Ethanol Can Contribute to Energy and Environmental Goals

Alexander E. Farrell,[1*] Richard J. Plevin,[1] Brian T. Turner,[1,2] Andrew D. Jones,[1] Michael O'Hare,[2] Daniel M. Kammen[1,2,3]

To study the potential effects of increased biofuel use, we evaluated six representative analyses of fuel ethanol. Studies that reported negative net energy incorrectly ignored coproducts and used some obsolete data. All studies indicated that current corn ethanol technologies are much less petroleum-intensive than gasoline but have greenhouse gas emissions similar to those of gasoline. However, many important environmental effects of biofuel production are poorly understood. New metrics that measure specific resource inputs are developed, but further research into environmental metrics is needed. Nonetheless, it is already clear that large-scale use of ethanol for fuel will almost certainly require cellulosic technology.

Energy security and climate change imperatives require large-scale substitution of petroleum-based fuels as well as improved vehicle efficiency (*1*, *2*). Although biofuels offer a diverse range of promising alternatives, ethanol constitutes 99% of all biofuels in the United States. The 3.4 billion gallons of ethanol blended into gasoline in 2004 amounted to about 2% of all gasoline sold by volume and 1.3% (2.5×10^{17} J) of its energy content (*3*). Greater quantities of ethanol are expected to be used as a motor fuel in the future because of two federal policies: a $0.51 tax credit per gallon of ethanol used as motor fuel and a new mandate for up to 7.5 billion gallons of "renewable fuel" to be used in gasoline by 2012, which was included in the recently passed Energy Policy Act (EPACT 2005) (*4*, *5*).

Thus, the energy and environmental implications of ethanol production are more important than ever. Much of the analysis and public debate about ethanol has focused on the sign of the net energy of ethanol: whether manufacturing ethanol takes more nonrenewable energy than the resulting fuel provides (*6*, *7*). It has long been recognized that calculations of net energy are highly sensitive to assumptions about both system boundaries and key parameter values (*8*). In addition, net energy calculations ignore vast differences between different types of fossil energy (*9*). Moreover, net energy ratios are extremely sensitive to specification and assumptions and can produce uninterpretable values in some important cases (*10*). However, comparing across published studies to evaluate how these assumptions affect outcomes is difficult owing to the use of different units and system boundaries across studies. Finding intuitive and meaningful replacements for net energy as a performance metric would be an advance in our ability to evaluate and set energy policy in this important arena.

To better understand the energy and environmental implications of ethanol, we surveyed the published and gray literature and present a comparison of six studies illustrating the range of assumptions and data found for the case of corn-based (*Zea mays*, or maize) ethanol (*11*–*16*). To permit a direct and meaningful comparison of the data and assumptions across the studies, we developed the Energy and Resources Group (ERG) Biofuel Analysis Meta-Model (EBAMM) (*10*). For each study, we compared data sources and methods and parameterized EBAMM to replicate the published net energy results to within half a percent. In addition to net energy, we also calculated metrics for greenhouse gas (GHG) emissions and primary energy inputs (table S1 and Fig. 1).

Two of the studies stand out from the others because they report negative net energy values and imply relatively high GHG emissions and petroleum inputs (*11*, *12*). The close evaluation required to replicate the net energy results showed that these two studies also stand apart from the others by incorrectly assuming that ethanol coproducts (materials inevitably generated when ethanol is made, such as dried distiller grains with solubles, corn gluten feed, and corn oil) should not be credited with any of the input energy and by including some input data that are old and unrepresentative of current processes, or so poorly documented that their quality cannot be evaluated (tables S2 and S3).

Sensitivity analyses with EBAMM and elsewhere show that net energy calculations are most sensitive to assumptions about coproduct allocation (*17*). Coproducts of ethanol have positive economic value and displace competing products that require energy to make. Therefore, increases in corn ethanol production to meet the requirements of EPACT 2005 will lead to more coproducts that displace whole corn and soybean meal in animal feed, and the energy thereby saved will partly offset the energy required for ethanol production (*5*, *18*).

The studies that correctly accounted for this displacement effect reported that ethanol and coproducts manufactured from corn yielded a positive net energy of about 4 MJ/l to 9 MJ/l. The study that ignored coproducts but used recent data found a slightly positive net energy for corn ethanol (*13*). However, comparisons of the reported data are somewhat misleading because of many incommensurate assumptions across the studies.

We used EBAMM to (i) add coproduct credit where needed, (ii) apply a consistent system boundary by adding missing parameters (e.g., effluent processing energy) and dropping extraneous ones (e.g., laborer food energy), (iii) account for different energy types, and (iv) calculate policy-relevant metrics (*19*). Figure 1 shows both published and commensurate values as well as equivalent values for the reference, conventional gasoline.

The published results, adjusted for commensurate system boundaries, indicate that with current production methods corn ethanol displaces petroleum use substantially; only 5 to 26% of the energy content is renewable. The rest is primarily natural gas and coal (Fig. 2). The impact of a switch from gasoline to ethanol has an ambiguous effect on GHG emissions, with the reported values ranging from a 20% increase to a decrease of 32%. These values have their bases in the same system boundaries, but some of them rely on data of dubious quality. Our best point estimate for average performance today is that corn ethanol reduces petroleum use by about 95% on an energetic basis and reduces GHG emissions only moderately, by about 13%. Uncertainty analysis suggests these results are robust (*10*). It is important to realize that actual performance will vary from place to place and that these values reflect an absence of incentives for GHG emission control. Given adequate policy incentives, the performance of corn ethanol in terms of GHG emissions can likely be improved (*20*). However, current data suggest that only cellulosic ethanol offers large reductions in GHG emissions.

The remaining differences among the six studies are due to different input parameters, which are relatively easy to evaluate within the simple, transparent EBAMM framework. For instance, most of the difference between the highest and lowest values for GHG emissions in our data are due to differences in limestone ($CaCO_3$) application rate and energy embodied in farm machinery (table S1). The former is truly uncertain; data for lime application and for the resulting GHG emissions are poor (*15*). In contrast, the higher farm machinery energy values are unverifiable and more than an order of magnitude greater than values reported elsewhere and calculated here, suggesting that the lower values are more representative (*10*) (table S3).

This analysis illustrates the major contribution of agricultural practices to life-cycle GHG emissions (34% to 44%) and petroleum inputs (45% to 80%) to corn ethanol, suggest-

[1]Energy and Resources Group, [2]Goldman School of Public Policy, [3]Renewable and Appropriate Energy Laboratory, University of California, Berkeley, CA 94720–3050, USA.

*To whom correspondence should be addressed. E-mail: aef@berkeley.edu

ing that policies aimed at reducing environmental externalities in the agricultural sector may result in significantly improved environmental performance of this fuel. For example, conservation tillage reduces petroleum consumption and GHG emissions as well as soil erosion and agrichemical runoff (*20*, *21*).

We use the best data from the six studies to create three cases in EBAMM: *Ethanol Today*, which includes typical values for the current U.S. corn ethanol industry and requires the fewest assumptions; *CO_2 Intensive*, which has its basis in current plans to ship Nebraska corn to a lignite-powered ethanol plant in North Dakota (*22*); and *Cellulosic*, which assumes that production of cellulosic ethanol from switchgrass becomes economic as represented in one of the studies (*16*).

The *Cellulosic* case presented here is a preliminary estimate of a rapidly evolving technology and is designed to highlight the dramatic reductions in GHG emissions that could be achieved. In addition, other biofuel technologies and production processes are in active development and, as the data become available, should be the subject of similar energy and environmental impact assessments.

For all three cases, producing one MJ of ethanol requires far less petroleum than is required to produce one MJ of gasoline (Fig. 2). However, the GHG metric illustrates that the environmental performance of ethanol varies greatly depending on production processes. On the other hand, single-factor metrics may be poor guides for policy. With the use of the petroleum intensity metric, the *Ethanol Today* case would be slightly preferred over the *Cellulosic* case (a petroleum input ratio of 0.06 compared with 0.08); however, on the GHG metric, the *Ethanol Today* case is far worse than *Cellulosic* (83 compared to 11). Additional environmental metrics are now being developed for biofuels, and a few have been applied to ethanol production, but several key issues remain unquantified, such as soil erosion and the conversion of forest to agriculture (*18*, *20*).

Looking to the future, the environmental implications of ethanol production are likely to grow more important, and there is a need for a more complete set of policy-relevant metrics. In addition, future analysis of fuel ethanol should more carefully evaluate ethanol production from cellulosic feedstocks, not least because cellulosic ethanol production is undergoing major technological development and because the cultivation of cellulosic feedstocks is not as far advanced as corn agriculture, suggesting more potential for improvement. Such advances may enable biomass energy to contribute a sizeable fraction of the nation's transportation energy, as some studies have suggested (*23*, *24*).

Our study yields both research and policy recommendations. Evaluations of biofuel policy should use realistic assumptions (e.g., the inclusion of coproduct credits calculated by a

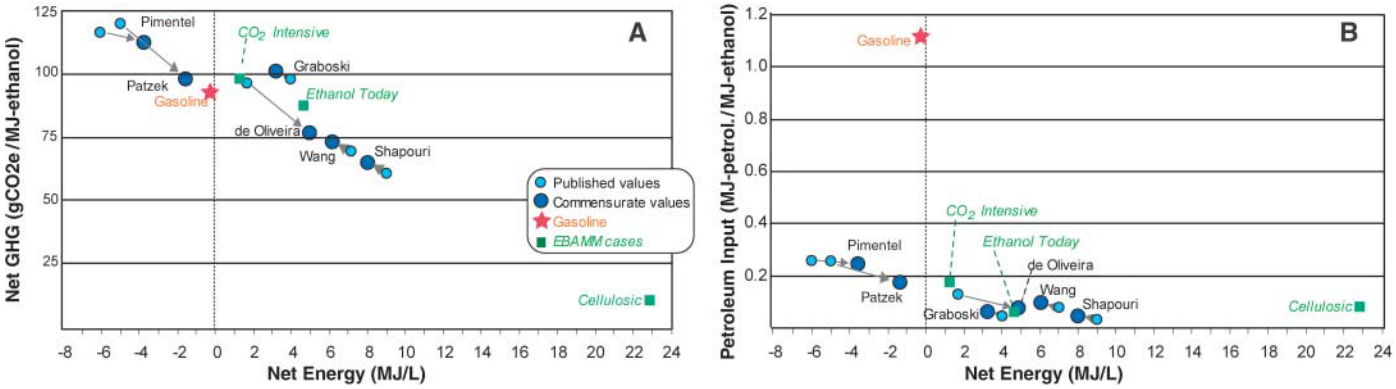

Fig. 1. (**A**) Net energy and net greenhouse gases for gasoline, six studies, and three cases. (**B**) Net energy and petroleum inputs for the same. In these figures, small light blue circles are reported data that include incommensurate assumptions, whereas the large dark blue circles are adjusted values that use identical system boundaries. Conventional gasoline is shown with red stars, and EBAMM scenarios are shown with green squares. Adjusting system boundaries reduces the scatter in the reported results. Moreover, despite large differences in net energy, all studies show similar results in terms of more policy-relevant metrics: GHG emissions from ethanol made from conventionally grown corn can be slightly more or slightly less than from gasoline per unit of energy, but ethanol requires much less petroleum inputs. Ethanol produced from cellulosic material (switchgrass) reduces both GHGs and petroleum inputs substantially.

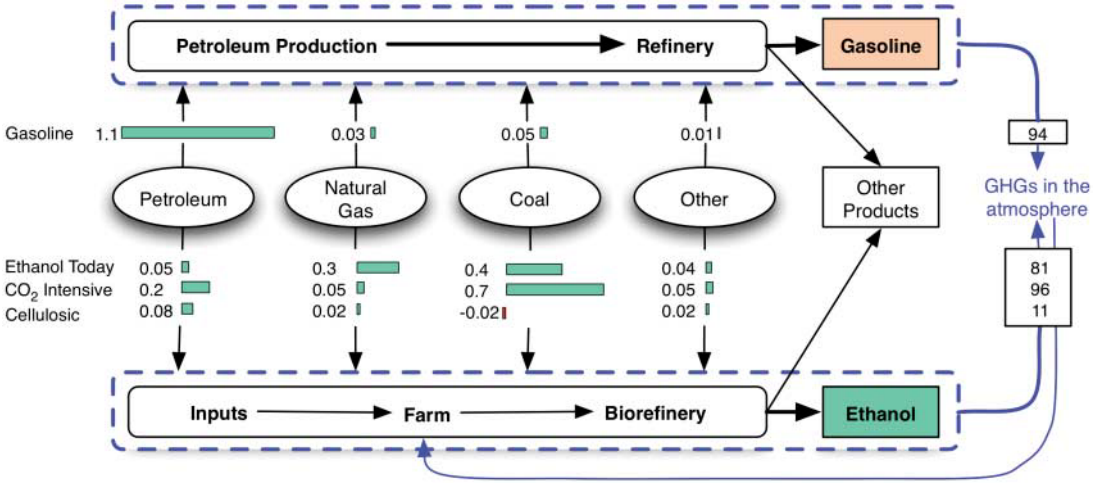

Fig. 2. Alternative metrics for evaluating ethanol based on the intensity of primary energy inputs (MJ) per MJ of fuel and of net greenhouse gas emissions (kg CO_2-equivalent) per MJ of fuel. For gasoline, both petroleum feedstock and petroleum energy inputs are included. "Other" includes nuclear and hydrological electricity generation. Relative to gasoline, ethanol produced today is much less petroleum-intensive but much more natural gas– and coal-intensive. Production of ethanol from lignite-fired biorefineries located far from where the corn is grown results in ethanol with a high coal intensity and a moderate petroleum intensity. Cellulosic ethanol is expected to have an extremely low intensity for all fossil fuels and a very slightly negative coal intensity due to electricity sales that would displace coal.

displacement method), accurate data, clearly defined future scenarios, and performance metrics relevant to policy goals like reducing greenhouse gas emissions, petroleum inputs, and soil erosion. Progress toward attaining these goals will require new technologies and practices, such as sustainable agriculture and cellulosic ethanol production. Such an approach could lead to a biofuels industry much larger than today's that, in conjunction with greater vehicle efficiency, could play a key role in meeting the nation's energy and environmental goals.

References and Notes

1. T. E. Wirth, C. B. Gray, J. D. Podesta, *Foreign Aff.* **82**, 132 (2003).
2. R. A. Kerr, R. F. Service, *Science* **309**, 101 (2005).
3. S. C. Davis, S. W. Diegel, *Transportation Energy Data Book* (Technical Report No. ORNL-6973, Oak Ridge National Laboratory, Oak Ridge, TN, 2004).
4. If only cellulosic ethanol production capacity is added, only 4.8 billion gallons will be required because of preferential credit provisions.
5. "Implications of Increased Ethanol Production for U.S. Agriculture" (Report No. 10-05, Food and Agricultural Policy Research Institute, Univ. of Missouri, Columbia, MO, 2005). Also available at www.fapri.missouri.edu/outreach/publications/2005/FAPRI_UMC_Report_10_05.pdf.
6. By convention, photosynthetic energy is ignored in this calculation.
7. H. Shapouri, J. A. Duffield, M. Wang, *Trans. ASAE* **46**, 959 (2003).
8. R. S. Chambers, R. A. Herendeen, J. J. Joyce, P. S. Penner, *Science* **206**, 789 (1979).
9. C. J. Cleveland, *Energy* **30**, 769 (2005).
10. Materials and methods are available as supporting material on *Science* Online. Additional information is available, including the working EBAMM model, at http://socrates.berkeley.edu/~rael/EBAMM.
11. T. Patzek, *Crit. Rev. Plant Sci.* **23**, 519 (2004).
12. D. Pimentel, T. Patzek, *Nat. Resour. Res.* **14**, 65 (2005).
13. M. E. D. De Oliveira, B. E. Vaughan, E. J. Rykiel, *Bioscience* **55**, 593 (2005).
14. H. Shapouri, A. McAloon, "The 2001 net energy balance of corn ethanol" (U.S. Department of Agriculture, Washington, DC, 2004). Also available at www.usda.gov/oce/oepnu.
15. M. Graboski, "Fossil energy use in the manufacture of corn ethanol" (National Corn Growers Association, Washington, DC, 2002). Also available at www.ncga.com/ethanol/main.
16. M. Wang, "Development and use of GREET 1.6 fuel-cycle model for transportation fuels and vehicle technologies" (Tech. Rep. ANL/ESD/TM-163, Argonne National Laboratory, Argonne, IL, 2001). Also available at www.transportation.anl.gov/pdfs/TA/153.pdf.
17. S. Kim, B. E. Dale, *Int. J. Life Cycle Assess.* **7**, 237 (2002).
18. M. A. Delucchi, "Conceptual and methodological issues in lifecycle analyses of transportation fuels" (Tech. Rep. UCD-ITS-RR-04-45, Univ. of California, Davis, 2004). Also available at www.its.ucdavis.edu/publications/2004/UCD-ITS-RR-04-45.pdf.
19. Factors eliminated were labor transportation, labor food energy, and process water energy. The first two were deemed outside the system boundaries. Process water energy was included in one study but was insufficiently documented. Factors added were farm machinery energy, inputs packaging, and effluent processing energy. The metric for petroleum use included crude oil used as a feedstock for gasoline, and the metric for GHGs included end-use (tailpipe) fossil emissions (*10*).
20. S. Kim, B. E. Dale, *Biomass Bioenergy* **29**, 426 (2005).
21. E. Tegtmeier, M. Duffy, *Int. J. Agric. Sustainability* **2**, 1 (2004).
22. More information is available at www.redtrailenergyllc.com.
23. R. D. Perlack, L. L. Wright, A. Turhollow, R. Graham, B. Stokes, D. Erbach, "Biomass as feedstock for a bioenergy and bioproducts industry: The technical feasibility of a billion-ton annual supply" (Tech. Rep. ORNL/TM-2006/66, Oak Ridge National Laboratory, Oak Ridge, TN, 2005). Also available at http://feedstockreview.ornl.gov/pdf/billion_ton_vision.pdf.
24. L. B. Lave, W. Griffin, H. McLean, *Issues Sci. Technol.* **18**, 73 (2001).

25. This research was made possible through support from the Energy Foundation and the Karsten Family Foundation (both to D.M.K.) and NSF's Climate Decision Making Center at Carnegie Mellon University (SES-034578) (to A.E.F.) and Graduate Research Fellowship program (to A.D.J.). The authors thank J. Thompson, D. Greene, M. DeLucchi, M. Wang, and an anonymous reviewer for assistance and valuable comments.

Supporting Online Material
www.sciencemag.org/cgi/content/full/311/5760/506/DC1
Materials and Methods
SOM Text
Figs. S1 and S2
Tables S1 to S3
References

17 October 2005; accepted 9 January 2006
10.1126/science.1121416

Optical Detection of DNA Conformational Polymorphism on Single-Walled Carbon Nanotubes

Daniel A. Heller,[1] Esther S. Jeng,[2] Tsun-Kwan Yeung,[2] Brittany M. Martinez,[2] Anthonie E. Moll,[2] Joseph B. Gastala,[2] Michael S. Strano[2]*

The transition of DNA secondary structure from an analogous B to Z conformation modulates the dielectric environment of the single-walled carbon nanotube (SWNT) around which it is adsorbed. The SWNT band-gap fluorescence undergoes a red shift when an encapsulating 30-nucleotide oligomer is exposed to counter ions that screen the charged backbone. The transition is thermodynamically identical for DNA on and off the nanotube, except that the propagation length of the former is shorter by five-sixths. The magnitude of the energy shift is described by using an effective medium model and the DNA geometry on the nanotube sidewall. We demonstrate the detection of the B-Z change in whole blood, tissue, and from within living mammalian cells.

Single-walled carbon nanotubes (*1*) are rolled sheets of graphene with nanometer-sized diameters that possess remarkable photostablity (*2*). The semiconducting forms of SWNTs, when dispersed by surfactants in aqueous solution, can display distinctive near-infrared (IR) photoluminescence (*3*) arising from their electronic band gap. The band-gap energy is sensitive to the local dielectric environment around the SWNT, and this property can be exploited in chemical sensing, which was recently demonstrated for the detection of β-D-glucose (*4*).

Among the molecules that can bind to the surface of SWNTs is DNA, which adsorbs as a double-stranded (ds) complex (*5*). Certain DNA oligonucleotides will transition from the native, right-handed B form to the left-handed Z form as cations adsorb onto and screen the negatively charged backbone (*6–9*). We now show that an analogous B-to-Z transition for a 30-nucleotide dsDNA modulates the dielectric environment of SWNTs and decreases their near-IR emission energy up to 15 meV. We have used this fluorescence signal to detect divalent metal cations that bind to DNA and stabilize the Z form. The thermodynamics of the conformational change for DNA both on and off the SWNT are nearly identical. These near-IR ion sensors can operate in strongly scattering or absorbing media, which we demonstrate by detecting mercuric ions in whole blood, black ink, and living mammalian cells and tissues.

Near-IR spectrofluorometry was performed on colloidally stable complexes of DNA-encapsulated SWNTs (DNA-SWNTs) buffered at a pH of 7.4 and synthesized by the noncovalent binding to the nanotube sidewall (*10*) of a 30–base pair single-stranded DNA (ssDNA) oligonucleotide with a repeating G-T sequence. This ssDNA can hydrogen bond with itself to form dsDNA. Several types of semiconducting SWNTs are present, but as we show below, they can be identified by their characteristic band gaps. The shift in band gap is similar for each type of SWNT, although there is a diameter dependence. After the addition of divalent cations, we observed an energy shift in the SWNT emission with a relative ion sensitivity of $Hg^{2+} > Co^{2+} > Ca^{2+} > Mg^{2+}$, which is identical for free DNA (Fig. 1A) (*11*). The shift can also be observed by monitoring SWNT photoabsorption bands (fig. S1). The fluorescence peak energy traces a monotonic, two-state equilibrium profile with increasing ionic strength for each case (*12*).

The removal of ions from the system via dialysis returns the emission energy to its initial value, which is indicative of a completely reversible thermodynamic transition (Fig. 1B and

[1]Department of Chemistry, [2]Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA.

*To whom correspondence should be addressed. E-mail: strano@uiuc.edu