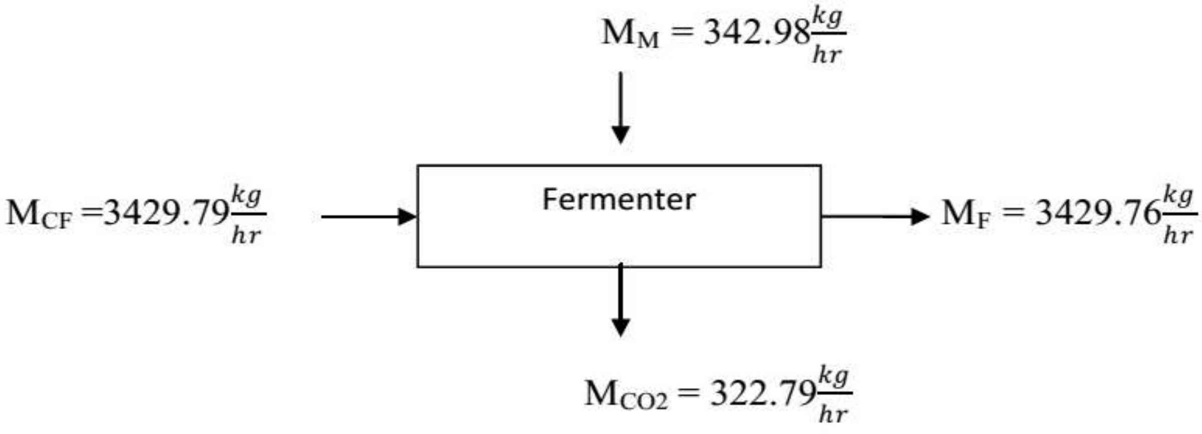
= 3919.76 *4.13*(132 - 25)

= 1732181.142kJ/hr.

Steam consumption, $Q = M_S \, Cp \, \Delta T + h_{lw}$

$$M_S = \frac{Q}{CP\Delta T + Hfw} = \frac{\mathbf{1732181.142kj/hr}}{\mathbf{4.13*107+2256.9}} = 641.8kg$$

5.2.4. Energy balance for fermenter



Fermentation is an exothermic reaction heat will be generated inside the fermenter and the outlet temperature is 30^0C. The energy balance in the fermenter at 0^0C reference temperature.

Data,

Cp of mix at 30^0C = 4.142kJ/kgK

Cp of CO_2 at 30^0C = 0.846kj/kgK

$$Q_{MIX} = Q_{CO2} + Q_F + Q$$

$$Q = Q_{MIX} - Q_{CO2} - Q_F$$

$Q = M_{MIX}\ CP_{MIX}\ \Delta T - M_{CO2}\ CP_{CO2}\ \Delta T - M_F CP_F\ \Delta T$

$CP_F = CP_{MIX}X_{MIX} + CP_{CO2}X_{CO2}$ → $X_{CO2,} = \frac{322.79}{3429.76+342.98} = 0.086$

$$X_{MIX} = 1- 0.086 = 0.914$$

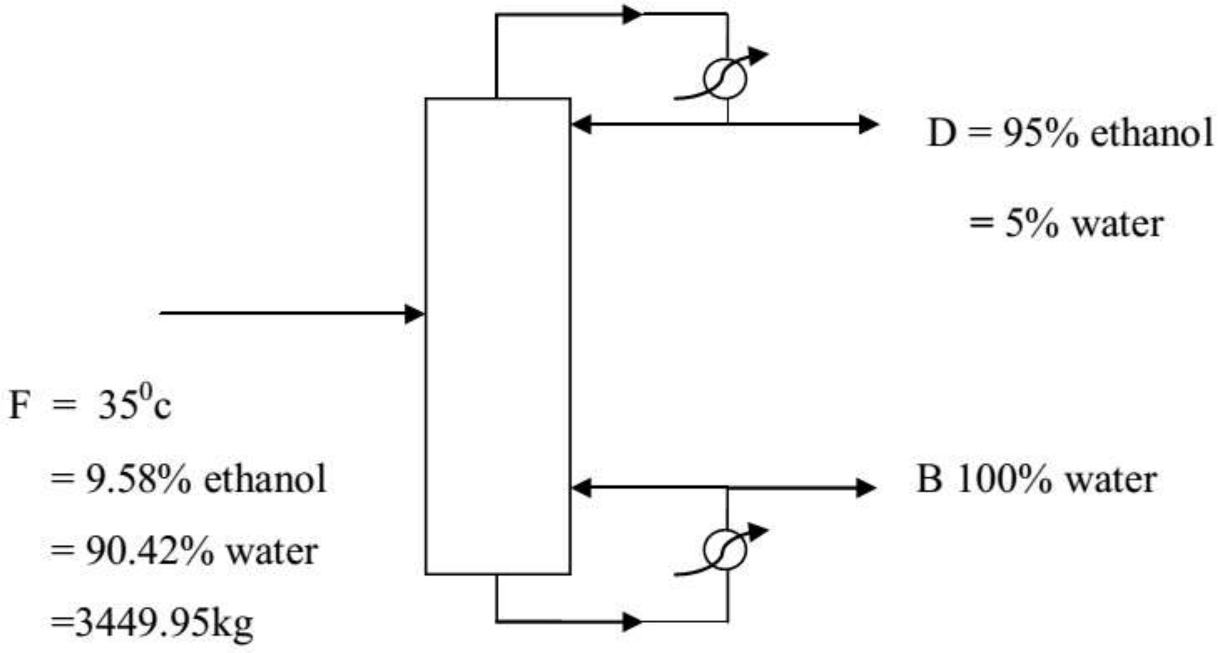
$$CP_F = 4.142*0.914 + 0.846*0.086 = 3.86kJ/kgK$$

$Q = M_{MIX}\ Cp_{MIX}\ \Delta T - M_{CO2}\ Cp_{CO2}\ \Delta T - M_F CP_{F\Delta}T$

$= 3772.74*4.142*(30-0) – 322.79*0.846*(30-0) – 3449.95*3.86*(30-0)$

$= 61104.05$Kj

5.2.5. Energy balance on distillation column



From ethanol component balance

$FX_F = DX_D$

3449.95*0.0958 = D*0.95, → D = (3449.95*0.0958)/ 0.95 = 347.9kg/hr.

W = F – D

= 3449.95 – 347.9, → = 3102.05kg/hr.

Energy balance

Basis 25^0c, 1hr

Heat capacity on top, Cp, distillate = 0.95*2.72 + 0.05*4.18 = 2.793kJ/kgK

Heat capacity on bottom Cp water = 4.18kJ/kg

Reflux ratio, R = 2.5, $R = \frac{L}{D} = 2.5$

$L = 2.5*D$

$$= 2.5*347.9 = 869.75\frac{kg}{hr}$$

$$V = L + D$$

$$= 869.75 + 347.9 \quad = 1217.65 kg/hr.$$

From vapor equilibrium data, Boiling point of 95% alcohol = $78.13^{0}C$

Input = Out put

At steady state $H_F = H_D + H_L + Q_C$

$$Q_C = H_F - H_D - H_L$$

Assuming complete condensation,

Enthalpy of Vapor = Latent + Sensible heat

$$H_V = M_V \lambda_V + M_V C_P \Delta T$$

$= 1217.65*789 + 1217.65*2.72*(78.13 - 25) \longrightarrow = 1136692.835 kJ/hr.$

Q_B = is determined from a balance over complete system,

Input = Out put

$$Q_B + H_F = Q_C + H_D + H_W$$

$$Q_B = Q_C + H_D + H_W - H_F$$

Heat capacity of feed

$$H_F = M_F.C_p.\ \Delta T$$

$= 3449.95*4.04*(35 - 25), \longrightarrow 139377.98 kJ/hr$

Heat capacity of bottom, $H_W = M_W.C_p.\ \Delta T$

$$= 3102.05*4.18*(100-25)$$

$$= 972492.675 kJ/hr$$

$Q_B = Q_C + H_D + H_W - H_F, \longrightarrow 1136692.835 + 0 + 972492.675 – 139377.98$

$$= 1969807.53\text{KJ/hr}$$

Q_B = re-boiler heat input

Q_C = condenser cooling

Q_B is supplied by condensing steam, Latent heat of steam at 274KN/M^3

$$\lambda v = 2174\text{KJ/kg}$$

Steam required, $\longrightarrow \frac{QB}{\lambda s} = \frac{1969807.53KJ/hr}{2174kj/kg} = 906.2kg/hr$

Q_C is removed by cooling water with a temperature rise of 30^{0}C

$$Q_C = M_W CP\Delta T$$

$$M_W = \frac{QC}{CP\Delta T} = \frac{1136692.8w}{4.18*30} = \frac{9064.5kg}{hr}.$$

CHAPTER SIX

6.1 SIZING AND DESIGN OF MAJOR PROCESS EQUIPMENT

Storage tank and pumps	dried fruit peel
Basis one hour	
Storage tanks for dried fruit peel	
Solid to be handled	
Density of solids	$1030 = \frac{Kg}{M^3}$
Temperature of solids	25^0C
Materials of construction	carbon steel
Capacity	75%

$$\rho = \frac{m}{v} = \longrightarrow , \ v = \frac{m}{\rho} , = \frac{3351.39kg/hr}{1003kg/M^3} = 0.3M^3$$

Required storage volume

$Vr = 0.30m^3/0.75 = 0.4m^3$

Storage tank for pretreatment

Slurry to be handled	mixture of water and fruit peel powder
Density of slurry	$1015kg/m^3$
Temperature of slurry	25^0C
Materials of construction	carbon steel
Capacity	75%

$$v = \frac{m}{\varrho} = \frac{3919.76kg/hr}{1015\frac{kg}{m^3}} = 3.8618m^3 = 3.87m^3$$

Required storage volume

$$V_r = \frac{v}{0.75} = \frac{3.87m^3}{0.75} = 5.16m^3$$

6.1.1. Storage tank for Fermentation,

Liquid to be handled	water and treated fruit peel mixture
Density of liquid	1015kg/m^3
Temperature of liquid	25^0C

Capacity

$$v = \frac{m}{\varrho} = \frac{3449.95kg/hr}{1015\frac{kg}{m^3}} = 3.39896m^3 = 3.4m^3$$

Required storage volume (Vr), → 3.4m^3/0.75, = 4.53m^3

6.1.2. Storage tank for hydrolyzed

Slurry to be handled	slurry of fruit peel and water mixture
Density of liquid	1015kg/m^3
Temperature of slurry	25^0C
Materials of construction	Carbon steel

Capacity

$$v = \frac{m}{\varrho} = \frac{3919.76kg/hr}{1015\frac{kg}{m^3}} = 3.8618m^3 = 3.87m^3$$

Required storage volume

$$V_r = \frac{v}{0.75} = \frac{3.87m^3}{0.75} = 5.16m^3$$

6.1.3. Storage tank for fermentation

Liquid to be handled	water and treated fruit peel mixture
Density of liquid	1015kg/hr
Temperature of liquid	25^0C

Capacity

$$v = \frac{m}{\varrho} = \frac{3449.95kg/hr}{1015\frac{kg}{m^3}} = 3.39896m^3 = 3.4m^3$$

Required storage volume

$$V_r = \frac{v}{0.75} = \frac{3.4m^3}{0.75} = 4.53m^3$$

Storage tank for ethanol

Liquid to be handled	Ethanol
Density of liquid	$790kg/m^3$
Temperature of liquid	25^0C
Materials of construction	carbon steel

Capacity

$$v = \frac{m}{\varrho} = \frac{330.5kg/hr}{790\frac{kg}{m^3}} = 0.42\ m^3$$

Required storage volume (Vr)

$$V_r = \frac{0.42}{0.75} = \frac{0.42}{0.75} = 0.56\ m^3$$

6.1.4. Storage tank for the mixing of water and fruit peel powder

Slurry to be handled	water and fruit peel powder mixture
Density of liquid	$0.1*1030 + 0.9*1000 = 1003kg/m^3$
Temperature of liquid	25^0C
Materials of construction	carbon steel

Capacity

$$\rho = \frac{m}{\nu} \ , v = \frac{m}{\rho} ,= \frac{\frac{304.64kg}{hr}}{1030kg/m^3} \ 0.2958\mathrm{m}^3 = 0.3\mathrm{m}^3$$

Required storage volume

$$V_r = \frac{v}{0.75} = \frac{0.3m^3}{0.75} = 0.4m^3$$

6.1.5. Storage tank for pretreatment

Slurry to be handled	mixture of water and fruit peel powder
Density of slurry	1015kg/m^3
Temperature of slurry	25^{0}C
Materials of construction	carbon steel

Capacity

$$v \ = \frac{m}{\varrho} = \frac{3351.39kg/hr}{1015\frac{kg}{m^3}} = 3.30186m^3 = 3.3m^3$$

Required storage volume (Vr)

$$V_r = \frac{v}{0.75} = \frac{3.3m^3}{0.75} = 4.4m^3$$

6.1.6. Storage tank for Ethanol

Liquid to be handled	Ethanol
Density of liquid	790kg/m^3
Temperature of liquid	25^{0}C
Materials of construction	carbon steel

Capacity

$$v \ = \frac{m}{\varrho} = \frac{330.5kg/hr}{790\frac{kg}{m^3}} = 0.42 \ m^3$$

Required storage volume (Vr)

$$V_r = \frac{0.42}{0.75} = \frac{0.42}{0.75} = 0.56\ m^3$$

Pump for delivering for mixing tank storage

Type	centrifuge pump
	Operating condition
Head	4m
Slurry to be handled	mixture of water and fruit peel powder
Density	1003kg/m^3
Temperature of liquid	25^0C
Materials of construction	carbon steel
Capacity	3.35m^3/hr

6.2. Design for distillation column

A continuous fractionating column is to design to separate 3449.95kg/hr. of ethanol water mixture with 9.58% ethanol and 90.42% water so as to give 99.9% ethanol and a waste of 100% water. A reflux ratio of 2.5 of product is assumed to be used. The column works at a vacuum of 0.4bar with a vapor velocity of 0.75m/s.

Molecular weight of ethanol = C_2H_5OH, $M_{WT,}$ = 2*12 + 5 + 16 +1 = 46gm/mol.

Molecular weight of water = H2O

= 18g m/mol.

Boiling point of ethanol = 78.13^0C = 351.13k

Boiling point of water = 100^0C = 373k

Feed mean molecular weight = 0.0958*46 + 0.9042*18, $\longrightarrow$ = 20.68gm/mol

Specific heat of feed = 0.0958*2.72 +0.9042*4.18 = 4.04kJ/kg.k

Water mole fraction on feed,

$$Y_F = \frac{\frac{90.42}{18}}{\frac{90.42}{18}+\frac{9.58}{46}} = \frac{5.0233}{5.0233 + 0.208} = 0.96 = 96\%$$

Water mole fraction in distillate

$$Y_F = \frac{\frac{5}{18}}{\frac{5}{18}+\frac{95}{46}} = \frac{0.278}{0.278+2.065} = 0.1187 = 11.87\%$$

Water mole fraction in bottom

$$Y_B = \frac{\frac{100}{18}}{\frac{100}{18}} = 1 = 100\%$$

Ethanol mole fraction in feed

$$X_F = \frac{\frac{9.58}{46}}{\frac{9.58}{46}+\frac{90.42}{18}} = \frac{0.208}{0.208+5.023} = 0.0398 = 3.98\%$$

Ethanol mole fraction in distillate

$$X_D = \frac{\frac{95}{46}}{\frac{95}{46}+\frac{5}{18}} = \frac{2.065}{2.065+0.278} = 0.8813 = 88.13\%$$

Ethanol mole fraction in bottom, $X_B = 0\%$

Reflux ratio = 2.5

Molar latent heat of mixture in feed

λ= 0.0958*790 + 0.9042*2376.7 = 2224.69kJ/kg

$$2224.69\text{kJ/kg} * \frac{1kg}{0.021kmol} = 105937.619kJ/kmol$$

$$= 105937.619\text{kJ/kmol}*2.39*10^{-1}\frac{kgcal}{kJ} = = 25319.09\text{kcal/KJ}$$

Boiling point (average) of feed

$= \Sigma X_i T_i$

= 0.0398*308 + (1- 0.0398)*308 = 332.52k = 59.50C

Heat capacity of feed

CP_F = 4.04kJ/kg.k

= 4.04kJ/kg.k*0.23kg/kmol

= 0.9292kcal/kg.K

$$q = \frac{C_p\ dT + \lambda}{\lambda}$$

$$= \frac{0.9292(332.52-298) + 25319.09}{25319.09}$$

= 1.0013kJ/kg.k

Intercept on y-axis,

$$= \frac{X_D}{R_{D+1}} = \frac{0.95}{2.5+1} = 0.27$$

Table 8 VLE Vapor equation data of ethanol water solution given below

X(liq.)	0.01900	0.0721	0.0966	0.1238	0.1661	0.2337	0.2608	0.3273
Y(vap.)	0.1700	0.3891	0.4375	0.4704	0.5089	0.5445	0.5580	0.5826

0.3965	0.5079	0.5198	0.5732	0.6763	0.7472	0.8943	0.8943
0.6122	0.6564	0.6599	0.6841	0.7385	0.7815	0.7815	0.8943

Feed in cold liquid

$$\text{Slope} = \frac{q}{q+1} = \frac{1.0013}{1.0013+1} = 0.5$$

XF = 0.0398,   XD = 0.8813, XB = 0

Figure 6.2 McCabe-Thiele diagrams to determine number of stage

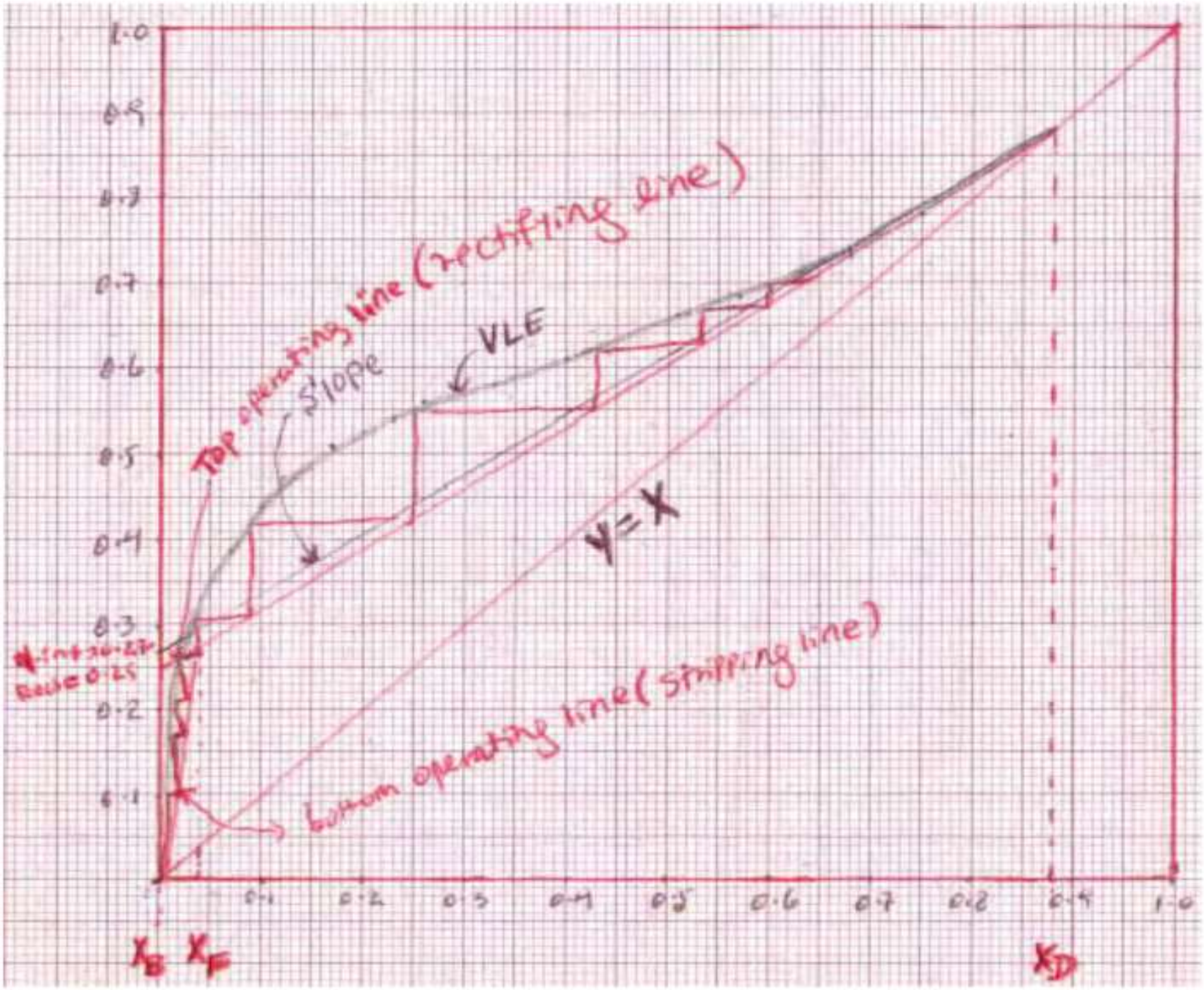


Figure 6.2 McCabe-Thiele diagrams to determine number of stage

With the above information, number of theoretical plate is 10 and feed is introduced at the 6 stages.

Diameter at the top

Temperature at the top is 85^{0}C (358k),

6.3. Condenser design

The condenser to be used is a horizontal condenser design to condense 247.9kg/hr of distilled ethanol at 25^{0}C by exchange with water at 20^{0}C and out let temperature of 30^{0}C. Fluid allocation is given tube side to water and shell side to ethanol.

Specification

Permissible pressure drop on both sides is 0.8bar

Fouling factor

Distilled ethanol = 0.0001m^{20}c/w

Water = 0.0003m^{20}c/w

The mean temperature of ethanol

$$=\frac{85+30}{2}=57.5\ ^0c=330.5k$$

At this temperature the C_P of ethanol is

$C_P = A + BT$

$$= 8.424 + 44.422*10^{-2}*330.5k$$

$$= 155.24kJ/kmol$$

$$= 155.24kJ/kmol*kmol/46$$

$$= 3.375kJ/kg.k$$

$$\text{Heat duty} = \frac{347.9kg/hr}{3600}*3.375(85-30) = 17.94kw$$

As the first trial the mean temperature of water is equal to the inlet temperature, thus Specific heat capacity of water at this temperature = 4.18kJ/kg.k

Energy balance of the previous

Mw = 9064.54kg/hr.

$$\frac{9604.54kg/hr}{3600s}*4.18(t_2-20) = 17.9kw$$

$t_2 = 21.61^0C$

The mean temperature of water is

$$t_2 = \frac{21.61+25}{2} = 23.31^0C$$

The specific heat capacity of water remains the same up to 50^0C, thus = 4.18kJ/kg.k

Over all coefficient

For condenser of this type the overall coefficients will be between 700-1000w/m^{20}C (Coulson vol IV, 2005). So, we start with 700 w/m^{20}C.

Condenser type and dimension

Even number tube pass is selected to simplify the pipe work

Start with one shell pass and two tube pass

$$\Delta T_{lm} = \frac{(85-23.31)-(30-20)}{ln\,[(85-23.31)/(30-20)]} = 13.1^0c$$

Hence,

$$R = \frac{85-30}{23.31-20} = 16.62$$

$$S = \frac{23.31-20}{85-20} = 0.05$$

From the graph of temperature correlation factor (Coulson vol IV, 2005)

Ft = 0.98

So $\Delta Tlm = 0.98 * 13.1 = 12.84^0C$

Heat transfer area,

$$A_u = \frac{Q}{U\Delta T} = \frac{17.94 * 10^3}{700 * 12.84} = 2m^2$$

Lay out

Use a splitting floating head heat exchanger for efficiency and ease of cleaning. Carbon steel is used since both fluids are not corrosive.

Assumed the following dimensions

Outside diameter = 19.05mm

Inside diameter = 14.83mm

Tube length = 4m since it is popular size

Pitch triangular = 23.81mm

Pitch / diameter = 1.25

Number of tubes

Area of one tube (neglecting thickness of tube sheets)

= πDL

= $3.14*19.05*10^{-3}*4$ = 0.2393m2

Number of tubes

$$=\frac{A_u}{\pi \mathrm{DL}}$$

$$=\frac{2}{0.2393}=8.36=9\text{tubes}$$

So far 2 passes, the tube per pass is

= 9/2 = 4.5 = 5 tubes,

Tube cross sectional area

$$=\frac{\pi \mathrm{D}^2}{4}$$

$$=\frac{3.14*(14.83*10)^{-3}}{4}$$

$$=0.00017\mathrm{m}^2$$

Area per pass

= 5*0.00017

= $0.00085m^2$

Volumetric flow rates,

$$= \frac{m_{H2O}}{\varrho_{H2O}} = \frac{9064.54}{3600} * \frac{1}{1000} = 0.0025\mathrm{m}^3/\mathrm{s}$$

Tube side velocity,

$$\mathrm{V_t} = \frac{0.0025}{0.00085} = 2.9\mathrm{m/s}$$

The velocity is satisfactory up to 4m/s to prevent fouling.

Bundle and shell diameter

One shell and two tube per pass from Coulson table

For two tubes pass of the triangular pitch K1 and n1 from the constant table (coulson volume IV, 2005)

K1 = 0.249

n1 = 2.207

$$\mathrm{D} = \mathrm{d_o}(\frac{N_t}{K_l})^{\frac{1}{n}}$$

$$= 19.05(\frac{10}{0.249})^{\frac{1}{2.207}}$$

$$= 101.53\mathrm{mm}$$

$$= 102\mathrm{mm}$$

For a split ring floating, the typical shell clearance is 50mm

D_b clearance = D_S-D_L = 50

D_S = 50+102= 152mm

Tube side heat transfer coefficient

$$\mathrm{R_e} = \frac{\varrho u d_i}{\mu} = \frac{1000*2.9*14.83*10^{-3}}{77*10^{-5}} = 55853$$

$$\mathrm{Pr} = \frac{\mu d_i}{k_f} = \frac{4.18*10^3*77*10^{-5}}{0.6} = 5.36$$

$$\frac{L}{d_i} = \frac{4000}{14.83} = 269.7$$

From the graph showing the tube side heat transfer factor Jh versus Re (Coulson vol IV, 2005)

$$J_h = 3.3*10^{-3}$$

$$Nu = J_h * Re*P^{0.33}$$

$$= 3.3*10^{-3}*55853*5.36^{0.33}$$

$$= 320.76$$

$$Nu = \frac{h_i d_i}{k_f}$$

$$h_i = \frac{0.6*320.76}{14.83*10^{-3}} = 12977.48 w/m^{2\ 0}c$$

Shell side heat transfer coefficient

Condensing vapor side

Kern’s method is used

For one tube passes of the shell side

k1 = 0.249

n1 = 2.207

$$D_b = D = d_o(\frac{N_t}{K_l})^{\frac{1}{n}}$$

$$= 19.05(\frac{10}{0.249})^{\frac{1}{2.207}} = 102mm$$

The bundle to shell clearance is around 50mm

Ds = 102 + 50 = 152mm

Baffle spacing

$$= \frac{Ds}{5} = \frac{152}{5} = 30.4 = 31mm$$

The area of the cross flow As, for the row of tubes at the shell equation

$$As = \frac{Pt - do}{Pt} *Ds*I_B$$

Where Pt = tube pitch

Do = outside tube diameter

Ds = shell inside diameter

IB = baffle spacing

$$As = \frac{23.81 - 19.05}{23.81} * 152 * 31$$
$$= 942 mm^2$$

For the equilateral triangle pitch arrangement, the shell side equivalent diameter

$$De = \frac{1.1}{d_0}(Pt^2 - 0.917{d_0}^2)$$
$$= \frac{1.1}{19.05}(23.81^2 - 0.917 * 19.05^2)$$
$$= 13.52mm$$

Volumetric flow rate on the shell side (ethanol side)

$$V = \frac{m}{\varrho}, \text{ where } \varrho = \frac{p}{RT} = \frac{0.4*10^2}{8.314*358} = 0.968$$

$$V = \frac{347.9}{3600*968} = 0.0000998 m^3/s$$

Shell side velocity

$$= \frac{volumetric \quad flow \ \ rate}{area} = \frac{0.0000998}{0.000942} = 0.11 m/s$$

$$Re = \frac{\varrho u d_i}{\mu} = \frac{790*0.11*13.52*10^{-3}}{1.8*10^{-3}} = 979.1$$

$$Pr = \frac{Cp\mu}{k} = \frac{4*10^{-3}*1.2*10^{-3}}{0.6} = 0.000008$$

Use baffle cut 25%, from the plot showing shell side heat transfer factor (coulson vol IV, 2005)

Jf = $1.8*10^{-2}$

$$Nu = \frac{h_s d_e}{k_f} \qquad \text{where } Nu = J_h * Re * Pr^{0.33}$$

$$= 1.8*10^{-2}*979.1*0.000008^{0.33}$$

$$= 0.37$$

$$d_e = 13.52*10^{-3}$$

$$k_f = 0.6$$

$$h_s = 0.37*0.6*13.52*10^{-3} = 0.003 \text{ w/m}^{2\ 0}\text{c}$$

Overall coefficient

$$\frac{1}{U_0} = \frac{1}{h_0} + \frac{1}{h_{0d}} + \frac{d_0 \ln \frac{d_0}{d_i}}{2k_w} + \frac{d_0}{d_i} * \frac{1}{h_{id}} + \frac{d_0}{d_i} * \frac{1}{h_{0d}}$$

Where h_0 = 0.003 w/m$^{2\ 0}$C

h_i= 12977.48w/m$^{2\ 0}$C

h_0d = 0.0001 w/m$^{2\ 0}$C (outside dirt coefficient)

h_id = 0.0003 w/m$^{2\ 0}$C

k_w = thermal conductivity of tube wall = 55 w/m$^{2\ 0}$c

$$= \frac{1}{0.003} + \frac{1}{0.0001} + \frac{19.05 \ln \frac{19.05}{14.83}}{2*55} + \frac{19.05}{14.83} * \frac{1}{0.0003} + \frac{19.05}{14.83} * \frac{1}{12977.48}$$

$$U_0 = 14615.24 \text{ w/m}^{2\ 0}\text{c}$$

Pressure drop

Number of tubes = 10

Number of pass = 2

Tubes inside diameter = 14.83mm

Tube side velocity, Vt = 2.9m/s

Re = 55853

From the graph showing tube friction factor (Coulson vol. 2005)

$J_h = 3.3*10^{-3}$

Hence, neglect viscosity correction factor

$$\Delta P_t = N_p[8j_f(\frac{L}{d_i})(\frac{\mu}{\mu_w})^{-m} + 2.5]\frac{\rho U_t^2}{2},$$ neglect viscosity correction factor

Where ΔPt = tube side pressure drop, N/m^2(pa)

Np = number of tube side passes.

Ut = tube side velocity, m/s

L = length of one tube

$$\Delta P_t = 2[8*3.3*10^{-3}(\frac{4000}{14.83}) + 2.5]\frac{1000*2.9^2}{2}$$

$= 80910 N/m^2$

= 0.8bar, it is satisfactory since within the specification

CHAPTER SEVEN

7.1. COSTING AND ECONOMICS

Before initiating the development of a process, at various stages in its development and before attempts the design of a process and plant it is the responsibility of the chemical engineer to make economic evaluation. The evaluation determines whether one should undertake the project, abandon it, continue with it (but with further research) or take it to the pilot plant stage.

Even if insufficient technical information is available to design a plant completely, we must still make and economic evaluation to determine if it is economically and financially feasible. A project economically feasible when it is more profitable than other competing project, and financially feasible when management can raise the capital for its implementation.

The economic evaluation of a process proceeds in several steps. These are:

- Preparing a process flow diagram
- Calculating mass and energy flows
- Sizing major equipment
- Estimating the production cost
- Forecast the product sales price
- Estimating the return on investment

The ultimate purpose for developing such a detailed process design and cost estimate is to determine the economics of ethanol production. The total capital investment (TCI) is first computed from the total equipment cost. Next, variable and fixed operating costs are determined. With these costs, we use a discounted cash flow analysis to determine the net present value (NPV) with a finite internal rate of return (IRR). This section describes the assumptions made in completing the discounted cash flow analysis.

For the cost estimation of the equipment of this plant design exchange rate is assumed i.e. 1US Dollar =34.0ET Birr. The cost indexes obtained from literatures are as follows:- The Marshal and Swift installed equipment index obtained is shown in the following table.

Table 9 Marshal and Swift installed equipment index

Year	Process industry index
1990	924
2001(July)	1352
2012	1780
2015	2000
2020 were extrapolated	from the earlier data

Cost data also obtained from table 9-50 of Perry’s chemical engineering hand book (7th edition) and Coulson volume 6 (4th edition) and equipment cost manipulation is based on Marshall Swift index of 1000.

New Cost = Base Costs * (New size /Base size)^n

$$\text{Present cost} = \text{original cost} * \frac{\text{index value at the present time}}{\text{Index value at the original cost was obtained}}$$

7.2. Total Capital Investment (TCI)

The next step is to determine the installed cost of that equipment. The installation cost can be determined by performing a detailed study of everything required to install the necessary equipment and make it operational.

The purchased cost for a given component reflects a baseline equipment size. As changes are made to the process, the equipment size required may be different than what was originally designed. Instead of re-costing in detail, an exponential scaling expression was used:

New Cost = Base Costs * (New size /Base size)^n

Where n is a characteristic scaling exponent (typically in the range of 0.6 to 0.7) based upon some characteristic of the equipment related to production capacity, such as flow or heat duty. Such scaled costs are easier to calculate and generally give nearly the same result as resizing the equipment for each scenario. The scaling exponent can be inferred from vendor quotes if multiple quotes are given for different sizes, obtained from a standard reference [73–74, 76].

Estimation of Purchased Estimate Cost

Calculation for estimation storage tank cost

-For VE-101, storage tank for fruit peel powder

-Theoretical capacity = 3.8m^3/hr

-Actual capacity = 0.4m^3/hr

-Quantity = 1

-Exponent =0.57

Thus,

$$C_2 = C_1 \left(\frac{S_2}{S_1} \right)^{n}$$

$$C_2 = 5000 * \left(\frac{0.4}{3.8} \right)^{0.57}$$

$$C_2 = \$\ 1385.69$$

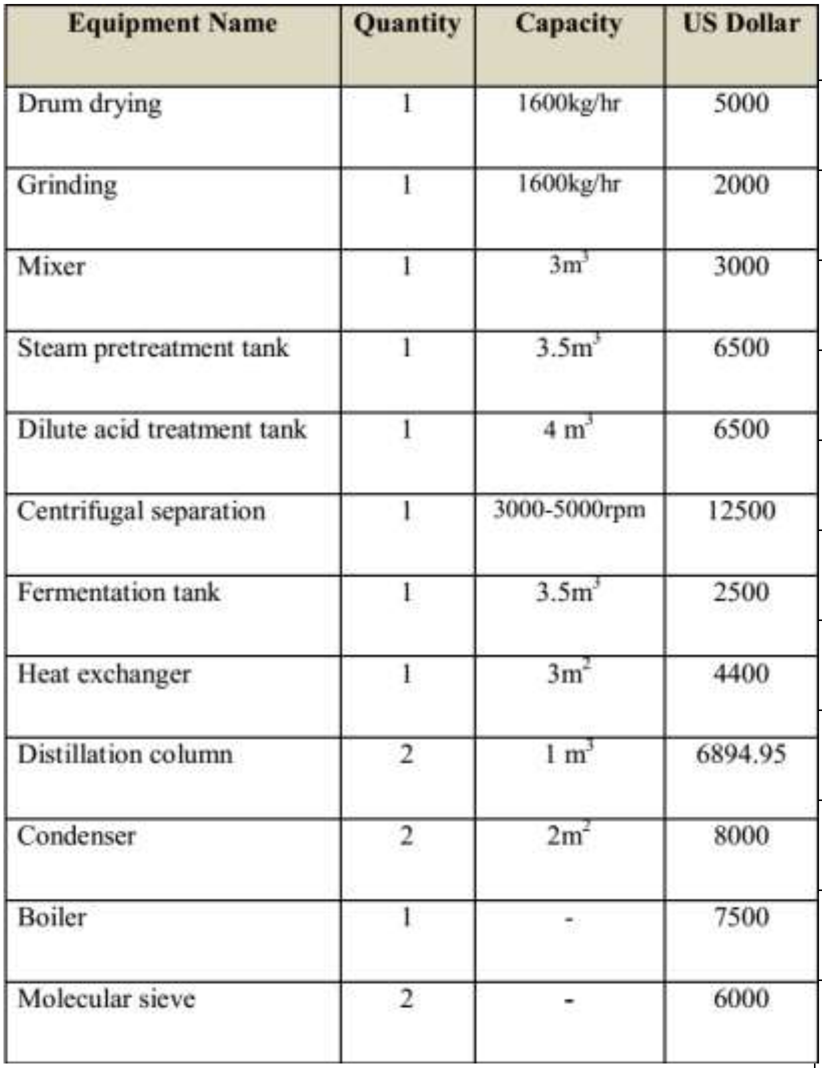
$$\text{Present cost} = \text{original cost} * \frac{present\ \ time\ \ index}{orginal\ \ (base\ \ year\ )index}$$

$$= \$\ 1385.69 * \frac{1780}{1000} = \$\ 2466.53$$

Table 10 estimation storage tank cost

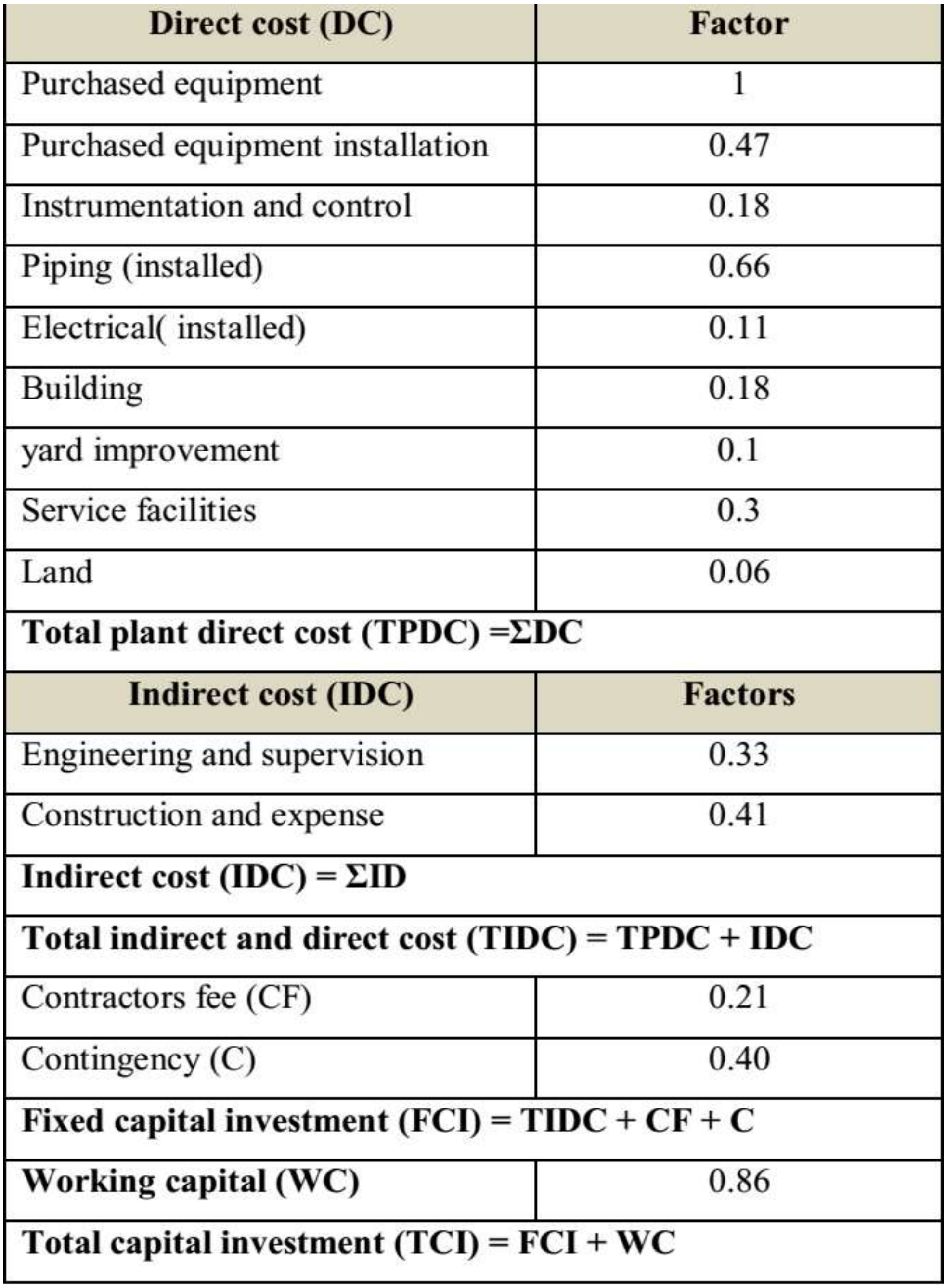
Equipment Name	Qua.	exponent	Actual capacity, m^3	Source	US Dollar	ET Birr
Fruit peel powder storage tank	1	0.57	0.4	Perry	2466.54	83862.3
Thank storage for fruit peel powder an dist. Water	1	0.57	4.47	Perry	8349.34	283877.5
Pretreatment storage tank	1	0.57	4.4	Perry	8274.56	281317
Dilute acid treated Tank	1	0.57	5.16	Perry	8582.10	291788.56
Fermented storage tank	1	0.57	4.53	Perry	8413.04	286042.8
Ethanol storage Tank	1	0.57	0.56	Perry	2988.00	101592.0
Total	1,328,478 ETB					

Table 11 Estimation of unit operation equipment



Equipment Name	Quantity	Capacity	US Dollar	
Drum drying	1	1600kg/hr	5000	170000
Grinding	1	1600kg/hr	2000	68000
Mixer	1	$3m^3$	3000	102000
Steam pretreatment tank	1	$3.5m^3$	6500	221000
Dilute acid treatment tank	1	$4\ m^3$	6500	221000
Centrifugal separation	1	3000-5000rpm	12500	425000
Fermentation tank	1	$3.5m^3$	2500	85000
Heat exchanger	1	$3m^2$	4400	149600
Distillation column	2	$1\ m^3$	6894.95	**234428.30**
Condenser	2	$2m^2$	8000	272000
Boiler	1	-	7500	255000
Molecular sieve	2	-	6000	204000
				Total **2,407,028.3** ETB

Table 12 Estimation costs: direct, indirect and total capital investment



Direct cost (DC)	**Factor**	ETB
Purchased equipment	1	33,238,361.39
Purchased equipment installation	0.47	15,583,503.3
Instrumentation and control	0.18	5,982,905.3
Piping (installed)	0.66	21,937,318.7
Electrical(installed)	0.11	3,647,214.5
Building	0.18	5,982,905.3
yard improvement	0.1	3,323,835.9
Service facilities	0.3	9,971,507.3
Land	0.06	1,994,301.8
Total plant direct cost (TPDC) =ΣDC		**101,709,385.5**
Indirect cost (IDC)	**Factors**	**Cost(ETB)**
Engineering and supervision	0.33	10,968,659.2
Construction and expense	0.41	13,627,727.8
Indirect cost (IDC) = ΣID		24,596,386.2
Total indirect and direct cost (TIDC) = TPDC + IDC		**126,305,773.2**
Contractors fee (CF)	0.21	6,980,055.9
Contingency (C)	0.40	13,295,343.7
Fixed capital investment (FCI) = TIDC + CF + C		146,581,173.0
Working capital (WC)	0.86	28,584,990.3
Total capital investment (TCI) = FCI + WC		**175,166,163.3**

7.3. Variable Operating Costs

Variable operating costs, which include raw materials, waste handling charges, and by-product credits, are incurred only when the process is operating. Quantities of raw materials used and wastes produced were determined using the material balance.

Table 13 direct production cost (variable cost)

Item			**Cost (ETH Birr)**
Raw materials		0.5Birr/kg*10968120kg	89,061,134.4
1	Operating labor(L)	84*1200*12	19,643,904.0
2	Direct supervisors and clerical labor	0.1L	1,964,390.4
3	Utilities(electric & water cost)	217573 + 18901	3,840,337.76
4	Maintenance and repair	0.06FCI	879,487,041.4
5	Operating supplies	0.01FCI	1,465,811.68
6	Laboratory changes	Not Applicable	
7	Patent and royalties	Not Applicable	
Total direct production cost = 7682906.4			Upgrade **124,770,399.9**

7.4. Fixed Operating Costs

Fixed operating costs are generally incurred in full whether or not the plant is producing at full capacity. These costs include labor and various overhead items. The number of employees was estimated by considering the likely degree of automation for each area and adding a reasonable number of management and support employees. Salaries were estimated by using commercially available salary. A 90% labor burden is applied to the salary total and covers items such as safety, general engineering, general plant maintenance, payroll overhead (including benefits), plant security, janitorial and similar services, phone, light, heat, and plant communications.

Table 14 Fixed operating costs

S. No	Items		Cost (ETH Birr)
1	Depreciation	0.1FCI	14,658,116.8
2	Local taxes	0.02FCI	2,931,623.5
3	Insurance	0.005FCI	732,904.7
4	Rent	0.08(land + building)	638,167.01
Total			**19,960,817.12**

Table 7.7 Plant overhead cost

S. No	Item		Cost (ETH Birr)
1	Plant overhead cost	2*8000*12	**3,118,080**

Manufacturing cost = direct production cost (variable) + fixed operating cost + plant overhead cost

= **124,770,399.9** + **19,960,817.12** + **3,118,080**

= 146,849,303.1

Table 15 General expense

S. No	Item		Cost(ETH Birr)
1	Administrative cost	0.5L = 0.5*1209600	9,821,952.0
2	Distribution and sell cost	0.2L = 0.2*1209600	3,928780.8
3	Research and development		NA
4	Financing interest (self-finance)		NA

Total			**13,750,732.8**

Total production cost = manufacturing cost + general expense

= 146,849,303.1 + 13,750,732.8

TPC = 160,600,035.9

Hence, Total production cost = **160,600,035.9** Birr

Variable cost = 124,770,399.9Birr

Fixed costs = fixed charges (except depreciation) + plant overhead cost

= 4,302,705.8 + 3,118,080

= 7,420,785.8

Depreciation cost = 14,581,116.83

General expense = 13,750,732.8

7.5. Economic evaluation

7.5.1. Net income, Payback time and return on investment

Gross earn cost

Current price of 99.9% ethanol = 37Birr/lit based on current price set by Sugar Corporation

So we took 37 Birr/lit

-Annual revenue = 37*6,000,000 = 222,000,000

-Total production cost = 160,600,035.9Birr

Gross annual profit = 222,000,000ETB - 160,600,035.9 = 61,399,965ETB

-Income tax on gross profit (30%) = 0.5(61,399,965) = 18,419,989.5ETB

-Net income = 42,979,976ETB

-Percent profit

$$\% \text{ profit} = \frac{Net\ income}{total\ \ production\ \ cost}$$

%profit 42,979,976/160,600,035 = 27%

Percent rate of return

-Net income = 42,979,976

Total capital investment = 175,166,164.5ETB

$$\text{-Rate of return, \% ROR} = \frac{Net\ income}{TCI} = 42{,}979{,}976/175{,}166{,}164 = 0.24$$

Payback period

Project life is assumed 14 years and we use straight line method

$$\text{Depreciation} = \frac{FCI}{14} = \frac{146{,}581{,}171}{14} = 10{,}470{,}083$$

-Payback period $= \frac{FCI}{profit\ \ + depreciation}$

$= \frac{146,581,171}{10,470,083+\ 42,979,976} = 2.78, appro\ two\ year$

CHAPTER NINE

9.1. CONCLUSIONS AND RECOMMENDATIONS

9.1.1. Conclusion

Hydrolysis of fruit peel waste was carried out with dilute acid and the optimum condition as well as interaction. Those all three factors were significant variables for the yield of ethanol. Very high and low acid concentration, temperature and retention time have negative effect on the yield of ethanol. Production of ethanol from fruit peels is feasible from the economic point of view in that its internal rate of return provides a return greater than the current rate of return. Moreover, the payback time is less than two years. The plant uses raw material from the municipality waste. Thus it brings no wastes that are dangerous to the environment and health. The by-product is also biodegradable and we can use it for the production of fertilizer. The waste also generates financial revenue in addition to protect the environment from disposed peel wastes in open yard landfill areas. The project economy plus its cost is analyzed and it’s viable to plant. The equipment cost and it equipment eractiion is taken from Perry Hand Book of chemical engineering, and Coulson and Richardson volume 5 fourth edition. The viability of the project is analyzed from its net profit.

9.1. 2. Recommendation

Further researches have to be done to improve the production of high quality and quantity of fruit peel ethanol. Alternative extraction methods of ethanol such as enzymatic extraction have to be done in order to investigate the variation that could be arise on the quality and quantity of the ethanol yield as a result of using different extraction methods. The material which useful to investigate the result is effectiveness is essential for further investigation on a lab scale Most of the solid wastes including fruit peel waste in our country have no or very low conversion to different usable products and as such among the major problems of health especially for cities such as Wolkite, and Gubre. Hence, it recommended that government or other investor's to recover this very valuable product as well as to contribute to the country in reducing the highly rising quantity of wastes. To conclude the recommendation, there is an urgent need for proper collection, documentation and assessment of fruit peel yields of orange, mango and banana as well as their seasonal variation in our country.

Reference

1) Armstrong S.R., 1999. Ethanol Brief Report on its Use in Gasoline.
2) Arnokd K. Ramesohl S. Fischerdick M. Merten F., 2005. Synopsis of German and European experience and state of the art of biofuels for transport.- Study commissioned by the
3) German GTZ; Wuppertal Institute.
4) Badge, P. C. (2002). Ethanol from cellulose a general review p. 17–21.
5) Blackwell, W. (2008). Fuel from Cellulose, Cheaper and With Better Yields than Ever Before.
6) Science Daily. Retrieved March 22, 2010.
7) Chandel, A.K., Es, C., Rudravaram, R., Narasu, M.L., Rao, L.V., Ravindra, P., 2007.
8) Economics and environmental impact of bioethanol production technologies.
9) Chandrakant,P., and Bisaria, V. S., 1998. Simultaneous bioconversion of cellulose and
10) Hemicellulose to ethanol. Critical Reviews in Biotechnology 18: 295-331.
11) D. Elango, M. Pulikesi, P. Baskarelingam, V. Ramamurthi and S, Sivanesan, 2007. Production of biogas from municipal solid waste with domestic sewage. Journal of Hazardous. Materials 141, 301-304.
12) Glasser, W.G., Wright, R.S., 1998. Steam-assisted biomass fractionation. II. Fractionation behavior of various biomass resources. Biomass and Bioenergy.
13) Göteborg. (2006), Continuous Ethanol Production from Dilute-acid Hydrolyzates.
14) Guffey, F.D., Wingerson, R.C., 2002. Fractionation of lignocellulosic biomass for fuel-grade ethanol production.
15) Himmel, M. E., et al., 2007. Biomass recalcitrance: Engineering plants and enzymes forbiofuels production. Science 315: 804-807.
16) Jacobson, M. Z. (2009). Effects of biofuels vs. other new vehicle technologies on air pollution, global warming, land use and water.
17) Mamma D., Kourtoglou E., Christakopoulos P., Fungal multienzyme production on industrial by-products of citrus-processing industry, Bioresource Technology 99 (2008) 2373- 2383.
18) Onuki, S. (2005). Bioethanol, Industrial production process and recent studies. USA Perry et al., chemical engineering hand book.
19) Nirbhay Gupta, 2008. Hydrolysis of Lignocellulosic Materials for Ethanol Production, National Institute of Technology, Rourkela.

20) Pimentel, D. (2003, June) “Ethanol Fuels: Energy Balance, Economics, and Environmental Impacts are Negative.”

21) Prasad, S., et al., 2007. Ethanol as an alternative fuel from agricultural, industrial and urban residues. Resources Conservation and Recycling 50: 1-39.

22) Solomon, B. D., et al., 2007. Grain and cellulosic ethanol: History, economics, and energy Policy. Biomass & Bioenergy 31: 416-425.

23) Coulson and Richardson book vol,(5) 4thedi.

24) Pour bafrani M., Talebnia F., Niklasson C., Taherzadeh M. J., Protective Effect of Encapsulation in Fermentation of Limonene-containing Media and Orange Peel Hydrolyzate, Int. J. Mol. Sci. 2007, 8, 777-787.

25) Macedo I.C.Leal M.R.L.V. Dasilva J.E.A.R., 2003. Greenhouse Gas (GHI) Emissions in the Production and Use o Ethanol in Brazil: Present Situation (2002). - Prepared for the secretariat of the State of Sao Paulo.

26) The ethanol in the end is blended with gasoline to improve the energy performance of vehicle and reduce air pollution download at URL. (http://www.nrel.gov/lab/pao/biomass_energy.html).

27) A bioethanol production from Municipal and industrial waste materials download at URL (http://www.ott.doc.gov/biofuels).