

# **Bioethanol : Industrial production process and recent studies**

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## **ABSTRACT**

Because of the recent increase in the gas price and interest in environmental issues, the demand of ethanol as substitute of gasoline is rapidly increasing. Basically, 5 steps are included in ethanol production composed of grinding, cooking, fermentation, distillation, and hydration. In each step, there are several ideas to improve its productivity and benefitability. In this paper, I put some explanation about industrial choice or idea. Also, many new studies are going on such as lignocellulosic biomass, immobilization cell system. While these new studies are very efficient, they are not mature to be utilized for industrial purpose. Also, bioethanol as energy source has some unclear aspects from the stand points of sustainable energy and its environmental stress. In this sense, still, there are so many concerns to clear to make bioethanol a real ideal energy source.

## **KEYWORDS**

Bioethanol, industrial process, sustainable energy source, lignocellulosic biomass, energy balance,

## **INTRODUCTION**

Humans have been producing ethanol for thousands years. According to the time flow, the area of ethanol has been extending dramatically. The very first time, ethanol existed only in alcoholic drinks. After some purification methods were established, the usage of ethanol highly extended. Then, now, ethanol is at the new step. The current increase in the gas price and interest in environmental problems, ethanol becomes highly attractive again. However, to use ethanol as a substitute of gasoline, there are so many problems on it. We have to establish large industrial ethanol plant. Also, an increase in the productive efficiency will be required. On this stand point, in this paper we examine the industrial process of ethanol production and the new studies to achieve more effective production. Also, we discuss its effectiveness from stand point of energy balance and environment issues.

## **1. PRODUCTION PROCESS**

For production process, I referred the Kohl's article.

### **1.1 Grinding Grain**

First, starch should be exposed from the peel of corn to contact with water. Also, grinding makes corn small pieces, which can increase its surface area. Then, the increase in its surface area can enhance the contact between starch and water. Two types of mills, a roller mill and a hammer mill, are usually employed. For an industrial use, a hammer mill is mostly used because of its accuracy and its application for large amount.

A roller mill has some roll pairs consisting of two rollers. Corn is pressed by two rollers and crushed into small pieces. Around the rolls there are some trenches to improve the effectiveness of the crush. Also, the rotating speeds of two rollers are different in order to generate more stress on the corn. Finally, screening is implemented at the bottom of the mill. Then, the fine particles can pass the screen, and the big particles, which cannot match the required size, become the subject of the grinding again.

Although the set up cost of a roller milling is relatively expensive, it consumes less energy than a hammer mill. However, it is less used than a hammer mill in a dry mill industry. There are some reasons. First, the maintenance of the appropriate roller gaps is very costly. Also, a roller mill has a difficulty to grind a small and grain with hard shell such as corn. Thus sometimes, it is not appropriate to grind corn.

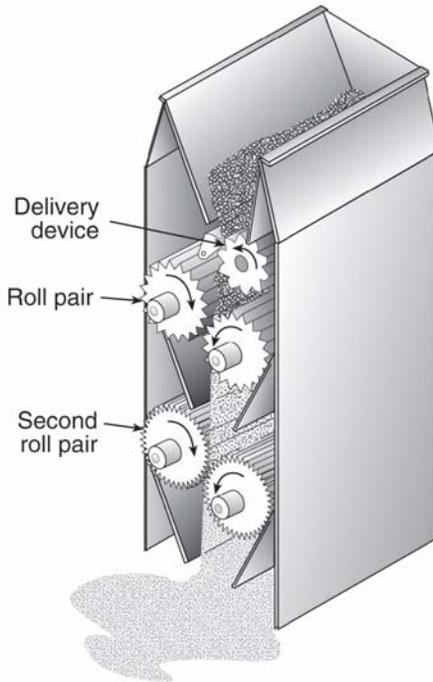


Figure 1 Roller mill (Kohl, 2003)

A hammer mill has several bar-like hammers in it. Rotating hammers hit corn to make them small particles. The rotating speed is set high enough, typically between 190 to 270 mph. The rotating hammers are covered with a screen. Only small particles can pass through the filter, and big particles keep being subject of grinding. Actually, the particle size is decided by the screen size.

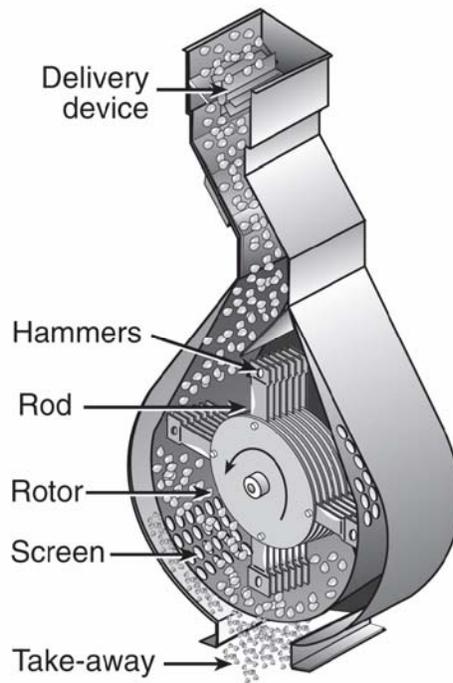


Figure 2 Hammer mill (Kohl, 2003)

The average particular size is very important for the industry because it determine the efficiency of the overall step. Basically, smaller particles are required. Smaller particles can absorb water and gelatinize easily. In other hand, if there are many big particles remain, they can reduce the efficiency. They cannot be saccharized on schedule, which means they will not be fermented. These big particles will be just impurities in the final product. In this sense, making same size particles is very significant. Also, small particles can increase the density of the dried distiller's grains with soluble (DDGS). This high density provides more effective transportation cost.

## 1.2 Cooking

There are so many parameters which can affect the enzymatic activities. To achieve the most effective productivity, the appropriate parameters, which can maximize the enzymatic activities and minimize the cost, are required. In an ethanol industry, the most closely controlled parameters are temperature and pH. Basically, the higher temperature gives the higher productivity. However, above a certain temperature, the enzyme starts loosing its activity. This is because the protein form of the enzyme is broken by the heat. Also, an enzyme has an optimal pH range. In the range, the enzyme shows the high production. However, if the pH changes drastically from the range, the enzyme looses its activity again. This phenomenon is same as one with high temperature, that is to say, the extreme pH can break enzyme formation and it cannot be recovered.

At the grinding step, the outer shell of grain is almost completely removed. Also, this step increases the surface area of each particle. These results make water penetrate through grain easily. However, there is still some undesirable area, which is hard to absorb water. To achieve effective enzymatic action, this micro-crystalline area should be removed. This is typically accomplished with two hot water processes. First, grain is treated with hot water, typically 85°C for between 20 to 60 minutes. Then, super heated water, typically 110°C, is introduced with high pressure.

With the first mixing with hot water, the starch absorbs water. Then, the structure of the micro-crystalline area becomes weak. Then, after introduction of super heated water with high pressure, this area is completely broken. Without this water treatment, this area cannot be broken, which means the efficiency of the enzymatic action is lost.

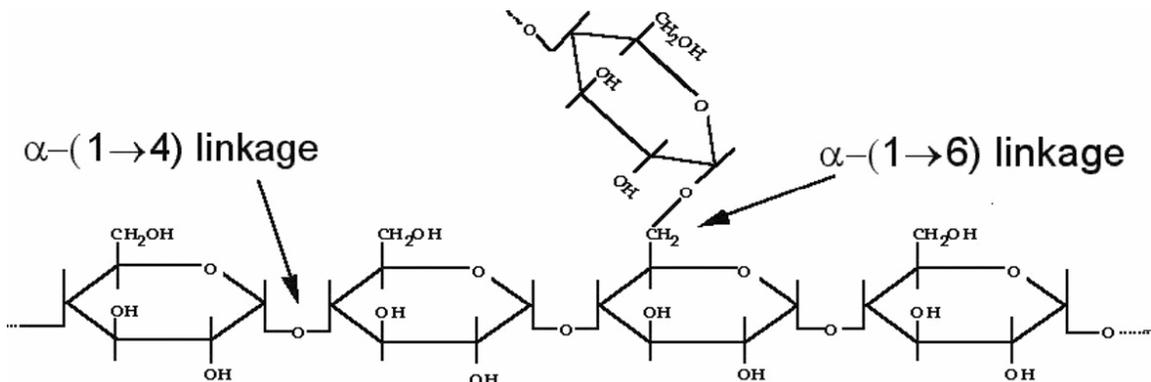


Figure 3 Starches (Kohl, 2003)

As shown in Figure 3, starch is a polymeric glucose. During the cooking step starch is hydrolyzed into fermentable sugars. In an ethanol industry, two enzymes are usually employed, endoenzyme *alpha-amylase* and exoenzyme *glucoamylase*. *Alpha-amylase* attacks the alpha-1, 4 linkages of starch. Then, starch is converted into dextrin shown in Figure 4. The longer incubation time and the higher concentration of *alpha-amylase* make it possible to obtain shorter dextrin with short time.

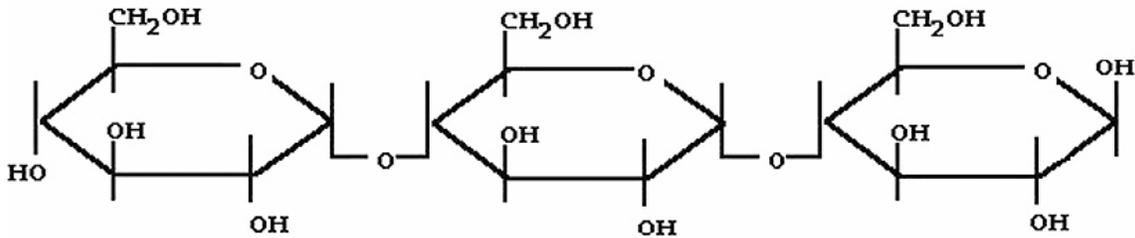


Figure 4 Dextrin (Kohl, 2003)

The length of the dextrin chain is well controlled. This is because it affects the productive efficiency. The shorter dextrin chain causes the lower viscosity. The lower viscosity can reduce the reaction time or electric cost.

After the first hydrolysis with *alpha-amylase*, *glucoamylase* works. *Glucoamylase* removes one glucose from dextrin. Thus, *glucoamylase* cuts linkage of dextrin from its end. This reaction is much slower than *alpha-amylase*. Generally, the enzymatic action of *alpha-amylase* is over 10 times faster than one of *glucoamylase*.

As stated above, *Alpha-amylase* attacks the alpha-1, 4 linkages of starch, so it does not have any effect on 1, 6 linkages. However, this will not be a big problem because the amount of 1, 6 linkages are much less than 1, 4 linkages. When 1, 6 linkages become the subject of hydrolysis, another kind of enzyme is employed.

### 1.3 Fermentation

Yeast is a facultative anaerobe. In an aerobic environment, it converts sugars into carbon dioxide and water. In an anaerobic environment, it converts sugars into carbon dioxide and ethanol. Thus, for an ethanol industry, it is important to exclude significant oxygen from its system.

This fermentation process is relatively slow process, so it is important for an industrial use to make it faster. Usually, a propagation tank is employed. In this tank, mash, water, enzymes, nutrients, and yeast are mixed to re-hydrate the yeast. The purpose of this tank is to get highly activate yeast. Preparing two propagation tanks, the activate yeast can be provided constantly.

If the propagation tank is not employed, a significant time lag will occur in the fermenter. This is very time consuming and causes losing an economical efficiency. Also, a propagation tank has a role to grow yeast in it, so using a propagation tank, producers can save the amount of yeast they have to buy from suppliers.

### 1.4 Stress management

There are some stress factors for yeast which have to be controlled by producers such as sugar concentration, ethanol concentration, temperature, bacterial infection, mycotoxins, and nutrient levels. Yeast is strong enough to tolerate each factor only if the stress is only one for example if the sugar concentration becomes higher than the desired level, the activity of yeast will slow down. However, as soon as the sugar concentration is recovered in the required range, its activity will recover. The most concerning situation is the case that two or more stresses appear simultaneously. In this case, yeast cannot tolerant the environment. The damage on yeast will be significant, which means if the stresses are removed, its activity will not come back again. In this sense, the stress management is very important.

#### 1.4.1 Temperature

Too high temperature kills yeast, and low temperature slows down yeast activity. Thus, to keep a specific range of temperature is required. However, fermentation is exothermic, so in this sense, only a cooling system can be on the issue.

Generally, there are two kinds of cooling systems, external and internal. Although internal cooling systems are easier to keep clean, external systems are usually employed at large facilities because of its large cooling capacities.

### **1.4.2 Sugars and Ethanol**

Simultaneous stresses on yeast should be avoided for fermentation, which means simultaneous increases in sugars and ethanol concentrations are not a good situation for yeast. As one of the way to avoid this situation, sometimes the simultaneous saccharification and fermentation (SSF) method is employed. The main idea of SSF is that as long as saccharification occurs with fermentation, the concentrations of sugars do not increase significantly. In this system an increase in the ethanol concentration can not be avoided, but as long as the stress factor is only one, this is still acceptable.

### **1.4.3 Lactic and Acetic acid**

Lactic and acetic acid are found in fermenter as byproducts produced by contaminated bacteria. Lactic acid is produced by *lactobacilli* bacteria, and acetic acid is produced by *acetobacter* and *gluconobacter* bacteria. These acids can cause loosing activity of yeast with high ethanol and sugars concentrations. To avoid these acids, producers have to remove contaminated bacteria. However, it is very difficult to achieve because the condition suitable for yeast is also suitable for those bacteria. Also, their growth rates are much faster than yeast. Currently, the best way to deal with them is to take care of the temperature and liquefaction very closely and to keep clean all equipments.

### **1.5 Distillation**

After fermentation, we have to make the purity of ethanol higher. Distillation is one of the steps of the purifications. Distillation is the method to separate two liquid utilizing 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, still, there are two materials in both layers, the liquid and the vapor layers.

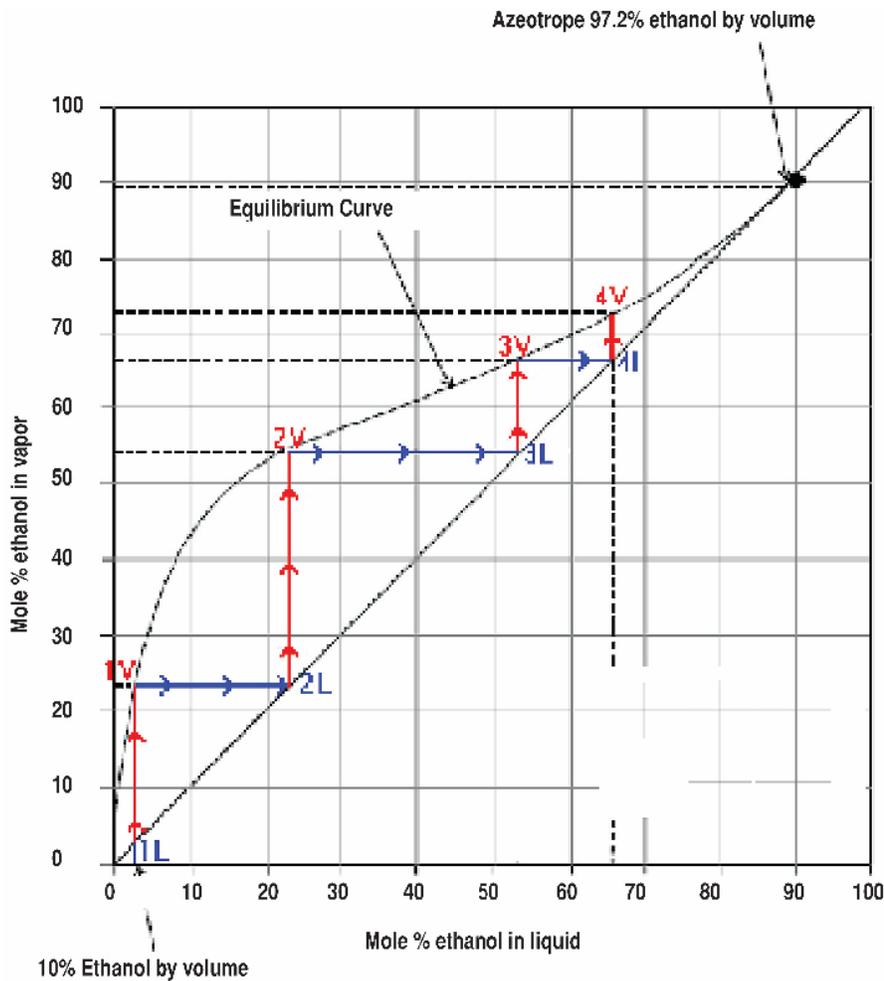


Figure 5 Distillation of ethanol/water system (Kohl, 2004)

Figure 5 shows a schematic distillation step. Let's say first, we have 10% v/v ethanol (1L on Figure 5). With distillation we can get vapor in which ethanol concentration becomes higher (1V). Then, we have to cool it down (2L). Now, we can get much higher ethanol concentrated liquid. With repeating this step (2L, 2V, 3L...), we can get more pure ethanol. After 20 to 24 steps, we can get 95% ethanol. However, theoretically, we cannot get more than 97.2% pure ethanol with distillation. This is because of the intermolecular interactions.

Since distillation process is the process of the multiple vaporization and concentration, it burdens on the cost. One of the factors which can save this cost is the initial concentration of ethanol. In this sense, to keep cost cheaper, some effort is required on the fermentation step.

## 1.6 Dehydration

As stated above, after traditional 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 for example ethanol and gasoline are mixed, 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.

### 1.6.1 Azeotropic distillation

In azeotropic distillation, a third chemical, called entrainer, is added into solution. In this ethanol case, usually benzene or cyclohexane is chosen. An entrainer has a strong chemical interacts with the chemical

which we want to separate. Thus, when an entrainer is introduced into solution, three phases appear. In the case of ethanol and water, one layer is almost pure water, another is pure ethanol, and the other is the mix of three compounds. However, some problems are included in this method. First, it is complicated. Next, it is easy to contaminate objective compounds with the entrainer. Also, safety issues of the entrainer remain such as flammability or toxicity.

### **1.6.2 Molecular sieves**

For the dehydration purpose, zeolite molecular sieves are usually employed. Molecular sieves have many pores. While the entrance of the pore is small, the inside of it is relatively large. The pore size of the molecular sieves used for ethanol dehydration is generally around 3 Angstroms. This is very ideal to dehydrate ethanol because the diameter of ethanol molecule is 4.4 Angstroms, and the diameter of water molecule is 2.8 Angstroms. Thus, this pore can catch water molecules while it cannot catch ethanol molecules.

Also, this reaction is not chemical reaction, so the regeneration of molecular sieves is relatively easy. The regeneration can be achieved by heating or low pressure.

In the ethanol industry, superheated 190 proof ethanol is passed through molecular sieves. If the pores are fully occupied with water, the superheated ethanol is sent to another molecular sieves tank, and the occupied molecular sieves are exposed under low pressure to regenerate.

While molecular sieves have more advantages than azeotropic distillation, still some problems remain. First, it requires high energy, which means it is costly. Also, high pressured ethanol is very flammable.

## **2. Lignocellulosic biomass**

So far, I stated about ethanol production from starch such as corn. However, the production process varies according to the materials. For example, for glucose from sugar cane or molasses, pretreatment step can be very simple because it does not require saccharification. In the other hand, for lignocellulosic biomass from bagasse, wheat straw, wheat husk, or wooden waste, one more pretreatment, solubilization of cellulose, is required. It is clear that in the future, the bioethanol from lignocellulosic biomass is getting more important from the environmental standpoint. This is because corn and sugar are food, but most of lignocellulosic biomass is not eatable. Many researchers are looking for new utilizations of this biomass. As one of these, the research for the pretreatment for lignocellulosic biomass is very active.

### **2.1 Acid treatment**

The one of the most common chemical pretreatment is adding sulfuric acid. There are lignin-hemicellulose networks in cellulose fibers. This network interrupts the enzymatic biodegradation of cellulose. To achieve more effective enzymatic hydrolysis, this network should be removed. In this sense, sulfuric acid can resolve hemicelluloses and activate the enzymatic activity to cellulose. Also, there are some advantages such as low cost and high reaction, and no acid-recovery system required (Esteghlalian et al., 1996).

### **2.2 Alkaline treatment**

Alkaline is also used to treat lignocellulosic biomass. In the case of pretreatment of corn stover by aqueous ammonia, 70-85% lignin was removed, and 40-60% of hemicelluloses were solubilized (Kim et al., 2003). The characteristic of alkaline treatment is that it can remove the lignin without having big effects on other components (McMillan, 1996).

### **2.3 Thermal treatment**

In many case, acid treatment is along with steam treatment. The purpose of steam treatment is to break the plant cell wall, which can interrupt enzymatic biodegradations. In this sense, it seems like that the higher temperature gives the better results. However, it is not simple. In the case of steam pretreatment of SO<sub>2</sub>-impregnated mixed softwoods (Stenberg et al., 1998), the sugar yield is increasing with the increase in

temperature until 210 °C. However, ethanol production is decreasing with the increase in temperature. They concluded this is because of the by-products as inhibitors. Therefore, the operating parameters should be chosen very carefully.

### 3. Immobilized cell system

Immobilized yeast cell system provides a high density in the reactor. This enables high flow rate and short time operation. It can be a big economical advantage. However, not so many immobilized systems are employed into the ethanol industry. This is because this system still has some weakness for example this system can change the yeast characteristic, it may affect on the flavor, and there are still some engineering problems. However, many researchers are working on this issue.

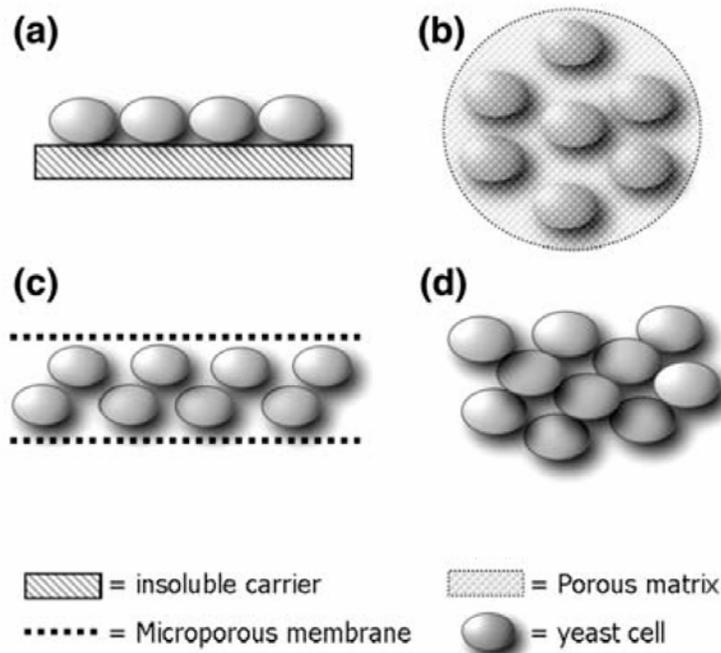


Figure 6 immobilization methods: (a) “attachment to a surface, (b) entrapment within a porous matrix, (c) contaminant behind a barrier, (d) self-agitation (Verbalen et al., 2006)

As one example of the entrapment within a porous matrix, a research shows that immobilized yeast by carrageenan produce ethanol 11.5 times higher than the free cells (Nigam, 2000).

#### 4. Energy balance of bioethanol

Table 1 Energy balance of bioethanol (Shapouri et al., 2003)

Study (year)	Corn Yield (t/ha)	Nitrogen Fertilizer Application Rate (kg/ha)	Nitrogen Fertilizer Production (MJ/kg)	Corn Ethanol Conversion Rate (L/kg)	Ethanol Conversion Process (MJ/L)	Total Energy Use <sup>[a]</sup> (MJ/L)	Coproducts Energy Credits <sup>[a]</sup> (MJ/L)	Net Energy Value <sup>[a]</sup> (MJ/L)
Pimentel (1991)	6.90	152	17.97	0.373	20.54	36.52 (LHV)	5.99	-9.34
Pimentel (2001)	7.97	145	16.05	0.373	20.94	36.53 (LHV)	5.99	-9.35
Keeney and DeLuca (1992)	7.47	151	18.16	0.381	13.51	25.42 (LHV)	2.25	-2.35
Marland and Turhollow (1990)	7.47	142	14.90	0.373	13.97	20.61 (HHV)	2.27	5.06
Lorenz and Morris (1995)	7.53	138	13.21	0.380	15.04	22.6 (HHV)	7.69	8.53
Ho (1989)	5.65	NR	NR	NR	15.89	25.09 (LHV)	2.93	-1.11
Wang et al. (1999)	7.84	147	10.09	0.380	11.39	19.08 (LHV)	4.17	6.27
AAFC (1999)	7.28	140	NR	0.401	14.05	19.01 (HHV)	3.92	8.31
Shapouri et al. (1995)	7.65	125	10.06	0.377	14.85	23.09 (HHV)	4.2	4.31
This study (2002)	7.84	145	8.80	0.396	14.43	21.53 (HHV)	4.01	5.88

<sup>[a]</sup> The midpoint or average is used when studies report a range of values.  
 LHV Low heat value = 21.18 MJ/L of ethanol. Keeney and DeLuca (1992) used 20.82 MJ/L of ethanol.  
 HHV High heat value = 23.40 MJ/L of ethanol. Lorenz and Morris (1995) used 23.44 MJ/L of ethanol.  
 NR Not reported.

Table 2 Energy balance of bioethanol (Shapouri et al., 1995)

Study/year	Corn yield	Nitrogen fertilizer application rate	Inputs for nitrogen fertilizer	Corn ethanol conversion rate	Ethanol conversion process	Total energy use	Coproducts energy credits	Net energy value
	bu/acre	lb/acre	Btu/lb	gal/bu	Btu/gal	Btu/gal	Btu/gal	Btu/gal
Pimentel (1991)	110	136.0	37,551	2.50	73,687 (LHV)	131,017	21,500	-33,517
Keeney and DeLuca (1992)	119	135.0	37,958	2.56	48,434 (LHV)	91,127	8,072	-8,431
Marland and Turhollow (1991)	119	127.0	31,135	2.50	40,105 (HHV)	73,934	8,127	18,324
Morris and Ahmed (1992)	120	127.0	31,000	2.55	46,297 (LHV)	75,297	24,950	25,653
Ho (1989)	90	NR	NR	NR	57,000 (LHV)	90,000	10,000	-4,000
This study (1995)	122	124.5	22,159	2.53	53,277 (HHV)	82,824	15,056	16,193
Average	113	129.9	31,961	NA	NA	NA	NA	2,373

Where HHV means “High heating value, which is the standard heat of combustion referenced to water of combustion as liquid water,” and LHV means “Low heating value, which is the standard heat of combustion referenced to water of combustion as water vapor.”

Table 1 and Table 2 show the energy balance of ethanol made from corn. Net energy value (NEV) is defined as “energy converted into ethanol or its coproducts minus energy used to produce ethanol.” Thus, if NEV is negative, which means we are losing energy by making ethanol. This is very important value for fuel ethanol. If producing fuel ethanol from corn is just energy consuming, there is no reason to keep producing. Actually, this issue is very controversial. The result is changing depending on the researchers or methods. This is because each assumption of researches is not always same.

First, according to the time of the research, some technologies are improving for example the corn yield is changing drastically. Ho reports 90 bushels/acre of corn yield in 1989, but the corn yield is improving to

122 bushels/acre in 1995. Fertilizer also is improving its efficiency. Its input and application rate tend to decrease.

Also, assumptions about ethanol conversion are very different among the studies. On Table 2, while the highest conversion is 78367 Btu/gallon, the lowest is 40105 Btu/gallon.

In addition, some coproducts, such as distillers' dried grains with soluble (DDGS), corn gluten meal (CGM), and corn gluten feed (CGF), contribute this difference. Some researchers include these coproducts in their calculation, and some do not (Shapouri et al., 1995). Therefore, currently, there is no clear conclusion about bioethanol energy balance. However, the overall NEV tends to increase (Figure 7).

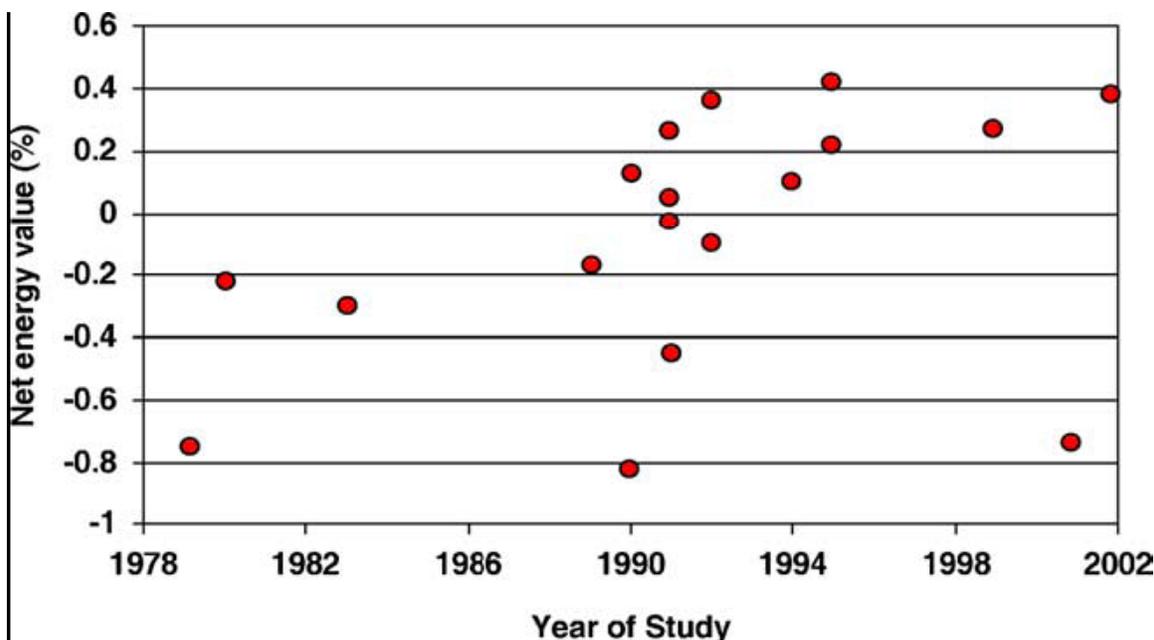


Figure 7 the change in the Net energy value calculations (Niven R.K., 2005)

Thus, we can imagine NEV may be positive with any calculation in the future with developments of the new technologies.

Besides, currently, while we are not sure the energy balance of bioethanol, it is also true. We can convert energy from domestic sources, such as coal and natural gas, into a high value liquid fuel that can reduce the usage of petroleum.

### 5. Negative sides of bioethanol

So far, I was trying to say the benefit of bioethanol. However, as everything has some negative side, bioethanol has also some deficit. Figure 8 shows some environmental impacts of ethanol in gasoline. Although, some of them may be exaggerated, but this approach is very important when we are considering bioethanol from overall environmental aspects. Corn production causes more soil erosion and uses more herbicides and insecticides. Also, wastewater from ethanol plant is also another big problem.

In addition, an increase in the demand of bioethanol may burden on our money. This is because, currently, ethanol production is supported by huge subsidies coming from our tax. Besides, an increase in the ethanol production means an increase in the demand of corn (Pimental D., 2003). This may cause an increase in the corn price. Today, corn is everywhere in our meal.

Therefore, there are still so many concerns to say bioethanol is a real ideal energy source.

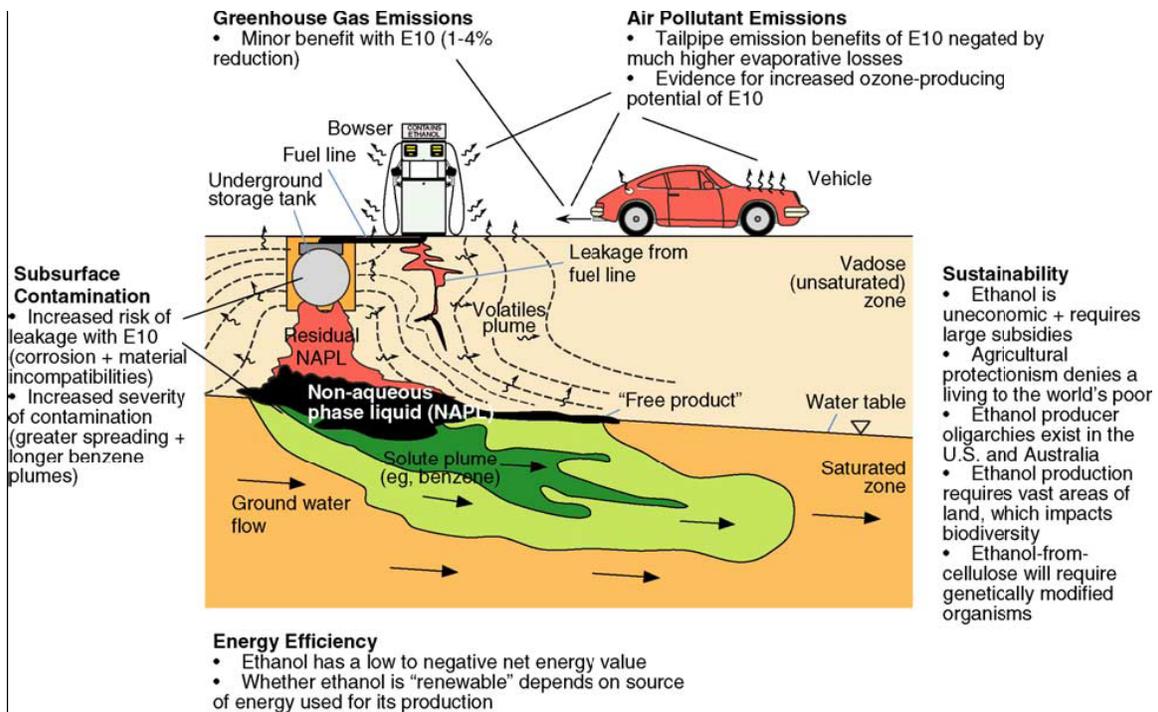


Figure 8 Environmental impacts of ethanol in gasoline (Niven R.K., 2005)

## Conclusion

I examined the bioethanol production process and its energy and environmental aspects. So many techniques are used in the industrial ethanol production process. However, the biggest concern of the process is its cost. A lot of researchers are working on bioethanol to improve its productive efficiency. Also, some of new technologies are very effective, but for industrial use, the balance between the cost and the effectiveness is very important.

On the other hand, the energy balance bioethanol is another big issue. The energy balance of bioethanol is not still very clear because of the differences among the each calculation method. However, it is true that the energy balance is improving according with time.

Unfortunately, not all aspects of bioethanol are positive. There are so many environmental concerns. Thus, to say bioethanol is a real ideal energy source, we have to solve various problems.

## Reference

- Esteghlalian, A., Hashimoto, A.G., Fenske, J.J., Penner, M.H. (1997) Modeling and optimization of the dilute-sulfuric-acid pretreatment of corn stover, poplar and switchgrass. *Bioresource Technology*, **59**, 129
- Kim, T.H., Kim, J.S., Sunwoo, C., Lee, Y.Y. (2003) Pretreatment of corn stover by aqueous ammonia. *Bioresource Technology*, **90**, 39
- Kohl, S. (2003, 2004) Technical Connections. Ethanol today
- McMillan, J.D. (1997) Bioethanol production: status and prospects. *Renewable Energy*, **10**, 295
- Nigam, J.N. (2000) Continuous ethanol production from pineapple cannery waste using immobilized yeast cell. *Journal of Biotechnology*, **80**, 189
- Niven, R.K. (2005) Ethanol in gasoline: environmental impacts and sustainability review article. *Renewable and Sustainable Energy Reviews*, **9**, 535
- Pimental, D., (2003) Ethanol Fuels: Energy Balance, Economics, and Environmental Impacts are Negative. *Natural Resources Research*, **12**
- Shapouri, H., Duffield, J.A., Graboski M.S. (1995) Estimating the net Energy Balance of Corn Ethanol. *An Economic Research Service Report*
- Shapouri, H., Duffield, J.A., Wang, M. (2003) The Energy Balance of Corn Ethanol Revisited. *American Society of Agricultural Engineers*, **46**, 959
- Stenberg, K., Tenborg, C., Galbe, M., Zacchi, G. (1998) Optimization of Steam Pretreatment of SO<sub>2</sub>-impregnated Mixed Softwoods for Ethanol Production. *J. Chem. Technol. Biotechnol.*, **71**, 299
- Verbelen, P.J., De Schutter, D.P., Delvaux, F., Vestrepin, K.J., Delvaux, F.R.(2006) Immobilized yeast cell systems for continuous fermentation applications. *Biotechnol Lett*, **28**, 1515