A First-Law Thermodynamic Analysis of the Corn-Ethanol Cycle

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This paper analyzes energy efficiency of the industrial corn-ethanol cycle. In particular, it critically evaluates earlier publications by DOE, USDA, and UC Berkeley Energy Resources Group. It is demonstrated that most of the current First Law net-energy models of the industrial corn-ethanol cycle are based on nonphysical assumptions and should be viewed with caution. In particular, these models do not (i) define the system boundaries, (ii) conserve mass, and (iii) conserve energy. The energy cost of producing and refining carbon fuels in real time, for example, corn and ethanol, is high relative to that of fossil fuels deposited and concentrated over geological time. Proper mass and energy balances of corn fields and ethanol refineries that account for the photosynthetic energy, part of the environment restoration work, and the coproduct energy have been formulated. These balances show that energetically production of ethanol from corn is 2–4 times less favorable than production of gasoline from petroleum. From thermodynamics it also follows that ecological damage wrought by industrial biofuel production must be severe. With the DDGS coproduct energy credit, 3.9 gallons of ethanol displace on average the energy in 1 gallon of gasoline. Without the DDGS energy credit, this average number is 6.2 gallons of ethanol. Equivalent CO_2 emissions from corn ethanol are some 50% higher than those from gasoline, and become 100% higher if methane emissions from cows fed with DDGS are accounted for. From the mass balance of soil it follows that ethanol coproducts should be returned to the fields.

KEY WORDS: Net energy, biorefinery, efficiency, coproduct, emissions, environment, cost.

INTRODUCTION

This paper analyzes energy efficiency of the industrial corn-ethanol cycle. In particular, it critically reviews the report by Farrell and others (2006a). This report is based on an Excel spreadsheet with cells containing numbers from three peer-reviewed papers (Patzek, 2004; Pimentel and Patzek, 2005; de Oliveira, Vaughan, and Rykiel, 2005) and four[3] gray-literature reports (Wang, 2001; Graboski, 2002; Shapouri, Duffield, and Wang, 2002; Shapouri and McAloon, 2004). The authors cite the only relevant peer-reviewed paper by Shapouri, Duffield, and Wang (2003) merely to rationalize their Footnote (6) that disposes of the calorific value of corn grain.

The report's supporting online material (Farrell and others, 2006c) is a Users' Manual that explains the spreadsheet assumptions and contents. The authors then perform certain arithmetic operations on the numbers they have stored in the spreadsheet, from which they draw their conclusions.

In order to arrive at their conclusions about corn ethanol, the authors selected the following path:

C1. Corn Grain Has No Energy. Calorific value of corn grain is omitted and not subtracted as a raw energy input to ethanol refineries.

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[3] The terse, 5-page report (Shapouri and McAloon, 2004) is incomplete and, e.g., corn ethanol yield must be inferred from (Shapouri, Duffield, and Wang, 2002).
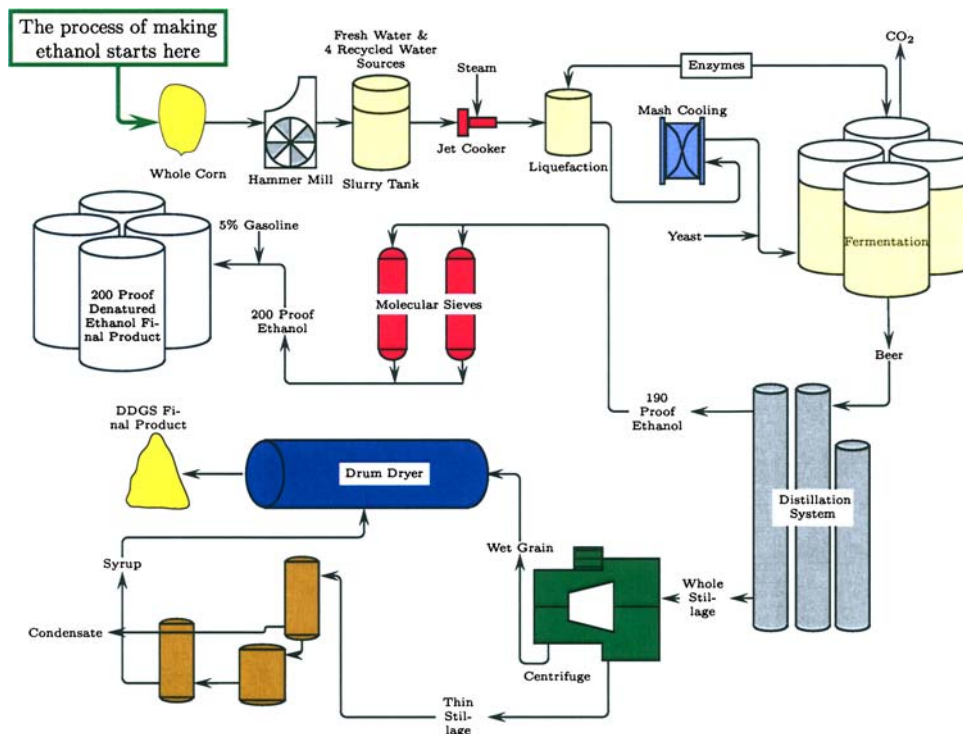
Figure 1. Schematic of dry grind corn ethanol plant. Note that after starch hydrolysis (liquefaction) to glucose, solid part of corn mash and oil could be separated physically from glucose liquor, and go straight to centrifuge and drying.

C2. Ethanol Yield Is High. Average yield of corn ethanol is increased by more than possible.

C3. Co-Products Receive Energy Credit. Roughly 30 to 50% of the fossil energy used to distill ethanol is subtracted from the biorefinery energy balance.[4]

C4. Results Are Consistent with Some Reports. The final results are consistent with the following reports: (Wang, Saricks, and Wu, 1997; Wang, 2001), (Graboski, 2002), and (Shapouri, Duffield, and Wang 2002; Shapouri and McAloon, 2004).

My thermodynamics paper was quoted because some of the numbers in the report's spreadsheet originated from it. The most important Part III of (Patzek, 2004) contains (i) the parameters classified in the spreadsheet as "NR" (for not reported), and (ii) a proper mass balance of soil and a free

energy (Second Law) balance of corn-ethanol cycle. This Second Law balance: (1) Naturally accounts for the free energy of starch (C1); (2) highlights limitations of the USDA ethanol yield estimate (C2); (3) naturally separates starch and ethanol from corn grain leftovers and coproducts (C3); and (4) calculates the ratio of the cumulative free energy consumed in ethanol production to mechanical work obtained from this ethanol to be up to 7:1, depending on the machine that transforms the chemical energy of ethanol into work (C4).

Here I will discuss at some length the scientific underpinnings of C1–C4 using only the First Law of thermodynamics.

ENERGY BALANCE OF ETHANOL REFINERY

I will focus on a modern dry grind ethanol refinery sketched in Figure 1. Because corn grain is a nascent or "baby" fossil fuel, it takes a lot of energy to transform it into ethanol.

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[4] Ethanol distillation is the single biggest expenditure of fossil energy in the corn-ethanol cycle, see Section *Energy Balance of Ethanol Refinery*.

To demonstrate this fact, I will start from quoting the best existing written performance guarantee by ICM, Inc., 310 North First Street, Colwich, Kansas 67030, (www.icminc.com):

(1) Ethanol yield: 2.80 gallons per bushel[5] (denatured)
(2) Natural gas use: 34,000 Btu per gallon of ethanol (denatured)
(3) Electricity use: 0.75 kWh per gallon of ethanol (presumably denatured too).[6]

After removing 5% of #14 gasoline, the yield is $2.8 \times 0.95 = 2.66$ gal/bu of ethanol, plus 2% of isobutyl and isopropyl alcohol (ASTM D5798-99). If the latter were true, there would be $2.66 \times 0.98 = 2.60$ gal/bu ethanol in the final mixture, which is an incredible 98% of the mean theoretical ethanol yield calculated (Patzek, 2006b). As long as the processed corn is old and dry (has less than 15% of moisture by weight) the yield guarantee can be met, otherwise it is unlikely.[7]

Natural gas use is $9.48/0.95 = 9.98$ MJ/L of gasoline-free product. Electricity use is $0.71/0.95 = 0.75$ MJ/L of gasoline-free product. As primary energy, this electricity is about 3 times more or 2.25 MJ/L. Primary fossil energy necessary to produce the product mixture is therefore 12.23 MJ/L or 15.5 MJ/kg.

Remark 1 Even in the most efficient ethanol refinery, one spends 15.5/26.7; that is, an equivalent of 58% of the low heating value of ethanol, on direct refining costs. This number should be compared with an average energy ratio for refining crude oil, $\sim 12\%$ for diesel fuel (or gasoline), in an average U.S. refinery.[8] Thus, excluding corn grain/ethanol transportation energy, it takes 5 times more fossil energy to produce corn ethanol in the best biorefinery than gasoline or diesel fuel from crude oil in an average petroleum refinery.

As shown in Figures 2 and 3, both based on the data published (Morris and Ahmed, 1992), ICM, Inc., (Patzek, 2004), and (Sheehan and others, 1998), the average fossil energy expended in ethanol refineries is 7 times that in petroleum refineries.

Remark 2 From a purely energetic point of view, corn grain refining to ethanol and the associated transport logistics are poor choices. Corn is a dispersed widely, low energy-density source, and it cannot be piped. Similarly, ethanol cannot be piped. Thus, energy costs of corn and ethanol transportation can be as high as 3 MJ/L of ethanol for a refinery on the East or West Coast.[9]

A careful look at Figure 1 reveals that starch liquefaction is the stage at which liquid glucose *could* be separated from corn grain solids and corn oil. The solid then could be sent directly to the centrifuge and drum drier. All of these operations do not involve distillation. Therefore, it is not entirely correct to subtract $4.1/0.95 = 4.3$ MJ/L of ethanol, or roughly 50% of the natural gas expenditure in an lCM plant. This subtraction also makes little sense based on (Patzek, 2004), where I argued that most corn processing co-products should be returned to the fields to limit the egregious irreversibility and unsustainability of industrial corn farming (Tegtmeier and Duffy, 2004).

SYSTEM BOUNDARIES, MASS, AND ENERGY BALANCE

Let me now discuss how Farrell and others (2006a, 2006c) have failed to define the system boundaries and perform proper mass and energy balances. The authors claim to use "commensurate system boundaries," to arrive at their net energy ratios for corn ethanol, but never define these boundaries, thus violating the strongest recommendations (Slesser, 1974, 1975; Hall and Day, 1977; Patzek, 2004). As stated clearly in (Patzek, 2004; Patzek,

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[5] With an unspecified moisture content.

[6] The actual energy bills paid by ethanol refineries in South Dakota point to about 40,000 Btu and 1.95 kWh per gallon of ethanol. Source: The South Dakota Public Utilities Commission, private comm., 7 April 2006.

[7] Note that the imprecise, ill-defined units used by the U.S. ethanol industry offer some leeway. For example, in a report on the Gopher dry mill plant in St. Paul, MN, (Anonymous, 2003), the mean ethanol yield is 2.5 gal/bu, but 1 bushel weighs 68.5 lbm, not 56 lbm, as it is supposed to (see page 4).

[8] Consistently with my analysis, I will use Sheehan and others (1998) estimate of primary energy spent on crude oil production (domestic and foreign), transport, refining, and finished diesel fuel transport. This estimate is listed in their table 3, page 11. The Fossil Energy Ratio = 1 MJ Fuel Energy/1.1995 MJ of

Fossil (Primary) Energy Input = 0.8337. The Fossil Energy ratio of crude oil refining is 0.065. figure 2, on page 13, rescales the components of table 1 to MJ/MJ of Fuel. In the rescaled units, the energy spent on refining is 0.12 of the energy in diesel fuel.

[9] *Estimating Ethanol Logistics Cost and Energy Use*. David Hirshfeld, pers. comm. MathPro, Washington, D.C., 27 Jan. 2006.
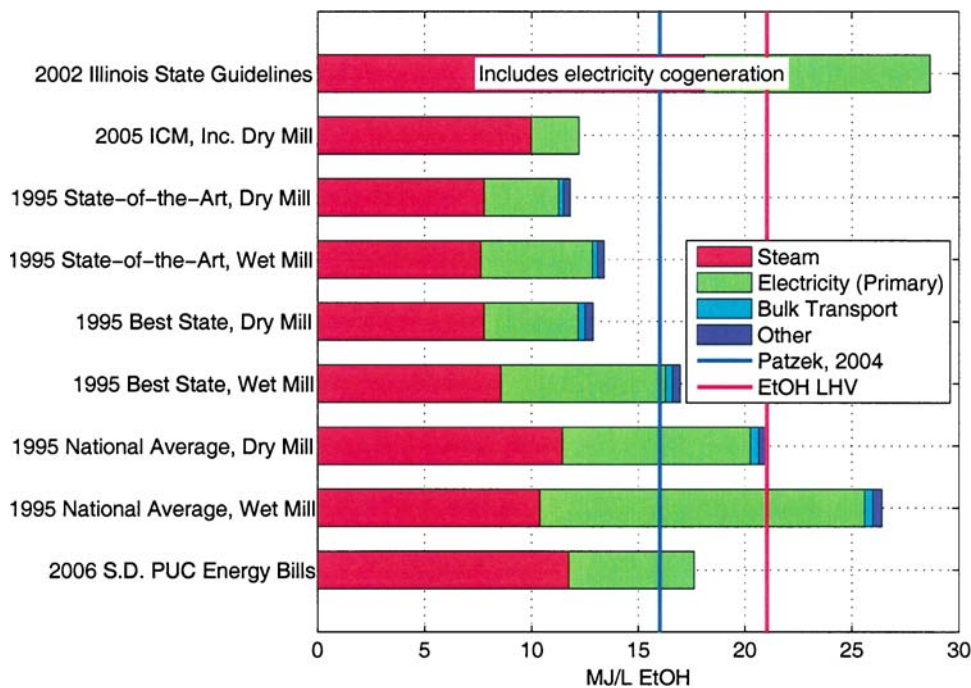
Figure 2. Fossil energy used in ethanol refineries. Left vertical line is my average estimate (Patzek, 2004). Other sources are: The ICM written guarantee, the 1995 update of Morris and Ahmed (1992), and www.iletohprefeas.com/include/input.pdf for the 2002 Illinois guidelines for potential ethanol plant builders. Low Heating Value (LHV) of ethanol; that is, amount of energy one obtains from combusting it in car engine, is right vertical line. ICM and Morris and Ahmed's (1992) data were discounted by taking out 5 volume percent of gasoline. Note that 1995 U.S. national average for dry mills is LHV of ethanol. Also note that my estimate (Patzek, 2004) is little better than "Best State" wet mill.

2006a), mass and energy inputs and outputs (fluxes) can be defined only *relative* to a system boundary. In other words, a system without a clear boundary cannot be described properly and the most fundamental axioms of science: mass and energy conservation will be violated.

Here, following Patzek (2004), the system boundary is defined as in Figure 4. Subsystem I encloses the corn fields[10] and plants. Subsystem I operates in annual cycles, and is refilled with the supply of corn seeds, soil nutrients, soil water, and heavy subsidies from ancient carbon fuels, minerals, and machinery. The 30-year average year-around solar *irradiance*[11] of a flat horizontal surface in Des Moines, Iowa, is 200 W/m^2. The corresponding annual irradiation of 1 ha therefore is 63,000 GJ. The all time highest average crop in Iowa has been

181 bushels/acre or 9700 kg of dry corn grain/ha. The biomass energy sequestered in this crop is 18.8 MJ kg^{-1} × 9700 kg ha^{-1} = 182 GJ ha^{-1}. Accounting for the stalk and roots, the total biomass energy is about 360 GJ ha^{-1}, or 360/63,000 = 0.006 of the annual *irradiation* energy. Thus, almost all solar energy is reflected, radiated, thermally conducted, and convected with water evaporated from the soil and plants. From the point of view of biomass sequestration the sun acts as a *catalyst* (Patzek and others, 2005). Subsystem I operates at two vastly different energy scales: The solar energy megascale, and the chemical/fossil energy microscale. The megascale solar energy balance is not pertinent to the chemical/fossil microscale energy balance performed here.

Subsystem II encloses ethanol refineries, their soil, and local surface and subsurface water resources. Subsystem III encloses machines that convert chemical energy in corn ethanol into a flow of electricity through fuel-cell cars or electrical power stations. Subsystem III is defined this way to

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[10] Additional field area for hybrid corn breeding also should be included.

[11] For definitions and details, see my Fall 2005 CE24 Lecture, http://petroleum.berkeley.edu/patzek/ce24/-Fall2005/Materials/PlantEfficiency.pdf
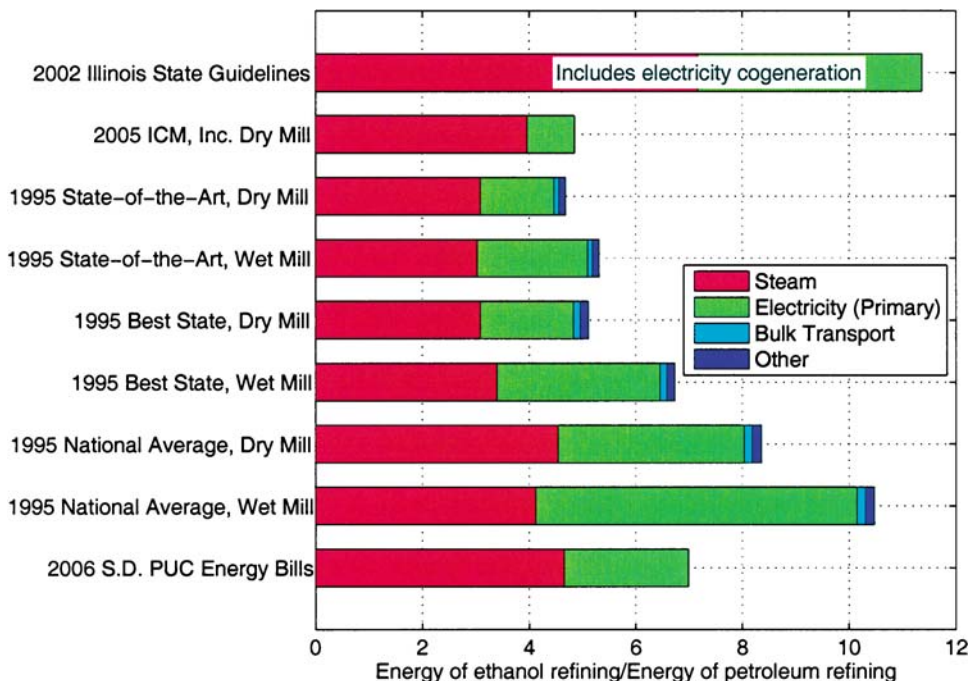
Figure 3. Ratio of energy used to refine corn grain to ethanol and energy used to refine crude oil to diesel fuel or gasoline. Calculations are based on data shown in Figure 2 and on NREL report (Sheehan and others, 1998). Mean ratio is 7.

keep the free-energy efficiency comparisons consistent among solar cells, wind turbines, and biofuel cycles, for details see Patzek (2004) and Patzek and Pimentel (2006). Subsystem III is not relevant to the discussion in this paper.

How to Analyze the Corn-Ethanol Cycle?

Any scientific analysis of an open, possibly steady-state, corn-ethanol system must fulfill these two old[12] principles of science that, when properly applied, account for all processes, old and new:

(1) The law of mass conservation (Lavoisier, ca. 1780)

(2) The law of energy conservation (Joule, Clausius, and Thomson, ca. 1840)

If the mass balance of the system is violated, so is the corresponding energy balance.

Following classical thermodynamics, (Planck, 1926; Stodola, 1927; Abbott and Van Ness, 1972), I will now write the steady-state mass and energy balances for Subsystems I and II and discuss the shortcomings of Equations (S-1)–(S-7) in (Farrell and others, 2006c). Both these balances will be written as

$$\sum \text{Inputs per unit area and time}$$
$$= \sum \text{Outputs per unit area and time}$$

Each of the mass and energy inputs will be specified in words.

The Mass Balances of Subsystems I–II

Farrell and others, (2006a, 2006c) have written no mass balances. The mass-balance terms, therefore, must be inferred from the corresponding terms in their energy balance. It turns out that Farrell and

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[12] Farrell and others (2006a) write this about (Patzek, 2004; Pimentel and Patzek, 2005): "[T]wo 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 (sic!) 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)."
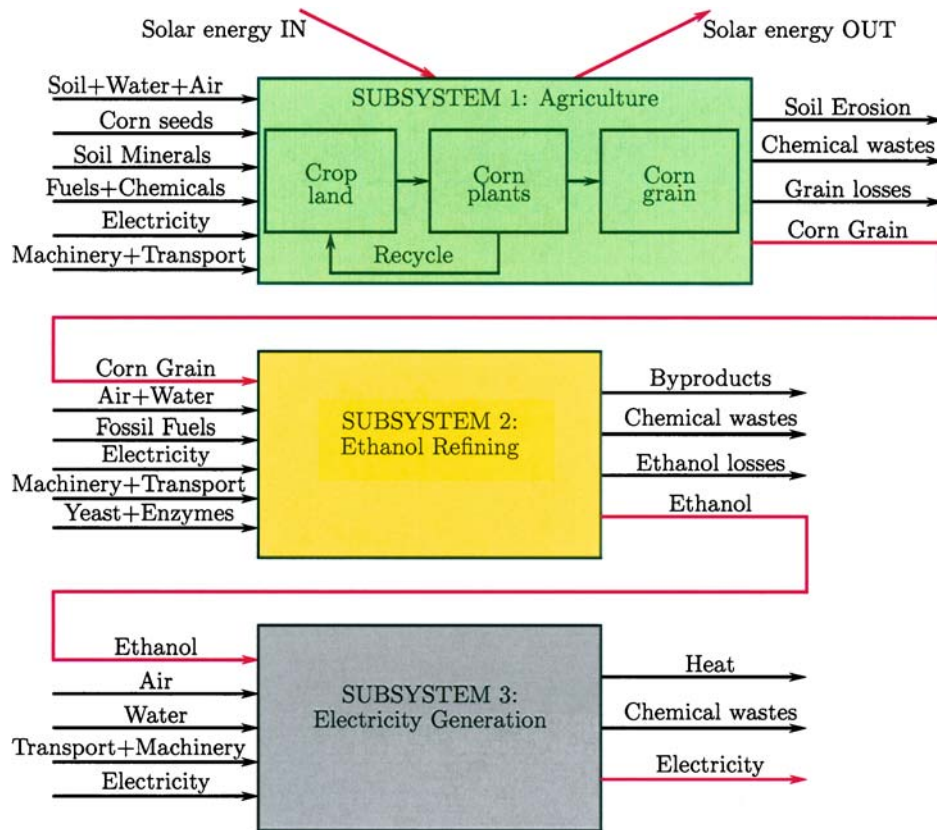
Figure 4. Corn → ethanol → electricity system consists of three subsystems in series. In these sub-systems, energy costs of labor have been omitted. Low-quality heat generated in Subsystems 1 and 2 also has been neglected. It is assumed that corn stalk is decomposed and recycled to improve soil structure. DDGS byproduct output of Subsystem 2, and CO_2 produced in Subsystems 1–3, become inputs to Subsystem 1, thus creating incomplete carbon cycle, and partially recycling other nutrients. Contaminated water outputs also can become inputs after purification, creating partial water cycle (see Patzek, 2004, Part III).

others have used some of the inputs and outputs in the mass balance of the industrial corn-ethanol cycle, but never closed this balance (their included steady-state inputs are labeled "(I)"). In other words, their calculations (Farrell and others, 2006a, 2006c) never conserve mass and, by implication, energy.

Properly speaking, all terms in the mass balance equations are fluxes and their units are kg m^{-2}, s^{-1}, or kg ha^{-1} s^{-1}, or kg ha^{-1} yr^{-1} (1 ha = 10,000 m^2):

Mass Balance of Corn Farming (Subsystem I)

$$
\begin{aligned}
&\text{1. Mass of Corn Seeds (I)} + \\
&\text{2. Mass of } CO_2 \text{ from Air} + \\
&\text{3. Mass of Mineral Uptake by Corn Plants (I)} + \\
&\text{4. Mass of Pesticide and Herbicide Uptake (I)} +
\end{aligned}
$$

$$
\begin{aligned}
&\text{5. Mass of Water In} = \\
&\text{6. Mass of Corn Plants (Grain (I)} + \text{Stalk} + \\
&\hspace{6cm} \text{Roots)} + \\
&\text{7. Mass of Effluent Liquids (Water} + \\
&\hspace{4cm} \text{Aqueous Chemicals)} + \\
&\text{8. Mass of Effluent Solids (Plant Parts)} + \\
&\text{9. Mass of Effluent Gases } (O_2, \ CO_2, \ H_2O, \ \text{etc.)}
\end{aligned}
\tag{2}
$$

Overall Mass Balance of Soil (Subsystem I)

$$
\begin{aligned}
&\text{1. Mass Corn Stalk} + \text{Roots} + \text{Other} \\
&\hspace{2cm} \text{Recycled Plant Parts/Animals} + \\
&\text{2. Mass of Weathered Minerals and Soil} \\
&\hspace{4cm} \text{from Inundations} + \\
&\text{3. Mass of Soil Restoration Materials} +
\end{aligned}
$$

4. Mass of Human Mineral Inputs to
Soil (I) =
5. Mineral Uptake by Plants and Animals +
6. Mass of Eroded Topsoil (Effluent +   (3)
Dust) +
7. Mass of Effluent Gases and Aerosols
(O_2, CO_2, CO, NH_3, NO_x, SO_x, etc.)

In industrial corn farming the soil mass balance is seldom steady-state because soil erosion and mineral withdrawal from soil mineral store may exceed mineral and plant inputs. Also, individual mineral component mass (and energy) balances must be performed separately. For example, the overall mass balance of human fertilizers:

Mass of Human Mineral Inputs =
Mass of Human Mineral Uptake by Corn
Plants +   (4)
Mass of Human Mineral Uptake by Soil +
Mass of Human Minerals in All Effluents

needs to be split into N, P, K, Mg, Ca, S, etc. mass balances, not all of which will be steady-state. For multiple examples of such calculations see Patzek and Pimentel (2006).

Mass Balance of Corn Processing (Subsystem II)

1. Mass of Corn Grain In +
2. Mass of Fossil/Synthetic Chemical
Inputs to Corn Processing (I) +
3. Mass of Yeast and Enzyme Inputs
to Corn Processing +
4. Mass of Water In +
5. Mass of O_2 from Air, SO_2, etc. =   (5)
6. Mass of Alcohols Out (I) +
7. Mass of DDGS Out (I) +
8. Mass of Other Distillation Byproducts +
9. Mass of Solid, Liquid, and Gaseous
Effluents from Corn Processing

The overall mass balance of corn processing is violated in Farrell and others (2006a, 2006c). Note that for 1 kg of corn grain input in a biorefinery there are 10–15 kg of process water inputs. Much of this water is evaporated, and some is recycled.

Terms 1, 6, 7, 8, and 9 in Equation (5) can be extracted from Equation (5) to yield just the balance

of *corn mass*:

Mass of Corn Grain In =
Mass of Alcohols Out (I) +
Mass of DDGS Out (I) +
Mass of Other Distillation Byproducts +   (6)
Mass of Some Solid, Liquid, and Gaseous
Effluents from Corn Processing

The Energy Balances of Subsystems I–II

Properly speaking, all terms in the energy balances below should have units of power fluxes $J\,m^{-2}\,s^{-1}$, or $MJ\,ha^{-1}\,crop^{-1}$, or $GJ\,ha^{-1}\,yr^{-1}$.

Energy Balance of Corn Farming (Subsystem I)

1. Energy in Corn Seeds (I) + Photosynthetic
Solar $h\nu\,m^{-2}\,s^{-1}$ +
2. Energy of CO_2 from Air +
3. Energy of Mineral/Chemicals Uptake by
Plants (I) +
4. Energy of Water In =
5. Energy of Corn Plants (Grain + Stalk +   (7)
Roots) +
6. Energy of Effluent Liquids (Water +
Aqueous Chemicals) +
7. Energy of Effluent Solids (Plant Parts) +
8. Energy of Effluent Gases (O_2, CO_2,
H_2O, etc.)

Note that some of the energy fluxes are close to zero (2), or are defined to be zero at standard conditions (4). The photosynthetic solar energy flux is a tiny fraction of solar irradiance. The fundamental energy balance (7) of corn farming is violated in (Farrell and others, 2006a, 2006c).

Overall Energy Balance of Soil (Subsystem I)

1. Net Solar Energy into Soil +
2. Energy of Corn Stalk + Roots + Other
Recycled Plant Parts/Animals +

3. Energy of Weathered Minerals and Their Aqueous Solutions $+$
4. Energy of Human Mineral Inputs $(I) +$
5. Soil Restoration Work $+$
6. Fossil Energy of Soil Reworking and Irrigation $(I) =$
7. Energy Stored in Soil Structure $+$ (8)
8. Energy of Mineral Uptake by Plants and Animals $+$
9. Energy of Eroded Topsoil (Effluent $+$ Dust) $+$
10. Energy of Effluent Gases and Aerosols (O_2, CO_2, CO, NH_3, NO_x, SO_x, etc.)

Note that the soil energy balance is seldom steady-state. The fundamental energy balance (8) of soil is violated in Farrell and others (2006a, 2006c).

Overall Energy Efficiency of Corn Farming (Subsystem I $+$ Environment)

If one assumes for simplicity that the calorific value of corn grain is equal to the solar energy sequestered as corn grain, then the overall energetic efficiency of industrial corn farming can be defined as:

$$\eta_{\text{corn grain}} = \frac{1}{1 + \sum \text{Farming Energy Inputs} + \sum \text{Restoration Work Inputs}}$$

$$\eta_{\text{corn grain}} = \frac{\text{Output Corn Energy}}{\text{Sequestered Solar Energy}}$$

$$\times \frac{1}{1 + \sum \text{Fossil/Environmental Energy Subsidy Fractions}} \quad (9)$$

where the dimensionless Farming Energy Inputs, Restoration Work Inputs, and their sum, Energy Subsidy Fractions, have the units of MJ/MJ in sequestered solar energy. The second term in Equation $(9)_2$ describes fossil energy inputs to industrial corn agriculture. In perfect solar-driven agriculture $\eta_{\text{corn grain}} = 1$.

Most energy balances ignore the environmental impacts of industrial farming, which are high (Tegtmeier and Duffy, 2004); exceptions are rare (Berthiaume, Bouchard, and Rosen, 2001; Patzek, 2004), Part III. The first sum in the denominator is about 0.2 (Patzek, 2004), Part I, or ~ 0.4 when the environmental impacts of direct fossil energy inputs to corn farming also are considered, see Part III. The second sum contains a relatively small Term 5 in Equation (8), and a large work term to restore the environment of the open corn fields Subsystem I. This work is external to Equation (8) and has not been included yet in (Patzek, 2004). The energy needed to perform restoration work must originate from the corn-ethanol cycle, other environmental resources, and fossil energy inputs. For example, the ethanol co-products can serve to restore the corn fields and get proper energy credit, see Section *Coproduct Energy Credit Revisited* for more discussion.

The second sum could certainly exceed 0.8 for the increasingly degraded industrial farming ecosystems (Ho and Ulanowicz, 2005). A conservatively low value[13] for Iowa today might be 0.4 (0.2 for the Subsystem I restoration work (Patzek, 2004) plus 0.2 for the environment restoration work). With this assumption,

$$\eta_{\text{corn grain}} = \frac{1}{1 + 0.2 + (0.2 + 0.2)} = 0.63 \quad (10)$$

Energy Balance of Corn Processing (Subsystem II)

To understand the delicate question of DDGS energy credits, we must perform the following detailed energy balance of the biorefinery in Figure 1:

1. Energy of Corn Grain $+$
2. Energy of Fossil/Synthetic Chemical Inputs to Corn Processing $(I) +$
3. Energy of Yeast and Enzyme Inputs to Corn Processing $+$
4. Energy of Water In $+$
5. Energy of O_2 from Air, SO_2, etc. $=$ (11)
6. Energy of Concentrated Alcohols Out $(I) +$
7. Energy of Dry DDGS Out $(I) +$
8. Energy of Other Distillation Byproducts $+$
9. Energy of Solid, Liquid, and Gaseous Effluents from Corn Processing

This overall energy balance of biorefinery is violated (Farrell and others, 2006a, 2006c).

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[13] It is difficult to grasp the scale of the ecosystem restoration problem. For example, in 1997, 20,500 gigatonnes/yr of N were injected into the U.S. environment from distributed human sources; one third was exported (Howarth and others 2002). More than 60 percent of our coastal rivers and bays in every coastal state of the continental United States are moderately to severely degraded by nutrient pollution. This degradation is particularly severe in the mid Atlantic states, in the southeast, and in the Gulf of Mexico (Howarth, 2000) Therefore, ground and surface water restoration will add to the Restoration Work Inputs another term that may be significantly larger than 1.

Remark 3 If we drop the requirement that the alcohols in Term 6 be concentrated and the DDGS in Term 7 be dry, Terms 1, 6, 7, 8, and 9 in Equation (11) can be extracted to balance just the *corn grain energy*, which tells us only that the energy of the *dilute* (8–12%) alcohol solution, plus the energy of the aqueous suspension of the non-starch solids and corn oil, balances almost exactly the energy in corn grain. This is approximately true because (1) the beer water and effluent CO_2 have almost no energy, and (2) starch cooking and hydrolysis consume some heat, but glucose fermentation generates an almost equal amount of heat.

The corn energy balance in the Slurry tank + Jet cooker + Liquefaction + Fermentation part of biorefinery is

$$
\begin{aligned}
\text{Energy in Corn Grain} = \\
\text{Energy in Corn Ethanol (I) \& Other} \\
\text{Alcohols} + \text{Energy in DDGS (I)} + \\
\text{Energy in Other Distillation Byproducts} + \\
\text{Energy in Some of Effluents}
\end{aligned} \quad (12)
$$

This corn energy balance in the refinery also is violated (Farrell and other, 2006a, 2006c).

Now we can check if the assertion in Remark 3 is correct, and the mass and energy balance Equations (6) and (12), are consistent with the data in the standard high heating values (Patzek, 2004). In keeping with the customary industry units, let me base the energy balance on 1 standard bushel of corn, or 56 lbm of corn grain that contains 15% of moisture by weight, or 21.6 kg of bone dry grain. From the calculations in Patzek (2006b), it follows that with *zero losses*.[14] The combined mass and energy balances now yield the following:

$$
\begin{aligned}
21.6\,\text{kg/bushel} \times 18.8\,\text{MJ/kg} \,(\text{Energy} \\
\text{in Corn Grain}) = \\
7.86\,\text{kg/bushel} \times 29.7\,\text{MJ/kg} \,(\text{Energy} \\
\text{in Corn Ethanol}) + \\
0.297 \times 21.6\,\text{kg/bushel} \times 18.8\,\text{MJ/kg} \\
(\text{Energy in nonstarch solids}) + \\
0.039 \times 21.6\,\text{kg/bushel} \times 39.5\,\text{MJ/kg} \\
(\text{Energy in corn oil}) + \\
0.045 \times 21.6\,\text{kg/bushel} \times 18.8\,\text{MJ/kg} \\
(\text{Energy in Losses})
\end{aligned} \quad (13)
$$

or

$$
\begin{aligned}
406\,\text{MJ/bushel} \,(\text{Energy in Corn Grain}) = \\
233\,\text{MJ/bushel} \,(\text{Energy in Corn Ethanol}) + \\
103\,\text{MJ/bushel} + 33\,\text{MJ/bushel} \,(\text{Energy} \\
\text{in DDGS}) + \\
18\,\text{MJ/bushel} \,(\text{Energy in Losses})
\end{aligned} \quad (14)
$$

Thus, the corn processing energy balance, consistent with the corresponding mass balance, is $406 \approx 387$ MJ/bushel; that is, it closes to within 5%. This is not bad at all, considering the inaccuracies in measuring the high heating values of the non-starch parts of corn grain that–mixed together form DDGS. Also the energy in mash cooking, starch liquefaction, and fermentation, as well as in the liquid and gaseous effluents has been neglected.

Note that at this stage we have balanced the *output* energy of dilute corn beer, and dilute solid suspension of the non-starch portion of corn grain and yeast, with the *input* energy of corn grain. This beer now must be *concentrated* from ~10% to 100% of ethanol, and the solids must be separated from water and dried. Ethanol concentration by multistage distillation is an extremely energy-intensive process. It is done in the Distillation and Drum Dryer section of the biorefinery in Figure 1. Almost *all* of the fossil energy in the biorefinery is spent on the beer distillation and DDGS separation and drying, see Section *Energy Balance of Ethanol Refinery* and Figure 2.

Remark 4 To close the complete biorefinery energy balance Equation (11), the fossil energy spent on distillation should be added as the second energy input after corn grain; that is, the input energy in yeast and enzymes will be neglected for now.

Now we are ready to perform the complete energy balance of the dry grind corn biorefinery. I will use the most optimistic ICM estimate of the distillation/drying energy, 15.5 MJ/kg of ethanol + butanol + isopropanol + etc. I will also charge the refinery with 1.5 MJ/kg in wastewater cleanup, and grain, alcohol and DDGS transportation costs.[15]

$$
\begin{aligned}
21.6\,\text{kg/bushel} \times 18.8\,\text{MJ/kg} \,(\text{Energy in} \\
\text{Corn Grain}) + \\
7.86\,\text{kg/bushel} \times (15.5 + 1.5)\,\text{MJ/kg} \\
(\text{Fossil Energy}) =
\end{aligned}
$$

---

[14] Note that I am using here the *maximum theoretical yield* of ethanol based on the real data presented (Patzek, 2006b). No industrial facility exceeds 85–95% of this yield for a long time. Thus, the counter-argument (Farrell and others, 2006b) is not completely correct.

[15] This energy cost was 2 times higher (Patzek, 2004).

7.86 kg/bushel $\times$ 29.7 MJ/kg (Energy in
Distillation Products) +
0.297 $\times$ 21.6 kg/bushel $\times$ 18.8 MJ/kg
(Energy in nonstarch solids) +   (15)
0.039 $\times$ 21.6 kg/bushel $\times$ 39.5 MJ/kg
(Energy in corn oil) +
All Energy Losses in Corn Processing

or

406 MJ/bushel (Energy in Corn Grain) +
134 MJ/bushel (Energy in Fossil Fuels) =
233 MJ/bushel (Energy in Distillation
Products) +   (16)
136 MJ/bushel (Energy in DDGS) +
171 MJ/bushel (All Energy Losses in Corn
Processing)

The overall biorefinery efficiency is defined as

$$\eta_{\text{ethanol}} = \frac{\text{Output Ethanol Energy}}{\sum \text{Refinery Energy Inputs}}$$

$$\eta_{\text{ethanol}} = \frac{\text{Output Ethanol Energy}}{\text{Input Corn Energy}}$$

$$\times \frac{1}{1 + \sum \text{Fossil/Environmental Energy Input Fractions}}$$

(17)

where the dimensionless Energy Input Fractions have the units of MJ/MJ in corn grain. The second term in Equation $(17)_2$ describes energy losses in a corn-ethanol biorefinery. A perfect solar driven corn-ethanol refinery with the maximum theoretical ethanol yield has $\eta_{\text{ethanol}} = 233/406 = 0.57$. In that refinery all coproducts would have to be recycled back to the corn fields to limit fossil energy inputs to agriculture (see Equation (9)).

At this stage, we can calculate *maximum* efficiency of the best possible ethanol refinery in two different ways:

(1) Without DDGS:

$$\eta_{\text{ethanol}} = \frac{233}{406 + 134} = 0.43 \qquad (18)$$

(2) Or, we can attempt to squeeze in the DDGS as another *finished fuel* (Which it is not! See the discussion in Section Coproduct Energy Credit Revisited.)

$$\eta_{\text{ethanol+DDGS}} = \frac{233 + 136}{406 + 134} = 0.68 \qquad (19)$$

Note that the best case ethanol refining is far less efficient than average petroleum refining ($\eta_{\text{gasonline}} = 0.88$). If one replaces the best ICM biorefinery with the 1995 National Average Dry Mill (see Fig. 2), the second term in Equation (16) increases from 134 to 220 MJ/bushel, and the average biorefinery efficiencies are 0.37 and 0.59, respectively.

To obtain the best overall efficiency of industrial corn-ethanol cycle, the biorefinery efficiencies in Equation (18) or (19) should be multiplied by the overall corn farming efficiency, Equation (10). We then get the following.

(1) (No DDGS coproduct credit):

$$\eta_1 = \eta_{\text{ethanol}} \times \eta_{\text{corn grain}} = 0.43 \times 0.63 = 0.27$$

(20)

(2) (Full DDGS coproduct credit):

$$\eta_2 = \eta_{\text{ethanol+DDGS}} \times \eta_{\text{corn grain}}$$

$$= 0.68 \times 0.63 = 0.43 \qquad (21)$$

These efficiencies are 0.23 and 0.37, respectively, for the average dry mill case. All examples shown in Figure 2 are compared in Figure 5. By including photosynthetic energy, but also a penalty for the restoration of corn fields, rivers, aquifers, etc., the overall corn-cycle efficiency is 3–4 times lower (without the DDGS energy credit), or ~2 times lower (with the DDGS energy credit), than the overall efficiency of gasoline production (0.833).

So, no matter how we do the calculations, we reach the following conclusion:

Remark 5 Fossil fuels must be conserved if our civilization is to survive a little longer (see Fig. 6). From thermodynamics it follows that ecological damage wrought by industrial biofuel production must be severe.

What Is Wrong with Net-Energy Analysis?

Equations (S-2) and (S-3) in Farrell and others (2006c) do not follow from *any* conceivable mass balance equation for a corn-ethanol system and are inconsistent with the fundamental energy balance Equations (7)–(12). In their net-energy analysis, Farrell and others (2006a, 2006c) did *not* (i) define the system boundaries, (ii) close mass balances and, consequently, (iii) conserve energy in violation of the First Law of Thermodynamics.

As already pointed out in Patzek (2004), most of the existing net-energy models of the energetics of industrial corn-ethanol cycle are based on nonphysical assumptions and *must* be corrected.
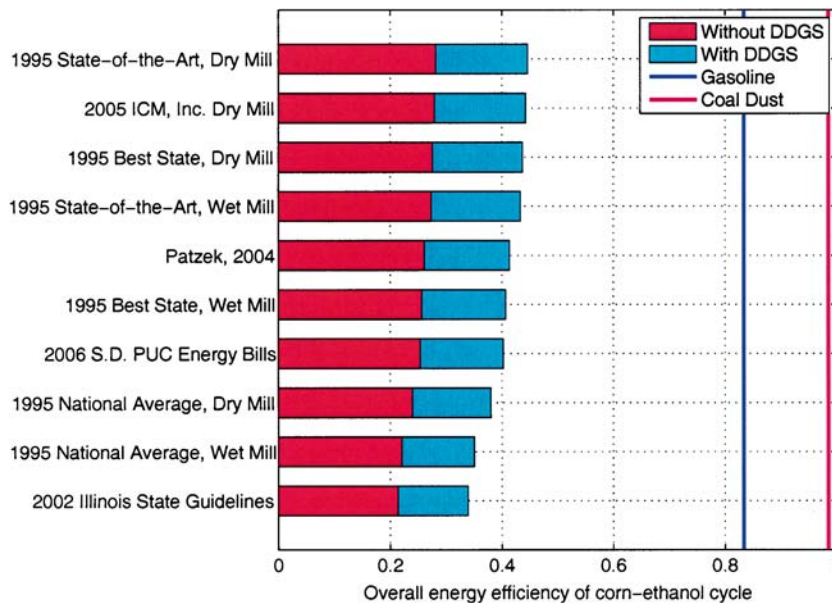
Figure 5. Overall energy efficiency of industrial corn-ethanol cycle. Data sources are listed in caption of Figure 2.

Remark 6 The net-energy models currently used to evaluate industrial biofuel cycles pick only those terms in the fundamental energy balances that justify *a posteriori* business or political outcomes. These models are favored by some engineers, managers, economists, and political scientists (see, e.g., Wang, Saricks, and Wu, 1997; Wang, 2001; Shapouri, Duffield, and Wang, 2002, 2003; Graboski, 2002;

Figure 6. Gallons of ethanol, produced in cycle driven by corn ethanol, needed to displace energy in 1 gallon of gasoline are calculated as $1/\eta_1/0.64$ or $1/\eta_2/0.64$. With full DDGS energy credit, 3.9 gallons of ethanol displace on average energy in 1 gallon of gasoline. Without DDGS energy credit, this average number is 6.2 gallons of EtOH. Note that 2006 PUC energy bills for South Dakota plants represent both averages.

Shapouri and McAloon, 2004; Farrell and others, 2006a), and lead to never-ending discussions (cf. Footnote 10) of the sort: "My net-energy *balance* (sic!) is better than yours because you did/did not include this or that term." The only hope to achieve progress in the comparison of relative merits of biofuel cycles is to use their *complete* energy balances, and define the *overall* energy efficiencies that account for the horrendous, widespread damage of the environment caused by these cycles (Patzek, 2004; Patzek and Pimentel, 2006; Pimentel and Patzek, 2005). It is time to move away from the ongoing and tedious fossil fuel net energy balance debate and on to the ecological problems that are poorly understood.

Coproduct Energy Credit Revisited

As highlighted in Footnote 10, there are serious disagreements whether the coproduct energy credits are justified. The reasons for their introduction and my arguments against them have been discussed in Section *Energy Balance of Ethanol Refinery*. Now we are ready to make more quantitative arguments:

(1) From a pure energy argument, see Equation (14), the energy embodied in a *fuel* made of bone-dry DDGS is 136/406 or 33% of the energy embodied in corn grain, whereas the ethanol energy is 233/406 or 57%.

(2) The *additional* refinery fossil energy inputs embodied in DDGS are $0.33 \times 233/136$ or 0.57 of the DDGS energy. The direct fossil energy embodied in harvested corn grain is about 0.2, see Equation (10). Therefore, 1 bushel of DDGS is equivalent to 3 bushels of corn in terms of its fossil energy content. One might give DDGS an energy credit, but only if one eliminates corn farming in proportion to the ratio of the respective energy contents. Thus, for 4 billion gallons of ethanol per year one would have to eliminate $0.95 \times 4 \times 10^9/2.5 \times 0.33 \times 3 = 1.6$ billion bushes of corn per year, or about 3.5–4 million hectares of farms that produce corn for feed. Otherwise, talk about DDGS "displacing" corn is meaningless.

(3) When one performs a mass balance of soil, Equation (3), as was done in Patzek (2004), one dicovers that to keep the soil from deterioration and ever-deepening dependence on synthetic fertilizers it is necessary to recycle as much plant matter as possible.[16] This was the thermodynamic reason for my rejection of these credits. No soil mass balance was done in Farrell and others (2006a, 2006c) and the references listed in C4.

(4) I have argued that DDGS should be returned back to the fields to limit the irreversibility of modern agriculture (see Section 3.12 in (Patzek, 2004)). Therefore, from my macro-ecological point of view, the DDGS energy credit is somewhat *negative*: The DDGS energy *output* of a biorefinery becomes an energy *input* to remote corn farms, minus the energy losses for processing, handling, transport, and spreading the DDGS on the fields. On the other hand, the diminished need for nitrogen fertilizer, decrease of soil erosion, and decrease of toxic water runoff from the fields, will improve energy efficiency of corn agriculture and subtract perhaps as much as 0.2 from the denominator of Equation (10).

(5) Finally, one might attempt to charge cows fed with DDGS with some or all methane emissions they cause. A single cow burps ∼600 L of methane per day (Kaharabata, Schuepp, and Desjardins, 2000). Assuming a 100-year time horizon, the greenhouse gas emissions from a cow are equivalent to 3 tonnes of CO_2 per year, an amount that would be generated by burning 1.9 tonnes (522 gal) of ethanol per year by a driver who consumes 12 gallons of E85 per week. For a 20-year time horizon, the equivalent CO_2 emissions from methane will be 2.7 times larger (Anonymous, 2002).

EQUIVALENT CO_2 EMISSIONS FROM THE CORN-ETHANOL CYCLE

My methodology for obtaining equivalent[17] CO_2 emissions from the industrial corn ethanol cycle is

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[16] The same argument applies with force to all large-scale schemes to cellulosic ethanol production (Patzek and Pimentel, 2006).

[17] Emissions of other gases, mostly nitrous oxide N_2O, ammonia NH_3, and methane CH_4, are converted to equivalent CO_2 emissions using their relative potencies in creating the greenhouse effect (Anonymous, 2002).

described in Patzek (2004). There are three differences between that analysis and the current one:

(1) Ammonium nitrate fertilizer is replaced with anhydrous ammonia and the respective emissions are decreased by 1/2.

(2) Emissions from humus oxidation in soil eroded by wind are included with the following assumptions: (a) topsoil contains 4% of humus (Stevenson, 1982); (b) humus contains 50% of C by weight (Stevenson, 1982), wind-eroded soil is enriched in humus by $(1.3 + 5)/2 \approx 3$ on average (Allison, 1973); (c) wind erodes only 1 mm of topsoil per year, or 10 tonnes/ha-yr (Pimentel, 2006); and (d) the airborne humus is completely oxidized.

(3) To make the comparisons meaningful, methane, gasoline, and diesel fuel are now charged with incremental 17% (2% more than before) emissions for their recovery, transportation, and processing.

With these assumptions, the specific emissions of equivalent CO_2 in grams per MJ in ethanol are shown in Figure 7. Note that the minimal CO_2 emissions from soil erosion are the second biggest source after ethanol refineries. These soil emissions are likely to be significantly higher on flat terrain with dry topsoil, such as that in South Dakota during drought.

The specific emissions from Subsystems I and II in the corn ethanol cycle are compared in Figure 8 with the equivalent emissions from other fossil fuels, methane, gasoline, and diesel fuel. It seems that the cumulative corn-ethanol emissions are 50% higher than those from ancient fossil fuels.

If one charges corn ethanol with equivalent CO_2 emissions from methane burped by the cows fed with DDGS, one adds at the minimum

$$0.33 \frac{\text{kg DDGS}}{\text{kg dry corn}} \times \frac{1}{0.364} \frac{\text{kg dry corn}}{\text{kg EtOH}} \times \frac{44}{30} \frac{\text{kg CO}_2}{\text{kg DDGS}}$$
$$\times \frac{0.12 \times 16}{44} \frac{\text{kg CH}_4}{\text{kg CO}_2 \text{ burped}} \times 56 \frac{\text{kg equiv. CO}_2}{\text{kg equiv. CH}_4}$$
$$\times \frac{1}{29.7} \frac{\text{kg EtOH}}{\text{MJ}} \times 1000 \approx 110 \frac{\text{g equiv. CO}_2}{\text{MJ in EtOH}} \quad (22)$$

or another 38% of equivalent CO_2 emissions over and above the gasoline emissions. The factor of 56 in the given equation comes from the relative potency of methane for the 20-year time horizon (Anonymous, 2002), and it was assumed that 12% of the gas burped by a cow is methane (Kaharabata, Schuepp, and Desjardins, 2000).
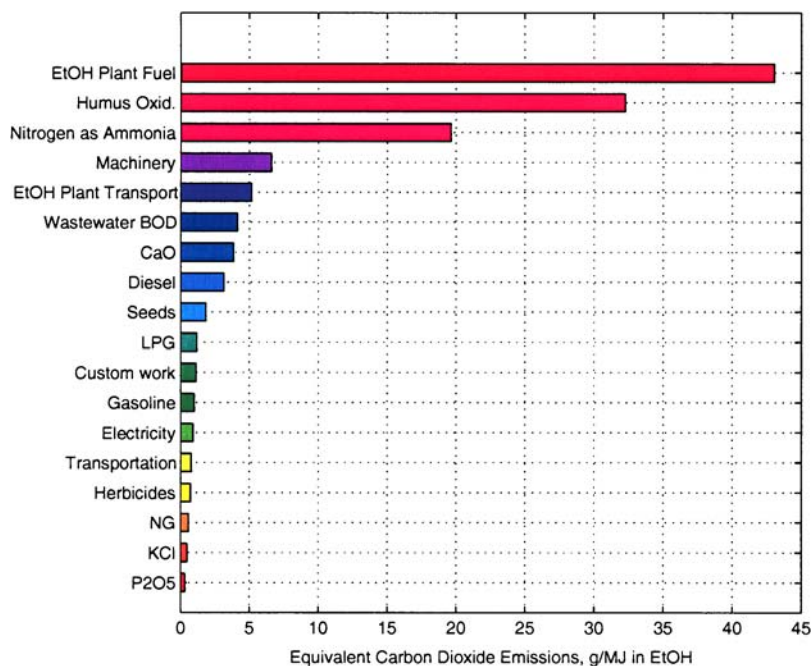

Figure 7. Equivalent CO_2 emissions from each major nonrenewable resource consumed by industrial corn-EtOH cycle.
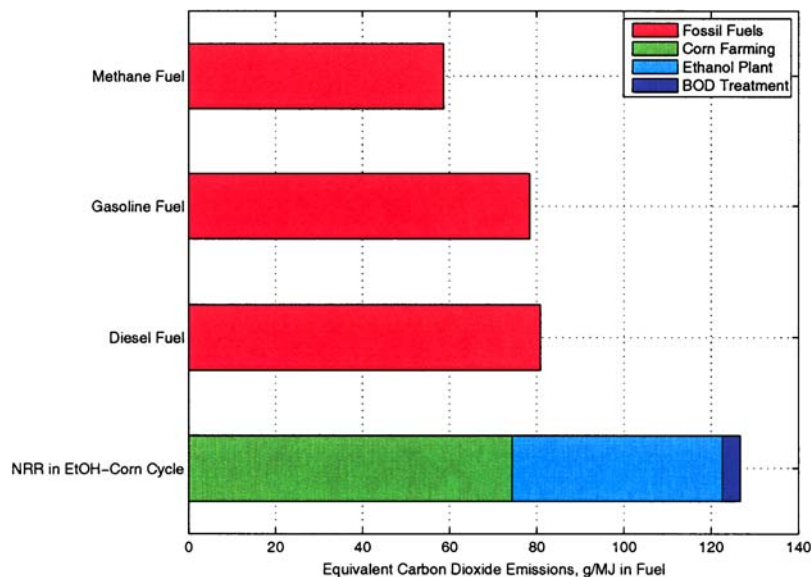
Figure 8. Equivalent CO_2 emissions from corn agriculture, corn ethanol production, and other fossil fuels. Corn-ethanol cycle emissions *double* if methane burped by cows fed with DDGS coproduct is accounted for.

If ethanol refineries switch from natural gas to coal, their GHG emissions will increase by at least 70–80%, (see table 19 ir Patzek, 2004), not counting the high energy costs of coal transport to the dispersed biorefineries.

SUMMARY AND CONCLUSIONS

This paper has been written in response to the Science Report by Farrell and others (2006a, 2006c) and the related gray-literature reports (Wang, 2001; Graboski, 2002; Shapouri, Duffield, and Wang, 2002; Shapouri and McAloon, 2004).

It has been shown here that the mass and energy calculations in (Farrell and others, 2006a) and, by extension, in (Wang and others, 1997; Wang, 2001; Shapouri, Duffield, and Wang, 2002, 2003; Shapouri and McAloon, 2004), violate the fundamental laws of mass and energy conservation. In particular, Equation (S-2) in Farrell and others (2006c), generates ethanol coproduct energy from nothing. This energy then could be used to drive a Carnot engine (Carnot, 1943), in direct contradiction the First Law of thermodynamics. In effect, (Farrell and others, 2006a) have constructed a perpetuum mobile of the first kind.

The energy cost of producing and refining carbon fuels in real time, for example corn and ethanol, is high relative to that of fossil fuels deposited and concentrated in geological time. Proper mass and energy balances of corn fields and ethanol refineries that account for photosynthetic energy, some of the environment restoration work, and the co-product energy have been formulated. These balances show that production of ethanol from corn is 2–4 times less favorable than production of gasoline from petroleum. Also, for thermodynamical reasons, ecological devastation wrought by the real-time industrial biofuel production *must* be severe.

The main conclusion of this paper is that the United States already has spent enough time, money, and natural and human resources on pursuing the mirage of replacing fossil fuels in aggregate (petroleum + natural gas + coal) with biomass. Better solutions lie on the demand side: limiting consumption, improving efficiency, consuming more locally, fostering local biofuel production, etc. These solutions are feasible, readily available, and usually ignored.

Finally, I believe we need to move the public discussion away from simplistic debate whether biofuels are good or bad to the more realistic question: At what level should we be producing biofuels? I do not think it is zero. Today biofuels replace a small fraction of transportation fuels and, unless we are successful in developing cellulose-based fuels (obviously feedstock, environmental and land use issues have

to be addressed here too), this fraction will remain small.

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