less γ is dropped to under 2 percent per annum. At $\gamma = 2$ percent, there appears to be little difficulty in keeping CO_2 concentrations down. Figure 2 shows some examples of the effects of varying these parameters.

The best estimates of climatic change resulting from increasing concentrations of atmospheric CO_2 indicate the occurrence of critical conditions some 50 years ahead, coincident with market penetration times for new energy sources. The large uncertainties in magnitude of the climate change predictions make the situation potentially even more critical, and the market penetration time results presented here suggest the need for immediate action if the change is to be averted. However, before undertaking the pursuit of such a radical step, we would be well advised to question further the validity of the market penetration time concept as it might apply to energy source replacement.

Marchetti's derivation of market penetration times (*2*) was based entirely on empirical evidence on transitions between the predominant use of various primary energy sources, such as from wood to coal and from coal to oil. His empirical fits to logistic curves are indeed impressive, as are those derived earlier by Fisher and Pry (*8*) for technology transfer rates. Although recommending a penetration time of 50 to 100 years for projecting future energy scenarios, Marchetti had no causal explanation for his results, and it is difficult to accept its global applicability and the irreducible value of market penetration time. Peterka (*4*) has provided a theoretical basis for the logistic curve (Eq. 1), but his analysis suggests that penetration times might not be bound to the 50-year time frame. Thus, put briefly, Peterka's model assumes that the two energy production systems are in economic competition and that, after a short initial period of venture capital use, the growth of production is limited by the amount of capital that can be generated solely from their own profits. This feature serves to limit the rate of growth of even a much less costly energy production system. However, if in fact the two energy sources are cost-competitive but are owned by the same controlling group (be it a government or a large corporation), Peterka's assumption would appear to break down, since profits from the old production system can be transferred to provide capital for the new.

Since immediate policy questions are strongly affected by the coupling of the CO_2 effect with market penetration time concepts, the applicability of the large market penetration time figure to the CO_2 question must be carefully scrutinized. As yet and perhaps because the market penetration idea in application to global energy systems is relatively new (*9*), it has not attracted the attention of economic theorists to whom we might appeal in order to establish or refute its predictive veracity.

J. A. LAURMANN
Division of Applied Mechanics,
Stanford University,
Stanford, California 94305

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6. The 56 percent is the fractional retention, omitting any contribution from slash burning of forests. If in fact deforestation has made significant contributions to atmospheric CO_2 release in the past, forest depletion in the future would lead to atmospheric CO_2 concentrations below those projected based on the use of the constant 56 percent rate that I have assumed here.
7. United States Energy Information Administration, *Annual Report to Congress*, vol. 2, *Projections of Energy Supply and Demand and Their Impacts* (Government Printing Office, Washington, D.C., 1977).
8. J. C. Fisher and R. H. Pry, "A simple substitution model for technological change" (Report 70-C-215, General Electric Company, Schenectady, N.Y., 1970).
9. Historical time trends for energy sources have been discussed much before Marchetti's quantitative analysis, as, for example, in P. C. Putnam, *Energy in the Future* (Van Nostrand, New York, 1953). I am indebted to a reviewer for pointing out this fact.
10. The 50-year figure is taken by Marchetti (*2*) to be a minimum value for market penetration time.
11. The results presented here are part of a continuing study being conducted for the Electric Power Research Institute, Palo Alto, Calif.; a partial description of this work, amplifying on the material alluded to here in (*5*), is to be published in an article entitled "Climate change from fossil fuel generated carbon dioxide and energy policy" in *Environment International*.

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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, cornstarch, 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 azeotrope (95.57 percent ethanol by weight) (*5*), (ii) distillation using a third component—either an organic solvent (*7*) or a strong salt solution (*8*)—to break up the azeotrope 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 the energy ratio drops precipitously, and as the azeotrope is approached the distillation energy input approaches the ethanol energy output. Additional energy is required to carry out the other distillations to break the azeotrope.

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 nondistillation 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 88° to 95°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 [$CaO + H_2O \rightarrow Ca(OH)_2$ + 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 $\rightarrow CaO + H_2O$], and 110 Btu's to evaporate the water released in regeneration. Hence, eight time more combustible energy (12,760 Btu's per pound for ethanol) is obtained than is used in the dehydration process.

Table 1. Comparison of alcohol-dehydrating agents.

Material	Ethanol (%)	
	Starting	Dehydrated
Cornstarch	73.7	99.0
Sucrose	72.5	90.7
Corn	77.0	97.7
Avicel (microcrystalline cellulose)	88.9	98.6
Whatman CF-11 cellulose	88.8	96.4
Buckeye CM cellulose	84.8	99.8
Corn residue	85.2	92.0
NaOH	80.7	97.6
$CaSO_4$	90.1	98.0

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 50 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 1235 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, Avicell 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 C_0 percent by weight was put into an insulated 300-ml 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 T_{col} 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 nonheated 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 C_0) 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 azeotrope (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 in-

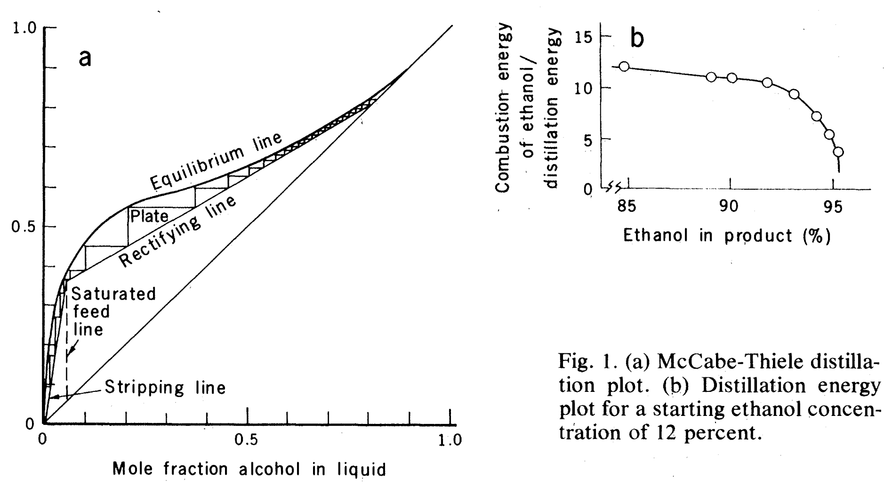


Fig. 1. (a) McCabe-Thiele distillation plot. (b) Distillation energy plot for a starting ethanol concentration of 12 percent.

dicates the potential use of grain to dehydrate alcohol before the grain is converted (by wet processing) to alcohol in a grain alcohol plant. The effectiveness of CM cellulose (Fig. 2c) suggests that other modified carbohydrate polymers such as superadsorbent starch ("superslurper") (*10*) might have the potential to dehydrate alcohol.

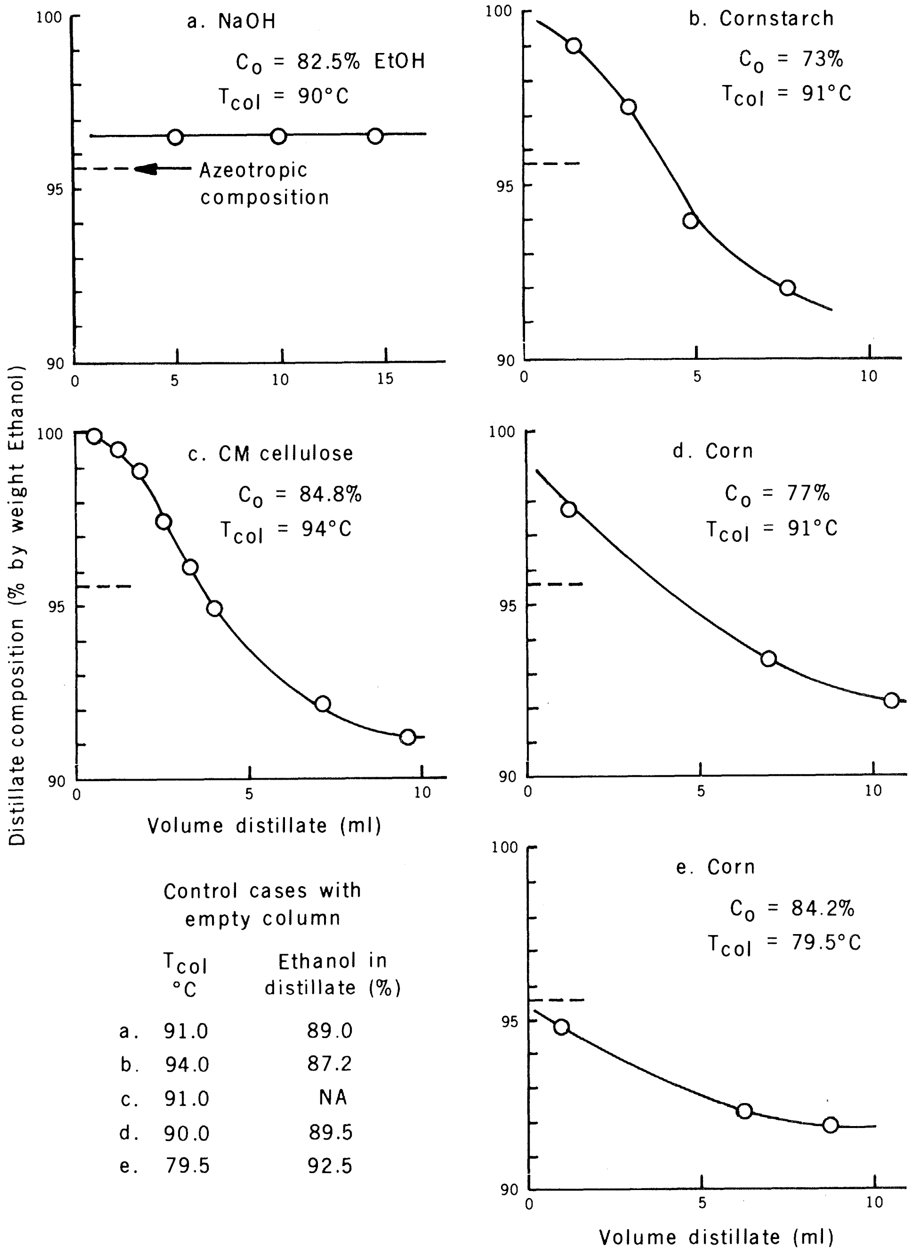
Column temperature has a significant effect on dehydration. At T_{col} = 91°C, corn readily dehydrates alcohol (Fig. 1d). At T_{col} = 79.5°C the dehydration capacity is diminished, even though the starting ethanol concentration is 7 percent higher. Similar phenomena were observed for other dehydrating agents. The vapor contact times are short: on the order 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 readily regenerated by heating and can be recycled. Furthermore, cellulosic materials, corn residue, and cornstarch are materials that would be available, or could be generated internally, in plants converting cellulosic residues or grains to alcohol. Another advantage of using organic rather than inorganic dehydrating agents is that the temperature of regeneration is lower for starch or cellulosics (60° to 110°C) than it is for CaO (160° to 170°C). Hence, lower temperature energy, not usable elsewhere in an alcohol production facility, could be utilized for regenerating a dehydrating agent such as cellulose or starch. This might result in further energy economy.

The principle of drying ethanol by a nondistillation process was demonstrated more than 40 years ago with CaO. Since other dehydrating agents work equally well, and processes for energy-efficient production of ethanol are now needed, it seems appropriate to suggest that research that was apparently discontinued in the 1930's be started again and carried forward.

MICHAEL R. LADISCH
KAREN DYCK

Laboratory of Renewable Resources Engineering, Purdue University, West Lafayette, Indiana 47907



Control cases with empty column

	T_{col} °C	Ethanol in distillate (%)
a.	91.0	89.0
b.	94.0	87.2
c.	91.0	NA
d.	90.0	89.5
e.	79.5	92.5

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 enrichment effect obtained with an empty column before runs (a) through (e).

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