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Dehydration of Ethanol:
New Approach Gives Positive Energy Balance

Abstract. Water was removed from aqueous ethanol by using cellulosic materials, starch, corn, and other agents. The combustion energy of the ethanol product can exceed the energy needed to carry out the dehydration by a factor of 10.

We have found a way to dehydrate ethanol in which the combustion energy of the ethanol product exceeds the energy needed to carry out the dehydration by a factor of 10. Drying of aqueous ethanol by materials such as cellulose, corn starch, shelled corn, corn (cellulosic) residue, mineral oxide, hydroxide, or sulfate results in a product that is up to 99.8 percent water-free.

Alcohols are made from either grains or biomass by first converting these materials to fermentable sugars (4). The sugars are then fermented, typically with yeast, to give a broth containing 6 to 12 percent ethanol along with small amounts of aldehydes, ketones, amyl alcohols (fusel oils), and methanol (5). The final step, distillation to water-free alcohol, consumes 50 to 80 percent of the energy used in a typical fermentation ethanol manufacturing process (1, 2). The energy intensity of traditional distillation techniques is frequently cited in criticizing the potential of biomass-derived ethanol as a liquid fuel (1-3).

Recovery of ethanol from the fermentation broth is at least a three-step process: (i) distillation of dilute aqueous alcohol to its azetropes (95.57 percent ethanol by weight) (5), (ii) distillation using a third component—either an organic solvent (7) or a strong salt solution (6)—to break up the azetropes and remove the remaining water, and (iii) distillation to separate water from the third component so that it can be recycled. Trace constituents, including pentanol (fusel oil) and methanol, can be removed by additional distillation, but this is not necessary for ethanol to be blended with gasoline (2).

Analysis of the ethanol-water distillation, using the McCabe-Thiele method for analysis of fractionation columns (9), indicated the energy-sensitive regimes. Energy consumption greatly increases with decreasing ethanol concentration in the feed below 4 percent alcohol, since a disproportionately larger quantity of feed must be vaporized to obtain the same amount of product. Current fermentation technology results in a product containing 5 to 12 percent ethanol (11), so this energy problem is avoided. Most of the energy consumption occurs in distilling above 85 percent ethanol, as shown by the equilibrium diagram in Fig. 1a. With increasing alcohol product concentration (92.2 percent by weight in Fig.
1a), the rectifying operating line approaches the equilibrium line. Hence, more theoretical plates (one step corresponds to one plate in Fig. 1a) are required. To obtain a column with a reasonable number of plates (fewer than 40) for producing ethanol of higher purity, the slope of the rectifying line must be increased. This requires a higher reflux ratio and therefore more energy input.

By constructing such diagrams and using appropriate mass and energy balances (9), we obtained the results plotted in Fig. 1b. The energy requirements in Fig. 1b are based on a reflux ratio 1.5 times the theoretical minimum for distillation of a saturated 12 percent ethanol feed. Figure 1b shows that the energy content of 12 percent alcohol, distilled to 90 percent purity, is 11 times the energy needed for distillation. Above 90 percent purity the energy ratio drops precipitously, and as the azetrope is approached the distillation energy input approaches the ethanol energy output. Additional energy is required to carry out the other distillations to break the azetrope.

The problem is to produce dehydrated ethanol in an energy-efficient manner, starting from 90 percent or lower concentrations. One solution is to use a non-distillation process. We found that aqueous ethanol can be dehydrated by preferential adsorption of water on adsorbents that are inexpensive and require relatively little energy for use or regeneration.

Initially, calcium oxide (CaO) was tried. Ethanol-water vapor was passed through a 20-ml condenser tube (heated at 98° to 99°C) filled with CaO. The vapor coming from the tube was condensed, collected, and then analyzed for water content by the Karl-Fischer (KF) water analysis procedure (12). Vapor with a starting composition of 89 percent ethanol and 11 percent water was successfully dehydrated in this way to give a product with 99+ percent ethanol. This result is not surprising since CaO is known to react with water [CaO + H₂O → Ca(OH)₂ + 2527 Btu's per pound of water] and would not be expected to react with ethanol. The energy efficiency of this approach is not intuitively obvious, however. The total energy consumed is 1577 Btu's per pound of alcohol: 1190 Btu's for distillation to 89 percent alcohol, 277 Btu's for heat of regeneration [Ca(OH)₂ → heat → CaO + H₂O], and 110 Btu's to evaporate the water released in regeneration. Hence, eight time more combustible energy (12,750 Btu's per pound for ethanol) is obtained than is used in the dehydration process.

Table 1. Comparison of alcohol-dehydrating agents.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ethanol (%)</th>
<th>Starting</th>
<th>Dehydrating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cornstarch</td>
<td>73.7</td>
<td>99.0</td>
<td></td>
</tr>
<tr>
<td>Sucrose</td>
<td>72.5</td>
<td>90.7</td>
<td></td>
</tr>
<tr>
<td>Corn</td>
<td>77.0</td>
<td>97.7</td>
<td></td>
</tr>
<tr>
<td>Avicel (microcrystalline cellulose)</td>
<td>88.9</td>
<td>98.6</td>
<td></td>
</tr>
<tr>
<td>Whatman CF-11 cellulose</td>
<td>88.8</td>
<td>96.4</td>
<td></td>
</tr>
<tr>
<td>Buckeye CM cellulose</td>
<td>84.8</td>
<td>99.8</td>
<td></td>
</tr>
<tr>
<td>Corn residue</td>
<td>83.2</td>
<td>92.0</td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>80.7</td>
<td>97.6</td>
<td></td>
</tr>
<tr>
<td>CaSO₄</td>
<td>90.1</td>
<td>98.0</td>
<td></td>
</tr>
</tbody>
</table>

Calcium oxide was reported to be capable of drying ethanol 40 years ago (13). By further experimentation, we found other alcohol dehydrating agents, some to our knowledge not previously reported in the literature, some of which are more energy-efficient than CaO. With the same experimental procedure used for CaO, we observed dehydration with the materials listed in Table 1. Although the water-adsorbing properties of cellulose and starch are known (14), preferential adsorption of water in the presence of ethanol was unexpected. Furthermore, the energy balance is more favorable than that obtained with CaO. For example, the heat of wetting of cellulose, on the order of 29 Btu's per pound (15), is less than the heat of reaction of CaO. The total energy requirement with cellulose as the dehydrating agent is 1255 Btu's per pound of alcohol: 1050 Btu's per pound for distillation (from 12 to 84.8 percent) and 185 Btu's per pound for cellulose dehydration. Hence, ten times more (combustible) energy is obtained than is used in obtaining the product. Quantitative properties of selected dehydrating agents are summarized in Fig. 2. These materials were heated before use: NaOH (pellets) at 90°C, cornstarch (Argo Division, Corn Products Co.) at 90°C, CM cellulose (type CLD, Buckeye Co.) at 110°C, Avicel and CF-11 at 60°C in a vacuum (30 inch-Hg), and corn (shelled and cracked) at 90°C. Aqueous ethanol at a concentration of Cₖ percent by weight was put into an insulated 300-mil round-bottom flask heated by an electric mantle. A jacketed column, 20 ml in volume, was placed vertically in the flask neck. The column was maintained at temperature Tₐ by using a Haake model FE circulating-water bath. A receiver, placed immediately at the outlet of the column, condensed and collected the vapor from the column. All non-heated parts of the apparatus were well insulated.

Before each run, ethanol was placed in the flask and the entire system was heated to steady state. After the heating, and before filling the column with dehydrating agent, control values were obtained. "Distillate" as well as the contents of the flask ("bottoms") at Cₖ were sampled and analyzed by the KF procedure for water. The results are indicated in Fig. 2. Preheated dehydrating agent was then quickly placed in the column. Weights of materials were NaOH, 15 g; cornstarch, 7.3 g; CM cellulose, 3.4 g; and corn, 7.5 g.

Sodium hydroxide (Fig. 2a) gave 96.5 percent ethanol. This is above the azetrope (95.6 percent) and considerably higher than the control value (89 percent). Hence, the enhancement of the ethanol concentration is due to dehydration and not solely to additional fractionation effects of the packing material in the column. Passage of ethanol vapors over starch (Fig. 2b) gives a dramatic dehydration, yielding 99 percent ethanol from a 73 percent starting concentration. Similarly, cracked corn kernels also dehydrate alcohol (Fig. 2d). This result indicates...
dicates the potential use of grain to dehy-
drinate alcohol before the grain is convert-
ed (by wet processing) to alcohol in a grain alcohol plant. The effectiveness of CM cellulose (Fig. 2c) suggests that oth-
er modified carbohydrate polymers such as superabsorbent starch (“supersturp-
ner”) (10) might have the potential to de-
hydrate alcohol.

Column temperature has a significant ef-
fect on dehydration. At TCOL = 91°C, corn readily dehydrates alcohol (Fig.
Id). At TCOL = 79.5°C the dehydration capa-
city is diminished, even though the start-
ing ethanol concentration is 7 per-
cent higher. Similar phenomena were ob-
served for other dehydrating agents. The vapor contact times are short: on the or-
der of 4 seconds for NaOH, 14 seconds for starch, 28 seconds for CM cellulose, and 5 seconds for corn.

From a practical point of view, the classes of compounds discussed in this report are attractive since they are read-
ily regenerated by heating and can be re-
cycled. Furthermore, cellulose materi-
als, corn residue, and corn starch are ma-
terials that would be available, or could be generated internally, in plants con-
verting cellulose residues or grains to al-
cohol. Another advantage of using or-
ganic rather than inorganic dehydrating agents is that the temperature of regenera-
tion is lower for starch or cellulose (60°C to 110°C) than it is for CaO (160°C to 170°C). Hence, lower temperature ener-

Fig. 2. Ethanol composition as a function of vapor condensed and collected after passage through a column containing the indicated dehydrating agent. Control cases show the enrich-
ment effect obtained with an empty column before runs (a) through (e).