Gaia Brief:

Ethanol Quality—Impurities in Distillation that Affect Ethanol as a Fuel

Water

Alcohol at 150 proof is the minimum required to fire a boiler. Alcohol at 170 proof is generally the minimum required to run a generator or an internal combustion engine (Blume, 2007)[1]. A fuel injection system requires at least 185 proof and preferably 192 proof ethanol (Blume, 2007)[2].

The Aprovecho Research Laboratory tests on the ethanol stoves performed for this study (Chapter 5) suggest that while ethanol at 100 proof will ignite, alcohol at 120 to 130 proof is the minimum necessary to support a stable flame and alcohol at 160 proof is necessary to obtain a robust flame).

Aldehydes and Ketones

The presence of these more volatile compounds in ethanol, while usually very low, can be significant if a distillery has not been operated properly or if the concentration of these compounds in the starting material was high. Aldehydes and ketones are generally concentrated in the head or foreshot in batch distillation and come off in the first 15% of the run (Blume, 2007). The head can be collected with the tail, the low wines that are produced at the end of batch distillation, and these can be redistilled to separate more ethanol from the impurities.

In continuous distillation the heads are distilled over into a separate column where they are refluxed. Heavier ethanol is separated from the lighter aldehydes in mid column and returned to the rectification column so as not to be lost. Condensate from the head or foreshot is referred to as high wines.

Industrial grade ethanol requires the separation of these lighter compounds. They do not affect quality or performance for engine fuel and probably would not affect performance for stove fuel, but their presence in the fuel may create the liability of aldehyde and acetaldehyde emissions, in whatever trace amounts that may be produced[3]. Therefore, if possible, these lighter compounds should be separated, if the distillery equipment is adequate to allow this to be easily done.

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[1] David Blume, pp. 196-197.

[2] David Blume, pp. 377.

[3] The Dometic ORIGO stove, precursor to the CleanCook stove, was tested for volatile emissions in the Chemtaur Laboratory in Johannesburg in January, 2002. Industrial grade ethanol was used. Less than 1 ppm/hr of formaldehyde or other aldehydes was detected. Less than 1 ppm of nitrous fumes or NOx was detected. A 35 m^3 room was tightly sealed and tests were conducted burning one- and two-burner stoves sufficient to combust 0.25 litres of fuel in each burner. An uncovered pot of water was placed on each burner. The nitrous fumes as well as carbon monoxide and carbon dioxide were determined with Dräger color-tubes. The formaldehyde or aldehydes were determined using a KLM color comparator. After the tests, the room was entered immediately. A slight burning of the eyes and nose was detected, indicating the aldehyde produced was probably acetaldehyde. There was not a detectable difference in the results of the two-burner test compared with the one-burner test with regard to aldehydes and nitrous fumes. The short term exposure limit (STEL) for formaldehyde is 2 ppm and for acetaldehyde is 150 ppm.

Acetic Acid

In bad fermentation batches, undesirable bacteria may produce high amounts of acetic acid, which has a low enough boiling point to be distilled with the last part of a run in batch distillation. High acetic acid together with low proof creates a corrosive fuel. If the alcohol is below a pH of 6.0 this is known to be acidic enough to cause problems in auto engines. For this reason, it is standard procedure to neutralize mash to pH 7.0 before distillation by adding lime.

Fusel Oil

Fusel oil is a mixture of higher alcohols such as amyl, isoamyl, propyl, isopropyl, butyl and isobutyl alcohols and acetic and lactic acids. The term fusel is German for "bad liquor". During distillation, fusel alcohols are concentrated in the "tails" at the end of the distillation run. They have an oily consistency, which is noticeable to the distiller, hence the term fusel oil (Blume, 2007).

Fusel oil production is affected both by fermentation and distillation. The quality and quantity of fusel oil generated during alcohol production depends on type and method of preparation of mash used for fermentation, condition and environment under which fermentation proceeds, choice of enzymes and method of removal of fusel oil during distillation. The yields of fusel oil obtained in a commercial plant may vary between 0.1% and 1% of alcohol produced on an absolute basis. Wheat or potato mash yield higher amounts of fusel oil than molasses or sugar cane juice. Fusel oil is a product with its own value. Esters obtained from alcohols of fusel oil can be used industrially as solvents, extractants, flavoring agents, plasticizers and for medicinal and perfume use (Güvenç, et al, 2007)[4].

While acetic acid can be corrosive, the various esters that comprise fusel oil are known to deposit gum or carbon on valves in automobile engines.

In the CleanCook stove pilot studies in Ethiopia, it was noticed that alcohol high in ester created problems with the fiber-filled fuel canister, leaving an oily crust of unburned carbon on the top of the exposed fiber at the mouth of the canister, which became progressively worse over several months of use of the contaminated fuel. This occurred with alcohol delivered to the Shimelba Refugee Camp from Finchaa Sugar Factory (Egziabher, et al., 2006)[5]. This layer of carbon inhibited the evaporation of alcohol from the canister, impeding the function of the canister by reducing the flow of fuel into the stove combustion chimney. After four to five months, these fuel canisters had to be replaced (Egziabher, 2006).

This report is available at http://www.projectgaia.com/page.php?page=resources.

[4] Güvenç, A., Kapucu, N., Kapucu, H., Aydoğan, Ö., Mehmetoğlu, Ű., 2007. Enzymatic esterification of isoamyl alcohol obtained from fusel oil: Optimization by response surface methodology, Ankara University, Ízmit-Kocaeli, Turkey, in Enzyme and Microbial Technology 40 (2007), pp. 778–785.

[5] Egziabher, A., Murren, J., O'Brien, C., An Ethanol-fueled Household Energy Initiative in the Shimelba Refugee Camp, Tigray, Ethiopia: A Joint Study by the UNHCR and the Gaia Association, January 2006, available at http://www.projectgaia.com/page.php?page=resources.

Figure 6: Compromised canister

Compromised CleanCook fuel canister, Shimelba Camp, 2006. Ethanol laden with fusel oil created an oily carbon build-up over a period of three to four months. More than normal amounts of fusel oil were detected in the ethanol fuel. The top of the canister was removed for this photo (Gaia Association).

In continuous distillation, fusel oil is extracted from the distillation column at the plate or level just above where its boiling point is achieved. Normally, fusel oil is harvested for sale as its own product. When the Gaia engineers questioned the Finchaa distillery about the apparent high fusel oil content of the alcohol delivered to Shimelba Camp, they learned that the distillery's fusel oil collection system was broken and that the alcohol delivered to them had been contaminated not only with normal trace quantities of fusel oil but also with previously collected fusel oil that had been dumped back into the alcohol to dispose of it. This represented an extreme case of fusel oil contamination. It provided, however, a useful lesson on the effects of fusel oil. When the Gaia engineers tested this contaminated alcohol by burning it on a ceramic plate, they noticed a distinct oily film deposited as a residue on the plate after the alcohol had burned.

Fusel oil may be separated from alcohol by use of a soft-wood charcoal filter. This was a traditional method of purifying beverage alcohols such as whiskey (Cowdery, 1994)[6]. Certain filter media may also be effective. Gaia Association in Ethiopia is researching this approach as a low-cost method for reducing fusel oil contamination of ethanol made in simple stills. Blume mentions commercially available pharmaceutical processors that will remove these impurities (Blume Distillation, 2010)[7].

Another method for removing fusel oil from beverage alcohol is to induce phase separation and to decant it (Guymon, 1958)[8]. A traditional method was to mix olive oil into alcohol and shake it well. Upon sitting, any fusel oil would collect on the surface of the mixture with the olive oil and could be poured off, after which the alcohol would be redistilled to remove the taste of oil (New American Cyclopaedia, 1870)[9].

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[6] Cowdery, Charles K., Whiskey Basics -- The Bourbon Country Reader, Volume 1, Number 5, April 1994, accessed on the web June 15, 2010 at http://home.netcom.com/~cowdery/articles/whiskey.html.

[7] Blume Distillation LLC, Confidential Private Placement Memorandum, February 1, 2010.

[8] Guymon, James F., Principles of Fusel Oil Separation and Decantation, American Society for Enology and Viticulture, 9:2:64-73 (1958).

[9] Dana, George and Charles A., eds., The New American Cyclopædia: A Popular Dictionary of General Knowledge, Ripley, January 1870.

Separating Impurities from Ethanol in the Distillation Process

Although impurities created in the distillation of alcohol are produced in only very small quantities, it is nevertheless desirable to use alcohol relatively free of impurities for household stove fuel use, to minimize the production of trace volatile organic compounds during combustion. This is all the more so because alcohol is easily and efficiently separated from its impurities in a controlled distillation process. Separation of trace contaminants is more easily achieved in continuous distillation. This is done without additional energy inputs, but simply as part of the distillation process. But contaminant-free alcohol can be produced in either batch or continuous distillation.

In batch distillation, impurities that boil below 171 degrees F are separated at the beginning of a run (the head or foreshot). These include aldehydes, ketones and other volatile trace components. Impurities boiling above 173 degrees F, such as fusel oil or higher alcohols, esters and acetic acid are separated at the end of the run (the tail). In quality beverage making, the head and tail of the distillation are rejected and only the “middle cut” is retained.

For fuel production, the tail of the distillation run can be added to the next batch for re-distillation. This is also referred to as the recycling of the “low wines” (Blume, 2007). This reduces the loss of the alcohol.

In the following table, the amount of the ethanol in the mash that is distilled off in the head, the middle cut (or the “heart”) and the tail can be seen. Most of the ethanol comes off in the middle cut (86.6%) but a considerable amount comes off in the head (5.5%) and the tail (5.1%). Thus, if this ethanol is redistilled, more of it is separated successfully from the impurities and less is wasted.

Table 1: Volume and alcohol content distribution in batch distillation

Fraction	Total volume (L)	Alcoholic strength (°GL)	Ethanol volume (L)	Fraction of the volume of alcohol in wine (%)
Original Wine	1000	8.5	85.0	100
Distillate head	7	67	4.7	5.5
Distillate heart	160	46	73.6	86.6
Distillate tail	20	21.5	4.3	5.1
Vinasse	813	0.3	2.4	2.8

In the production of Brazilian cachaça or sugar cane rum, the head and the tail are both discarded, as not suitable for quality cachaça (Maia and Campelo, 2005)[10].

In continuous distillation, impurities with higher boiling points than pure alcohol are taken off in the rectification column at the level where the impurity condenses. In a properly working plate column, the top plate in the column will be at 173 degrees F, the boiling point of alcohol, and the bottom plate in the

[10] Maia, Amazinle Biagione Ribeiro de Abreu, Campelo, Eduardo Antonio Pinto, Tecnologia da cachaça de Alambique, Belo Horizonte: SEBRAE/MG; SINDIBEBIDAS, 2005.

column will be at 212 degrees F, the boiling point of water. Fusel oil will come off at the plate where its boiling point is no longer reached and where it condenses onto the plate. It may be collected from the plate and removed from the distillation column. This is the most consistently effective means for fusel oil separation.

Figure 7: Metahara Distillery Rectifier Column and Fusel Oil Decanter

Figure 7: The rectifier column (left photo) stands between the stripper column and the aldehydes column. On the right side of the rectifier column, outlets at varying heights take off compounds such as the alcohols of fusel oil. The more volatile first fraction (heads) of the distillation is distilled over into the aldehydes column (on right side of photo). The ethanol in the heads is returned to the middle column for further distillation.

Fusel Oil is siphoned from the rectifier column and stored in the fusel oil decanter (right photo) for sale as its own valuable product.