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# Agri-Fuel Potentials of Butanol/Acetone Production:

## An Alternative to Ethanol for a Gasoline Substitute

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### Abstract

Butanol and acetone can be produced via a fermentation process similar to ethanol. Whereas ethanol fuels require strict observance of federal and state alcohol laws, butanol and acetone are not so regulated. These and other advantages may make the production of butanol/acetone fuels an alternative choice for a gasoline substitute.

### 1. INTRODUCTION

One of the problems of producing ethanol via the fermentation method is that the resulting ethanol is in an aqueous solution. To be useful, the ethanol and water must be separated. This is usually done by distilling off the ethanol, which is an energy intensive process. For example, to distill one liter of ethanol suitable for gasohol requires  $0.80 \times 10^7$  joules of energy in a well engineered, efficient system. One liter of ethanol contains  $2.35 \times 10^7$  joules of combustible energy. Therefore for each resulting 100 units of energy inherent in the ethanol it takes 34 units of energy to separate it from the water.

To solve the problem of intensive energy requirements for separation, there have been several avenues of attack. One has been to improve the efficiency of the distillation process. However, there is a thermodynamic limit for improving this efficiency. As the theoretic limit of efficiency is approached, the subsequent costs in hardware will escalate rapidly.

### 2. REGULATION

Another approach to improve the ethanol production efficiency has been to use distillation in combination with concentrating solar collectors, so that the distillation energy is "free". However, this greatly increases the initial equipment capital costs. In order to maintain control of the distillation process, a large high temperature thermal storage system is required.

Still another approach has been to make more efficient use of the ethanol by-products. By improving the useful value of the by-products (usually used as a protein source for feeds) the distillation costs can be compensated.

While all these approaches are useful and productive they serve only to minimize the costs of distillation; they do not eliminate them. This is because inherently water and ethanol are totally miscible in one another. In other words, they mix so well that distillation has been the only practical way to separate them. This is a basic limiting energy constraint of the present ethanol production process of distillation.

Another important constraint on ethanol production is that of regulation. The Bureau of Alcohol, Tobacco and Firearms, a Federal agency, is responsible for the regulation and monitoring of all ethanol production in the United States. There also exists a number of State and local agencies which also regulate and monitor ethanol production. These various agencies have been set up to basically monitor the production of beverage grade ethanol. While some ethanol plants are now being set up to produce fuel grade ethanol, which is not the same as beverage grade quality, nonetheless the same regulations presently apply to both methods and can create administrative difficulties. The problems lie in the fact that beverage quality ethanol production and distribution may differ significantly from fuel grade ethanol.

### 3. TRADITIONAL ETHANOL

The choice of ethanol has been one of tradition, rather than one of optimization. The dual use of ethanol as beverage and fuel has allowed the convenience of a single technology to be used for both purposes, which is not necessarily an optimized choice as far as energy production is concerned. The economic constraints to optimize ethanol production as a beverage are not used necessarily the same constraints that apply to ethanol as a fuel. While ethanol can be used as a fuel, it is not necessarily the optimum fuel choice to be produced from agricultural resources. There exists a number of combustible chemicals which should be considered which can be produced via fermentation that offer improved fuel characteristics over ethanol and improved production characteristics over ethanol.

The following is an examination of one of these other choices, namely the production of n-butanol and acetone from agricultural resources.

### 4. N-BUTANOL FERMENTATION

The organism called *Clostridium acetobutylicum* converts hexose sugars into n-butanol, acetone, and ethanol in ratios of 6:3:1 respectively. This is done in a process similar to methane digestion in that *Clostridium acetobutylicum* is an anaerobic bacterium. This means that it lives in the absence of free oxygen. Other by-products of this anaerobic digestion are carbon dioxide gas, hydrogen gas, and protein enriched stillage, more or less identical to the stillage obtained from ethanol production.

In Table 1 are shown the comparative physical characteristics of ethanol, acetone, and n-butanol. The specific gravities of all three are very close, less than 3%

different. However, due to the increased molecular size, acetone and n-butanol have respectively 11% and 24% more heats of combustion per liter than ethanol. As a comparison, note that gasoline has a heat of combustion of  $3.45 \times 10^7$  joules per liter. While ethanol has a combustion value 32% lower than gasoline, acetone and n-butanol are only 24% lower and 15% lower respectively.

TABLE 1. COMPARISONS OF ETHANOL,  
BUTANOL & ACETONE

|   | <u>Ethanol</u>                 | <u>n-Butanol</u>              | <u>Acetone</u>                |
|---|--------------------------------|-------------------------------|-------------------------------|
| Specific gravity<br>(water = 1.000)       | 0.789                          | 0.810                         | 0.790                         |
| Boiling point                             | 78.5°C                         | 117.25°C                      | 56.2°C                        |
| Freezing point                            | -117.3°C                       | -89.5°C                       | -95.4°C                       |
| Molecular weight                          | 46                             | 74                            | 58                            |
| Heat of combustion<br>(@ 20°C, 1<br>atm.) | 2.35 x<br>10 <sup>7</sup> j/l* | 2.92 x<br>10 <sup>7</sup> j/l | 2.61 x<br>10 <sup>7</sup> j/l |

\* joules per liter, 100% pure substance

In Table 2 are shown the fuel products of ethanol fermentation and n-butanol/acetone production. While ethanol production produces 25% more liquid volume, it produces only 6% more liquid fuel value. However when the energy of the hydrogen gas is included into this energy ledger we find the fuel energy output of ethanol production and the total fuel energy output of butanol production are nearly identical.

It is important to note the quality of the fuels produced in the two different fermentation processes. According to a number of tests performed by the National Bureau of Standards in 1945, butanol/acetone fuel combinations have fuel characteristics in the middle ground between ethanol and gasoline.\*\* This would make butanol/acetone fuels a more reasonable alternative fuel choice for engines originally designed for gasoline consumption.

\*\* Journal of Research of the National Bureau of Standards, Volume 35, December 1945, "Utilization of Non-Petroleum Fuels in Automotive Engines", by Jesse Duck and Clarence Bruce, Research Paper #RP 1681.

TABLE 2. RELATIVE ENERGY PRODUCTION FROM  
1 BUSHEL OF CORN

ETHANOL FERMENTATION

|                                      |                            |
|--------------------------------------|----------------------------|
| Combustable products of fermentation | 11.4 liters ethanol        |
| Combustion value                     | $26.79 \times 10^7$ joules |

n-BUTANOL FERMENTATION

|                                      |  |
|--------------------------------------|--|
| Combustable products of fermentation | 5.47 liters n-butanol                                |
|                                      | 2.74 liters acetone                                  |
|                                      | <u>0.91 liters ethanol</u>                           |
| Subtotal                             | 9.12 liters liquid fuel                              |
|                                      | 0.27 kilograms of hydrogen gas                       |
| Combustion value                     | $15.97 \times 10^7$ joules n-butanol                 |
|                                      | $7.15 \times 10^7$ joules acetone                    |
|                                      | $2.13 \times 10^7$ joules ethanol                    |
|                                      | <u><math>0.85 \times 10^7</math> joules hydrogen</u> |
| TOTAL                                | $26.10 \times 10^7$ joules                           |

In Table 3 are shown the solubilities of acetone, ethanol, and n-butanol in water. Of the three substances, ethanol and acetone are completely miscible in water. However, n-butanol is only slightly soluble in water. Once the water has become saturated with n-butanol, the remainder will layer out and float on the top. This effect can be enhanced by "salting out" the alcohol. That is, by adding salt, sodium chloride, the solubility of butanol in water is further decreased. When this happens, the butanol will layer out at 160 proof and float on top of the solution.

TABLE 3. SOLUBILITY

| <u>Substances</u>         | <u>Miscibility</u>               |
|---------------------------|----------------------------------|
| Ethanol in water          | in all proportions               |
| Acetone in water          | in all proportions               |
| n-butanol in water (20°C) | <u>Water layer</u> - 92.2% water |
|                           | 7.8% n-butanol                   |
|                           | <u>Alcohol layer</u> -           |
|                           | 20% water                        |
|                           | 80% n-butanol                    |

At 160 proof (80% n-butanol, 20% water) n-butanol has an approximate combustion value of  $2.41 \times 10^7$  joules per liter and a specific gravity of 0.842. In other words, the heat of combustion for 160 proof n-butanol is about equal to 200 proof ethanol. In an internal combustion engine this water may be useful to help minimize temperatures to help reduce NO<sub>x</sub> emissions.

The bacterium that accomplishes this conversion is often found in farmyard soils. Clostridium acetobutylicum (and also Clostridium sacchrobutyl acetonicum liquefaciens) is closely related to Clostridium botuli, the "bug" that causes botulism poisoning in improperly canned foods. The acetobutylicum is anerobic, grows optimumly at 37°C, and belongs to the family of rod-shaped motile bacteria.

To ferment starches to n-butanol, the corn is prepared up to the point of yeast inoculation identical to ethanol production methods. In other words, if materials containing starches are used, the starches have to be hydrolized into sugars. After saccharification is complete, the acetobutylicum is added to the mash with ammonia nitrogen, and the mash is covered to prevent oxygen poisoning, much like a methane generator. Fermentation then proceeds while the mash is maintained at proper temperature and ph for approximately 48 hours.

## 5. RECOVERY OF PRODUCTS

Recovery of the fermentation products can be accomplished in several ways. The traditional technique is by fractional distillation. However, for fuel purposes, the fractional distillation need not proceed along conventional lines. In other words, it is not necessary to produce pure n-butanol, pure acetone, or pure ethanol thru an extensive fractional distillation process. As long as most of the water is removed, the relative impurities are unimportant.

Another method of recovery which may be utilized is that of the molecular sieve. Zeolite, and other similar materials, allow the smaller water molecules to pass through, but not the larger molecules of butanol, acetone and ethanol. They would be left behind in a liquid mixture, which is fine for fuel purposes.

A third way to recover the products of fermentation is to take advantage of the fact of n-butanol's limited solubility in water. As was mentioned before, in a binary system, water will absorb n-butanol until it is saturated with about 7 - 8% n-butanol. After the water is saturated, any excess butanol will layer out at the top in a 20% water, 80% n-butanol combination. However, in the presence of acetone and ethanol, and a small amount of salt, n-butanol will layer out before saturating the water at the 8% n-butanol level. Thus, a stripper still or pot still could concentrate the n-butanol in solution enough to take advantage of its partial solubility characteristics. This layer of butanol will be 160 proof n-butanol with acetone and ethanol impurities. For fuel purposes, this impure condition of the n-butanol is not a major concern. Thus the n-butanol layer could be decanted off the top of the mash. This is

important because a significant fraction of the fuel produced by the fermentation process might not require distillation to be recovered.

After the butanol layer is decanted, the remaining mash will be made up of acetone, ethanol, water, salt and wet stillage. The acetone then can be distilled out at a very modest energy cost due to the fact that the vapor point of acetone is at 56.2° C. Much less energy is required to distill out acetone as, say for example, ethanol whose vapor point is 78.5°C. The remaining ethanol would be left in solution due to the small amount available for recovery.

## 6. HYDROGEN BY-PRODUCT

One of the interesting facets of butanol production is the hydrogen gas by-product. Both hydrogen and carbon dioxide are gaseous by-products of this fermentation method. Hydrogen will represent approximately 40% of this by-product gas by volume. The energy available in the hydrogen that is given off could be useful in supplementing the energy required to run the system or it could be separated out and sold, depending on the economics. Reference (6) in the bibliography cites these tests.

## 7. HISTORY

Prior to WWII n-butanol was produced on a large scale in the United States specifically in Terra Haute, Indiana and Peoria, Illinois. However at that time it was not valued as a fuel, but rather as a chemical feed stock for rubber production. Prior to that, it was the main source of acetone for explosives for England during WWI. After WWII, petroleum became cheap and plentiful, and the

production of butanol/acetone via fermentation dropped dramatically. So while the production of butanol via fermentation has been a known process since about 1910, the production of butanol as a fuel is a relatively new concept for chemical plant designers.

## 8. SUMMARY

While all the elements of butanol production have worked in and of themselves at various times, they have not yet been melded together into a small scale fuel production system. As has been shown, butanol/acetone fuels offer advantages over ethanol based fuels. Furthermore, there appears to be some system advantages in the recovery of butanol that could be capitalized on in such a fuel production system.

The preceding has been only a general outline of the potentials of n-butanol/acetone production from agricultural resources. I hope that by presenting this information, attention is drawn to the potentials of butanol production for fuel and that the necessary work to refine fuel system production of butanol can be then be undertaken.

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## ABOUT THE AUTHOR

Randall Noon is an Assistant Director of the Kansas Energy Office in charge of the Energy Research and Resource Development Division. He holds BS and MS degrees in mechanical engineering from the University of Missouri, and is professionally licensed both in the United States and Canada. Among others, he is currently involved in a project to set up a mechanized, energy forest plantation in Southeastern Kansas utilizing orphaned strip mined land. Mr. Noon and his family reside in Topeka, Kansas.