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DISTILLATION OF ETHANOL IN THE BIOETHANOL PRODUCTION

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Аннотация. В работе рассматриваются технологические аспекты выделения этилокого спирта из бражки при проихводстве топливного спирта.

Ключевые слова: топливный спирт, дистилляция, бражка, абсолютирование.

Introduction

In general, all bioethanol production methods require a separation of ethanol and dehydration for fuel grade ethanol. There are three independent routes for producing fuel grade ethanol from lignocellulosic biomass:

1. Aqueous-phase biomass hydrolysis route – fermentation of an aqueous solution of C-5,6 sugars described;
2. Gasification route – fermentation of syngas;
3. Gasification route – catalytic conversion of syngas.

Routes 1 and 2 are aqueous-phase microbial fermentation methods and the end product in these techniques is a mash containing 10% to 12% ethanol in water. In the first route, all non-fermentable solids from the biomass hydrolyzate and yeast cells remain in the fermented solution, which is commonly known as "beer." In the second route, where syngas (a mixture of CO, H2 and CO2) is fermented, buffering salts, and microorganisms used will remain in the solution. In the third route, where syngas is converted to ethanol using a metal-based chemical catalysis system at high temperature, the conversion is usually not as selective as in biochemical routes. This route generally provides ethanol together with methanol, some higher alcohols, ethers, ethylene glycol and a small amount of hydrocarbons. A fractional distillation technique can be used to separate out ethanol from this mixture.

Distillation of the Beer

Processing of beer produced from the fermentation of C-5,6 sugar solution by distillation and then drying to fuel grade ethanol is a mature technology. These techniques are well developed as corn-and sugarcane-based first generation bioethanol is in wide use as a blend in fuel in the United States, Brazil and a few other countries. These techniques developed for first generation ethanol are generally applicable to cellulosic ethanol as well.

How Distillation Works

Absolute ethanol boils at 78.5°C and water boils at 100°C at standard atmospheric pressure. Ethanol has a higher vapor pressure than water; in other words, it takes less energy to convert ethanol to ethanol vapor than water to steam. When ethanol and water are mixed the boiling temperature varies and falls between the boiling points of pure ethanol and water. When we boil a mixture of ethanol and water, more ethanol vapor rises from the vessel than water vapor. The compositions of liquid and the vapor produced at different temperatures can be plotted against the temperature; this graph is known as the phase diagram, which is shown in Figure 1. If

we can capture vapor and condense the vapor, the condensate has a higher concentration of ethanol than the original mixture. Now we can boil this condensed liquid and capture the vapor and re-condense the vapor. This second condensed vapor will have even a higher proportion of ethanol. This process is called rectifica-tion, and can be repeated until most of the ethanol is drawn off. However, things are not that simple in the case of ethanol water, and this solution forms a minimum-boiling azeotrope at the composition of 89.4 mol% ethanol and 10.6 mol% water. At this composition vapor phase and liquid phase both will have the same composition as shown in Figure 1. The azeotrope mixture will boil at 78.2°C at standard atmospheric pressure and ethanol cannot be further concentrated by simple fractional distillation when it reaches this composition.

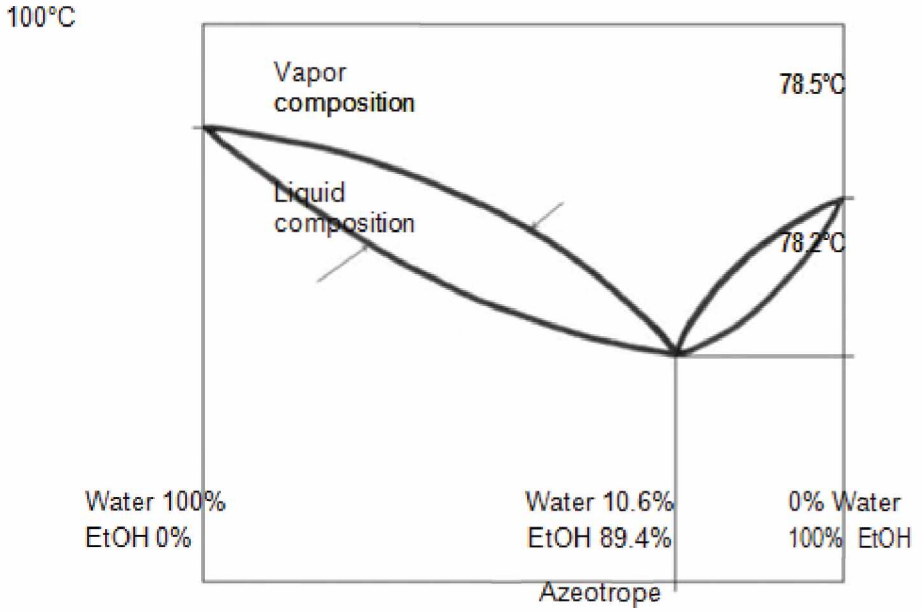

Figure 1 Ethanol-water phase diagram showing the minimum-boiling azeotrope of composition of 89.4 mol% ethanol and 10.6 mol% water; the azeotrope mixture will boil at 78.2°C and standard atmospheric pressure.

There are several methods that can be used to further enrich ethanol from an azeotrope composition mixture; the two common methods are:

1. Introduction of a third component called an entrainer that will affect the volatility of one of the azeotrope constituents more than the other. When an entrainer is added to a binary azeotrope the mixture will form a ternary azeotrope. Benzene or cyclohexane can be used as an entrainer for further concentration of ethanol.

2. Use of dehydration agents such as molecular sieves to selectively absorb water from the mixture. This is a widely applied technology in drying distilled ethanol to fuel grade ethanol.

Further enrichment of ethanol to ~99.5% fuel grade ethanol is also known as dehydration.

Conventional Ethanol Distillation System

The solid particulate matter such as yeast cells and non-fermented residual solids in the fermented solution are first removed by cen-trifugation or filtration. Then distillation of the fermented solution, or "beer," is the next step in the

separation of ethanol from this ethanol-water mixture. A conventional ethanol distillation system is a combination of three columns as shown in Figure.2.

The first column is known as beer column or stripping column and the second column is known as rectifying or refining column, and the third column is called side stripper. In the conventional separation process, fermented mixture, or beer, is first passed through a beer column. This column essentially behaves as a steam stripping column and produces a vapor stream having an ethanol composition between 40% and 60% by mass. The bottoms stream leaving the beer column is composed mainly of water, with some residual solids. The vapor stream leaving the beer column then enters the second column known as the rectifying column. The bottoms product leaving the rectifying column can go to a separate stripping column known as the side stripper column. The distillate leaving the rectifying column is normally near the azeotropic composition (89.4 mol% ethanol and 10.6 mol% water). This distillate stream then undergoes dehydration to produce fuel grade ethanol product [1, 2].

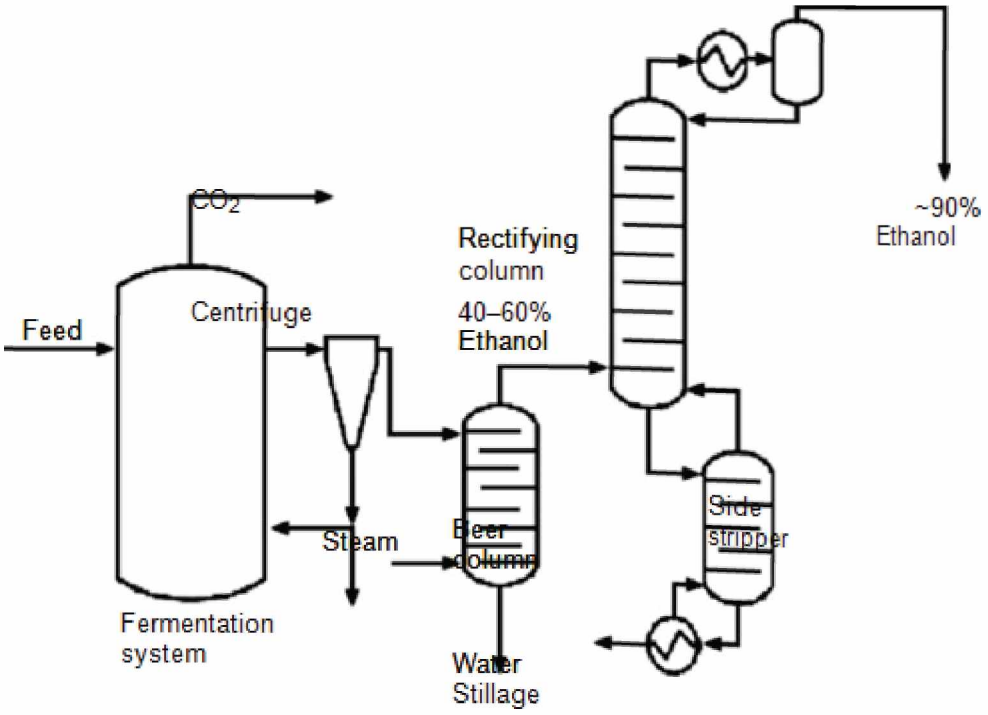

Figure 2 Conventional ethanol distillation set up with beer column, rectifying column, and side stripper. (Adopted with permission from reference [3]; copyright 2012 Elsevier).

Beer Column or Stripping Column

The beer or stripping column is used in the initial separation of ethanol from fermented sugar solution or beer. The distillation sys-tem is fed with the fermentation process product that contains 10% to 12% alcohol in water. Most of the non-fermentable solids from the biomass hydrolyzate and yeast cells can be removed from the fermentation broth by centrifugation. However, some small solid particulate matter may remain in beer, which is introduced from the top of the column, and the steam is introduced from the bot-tom of the column as shown in the Figure 2. A stack

of sieve trays inside the column help to enhance the vapor-liquid contact and separation. A top and side view of a sieve tray used in ethanol distillation columns is shown in Figure 3. One side of the sieve tray is open and allows downward draft, and the other catches the down coming liquid from the sieve tray just above this tray. Typically 19–20 sieve trays are used in the beer column. As vapor rises and the beer falls through trays, heat from the vapor causes alcohol to evaporate. The tray-by-tray vaporization/condensation continues, moving the ethanol concentration lower at each descending tray. At the bottom of the column, the remaining beer (minus alcohol) is called whole stillage and is sent to the whole stillage tank for centrifugation. The countercurrent flow removes nearly all the ethanol from the feed to the beer column. Ethanol-water vapor exiting from the top of the column contain 40–60% alcohol by volume. Typical temperature at the top of the beer column is about 70–74°C, whereas the bottom is about 85–88°C.

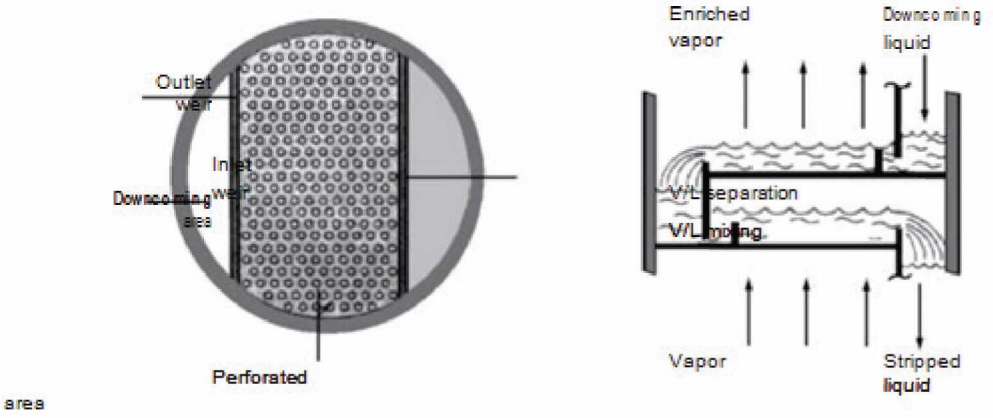

Figure 3 Top and side view of a sieve tray.

Rectifying or Refining Column

The rectifying column, sometimes called the refining column, is used in the second stage of separation, which also has a stack of sieve trays to boost the separation of ethanol and water. Alcohol from the top of the beer column, now in vapor form, is fed into the bottom of the rectifier column, providing the heat source for the rectifier column. The alcohol continues to rise and more water is removed, increasing to approximately 90% alcohol out of the top of the rectifier column. After the alcohol vapors leave the top of the rectifier column they enter the condenser, where the vapors are condensed. Two-thirds of the 90% alcohol produced here is returned to the top of the rectifier column as 90% reflux. The remaining third of the alcohol is sent to the azeotropic ethanol-water mixture (89.4 mol% ethanol and 10.6 mol% water) storage tank. Temperature at the top of the rectifier column is around 68–71°C, whereas in the bottom of the column it is about 85–88°C. The azeotropic mixture is then dried to make nearly anhydrous fuel grade ethanol (99–99.8 wt%) in the next stage.

Side Stripper Column

The side stripper is an additional alcohol recovery column con-nected to the rectifying column. Rectifier bottoms are pumped into the top of the side stripper column and steam and/or cook flash from the flash vessel is injected into the bottom.

As the rectifier bottoms fall through the trays, the steam rises and removes any remaining alcohol. The alcohol vapors from the top of the side strip-per are carried back to the bottom of the rectifier column. Liquid from the bottom of the side stripper is pumped back into the cook system. Temperature at the bottom of the side stripper column is 85–88°C, whereas the top of the column is around 65–68°C.

Steam Generation for Distillation Process

The steam required for the distillation of cellulosic ethanol is gen-erated in a boiler by burning solid biomass wastes. According to the NREL cellulosic ethanol process design technical report, extra steam generated in the boiler can be used to produce electricity using a turbogenerator [4]. This NREL technical report gives steam generation requirements and operating conditions for a corn stover cellulosic ethanol plant with a capacity of 2,205 dry US ton/day.

The purpose of the combustor, boiler, and turbogenerator sub-system is to burn various organic byproduct streams to produce steam and electricity. Combustible byproducts include all of the lignin and the unconverted cellulose and hemicellulose from the feedstock, biogas from anaerobic digestion, and biomass sludge from waste water treatment. Burning these byproduct streams to generate steam and electricity allows the plant to be self-sufficient in energy, reduces solid waste disposal costs, and generates additional revenue through sale of excess electricity.

Design Basis of the Boiler

The 2011 NREL corn stover ethanol plant proposal suggests the use of a combustor capable of handling wet solids, where a fan moves air into the combustion chamber [4]. According to this design, treated water enters the heat exchanger circuit in the combustor, where it is boiled and superheated to high-pressure steam. A multistage turbine and a generator can be used to generate electricity from high-pressure steam. Steam extracted from the turbine at two different conditions is available for use in the ethanol distillation process. In the final stage of the turbine, the remaining steam is taken down to a vacuum and condensed with cooling water for maximum energy conversion. The condensate is returned to the boiler feed water system along with condensate from the various heat exchangers in the process. The steam turbine turns a generator that produces AC electricity for all users in the plant. The balance of electricity is assumed to be sold to the grid, providing a co-product credit.

NREL technical analysis recommended a Towerpak Stirling power boiler system for the generation of steam from solid waste with 44% moisture content [4]. This system features a live-bottom grated fuel bin to ensure drying and complete combustion of the wet solid fuel. The system was quoted to produce 525,000 lb/h (239,000 kg/h) of steam at 850°F (454°C) and 900 psig in the 2,205 dry corn stover US ton/day plant. Boiler efficiency, defined as the percentage of the feed heating value that is converted to steam heat, is ~80%.

Flue gas from the combustor can be used to preheat the entering combustion air which enters a spray dryer for flue gas desulfuriza-tion (FGD). All of the sulfur entering the combustor is converted to sulfur dioxide, and its concentration in the flue is expected to be >1,800 ppm. This level of SO2 requires FGD. The proposed flue gas desulfurization technique involves spraying lime (calcium hydroxide) into the

flue gas as a 20 wt% slurry at 20% stoichiometric excess. Thereby flue gas desulfurization converts 92% of the SO2 into calcium sulfate, which falls out the bottom of the spray dryer.

In a cellulosic ethanol plant of this capacity, carbon monoxide is assumed to be generated at a rate of 0.31 kg/MWh, nitrogen oxide (Nox) is generated at 0.31 kg/MWh. NOx formation is a complicated mechanism and depends on the feed, combustion temperatures, excess air rate, combustor design, and the presence of flue gas cleanup devices like flue gas desulfurization [5].

Additionally, according to the NREL proposed design of the combustor-boiler system, of the superheated steam leaving the boiler, 12% is extracted from the turbine at 175 psig (13 atm) and 268°C (514°F) for feeding to the pretreatment reactor and the boiler feed water economizer. An additional 35% is extracted at 125 psig (9.5 atm) and at 164°C (327°F), which is used in the distillation and in the deaerator. The rest of the steam is condensed at −13 psig (0.1 atm). The condensate is pumped back to the boiler.

Studies on Development of Hybrid Systems for Ethanol Distillation

Even though distillation and dehydration are well tested and mature technologies, there is plenty of room for further improvements. One major drawback in current technology is the amount of energy required to distill ethanol out of beer, which normally contains only 10–12% ethanol and yet can be as high as 40% of the energy content of the ethanol [6]. Therefore, energy saving improvements in distillation is still a high demand research area. Several interesting developments are reported in recent literature providing insight into new directions in ethanol distillation research. Much of the new research on ethanol distillation is in application of pervapora-tion techniques, or incorporation of pervaporation into distillation.

Pervaporation is a method for separation of liquids by partial vaporization through a membrane. This technique allows preferential vaporization of the more volatile component, which is ethanol, and therefore pervaporation is less energy consuming than straight distillation. Many research groups have attempted to develop hybrid systems with pervaporation and distillation. Generally, two types of hybrid processes have been investigated. Several studies have attempted to generate optimal designs for using pervaporation as the dehydration stage following distillation. Other studies have integrated the pervaporation process directly with other separation processes using complex recycle streams and energy integration. Progress in this area till 1999 has been reviewed by Lipnizki et al. [7]; different approaches to integrate pervaporation with etha-nol distillation process is included in their review paper. Then in 2010, Frolkova and Raeva provided a comprehensive review of methods available for ethanol dehydration [8]. Their discussion also included a hybrid pervaporation-distillation process for breaking the ethanol-water azeotrope. The applications of optimization methods for the distillation process are rare in the literature reports. However, in one study Szitkai et al. attempted to optimize the performance of a hybrid distillation-pervaporation process for ethanol separation [9]. Their study employed a mixed-integer nonlinear programming (MINLP) approach to minimize the total annual cost.

Various approaches for integration of pervaporation for the recovery of biomass

fermentation products are reviewed in a 2005 review article [10]. The review also presented several original processes employing both hydrophobic and hydrophilic membranes in conjunction with distillation to improve process efficiency. More recently, this group proposed an innovative process which com-bines distillation and vapor permeation to improve process energy efficiency [11, 12]. Several variations were proposed but the general idea was to exploit the selective nature of the vapor permeation membrane together with vapor compression to improve separation performance and reduce energy load. Then, Del Pozo Gomez et al. proposed a novel pervaporation process, in which both vapor and liquid streams were fed to a modified pervaporation module [13, 14]. The vapor and liquid phases were separated by a conductive wall and only the liquid was exposed to the membrane surface. As the liquid permeates through the membrane, heat is lost. Conventionally, this would cause a temperature drop, decreasing the permeation flux. However, in the proposed process, the heat lost due to permeation is supplied by the partial condensation of the vapor stream.

There are few examples of similar approaches; in one case Fontalvo et al. suggested that a two-phase vapor–liquid mixture be contacted directly with a membrane surface [15, 16]. Again, the goal was that condensation of the vapor should provide energy to augment the pervaporation process. Further, the presence of both phases would increase the turbulence at the membrane surface, thereby decreasing concentration polarization effects.

In another example, Haelssig and coworkers proposed a hybrid membrane separation system to replace the rectifying column and dehydration system in the ethanol recovery process [3]. A schematic representation of this separation system is shown in Figure 4.

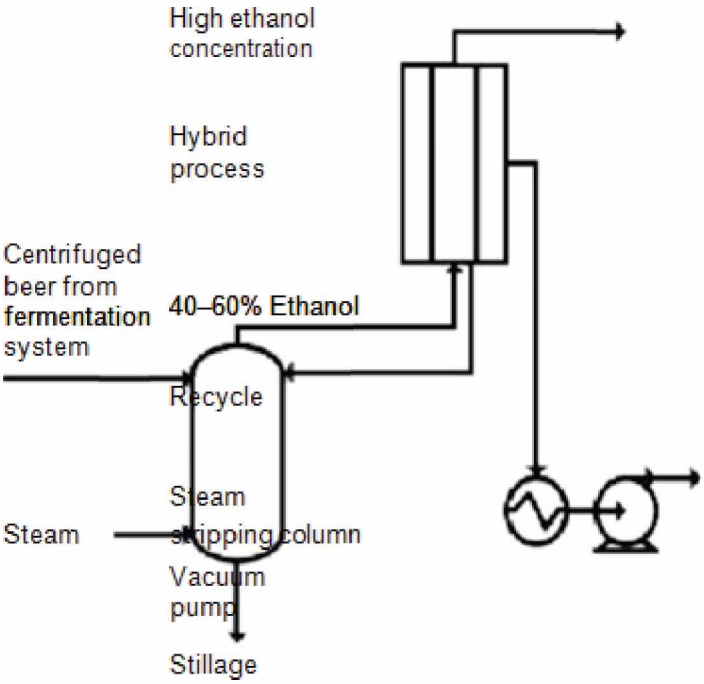

Figure 4 Overview of the proposed hybrid separation process. (Adapted with permission from reference [3]; copyright 2012 Elsevier).

In the new process, the vapor stream leaving the beer column enters the bottom of a vertically oriented membrane unit and flows upwards through the module. As in a rectifying column, the vapor partially condenses and refluxes in the system at the top of the membrane unit. The liquid reflux flows down the sur-face of the membrane through the action of gravity. This leads to countercurrent contacting of the vapor and liquid phases, allow-ing enrichment of the volatile components in the vapor phase. A vacuum is maintained on the permeate side of the membrane to keep a driving force for the selective pervaporation of water. The pervaporation process is associated with a heat loss, since the permeating species must be vaporized. Thus, an energy flux also drives the partial condensation of the vapor phase. Clearly, the process includes aspects of distillation, dephlegmation and pervaporation. For this reason, the process will be referred to as membrane dephlegmation.

Haelssig and coworkers anticipated that the membrane dephleg-mation process is capable of producing a concentrated ethanol stream above the azeotropic composition. Of course, the combination of the rectifying column and the dehydration system in the conventional separation process also produces dehydrated ethanol. However, two separate units are required and it is expected that the use of a single unit will reduce the capital investment and simplify the whole process [3].

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