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

BY

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By

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Declaration

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

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List of Acronyms

AFEX	Ammonia Fiber Explosion
ANOVA	Analysis of Variance
CO	Carbon monoxide
CO_2	Carbon dioxide
DC	Direct Cost
DCFR	Discounted Cash Flow Return
ESDA	Ethiopia Sugar Development Agency
E10	Ethanol mixture that contain 10% ethanol and 90% unleaded gasoline
FCI	Fixed Capital Investment
FPL	Forest Products Laboratory
GHG	Green House Gas
MTBE	Methyl tertiary butyl ether
IDC	Indirect Cost
IRR	Internal Rate of Return
NPV	Net Present Value
NOx	Nitrogen oxides
PAN	Peroxyacetyl nitrate
pH	power of Hydrogen
PM	Particulate matter
ROR	Rate of Return
SDA	Sugar Development Agency
SNNP	South Nation and National People
TCI	Total Capital Investment
TDC	Total Direct Cost
TPDC	Total Plant Direct Cost
USDA	United States Development Agency
U.S	United State
VLE	Vapor Liquid Equilibrium
VOCs	volatile organic compounds
WC	Working Capital

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Abstract

Waste disposal has become one of the major concerns for our city, Addis Ababa. 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 3-5 cm sizes for easy drying and grinding. Sample drying was carried out in oven (60^0C for 72hr) to obtain easily crushable material. After drying, each of the samples was milled separately. The maximum particle sizes of the ground mixed sample were 2 mm.

Laboratory experiments of 16 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, 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 by pycnometer (specific gravity bottle). 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^oC (Perry Chemical Engineering Handbook).

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). Box-Behnken was applied to study the interaction effects, to see the contour and surface plot. The optimum results were obtained at 0.74%v/v acid concentration, 101.69^0C temperature and 11.54min retention time. Under these condition 48% 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) 52.6% and the payback period of the project is estimated to be 2years.

Chapter One

Introduction

1.1. Background

The production of ethanol from lignocellulosic 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 lignocellulosic 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, inevitable depletion of the world's energy supply, and the unstable oil market (such as the energy crisis of the 1970s) have renewed the interest of society in searching for alternative fuels (Himmel et al., 2007; Solomon et al., 2007). 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. The first two groups of raw materials are currently the main resources for ethanol production, but concomitant growth in demand for human feed similar to energy could make them potentially less competitive and perhaps expensive feedstocks in the near future, leaving the cellulosic materials as the only potential feedstock for production of ethanol (Taherzadeh and Karimi, 2007). 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, 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

Energy is one of the most fundamental parts of our universe. We use energy to do work. Energy lights our cities. Energy powers our vehicles, trains, planes and rockets. Energy warms our homes, cooks our food. Energy powers machinery in factories and tractors on a farm. Everything we do is connected to energy in one form or another. Energy is defined as: "the ability to do work". Work means moving something, lifting something, warming something, lighting something. All these are a few of the various types of work.

All energy sources have an impact on the environment. Concerns about the greenhouse effect and global warming, air pollution, and energy security have led to increasing interest and more development in renewable energy sources such as bio-fuel, solar, wind, geothermal, and hydrogen.

But we'll need to continue to use fossil fuels and nuclear energy until new, cleaner technologies can replace them.

In the worldwide economy much focus has been laid on the rising oil price which has become a hot topic. The rising oil price has increased the interest of finding other possible ways to produce fuel. And the production of bio-ethanol has grown steadily during the last 25 years.

The aim of this thesis was to investigate the possibility of using and transforming fruit peel waste to something valuable, namely ethanol using the fungus S*accharomyces cerevisiae* as ethanol producing organism.

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. The situation is exacerbated in slums where households cannot make use of garbage collection containers. 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

The overall objectives of this work were:-

- 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* ***c****cerevisiae*) and distillation method.
- To protect the environment from fruit peel wastes and there by generating financial revenue from waste.
- 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

Literature Review

2.1. Introduction

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 bio-fuels 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).

Biodiesel: - is an ester that can be made from several types of oils, such as vegetable oils and animal fats. Biodiesel is typically used as a blend 20 percent biodiesel and 80 percent petroleum diesel called B20. B20 can be used in a conventional diesel engine with essentially no engine modifications. There is also a growing interest in using biodiesel where workers are exposed to diesel exhaust, in aircraft to control local pollution near airports, and in locomotives that face restricted use unless emissions can be reduced (Rainner J and Dominik R, 2007).

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).

Ethanol is a clean-burning, high-octane fuel that is produced from renewable sources. Because ethanol can be produced domestically in most countries, it helps reduce dependence upon foreign sources of energy for these countries. 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. Similar to the case of biodiesel, adding ethanol to gasoline "oxygenates" the fuel. It adds oxygen to the fuel mixture so that it burns more completely and reduces polluting emissions such as carbon monoxide (Cellulosic Ethanol, 2010).

2.2. The history of fuel ethanol

The use of ethanol as an automobile fuel is not a new invention. Already in 1908, Ford's model T could be adjusted to run on either gasoline or alcohol (DiPardo, 2000). However, after World War II the interest in using ethanol as a fuel declined because cheap gasoline made from petroleum was available. In the 1970's, the interest in fuel ethanol was renewed due to the oil crisis (DiPardo, 2000). More recently, ethanol has become used as an additive in gasoline. MTBE (methyl tertiary butyl ether) is used as a gasoline additive to increase the oxygen content and the octane number. During the last few years, the use of MTBE has been banned in several states in the USA due to the risk of contamination of water. Many companies have replaced MTBE with ethanol to give the gasoline similar clean burning and octane boosting properties as MTBE-blended gasoline (F.O. Licht's World ethanol and biofuels report 2006; Sun and Cheng, 2002). Today there are several flexifuel automobile models (vehicles that can run on mixtures of ethanol and gasoline containing up to 85% ethanol) available from various manufacturers (BAFF, 2006).

About 99% of the fuel ethanol is produced from cultivated crops (BAFF, 2006). Brazil has for a long time been the leading ethanol producer of the world. However, during the last years USA has increased its production and today both countries have an annual production of about 16 000 000 m^3 (F.O. Licht's World ethanol and biofuels report, 2006). The Brazilian ethanol is mainly produced from sugarcane. Brazil is the world leader in the use of ethanol as an automobile fuel. In Brazil, the ordinary gasoline, which is used in about 7, 000, 000 cars, contains about 24%

ethanol. In addition, 4, 000, 000 automobiles drive on a blend of 95% ethanol and 5% water (BAFF, 2006). In the USA, ethanol is mainly produced from corn.

In Sweden, about 55 000 m^3 of fuel ethanol is produced per year from wheat and about 18 000 m^3 from spent sulfite liquor (Agroetanol AB, 2006; Jordbruksverket, 2006). In Sweden, the ordinary gasoline typically contains 5% ethanol and the number of flexifuel automobiles is increasing (Jordbruksverket, 2006). The Swedish ethanol production does not cover the demand and therefore Sweden is a net importer of ethanol. However, initiatives have been taken to increase the future national ethanol production. In 2004 an ethanol-from-lignocellulose pilot plant was inaugurated in the city of Örnsköldsvik. Agro-ethanol plans to expand its production of ethanol from grain with 150, 000 m^3 in 2008.

2.3. Bio-ethanol and Its Application as a Fuel

Ethanol, also known as ethyl alcohol with the chemical formula C_2H_5OH, is a flammable, clear, colorless and slightly toxic chemical compound with acceptable odour. It can be produced either from petrochemical feedstocks by the acid-catalyzed hydration of ethene, or from biomass feedstocks through fermentation. On a global scale, synthetic ethanol accounts for about 5-10% of total production while the rest is produced from fermentation of biomass mainly sugar crops, e.g. cane and beet, and of grains (mainly corn) (Licht,2006).

Ethanol as a neat fuel or even in the blended form with gasoline has a long history as automotive fuel. In 1860, German inventor Nicholas Otto used ethanol as a fuel in an early prototype of an internal combustion engine because it was widely available throughout Europe for use in spirit lamps. A few years later, Henry Ford built his first automobile with an engine that could run on ethanol. In 1908, Ford unveiled his Model T engine equipped with carburetors that could be adjusted to use alcohol, gasoline or a mixture of both fuels (Solomon et al., 2007). Ethyl alcohol as "the fuel of the future" was presented by him for the first time. In 1925, he told the New York 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

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. World Market of Ethanol

Today, bio-ethanol is the most dominant bio-fuel and its global production showed an upward trend over the last 25 years with a sharp increase from 2000. As of 2005, worldwide production capacity for bio-ethanol fuel was about 45 billion liters per year, with approximately 15% annual growth between 2000 and 2005. This value increased to 49 billion liters in 2006, when the Americans produced 75% of the total world ethanol output, followed by Asia/Pacific and Europe/Africa with respective values of 15 and 10% (Licht, 2006). The industrial alcohol market showed a rather modest rate of growth similar to the increase in Gross Domestic Product in many countries. The market for beverage alcohol in most developed countries is stagnating, due to increased health awareness. Fuel ethanol production is predicted to have the strongest increase in the Americans, where the production is expected to rise to around 75 billion liters by 2015, representing about 42 billion liters increase in the projection period. In Asia this value is anticipated to increase to 8 billion liters during the same period, and in Europe, with the policy of increasing the share of bio-fuels in the transportation sector, the production will rise strongly. Therefore, total output in 2015 is forecast to reach over 115 billion liters (Licht, 2006).

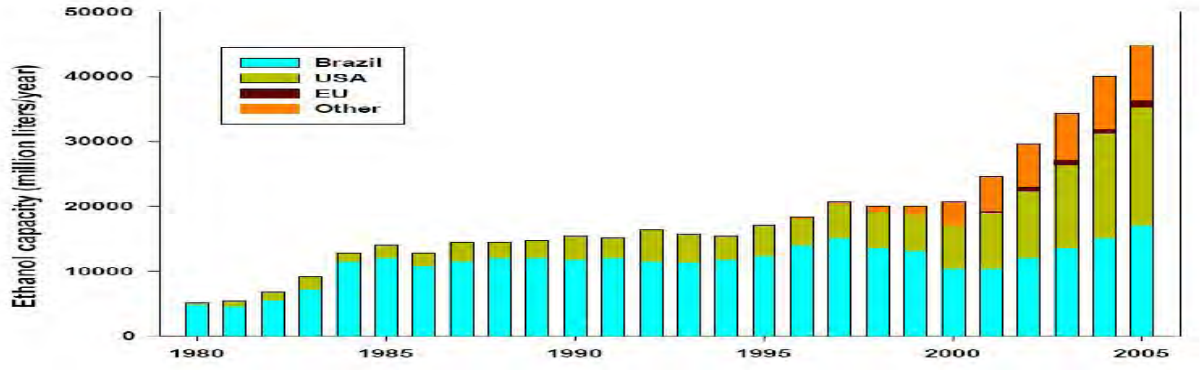


Figure 2.1 Annual ethanol productions by the major producers, adapted from Mabee (2007)

In 2009, production of fuel ethanol reached an estimated 76 billion liters, an increase of 10 percent over 2008. The United States and Brazil accounted for 88 percent of global ethanol production in 2009. Most of the increased production occurred in the United States (Licht, 2006).

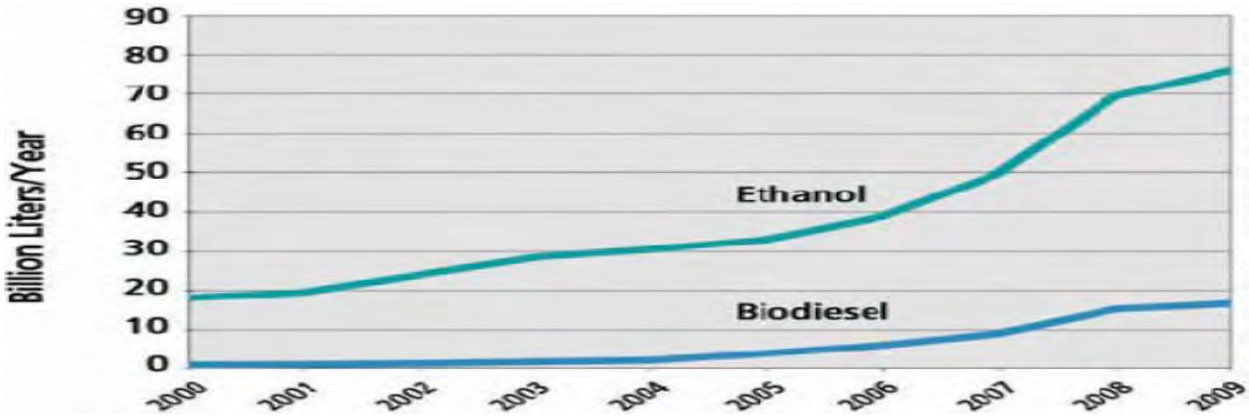


Figure 2.2 Ethanol and Biodiesel production, 2000 – 2009

After a significant downturn in the U.S. fuel ethanol market in 2008, U.S. production rose 16 percent to about 41 billion liters in 2009, accounting for approximately 54 percent of global ethanol production. According to one estimate, U.S. ethanol (which is mostly corn-based) displaced more than 360 million barrels of imported oil for gasoline production. The highest sugar prices in years, combined with adverse weather conditions in a major producing region, resulted in a drop in Brazil's ethanol production from 27.1 billion liters in 2008 to 26.3 billion liters in 2009. All ethanol produced in Brazil is from sugar cane. All fueling stations in Brazil sell both pure ethanol and gasohol, a 25 percent ethanol/75 percent gasoline blend. Flex-fuel cars, which can use pure ethanol, gasoline, or any blend of the two, provide the flexibility to choose fuel based on price at the pump. They have been widely embraced by drivers and represent more than 95 percent of all new cars sold in Brazil. In recent years, significant global trade in fuel ethanol has emerged, with Brazil being the leading exporter. However, Brazilian ethanol export declined by almost 31 percent in 2009. International demands declined in great part because of the global economic crisis (Licht, 2006).

2.5. 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. This mixture is called hydrous ethanol. If the remaining water is removed in further process, the ethanol is called anhydrous ethanol and suitable for blending with gasoline. Ethanol is "denatured "prior to leaving the plant to make it unfit for human consumption by addition of small amount of products such as gasoline (ESDA, 2005).

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 2.1 Projected ethanol production by year in million liters

S. Industry	2009/10	2010/11	2011/12	2012/13	2013/14
Fincha	6.9	13.2	15.7	17.1	21.5
Methara	8.9	12.8	17.5	21.3	21.3
Wonji	-	-	10.6	10.6	10.6
Tendaho	-	15.9	30.1	43.6	55.4
Total	15.8	41.9	73.9	92.6	108.8

Source: Ethiopian Sugar Agency, 2009

2.6. 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).

The statistical tables show that 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).

The census data reveals that about half of the permanent crops produced in Ethiopia were used for sale and the remaining for household consumption and other purposes. Thus 51% of the crop was sold and 44% was consumed at home. The utilization by crop type within the permanent crop group ranges between 31% and 72% for household consumption and between 24% and 63% for sale. Permanent crop utilization by region is mainly similar to the country's pattern (CSAE, 2003).

2.7. 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.

Climate and soil type determine the types and amounts of plants that can be grown in different geographic areas. Another important consideration is feedstock logistic is the steps necessary to move feedstocks from fields or collection areas to ethanol production plants. For agricultural and forestry feedstocks, these steps include harvesting, transportation, storage, and preprocessing (Cellulosic Ethanol, 2010).

The use of ethanol as an alternative motor fuel has been steadily increasing around the world for a number of reasons. Domestic production and use of ethanol for fuel can decrease dependence on foreign oil, reduce trade deficits, create jobs in rural areas, reduce air pollution, and reduce global climate change carbon dioxide buildup. Ethanol, unlike gasoline, is an oxygenated fuel that contains 35% oxygen, which reduces particulate and NO_x emissions from combustion. The following are different type's feedstocks for ethanol production (Cellulosic Ethanol, 2010).

2.7.1. 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. However, since sugar materials are in the human food chain, these materials are usually too expensive to use for ethanol production (J. Janick and P.C. Badger, 2002).

One example of a sugar feedstock is sugarcane. Brazil developed a successful fuel ethanol program from sugarcane for a number of reasons: (1) Brazil conventionally relied heavily on imported oil for transportation fuels, which caused a severe economic drain on the country; (2) Brazil can attain very high yields of sugarcane; and (3) Brazil has also experienced periods of poor sugar markets. As a result, the Brazilian government established programs supportive of the industry with the result that Brazil has been able to successfully produce and use sugarcane for fuel ethanol production (J. Janick and P.C. Badger, 2002).

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).

2.7.2. 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. Being abundant and outside the human food chain makes cellulosic materials relatively inexpensive feedstocks for ethanol production (P.C. Badger, 2002).

The global production of plant biomass, with over 90% lignocelluloses content, is estimated to be about 2×10^{11} tons/year, where about $8\text{-}20\times10^{9}$ tons of primary biomass remain potentially accessible annually (Lin and Tanaka, 2006). Over the last few decades, extensive attention has been devoted to research on the conversion of lignocellulosic materials to ethanol. Lignocelluloses are complex mixtures of carbohydrate polymers, namely cellulose, hemicelluloses, lignin, and a small amount of compounds known as extractives (Prasad et al., 2007).

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 overcome the two main bottlenecks for the first generation feedstock: adversely effects on food prices, and inability to scale (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 crystalline region in which the linear molecules of cellulose are

bonded laterally by hydrogen bonds is characterized by the cellulose lattice which extends over the entire cross-section of the micro-fibrils. This crystalline region is bounded by a layer of cellulose molecules that exhibit various degrees of parallelism. The less ordered region is called the Para-crystalline or amorphous region. The disordered region allows disintegration of the cellulose by hydrolysis into rod-like particles with aqueous, non-swelling, strong acid. Micro-fibrils build up fibrils and finally cellulose fibers. As a consequence of its fibrous structure and strong hydrogen bonds cellulose has a high tensile strength and is insoluble in most solvents. Orientation of the linkages and additional hydrogen bonding makes the polymer rigid and difficult to break (Hamelinck, C.N.et al, 2005; Sjostrom, E., 1981).

The molecular arrangement of this fibrillar bundle is sufficiently regular that cellulose exhibits a crystalline X-ray diffraction pattern. Typically, cellulose chains in primary plant cell walls have degrees of polymerization in the range of 5,000 to 7,500 glucose monomer units, with the degree of polymerization of cellulose from wood being around 10,000 and around 15,000 from cellulose cotton. 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).

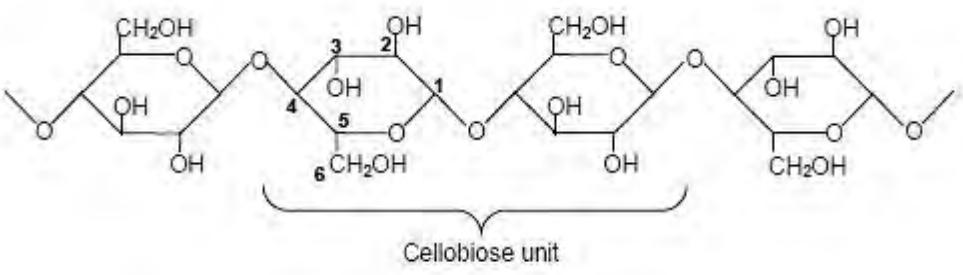


Figure 2.3 Schematic illustration of the cellulose chain

Hemicelluloses: were originally believed to be intermediates in the biosynthesis of cellulose. Today it is known, however, that hemicelluloses belong to a group of heterogeneous polysaccharides which are formed through biosynthetic routes different from that of cellulose. In contrast to cellulose which is a homo-polysaccharide, hemicelluloses are hetero-polysaccharides. 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. Some hemicelluloses contain mostly xylan, whereas others contain mostly glucomannans. Among softwood hemicelluloses there are galactoglucomannans, arabinoglucuronoxylan, and arabinogalactan, meanwhile hardwood hemicellulose comprises mainly glucuronoxylans and glucomannan(Saha, B.C. and Bothast, R.J., 1997).

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).

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).

When dried citrus peels are rich in cellulose, hemicelluloses, proteins and pectin, the fat content is however low (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). A disadvantage is that like orange peels have a very low nutritional content which reduce its value as livestock feed (Dhillon S. S et al., 2004).

New techniques are developed and being proposed as an alternative to transform the food processing material by microorganisms to valuable products such as biogas, ethanol, citric acid, chemicals, various enzymes, volatile flavoring compounds, fatty acids and microbial biomass (Dhillon S. S et al., 2004). An alternative way to utilize citrus processing waste is to produce ethanol or other valuable products by fermenting the sugars in peel hydrolyzate. One of the main obstacles for using such as orange peel waste for fermentation is its content of peel oil. More

than 95% is of the peel oil is D-limonene (hereafter called limonene). Limonene is extremely toxic to fermenting microorganisms (Pourbafrani M et al., 2007).

Even at concentrations as low as 0.01% (w/v) limonene has an immense antimicrobial effect which results in the failure of fermenting hydrolyzate with higher limonene concentrations. To overcome this obstacle the limonene has to be removed from the medium by e.g. filtration or aeration for a successful fermentation (Pourbafrani M et al., 2007). One report showed that the limonene concentration in the hydrolyzate was 0.52% (v/v), in enzymatic hydrolyzed orange peels. In the investigation a solid concentration of 12% was used (Pourbafrani M et al., 2007).

The major component wet fruit peel wastes are approximately 80% water, 6% soluble sugars, 5% cellulose and hemicelluloses, 4% pectin and 0.8% limonene (Welyang Z et al., 2008).

2.7.3. 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. Cereal grains commonly used in the US for ethanol production include maize and wheat. 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).

2.8. 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. It can also be obtained via ethylene or acetylene, from calcium carbide, coal, oil gas, and other sources. The two primary ways of producing fuel ethanol from cellulosic feedstock are: Biochemical conversion process and Thermo chemical conversion process (Cellulosic ethanol, 2010).

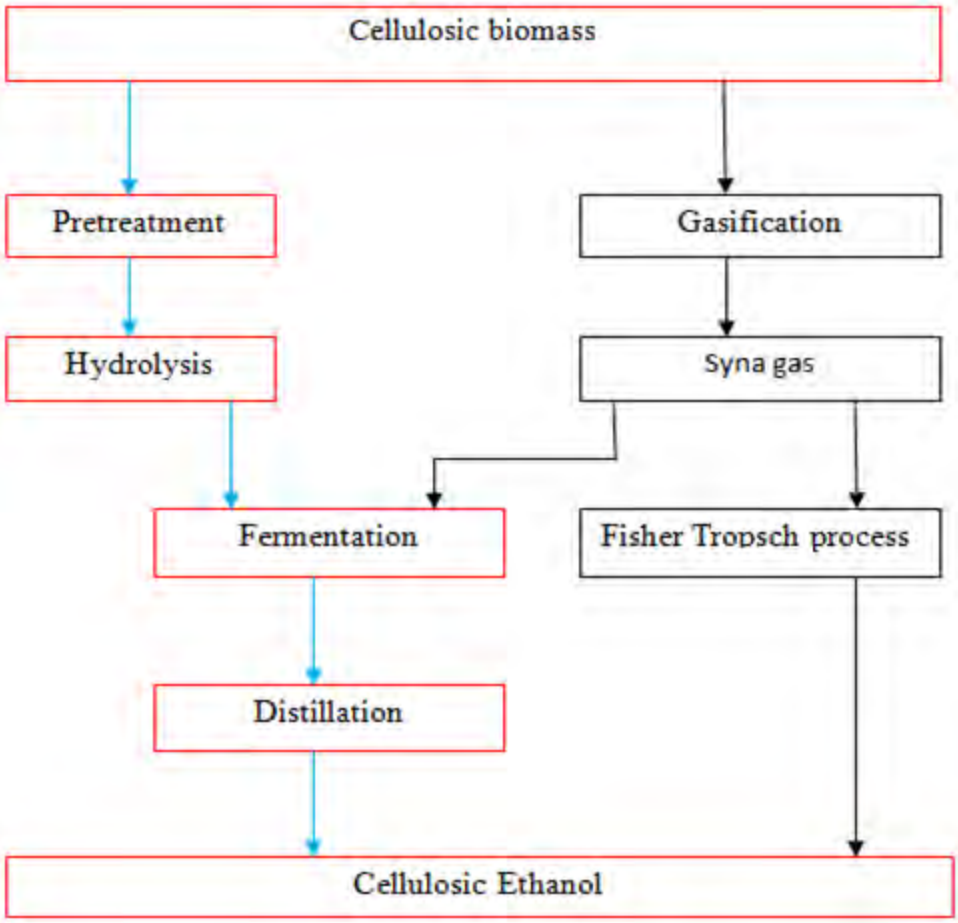


Figure 2.4 Schematic diagram of cellulosic ethanol production

2.8.1. 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).

2.8.1.1. 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 effect of pretreatment of lignocellulosic materials has been recognized for a long time. 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).

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. Vibratory ball milling has been found to be more effective in breaking down the cellulose crystallinity of spruce and aspen chips and improving the digestibility of the biomass than ordinary ball milling. The power requirement of mechanical comminution of agricultural materials depends on the final particle size and the waste biomass characteristics (Nirbhay Gupta, 2008).

Ozonolysis: Ozone can be used to degrade lignin and hemicellulose in many lignocellulosic materials such as wheat straw, bagasse, green hay, peanut, pine, cotton straw, and poplar sawdust. The degradation was essentially limited to lignin and hemicellulose was slightly attacked, but cellulose was hardly affected. Ozonolysis pretreatment has the following advantages: it effectively removes lignin; it does not produce toxic residues for the downstream processes; and the reactions are carried out at room temperature and pressure. However, a large amount of ozone is required, making the process expensive (Nirbhay Gupta, 2008).

Pyrolysis*:* Pyrolysis has also been used for pretreatment of lignocellulosic materials. When the materials are treated at temperatures greater than 300°C, cellulose rapidly decomposes to produce gaseous products and residual char. The decomposition is much slower and less volatile products are formed at lower temperatures. Mild acid hydrolysis (1 N H_2SO_4, 97 °C, 2.5 h) of

the residues from pyrolysis pretreatment has resulted in 80–85% conversion of cellulose to reducing sugars with more than 50% glucose .The process can be enhanced with the presence of oxygen.

When zinc chloride or sodium carbonate is added as a catalyst, the decomposition of pure cellulose can occur at a lower temperature (Nirbhay Gupta, 2008).

Chemical Pretreatment

Acid catalyzed: Concentrated acids such as H_2SO_4 and HCl have been used to treat lignocellulosic materials. Although they are powerful agents for cellulose hydrolysis, concentrated acids are toxic, corrosive and hazardous and require reactors that are resistant to corrosion. In addition, the concentrated acid must be recovered after hydrolysis to make the process economically feasible. 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. The digestibility of NaOH-treated hardwood increased from 14% to 55% with the decrease of lignin content from 24–55% to 20%. However, no effect of dilute NaOH pretreatment was observed for softwoods with lignin content greater than 26%. Dilute NaOH pretreatment was also effective for the hydrolysis of straws with relatively low lignin content of 10–18% used the combination of irradiation and 2% NaOH for pretreatment of corn stalk, cassava bark and peanut husk. Ammonia was also used for the pretreatment to remove lignin and an ammonia recycled percolation process for the pretreatment of corn cobs/stover mixture and switchgrass. The efficiency of delignification was 60–80% for corn cobs and 65–85% for Switch grass (Nirbhay Gupta, 2008).

Organosolv Process: In the organosolv process, an organic or aqueous organic solvent mixture with inorganic acid catalysts (HCl or H_2SO_4) is used to break the internal lignin and hemicellulose bonds. The organic solvents used in the process include methanol, ethanol, acetone, ethylene glycol, and triethylene glycol and tetrahydrofurfuryl alcohol. Organic acids such as oxalic, acetylsalicylic and salicylic acid can also be used as catalysts in the organosolv process. At high temperatures, the addition of catalyst was unnecessary for satisfactory delignification. Usually, a high yield of xylose can be obtained with the addition of acid. Solvents used in the process need to be drained from the reactor, evaporated, condensed and recycled to reduce the cost. Removal of solvents from the system is necessary because the solvents may be inhibitory to the growth of organisms, hydrolysis, and fermentation (Nirbhay Gupta, 2008).

Oxidative Delignification: Lignin biodegradation could be catalyzed by the peroxidase enzyme with the presence of H_2O_2. The pretreatment of cellulosic biomass with hydrogen peroxide greatly enhanced its susceptibility to enzymatic hydrolysis. About 50% lignin and most hemicellulose were solubilized by 2% H_2O_2 at 30 °C within 8 h, and 95% efficiency of glucose production from cellulose was achieved in the subsequent saccharification by cellulase at 45 °C for 24 h (Nirbhay Gupta, 2008).

Physico-Chemical Pretreatment

Ammonia Fiber Explosion (AFEX): AFEX is Physico-chemical pretreatment in which lignocellulosic materials are exposed to liquid ammonia at high temperature and pressure for a period of time and then pressure is swiftly reduced. The concept of AFEX is similar to steam

explosion. In a typical AFEX process, the dosage of liquid ammonia is 1-2 kg ammonia /kg dry biomass, temperature 90ºC, and residence time 30 minutes. AFEX pretreatment can significantly improve the saccharification rates of various herbaceous crops and grasses. It can be used for the pretreatment of many lignocellulosic materials including alfalfa, wheat straw, wheat chaff, barley straw, corn stover, rice straw municipal solid waste, softwood newspaper, coastal Bermuda grass, switch grass, aspen chips and bagasse. The AFEX pretreatment does not significantly solubilize hemicellulose compared to acid pretreatment and acid-catalyzed steam explosion. The composition of materials after AFEX pretreatment was essentially the same as the original materials. Over 90 % hydrolysis of cellulolse and hemicellulose has been obtained after AFEX pretreatment of Bermuda grass and bagasse. To reduce the cost and protect to environment, ammonia must be recycled after the pretreatment. The ammonia pretreatment does not produce inhibitors for the downstream biological processes, so water wash is not necessary. AFEX pretreatment does not require small particle size for better efficiency (Holtzapple *et al.*, 1990).

CO_2 Explosion: Similar to steam and ammonia explosion pretreatment, CO_2 explosion is also used for the pretreatment of ligocellulosic materials. It was hypothesized that CO_2 would form carbonic acid and increase the hydrolysis rate. Dale and Moreira (1982) used this method to pretreat alfalfa (4 kg CO_2/ kg fiber at the pressure of 5.62 MPa) and obtained 75 % of the theoretical glucose released during 24 h of enzymatic hydrolysis. The yields were relatively low compared to steam or ammonia explosion pretreatment, but high compared to the enzymatic hydrolysis without pretreatment. Compared CO_2 explosion with steam and ammonia explosion for pretreatment of recycled paper mix, sugarcane bagasse and repulping waste of recycled paper and found that CO_2 explosion was more cost effective than ammonia explosion and did not cause the formation of inhibitory compounds and could occur in steam explosion (Holtzapple *et al.*, 1990).

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^{o}C and residence time of 10 to 40 minutes gives highest yield of ethanol (Solomon, 2007).

The advantages of steam explosion pretreatment include the low energy requirement compared to mechanical comminution and no recycling or environmental costs. The environmental mechanical methods require 70 % more energy than steam explosion to achieve the same size reduction. Steam explosion is recognized as one of the most cost effective pretreatment process for hardwoods and agricultural residues, but it is less effective for softwoods. Limitations of steam explosion include destruction of a portion xylan fraction, incomplete disruption of the lignin-carbohydrate matrix and generation of compounds that may be inhibitory to microorganisms used in downstream processes. Because of the formation of degradation products that are inhibitory to microbial growth, enzyme hydrolysis and fermentation, pretreated biomass needs to be washed by waster to remove the inhibitory materials along with water soluble hemicellulose (McMillan, 1994).

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.The pretreatment of wheat straw by 19 white-rot fungi and found that 35% of the straw was converted to reducing sugars by *Pleurotus ostreatus* in five weeks. Similar conversion was obtained in the pretreatment by *Phanerochaete sordida* and *Pycnoporus cinnabarinus* in four weeks (Nirbhay Gupta, 2008).

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, H_2O_2 producing enzymes and quinine reducing enzymes can also degrade lignin. The advantages of biological pretreatment include low energy requirement and mild environmental

conditions. However, the rate of hydrolysis in most biological pretreatment processes is very low (Nirbhay Gupta, 2008).

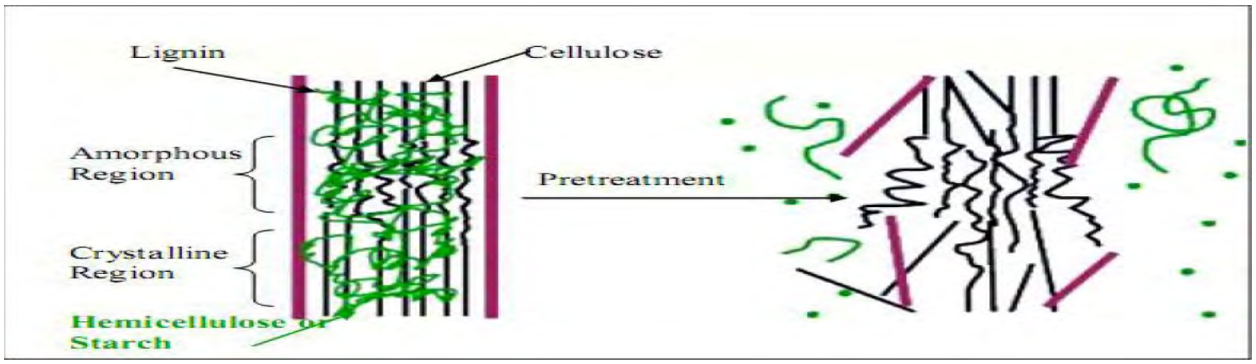


Figure 2.5 Schematic Representation on Biomass Pre-Treatment (Mosier et al, 2004)

2.8.1.2. 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. The rest of hemicelluloses are degraded to weak acids, furan derivates, and phenolics. These compounds, however, are potential fermentation inhibitors (Cellulosic Ethanol, 2010).

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).

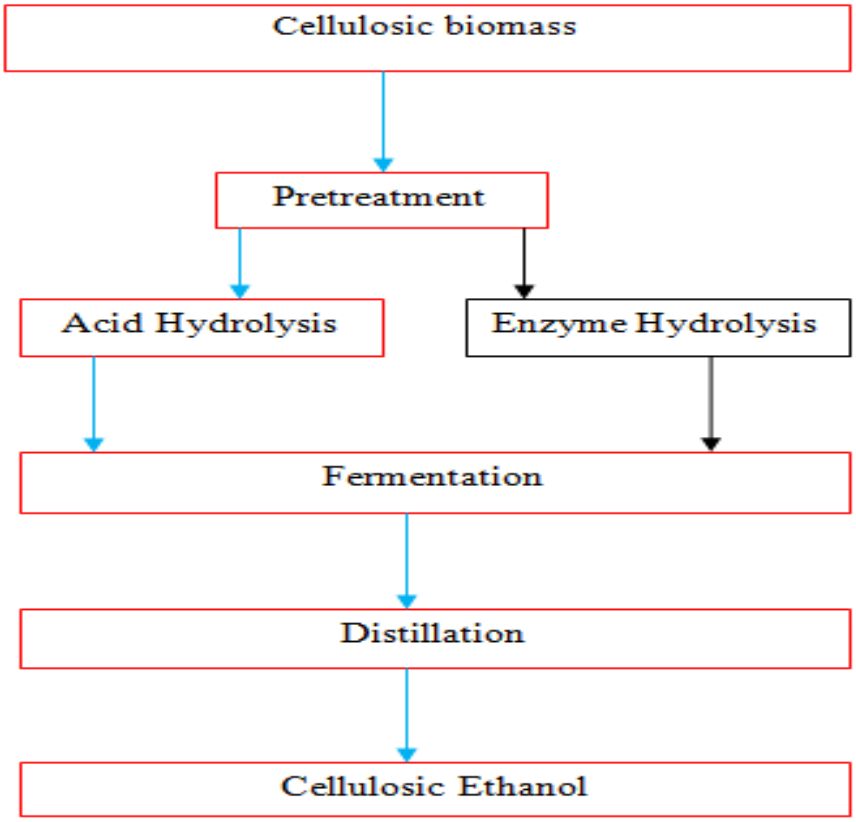


Figure 2.6 Hydrolyzed methods for cellulosic feedstocks

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. Acid pretreatment for ethanol production was developed in Germany in the 19th century. In the United States, the U.S. Forest Service, Forest Products Laboratory (FPL) conducted extensive research using acid pretreatment for ethanol production from wood (Zhu et al., 2008).

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).

$$(C_6H_{10}O_5)_n + nH_2O \longrightarrow nC_6H_{12}O_6 \qquad \Delta H=22.1n \text{ kJ/mol}$$

$$(C_5H_8O_4)_m + mH_2O \longrightarrow mC_5H_{10}O_5 \qquad \Delta H=79.0m \text{ kJ/mol}$$

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. Not only does sugar degradation reduce sugar yield, but the furfural and other degradation products can be poisonous to the fermentation microorganisms. (Mohammad, 2008) the optimum results of ethanol yield from citrus peel waste were obtained at a temperature of 116 ^{o}C, 1 % sulfuric acid concentration, and 12.5 min retention time (Cellulosic Ethanol, 2010).

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. Since 5-carbon sugars degrade more rapidly than 6-carbon sugars, one way to decrease sugar degradation is to have a two-stage process. The first stage is conducted under mild process conditions to recover the 5-carbon sugars while the second stage is conducted under harsher conditions to recover the 6-carbon sugars. Unfortunately, sugar degradation is still a problem and yields are limited (Cellulosic Ethanol, 2010).

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. One concentrated acid process was first developed by USDA and further refined by Purdue University and the Tennessee Valley Authority. 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).

This material is then dewatered and dried with the effect that the acid concentration in the material is increased to about 70%. After reacting in another vessel for 1 to 4 hr at 100ºC, the reactor contents are filtered to remove solids and recover the sugar and acid. The sugar/acid solution from the second stage is recycled to the first stage to provide the acid for the first stage hydrolysis. The sugars from the second stage hydrolysis are thus recovered in the liquid from the first stage hydrolysis (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. Without acid recovery, large quantities of lime must be used to neutralize the acid in the sugar solution. This neutralization forms large quantities of calcium sulfate, which requires disposal and creates additional expense (Cellulosic Ethanol, 2010).

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. Cellulolytic enzymes were discovered during World War II when American scientists found the agent that was responsible for army clothing deterioration in the jungles of the South Pacific. 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. Then, J-glucosidase hydrolyses cellobiose to glucose (Sun and Cheng, 2002). However, a 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. There are a wide range of different pretreatment methods. Steam explosion and dilute-acid pretreatment are among the most common (Sun and Cheng, 2002). The

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 by-product 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 Fermentaion (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). It has also been proved that J- glucosidase can be inhibited by glucose (Holtzapple et al., 1990). Another drawback is that SHF is a two-step process. To reduce the risk for enzyme inhibition and reduce the number of process steps, SSF can be used. In SSF, hydrolysis and fermentation occur at the same time, which means that the glucose that is generated is immediately consumed by the fermenting microorganism and inhibition of J-glucosidase is therefore prevented. The disadvantage of the SSF process is that the optimal temperatures for the cellulases and the fermenting microorganism are not the same so the selected temperature is a compromise, which means that neither hydrolysis nor fermentation will be performed under optimal conditions (Lynd et al., 2005).

Recently, efforts have been made to combine cellulase production, hydrolysis and fermentation in one single step. This concept is called Consolidated Bio-Processing (CBP) and the aim is to create a microorganism that is able to perform these three steps simultaneously (Lynd et al., 2005). There are two different strategies to create a CBP microorganism: A naturally occurring cellulolytic microorganism can be modified by genetic engineering to gain important properties, such as the ability to give high ethanol yields, or alternatively a non-cellulolytic microorganism that gives high ethanol yields can be altered by genetic engineering to express heterologous cellulases (Lynd et al., 2005).

Today, most research efforts are focused on the enzymatic hydrolysis because of the high development potential. The dilute-acid and concentrated-acid hydrolysis are relatively mature techniques for which no major improvements are likely to happen. Nevertheless, the enzyme cost

is still high for the enzymatic process. The cost of enzyme in the SSF and SHF processes has been calculated to be 10-20% of the total ethanol production cost (Wingren et al., 2005).

$$(C_6H_{10}O_5)_n + H_2O \text{ (Alpha- + Gluco-Amylases)} \longrightarrow C_6H_{12}O_6$$

2.8.1.3. 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. Yeasts are minute, often unicellular, fungi. 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. Some examples of non-conventional yeasts include *Kuyberomyces lactis, Yarrowia lipolytica, Hansenula polymorpha and Pichia pastoris* (Cellulosic ethanol, 2010).

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).

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

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

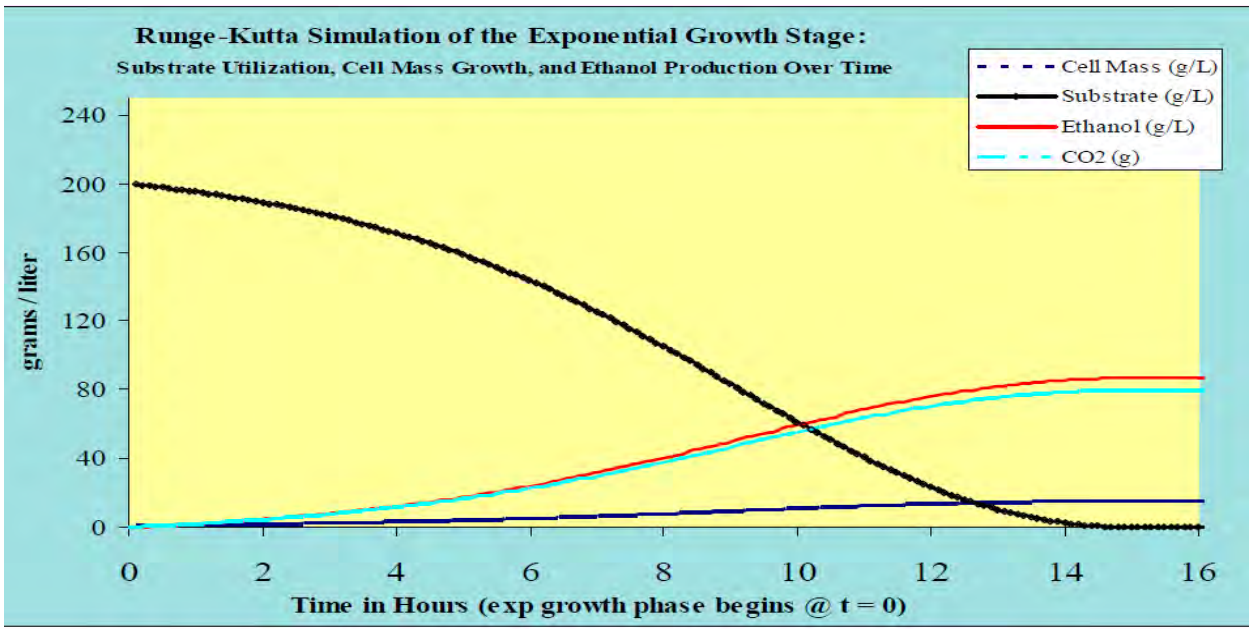


Figure 2.7 Glucose, Alcohol, CO_2, Cell Mass Levels during Fermentation (Source: N. Mosier and M. Ladisch).

2.8.1.4. 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).

2.8.1.5. 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).

2.8.2. Thermo-chemical Conversion Process

This process route includes production of synagas using gasification of the biomass, and fermentation or catalytic synthesis of the synagas to produce ethanol. The process begins with biomass gasification where, under a controlled oxygen supply, cellulose, hemicellulose, and lignin are converted to synthesis gas (synagas), primarily CO, CO_2 and H_2. This synagas 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^{o}C. Although fermentation; convert the synagas mixture into ethanol using organisms and separate ethanol from water (Cellulosic ethanol, 2010).

2.9. The Benefits of Fuel Ethanol

A major benefit of a well-functioned bio-fuel system is that it eliminates and converts organic waste into useful and valuable products. One of the main benefits with bio-ethanol is the replacement of expensive fossil fuel. Some advantages are connected to waste removal, like improving hygienic conditions. Protection of soil, water, air and woody vegetation can be mentioned as environmental advantages. If the actual conditions are satisfactorily, the bio-ethanol technology can contribute to conservation and development (Galbe and Zacchi, 2002).

The fact that a bio-ethanol production can be building and operated locally creates opportunities to decrease the waste solid collection volume and land disposal costs. Furthermore, the technology has also a potential to create job opportunities locally for several thousands of people (Galbe and Zacchi, 2002).

Over the last 150 years, human activities have caused a dramatic increase in the emission of a number of greenhouse gases such as CO_2, which has led to changes in the equilibrium of the earth's atmosphere. Fuel ethanol is suggested as a sustainable fuel which can be produced from renewable resources and led to maintain or even reduce the level of greenhouse gases (Galbe and Zacchi, 2002).

Finally, the standard of living can be enhanced which directly contributes to social and economical development of the country (Galbe and Zacchi, 2002).

Chapter Three

Material and Methods

The experiments of production of ethanol from fruit peel were carried out in the laboratory of Chemical Engineering Department at the Institute of Technology, Addis Ababa University.

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 hydrolyzates 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

- 98% Sulfuric Acid (H_2SO_4):- used as a pretreatment and hydrolysis fruit peel.
- Sodium Hydroxide (NaOH):- used to adjust the pH of soluble cellulose and hemicelluloses before fermentation.
- Yeast extracts (Agar):- used as media preparation.
- Urea: - used as media preparation.
- Dextrose sugar: - used as media preparation.
- Mg SO_4.7 H_2O:- used as media preparation.
- Yeast (*Saccharomyces cerevisiae*).

3.2. Procedure of Experiment

The study was aimed at optimization of acid hydrolysis in the production of ethanol from fruit peel. Fruit peels were collected from juice house in Addis Ababa. They were collected in plastic bags and transported to the laboratory of environmental engineering 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 3kg was used for the sample preparation. They were cut by knife into pieces of about 3-5 cm length for drying and grinding. Sample drying was carried out in oven

(60^0C for 72hr) to obtain easily crushable material. After drying, each of the samples was milled separately. The maximum particle sizes of the ground mixed sample were 2 mm. The sample of larger particle size than 2 mm was ground over and over again until all particle size became 2 mm. The sample was kept at low temperature until the next stage of experiment. Grinding of fruit peel into powder form increases the surface area of the sample which enhances the contact between hemicellulose and cellulose with dilute acid to reduce cellulose crystallinity.

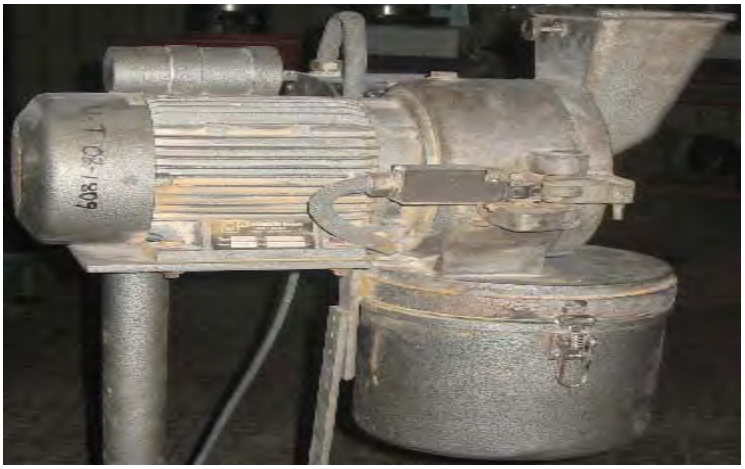


Figure 3.1 Grinding Machine

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 by-product 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 121^oC temperatures. Flow through processes steam at temperature of 121^oC 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

became 0 bars. The retention time for every batch was 15min. Finally the samples was kept in autoclave for the given pretreatment time and temperature and allowed to cool.

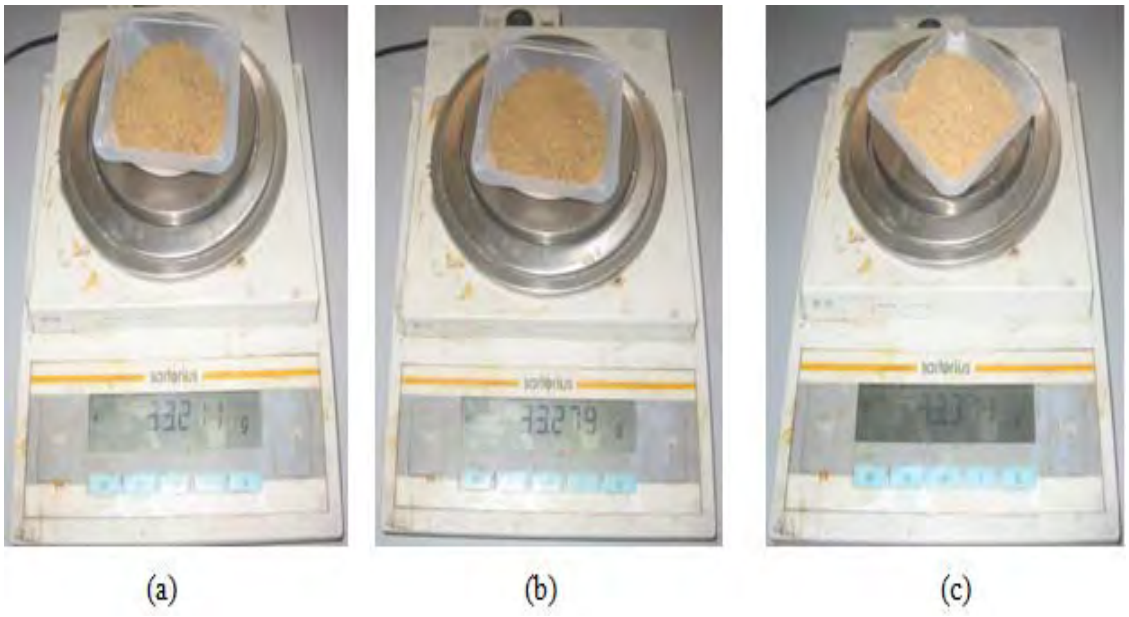


Figure 3.2 (a) Mango peel, (b) Banana peel and (c) Orange peel sample

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^{o}C for 15 minutes.
- 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 3.3 **(**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 25 minutes), hydrolysis temperature (100 to 132^{o}C), and acid concentration (0.5 to 1%).

Table 3.1 Minimum and Maximum values of parameters

Factors	Minimum	Maximum
Hydrolysis time(minutes)	5	25
Hydrolysis temperature ^{0}C	100	132
Acid concentration(% by volume of distilled water)	0.5	1

Table 3.2 Experimental design formulated for hydrolysis stage

S. Number	Actual Value			S. Number	Actual Value		
	Acid con.	Temp.	Time		Acid con.	Temp.	Time
1	0.50	100.00	15.00	9	0.50	116.00	5.00
2	0.75	132.00	5.00	10	0.75	116.00	15.00
3	0.50	132.00	15.00	11	0.75	116.00	15.00
4	1.00	116.00	5.00	12	0.75	100.00	5.00
5	1.00	132.00	15.00	13	0.75	116.00	15.00
6	0.50	116.00	25.00	14	0.75	116.00	15.00
7	0.75	132.00	25.00	15	0.75	100.00	25.00
8	1.00	116.00	25.00	16	1.00	100.00	15.00

Figure 3.4 (a) Hydrolysis in the reactor (b) Sample ready for hydrolysis

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 for 5 to 25min.
- After hydrolysis, neutralize with 10 M NaOH until the pH became around 7.
- 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 3.5 (a) Sample ready for centrifugal separation (b) Centrifuge Machine

3.2.3.1. 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 3.6 pH meter

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 equipments that were used for fermentation purposes were sterilized (autoclaved). The sterilization was carried out at a temperature of 121^{o}C for 15 minutes.

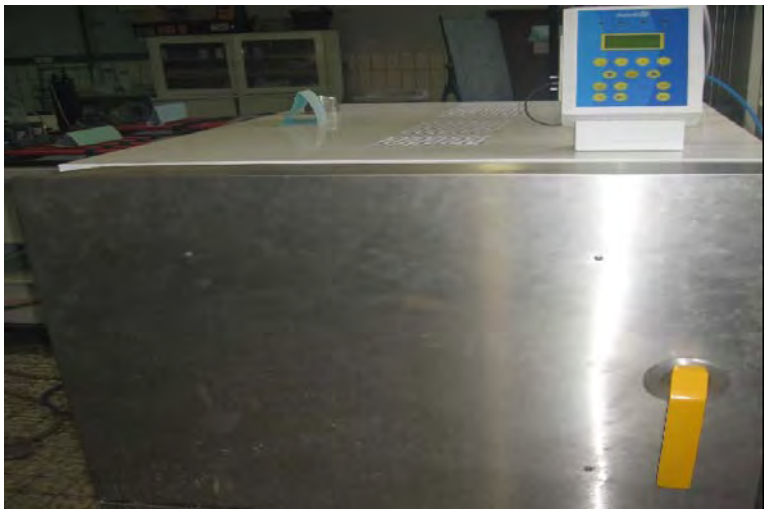


Figure 3.7 Sterilization equipment

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, pH 5.5 with 200 rpm stirring condition for 3 days. Before conducting fermentation I had the preparation of media for the yeast. In order to prepare the media I should had the favorable condition for yeast growth or to supply the required amount of nutrients. Mix the following nutrients in there proportion.

Media Preparation

- For preparing 100 ml media, I add
- ✓ Sugar (Dextrose) = 10 gm
- ✓ Yeast extract = 0.2 gm
- ✓ Urea = 1.0gm
- ✓ Make up water = 100 ml
- ✓ Mg SO_4.7 H_2O = 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 then placed in a shaking incubator for 24 hours, a temperature of 30^{o}C and 200rpm.

(a) (b)

Figure 3.8 (a) Shaker incubator (b) media after 24hr incubation

The Procedure for Fermentation

- The sample was conditioned to temperature of 30^{o}C 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^{o}C, 1 hour and 120 rpm.
- Set autoclavable reactor at 30^{o}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^{o}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.

(a) (b)

Figure 3.9 (a) Fermentation setup (b) Sample ready for fermentation

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 ^{o}C for 3hrs.

Components of experimental setup

- Distillation vessel
- Special top-fit of distillation vessel
- Condenser
- 90^{o} 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^{o}C and a distillation time of 3 hours.

Figure 3.10 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^{o}C. Weigh the pycnometer (specific gravity bottle) with stopper after cleaning, drying and note the weight as X_1 at 20^{o}C. Filled the pycnometer with distilled water and take the weight of the water at 20^{o}C and note as X_3. Make the pycnometer empty, clean, dry and then filled with sample (alcohol) of the experimental result. Determine the weight of the sample at 20^{o}C and note as X_2. 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.

$$\text{Specific gravity of sample} = (X_2-X_1)/(X_3-X_1)$$

Where: X_1- weight (g) of empty pycnometer

X_2- weight (g) of pycnometer + sample

X_3 - weight (g) of pycnometer + water

Figure 3.11 Pycnometer (Specific gravity bottle)

3.3. Data Analysis

Design expert® 7 software experimental method was used to determine the effect of three operating variables of the acid hydrolysis in ethanol production from fruit peel. These were time, temperature and acid concentration. The response variable was ethanol yield. Significance of the result was set from analysis of variance (ANOVA).

Chapter Four

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 density using hydrometer and pycnometer to know the yield of ethanol concentration. The results are indicated below, table 4.1 (using Hydrometer) 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 4.1 Yield of ethanol (Hydrometer)

Run No	Densities(g/ml^3)	Yield of ethanol (%)	Run No	Densities(g/ml^3)	Yield of ethanol (%)
1	0.92	43	9	0.93	38
2	0.92	43	10	0.89	57
3	0.92	43	11	0.89	57
4	0.93	38	12	0.93	38
5	0.93	38	13	0.89	57
6	0.91	48	14	0.90	52
7	0.93	38	15	0.91	48
8	0.92	43	16	0.93	38

Table 4.2 Yield of ethanol (Pycnometer)

Run No	Densities(g/ml^3)	Yield of ethanol (%)
1	0.92746	43.5
2	0.92741	43.5
3	0.92684	44
4	0.93104	42
5	0.93101	42
6	0.91271	50.5
7	0.93256	41.5
8	0.92533	44.5
9	0.93516	40
10	0.89432	58.5
11	0.89241	59.5
12	0.93637	39.5
13	0.89652	57.5
14	0.90935	52
15	0.91825	48
16	0.93834	38.5

As shown on the above two table (table 4.1 and 4.2) the yield of ethanol concentration (%) are different since hydrometer are read two digit after point where as the pycnometer are measured using the sensitive balance and produce five digit after point. From those two table result above the pycnometer result were read exactly from Perry Chemical Engineering Handbook. Due to this reason the pycnometer are more accurate than that of hydrometer measurement. Hence the discussions continue depend on the result from pycnometer.

From the result shown above (table 4.2) the maximum yields are run number: 11, 10, 13, 14 and 6 descending order. The minimum results were obtained at run number: 16, 12 and 9.

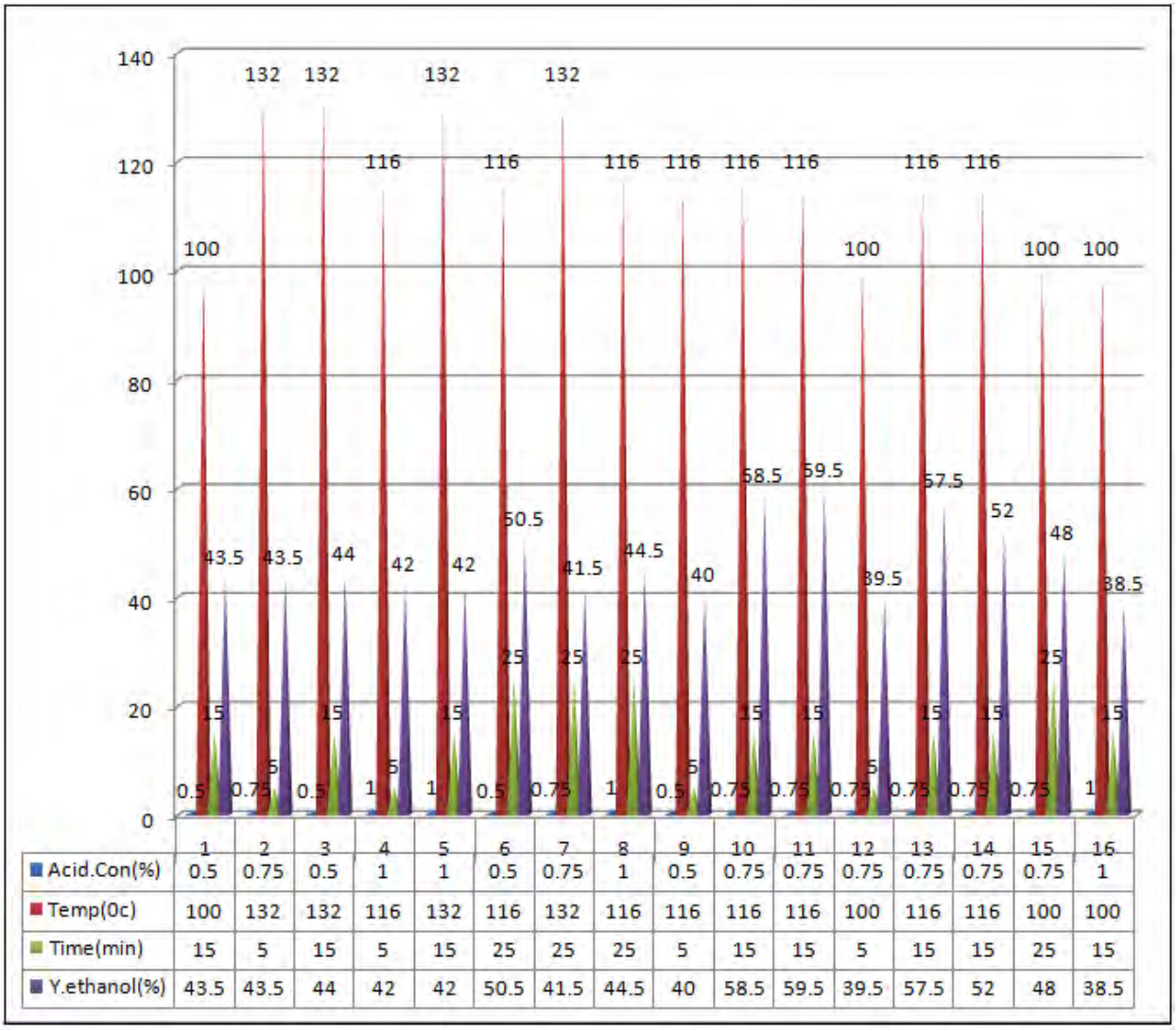


Figure 4.1 Ethanol yield and parameters condition

As we see from the above figure 4.1 high yield of ethanol were observed at 0.75% acid concentration, at 116^0C 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 16 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 4.3 Result using Design expert® 7 software

Run No	Acid conc.(% by weight)	Temperature (^{0}C)	Time (min)	Yield of Ethanol (%)
1	0.5	100	15	43.5
2	0.75	132	5	43.5
3	0.5	132	15	44
4	1	116	5	42
5	1	132	15	42
6	0.5	116	25	50.5
7	0.75	132	25	41.5
8	1	116	25	44.5
9	0.5	116	5	40
10	0.75	116	15	58.5
11	0.75	116	15	59.5
12	0.75	100	5	39.5
13	0.75	116	15	57.5
14	0.75	116	15	52
15	0.75	100	25	48
16	1	100	15	38.5

The resulting data obtained on table 4.3, were analyzed using Design expert® 7 software to decide the effects of operating parameters; acid concentration, temperature and time. The

dependent variable used as a response parameter was the yield of ethanol. All experiments were carried out in a randomized order to minimize the effect of unexpected variability in the observed response due to extraneous factors.

Design Summary for ethanol production with two levels and three factors. The design model of the experiments are quadratic polynomial and the center point is zero using Design expert® 7 software.

Table 4.4 Design Summary of factorial designs

Design Summary of Design expert® 7 software	
Study type	Response surface
Initial design	Box-Behnken
Design model	Quadratic polynomial
Run	16
Block	No block

To determine whether or not the quadratic model is significant, it was crucial to perform analysis of variance (ANOVA), table 4.5. The probability (P-values) values were used as a device to check the significance of each coefficient, which also showed the interaction strength of each parameter. The smaller the P-values are, the bigger the significance of the corresponding coefficient.

Table 4.5 Analysis of variance (ANOVA) for the quadratic model

Source	Sum of square	Degree of freedom	Mean square	F-value	P-value Prob>F
Model	686.06	9	76.23	10.08	0.0054*
A-Acid conc.	15.13	1	15.13	2.00	0.2070
B-Temp.	0.28	1	0.28	0.037	0.8534
C-Time	47.53	1	47.53	6.29	0.0461
AB	2.25	1	2.25	0.30	0.6051
AC	16.00	1	16.00	2.12	0.1960
BC	27.56	1	27.56	3.64	0.1048
A^2	189.06	1	189.06	25.00	0.0025
B^2	256.00	1	256.00	33.85	0.0011
C^2	132.25	1	132.25	17.49	0.0058
Residual	45.37	6	7.56		
Lack of fit	11.69	3	3.90	0.35	0.7961
Pure error	33.69	3	11.23		
Cor total	731.44	15			

F- Value is a test for comparing model variance with residual (error) variance. If the variances are close to the same, the ratio will be close to one and it is less likely that any of the factors have a significant effect on the response. It is calculated by Model Mean Square divided by Residual Mean Square. Here the Model F-value of 10.08 implies the model is significant. There is only a 0.54% chance that a "Model F-Value" this large could occur due to personal error or disturbance. Probability values and/ or "Prob > F" values less than 0.0500 indicate model terms are significant. In this case C (time), A^2 (acid concentration), B^2 (temperature), C^2 (time) are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

The lack of fit F-value of 0.35 implies the lack of fit is not significant relative to the pure error. There is a 79.61% chance that a lack of fit F-value this large could occur due to noise. Non significant lack of fit is good.

Coefficient of Variation, the standard deviation expressed as a percentage of the mean; Predicted Residual Error Sum of Squares, which is a measure of how the model fits each point in the design; the R-Squared, measure of the amount of variation around the mean explained by the model; Adj R-Squared that is a measure of the amount of variation around the mean explained by the model, Pred R-Squared, a measure of the amount of variation in new data explained by the model, and Adequate Precision, this is a signal to disturbance ratio due to random error, presented in the table 4.6, below, are used to decide whether the model can be used or not.

Table 4.6 Model adequacy measures

Standard deviation	2.75	R-squared	0.9380
Mean	46.56	Adj R-squared	0.8449
C.V.%	5.91	Pred R-squared	0.6625
PRESS	246.89	Adeq Precision	8.739

The "Pred R-Squared" of 0.6625 is as close to the "Adj R-Squared" of 0.8449 in less than 0.2 difference as one might expect. "Adeq Precision" measures the signal to disturbance ratio due to random error. A ratio greater than 4 is desirable. Here ratio of 8.739 indicates an adequate signal. Therefore, this model can be used to navigate the design space.

The regression coefficients and the corresponding 95% CI (Confidence Interval) High and Low were presented in table 4-7 below. If zero was in the range High and Low 95% Confidence Interval, the factors has no effect. From the 95% CI High and Low values of each model term, it could be concluded that the regression coefficients of acid concentration and the interaction terms of time and acid concentration have highly significant effect in ethanol production.

Table 4.7 Regression coefficients and the corresponding 95% CI High and Low

Factors	Coefficient of estimate	Standard error	95% CI low	95% CI high
Intercept	56.88	1.37	53.35	60.24
A-acid con.	-1.38	0.97	-3.75	1.00
B-temper.	0.19	0.97	-2.19	2.57
C-time	2.44	0.97	0.058	4.82
AB	0.75	1.37	-2.61	4.11
AC	-2.00	1.37	-5.36	1.36
BC	-2.63	1.37	-5.99	0.74

By the designed experimental data from table 4.3, the quadratic polynomial model for ethanol production from fruit peel by dilute acid hydrolysis was retreated and shown as below:

Equation in terms of coded factors:

Yield of Ethanol = +56.88 -1.38*A + 0.19*B + 2.44*C + 0.75*A*B -2.00*A*C – 2.63*B*C - $6.87*A^2 – 8.00*B^2 – 5.75*C^2$

Equation in terms of actual factors:

Yield of Ethanol = -460.56250 + 149.75000*Acid concentration + 7.36719*Temperature + 4.47188*Time + 0.18750*Acid concentration*Temperature – 0.80000*Acid concentration*Time -0.016406*Temperature*Time – 110.00000*Acid $concentration^2 – 0.031250*Temperature^2 – 0.057500*Time^2$

The actual versus predicted values using model in the above equation (in terms of actual factors) are tabulated in table 4-8.

Table 4.8 Actual versus model Predicted of ethanol yield

Diagnostic case statistics								
Run No	**Actual value (%)**	**Predicted Value (%)**	**Residual**	**Leverage**	**Internally studentized residual**	**Externally studentized residual**	**Influence on fitted value**	**Cooks distance**
1	43.50	43.94	-0.44	0.750	-0.318	-0.293	-0.507	0.030
2	43.50	43.5	0.000	0.750	0.000	0.000	0.000	0.000
3	44.00	42.81	1.19	0.750	0.864	0.842	1.459	0.224
4	42.00	42.44	-0.44	0.750	-0.318	-0.293	-0.507	0.030
5	42.00	41.56	0.44	0.750	0.318	0.293	0.507	0.030
6	50.50	50.06	0.44	0.750	0.318	0.293	0.507	0.030
7	41.50	43.12	-1.62	0.750	-1.182	-1.232	*-2.13	0.419
8	44.50	43.31	1.19	0.750	0.864	0.842	1.459	0.224
9	40.00	41.19	-1.19	0.750	-0.864	-0.842	-1.459	0.224
10	58.50	56.88	1.63	0.250	0.682	0.649	0.374	0.016
11	59.50	56.88	2.63	0.250	1.102	1.127	0.650	0.040
12	39.50	37.87	1.63	0.750	1.182	1.232	*2.13	0.419
13	57.50	56.88	0.63	0.250	0.262	0.241	0.139	0.002
14	52.00	56.88	-4.88	0.250	-2.047	-3.402	-1.964	0.140
15	48.00	48.00	0.000	0.750	0.000	0.000	0.000	0.000
16	38.50	39.69	-1.19	0.750	-0.864	-0.842	-1.459	0.224
* exceeds limits								

To see how well the model satisfies the assumptions of the analysis of variance (ANOVA), the plots of residuals versus predicted (Table 4.8) were analyzed.

Normal probability plot of the raw data used to check the assumption of normality when using t-test. In the analysis of variance, it is usually more effective (and straight forward) to do this with the residuals. This shown below resembles a straight line. In visualizing the straight line, place more emphasis on the central values of the plot than on the extremes.

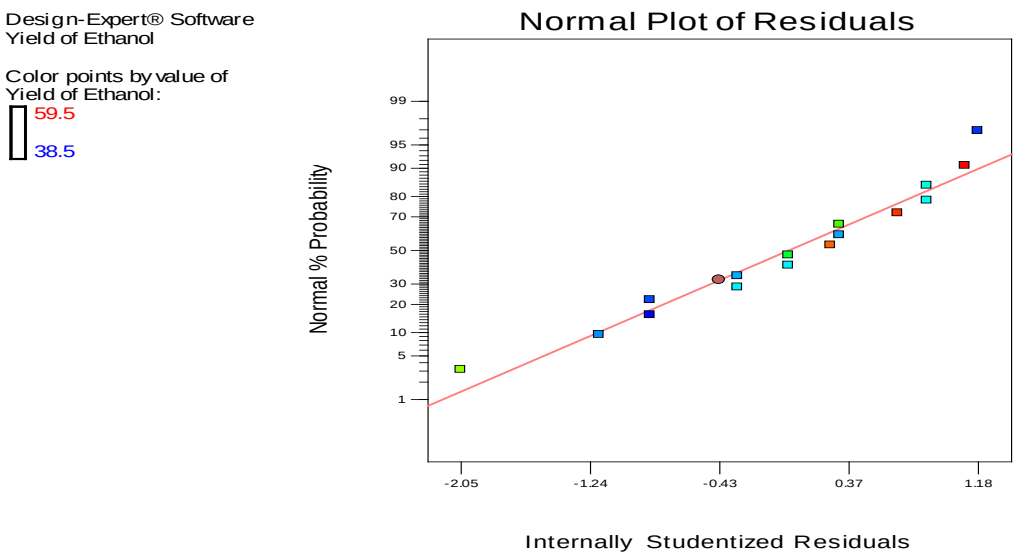


Figure 4.2 Normal plots of residuals

From the plot as shown above, the normal probability plot indicates the residuals following a normal distribution, in the case of this experiment the points in the plots shows fit to a straight line in the figure, this shows that the quadratic polynomial model satisfies the assumptions analysis of variance (ANOVA) i.e. the error distribution is approximately normal.

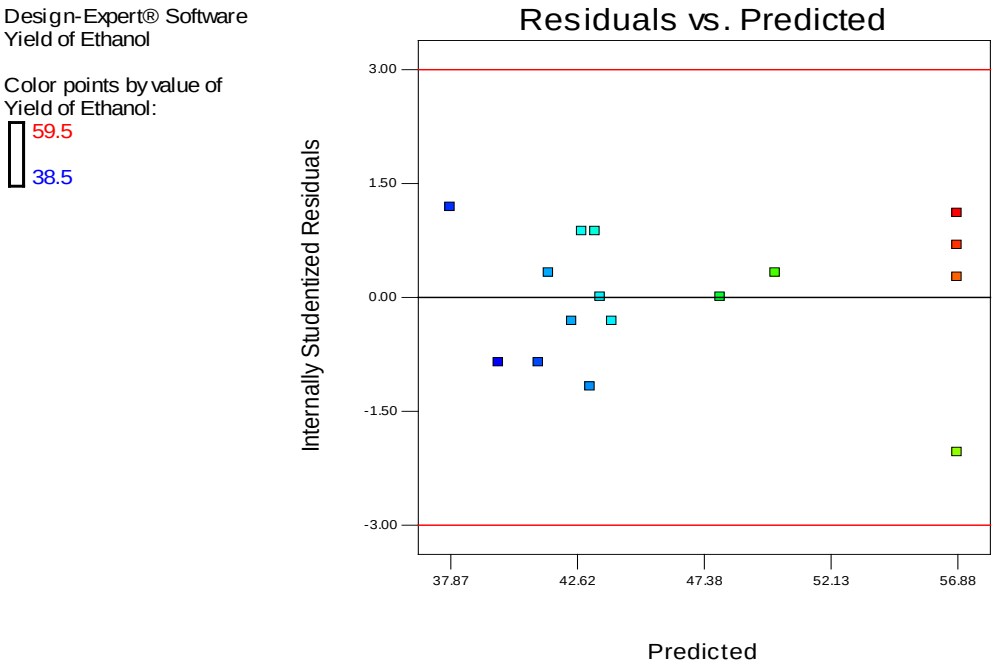


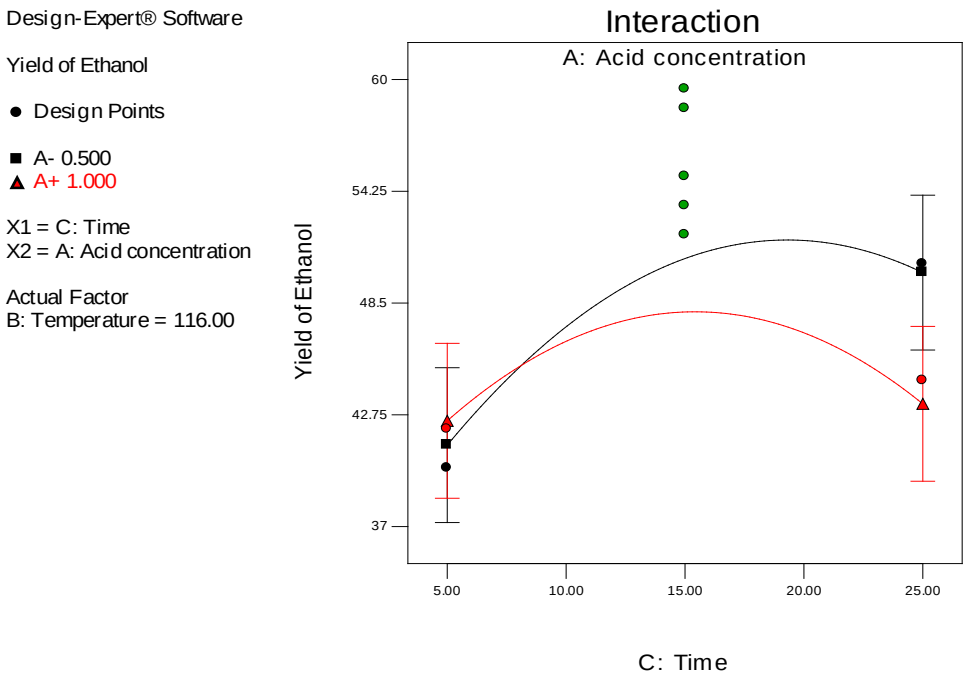
Figure 4.3 Residual versus predicted values

If the model is correct and the assumptions are satisfied, the residuals should be structure less; in particular, they should be unrelated to any other variable including the predicted response. A simple check is to plot the residuals versus the fitted (predicted) values. A plot of the residuals versus the rising predicted response values tests the assumption of constant variance. The plot shows random scatter which justifying no need for an alteration to minimize personal error.

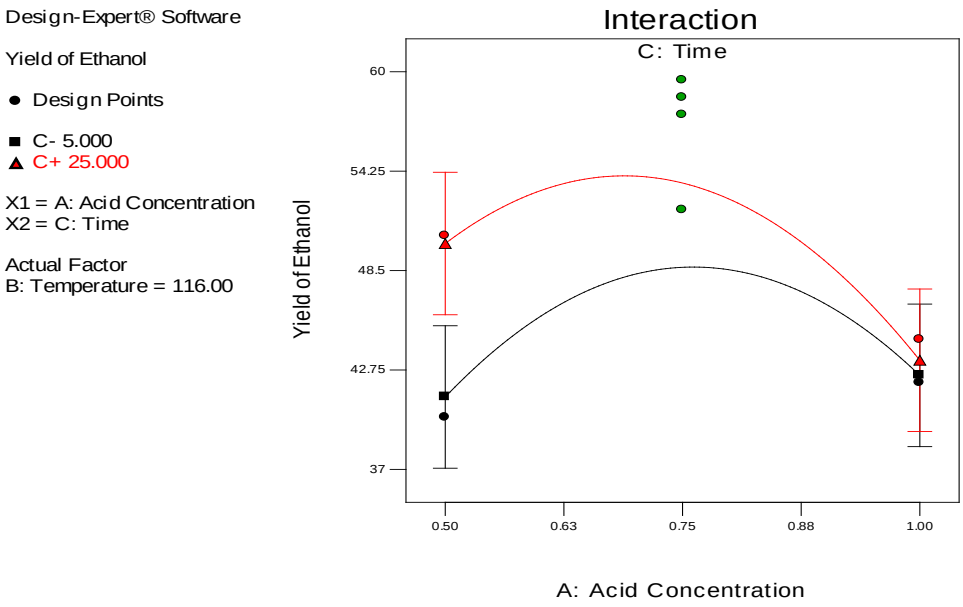
4.2. Effects of Experimental Variables on Hydrolysis

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 (4.4), (4.5) and (4.6) below as a function of the interactions of any two of the variables by holding the other value of the variable at middle.

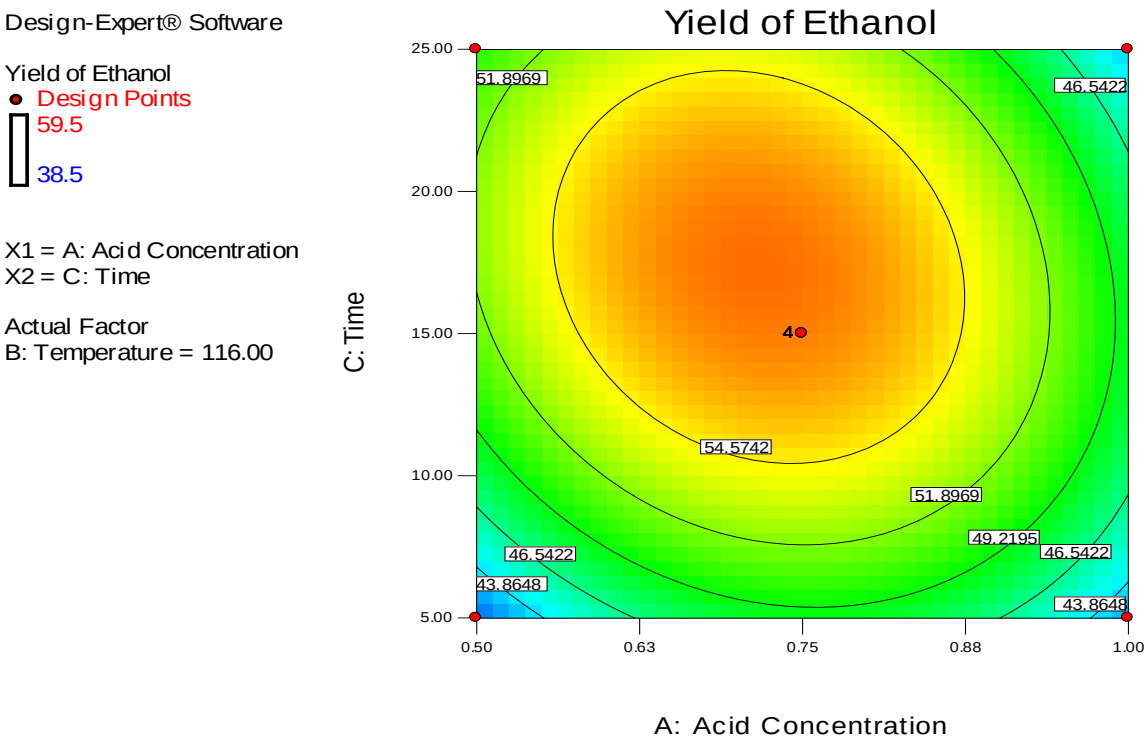
For the interaction figures, black and red line indicates low and high level of parameters respectively.



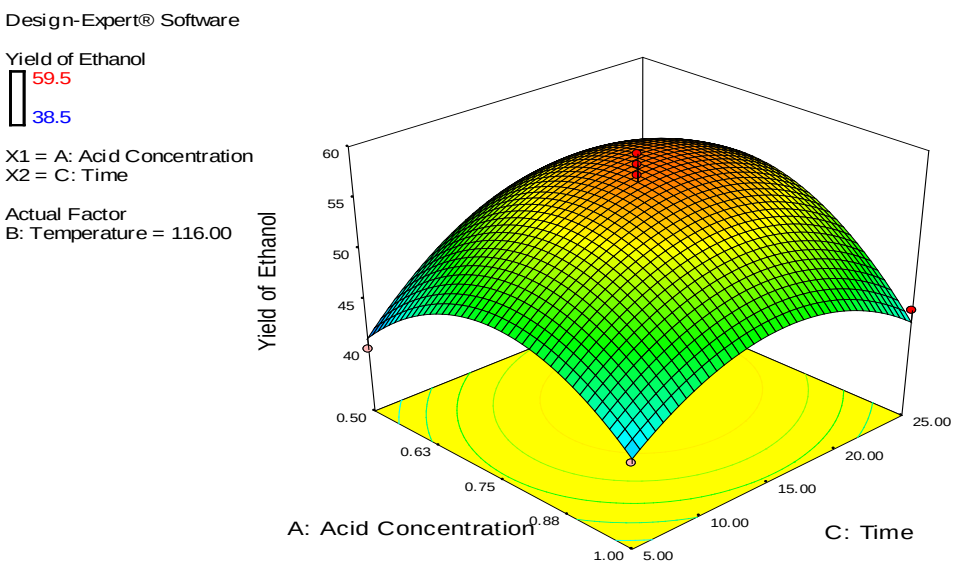
(a) The effects of time and acid concentration (fixed) on the yield of ethanol, when the temperature was at the center point



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



(c) Contour plots of the effects of acid concentration and time on ethanol yield



(d) Response surface plots of the effects of acid concentration and time on ethanol yield

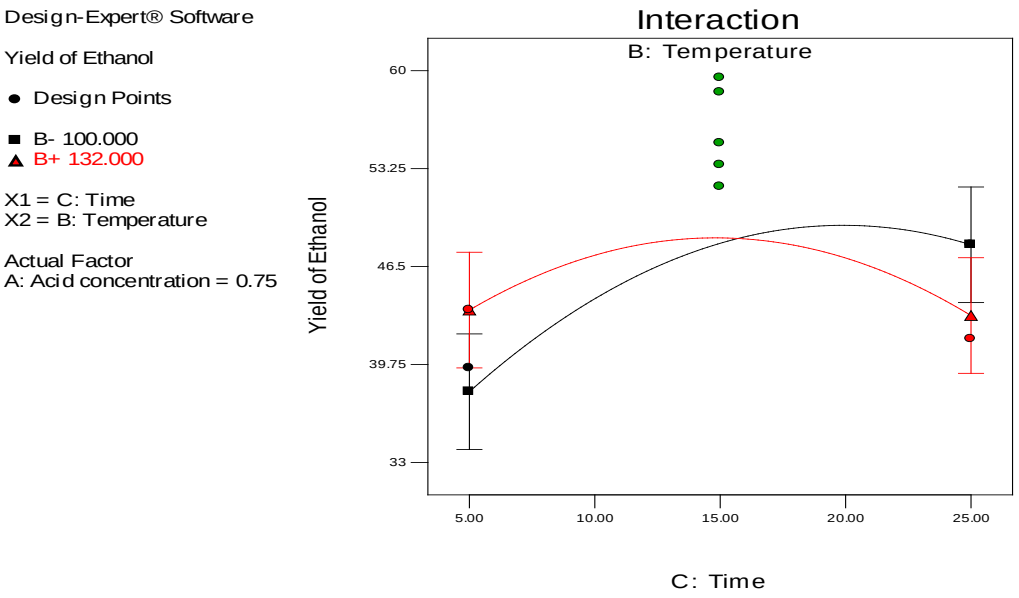
Figure 4.4 Effect of acid concentration and time on the yield of ethanol when temperature was at the center point (a, b, c & d)

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.

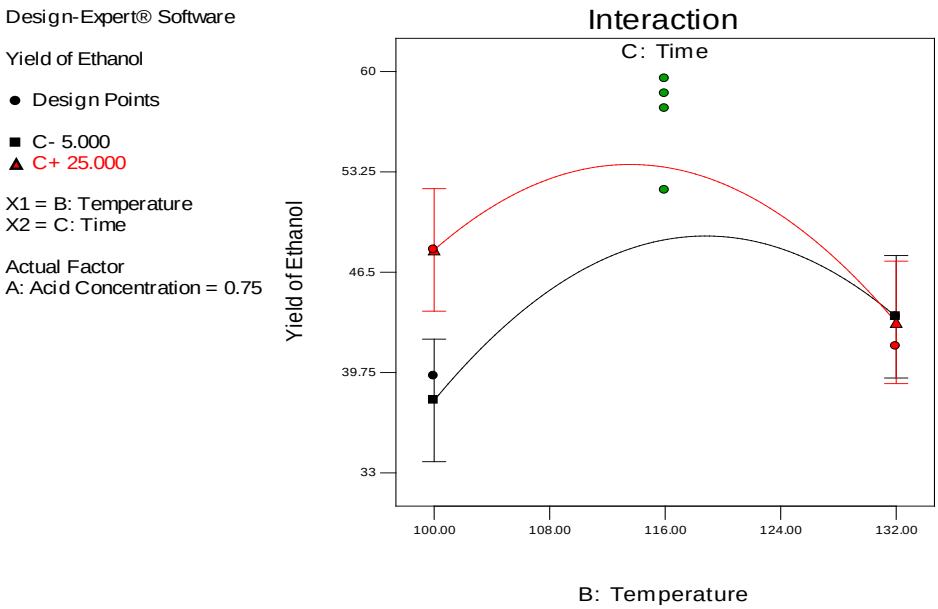
Contour plot graph showing predicted response of ethanol yield as a function of hydrolysis time and acid concentration was shown in figure 4.4 (c). As hydrolysis time increases at lower level of acid concentration and as acid concentration increases at low level of time gives a positive effect on the yield of ethanol.

The response surface figure 4.4 (d), obtained from hydrolysis time and acid concentration was conical shape. Hence from the result, there were well defined optimums operating conditions. As hydrolysis time increases at lower level of acid concentration and as increase level of acid

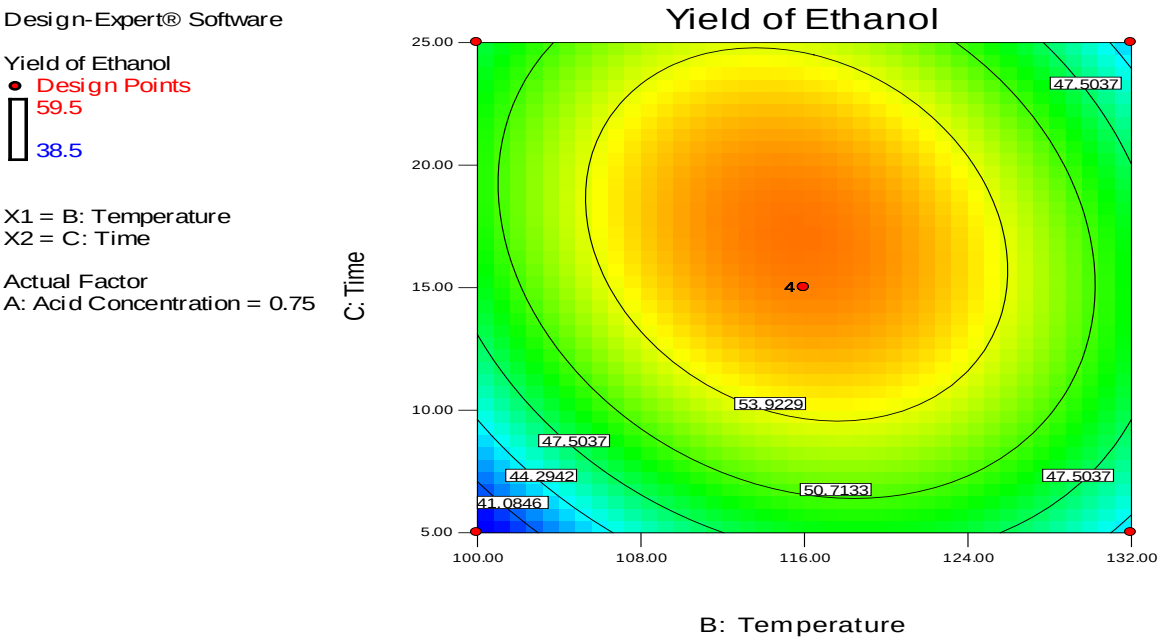
concentration and lower level of time gives a positive effect on the yield of ethanol. The response surface suggests that there were dominance interactions of these two factors.



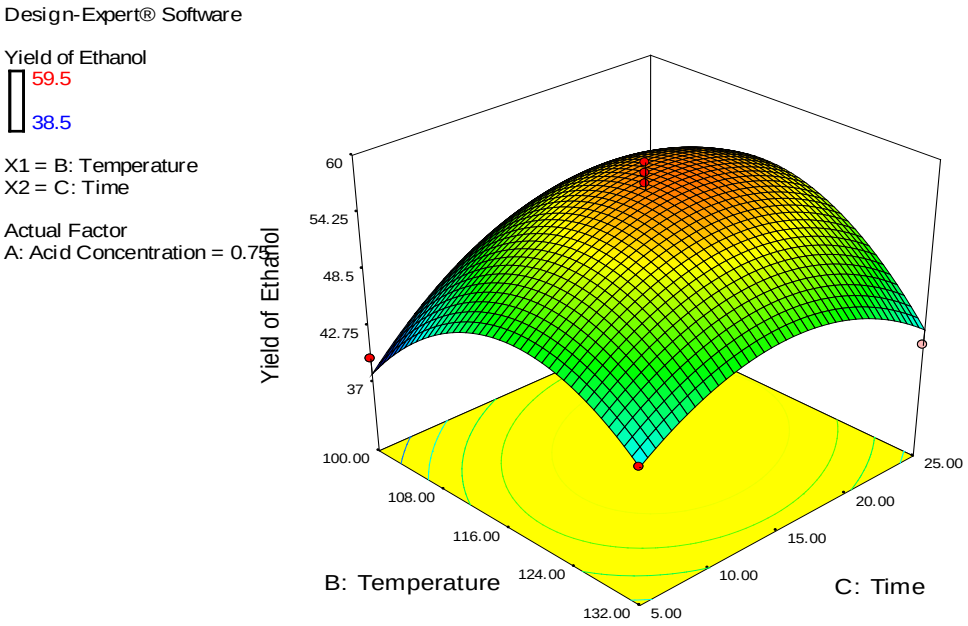
(a) The effect of time and temperature (fixed) on the yield of ethanol, when acid concentration was at the center point



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



(c) Contour plots of the effects of time and temperature on the yield of ethanol



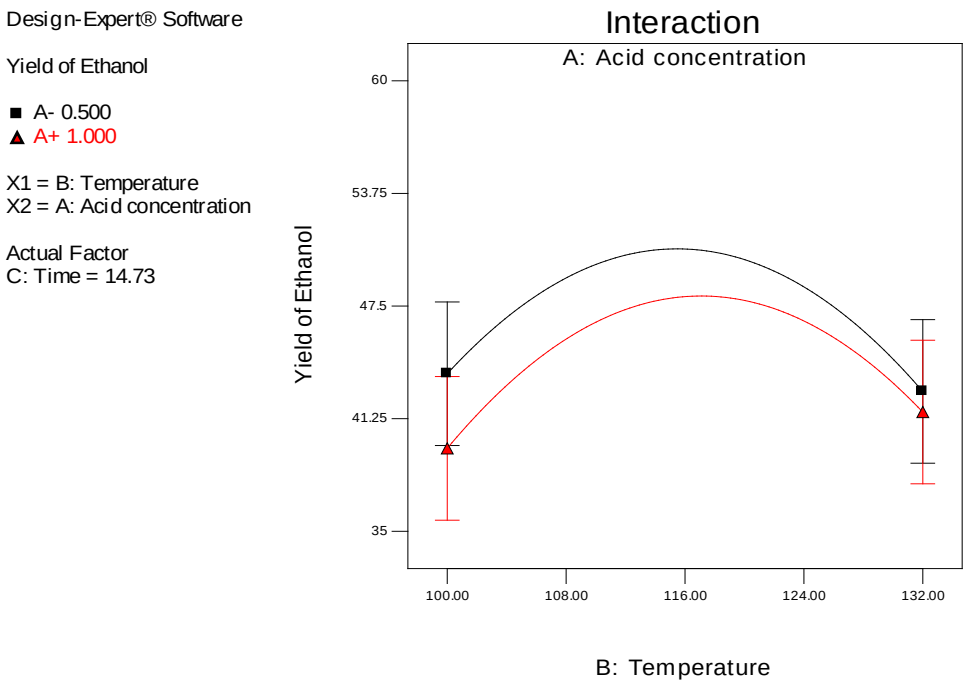
(d) Response surfaces plot of the effects of temperature and time on the yield ethanol

Figure 4.5 Effect of temperature and time on yield of ethanol when acid concentration was at the center point (a, b, c & d)

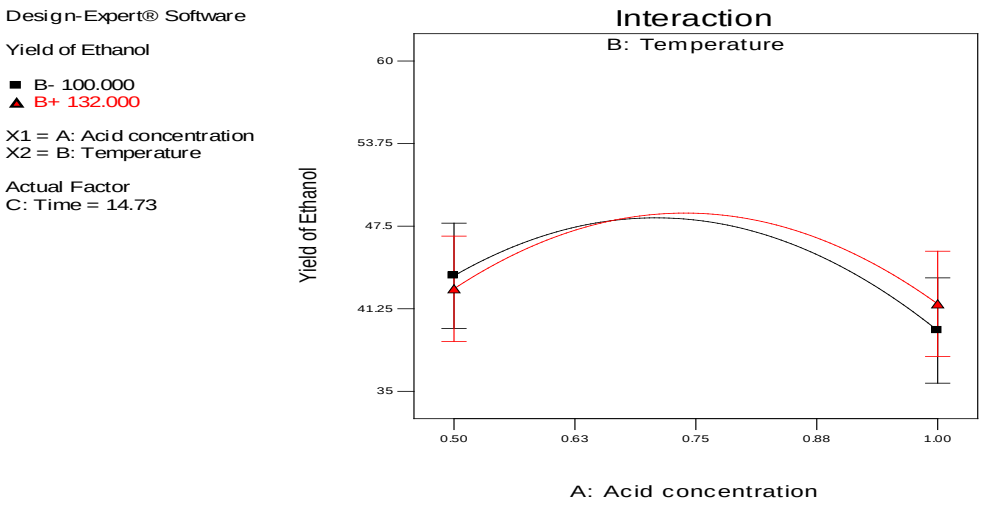
The effects of acid concentration and temperature on the yield of ethanol, acid concentration was selected at the center point, are shown in figure 4.5 (a) and (b). When the levels of temperature increase hydrolysis resulted in higher yield of ethanol. However, as you seen from the graph after some increments of temperature, the yield of ethanol became decreases since the possible formation of other molecules instead of glucose formation due to high temperature. Similarly, at low and high time, the yield of ethanol decrease.

From the contour plot graph showing predicted response of ethanol yield as a function of hydrolysis time and hydrolysis temperature was shown in figure 4.5 (c). As hydrolysis time increases at lower level temperature gives positive effect on the yield of ethanol and it decrease when the hydrolysis time and temperature became higher and higher.

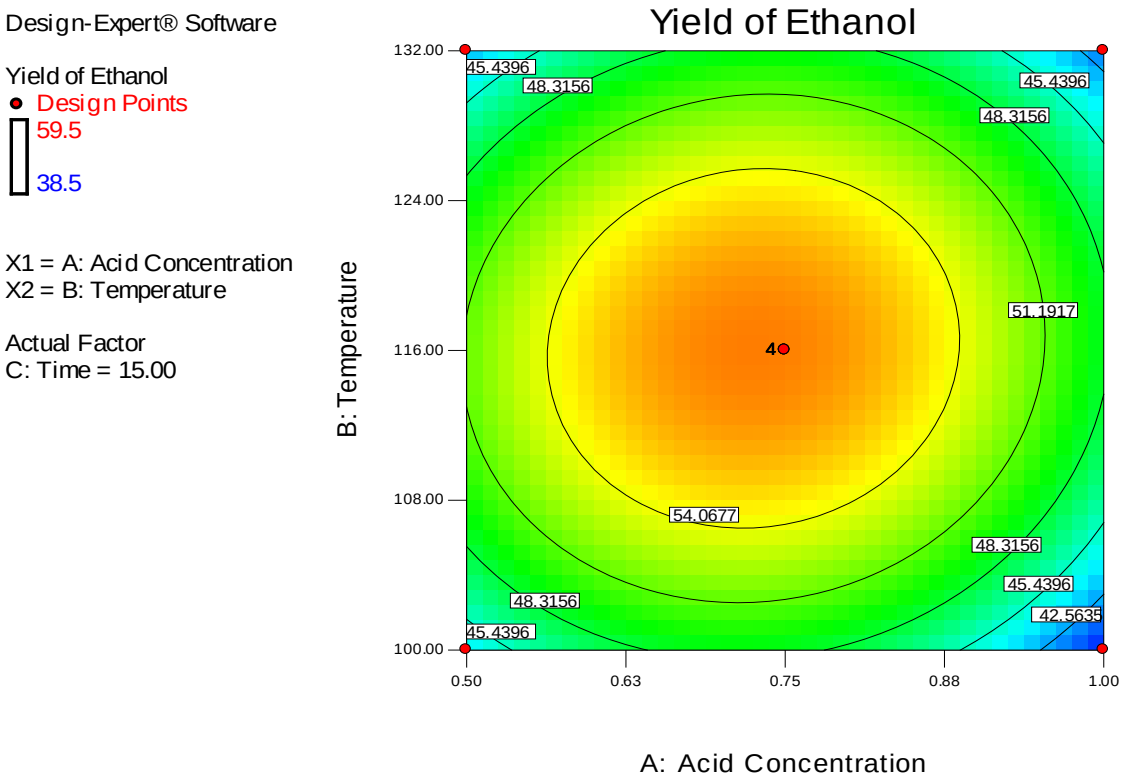
The response surface figure 4.5 (d), obtained from hydrolysis time and hydrolysis temperature was conical shape. It suggests that there were well-defined optimum operating conditions. The response optimized value for the production of ethanol was based on both in hydrolysis time and temperature.



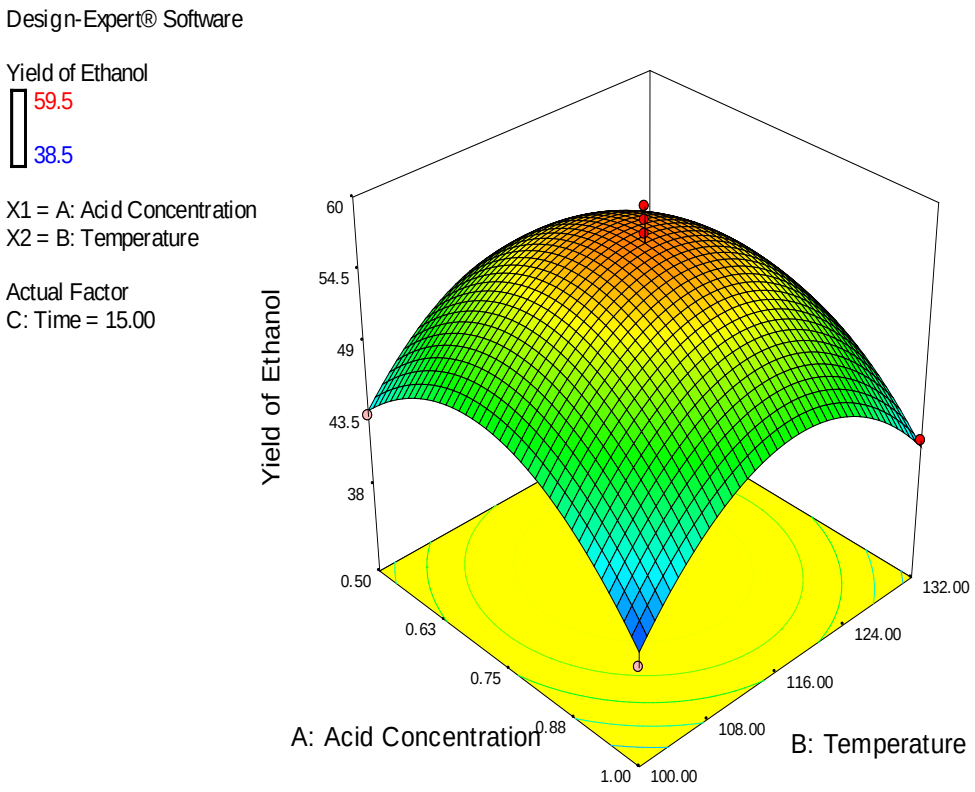
(a) The effects of temperature and acid concentration (fixed) on the yield of ethanol, when and time was at the center



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



(c) Contour plots of the effects acid concentration and temperature



(d) Response surface plots of the effects acid concentration and temperature

Figure 4.6 Effect of temperature and acid concentration on the yield of ethanol when time was at the center point (a, b, c & d)

At the lower and higher levels of temperature and acid concentration, the production of ethanol yield decrease since it has effect of the hydrolysis treatment. At lower temperature and acid concentration 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 temperature and acid concentration have strong relationship for the yield of ethanol production.

Contour plot graph showing predicted response of ethanol yield as a function of hydrolysis temperature and acid concentration was shown in figure 4.6 (c). As hydrolysis temperature

increases at lower level of acid concentration and as acid concentration increases at low level of temperature gives a positive effect on the yield of ethanol.

The response surface figure 4.6 (d), obtained from hydrolysis temperature and acid concentration was conical shape. Hence from the result, there were well defined optimums operating conditions. As hydrolysis temperature increases at lower level of acid concentration and as increase level of acid concentration and lower level of temperature gives a positive effect on the yield of ethanol. The response surface suggests that there were dominance interactions of these two factors.

4.3. Optimizations

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

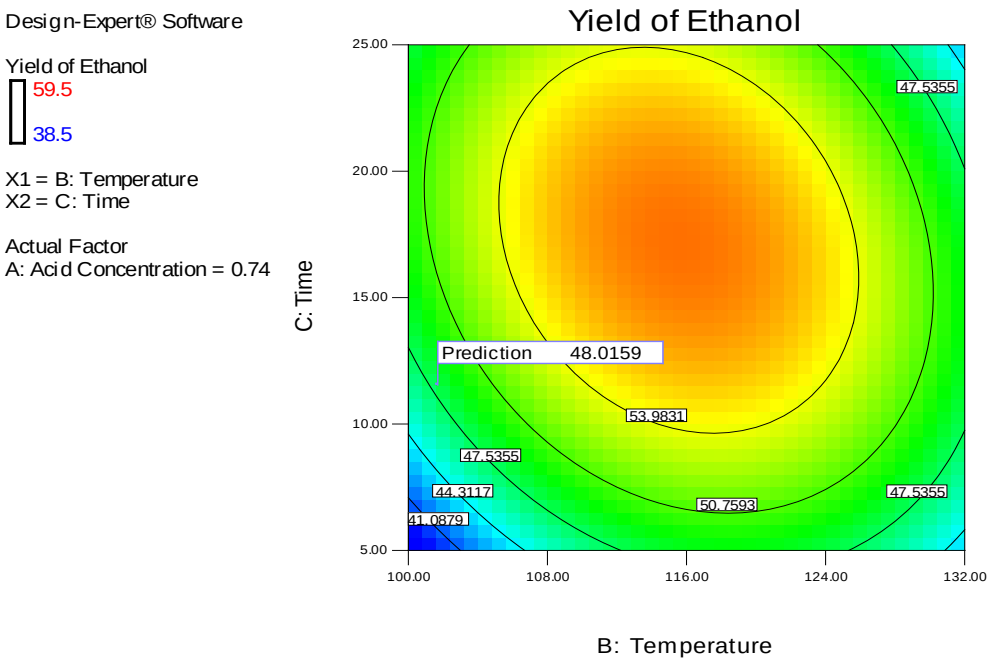
Table 4.9 Optimization criteria for optimum yield of ethanol

Parameters	Purpose	Minimum value	Maximum value
Acid concentration (%)	Minimize	0.5	1
Temperature (^{0}c)	Minimize	100	132
Time (min)	Minimize	5	25
Yield of Ethanol (^{0}c)	Maximize	40	63.5

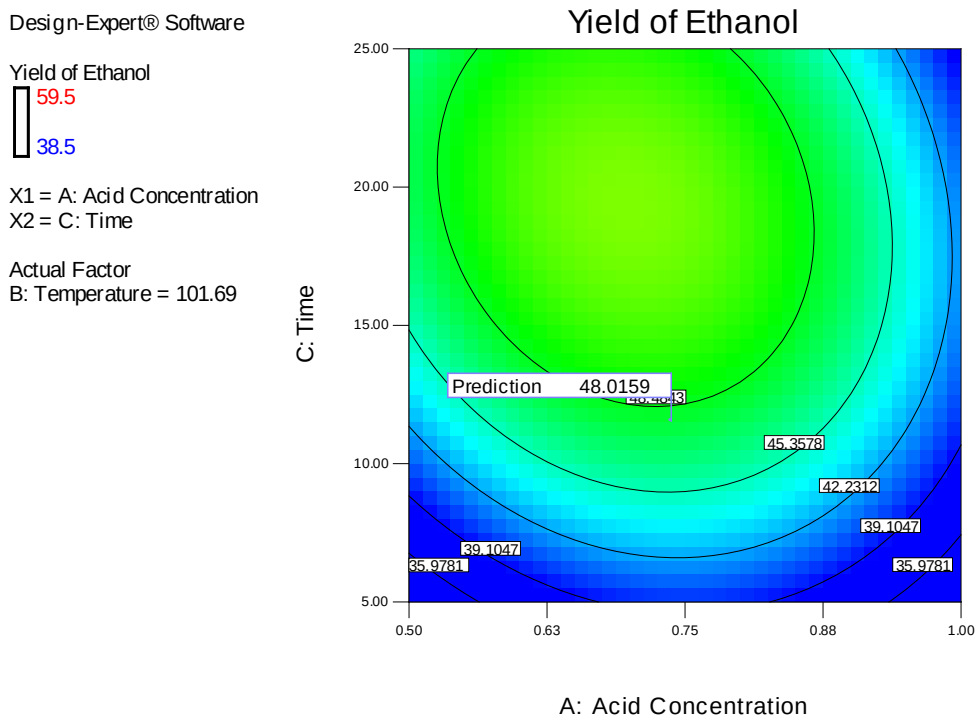
The optimum possible solutions in hydrolysis for different parameters for ethanol production and corresponding surface plot are presented in table 4.10 and figure 4.7 below.

Table 4.10 Optimum possible solutions

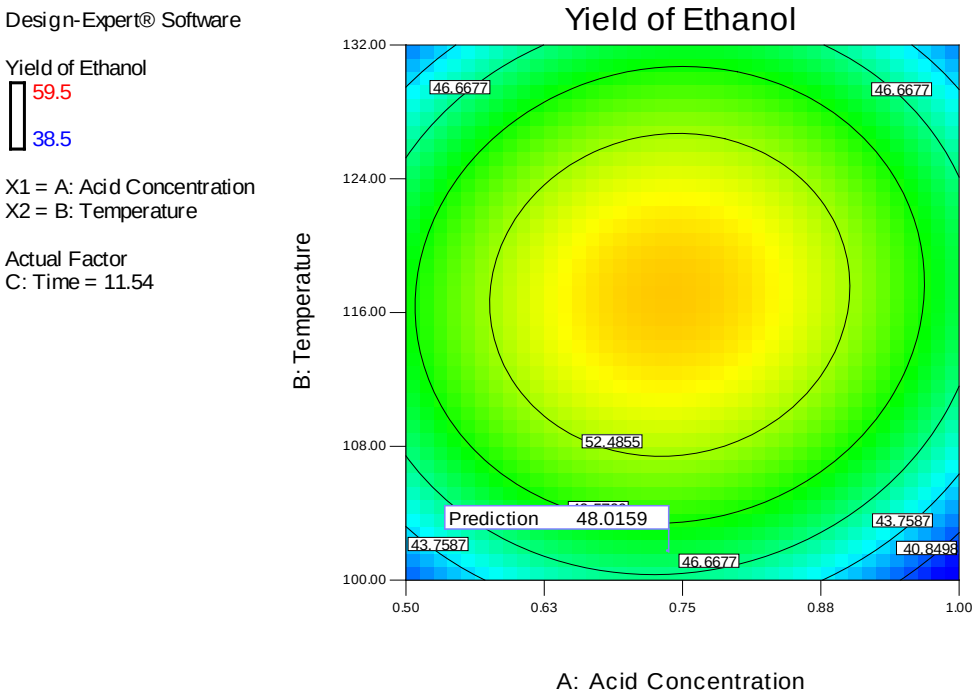
Run No	Acid Conc. (%)	Temp.(^{0}c)	Time (min)	Yield of ethanol	Desirability
1	0.74	101.69	11.54	48.0159	1.000(selected)
2	0.80	119.48	8.82	52.9000	1.000
3	0.92	120.09	20.54	50.8466	1.000
4	0.57	101.35	13.91	47.2869	1.000
5	0.58	106.94	6.26	43.1988	1.000
6	0.56	122.56	18.08	52.6954	1.000
7	0.64	117.87	24.47	53.7368	1.000
8	0.66	100.12	18.10	49.9463	1.000
9	0.73	125.21	22.16	52.1705	1.000
10	0.57	117.85	18.50	54.7933	1.000
11	0.61	116.35	14.17	55.1896	1.000
12	0.93	113.77	14.44	52.0913	1.000
13	0.68	106.42	5.87	44.9027	1.000
14	0.64	105.82	13.54	52.1453	1.000
15	1.00	114.12	5.53	42.7498	1.000
16	0.94	126.80	5.78	44.7928	1.000


Design-Expert® Software
Yield of Ethanol
59.5
38.5
X1 = B: Temperature
X2 = C: Time
Actual Factor
A: Acid Concentration = 0.74
Yield of Ethanol
C: Time
B: Temperature
Prediction 48.0159
47.5355
53.9831
47.5355
44.3117
50.7593
47.5355
41.0879
25.00
20.00
15.00
10.00
5.00
100.00
108.00
116.00
124.00
132.00

(a)

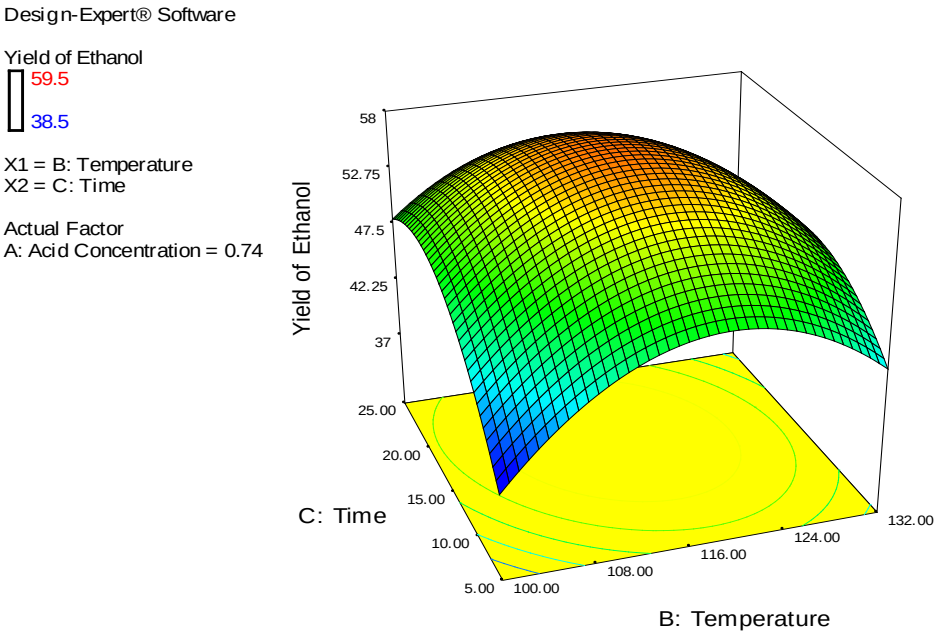

Design-Expert® Software
Yield of Ethanol
59.5
38.5
X1 = A: Acid Concentration
X2 = C: Time
Actual Factor
B: Temperature = 101.69
Yield of Ethanol
C: Time
A: Acid Concentration
Prediction 48.0159
45.3578
42.2312
39.1047
39.1047
35.9781
35.9781
25.00
20.00
15.00
10.00
5.00
0.50
0.63
0.75
0.88
1.00

(b)

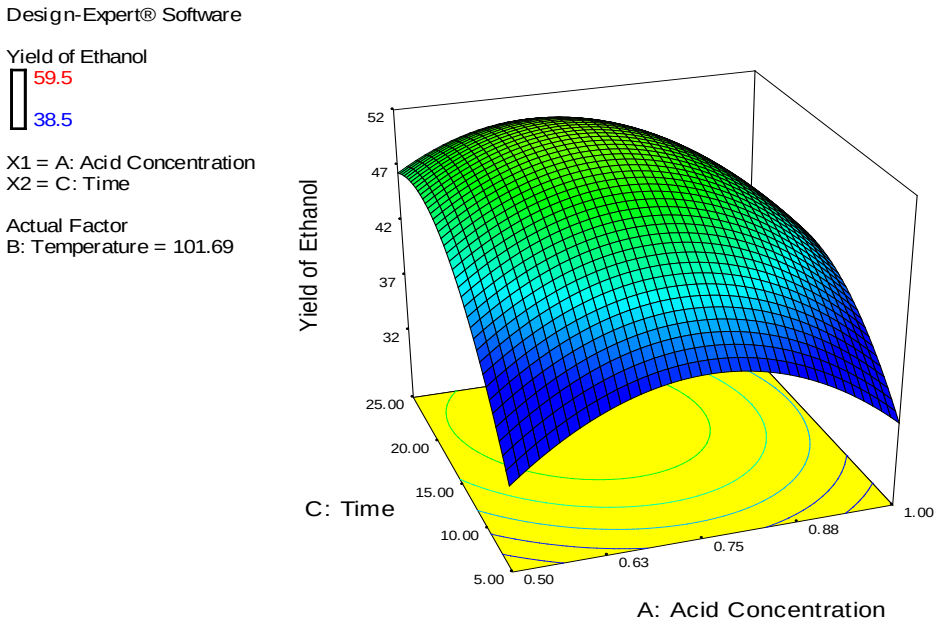


(c)

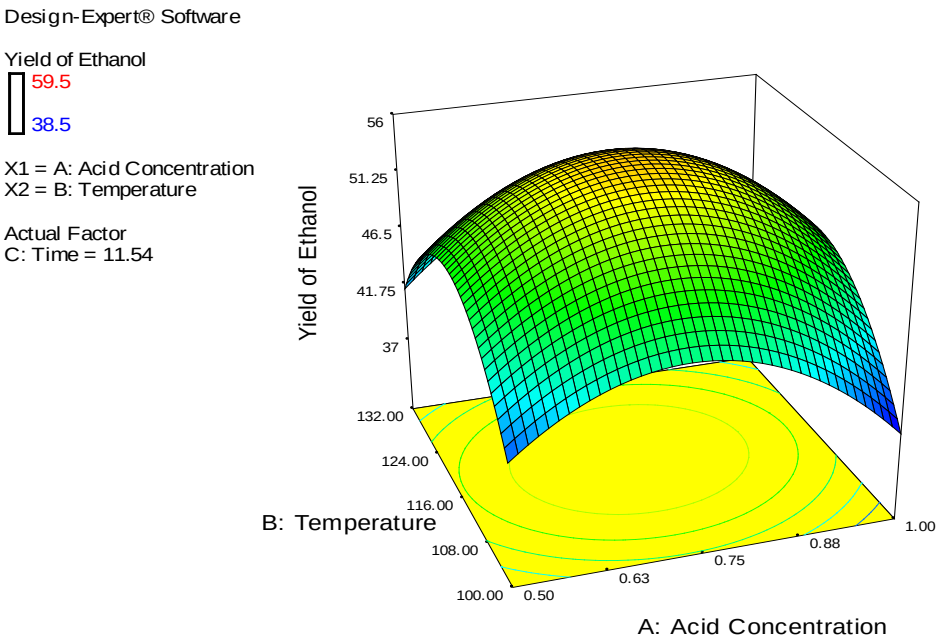
Figure 4.7 (a), (b) and (c) optimization of contours plot in ethanol yield



(a)



(b)



(c)

Figure 4.8 (a), (b) and (c) surfaces plot of possible optimum solutions

4.4. Validation of the model

According to the two-level factorial design result using Design-Expert® 7 software, an experiment with hydrolysis acidic concentration, temperature and time were conducted in order to study the outcome or effect of the factorial design. The experiment was carried out at the optimized conditions. As you see from figure 4.7 and 4.8 (a), (b) and (c) above, ethanol yield of average predicted value was 48.02%. As a result, the model was considered to be accurate and reliable for predicting the yield of ethanol from fruit peel using dilute acid hydrolysis. Based on the second-order models, numerical optimization was carried out to maximize the yield of ethanol, using the response optimizer in Design expert®7. The optimal values of test variables were calculated as 11.54 min, 101.69 °C and 0.74% v/v acid concentration. The analyses show that the average yields of ethanol is 48%.

Chapter Five

Material and Energy Balance

Material quantities, as they pass through processing operations, can be described by material balances. Such balances are statements on the conservation of mass. Similarly, energy quantities can be described by energy balances, which are statements on the conservation of energy. If there is no accumulation, what goes into a process must come out. This is true for batch operation. It is equally true for continuous operation over any chosen time interval.

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) = $\frac{total\ \ capacity}{24*300}$ = $\frac{3*10^6\ lit}{\frac{24hr}{day}*300\,day}$ = 416.67 lit/hr = 110.23gal/hr

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

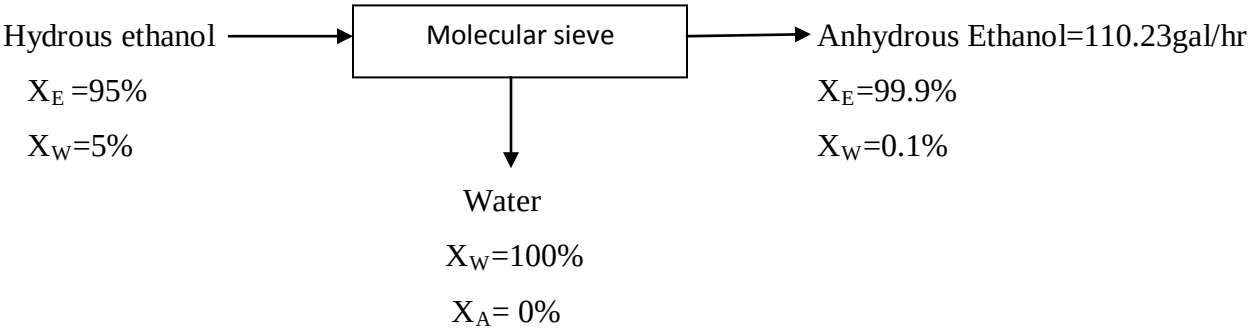
$$= 6.61\frac{lb}{gal}*110.23\frac{gal}{hr} = 728.6203\frac{lb}{hr}$$

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

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

Material balance for Molecular sieve

It is the equipment which following the distillation column and bring the ethanol concentration from 95% to 99.9%.



Where X_E= Percentage of Ethanol

X_W= Percentage of water

Hydrous ethanols (gal/hr) enter into sieve = $\frac{Anhydrous\ \ Ethanol}{(1-hydrous\ \ ethanol\ \ fraction\ )}$

$$= \frac{110.23\ gal/hr}{(1-0.05)} = 116.03\text{gal/hr} = 347.9\frac{kg}{hr} = 2504.88\frac{ton}{yr}$$

The water that is trapped by the molecular sieve is

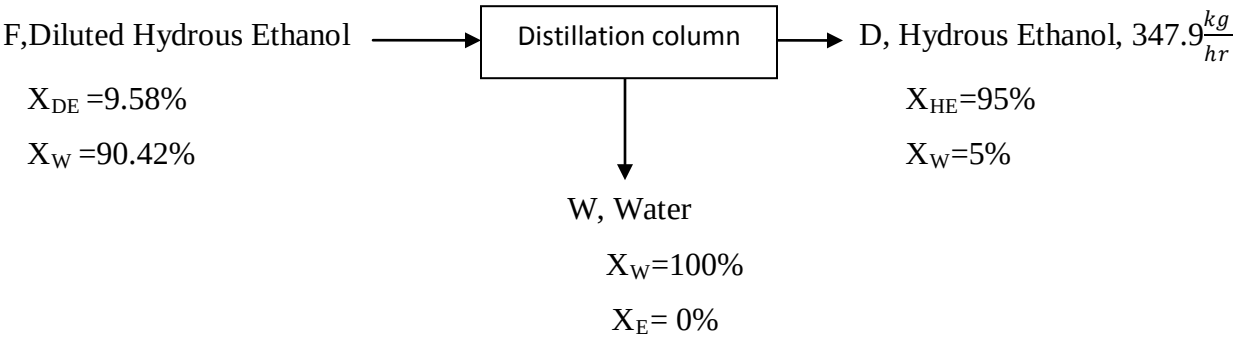
Mass flow rate of hydrous ethanol = Mass flow rate of water leave sieve + Mass flow rate of anhydrous ethanol leave the sieve

$$M_{HE} = M_W + M_{AE}$$

$$M_W = M_{HE} - M_{AE} = 347.9\text{-}330.5 = 17.4\frac{kg}{hr} = 125.28\frac{ton}{yr}$$

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 X_{DE} = fraction of diluted hydrous ethanol

X_W = fraction of dilute hydrous ethanol and hydrous ethanol

X_{HE} = fraction of hydrous ethanol

From ethanol component balance

$$F*X_F = W*X_E + D*X_{HE}$$

$$F=\frac{W*X_E + D*X_{HE}}{X_F} = \frac{0 + 347.9*0.95}{0.0958} = 3449.95\frac{kg}{hr} = 24839.64\frac{ton}{yr}$$

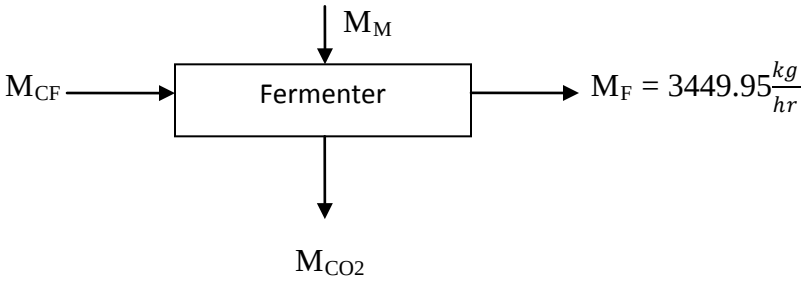
From which,

$$W = F-D$$

$$=3449.95-347.9 = 3102.05\frac{kg}{hr} = 22334.76\frac{ton}{yr}$$

Material Balance for Fermentation

Total material balance in the fermenter



Where M_{CF} = mass of centrifuge (filter) mash

M_M =mass of media

M_{CO2} = mass of co_2 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 I take the value i.e 97% efficiency.

$$\frac{M_{GF}}{180} = \frac{347.9}{2*46}$$

$$M_{GF} = \frac{347.9*180}{88} *0.97 = 660.25\frac{kg}{hr} = 4753.8\frac{ton}{yr}$$

And the amount of carbon dioxide produced is

$$\frac{660.25}{180} = \frac{MCO_2}{88}$$

$$M_{CO2} = \frac{660.25*88}{180} = 322.79\frac{kg}{hr} = 2324.09\frac{ton}{yr} \text{ of } CO_2$$

produced

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

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

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

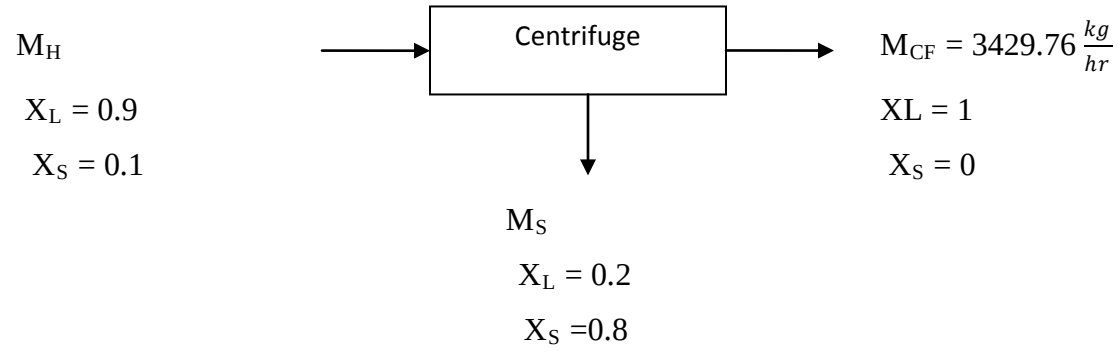
$$1.1\ M_{CF} = 3772.74\frac{kg}{hr}$$

$$M_{CF} = 3429.76\frac{kg}{hr}$$

$$M_M = 342.98\frac{kg}{hr} = 2469.46\frac{ton}{yr}$$

Material Balance for Centrifugal separation

Centrifuge is used for separating insoluble solid from liquid. Moisture content of centrifuge solid is 20%.



Where M_H = mass flow rate of acid treated fluid

M_S = mass flow rate of bottom centrifuge solid

M_{CF} = mass flow rate of the centrifuge fluid.

From the solid component balance

$$M_H X_S = M_S X_S$$

$$M_H*0.1 = M_S X_S$$

From the liquid

$$M_H X_L = M_S X_L + M_{SF} X_L$$

$$M_H*0.9 = M_S *0.2 + 3429.76*1$$

Substitute and solve

$$\frac{MS\ XS * 0.9}{0.1} = M_S*0.2 + 3429.76*1$$

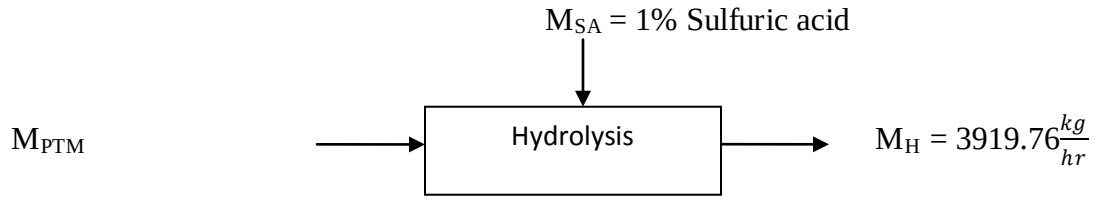
$$\frac{MS*0.8 * 0.9}{0.1} = 0.2M_S + 3429.76$$

$$M_S = 489.97\frac{kg}{hr}$$

$$M_H = \frac{489.97*0.8}{0.1} = 3919.76\frac{kg}{hr} = 28222.27\frac{ton}{yr}$$

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 $\longrightarrow$ 1 mole of glucose for 100% conversion.

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

$$\frac{M_{PTM}}{162} = \frac{3919.76}{180}$$

$$M_{PTM} = \frac{3919.76*162}{180} * 0.95 = 3351.39\frac{kg}{hr} = 24130\frac{ton}{yr}$$

Applying total mass balance

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

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

$$= 3919.76 - 3351.39$$

$$= 568.37\frac{kg}{hr} = 4092.26\frac{ton}{yr} \text{ of 1\% dilute sulfuric acid.}$$

From this component of mass of sulfuric acid

$$= 0.01*568.37$$

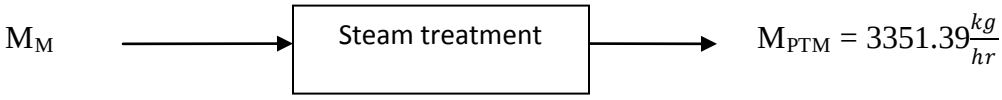
$$= 5.6837\frac{kg}{hr} = 40.92\frac{ton}{yr} \text{ of sulfuric acid}$$

And

$$= 0.99*568.37\frac{kg}{hr} = 562.69\frac{kg}{hr} = 4051.37\frac{ton}{yr} \text{ distilled water}$$

Mass balance for pretreatment

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



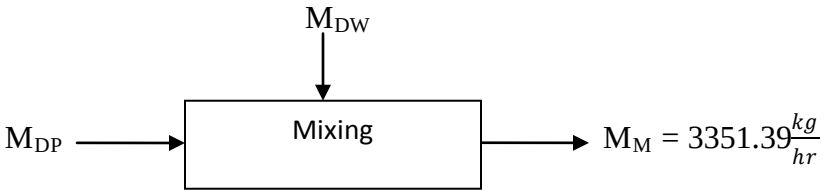
Where M_M =Mass flow rate of mixture

$$M_M = M_{PTM}$$

$$M_M = 3351.39\frac{kg}{hr} = 24130\frac{ton}{yr}$$

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

$$M_{in} = M_{out}$$

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

$$M_{DP} + 10M_{DP} = 3351.39\frac{kg}{hr}$$

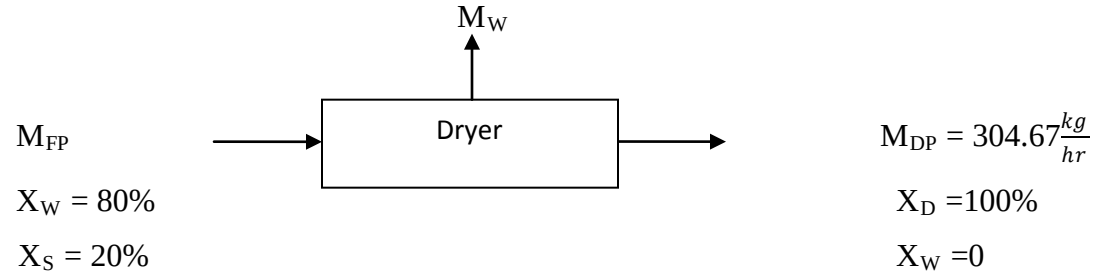
$$11M_{DP} = 3351.39\frac{kg}{hr}$$

$$M_{DP} = \frac{3351.39\frac{kg}{hr}}{11} = 304.67\frac{kg}{hr} = 2193.62\frac{ton}{yr}$$

$$M_{DW} = 10*304.67\frac{kg}{hr} = 3046.72\frac{kg}{hr} = 21936.38\frac{ton}{yr}$$

Material balance for dryer

It is used to dry the wet fruit peel i.e. to make agreeable for easily crushing.



Where M_{FP} = mass flow rate of wet fruit peel

X_W = fraction of distilled water in fruit peel

X_S = fraction of solid in fruit peel

M_{DP} = mass flow rate of dry fruit peel

X_D = fraction of dry fruit peel

Component mass balance for fruit peels

$$M_{FP}\ X_S = M_{DP}\ X_D$$

$$M_{FP} = \frac{304.67*1}{0.2} = 1523.35\frac{kg}{hr} = 10968.12\frac{ton}{yr}$$

From over all material balance

$$M_{FP} = M_W + M_{DP}$$

$$M_W = 1523.35\frac{kg}{hr} - 304.67\frac{kg}{hr} = 1218.68\frac{kg}{hr} = 8774.5\frac{ton}{yr}$$

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.

Basis one operation hours

Energy balance for dryer

The dryer is dried the sample by 105^0c from 20^0c

$T = 20^0c$ → Dryer → $T = 105^0c$

The energy required is

$$Q = m\ Cp\ \Delta T$$

Where m =mass of wet fruit peel

Cp = specific heat of wet fruit peel

$\Delta T = T_f - T_i$

Mass of fruit peel from material balance = $1523.35\frac{kg}{hr}$

$$Cp = C_{pf} * X_f + C_{pf} * X_w$$

$$= 3.90*0.2 + 4.18*0.8 = 4.124\frac{kJ}{kg.k}$$

$$Q = m\ Cp\ \Delta T$$

$$= 1523.35\frac{kg}{hr} * 4.124\frac{kJ}{kg.k} * (105\text{-}20)^0k$$

$$= 533995.109\frac{kJ}{hr}$$

Energy Balance for Mixing

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

$M_{DW} = 3046.72\ \frac{kg}{hr}$

$T = 25^0c$, $M_{DP} = 304.67\frac{kg}{hr}$ → Mixing → $T = 121^0c$, $M_M = 3351.39\ \frac{kg}{hr}$

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

The heat required for mixing is

$$Q = M_M\ Cp\ \Delta T$$

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

$$= 69625.117\frac{kJ}{hr}$$

Energy balance on steam treatment

It is the energy used for pretreatment.

$T = 25^0c$ → Steam treatment → $T = 121^0c$

The heat required for steam pretreatment is

$$Q = m\ Cp\ \Delta T$$

Where m = mass of fruit peel

Cp = specific heat of wetted fruit peel

$\Delta T = T_f - T_i$

$$Q = m\ Cp\ \Delta T$$

$$= 3351.39\ \frac{kg}{hr} * 4.124 * (121\text{-}25)\ ^0k$$

$$= 1326828.707\frac{kJ}{hr}$$

Steam consumption

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

$$M_S = \frac{Q}{Cp\ \Delta T + hfw}$$

$$= \frac{1326828.707}{4.124*(121-25)+2256.9} = 500.16kg$$

Energy balance for Hydrolysis

It is the energy used for hydrolyse cellusose to glucose

$M_{SA\text{-}W} = 568.37\ \frac{kg}{hr}$

$T = 25^0c$ → Hydrolysis → $T = 132^0c$

$M_{PTM} = 3351.39\frac{kg}{hr}$ $\qquad$ $M_H = 3919.76\ \frac{kg}{hr}$

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

The heat required for hydrolysis is

$$Q = M_H\ Cp\ \Delta T$$

$$= 3919.76 * 4.13 * (132 - 25)$$

$$= 1732181.142 \frac{kJ}{hr}$$

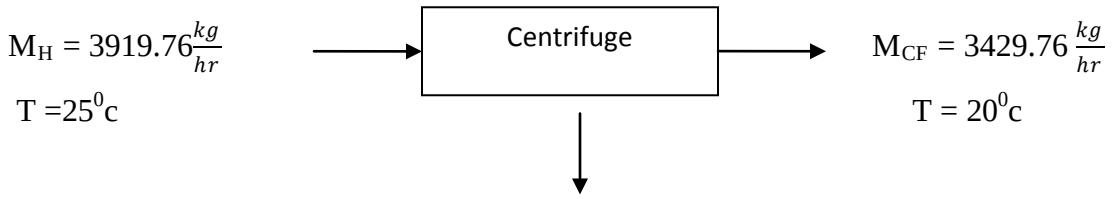
Steam consumption

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

$$M_S = \frac{Q}{Cp \, \Delta T + hfw}$$

$$= \frac{1732181.142}{4.13 * (132 - 25) + 2256.9} = 641.83kg$$

Energy balance for centrifugal separation



$$M_S = 489.97 \frac{kg}{hr}$$

$$T = 20^0 c$$

$$C_{PS} = \frac{489.97 * 0.8 * 4.124 + 489.97 * 0.2 * 4.18}{489.97} = 4.135 \frac{kJ}{kg.k}$$

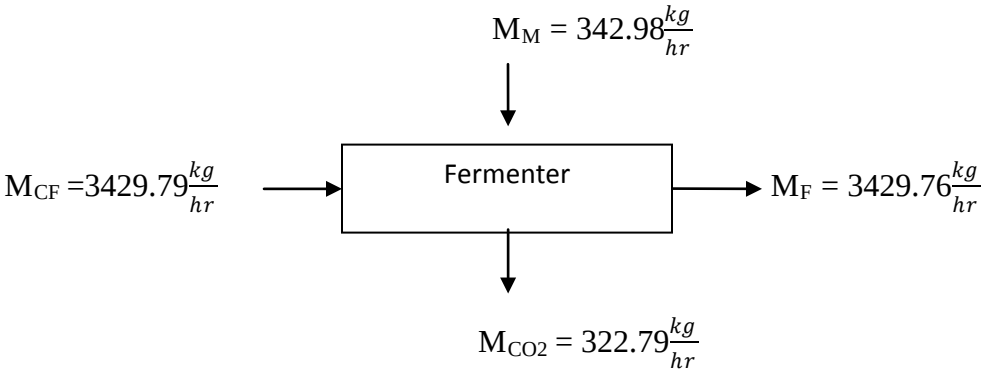
Heat released during the separation can be computed as

$$Q = M_S \, Cp \, \Delta T + M_{CF} \, Cp \, \Delta T$$

$$= 489.97 * 4.135 * (25-20) + 3429.76 * 4.18 * (25-20)$$

$$= 81812.11 \frac{kJ}{hr}$$

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 = $4.142\frac{kJ}{kg.k}$

Cp of CO_2 at 30^0C = $0.846\frac{kJ}{kg.k}$

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

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

$$Q = M_{MIX}\, Cp_{MIX}\, \Delta T - M_{CO2}\, Cp_{CO2}\, \Delta T - M_F\, C_{PF}\, \Delta T$$

$$C_{PF} = C_{PMIX}\, X_{MIX} + C_{PCO2}\, X_{CO2}$$

$$X_{CO2} = \frac{322.79}{3429.76+342.98} = 0.086$$

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

$$C_{PF} = 4.142*0.914 + 0.846*0.086$$

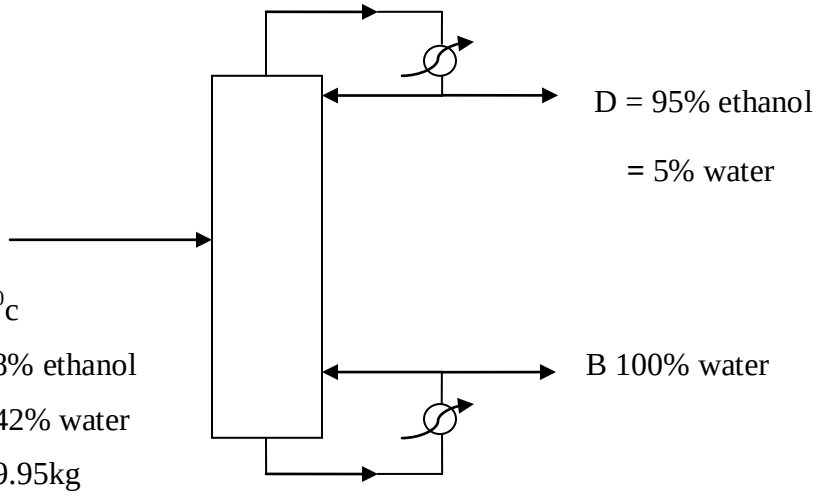
$$= 3.86\frac{kJ}{kg.k}$$

$$Q = M_{MIX}\, Cp_{MIX}\, \Delta T - M_{CO2}\, Cp_{CO2}\, \Delta T - M_F\, C_{PF}\, \Delta T$$

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

$$= 61104.05kJ$$

Energy balance on distillation column



From ethanol component balance

$$FX_F = DX_D$$

$$3449.95*0.0958 = D*0.95$$

$$D = \frac{3449.95*0.0958}{0.95} = 347.9\frac{kg}{hr}$$

$$W = F - D$$

$$= 3449.95 - 347.9$$

$$= 3102.05\frac{kg}{hr}$$

Energy balance

Basis 25^0c, 1hr

Heat capacity on top

$$\text{Cp, distillate} = 0.95*2.72 + 0.05*4.18 = 2.793\frac{kJ}{kg.k}$$

Heat capacity on bottom

$$\text{Cp water} = 4.18\frac{kJ}{kg}$$

Balance around the main condenser

$$\text{Reflux ratio, R} = 2.5$$

$$R = \frac{L}{D} = 2.5$$

$$L = 2.5*D$$

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

$$V = L + D$$

$$= 869.75 + 347.9$$

$$= 1217.65\frac{kg}{hr}$$

From vapor equilibrium data

$$\text{Boiling point of 95\% alcohol} = 78.13^0\text{C}$$

At steady state

$$\text{Input} = \text{Out put}$$

$$H_F = H_D + H_L + Q_C$$

$$Q_C = H_F - H_D - H_L$$

Assuming complete condensation

$$\text{Enthalpy of Vapor} = \text{Latent} + \text{Sensible heat}$$

$$H_V = m_v\lambda_v + m_v c_p \Delta T$$

$$= 1217.65*789 + 1217.65*2.72*(78.13 - 25)$$

$$= 1136692.835\frac{kJ}{hr}$$

Q_B = is determined from a balance over complete system.

$$\text{Input} = \text{Out put}$$

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

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

Heat capacity of feed

$$H_F = m_F.Cp.\ \Delta T$$

$$= 3449.95*4.04*(35 - 25)$$

$$= 139377.98\frac{kJ}{hr}$$

Heat capacity of bottom

$$H_W = m_W.Cp.\ \Delta T$$

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

$$= 972492.675\frac{kJ}{hr}$$

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

$$= 1136692.835 + 0 + 972492.675 – 139377.98$$

$$= 1969807.53\frac{kJ}{hr}$$

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

λ_v = 2174KJ/kg

Steam required

$$M_S = \frac{Q_B}{\lambda_s} = \frac{1969807.53\frac{kJ}{hr}}{2174\,\text{KJ/kg}} = 906.1\frac{kg}{hr}$$

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

$$Q_C = m_W C_P \Delta T$$

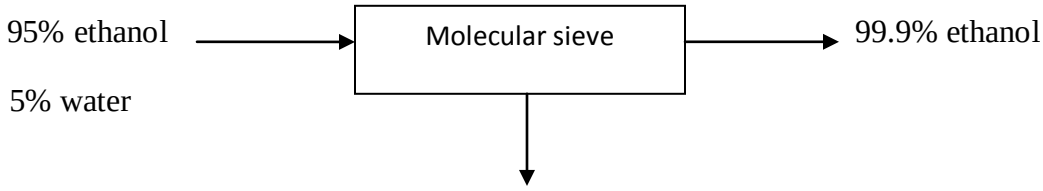
$$m_W = \frac{Q_c}{C_p\ \Delta T}$$

$$= \frac{1136692.835}{4.18*30}$$

$$= 9064.54\frac{kg}{hr}$$

Energy balance for molecular sieve

Adsorption takes place at 95%



$$Cp = CpetXet + CpwXw$$

$$= 2.72*0.95+4.18*0.05$$

$$= 2.79\frac{kg}{kgk}$$

$$Q = mCp\Delta T$$

$$= 330.5*2.79*(95-20)$$

$$= 69157.13\frac{kJ}{hr}$$

Chapter Six

Specification and Design of Major Process Equipment

Storage tank and pumps

Basis one hour

Storage tanks for dried fruit peel

Solid to be handled	dried fruit peel
Density of solids	$1030\frac{kg}{m^3}$
Temperature of solids	25^0C
Materials of construction	carbon settle

Capacity

$$\varrho = \frac{m}{v}$$

$$v = \frac{m}{\varrho} = \frac{304.67kg/hr}{1030\frac{kg}{m^3}} = 0.2958m^3 = 0.3m^3$$

Required storage volume

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

Storage tank for pretreatment

Slurry to be handled	mixture of water and fruit peel powder
Density of slurry	$1015\frac{kg}{m^3}$
Temperature of slurry	25^0C
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

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

Storage tank for hydrolyzed

Slurry to be handled	slurry of fruit peel and water mixture
Density of liquid	$1015\frac{kg}{m^3}$
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

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

Storage tank for Fermentation

Liquid to be handled	water and treated fruit peel mixture
Density of liquid	$1015\frac{kg}{m^3}$
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

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

Storage tank for Ethanol

Liquid to be handled	Ethanol
Density of liquid	$790\frac{kg}{m^3}$
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

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

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 = $1003\frac{kg}{m^3}$
Temperature of liquid	25^0C
Materials of construction	carbon steel

Capacity

$$v = \frac{m}{\varrho} = \frac{3351.39 kg/hr}{1003\frac{kg}{m^3}} = 3.3414 m^3 = 3.35\ m^3$$

Required storage volume

$$V_r = \frac{v}{0.75} = \frac{3.35\ m^3}{0.75} = 4.47 m^3$$

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	$1003\frac{kg}{m^3}$
Temperature of liquid	25^0C
Materials of construction	carbon steel
Capacity	$3.35 m^3$/hr

Pump for delivering from pretreatment storage

Type	centrifugal pump
Operating condition	
Head	4m
Slurry to be handled	mixture of water and fruit peel powder
Density	$1003\frac{kg}{m^3}$
Temperature	25^0C
Materials of construction	carbon steel
Capacity	$3.3 m^3/hr$

Pump for delivering from dilute acid treated tank

Type	centrifugal pump

Operating condition

Head	4m
Liquid to be handled	slurry of water and fruit peel powder
Density	$1003\frac{kg}{m^3}$
Temperature of liquid	25^0C
Capacity	$3.87m^3/hr$

Pump for delivery from fermented tank

Type centrifugal pump

Operation condition

Head	4m
Liquid to be handled	filter of water and peel powder
Density	$1000\frac{kg}{m^3}$
Temperature	25^0C
Capacity	$3.4m^3/hr$

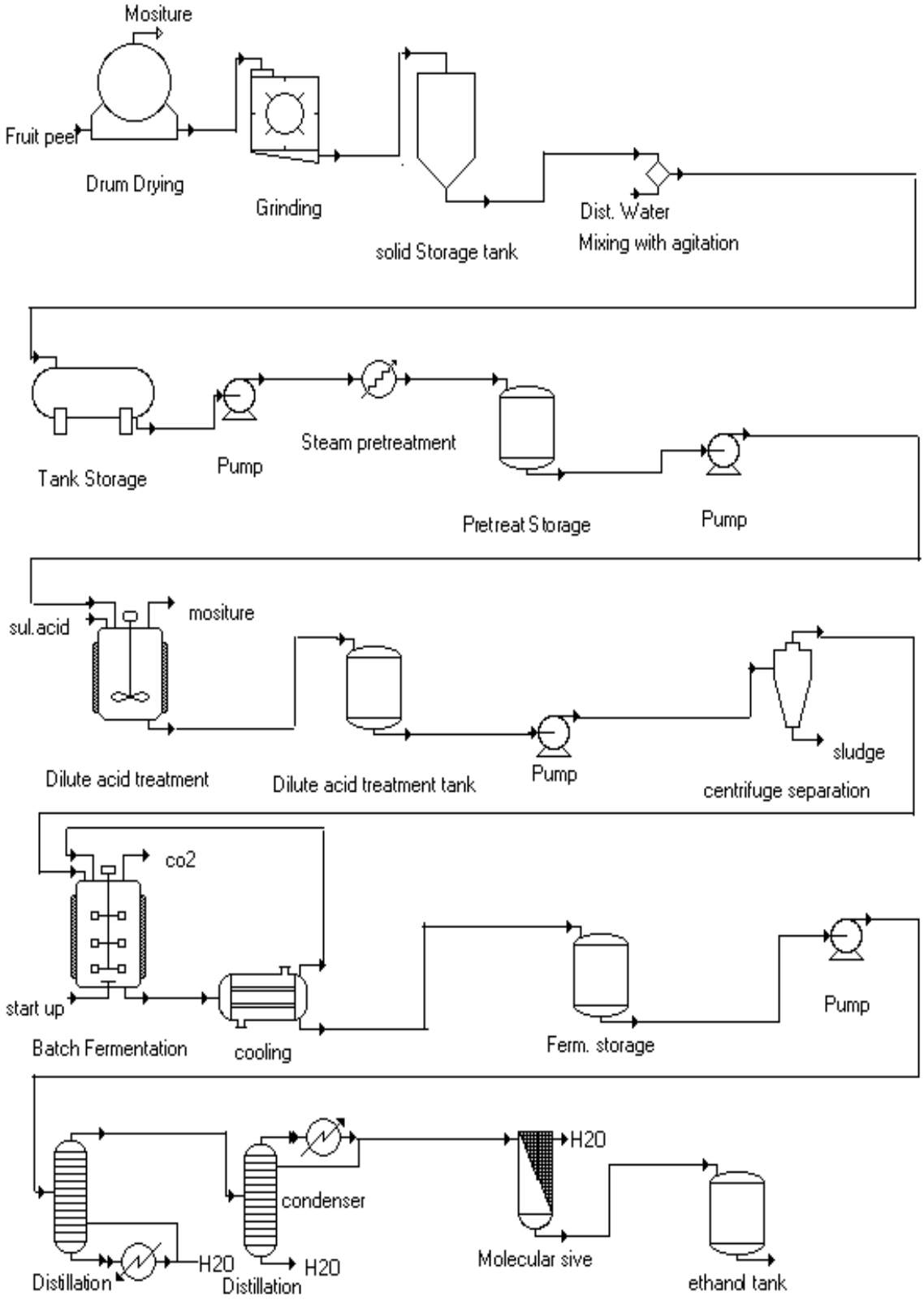


Figure 6.1 Process flow sheet for ethanol production from fruit peel waste (super pro design)

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

= 2*12 + 5 + 16 +1

= 46gm/mol

Molecular weight of water = H_2O

= 2 + 16

= 18gm/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

= 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

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

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

= $25319.09\frac{kcal}{kJmol}$

Boiling point (average) of feed

= $\Sigma X_i T_i$

= 0.0398*308 + (1- 0.0398)*308 = 332.52k = 59.5^0C

Heat capacity of feed

C_{PF} = 4.04kJ/kg.k

= 4.04kJ/kg.k*0.23$\frac{kg}{kmol}$

= 0.9292$\frac{kcal}{kg.k}$

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

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

= 1.0013kJ/kg.k

Intercept on y-axis

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

Vapor equation data of ethanol water solution given below

Table 6.1 VLE data for ethanol water solution

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

X(liq.)	0.3965	0.5079	0.5198	0.5732	0.6763	0.7472	0.8943
Y (vap.)	0.6122	0.6564	0.6599	0.6841	0.7385	0.7815	0.8943

Feed in cold liquid

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

$X_F = 0.0398$, $X_D = 0.8813$, $X_B = 0$

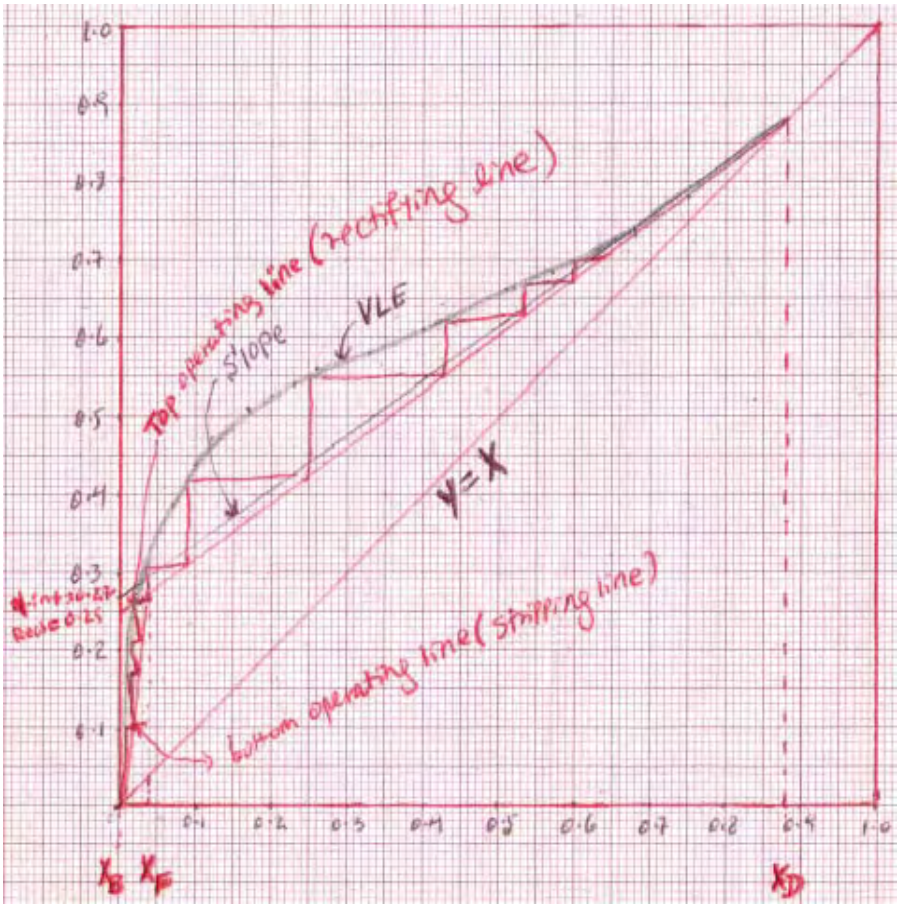


Figure 6.2 McCabe-Thiele diagrams to determine number of stage

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 85^0C (358k), assumed

Assuming ideal gas behavior

$V = \frac{nRT}{p}$, where n is taken the vapor load at V = L+D =1217.65kg/hr

$V = \frac{1217.65*0.95}{46} + \frac{1217.65*0.05}{18} = 28.53$kmol/hr

R= 0.082atm.m^3/kmol.k

P= 0.4atm

$V = \frac{\frac{28.53\text{kmol}}{\text{hr}}*0.082*358}{0.4} = 2093.82 m^3/hr$

Cross sectional area

$A_S = \frac{V}{linear\ \ velocity} = \frac{\frac{2093.82 \text{m}3}{\text{hr}}}{\frac{0.75m}{s}*\frac{3600\,s}{hr}} = 0.78m^2$

Diameter at the top

$D = \sqrt{\frac{4A}{\Pi}} = \sqrt{\frac{4*0.78}{\Pi}} = 0.997$m

Bottom diameter of column

Temperature of the bottom is 100^0C (373k)

$V = \frac{nRT}{p}$, where $n = \frac{m_B}{18} = \frac{3102.05}{18} = 172.34$

R= 0.082atm.m^3/kmol.k

P = 0.4atm

T = 373k

$V = \frac{172.34*0.082*373}{0.4} = 13177.98\frac{m^3}{hr}$

Cross sectional area

$A = \frac{V}{linear\ \ velocity} = \frac{13177.98\frac{m^3}{hr}}{0.75*3600} = 4.88m^2$

$D = \sqrt{\frac{4A}{\Pi}} = \sqrt{\frac{4*4.88}{\Pi}} = 2.49$m

Area of down flow

The weir length is assumed 0.77D = 0.77*2.49 = 1.9173m

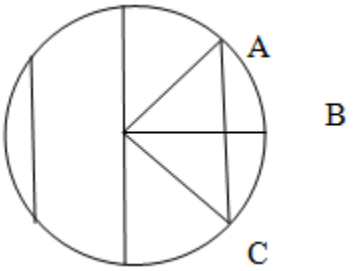


Figure 6.3 plate diagram showing weir length and down flow section plate design trial

Here, a = 0.5*weir length

= 0.5*1.9173

= 0.95865m

Down flow area = area OABC – area OAC

The angle subtended by the down flow area = 180*0.95865 =172^0

Area of OABC = $\frac{172}{360}$* $\frac{\prod D^2}{4}$ = $0.375D^2$

Area of OAC = ½ *0.77D*D/2 cos ($\frac{172}{2}$) = $0.0134D^2$

Down flow area = $0.375D^2$ - $0.0134D^2$ = $0.3616D^2$

=$2.24m^2$

Plate Design

Provision Column diameter, D_0 = 1m

Column area, $A_L = 0.98m^2$

Down flow area, $A_d = 0.24m^2$

Net area, $A_n = A_L - A_d$

$= 0.98-0.24$

$= 0.74m^2$

Active area, $A_a = A_L-2\ A_d$

$= 0.98-2*0.24$

$= 0.5\ m^2$

Hole area, A_h taken 10% of A_a, trial

$A_h = 0.1*0.5 = 0.05m^2$

Weir length = 0.77m

Take: weir height = 50mm

Hole diameter = 5mm

Plate thickness = 5mm

Molecular weight of feed = % of ethanol*M.wt of ethanol + % of water*M.wt of water

$= 0.0958*46 + 0.9042*18$

$= 20.6824$

Feed = $\frac{3449.95}{20.6824} = 166.81\frac{kmol}{hr}$

A mass balance of ethanol gives

Top product, D = $166.81*\frac{0.0958}{0.95} = 16.82\frac{kmol}{hr}$

Vapor rate, V = D (1+R) = 16.82 (1+2.5) = $58.87\frac{kmol}{hr}$

An overall mass balance gives

Bottom product, B = 166.81 – 16.82 = $149.99\frac{kmol}{hr}$

Slope of the bottom operating lines

Slope = $\frac{Lm'}{Vm'} = 0.5$

And Vm' = Lm' – B, from which

Vapor flow below feed, Vm' = Lm' – B

$$Vm' = 0.5 - B$$

$$Vm' = \frac{B}{0.5} = \frac{149.99}{0.5} = 299.98\frac{kmol}{hr}$$

$$Lm' = 0.5 * Vm'$$

$$= 0.5 * 299.98 = 149.99\frac{kmol}{hr}$$

Check weeping

Maximum volumetric flow rate

$$= \frac{\frac{149.99 kmol}{hr} * \frac{18 kg}{kmol}}{3600 s * \frac{1hr}{60s} * 0.97988 kg/m3}$$

$$= 0.77\frac{m^3}{s}$$

Maximum liquid rate

$$= \frac{\frac{149.99 kmol}{hr} * \frac{18 kg}{kmol}}{3600 s * \frac{1hr}{60s}}$$

$$= 44.997\frac{kg}{s}$$

Maximum liquid rate at 70% turn down

$$= 44.997\frac{m^3}{s} * 0.7$$

$$= 31.5\frac{kg}{s}$$

Weir liquid crest

The height of the liquid crest over the weir as per the fracis weir formula for the segmental down corner is

Maximum $h_{ow} = 750(\frac{L_w}{\varrho I_L})^{2/3}$

Where L_w = liquid folw rate

I_w = weir length = 0.77m

h_{ow} = weir crest, mm liquid

$= 750(\frac{0.14}{979.88 * 0.77})^{2/3}$ = 2.43mm liquid

Minimum $h_{ow} = 750(\frac{0.098}{979.88 * 0.77})^{2/3}$ = 1.92mm liquid

At minimum rate $h_w + h_{ow}$

= 50+1.92 = 51.92

K_2 = 30.2, from weep point correlation graph (Coulson volume, IV 2005)

The minimum vapor velocity through the holes (weep point)

$$V_h(\min) = \frac{k2-0.9(25.4-dh)}{(\varrho_v)^{1/2}}$$

$$= \frac{30.2-0.9(25.4-5)}{979.88^{1/2}}$$

$$= 0.38\text{m/s}$$

Actual minimum vapor velocity

$$= \frac{minimum\ \ vapor\ \ rate}{A_h}$$

Where, min vapor rate = $\frac{299.98kmol\ /hr*46}{0.72*3600} = 5.32\frac{m^3}{s}$

$$= \frac{5.32*0.7}{0.05m^2}$$

$$= 74.48\text{m/s}$$

So, minimum operating rate will be well above weep point

Plate pressure drop

Maximum vapor velocity through holes

$$V_h = \frac{maximum\ \ volumetric\ \ flow\ rate}{hole\ area} = \frac{0.77}{0.05} = 15.4\text{m/s}$$

The orffice coefficient from the graph showing discharge coefficient of sieve plate (coulson volume IV 2005)

$$\frac{A_h}{h_a} = \frac{0.05}{0.5} = 0.1 = 10\%$$

$$\frac{\text{plate thickness}}{\text{hole diameter}} = \frac{5mm}{5mm} = 1$$

Hence at 1 and 10% from the graph, C_0 = 0.84, orifice coefficient

The pressure drop through the plate is

$$h_d = 51\left(\frac{V_n}{C_0}\right)^2 \frac{\varrho_v}{\varrho_L}$$, density of vapor = 0.95*790 + 0.05*1000 = 800.5kg/m^3

$$= 51\left(\frac{15.4}{0.84}\right)^2 \frac{0.8005}{979.88}$$

$$= 14.0\text{mm}$$

The residual head can be calculated by the simple equation proposed by Hunt eta al (Coulson Vol,IV 2005)

$$h_r = \frac{12.5*10^3}{\varrho_L}$$

$$= \frac{12.5*10^3}{979.88}$$

$$= 12.76\text{mm liquid}$$

Therefore total pressure drop of the plate

$$h_t = h_d + (h_w + h_{ow}) + h_r$$

$$= 14.0+51.92+12.76$$

$$= 78.68\text{mm liquid}$$

Down comer liquid back up

Down comer pressure loss

h_{ap} is the height of the bottom edges of the apron above the plate

$$h_{ap} = h_w\text{-}10 = 50\text{-}10 = 40\text{mm}$$

The clearance area under the down corner given by

$$A_{ap} = h_{ap}*I_w$$

$$= 40\text{mm}*0.77*10^3$$

$$= 0.0308\text{mm}^2\text{, this is less than the down corner area}$$

$$A_d = 0.24\text{m}^2$$

This is less than the down corner area, $A_d = 0.24\text{m}^2$

The main resistance to flow caused by the constriction at the down corner out let i.e the head loss in the down comer is estimated by Cicalese et al (Coulson vol IV,2005)

$$h_{dc} = 166\left(\frac{L_{wd}}{\varrho_L A_{ap}}\right)^2$$

$$= 166\left(\frac{44.997}{979.88*0.0308}\right)^2$$

$$= 369\text{mm}$$

In terms of clear liquid the down comer back up is given by

$$h_b = (h_w + h_{ow}) + h_t + h_{dc}$$

$$= 51.92+78.68+369$$

$$= 4006\text{mm} = 0.4\text{m}$$

Let us checking tray spacing

$$= 0.4 < \frac{1}{2}\text{(plate spacing + weir length)}$$

$$= 0.4 < \frac{1}{2}(h_w + I_w)$$

$= 0.4 < \frac{1}{2}(0.05 + 0.77)$

$= 0.4 < 0.41$, tray spacing is acceptable

Let us check also residence time as per the method proposed by Thomas and Shah (coluson vol IV, 2005).

$$t_r = \frac{A_d * h_{bc} * \varrho_L}{L_{wd}}$$

$$= \frac{0.24 * 0.4 * 979.88}{44} = 3.67\text{sec}$$

The recommendation is greater than 3sec so residence time is satisfactory

Entrainment checking

Vr = maximum volumetric flow rate/net area

$$= \frac{0.77}{0.74} = 1.04\text{m/s}$$

We know that $u_f = k_L \sqrt{\frac{\varrho_L - \varrho_V}{\varrho_V}}$, $k_L = f(F_{LV}$, plate spacing)

Where $F_{LV} = \frac{L_w}{V_w}\sqrt{\frac{\varrho_V}{\varrho_L}}$, and $\frac{L_w}{V_w}$ = slope =1.01

$\varrho_v = 0.8005$ at 135^0C, $\varrho_L = 979.88$ at 135^0C

$$F_{LV} = 1.01\sqrt{\frac{0.8005}{979.88}} = 0.03$$

From the graph showing flood velocity vs sieve plates (coulson vol IV, 2005)

$K_L = 0.09$

$$V_f = 0.09\sqrt{\frac{979.88 - 0.8005}{0.8005}}$$

$= 3.15$m/s

Hence the % flooding is

$$\frac{U_v}{U_f} = \frac{1.04}{3.15} = 0.33 = 33\%$$

From the entrainment correlation graph (Coulson vol IV), the entrainment correlation is

$\Psi = 0.005$, which is well below 0.1

Tray lay out- use cartridge type construction. Allowing 50mm un-perforated strip round plate edge; 50mm wide calming zone.

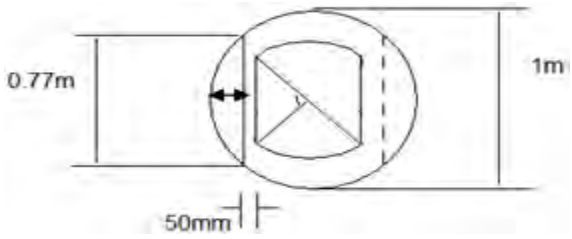


Figure 6.4 Tray layout of plate

Perforated area

From the above figure

$$\frac{L_w}{D_c} = \frac{0.77}{1} = 0.77$$

Calculate, L_h = 1000mm – 770mm – 50mm = 180mm = 0.18m

$\frac{L_w}{D_c} = \frac{0.77}{1} = 0.77$

$\frac{L_h}{D_c} = \frac{0.18}{1} = 0.18$

From the relation between angle subtended by chord, chord height and chord length (Coulson vol IV) the angle is 88^0.

Angle subtended at plate edge by un-perforated strip

$= 180^0 - 88^0 = 92^0$

Mean length of un-perforated edge strip

$= (1 - 50*10^{-3})\ \pi \frac{92}{180} = 1.53m$

$= 1.53m$

Area of un-perforated edge strip

$= 50*10^{-3}*1.53 = 0.0765m^2$

Mean length of calming zone

$= (1 - 50*10^{-3})*\sin\frac{92}{2} = 0.68m$

$= 0.68m$

Area of calming zone

$= 2(0.68*50*10^{-3})$

$= 0.068m^2$

Total area of perforation

A_p = 0.5- 0.0765- 0.068

= 0.3555m^2

Area ratio, $\frac{A_h}{A_p} = \frac{0.05}{0.3555}$ = 0.14

From the hole and pitch relation graph (Coluson vol, 2005, p = 575)

$\frac{I_p}{d_h}$ = f ($\frac{A_h}{A_p}$) = 2.6, satisfactory between 2.5- 4.0

No of holes

Area of one hole = $\frac{\pi * d^2}{4} = \frac{\pi * (5 * 10^{-3})^2}{4}$ = 1.9634*$10^{-5}$$m^2$

Area of all holes, A_h = 10% of active area

= 0.1*0.5 = 0.05

No of holes = $\frac{A_h}{A_{single\ \ hole}} \frac{0.05}{1.9634 * 10^{-5}}$ = 2547holes

Plate spacing:-

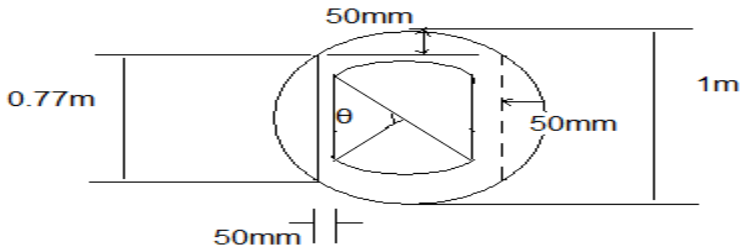


Figure 6.5 Proposed final layout of a plate

Plate no = 1

Turn down = 70%

Plate ID = 1

Plate material = mid steel

Hole size = 5mm

Down comer = material mild steel

Hole pitch = 12.5mm triangle

Plate spacing = 0.5m

Active hole = 2547

Plate thickness = 5mm

Plate pressure drop:-

= 80mm of liquid

= ϱgh

= 979.88*9.81*0.08

= 0.77kpa

Condenser design

The condenser to be used is a horizontal condenser design to condense 247.9kg/hr of distilled ethanol at 25^0C by exchange with water at 20^0C and out let temperature of 30^0C. 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 = $0.0001 m^2\ ^0c/w$

Water = $0.0003\ m^2\ ^0c/w$

The mean temperature of ethanol

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

At this temperature the c_p of ethanol is

$Cp = A + BT$

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

$= 155.24kJ/kmol$

$= 155.24kJ/kmol*kmol/46$

$= 3.375kJ/kg.k$

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

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

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

$t_2 = 21.61^0$C

The mean temperature of water is

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

The specific heat capacity of water remains the same up to 50^0C, thus

= 4.18kJ/kg.k

Table 6.2 Thermodynamic properties for characterizing ethanol and water

Ethanol	**Inlet**	**Mean**	**Outlet**
Temperature,^{0}C	85	57.5	30
Specific ,kJ/kg.k	3.37	3.375	3.9
Density, kg/m^3	790	789	789
Water	**Inlet**	**Mean**	**Outlet**
Temperature,^{0}C	20	23.31	21.61
Specific ,kJ/kg.k	4.18	4.18	4.18
Density, kg/m^3	1000	1000	1000

Over all coefficient

For condenser of this type the overall coefficients will be between 700-1000w/m^2.^{0}C (Coulson vol IV, 2005). So, we start with 700 w/m^2 ^{0}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)

$$F_t = 0.98$$

So ΔT_{lm} =0.98*13.1 = 12.84^{0}c

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)

$= \pi DL$

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

$= 0.2393 m^2$

Number of tubes

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

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

So far 2 passes, the tube per pass is

$= 9/2$

$= 4.5 = 5$ tubes

Tube cross sectional area

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

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

$= 0.00017 m^2$

Area per pass

$= 5*0.00017$

$= 0.00085\ m^2$

Volumetric flow rates

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

Tube side velocity, $V_t = \frac{0.0025}{0.00085} = 2.9 m/s$

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)

$K_1 = 0.249$

$n_1 = 2.207$

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

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

$= 101.53mm$

$= 102mm$

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

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

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

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

From the graph showing the tube side heat transfer factor J_h versus R_e (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

$k_1 = 0.249$

$n_1 = 2.207$

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

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

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

I_B = baffle spacing

$$As = \frac{23.81\ -19.05}{23.81} * 152 * 31$$

$$= 942mm^2$$

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)

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

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

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

$= 0.37$

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

$k_f = 0.6$

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

$h_i = 12977.48$w/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

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

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

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

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

N_p = number of tube side passes.

U_t = 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

Shell side

Shell diameter, Ds = 152mm

Equivalent diameter, De = 13.52mm

Tube length, L = 4m

Baffle spacing, I_B = 942mm

Reynolds number, Re = 979.1

Shell side velocity, Us = 0.11m/s

From the graph showing shell side friction factor versus Reynolds (coulson vol IV, 2005)

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

$\Delta P_t = 8j_f(\frac{D_s}{D_e})(\frac{L}{I_B})\frac{\varrho U_s^2}{2}(\frac{\mu}{\mu_w})^{-m}$, neglect viscosity correction factor

$= 8*1.8*10^{-2}(\frac{152}{13.52})\ (\frac{4}{942*10^{-6}})\ (\frac{800.5*0.11^2}{2})$

$= 33293 N/m^2$

= 0.34bar, satisfactory, since it is below 0.8bar (allowable pressure).

The proposed design

Split ring, floating head, 1sheel pass, 2 tube pass

9tubes, 4m long 19.05mm outside diameter, 14.83mm inside diameter, triangular pitch 23.81mm.

Heat transfer area = 2.393m^2(based on outside diameter)

Shell inside diameter 152mm, baffle spacing = 942mm^2, 25% baffle cut

Tube side coefficient = 12977.48 $w/m^{2\,0}c$

Shell side coefficient =0.003 $w/m^{2\,0}c$

Over all coefficient estimated = 700$w/m^{2\,0}c$

Over all coefficient calculated =15615.24 $w/m^{2\,0}c$

Dirt/fouling factor

Tube (water) = 0.0003 $w/m^{2\,0}c$

Shell side (ethanol water mixture) = 0.0001 $w/m^{2\,0}c$

Pressure drop

Tube side, calculated = 0.8bar,

Shell side, calculated = 0.34bar

Chapter Seven

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, I 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.

7.1. About Cost-Year Indices

For the cost estimation of the equipment of this plant design exchange rate is assumed i.e. 1US Dollar =17.76ET 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 7.1 Marshal and Swift installed equipment index

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

Cost data also obtained from table 9-50 of Perry's chemical engineering hand book (7^{th} edition) and Coulsin volume 6 (4^{th} edition) and equipment cost manipulation is based on Marshall swift index of 1000.

$$\text{New Cost} = \text{Base Costs} * (\text{New size} / \text{Base size})^{n}$$

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

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.

There are as many methodologies for computing the total installed cost of capital equipment as there are textbooks on plant economics. The matter of which method is "correct" is of course open for debate; however, at this level of detail, each methodology is generally considered as good as the next.

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:

$$\text{New Cost} = \text{Base Costs} * (\text{New size} / \text{Base size})^{n}$$

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

The attachment shown below is to show the calculation for present cost of equipments based on the Marshall Swift cost index of 1000.

Attachment 1

-Calculation for estimation of pump cost

-Identification number P101

-Unit power, given = 10hp (Perry chemical engineering hand book)

-Unit power, actual = 0.042

-Exponent, n = 0.3 (Perry chemical engineering hand book)

-Cost in $ = 4000

-Calculation

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

Where

C_2 = cost with capacity S_2

C_1 = cost with capacity S_1

$$C_2 = 4000 * \left(\frac{0.042}{10} \right)^{0.3}$$

C_2 = $ 774.52

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

$$= \$\ 774.52 * \frac{1780}{1000}$$

= $ 1378.65

Likewise estimation of the remaining pumps cost calculated and tabulated below.

Table 7.2 Estimation of equipment cost for fluid pumps

Identification no	Quantity	Exponent	Unit hp	Source	US Dollar	ET Birr
Pump 101	1	0.3	0.042	Perry	1378.65	24484.82
Pump 102	1	0.3	0.026	Perry	1193.91	21203.84
Pump 103	1	0.3	0.084	Perry	1697.32	30144.40
Pump 104	1	0.3	0.02	Perry	1103.54	19598.87
					Total pump cost	95431.93

Attachment 2

Calculation for estimation storage tank cost

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

-Theoretical capacity = 3.8 m^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 7.3 Estimation equipment cost of storage tanks

Equipment Name	quantity	exponent	Actual capacity, m^3	source	US Dollar	ET Birr
Fruit peel powder storage tank	1	0.57	0.4	Perry	2466.54	43805.75
Thank storage for fruit peel powder an dist. water	1	0.57	4.47	Perry	8349.34	148284.28
Pretreatment storage tank	1	0.57	4.4	Perry	8274.56	146956.19
Dilute acid treated tank	1	0.57	5.16	Perry	8582.10	152418.10
Fermented storage tank	1	0.57	4.53	Perry	8413.04	149415.59
Ethanol storage tank	1	0.57	0.56	Perry	2988.00	53066.88
					Total storage tank cost	693946.79

Attachment 3

Table 7.4 Estimation of unit operation equipment cost

Equipment Name	Quantity	Capacity	US Dollar	ET Birr
Drum drying	1	1600kg/hr	5000	88800
Grinding	1	1600kg/hr	2000	35520
Mixer	1	$3m^3$	3000	53280
Steam pretreatment tank	1	$3.5m^3$	6500	115440
Dilute acid treatment tank	1	$4\ m^3$	6500	115440
Centrifugal separation	1	3000-5000rpm	12500	222000
Fermentation tank	1	$3.5m^3$	2500	44400
Heat exchanger	1	$3m^2$	4400	78144
Distillation column	2	$1\ m^3$	6894.95	122454.41
Condenser	2	$2m^2$	8000	142080
Boiler	1	-	7500	133200
Molecular sieve	2	-	6000	106560
Total cost of process equipment				1257318.41

Attachment 4

Once the total equipment cost has been determined in the year of interest, I must add several other direct and indirect costs to determine the total capital investment (TCI). Project contingency and construction activities, and other costs related to construction are computed relative to the total direct cost (TDC) and give the fixed capital investment (FCI) when summed. The sum of FCI and the working capital for the project is the total capital investment (TCI).

Table 7.5 Estimation costs: direct, indirect and total capital investment

Direct cost (DC)	**Factor**	**Cost (ETB)**
Purchased equipment	1	2046697.13
Purchased equipment installation	0.47	961947.65
Instrumentation and control	0.18	368405.48
Piping (installed)	0.66	1350820.12
Electrical(installed)	0.11	225136.68
Building	0.18	368405.48
yard improvement	0.1	204669.71
Service facilities	0.3	614009.14
Land	0.06	122801.83
Total plant direct cost (TPDC) =ΣDC		6262893.22
Indirect cost (IDC)	**Factors**	**Cost (ETB)**
Engineering and supervision	0.33	675410.05
Construction and expense	0.41	839145.82
Indirect cost (IDC) = ΣID		1514555.87
Total indirect and direct cost (TIDC) = TPDC + IDC		7777449.09
Contractors fee (CF)	0.21	429806.4
Contingency (C)	0.40	818678.85
Fixed capital investment (FCI) = TIDC + CF + C		9025934.34
Working capital (WC)	0.86	1760159.53
Total capital investment (TCI) = FCI + WC		10786093.87

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 7.6 direct production cost (variable cost)

Item			Cost (ETH Birr)
Raw materials		0.5Birr/kg*10968120kg	5484060
1	Operating labor(L)	84*1200*12	1209600
2	Direct supervisors and clerical labor	0.1L	120960
3	Utilities(electric & water cost)	217573 + 18901	236474
4	Maintenance and repair	0.06FCI	541556.06
5	Operating supplies	0.01FCI	90259.34
6	Laboratory changes	Not Applicable	
7	Patent and royalties	Not Applicable	
Total direct production cost = 7682906.4			

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 7.7 Fixed operating costs

S. No	Items		Cost (ETH Birr)
1	Depreciation	0.1FCI	902593.43
2	Local taxes	0.02FCI	180518.69
3	Insurance	0.005FCI	45129.67
4	Rent	0.08(land + building)	39296.58
		Total fixed charges	1167538.37

Table 7.8 Plant over head cost

S. No	Item		Cost (ETH Birr)
1	Plant over head cost	2*8000*12	192000

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

= 7682906.4 + 1167538.37+ 192000

= 9042444.77

Table 7.9 General expense

S. No	Item		Cost(ETH Birr)
1	Administrative cost	0.5L = 0.5*1209600	604800
2	Distribution and sell cost	0.2L = 0.2*1209600	241920
3	Research and development		Not Applicable
4	Financing interest (self finance)		Not Applicable
	Total general expense		846720

Total production cost = manufacturing cost + general expense

= 9042444.77 + 846720

= 9889164.77

TPC = 9889164.77

Hence, Total production cost = 9889164.77Birr

Variable cost = 7682906.4Birr

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

= 264944.94 + 192000

= 456944.94Birr

Depreciation cost = 902593.43Birr

General expense = 846720

7.5. Economic evaluation

7.5.1. Net income, Payback time and return on investment

Gross earn cost

Current price of 99.9% ethanol = 8-12Birr/lit based on current price set by Sugar Corporation Agency. So I took 6 Birr/lit.

-Annual revenue = 6*3000000

= 18000000Birr

-Total production cost = 9889164.77Birr

-Gross annual profit = 18000000 - 9889164.77Birr

= 8110835.23Birr

-Income tax on gross profit (30%) = 0.3*8110835.23

= 2433250.57Birr

-Net income = 8110835.23- 2433250.57

= 5677584.66Birr

-Percent profit

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

$$= \frac{5677584\ .66}{9889164\ .77}$$

$$= 0.5741$$

$$= 57.41\%$$

Percent rate of return

-Net income = 5677584.66

-Total capital investment = 10786093.87

-Rate of return, % ROR = $\frac{Net\ income}{TCI}$

$= \frac{5677584.66}{10786093.87}$

$= 0.5264$

$= 52.64\%$

Payback period

-Project life is assumed 10 years and we use straight line method

-Depreciation = $\frac{FCI}{10} = \frac{9025934.34}{10} = 902593.43$

-Payback period = $\frac{FCI}{profit + depreciation} = \frac{9025934.34}{5677584.66 + 902593.43} = 1.37$years

So, the payback period of the project is estimated to be 2years

7.6. Discounted Cash Flow Return (DCFR)

The discount flow rate of return is the return obtained from an investment in which all investment and cash flows are discounted. It is determined by setting the NPW equation equal to zero and solving for the discount rate that satisfies relation (Timerhouse, 2007). I calculate the discounted rate of return or DCFR of the project and values at individual years, considering the plant capacity starting with 75% capacity at the first year and 90% capacity in the second year and with 100% capacity the remaining project life. Detail manipulation of the first three year is shown below:-

First year

-Percent rate of operating time = 75%

-Product rate = 75%*annual production = $0.75*3*10^6 = 2.25*10^6$

-Variable cost = 75%*variable cost = 0.75*7682906.4= 5762179.8

-Fixed cost = fixed charges (except depreciation) + plant over head cost = 456944.94

-General expense = 846720

-Depreciation = 0.05*FCL (as pre MACRS depreciation rate)

= 0.05*902593.43 = 45129.67

-Total product cost = Variable cost + Fixed cost + General expense

= 5762179.8+ 456944.94+ 846720

= 7065844.74

-Annual Sale = Price per liter * Annual product = $6*2.25*10^6$ = 13500000

-Gross profit = Annual sale – Total product cost

= 13500000 - 7065844.74

= 6434155.26

-Net income = Growth profit – Income tax

= 6434155.26– (0.3*6434155.26)

= 4503908.68

-Cash flow = Net income + Depreciation

= 4503908.68+ 45129.67

= 4549038.35

-IRR = 0.6

-Discount factor = $(1 + IRR)^{-n}$

= $(1 + 0.6)^{-1}$

= 0.63

-Present Value = Cash flow *Discount factor

= 4549038.35*0.63

= 2865894.16

Second year

-Percent rate of operating time = 90%

-Product rate = 0.9* annual production = $0.9*3*10^6$ = 2700000

-Variable cost = 0.9* variable cost = 0.9*7682906.4= 6914615.76

-Fixed cost = fixed charges (except depreciation) + plant over head cost = 456944.94

-General expense = 846720

-Depreciation = 0.095*FCL (as pre MACRS depreciation rate)

= 0.095*902593.43

= 85746.38

-Total product cost = Variable cost + Fixed cost + General expense

= 6914615.76+ 456944.94+ 846720= 8218280.7

-Annual Sale = Price per liter * Annual product = 6*2700000 = 16200000

-Gross profit = Annual sale – Total product cost

= 16200000 - 8218280.7

= 7981719.3

-Net income = Growth profit – Income tax

= 7981719.3– (0.3*7981719.3)

= 5587203.51

-Cash flow = Net income + Depreciation

= 5587203.51 + 85746.38

= 5672949.89

-IRR = 0.6

-Discount factor = $(1 + IRR)^{-n}$

= $(1+0.6)^{-2}$

= 0.39

-Present Value = Cash flow *Discount factor

= 5672949.89*0.39

= 2212450.46

Third year

-Percent rate of operating time = 100%

-Product rate = $3*10^6$

-Variable cost = 7682906.4

-Fixed cost = 456944.94

-General expense = 846720

-Depreciation = 0.09*FCL (as pre MACRS depreciation rate)

= 0.09*902593.43

= 81233.41

-Total product cost = 8986571.34

-Annual Sale = $6*3*10^6$ = 18000000

-Gross profit = Annual sale – Total product cost

= 18000000 - 8986571.34

= 9013428.66

-Net income = Growth profit – Income tax

= 9013428.66– (0.3*9013428.66)

= 6309400.06

-Cash flow = Net income + Depreciation

= 6309400.06 + 81233.41

= 6390633.47

-IRR = 0.6

-Discount factor = $(1 + IRR)^{-n}$

= $(1+0.6)^{-3}$

= 0.24

-Present Value = Cash flow *Discount factor

= 6390633.47*0.24

= 1533752.03

For the remaining periods of the project life, summary of economic data is given in the following table

Table 7.10 Summary of economic data used in the DCFR profitability analysis

Year	Product rate (%)	Sales revenue, SR (10^6/yr)	Total product cost, TPC ($/yr)	SR – TPC ($/yr)	Depreciation
1	0.75	13.5	7065844.74	6434155.26	45129.67
2	0.9	16.2	8218280.7	7981719.3	85746.38
3	1.0	18	8986571.34	9013428.66	81233.41
4	1.0	18	8986571.34	9013428.66	76720.44
5	1.0	18	8986571.34	9013428.66	72207.47
6	1.0	18	8986571.34	9013428.66	67694.51
7	1.0	18	8986571.34	9013428.66	67694.51
8	1.0	18	8986571.34	9013428.66	67694.51
9	1.0	18	8986571.34	9013428.66	67694.51
10	1.0	18	8986571.34	9013428.66	67694.51
Sum	9.65	173.7	87176696.16	86523303.84	699509.92

Thus,

$$0 = -TCI + 0.7\Sigma (S_j - C_{oj} - d_i) (1 + i)^{-j} + \Sigma d_j (1+i)^{-j}$$

Where

TCI = total capital investment

S_j = the values of sales in year j

C_{oj} = the total product cost not including depreciation

d_i = depreciation in year j as per the MACRS factor for 10years

$$0 = -TCI + 0.7\Sigma (S_j - C_{oj} - d_i) (1 + i)^{-j} + \Sigma d_j (1+i)^{-j}$$

$$0 = -10786093.87+0.7(173.7*10^6 -87176696.16 - 699509.92) (1 + i)^{-10} + 699509.92(1+i)^{-10}$$

$$10786093.87 = 60076655.74(1 + i)^{-10} + 699509.92(1+i)^{-10}$$

$$10786093.87 = 60776165.66(1+i)^{-10}$$

$$I = 0.19$$

Therefore at I = 0.19 the sum will be 0 with several iterations as shown in the table above. This value is accepted as per the suggested values for risk and minimum acceptable return in investment for investment types in which everything new and an investment seeking high marketing effort (Timmerhouse, 1991).

Cash flow

Assumption

It was assumed the plant would cease production after ten years of operation and at that time the land would be sold for the same price it was purchased for, the working capital would be sold at its estimated value and the plant equipment would have no salvage value. No money was borrowed. It will be assumed that all moneys invested must earn 10% per year. The net present value (NPV) is obtained.

$$\text{NPV} = \sum_{-2}^{10} \frac{(cash\ flow)_n}{(1+r)^n}$$

Where, n is year of operation

r is interest rate.

Start up expense is 10% of fixed capital.

The others fixed capital investment, working capital, depreciation gross profit, income tax, and operating, maintenance and indirect costs were calculated previously above.

With this condition cash flow cart made is shown on the next page.

From the cash flow chart the net present value is positive, so that the plant should be constructed.

Table 7.11 Cash flow chart

Year of operation	**-2**	**-1**	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Land	-122802												122802
Fixed capital	-3008645	-6017290											
Working capital			-1760160										1760160
Sales				13500000	16200000	18000000	18000000	18000000	18000000	18000000	18000000	18000000	18000000
Start up expenditure			-902593										
Operating, maint. & direct cost (total product cost)				-7065844.7	-8218280.7	-9889164.8	-9889164.8	-9889164.8	-9889164.8	-9889164.8	-9889164.8	-9889164.8	-9889164.8
Gross profit			-902593	6434155.3	7981719.3	9013428.7	9013428.7	9013428.7	9013428.7	9013428.7	9013428.7	9013428.7	9013428.7
Cumulative gross profit			-902593	5531562.3	13513281.6	22526710.3	31540139	40553567.7	49566996.4	58580425.1	67593853.8	76607282.5	85620711.2
Depreciation			0	-45130	-85746	-81233	-76720	-72207	-67695	-67695	-67695	-67695	-67695
Gross profit - depreciation			-902593	6389025.3	7895973.3	8932195.7	8936708.7	8941221.7	8945733.7	8945733.7	8945733.7	8945733.7	8945733.7
Income tax			270777.9	-1916707.6	-2368792	-2679658.7	-2681012.6	-2682366.4	-2683720.1	-2683720.1	-2683720.1	-2683720.1	-2683720.1
Net profit			-631815.1	4472317.7	5527181.3	6252537	6255696.1	6258855.3	6262013.6	6262013.6	6262013.6	6262013.6	6262013.6
Cumulative net profit			-631815.1	3840502.6	9367683.9	15620220.9	21875917	28134772.3	34396785.9	40658799.5	46920813.1	53182826.7	59444840.3
Cash flow	-3131447	-6017290	-2391975.1	4517447.7	5612927.3	6333770	6332416.1	6331062.3	6329708.6	6329708.6	6329708.6	6329708.6	8212670.6
Cumulative cash flow	-3131447	-9148737	-11540712	-7023264.3	-1410337	4923433	11255849.1	17586911.4	23916620	30246328.6	36576037.2	42905745.8	51118416.4
Net present value	-3789050.8	-6619019	-2391975	4144447.4	4100319.5	3242890.2	2085805.1	1264972.7	709918.9	388221.7	210791.1	103150.2	70182
Cumulative present value	-3789050.8	-10408069.8	-12800044.8	-8655597.4	-4555277.9	-1312387.7	773417.4	2038390.1	2748309	3136530.7	3347321.8	3450472	3520654

Chapter Eight

Environmental Impact of Bio-ethanol

8.1. Green house emission

One of the major drivers of bio-fuel promotion worldwide is the concern about climate change and the potential of bio-fuels to reduce GHG emissions. Although it is incontestable that the use of bio-ethanol is able to reduce GHG emissions significantly when compared to fossil fuels, assessments of quantified GHG reductions are useful and necessary. However, the GHG balance for bio-ethanol is highly variable and includes emissions of cultivation, transport, conversion process and distribution. Further, the GHG reduction potential depends on type of feedstock, agricultural practices, site productivity, conversion technology and finally on the whole design of the study (Dominik R. and Rainer J., 2007).

Detailed studies, indicating GHG reductions by using neat or blended bio-ethanol are given by WWI (2006) and OECD/IEA (2004). They show reductions of up to 96% for anhydrous bio-ethanol in Brazil (Macedo et al., 2003) from sugar cane.

Apart from sugar cane, other combinations of bio-fuel feedstock and conversion processes can reduce well to wheels CO_2 equivalent GHG emissions to near zero, too. An example therefore is enzymatic/acid hydrolysis of cellulose where ethanol is produced and biomass is used as process fuel (OECD/IEA).

In contrast, ethanol from corn shows very small GHG reductions with in all potential feedstock options (WWI 2006).Using commercial processes, the use of ethanol derived from grains, brings a 20% to 40% reduction in well to wheels CO_2 equivalent GHG emissions, compared to gasoline(OECD/IEA).

8.2. Toxic Exhaust Emissions

The major part of engine exhaust streams during ethanol combustion consists of the components nitrogen, carbon dioxide and water. All three components are non toxic to human health. However, about 1.4% of petrol engine exhaust emissions are composed of more or less harmful substances to human health (Mittelbach and Remschmidt, 2004).

Apart from the above mentioned emissions, fuel combustion emits particulate matter (PM), volatile organic compounds (VOCs), nitrogen oxides (NOx), carbon monoxide (CO) and a variety of other toxic air pollutants. VOCs and NOx are precursors for tropospheric ozone.

Momentary weather conditions and local geographic characteristics influence the impact of these air pollutants. Ozone formation e.g. occurs more easily during hot weather. Also toxic air pollutants are more evident under hot weather conditions. They can be emitted either by the engine exhausts or by evaporation from fuel storage and fuel handling since ethanol has high volatile and generally increases evaporative emissions of gaseous hydrocarbons. As opposed to this, carbon monoxide is a larger problem in cold weather and at high altitudes (Dominik R. and Rainer J., 2007).

To assess the environmental impact of substituting petrol with ethanol, both fuels have to be compared regarding their emissions. Harmful engine exhaust emissions from combustion of ethanol are generally lower when compared to the tailpipe emissions of fossil petrol. This ethanol can reduce certain vehicle pollutant emissions which exacerbate air quality problems, particularly in urban areas (Dominik R. and Rainer J., 2007).

Among the biggest benefits from using ethanol is the high reduction potential of carbon monoxide emissions. The use of E10 (ethanol mixture that contain 10% ethanol and 90% unleaded gasoline) is reported to achieve a 25% or greater reduction in carbon monoxide emissions due to the increased oxygen content of ethanol (OECD/IEA 2004). Ethanol contains approximately 35% oxygen which promotes a more complete combustion of the fuel. Thus, in some countries, ethanol is used as oxygenate for fossil petrol and is increasingly replacing the oxygenate MTBE (methyl tertiary butyl ether) due to the high ground water contamination potential of MTBE.

On the other hand ethanol-blended petrol emits higher evaporative hydrocarbons and other volatile organic compounds than petrol. When ethanol is added to gasoline, evaporative VOCs can increase due to the higher vapor pressure, measured as Reid vapor pressure of the ethanol mixture. Generally, adding the first few per cent of ethanol triggers the biggest increase in volatility. Raising the ethanol concentration further does not lead to significant further increases (and in fact leads to slight decreases), so that blends of 2%, 5%, 10% and more have a similar impact (OECD/IEA 2004).

Impacts of ethanol on nitrogen oxides (NOx) are generally minor and can either be increased or decreased, depending on conditions. NOx emission from combustion of ethanol blends range from a 10% decrease to a 5% increase over emissions from gasoline (OECD/IEA). However, if

the full life cycle of ethanol is considered, NOx emissions can be significantly higher mainly due to emissions from feed stock production. NOx is released from fertilizers used to grow bio-energy crops and is emitted mostly outside urban areas (Dominik R. and Rainer J. , 2007).

When gasoline is blended with ethanol, emissions of most toxic air pollutants decrease. This is primarily due to the dilution effect of ethanol which substitutes some part of gasoline which emits toxic air pollutants. For instance, toxic emissions of benzene, 1, 3 butadiene, toluene and xylene decrease when ethanol is added. Benzene is a carcinogen, while olefins and some aromatics which are emitted by the combustion of fossil fuels as well are precursors to ground level ozone. While few studies have looked at the impacts on pollution levels from high blends, it appears that impacts are similar to those from low blends (WWI 2006).

The above mentioned toxics benzene, 1, 3 butadiene, toluene and xylene which are emitted by the combustion of fossil fuels are considered to be more dangerous than emissions of ethanol combustion. During ethanol fuel combustion, emissions of the toxic air pollutants acetaldehyde, formaldehyde and peroxyacetyl nitrate (PAN) increase relative to straight gasoline. Acetaldehyde is emitted most but it is a less reactive and less toxic pollutant than formaldehyde. PAN is an eye irritant and is harmful to plants. No one of these pollutants is present in the unburned fuel, as they are only created as byproducts of incomplete combustion (WWI 2006).Nevertheless, impacts of acetaldehyde and PAN seem to be minor as emissions are relatively low compared to other sources and as they can be efficiently removed by a vehicle's catalytic converter (Arnold et al., 2005).

Strict emissions control standards for cars and trucks will tend to mute the air quality impacts of bio-ethanol, since manufacturers are required to build vehicles that meet these standards under a range conditions (Dominik R. and Rainer J., 2007).

8.3. Other environmental impact of bio-ethanol

Determining the direct environmental effects of ethanol production is complex. Environmental effects of using bio-ethanol vary, depending on the fuel itself, vehicle technology, vehicle tuning and driving procedure. Also agricultural production practices and the design of ethanol production plants differ largely (Dominik R. and Rainer J., 2007).

Water Issues

Water issues are an important concern of both, ethanol processing and use of ethanol. The water consumption for the production of bio-ethanol is considerable high. There by, much water is used for feedstock production. The amount of water used for agriculture depends on the humidity/aridity of the cultivated region and on the water demand of the feedstock type. But also for the conversion process much water is needed. The quantity of water needed for the ethanol production process much water is needed. The quantity of water needed for the ethanol production process depends on the design of the production plant. Modern technology and design can substantially reduce the amount of fresh water needed by a standard alone ethanol plant. There is zero discharge plants in operation that recycle virtually all of the water used in production, limiting the need for large supplies (Dominik R. and Rainer J., 2007).

Most plants are designed with in house water treatment systems for supply and discharge. However, there are always three water uses in a typical ethanol plant. The first water use in a typical ethanol plant is non contact water, primarily used for cooling. The second use is for liquefaction of the feedstock. Water must be clean and treated so that there is no microbiological contamination in the fermentation process. Thirdly, ethanol processing also results in large volumes of nutrient rich waste water that, if not cleaned and recycled, can speed eutrophication of local rivers and streams by affecting the water's dissolved oxygen content. In addition, sugar mills must be flushed every year, putting huge amounts of organic matter in to local water ways (WWI 2006).

Apart from the water consumption during the ethanol production process, water contamination impacts of released ethanol are an important environmental issue as well. Since ethanol is a naturally occurring substance produced during the fermentation of organic matter it is expected to rapidly biodegrade in essentially all environments (Ulrich 1999). Thus pure ethanol poses no threat to surface water and ground water and is much less harmful in case of spilling and leakage compared to fossil fuel which is highly toxic. When gasoline, which is blended with ethanol, contaminates soil or water, ethanol is the first component to quickly, safely and naturally biodegrade. At the same time, studies have shown that the rapid breakdown of ethanol depletes the oxygen available in water and soil, actually slowing the breakdown of gasoline. This may increase the impact of petrol spillage on the environment in two ways. First, the harmful

chemicals in gasoline persist longer in the environment than without ethanol. Second, as gasoline breaks down more slowly, it can travel farther (up to 2.5 times) in the marine environment, affecting a greater area (WWI 2006). Although these effects of ethanol gasoline mixtures are negative to the environment, it also to be considered that the total percentage of petrol released to the environment is reduced by the percentage of harmless ethanol. Depending on the blended percentage, this is a great advantage of gasoline which is highly blended with bio-ethanol.

Attention has to be paid, if ethanol is spilled to previously contaminated soils as it can remobilize the gasoline. Since this problem is most likely to happen concentrated at gasoline terminals, it can easily avoided with precautionary measures. Therefore regulations for the handling with both fuels have to be applied (Dominik R. and Rainer J., 2007).

Human Health

Ethanol is an important component of alcoholic beverages. It has been part of the human diet and the human environment for thousands of years. In low quantities and concentrations it is not harmful to human health, but pure or highly concentrated ethanol can permanently damage living tissue. Pure ethanol is a tasteless liquid with a strong and distinctive odor. It produces a characteristics heat like sensation when brought in to contact with the tongue or mucous membranes (Dominik R. and Rainer J., 2007).

Although low quantities of ethanol are not toxic to human health, concerns about the possible health consequences of using ethanol as transport fuel have been raised. These concerns mainly include the inhalation of ethanol vapors by using ethanol pure of blended in transport applications. Prediction of blood ethanol concentrations following exposure to ethanol vapors must consider several factors: (a) the concentration of ethanol in air, (b) the duration of exposure, (c) breathing rate, (d) absorption of ethanol across the lungs and (e) the body's elimination rate of ethanol. Nevertheless, it is highly unlikely that exposure to airborne ethanol associated with gasoline use could produce toxic effects. The reasons for this are the tiny doses that might be received and the body's rapid elimination of ethanol (Armstrong 1999). For instance, ethanol vapors might be inhaled at gasoline stations while fueling vehicles, but this exposure would be relatively brief, no more than five minutes. However, workmen of petrol stations can be exposed to vapors for many hours, since these vapors are released to the ambient air of the fuel station.

Another concern for human health of using ethanol as fuel could be toxic emissions by the combustion process. The fuel is low in sulfur and aromatic compounds and thereby it considerably reduces the emissions of the gases that are harmful to the climate and human health. Harmful engine exhaust emissions from combustion of ethanol and ethanol blends are generally lower when compared to the tail pipe emissions of fossil petrol (Dominik R. and Rainer J., 2007).

Chapter Nine

Conclusions and Recommendations

9.1. Conclusion

Hydrolysis of fruit peel waste was carried out with dilute acid and the optimum condition as well as interaction, contour and response surface plot were examined by using Box-Behnken. 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.

9.2. 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.

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 Addis Ababa. 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.

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Appendices

Appendix A: Properties of Ethanol

Acidity (Pka)	15.9 (H + from OH group)
Appearance	Colorless
Boiling point	78.4^0C (351.6k)
Density and phase	0.789g/cm^3, liquid
Dipole moment	1.69D(gas)
Melting point	-114.3^0C(158.8k)
Molecular formula	C_2H_5OH
Latent heat of Vaporization	
Btu/gal at 60^0C	2378
Btu/Ib at 60^0F	396
Specific heat, Btu/Ib ^{0}F	0.57
Specific gravity, 60^0F/60^0F	0.794
Solubility in water	Fully miscible
Viscosity	1.200cp at 20^0C

Appendix B: Density of Ethyl alcohol

%	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	%	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
0	0.99973	0.99913	0.99823	0.99708	0.99568	0.99406	0.99225	50	0.92126	0.91776	0.91384	0.90985	0.90580	0.90168	0.89750
1	785	725	636	520	379	217	034	51	0.91943	555	160	760	353	0.89940	519
2	602	542	453	336	194	031	0.98846	52	723	333	0.90936	534	125	710	288
3	426	365	275	157	014	0.98849	663	53	502	110	711	307	0.89896	479	056
4	258	195	103	0.98984	0.98839	672	485	54	279	0.90885	485	079	667	248	0.88823
5	098	032	0.98938	817	670	501	311	55	055	659	258	0.89850	437	016	589
6	0.98946	0.98877	780	656	507	335	142	56	0.90831	433	031	621	206	0.88784	356
7	801	729	627	500	347	172	0.97975	57	607	207	0.89803	392	0.88975	552	122
8	660	584	478	346	189	009	808	58	381	0.89080	574	162	744	319	0.87888
9	524	442	331	193	031	0.97846	641	59	154	752	344	0.88931	512	085	653
10	393	304	187	043	0.97875	685	475	60	0.89927	523	113	699	278	0.87851	417
11	267	171	047	0.97897	723	527	312	61	698	293	0.88882	446	044	615	180
12	145	041	0.97910	753	573	371	150	62	468	062	650	233	0.87809	379	0.86943
13	026	0.97914	775	611	424	216	0.96989	63	237	0.88830	417	0.87998	574	142	705
14	0.97911	790	643	472	278	063	829	64	006	597	183	763	337	0.86905	466
15	800	669	514	334	133	0.96911	670	65	0.88774	364	0.87948	527	100	667	227
16	692	552	387	199	0.96990	760	512	66	541	130	713	291	0.86863	429	0.85987
17	583	433	259	062	844	607	352	67	308	0.87895	477	054	625	190	747
18	473	313	129	0.96923	697	452	189	68	074	660	241	0.86817	387	0.85950	407
19	363	191	0.96997	782	547	294	023	69	0.87839	424	004	579	148	710	266
20	252	068	864	639	395	134	0.95856	70	602	187	0.86766	340	0.85908	470	025
21	139	0.96944	729	495	242	0.95973	687	71	365	0.86949	527	100	667	228	0.84783
22	024	818	592	348	087	809	516	72	127	710	287	0.85859	426	0.84986	540
23	0.96907	689	453	199	0.95929	643	343	73	0.86888	470	047	618	184	743	297
24	787	558	312	048	769	476	168	74	648	229	0.85806	376	0.84941	500	053
25	665	424	168	0.95895	607	306	0.94991	75	408	0.85088	564	134	698	257	0.83809
26	539	287	020	738	442	133	810	76	168	747	322	0.84891	455	013	564
27	406	144	0.95867	576	272	0.94955	625	77	0.85927	505	079	647	211	0.83768	319
28	268	0.95996	710	410	098	774	438	78	685	262	0.84835	403	0.83966	523	074
29	125	844	548	241	0.94922	590	248	79	442	018	590	158	720	277	0.82827
30	0.95977	686	382	067	741	403	055	80	197	0.84772	344	0.83911	473	029	578
31	823	524	212	0.94890	557	214	0.93860	81	0.84950	525	096	664	224	0.82780	329
32	665	357	038	709	370	021	662	82	702	277	0.83848	415	0.82974	530	079
33	502	186	0.94860	525	180	0.93825	461	83	453	028	599	164	724	279	0.81828
34	334	011	679	337	0.93986	626	257	84	203	0.83777	348	0.82913	473	027	576
35	162	0.94832	494	146	790	425	051	85	0.83951	525	095	660	220	0.81774	322
36	0.94986	650	306	0.93952	591	221	0.92843	86	697	271	0.82840	405	0.81965	519	067
37	805	464	114	756	390	016	634	87	441	014	583	148	708	262	0.80811
38	620	273	0.93919	556	186	0.92808	422	88	181	0.82754	323	0.81888	448	003	552
39	431	079	720	353	0.92979	597	208	89	0.82919	492	062	626	186	0.80742	291
40	238	0.93882	518	148	770	385	0.91992	90	654	227	0.81797	362	0.80922	478	028
41	042	682	314	0.92940	558	170	774	91	386	0.81959	529	094	655	211	0.79761
42	0.93842	478	107	729	344	0.91952	554	92	114	688	257	0.80823	384	0.79941	491
43	639	271	0.92897	516	128	733	332	93	0.81839	413	0.80983	549	111	669	220
44	433	062	685	301	0.91910	513	108	94	561	134	705	272	0.79835	393	0.78947
45	226	0.92852	472	085	692	291	0.90884	95	278	0.80852	424	0.79991	555	114	670
46	017	640	257	0.91868	472	069	660	96	0.80991	566	138	706	271	0.78831	388
47	0.92806	426	041	649	250	0.90845	434	97	698	274	0.79846	415	0.78981	542	100
48	593	211	0.91823	429	028	621	207	98	399	0.79975	547	117	684	247	0.77806
49	379	0.91995	604	208	0.90805	396	0.89979	99	094	670	243	0.78814	382	0.77946	507
								100	0.79784	360	0.78934	506	075	641	203

*For data from −78° to 78°C, see p. 2-142, Table 2N-5, *American Institute of Physics Handbook*, McGraw-Hill, New York, 1957. See Tables 2-214 and 2-305 for pure component densities.

Appendix C: Typical over all coefficients

Shell and tube exchangers		
Hot fluid	Cold fluid	U (W/m^2°C)
Heat exchangers		
Water	Water	800–1500
Organic solvents	Organic solvents	100–300
Light oils	Light oils	100–400
Heavy oils	Heavy oils	50–300
Gases	Gases	10–50
Coolers		
Organic solvents	Water	250–750
Light oils	Water	350–900
Heavy oils	Water	60–300
Gases	Water	20–300
Organic solvents	Brine	150–500
Water	Brine	600–1200
Gases	Brine	15–250
Heaters		
Steam	Water	1500–4000
Steam	Organic solvents	500–1000
Steam	Light oils	300–900
Steam	Heavy oils	60–450
Steam	Gases	30–300
Dowtherm	Heavy oils	50–300
Dowtherm	Gases	20–200
Flue gases	Steam	30–100
Flue	Hydrocarbon vapours	30–100
Condensers		
Aqueous vapours	Water	1000–1500
Organic vapours	Water	700–1000
Organics (some non-condensables)	Water	500–700
Vacuum condensers	Water	200–500
Vaporisers		
Steam	Aqueous solutions	1000–1500
Steam	Light organics	900–1200
Steam	Heavy organics	600–900

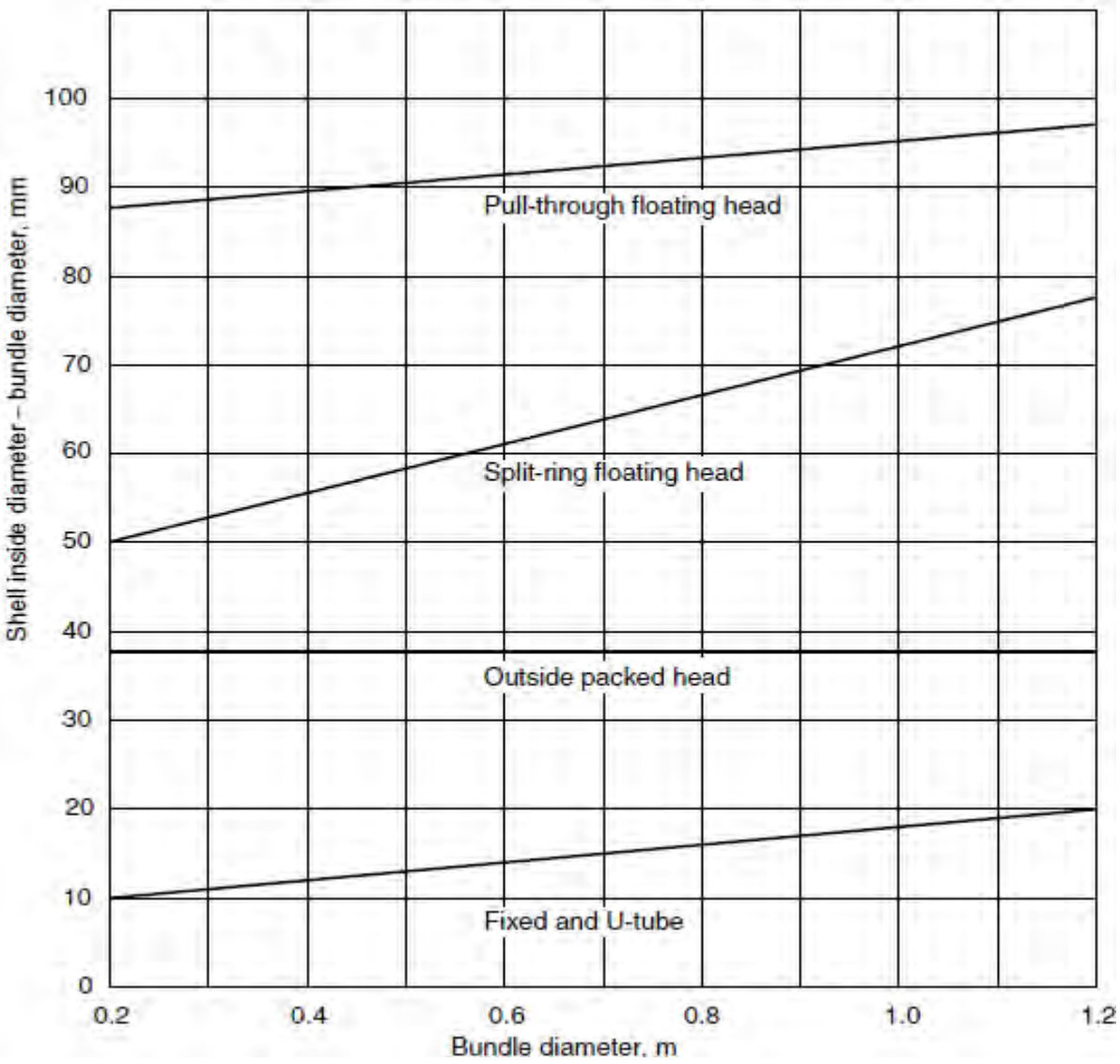
Appendix D: Fouling factor coefficient

Fluid	Coefficient ($W/m^2{}^\circ C$)	Factor (resistance) ($m^2{}^\circ C/W$)
River water	3000–12,000	0.0003–0.0001
Sea water	1000–3000	0.001–0.0003
Cooling water (towers)	3000–6000	0.0003–0.00017
Towns water (soft)	3000–5000	0.0003–0.0002
Towns water (hard)	1000–2000	0.001–0.0005
Steam condensate	1500–5000	0.00067–0.0002
Steam (oil free)	4000–10,000	0.0025–0.0001
Steam (oil traces)	2000–5000	0.0005–0.0002
Refrigerated brine	3000–5000	0.0003–0.0002
Air and industrial gases	5000–10,000	0.0002–0.0001
Flue gases	2000–5000	0.0005–0.0002
Organic vapours	5000	0.0002
Organic liquids	5000	0.0002
Light hydrocarbons	5000	0.0002
Heavy hydrocarbons	2000	0.0005
Boiling organics	2500	0.0004
Condensing organics	5000	0.0002
Heat transfer fluids	5000	0.0002
Aqueous salt solutions	3000–5000	0.0003–0.0002

Appendix E: Standard dimension for steel tubes

Outside diameter (mm)	Wall thickness (mm)				
16	1.2	1.6	2.0	—	—
20	—	1.6	2.0	2.6	—
25	—	1.6	2.0	2.6	3.2
30	—	1.6	2.0	2.6	3.2
38	—	—	2.0	2.6	3.2
50	—	—	2.0	2.6	3.2

Appendix F: Shell -bundle clearance



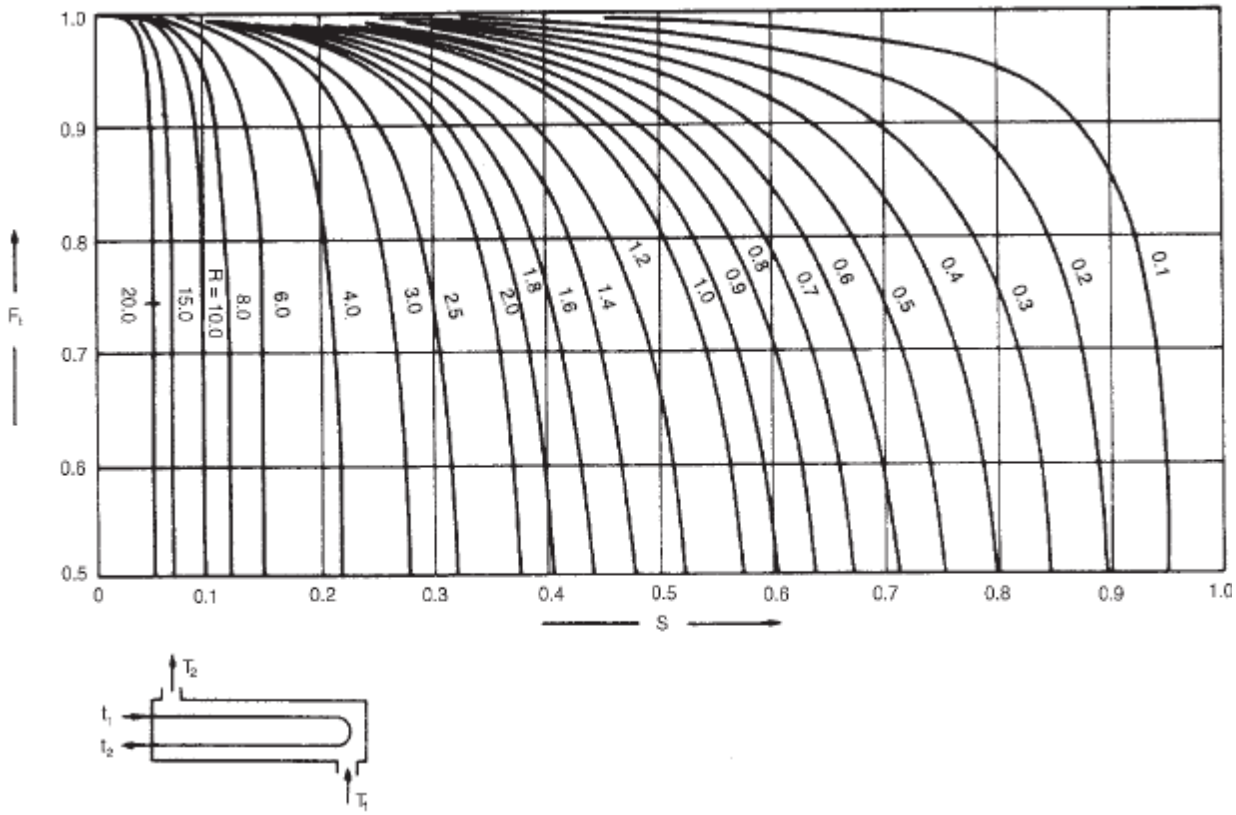
Appendix G: Constant use for pitch

Triangular pitch, $p_t = 1.25d_o$					
No. passes	1	2	4	6	8
K_1	0.319	0.249	0.175	0.0743	0.0365
n_1	2.142	2.207	2.285	2.499	2.675
Square pitch, $p_t = 1.25d_o$					
No. passes	1	2	4	6	8
K_1	0.215	0.156	0.158	0.0402	0.0331
n_1	2.207	2.291	2.263	2.617	2.643

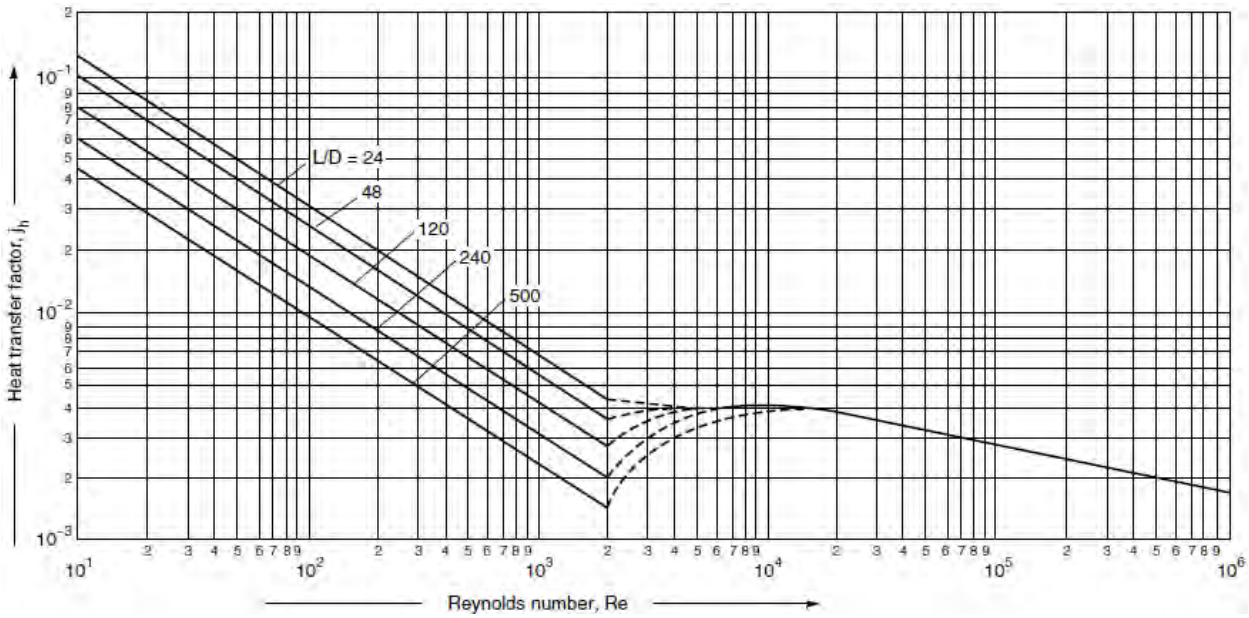
Appendix H: Typical baffle clearance and tolerance

Shell diameter, D_s	Baffle diameter	Tolerance
Pipe shells		
6 to 25 in. (152 to 635 mm)	$D_s - \frac{1}{16}$ in. (1.6 mm)	$+\frac{1}{32}$ in. (0.8 mm)
Plate shells		
6 to 25 in. (152 to 635 mm)	$D_s - \frac{1}{8}$ in. (3.2 mm)	$+0, -\frac{1}{32}$ in. (0.8 mm)
27 to 42 in. (686 to 1067 mm)	$D_s - \frac{3}{16}$ in. (4.8 mm)	$+0, -\frac{1}{16}$ in. (1.6 mm)

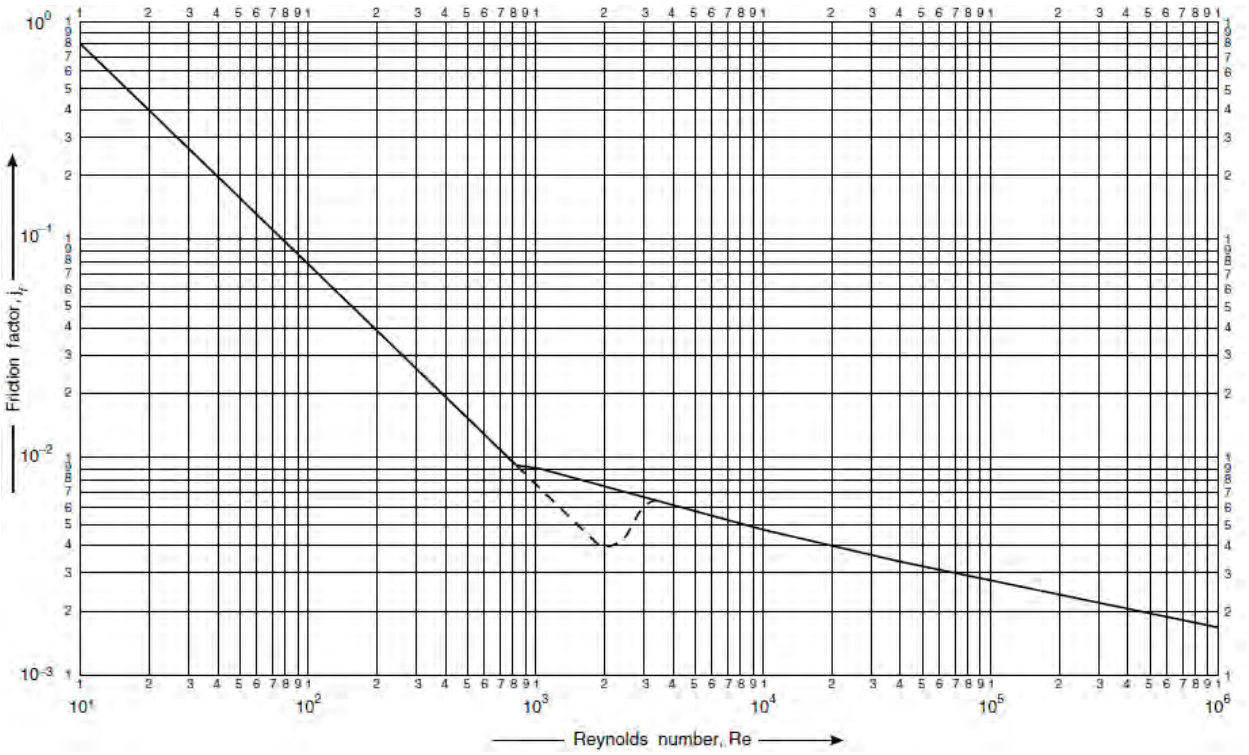
Appendix I: Temperature correction factor for one shell pass, two or more even tube pass



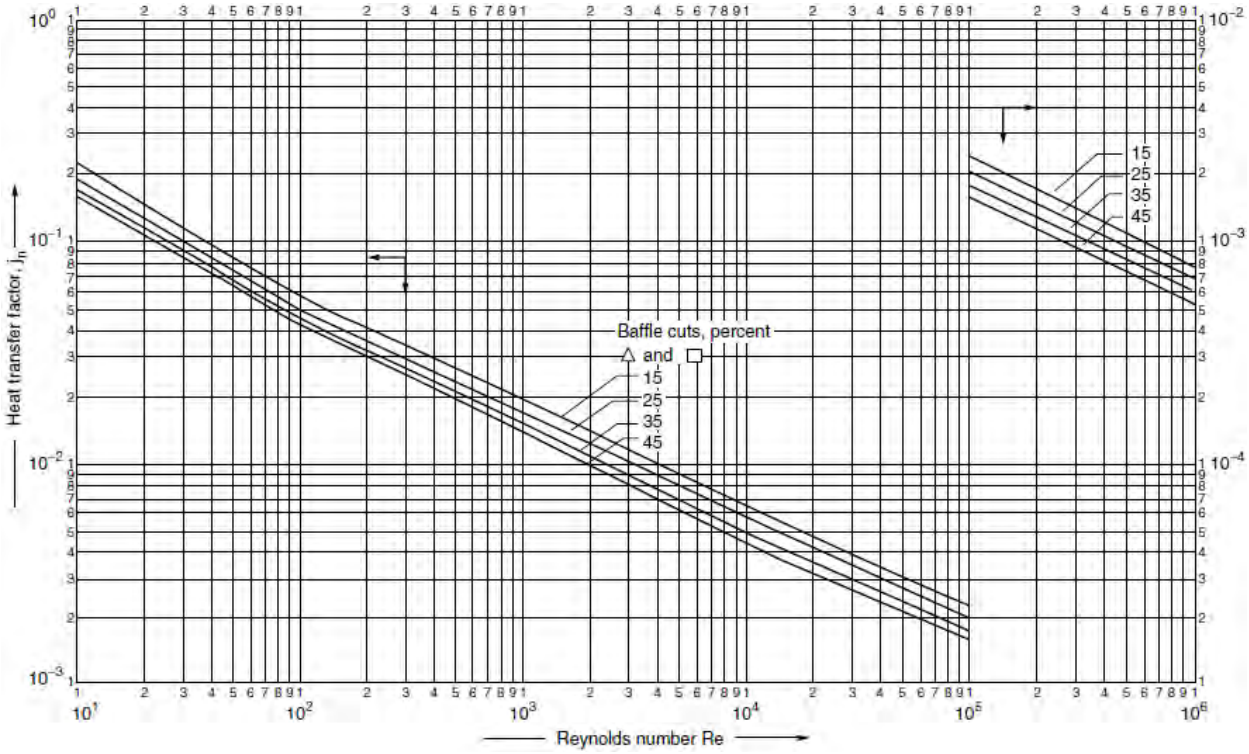
Appendix J: Tube side heat transfer factor



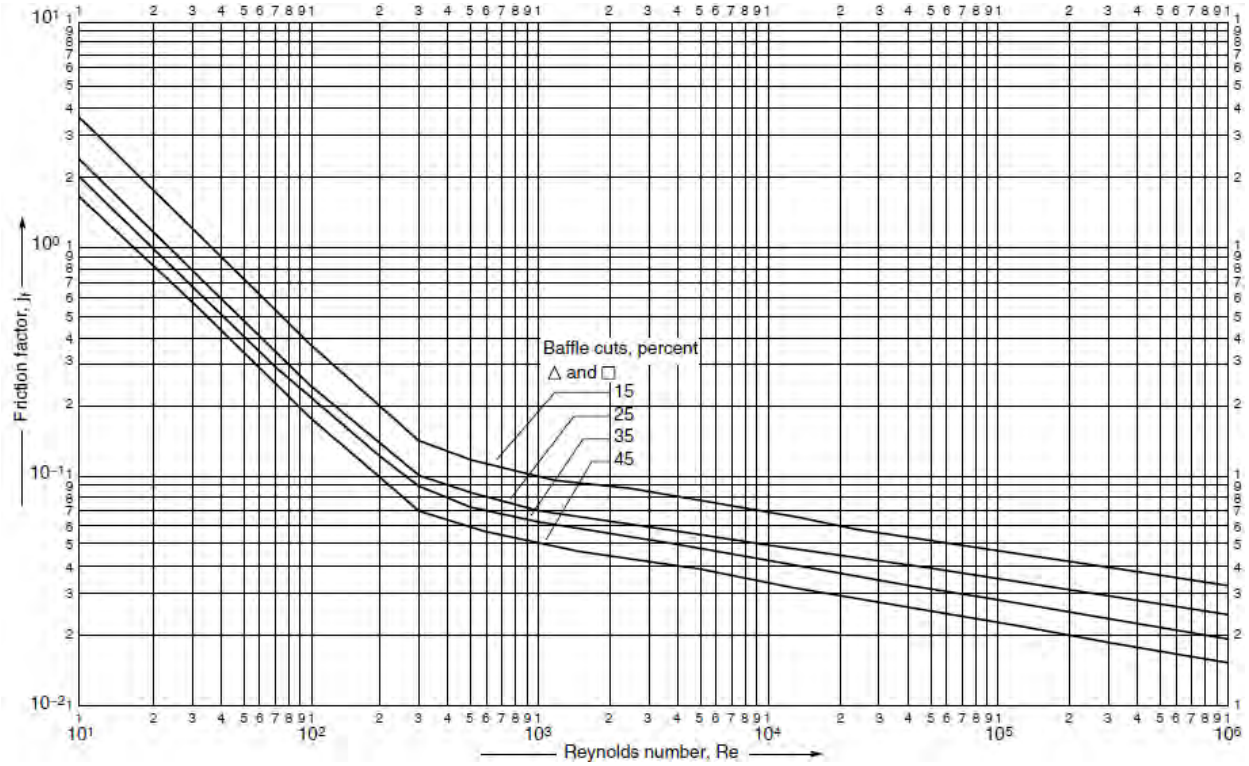
Appendix K: Tube side friction factor



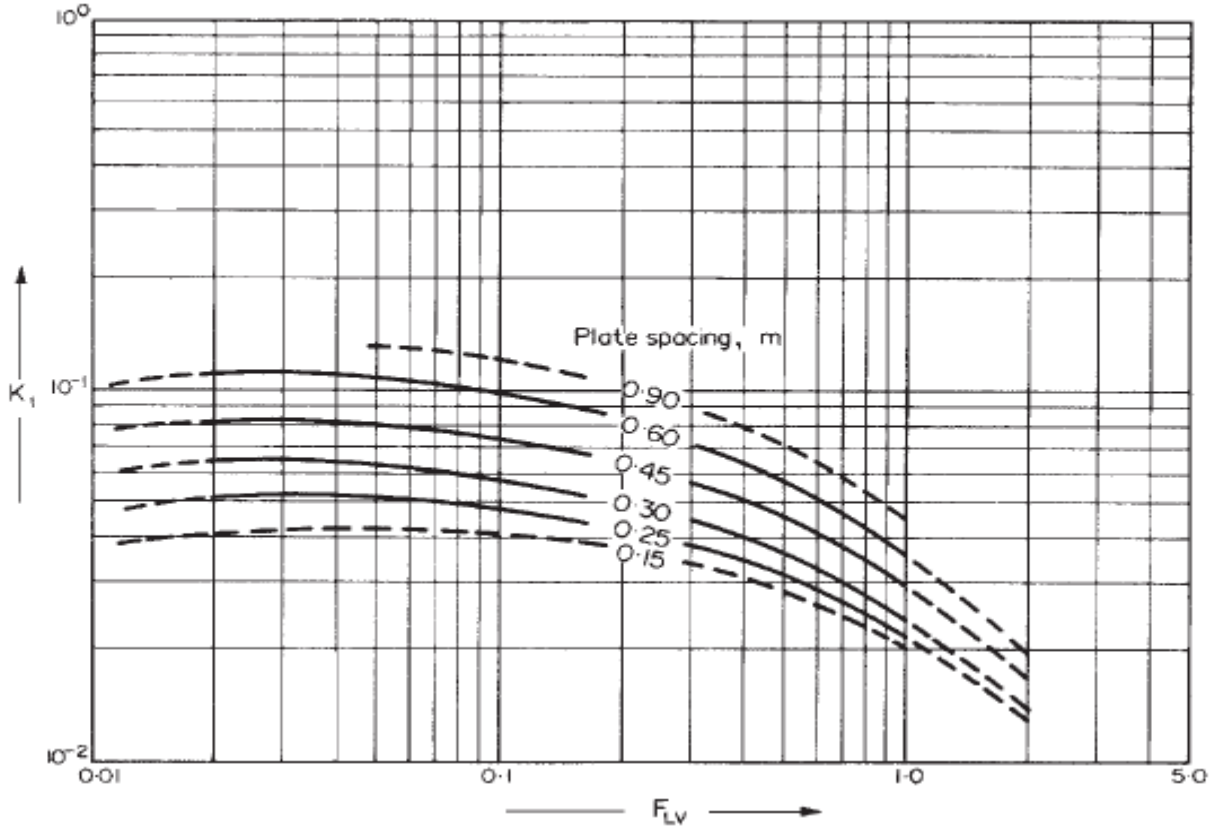
Appendix L: Shell-side heat-transfer factors, segmental baffles



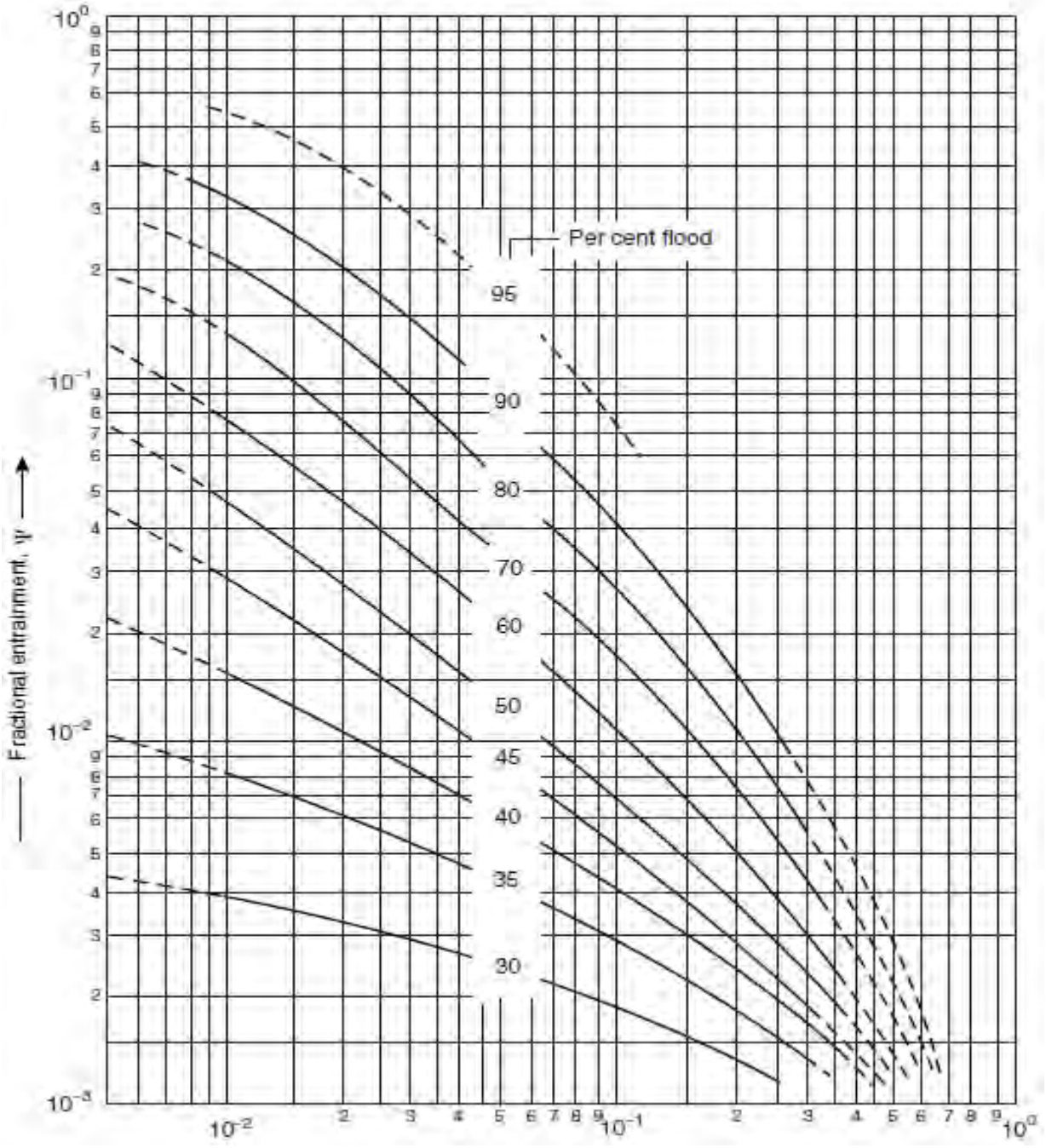
Appendix M: Shell-side friction factors, segmental baffles



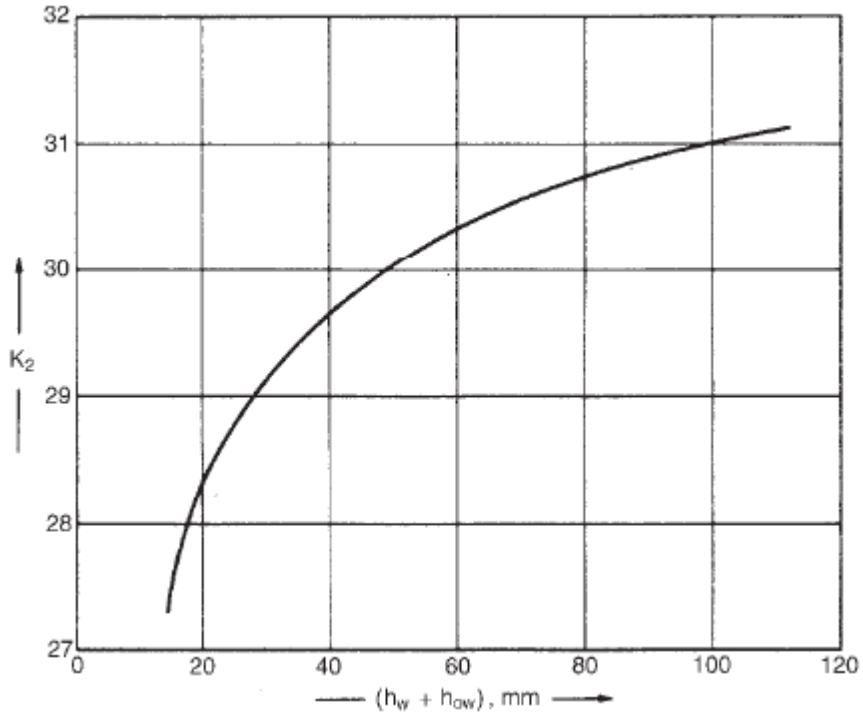
Appendix N: Flooding velocity, sieve plates



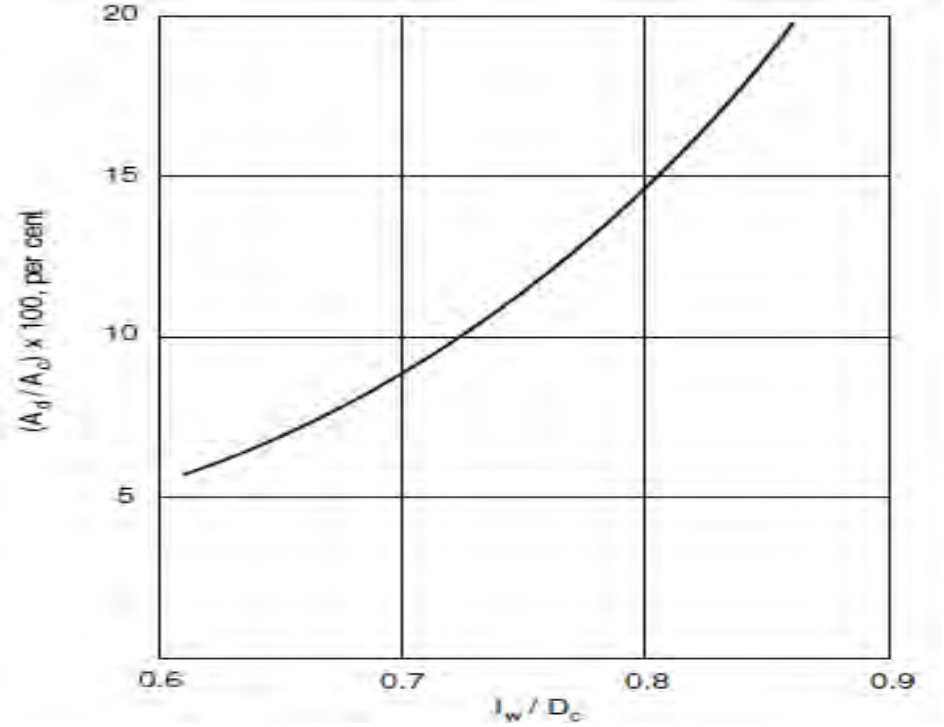
Appendix O: Entrainment correlation for sieve plates



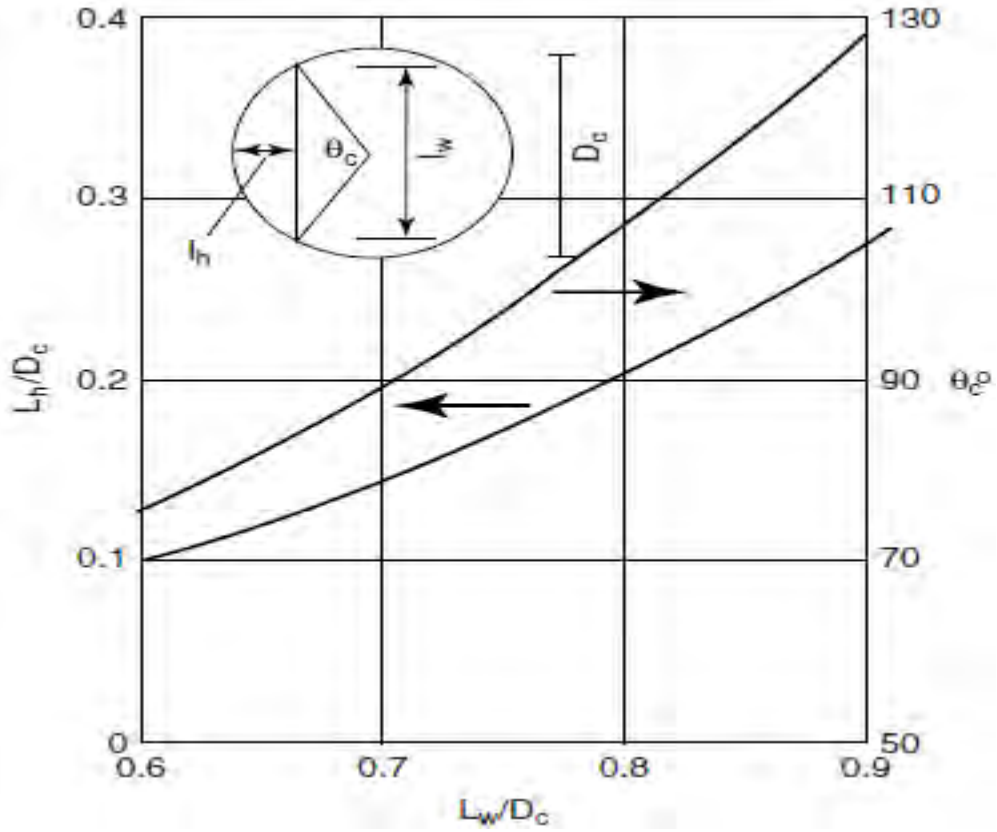
Appendix P: Weep-point correlation



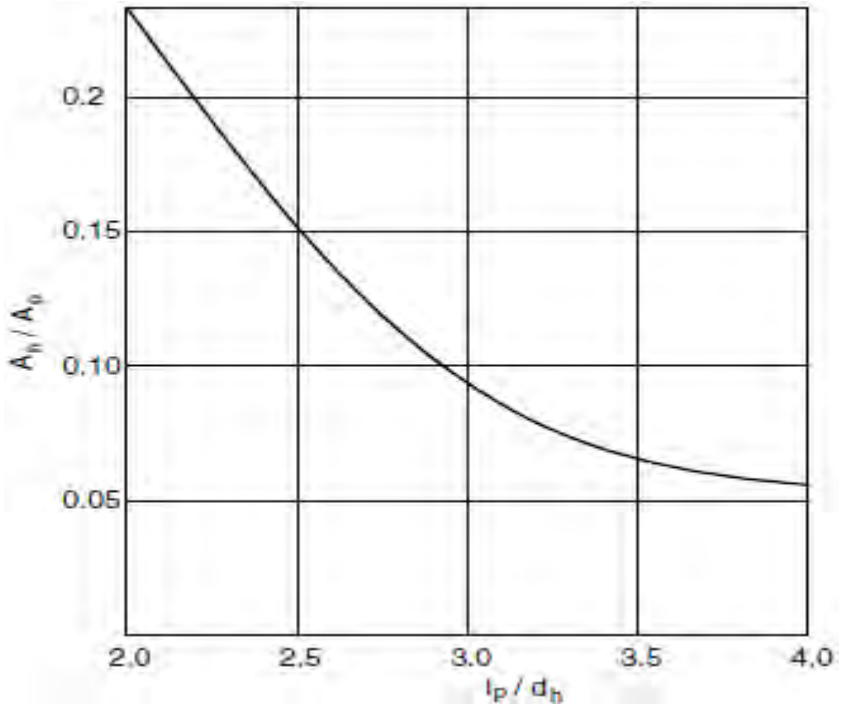
Appendix Q: Relation between down comer area and weir length



Appendix R: Relation between angle subtended by chord, chord height and chord length



Appendix S: Relation between hole area and pitch



Appendix T: Discharge coefficient, sieve plates