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Thermodynamics of the Corn-Ethanol Biofuel Cycle

Tad W. Patzek*
Department of Civil and Environmental Engineering, 210 Ericsson Building, MC 1716,
University of California, Berkeley, CA 94720, USA

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*Corresponding author. E-mail: patzek@patzek.berkeley.edu

This article defines sustainability and sustainable cyclic processes, and quantifies the degree of non-renewability of a major biofuel: ethanol produced from industrially grown corn. It demonstrates that more fossil energy is used to produce ethanol from corn than the ethanol's calorific value. Analysis of the carbon cycle shows that all leftovers from ethanol production must be returned back to the fields to limit the irreversible mining of soil humus.

Thus, production of ethanol from whole plants is unsustainable. In 2004, ethanol production from corn will generate 8 million tons of incremental CO_2, over and above the amount of CO_2 generated by burning gasoline with 115% of the calorific value of this ethanol. It next calculates the cumulative exergy (available free energy) consumed in corn farming and ethanol production, and estimates the minimum amount of work necessary to restore the key non-renewable resources consumed by the industrial corn-ethanol cycle. This amount of work is compared with the maximum useful work obtained from the industrial corn-ethanol cycle. It appears that if the corn-ethanol exergy is used to power a car engine, the minimum restoration work is about 6 times the maximum useful work from the cycle. This ratio drops down to 2 if an ideal fuel cell is used to process the ethanol. The article estimates the U.S. taxpayer subsidies of the industrial corn-ethanol cycle at \$3.8 billion in 2004. The parallel subsidies by the environment are estimated at \$1.8 billion in 2004. The latter estimate will increase manifold when the restoration costs of aquifers, streams, and rivers, and the Gulf of Mexico are also included. Finally, the article estimates that (per year and unit area) the inefficient solar cells produce ∼100 times more electricity than corn ethanol. There is a need for more reliance on sunlight, the only source of renewable energy on the earth.

Keywords biofuel, ethanol, fossil fuels, corn, sustainability, thermodynamics, energy, entropy, exergy, solar

1. INTRODUCTION

In the Preface to *What is Life?*—one of the great science classics of all times—Erwin Schrödinger (1967) observed: “A scientist is supposed to have a complete and thorough knowledge, at first hand, of *some* subjects and, therefore, is usually expected not to write on any topic of which he is not a master. This is regarded as a matter of *noblesse oblige*.”

The principle of non-interference with the far-away fields of science often precludes the scientists from seeking to explain the *universal* aspects of science, which are of paramount importance to the society at large. For example, the sophisticated technological models of biofuel production, for example, (Hemelinck, 2004), cannot be formulated alone, without welding them first to a detailed analysis of the possibilities of depleting the environment in the long-term and destroying the valuable ecosystems. This example is not merely of academic interest. A *United Nations Bioenergy Primer* (Kartha and Larson, 2000) states: “In the most biomass-intensive scenario, [modernized] biomass energy contributes . . . by 2050 . . . about one half of total energy demand in developing countries. . . . The IPCC’s[1] biomass intensive future energy supply scenario includes 385 million hectares of biomass energy plantations globally in 2050 (equivalent to about one quarter of current planted agricultural area), with three quarters of this area established in developing countries.” The magic word “sustainable” appears 130 times in this *Primer*, without ever being defined.[2] What will happen if the developing countries entrust their fragile ecosystems and societies to a fundamentally flawed, unsustainable energy supply scheme? What if the distributed generation of solar power is a significantly better alternative to fossil fuels and biofuels?

So here I renounce the noblesse and embark on a synthesis of facts and theories related to the production of a common biofuel, ethanol from corn, albeit with second-hand knowledge of some of these facts—and at a risk of making a fool of myself. I hope that some or most of this article will be read by the concerned farmers, engineers, environmentalists, and policy makers. In particular I wish to reach the fellow scientists, who—for most part—remain blissfully unaware of the astronomical *real* problems with supplying energy to over 6 billion people, but who often vigorously analyze the peripheral issues (which in addition are tackled in isolation and out of context).

Most traditional biofuels, such as ethanol from corn, wheat, or sugar beets, and biodiesel from oil seeds, are produced from classic agricultural food crops that require high-quality agricultural land for growth. A significant portion of the sunlight these crops capture is diverted to produce seeds and store sugar, and their growing seasons are short. The net energy yield of corn,[3] 80–100 GJ/ha-crop (Part I of this article), is significantly lower that those[4] of perennial crops and grasses (200–300 GJ/ha-crop), and sugarcane (∼400 GJ/ha-crop) (Rogner, 2000). Also, the environmental costs of annual crops are very high: they cause more soil erosion (up to 100-fold), require 7–10 times more pesticides, and more fertilizers than perennial grasses or wood (Berndes *et al.*, 2003). Finally, industrial *manufacturing* of hybrid seeds is very energy-intensive.

In this article, I will describe in some detail the unfavorable thermodynamics of the industrial production of ethanol from one particular food crop, corn. I will use the Second Law of thermodynamics to track what is happening to us (or, is it U.S.?) as mere years pass, and the precious resources the sun and the earth have been making and storing for millions of years are being squandered in front of our eyes.

1.1. Corn Highlights

The United States is the single largest corn producer in the world. Large overproduction of subsidized cheap corn forces corn producers and processors to invent new ingenious uses for their product. In terms of their large negative impact on the society and the environment, two corn products—ethanol and high-fructose syrup—stand out (Pollan, 2002; Elliot *et al.*, 2002). Almost 20% of U.S. corn production is now diverted to produce ethanol. Hence, in this article I will *de facto* argue that U.S. corn production should be reduced by at least 20% with significant benefits to the taxpayers and the planet. A telegraphic description of the U.S. corn farming and processing is as follows:

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[1] Intergovernmental Panel on Climate Change.

[2] The endlessly repeated harvest of whole plants that grow on the same soil would have to be sustainable.

[3] The energy of dry corn grain minus the fossil energy inputs per hectare and per crop.

[4] The reported net energy yields of perennial grasses, sugarcane, *etc.*, seem somewhat high.

- Corn is the single largest U.S. crop.
- Corn is farmed on ~28 million hectares, more than twice the area of England and Wales, and a bit less than 1/4 of all harvested cropland in the United States.
- The average yield of moist corn grain is ~8600 kg/ha.
- 44% of world's corn is produced in the U.S., 1% in Canada.
- All U.S. corn fields are fertilized.
- Corn requires more fertilizer than any other crop.
- Corn erodes soil much faster than it can rejuvenate by natural processes.
- Corn needs 50–100 cm water; 15% of corn is irrigated.
- Corn farmers receive $10 billion in price subsidies.
- Over 12 billion liters of corn ethanol will be produced in the United States in 2004.
- U.S. goal: Produce 20 billion liters of ethanol from corn annually.
- Ethanol producers receive ~$3.8 billion annually from the federal government and state governments, and extract ~$1.8 billion from the environment.

1.2. Energy Inputs to Corn Production

Fossil energy is essential to industrial agriculture. The following are the major energy inputs to industrial corn farming:

- Nitrogen fertilizers (all fossil energy).
- Phosphate, potash, and lime (mostly fossil energy).
- Herbicides and insecticides (all fossil energy).
- Fossil fuels: diesel, gasoline, liquified petroleum gas (LPG), and natural gas (NG).
- Electricity (almost all fossil energy).
- Transportation (all fossil energy).
- Corn seeds and irrigation (mostly fossil energy).
- Machinery, roads, silos, plants (mostly fossil energy).
- Labor (mostly fossil energy)

Corn produced at a large expense of fossil energy is then transformed, with even more fossil energy, into pure ethanol.

1.3. Layout

This article is divided into five parts, each of which can be read more or less independently. In Part I, I discuss the mass balance of corn processing, and the energy and mass balances of corn farming and ethanol production. Any First Law analysis of the corn-ethanol production process is *fundamentally incomplete*, and gives rise to confusion and arguments, which become moot once a more complete Second Law analysis is performed. Therefore, in Part II, I overview the fundamentals of thermodynamics, define the linear processes and cycles, irreversibility and sustainability, as well as *exergy* (the free energy available relative to the environmental conditions). In Part III, I apply the concepts developed in Part II to the industrial corn-ethanol cycle and answer the following questions:

1. Is ethanol production from corn a sustainable process?
2. If it is not sustainable, how unsustainable is it?
3. Can process changes result in making ethanol production from corn sustainable?

In particular, in Part III, I discuss the Carbon Cycle, the Water Cycle, the Ideal and Industrial Corn-Ethanol Cycles, and calculate the minimum work required to restore the nonrenewable resources consumed to produce corn ethanol. In Part IV, I estimate the various subsidies lavished on the transnational agribusiness corporations by the U.S. federal and local governments, and the huge subsidy extracted by these corporations from the U.S. environment: the rural population, soil, groundwater, rivers, the Gulf of Mexico, air, plants, and wildlife. Part V lists all major conclusions from this work.

Through my analysis, I hope to put to rest the sweeping statements made by some scientists, such as the following (Deluga *et al.*, 2004):

> Fast and efficient fuel reforming is one of the critical steps in producing H_2 for fuel cells and the "hydrogen economy," and ethanol is now the most available and economically renewable fuel.
>
> . . . Recent studies indicate that the energy in the fuel-ethanol is at least 1.34 times the energy used in its production.

PART I: MASS AND ENERGY BALANCE

1. Introduction

Here, I revisit the classical story of ethanol from corn: the cumulative mass and energy balance of corn farming and subsequent ethanol production. There have been several well-known predecessors who told their versions of this story before. Professor David Pimentel is the world-famous agricultural expert from Cornell University, author of the CRC *Handbook of Energy Utilization in Agriculture* (Pimentel, 1990), the book *Food, Energy, and Society* (Pimentel, 1996), and dozens of publications on the subjects of ethics and energy efficiency of agriculture, for example: Pimentel *et al.* (1988), Pimentel and Dazhong (1990), Pimentel (1991), Pimentel *et al.* (1994), Pimentel (2001). Here I will use only his most recent analysis of production of corn-ethanol (Pimentel, 2003). Doctor Michael Wang, Christopher Saricks, and May Wu are the authors of the 1997 Argonne National Laboratory Report, *Fuel-Cycle Fossil Energy Use and Greenhouse Gas Emissions of Fuel Ethanol Produced from the U.S. Midwestern Corn* (Wang *et al.*, 1997), which told quite a different version of the corn-ethanol story. Doctor Hosein Shapouri, James Duffield, and Michael Wang co-wrote the most recent 2002 USDA Report: *The Energy Balance of Corn Ethanol: An Update* (Shapouri *et al.*, 2002), which was less rosy than the Argonne Report, but considerably more optimistic than Professor Pimentel's analysis. I joined the corn-ethanol story in late 2002, after reading the thought-provoking book, *Food, Energy, and Society* by Pimentel. Subsequently, in Spring 2003, I decided to teach a Freshman Seminar at Cal on the subject of corn ethanol, and published with the students our own version of the story, *Ethanol from Corn: Clean Renewable Fuel for the Future, or Drain on Our Resources and Pockets?* (Patzek *et al.*, 2004), highly critical of the Argonne Report, and also critical of the 2002 USDA Report.

The new twist in my current story is the consistent split of all energy flows into the *specific energies* in MJ/kg, and the *mass fluxes* in kg/ha-crop.[5] This split will make my explanations clearer, and the possible errors easier to spot and correct. However nicely told, the classical ethanol-from-corn story is fundamentally incomplete and should be treated as Part I of the *Ethanol Biofuel Trilogy*. Parts II and III of this Trilogy must be told in the somewhat exotic language of the Second Law of thermodynamics, which describes the passage of Time and limits the possible directions of natural and industrial processes.

2. Mass Balance of Corn

Mass will be usually expressed in kilograms per hectare. One hectare is 10000 m^2 or 2.47 acres.

It is safe to assume that the average corn yield in the United States has increased 5-fold over the last 70 years (NASS, 2204b). For example, in Indiana (Nielsen, 2002), the average corn yield was ~ 30[6] bushels per acre in 1930 and 156 bushels per acre in 2001. The steadily improving yield resulted mostly from the increased fertilizer use and better corn genetics.

In 2001–2003, corn in the United States was harvested from $\sim 28 \times 10^6$ hectares (NASS, 2004a). The average corn yield varied from 130 bushels per acre in 2002, to 138.2 bushels/acre in 2001 and 142.2 bushels/acre in 2003 (NASS, 2004a).

Definition 1. One equivalent bushel is defined as 56 pounds (25.4 kg) of corn grain that contains 15 percent of moisture by weight (Bender and Hill, 1997).

Therefore, the mean corn yield over the last 3 years was just below 8600 kg/ha of *moist* corn grain, or $8600 \times 0.85 = 7300$ kg/ha of *dry* corn grain.

Because ethanol (EtOH) is made from the hydrolyzed starch with the theoretical efficiency of 0.51, 1 kg of dry corn grain may yield $0.66 \times 0.51 = 0.337$ kg of water-free EtOH with zero losses (see Table 1). Therefore, from 1 hectare, one may theoretically produce 2460 kg EtOH, given the dry corn yield above. Of course there are losses in the corn-to-ethanol conversion process, and the practical efficiency will be lower.

Remark 1. In the U.S., the customary unit of reporting efficiency of corn conversion to ethanol is gallons EtOH per bushel, e.g., (Shapouri *et al.*, 2002). With the standard EtOH density of 0.796 kg/L, the theoretical efficiency of 0.337 kg EtOH/kg dry grain (0.423 L EtOH/kg dry grain) yields 2.85 gallons EtOH/dry bushel = 2.42 gallons EtOH/equivalent bushel of corn with 15% moisture.

3. Major Energy Inputs to Corn Production

Most energy inputs will be expressed in MJ/kg of active ingredient in the input. For example, ammonia contains 82% nitrogen (active component); therefore, the specific energy input in MJ to obtain one kg of ammonia will be divided by 0.82.

TABLE 1

Average dry mass composition of corn grain (White and Johnson, 2003)

Component	% by mass
Starch	66
Oil	3.9
Gluten feed (21% protein)	24
Gluten meal (60% protein)	5.7
Losses	0.4

3.1. Field Chemicals

- **Nitrogen** is a component of many important structural, genetic, and metabolic compounds in plant cells. It is a major component of chlorophyll, amino acids, cell energy carriers (ATP/ADP), and genetic material (DNA/RNA).
- **Phosphorus** is one of the primary structural components of cell membranes. It is involved in photosynthesis (ADP/ATP), synthesis of proteins and vitamins, and it occurs in important enzymes.
- **Potassium** activates enzymes that produce proteins and sugars. It maintains water content and, hence, the turgor (rigidity) of plant cells.
- **Calcinated lime** is used to increase the pH of soil acidified by nitrogen fertilizer. The ideal pH for corn is 6.6.
- **Herbicides**, such as Atrazine, Acetochlor, S-Metolachlor, Dicamba, Nicosulfuron, and so on are used to protect corn from weeds.
- **Insecticides**, such as Chlorpyrifos, Terbufos, Carbofuran, Tefluthrin, and so on are used to protect corn from insects.

The average application rates of major field chemicals used in corn farming are reported in Table 2.

TABLE 2

Average application rates of corn field chemicals in 2001 (NASS, 2002)

Compound	True kg/ha	Fraction ha w/applied	Mean kg/ha
N	148.8	0.96	142.8
P_2O_5[a]	62.5	0.79	49.4
K_2O[a]	93.5	0.65	60.8
Herbicides	2.54	0.98	2.49
Insecticides	1.08	0.29	0.31

[a] USDA (NASS, 2002) reports "P" and "K" but, according to Ms. Barbara Tidwell of the NASS/MISO Customer Service, they mean P_2O_5 and K_2O.

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[5] The notation kg/ha-crop stresses that the time unit in the average fluxes is the duration of a single crop, *e.g.*, 120 days in the case of corn plants.

[6] The lowest average yield of corn in the U.S., ~18.2 bushels/acre, was recorded in 1901 and 1934, USDA, http://usda.mannlib.cornell.edu/data-sets/-crops/96120/trackrec2003.txt

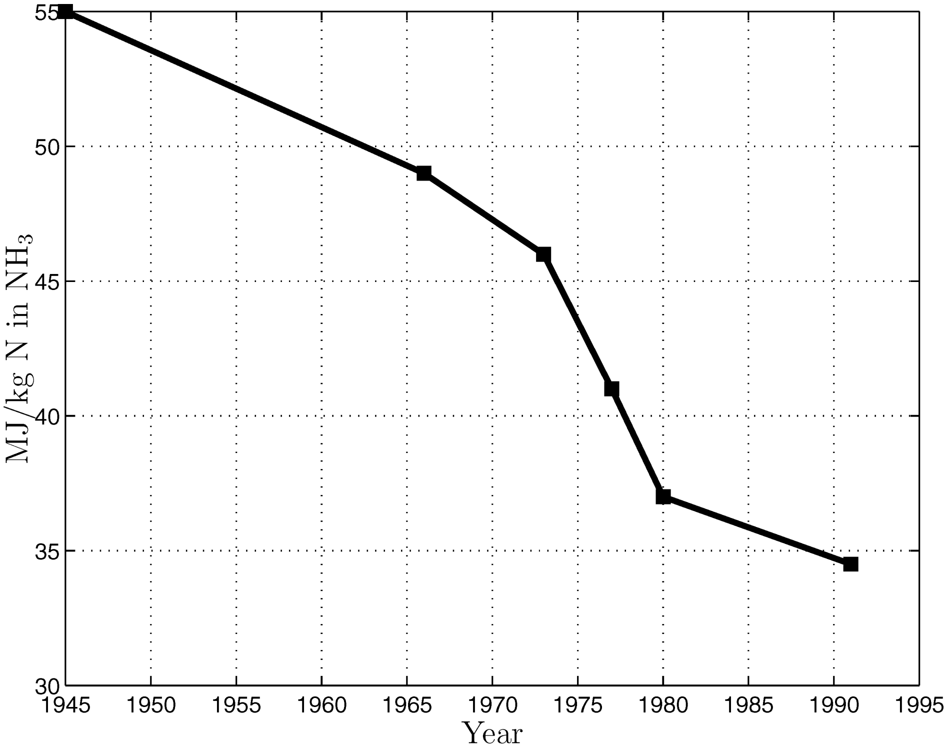

FIG. 1. History of energy efficiency of ammonia production in MJ/kg N. Source: G. Kongshaug (1998).

3.1.1. Specific energy requirements for nitrogen fertilizer. Nitrogen fertilizers are derived from ammonia, nitric acid, and carbon dioxide. Practically all ammonia is produced from natural gas and nitrogen in the Haber-Bosch process (Worrell *et al.*, 1994, Kongshaug, 1998; Worrell *et al.*, 2000). The energy efficiency of the Haber-Bosch process has been improved by 1/3 over the last 60 years, see (see Figure 1). Therefore, the age of the ammonia-producing plant does matter. Ernst Worrell *et al.* (2000) have compiled the ages and outputs of the 44 largest U.S. ammonia plants (see Figure 2). Most of these plants were built in the 1960s, and some were later modernized and expanded. The fact is that the major U.S. plants were built 40 years ago, and some were revamped 20–30 years ago. Another example comes from Europe: In 1995, ammonia synthesis in modern European plants consumed approx. 36.93 MJ/kg N, whereas older plants needed about 43.08 MJ/kg N (Biermann *et al.*, 1999).

Remark 2. For nitrogen fertilizer production, I will use the average efficiency of 30-year-old plants. I will also assume that all nitrogen fertilizer applied to the U.S. corn fields is represented by ammonium nitrate.

Kongshaug (1998) analyzed energy efficiency of ammonia production and divided ammonia plants into three classes: "Modern," "Average European plants," and "30-year-old plants." Using his terminology, the major nitrogen fertilizers are produced with the following specific energy inputs *per unit mass of nitrogen* in them.

Ammonia, NH_3, has 82% of nitrogen by mass. Following Kongshaug (1998), I will assume the following *net* energy consumption to produce ammonia:

$$\begin{array}{r} \text{30 Years Old 47 MJ/kgN} \\ \text{Average Europe 39 MJ/kgN} \\ \text{Modern 34.5 MJ/kgN} \end{array} \quad [1]$$

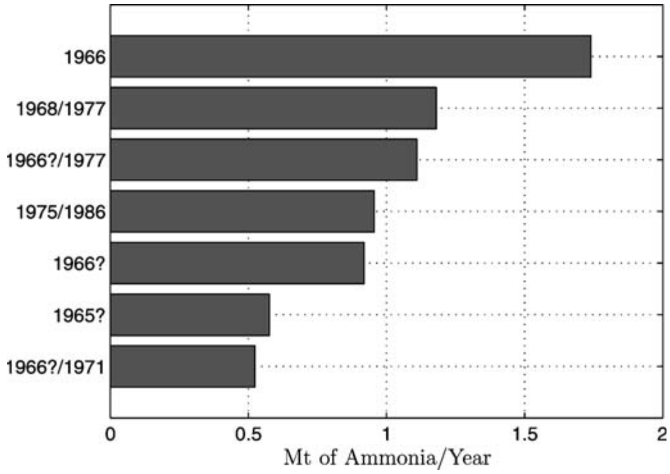

FIG. 2. Together, these seven largest plants produce 40% of the U.S. ammonia. The first dates refer to plant opening. Some of the plants were later expanded and revamped, as indicated by the second dates. Source: Ernst Worrell *et al.* (2000).

Urea, $CO(NH_2)_2$, has 45% of nitrogen by mass, and is obtained from ammonia and carbon dioxide: $2NH_3 + CO_2 \rightarrow CO(NH_2)_2 + H_2O$. The net energy consumption (Kongshaug, 1998) is:

$$\begin{aligned} \text{30 Years Old Ammonia } + 10 &= 57\ \text{MJ/kgN} \\ \text{Average Europe Ammonia } + 9 &= 48\ \text{MJ/kgN} \\ \text{Modern Ammonia } + 7.2 &= 42\ \text{MJ/kgN} \end{aligned} \quad [2]$$

Ammonium Nitrate, NH_4NO_3, has 35% nitrogen by mass, and is produced from nitric acid and ammonia: $HNO_3 + NH_3 \rightarrow NH_4NO_3$. Nitric acid is obtained by burning ammonia over catalyst to produce NO_x. One of the by-products of ammonium nitrate production is nitrous oxide N_2O, a potent greenhouse gas. With 97% conversion of ammonia to AN, the energy consumption is

$$\begin{aligned} \text{30 Years Old Ammonia } + 4 &= 51\ \text{MJ/kgN} \\ \text{Average Europe Ammonia } + 2 &= 41\ \text{MJ/kgN} \\ \text{Modern Ammonia } + 0.43 &= 35\ \text{MJ/kgN} \end{aligned} \quad [3]$$

3.1.2. Other energy inputs to fertilizer production. Primary particulation of fertilizers is carried out in prilling and granulation processes. The granulation units can also be used for a second pass of product building blocks (for mixed fertilizers), in addition to compaction and bulk blending units. The energy requirement for primary particulation is ~0.25–0.5 MJ/kg product, and for secondary granulation and compaction 0.7–1.1 MJ/kg product (Kongshaug, 1998). Here I have used 0.5 MJ/kg of AN. The energy costs of natural gas recovery, compression, purification and transportation, and fertilizer packaging, if any, are estimated cautiously at 2 MJ/kg N. The various estimates of net energy inputs into nitrogen fertilizer production are shown in Figure 3 and listed in Table 3. In all the tables, the estimates by Shapouri *et al.* come from their 2002 report (Shapouri *et al.*, 2002), by Wang *et al.* (1997), and by Berthiaume *et al.* (2001). Because Berthiaume *et al.* have reported only the specific exergy consumption, I have used my energy consumption estimates to represent theirs. I have also corrected and/or amended the various estimates as noted in what follows.

TABLE 3
Specific energy consumption and application rates of nitrogen fertilizer

Active ingredient	Specific energy MJ/kg	Application rate kg/ha	Source
N	63.43	148.0	Pimentel, 2003
N	54.43	148.8	Patzek, 2004
N	43.00	140.0	Shapouri *et al.*, 2002
N	49.06	153.0	Wang *et al.*, 1997
N	54.43[a]	150.0	Berthiaume *et al.*, 2001

[a] Berthiaume *et al.* (2001) do not give the specific N, P, K, Ca fertilizer energies, only the specific exergies. I have *assumed* that the specific energies of Berthiaume *et al.* are equal to my estimates, and used their reported application rates.

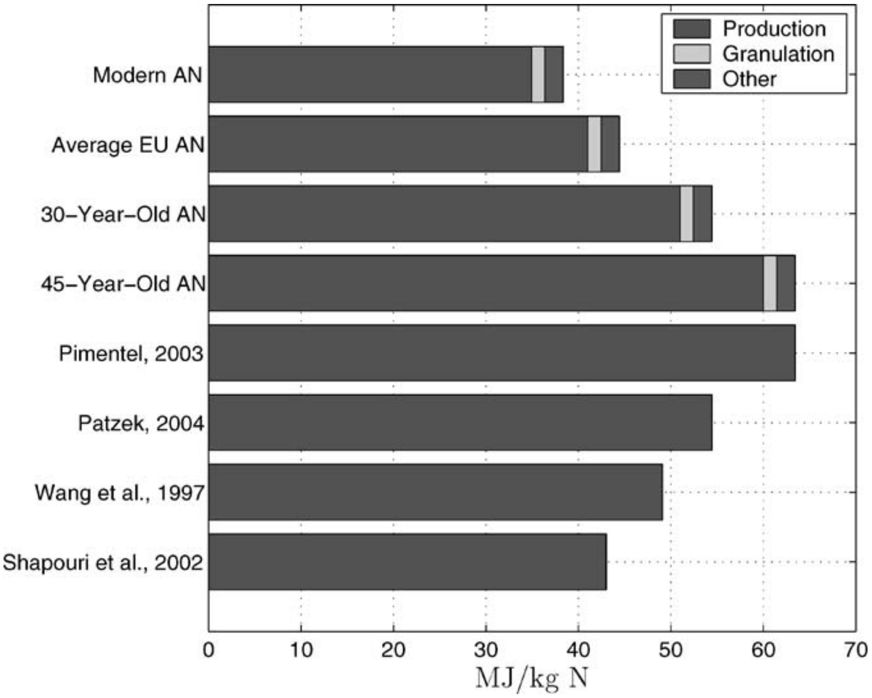

FIG. 3. The various estimates of the unit energy consumption to produce ammonium nitrate (AN). The estimates by Shapouri *et al.* are listed in Shapouri *et al.* (2002), by Wang *et al.* in Wang *et al.* (1997), and Pimentel's (2003) estimate of 78.1 MJ/kg N was adjusted down to the 45-year-old AN.

3.1.3. Specific energy requirements for phosphorus fertilizers. Phosphate and phosphoric acid are produced from the igneous *fluorapatite* $Ca_{10}(PO_4)_6(F, OH)_2$, and the sedimentary *francolite* $Ca_{10}(PO_4)_{6x}(CO_3)_x(F, OH)_{2+x}$. For example, superphosphate may be produced as follows:

$$\begin{aligned} 2Ca_3(PO_4)_2 + 6H_2SO_4 &\rightarrow 4H_3PO_4 + 6CaSO_4 \\ Ca_3(PO_4)_2 + 4H_3PO_4 &\rightarrow 3\,\underbrace{Ca(H_2PO_4)_2}_{\text{superphosphate}} \end{aligned} \qquad [4]$$

Calcium sulphate (gypsum) produced in reaction $(4)_1$ may be precipitated as a *dihydrate*, using milder conditions, 26–32% P_2O_5 at 70–80°C, or a *hemihydrate*, using 40–52% P_2O_5 at 90–110°C. Even though it demands more energy, the hemihydrate reaction is preferred because it optimizes use of sulfuric acid. The energy costs of gypsum disposal are omitted here.

Unlike the European Fertilizer Manufacturers Association (EFMA), which maintains an informative website, the United States does not have clear statistics on the types of phosphorus (and other) fertilizers used. From the USGS and U.S. Census Bureau documents, for example, Jasinski (2002) and references therein, it may be deduced that calcium phosphates (triple superphosphate and single superphosphate) dominate in the United States, followed by di-ammonium phosphate (DAP).

Just as with nitrogen fertilizers, phosphate fertilizers have different contents of active ingredient, here P_2O_5. For example, triple superphosphate is 46% P_2O_5, single superphosphate 18–20%, and di-ammonium phosphate 46%.

In this analysis, I will use the single superphosphate as the reference phosphorus fertilizer. The typical energy consumption for the 30-year-old technology is given by Kongshaug (1998) (see Table 4). In contrast to the energy input for nitrogen fertilizer, the data for phosphorus vary widely between 5.1 MJ/kg P_2O_5 and 26.4 MJ/kg P_2O_5 (Pimentel and Dazhong, 1990). EFMA uses 15.8 MJ/kg P_2O_5 (Biermann *et al.*, 1999).

Using the data in Table 4, the typical U.S. energy consumption is $0.3 + 6.5 = 6.8$ MJ/kg P_2O_5 as single superphosphate. The specific energy consumption for phosphorus and its application rates are listed in Table 5.

3.1.4. Specific energy requirements for potassium fertilizers. The energy requirements for potassium vary from 4.0 MJ/kg K_2O (Mudahar and Hignett, 1982) to 13.7 MJ/kg K_2O (Patyk and Reinhardt, 1997). EFMA uses 9.3 MJ/kg K_2O (Biermann *et al.*, 1999). The typical energy requirements to produce different potassium fertilizers are listed in Table 6. Here I will use the muriate of potash (MOP), or KCl, as the typical potassium fertilizer. Production of KCl is mainly carried out by shaft mining and beneficiation. The most energy efficient potash processes, based on a high quality sylvanite salt, require only 1.5 MJ/kg MOP (2.5 MJ/kg K_2O). The energy consumption, however, varies a lot, and estimates up to 6 MJ/kg MOP are reported for mining of more mixed salts (Kongshaug, 1998).

TABLE 5
Specific energy consumption and applications rates of phosphorus fertilizers

Active ingredient	Specific energy MJ/kg	Application rate kg/ha	Source
P_2O_5	17.44	53.0	Pimentel, 2003
P_2O_5	6.80	62.5	Patzek, 2004
P_2O_5	4.76	54.0	Shapouri *et al.*, 2002
P_2O_5	11.40	56.0	Wang *et al.*, 1997
P_2O_5	6.80	55.0	Berthiaume *et al.*, 2001

Here I will treat KCl as an admixture to a superphosphate fertilizer, and give it an identical energy consumption of 6.8 MJ/kg K_2O. The specific energy inputs and application rates for the potassium fertilizers are listed in Table 7.

3.1.5. Specific energy requirements for calcinated lime. Lime must be added to de-acidify soil after heavy use of nitrogen fertilizers. Calcinated lime, CaO, is obtained from limestone and dolomites. The calcination process is energy-intensive, and generates one mole of CO_2 per one mole of CaO. EFMA uses 2.97 MJ/kg CaO (Biermann *et al.*, 1999), but here I will follow the Australian Academy of Sciences and assume that only 1.75 MJ/kg CaO is used to produce calcinated lime.

Lime application rate is not commonly reported by the USDA. The suggested application rate is 1.8 times the application rate of nitrogen (Tisdale *et al.*, 1985), but there are reports of several times higher application rates (*e.g.*, Pimentel, 2003).

The total application rates of nitrogen, phosphorus, and potash fertilizers, as well as that of calcinated lime are shown in Figure 4.

3.1.6. Specific energy requirements for herbicides and insecticides. There are many active ingredients in commercial herbicides and insecticides, but all have very high specific

TABLE 4
Energy consumption in superphosphate production (Kongshaug, 1998)

Process	MJ/kg P_2O_5
Phosphate mining	>0.3
Apatite mining	2.9
Dihydrate process	2.5
Hemihydrate process	6.5

TABLE 6
Energy consumption in potassium fertilizer production (Kongshaug, 1998)

Fertilizer	K%	MJ/kg K_2O
Chloride	52	6.8 (additive to phosphates)
Sulphate	49	Not reported
Nitrate	45	13.5 (KNO_3 solution evaporation) 43 MJ/kg N

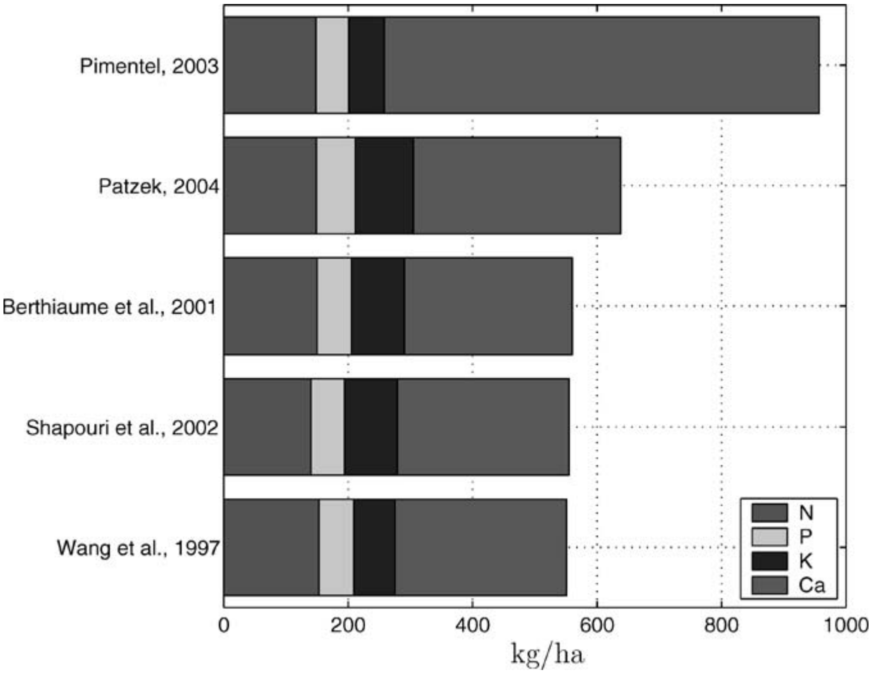

FIG. 4. The total fertilizer application rates listed in Tables 3, 5, 7, and 8.

energy requirements for their production. Here I have used the data collected in Table 5 in Shapouri *et al.*'s report (2002).

The specific energy inputs and application rates of herbicides and insecticides are listed in Tables 9 and 10. The overall application rates of herbicides and insecticides are also shown in Figure 5.

3.2. *Specific Energy Requirements for Fossil Fuels*

A unit mass of a fossil fuel gives out a specific amount of heat (its *calorific value*) when burned. The *Low* Calorific Value or *Net* Calorific Value (NCV) of a fossil fuel assumes that combustion products contain the water of combustion as vapor. The heat contained in this water is not recovered. Outside of power stations and fuel cells, water remains as vapor after combustion. Therefore, I use the low calorific values of all liquid fuels. The *High* Calorific Value or *Gross* Calorific Value (GCV) assumes that combustion water is entirely condensed. The heat contained in this water is recovered. Shapouri *et al*. (2002) seem to use GCV for all fuels. Wang *et al*. (1997) give only the total amount of energy for each fossil fuel; therefore, their specific values are back-calculated for each fuel and agree with my estimates.

TABLE 7
Specific energy consumption and application rates of potassium fertilizer

Active ingredient	Specific energy MJ/kg	Application rate kg/ha	Source
K_2O	13.77	57.0	Pimentel, 2003
K_2O	6.80	93.5	Patzek, 2004
K_2O	8.71	85.0	Shapouri *et al*., 2002
K_2O	5.30	66.0	Wang *et al*., 1997
K_2O	6.80	85.0	Berthiaume *et al*., 2001

TABLE 8
Specific energy consumption and application rates of calcinated lime

Active ingredient	Specific energy MJ/kg	Application rate kg/ha	Source
CaO	1.33	699.0	Pimentel, 2003
CaO	1.75	333.0[a]	Patzek, 2004
CaO	1.70	276.0	Shapouri *et al*., 2002
CaO	1.70	276.0[b]	Wang *et al*., 1997
CaO	1.75	270.0	Berthiaume *et al*., 2001

[a] Shapouri *et al.*'s data (Table 2 in Shapouri *et al.* (2002)) with the two zero entries omitted.
[b] Wang *et al.* (1997) does not report lime use; their estimates have been corrected by adding the lime use reported by Shapouri *et al.* (2002).

TABLE 9
Specific energy consumption and application rates of herbicides

Specific energy MJ/kg	Application rate kg/ha	Source
422.00	2.10	Pimentel, 2003
261.00	2.54	Patzek, 2004
261.00	4.73	Shapouri *et al*., 2002
237.30	3.07	Wang *et al*., 1997

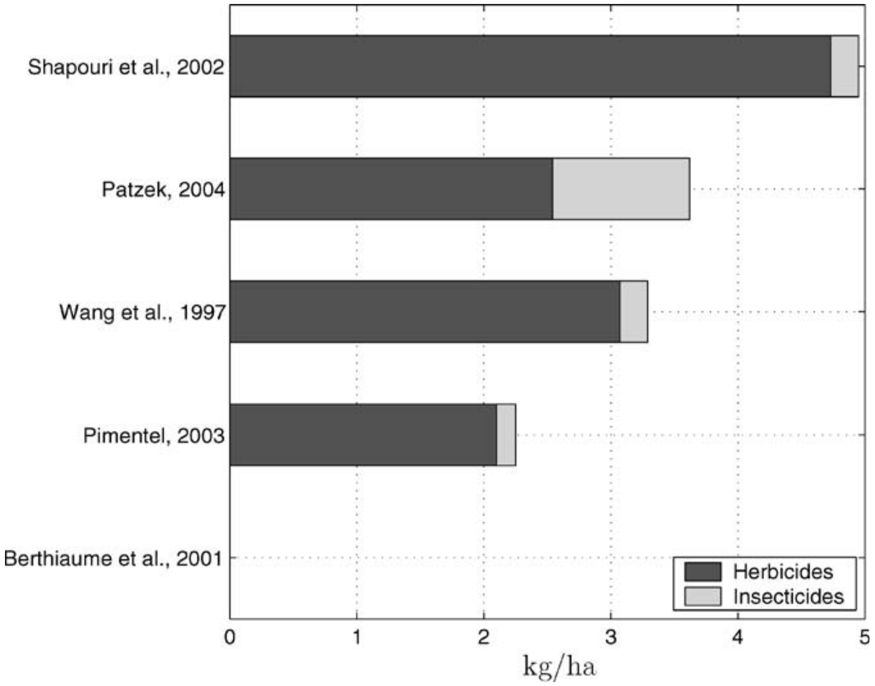

FIG. 5. The total herbicide and insecticide application rates listed in Tables 9 and 10.

After deciding on a low calorific value for each fossil fuel, one needs to find the standard values for "average" gasoline, diesel fuel, LPG, and natural gas. Finding consensus was more difficult than I expected. The International Energy Agency's (IEA) standards up to the year 2000 are listed in Table 11. IEA changed its standards for gasoline equivalent and diesel fuel equivalent in 2003. For comparison, I am also quoting some NCV values from a technical paper by AES, a U.S. energy company (AES, 2004). For gasoline and diesel fuel equivalents, I simply averaged the three estimates in Table 11. For reference, the standard densities of liquid fuels used in this work are: gasoline, 0.7374 kg/L; diesel fuel, 0.8400 kg/L; LPG, 0.5422 kg/L; natural gas, 0.6653(5) kg/sm^3.

The calorific values and average volumes of fossil fuels used in corn farming are listed in Tables 12–15. The cumulative volumes of all fossil fuels are shown in Figure 6.

Notice that not all sources account for all five fossil fuels, especially for LPG and natural gas. Both LPG and natural gas are used for corn drying and as fuel to power water pumps in irrigation. Their uses vary greatly from one state to another, and from one season to another (see Figure 7).

3.3. *Use of Electricity*

The average electric energy spent on farming 1 hectare of corn is listed in Table 16. Shapouri *et al*. (2002) attempted to include the efficiency of fossil energy conversion into electricity in their estimates. I have not done it here in the energy balance, but will consider all the steps in free energy conversion in the exergy balance in Part III. The average and the state data are compared in Figure 8. As with natural gas, variability in electricity use is very large.

3.4. *Averages can be Misleading . . .*

- Depending on the weather, *state-to-state* (regional) and *year-to-year* (temporal) variations in the use of

TABLE 10
Specific energy consumption and application rates of insecticides

Specific energy MJ/kg	Application rate kg/ha	Source
422.00	0.15	Pimentel, 2003
268.40	1.08	Patzek, 2004
268.40	0.22	Shapouri *et al*., 2002
243.00	0.22	Wang *et al*., 1997

TABLE 11
Standard Net Calorific Values of major fossil fuels (IEA, 2000; AES, 2004)

Fuel	Net Calorific Value
1 kg oil equiv. (oe)	41.868 MJ
1 kg coal equiv. (ce)	29.3 MJ
1 kg gasoline equiv.	1.070 kg oe = 44.8 MJ (46.8[a], 48.6[b])
1 kg diesel equiv.	1.035 kg oe = 43.3 MJ (45.7[a], 43.0[b])
1 kg LPG equiv.	1.130 kg oe = 47.3 MJ
1 kg NG	54 MJ (my estimate)

[a] The revised 2003 estimate by the International Energy Agency.
[b] 2004 estimate by Alternate Energy Systems.

TABLE 12

Calorific values and specific volumes of gasoline used in corn farming

Calorific value MJ/kg	Volume L/ha	Source
56.32	56.0	Pimentel, 2003
47.00	29.0	Patzek, 2004
59.10	29.0	Shapouri *et al.*, 2002
47.00	30.6	Wang *et al.*, 1997
0.00	0.0	Berthiaume *et al.*, 2001

TABLE 13

Calorific values and specific volumes of diesel fuel used in corn farming

Calorific value MJ/kg	Volume L/ha	Source
50.24	90.0	Pimentel, 2003
44.00	80.0	Patzek, 2004
53.97	82.1	Shapouri *et al.*, 2002
44.00	77.5	Wang *et al.*, 1997
44.00	71.0	Berthiaume *et al.*, 2001

TABLE 14

Calorific values and specific volumes of Liquified Petroleum Gas (LPG) used in corn farming

Calorific value MJ/kg	Volume L/ha	Source
0.00	0.0	Pimentel, 2003
47.30	47.0	Patzek, 2004
52.60	59.0	Shapouri *et al.*, 2002
47.30	32.4	Wang *et al.*, 1997
47.30	252.0[a]	Berthiaume *et al.*, 2001

[a] Large quantities of LPG are used to dry wet corn in Quebec.

TABLE 15

Calorific values and specific volumes of natural gas used in corn farming

Calorific value MJ/kg	Volume sm^3/ha	Source
0.00	0.0	Pimentel, 2003
55.00	21.3	Patzek, 2004
61.90	14.0	Shapouri *et al.*, 2002
55.00	36.1	Wang *et al.*, 1997
0.00	0.0	Berthiaume *et al.*, 2001

TABLE 16

Specific electric energy inputs to corn farming

Amount kWh/ha	Source
39.9	Pimentel, 2003
191.0	Patzek, 2004
207.6	Shapouri *et al.*, 2002
24.1	Wang *et al.*, 1997
132.0	Berthiaume *et al.*, 2001

electricity, liquid petroleum gas, and methane can be extreme.

- Therefore, a *single calculation* of energy efficiency of corn production for all states and all years is insufficient for the generalizations readily made from such a calculation. In other words, in the same corn growing season, the energy balance of corn ethanol production may be highly unfavorable in one state, and only somewhat unfavorable in another one.

3.5. *Energy in Human Labor*

Average labor time is 6.2 hrs/ha per growth season (Pimentel, 2003). I will assume that a physical worker is on a 4000 kcal/day diet. The specific energy to sustain a worker is then

$$4 \times 10^6 \text{ cal/day } \times 4.186 \frac{\text{J}}{\text{cal}} \times \frac{1}{24} \frac{1}{\text{hr}} = 0.7 \frac{\text{MJ}}{\text{hr}}, \qquad [5]$$

and it is negligible.

In my estimate, I have used Shapouri *et al.*'s (2002) custom labor estimate plus the worker sustenance energy (see Figure 9).

3.6. *Energy in Corn Seeds*

The production of *hybrid* corn seeds is very energy intensive (Pimentel, 2004a). Two corn genotypes are needed. The pollen from one genotype is used, and the pollen from the other genotype must be prevented from pollinating the genotype from which the corn seed will be harvested. Because of all these manipulations, about 7 times *more* energy is required to produce hybrid seeds compared with the energy in the same mass of corn grain.

The following data have been used to estimate the specific energy requirements for corn seeds:

- The seed rate is 57,000 (Corn Belt)–74,000 (West) seeds per ha (White and Johnson, 2003), p. 255.
- The mean weight of 1000 corn seeds is 0.332 kg (White and Johnson, 2003), p. 202.
- The caloric value of corn grain with 13–15% moisture is 15–16 MJ/kg.
- The production of hybrid corn requires about 104 MJ/kg (Heichel, 2004).

Both Shapouri *et al.* (2002), and Wang *et al.* (1997) ignored the hybrid seed energy, and assigned just the diesel fuel energy

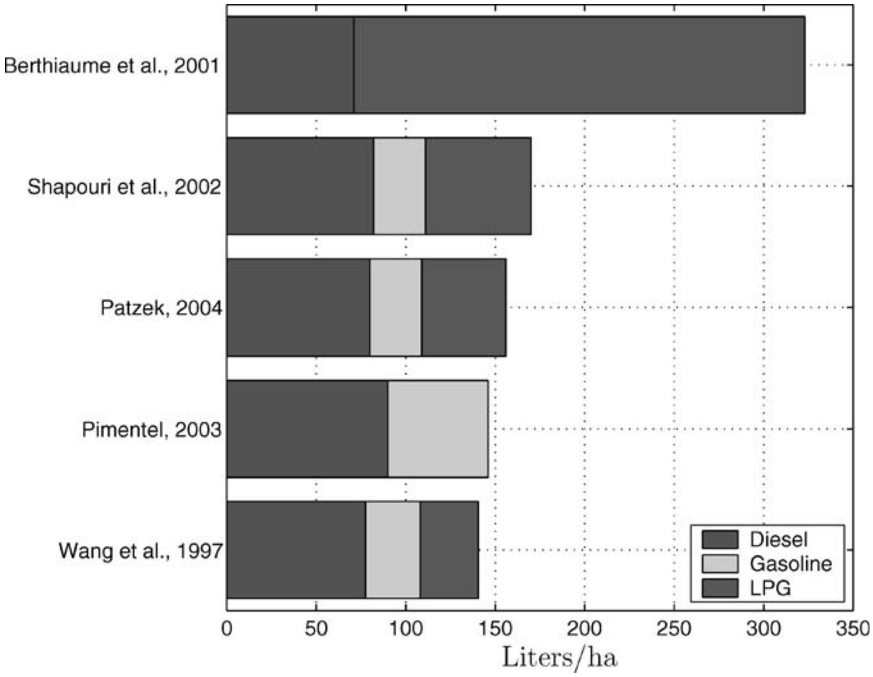

FIG. 6. The total fossil fuel volumes listed in Tables 12–15.

for planting the seeds. I have amended their calculations with the seed energy, based on their reported seed rates, and moved their estimates of diesel fuel use in corn planting to the fuel category.

3.7. *Energy in Irrigation*

Corn gets water mostly from rainfall, but some irrigation is generally required. In a dry season, the use of irrigation systems may increase substantially, as seen from the electricity use by

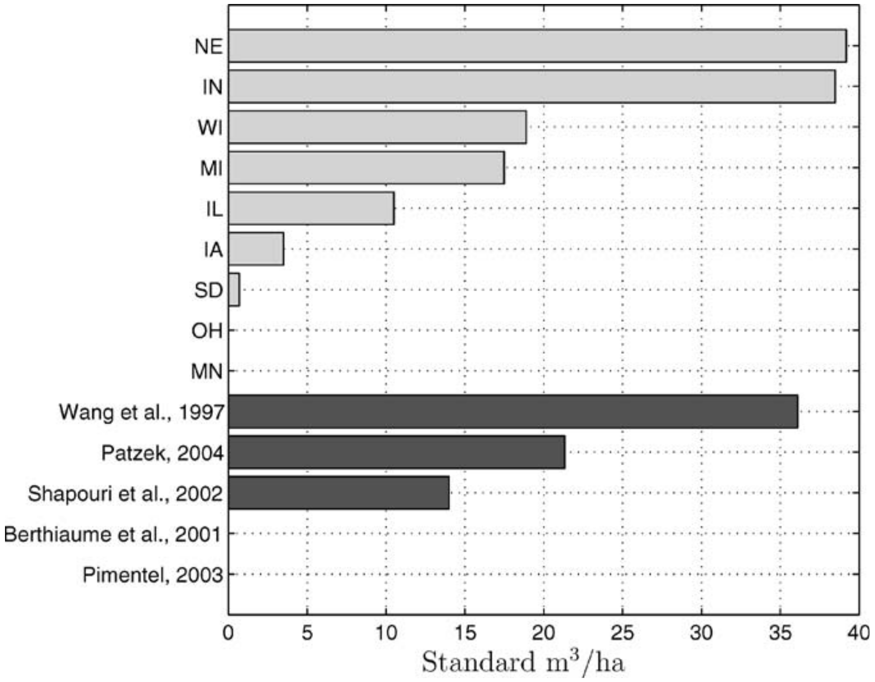

FIG. 7. By-state and average use of methane in corn farming. The 1996 methane volume data from the largest corn-producing states are from Shapouri *et al.* (2002). Note the large variability of methane use depending on wet/dry weather.

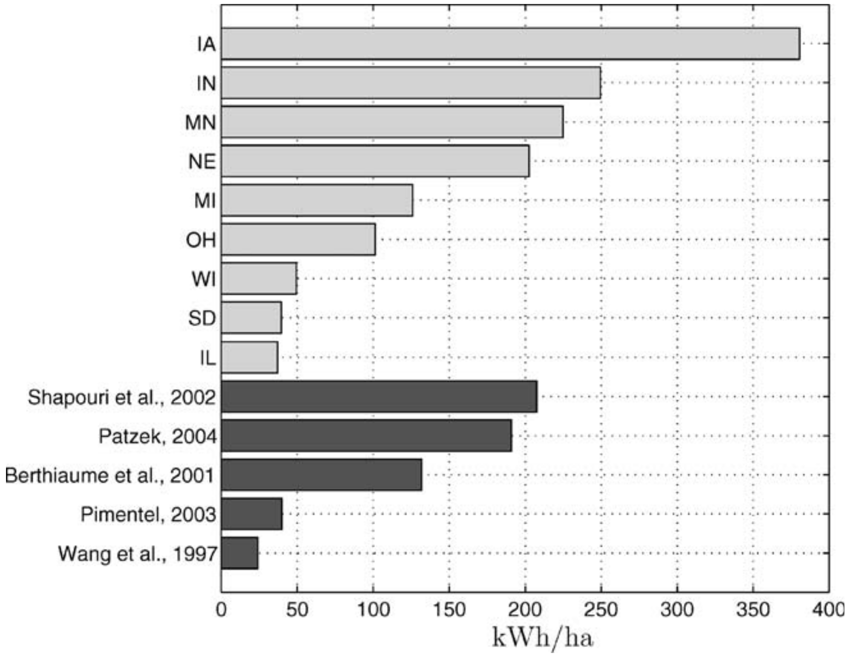

FIG. 8. By-state and average use of electricity in corn farming. The 1996 electricity data from the largest corn-producing states are from Shapouri *et al.* (2002). Note the large variability of electricity use depending on wet/dry weather.

state, reported in Figure 8. I have made the following assumptions to estimate the energy cost of corn irrigation:

- Only 15% of crop is irrigated, USDA-NASS, 1997 (Pimentel, 2003).
- On average 8.1 cm of water is used per acre, USDA-NASS, 1997 (Pimentel, 2003).
- Water is pumped on average from the depth of 100 m.
- Pump efficiency, *etc*., is 0.75.

Then the specific energy requirement for irrigation is

$$\frac{1\ \mathrm{m}}{100\ \mathrm{cm}} \times 10,000\frac{\mathrm{m}^2}{\mathrm{ha}} \times 1000\frac{\mathrm{kg}}{\mathrm{m}^3} \times 100\ \mathrm{m} \times 9.81\frac{\mathrm{m}}{\mathrm{s}^2}/0.75 = 131\ \mathrm{MJ/cm\text{-}ha} \qquad [6]$$

I have lowered Pimentel's (2003) estimate of irrigation energy to my estimate. Both Shapouri *et al*., and Wang *et al*. buried the

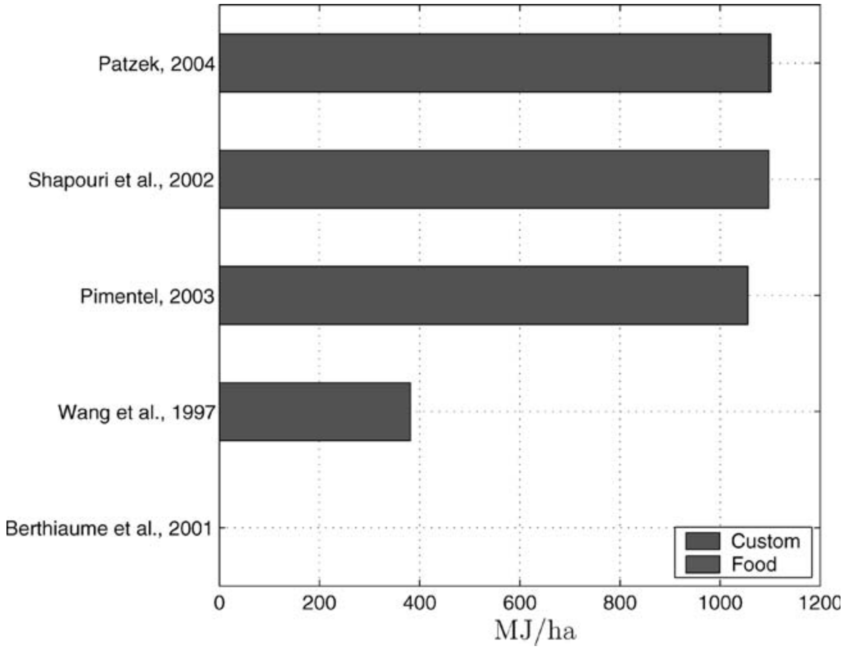

FIG. 9. Energy use in labor.

TABLE 17

Specific energy used in transportation related to corn farming. Source: Wang *et al.* (1997)

Category	Plant → Center	Center → Mixer	Mixer → Farm
Travel distance (km one way)	1700/850	80	50
Mode	barge/ rail	Class 8b truck	Class 6 truck
Energy use (kJ/kg)	71	25	53

Total energy use is 720 kJ/kg of field input materials or ∼400 MJ/ha + Commute of Personnel.

irrigation energy in their use of electricity and methane, so they account for the irrigation indirectly, for the particular mixture of states and weather they considered. Because I use Shapouri *et al.*'s estimates for the fossil fuels, I have not included the irrigation energy in my calculations.

3.8. *Energy in Transportation*

The specific energy use in transportation related to corn farming has been estimated by Wang *et al.* (1997) (see Table 17). The total energy use is about 720 kJ/kg of field chemicals (fertilizers, lime, fuel, *etc.*) transported into the field (∼400 MJ/ha-crop), plus personal commutes. This estimate is sensitive to the number of commutes to and from the field by personnel using motor vehicles.

3.8.1. Personal commute. At 6.2 hr/ha/crop of labor, 20 l/100 km gasoline use, and a 30 km round trip, the energy cost of commuting is

$$\frac{6.2}{9}\,\frac{\text{hr/ha/crop}}{\text{hr work day}} \times 60\ \text{km} \times 20\,\frac{\text{liter}}{100\ \text{km}} \times \frac{1}{100} \times 0.74\,\frac{\text{kg}}{\text{liter gasoline}} \times 47\,\frac{\text{MJ}}{\text{kg gasoline}} = 288\ \text{MJ/ha-crop} \qquad [7]$$

Therefore a single commute *nearly doubles* the overall transportation energy costs. This issue should be investigated further.

3.9. *Machinery and Infrastructure*

Industrial agriculture requires heavy machinery (trucks, tractors, ploughs, *etc.*), which must be replaced periodically. Industrial agriculture also requires extensive infrastructure with a large environmental footprint (access roads, silos, pumps, driers, electricity generators, air-conditioners, *etc.*). The unit fossil energy input as hardware has been estimated at ∼110 MJ/kg by Pimentel (2003). This estimate is roughly twice the energy required to produce 1 kg of steel. For the highly perfected, machined steel in farm equipment, it is a reasonable estimate and I accept it. The mass of hardware assigned by Pimentel to corn farming is 55 kg/ha, and I accept it, too.

Both Shapouri *et al.* (2002) and Wang *et al.* (1997) omit this input altogether, but I have not amended their calculations.

3.10. *Fossil Energy Inputs into Corn Production*

The specific fossil energy requirements in industrial corn farming are shown in Figure 11. A few comments are in order.

- The lowered Pimentel's (2003) estimate of fossil fuel energy plus irrigation is identical with that of Shapouri *et al.*

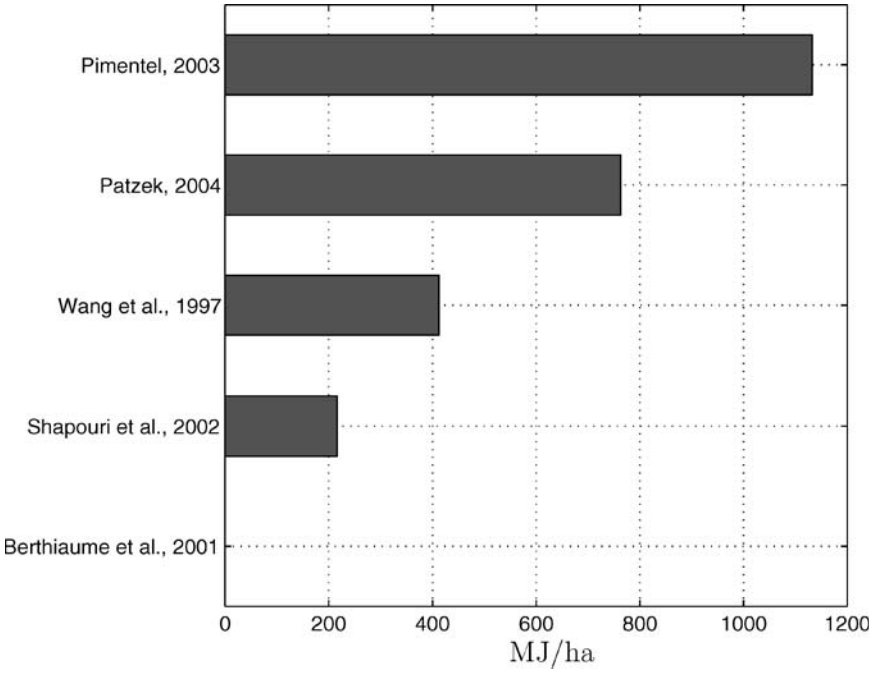

FIG. 10. Specific energy use in transport related to corn farming. Note that Pimentel's estimate may contain an additional single commute to and from the field.

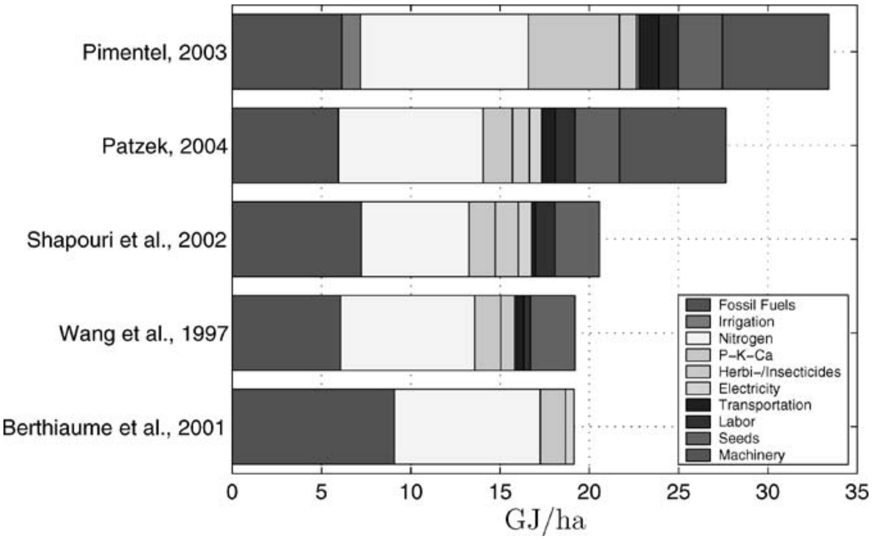

FIG. 11. Major fossil energy inputs into corn farming.

- The lowered Pimentel's (2003) estimate of nitrogen fertilizer energy is higher than the uncorrected one by Shapouri *et al.*, which is too low. My estimate is in the middle.
- Pimentel's (2003) lime application rate is twice those of everyone else's. It reflects the 1997 USDA average.
- Pimentel's (2003) transportation energy is higher than everyone else's. It may reflect 1–2 more commutes/ha/crop, see Figure 10.
- Shapouri and Wang *et al.* have underestimated the fossil energy in seeds and left out the machinery and infrastructure.
- I have added my seed energy estimate to their inputs, but left the machinery out.
- Berthiaume *et al.* (2001) have not included several of the energy inputs in corn farming, so their estimate is presented here only for comparison.
- The estimates of fossil energy inputs range from 19 GJ/ha (Wang) to 33 GJ/ha (Pimentel). My estimate is 27 GJ/ha.
- Wang *et al.*'s estimates are consistently too low. Shapouri *et al.*'s and my estimates are almost identical. The only significant difference is the inclusion of machinery into my estimates.
- The fossil energy use in corn farming is large and equivalent to 0.4 (Wang *et al.*) to 0.7 (Pimentel) metric tons of gasoline per hectare and per crop.
- The average energy use in corn farming does not tell the whole story because of the very large variability of energy use by state, depending on the local weather conditions.
- All estimates, including mine, have had errors and/or omissions at one stage or another. I hope that by bringing the approaches of all authors into a common framework, most of the deficiencies of the prior analyses have been eliminated.

3.11. Solar Energy Input into Corn Production

The amount of solar energy that irradiates 1 average hectare of corn field in the United States during the growth season is gigantic, and it dwarfs all fossil energy inputs *and* the calorific value of the 8600 kg of corn grain harvested from this hectare (see Figure 12). In fact, during the 120-day growth season, only $\sim$1% of the solar energy is converted by corn plants into biomass (Biermann *et al.*, 1999). In contrast, solar cells can collect sunlight all year long (see Appendix C). On an annual basis, the solar efficiency of corn plants drops by a factor of 3, that is, only $\sim$0.3% of the solar energy is captured by an average corn crop. In summary, the solar energy does *not* limit corn production—soil, water, and the dissolved nutrients do. I will discuss this crucially important point later. Here it suffices to say that if the sun were the limiting factor, the Sahara desert would be the best place to grow corn (Georgescu-Roegen, 1971).

3.12. Soil Humus and Micro-Element Depletion by Corn Production

Because good soil quality sustains farming, one needs to account for the extraction by corn plants of soil humus and metals.

Definition 2. **Humus** is the soil component that develops over time by the decomposition of organic matter.

Soil humus is among the principal carbon pools on continents. One hectare of corn produces 8600 kg of corn grain, *cf.* Section 2, and 8600 kg of stalk, leaves and roots (Pimentel, 2004a). By scaling Michaud's (1995) results to the average U.S. corn yield, I have estimated that about 2600 kg/ha-crop of soil humus is extracted by the corn monoculture grown on tilled soil. Similarly, I have calculated that decomposing all 8600 kg

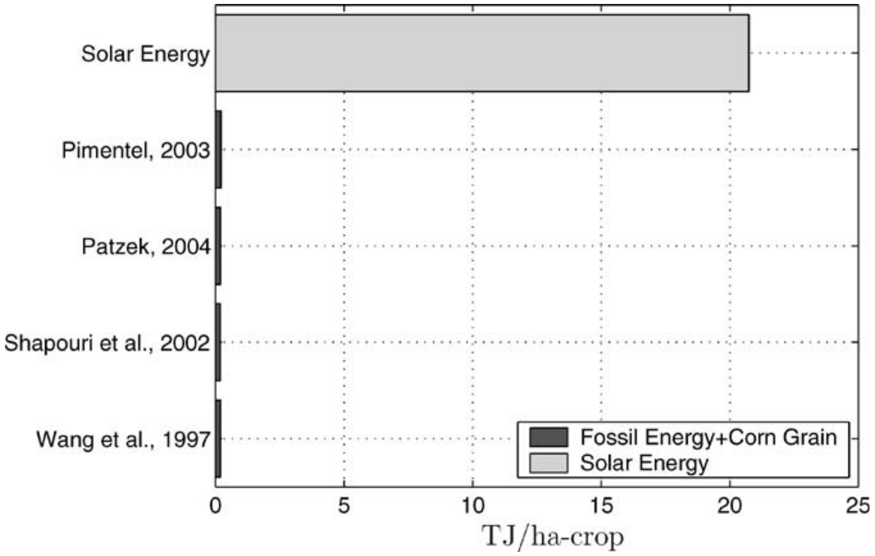

FIG. 12. Comparison of the cumulative solar energy input and the fossil + grain energy inputs per hectare and per crop (120 days).

of plant parts returns about 2100 kg/ha of humus (4:1 ratio). Therefore, with the full decomposition of plant leftovers, corn depletes ∼500 kg/ha-crop of humus.

The net humus depletion of 500 kg/ha-crop could be replenished by returning to the field 2000 kg/ha of corn grain leftovers from ethanol production. Otherwise, industrial corn farming is also *soil mining*, in addition to being crude oil, natural gas, and coal mining. I will come back to this point when I discuss the energy credits for ethanol production assumed by Wang *et al.* and Shapouri *et al.*

Based on the information in Troeh and Thompson (1993), Prof. Pimentel (2004b) has calculated that only 1630 kg of humus would be added to the soil from the 8600 kg/ha of corn residues. On the other hand, he points out that with appropriate field practices[7] and *continuous use* of synthetic fertilizers, it is possible to keep soil humus at a constant value. The 20-year study of conventional corn and soybean production system in Rodale, Pennsylvania, following Penn. State recommendations, confirms that the soil humus has remained relatively constant at about 1.7% of soil carbon over most of the 20 years. At Rodale, the application rate of synthetic nitrogen fertilizer has been 140 kg/ha; phosphorus and potassium have been applied as well.[8]

Prof. Pimentel (2004b) also points out that harvesting about 9000 kg/ha of corn grain removes ∼50 kg/ha of N and ∼8 kg/ha of P. Currently farmers are applying ∼150 kg/ha of N and ∼50 kg/ha of P. The additional ∼9000 kg/ha of corn stover contains ∼34 kg/ha of N. Back in the 1930s and 1940s, with corn yields below 2000 kg/ha, only 11 kg/ha of N was harvested with the grain. However, nitrogen was also being lost by leaching, denitrification, and erosion. With soil erosion rates of 20 to 30 t/ha/yr, from 50 to 90 kg/ha of nitrogen were being lost by erosion alone. Since then, soil erosion rates in U.S. corn fields have declined to 10 to 15 t/ha/yr. Soil erosion is deadly when it comes to nutrient and water loss (Larson, 1979; Lindstrom *et al.*, 1979).

All corn plant parts, other than the starch in corn grain, should be decomposed and recycled to recover their N, P, K, C, Ca, Mg, Zn, B, Cu, Mn, and so on, and diminish the degree of unsustainability of corn farming. However, most of the nitrogen and phosphorus and some other nutrients are translocated from vegetative plant parts to the developing grain later in the season. A corn crop harvested with no recycling removes more than 2 times as much nitrogen, 3 times as much phosphorus, and 10 times as much potassium as when this crop is harvested for grain (Wheaton *et al.*, 1993). It also removes most of the soil metals essential to the well-being of corn plants. The need to recycle plant parts and limit soil erosion largely negates the now fashionable attempts to produce ethanol from whole corn plants by harvesting everything from the corn field (see *e.g.*, NREL, 2002; Sheehan *et al.*, 2004). Every ecosystem on earth is highly optimized to recycle almost all mass it generates; otherwise life would not persist.

4. Major Energy Inputs to Ethanol Production

Conversion of corn grain into 100% ethanol (EtOH) is a fossil energy-intensive process, which also generates significant gas emissions, as well as liquid and solid waste. Here I consider only wet-milling of corn to convert it into glucose, which is subsequently fermented to industrial beer, and distilled to 96% ethanol. The final water removal is achieved in molecular sieves that exclude water, or by distillation with benzene; see Eq. (8). Fermentation is equivalent to catalytic burning in which 49%

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[7] Good field practices might include: (1) Soybean/corn crop rotation to naturally bind nitrogen and limit synthetic fertilizer use; (2) Corn stover decomposition in the field to conserve soil nutrients and limit erosion; and (3) Moderate soil tilling to diminish loss of soil carbon and erosion.

[8] Part II shows that the use of synthetic fertilizers makes farming unsustainable.

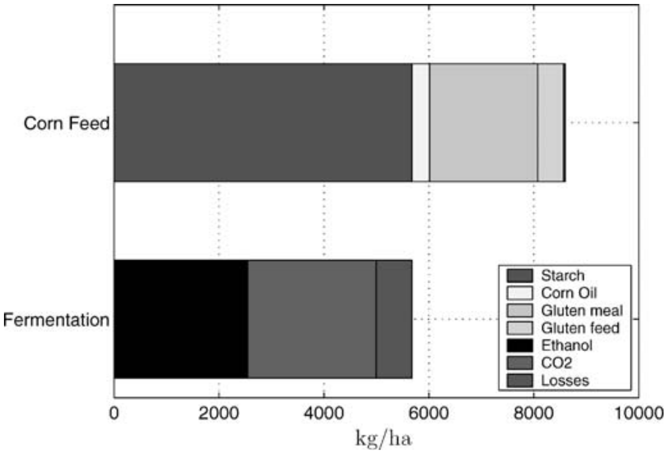

FIG. 13. The result of practical corn conversion into ethanol is 0.372 L EtOH/kg dry corn grain = 2.50 gal EtOH **dry** bushel = 2.18 gal EtOH **wet** bushel with 15% moisture.

of the input glucose is converted into carbon dioxide. This is why ethanol is often called "half-burned gasoline." Dry milling is energetically similar, and need not be considered.

$$\underbrace{\text{Corn Grain}}_{\substack{\text{Steeping}\\ \text{Grinding}\\ \text{Germ Separation}}} \rightarrow \underbrace{\text{Starch}}_{\substack{\text{Gluten}\\ \text{Liquefaction}\\ \text{Saccharification}}} \rightarrow \underbrace{\text{Glucose}}_{\substack{\text{Fermentation}\\ CO_2}} \rightarrow \underbrace{\text{Ethanol}}_{\substack{\text{Distillation}\\ \text{Dehydration}}} \qquad [8]$$

4.1. *Corn Mass Balance Revisited*

In Section 2, I calculated the theoretical efficiency of corn conversion into ethanol, in which every step is 100% efficient. Here, based on my estimates and conversations with industrial chemists, I will assume that the conversion of corn grain into 100% ethanol incurs 12% losses by mass (see Figure 13). This assumption will not influence any of my major conclusions, and may be relaxed if sufficient counter-arguments are made.

Four important conclusions can be drawn from Figure 13:

1. The correct high yield of ethanol from corn is now 0.372 L EtOH/kg dry corn grain, or 2.5 gallons of EtOH per 56 lbs of dry corn grain ("dry bushel").
2. The USDA estimate of 2.66 gallons/bushel (Shapouri *et al*., 2002) is too high, and cannot be accepted based on the mass balance of corn with the average composition from the Corn Chemistry & Technology Handbook (White and Johnson, 2003); see Table 1.
3. The downward correction of the USDA estimate will lower the overall energy efficiency of the corn-to-ethanol conversion process.
4. The reported field corn yields must be multiplied by 0.85 to convert the harvested corn to water-free or "dry" corn (see Figure 14).

4.2. *Transport in Ethanol Plants*

Transport of materials and people in-and-out of an ethanol plant requires energy, and there is some disagreement between Pimentel and Patzek on one hand, and Shapouri *et al*. and Wang *et al*. on the other. Here it suffices to state that

- Corn grain (8600 kg/ha) and fuel (*e.g*., ~1200 kg/ha of coal) must be transported *in*.
- Ethanol (~2200 kg/ha), gluten meal and feed (~2600 kg/ha) must be transported *out*.

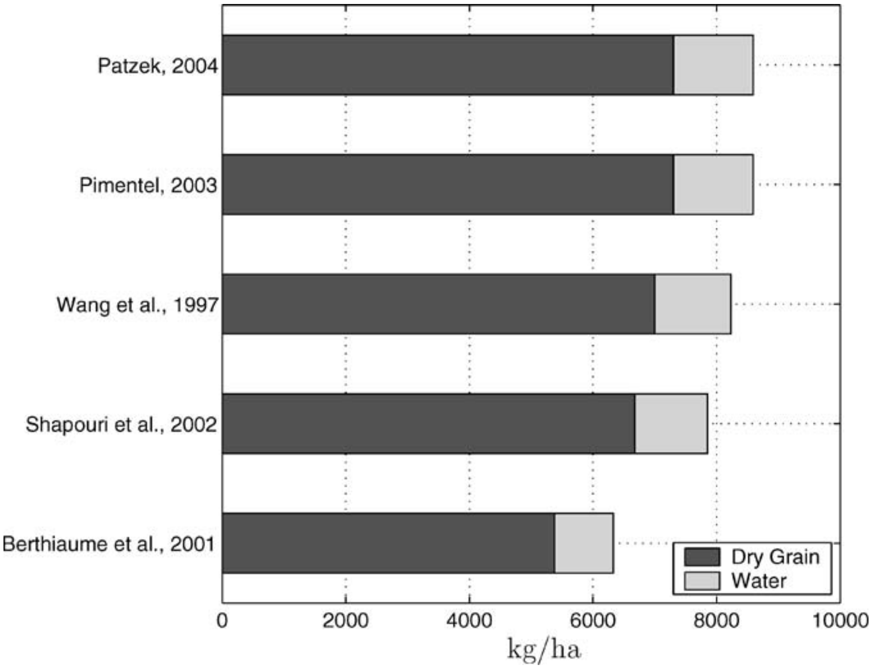

FIG. 14. Average wet and dry corn yields.

TABLE 18

Ethanol yield, specific energy inputs, and energy credits

Yield L/ha	Yield GJ/ha	Transport MJ/L	Fuel MJ/L	Total Inputs MJ/L	Credits MJ/L	Source
2706	57.51	1.32	14.75	16.07	1.88	Pimentel, 2003
2706	57.51	1.74	14.45	16.19	0.00	Patzek, 2004
2484	52.79	0.44	14.45	14.89	5.89	Shapouri *et al*., 2002
2603	55.32	0.43	13.96	14.39	5.38	Wang *et al*., 1997
2002	42.55	0.00	17.18	17.18	0.00	Berthiaume *et al*., 2001

- Workers must travel *in-and-out*.
- Both Shapouri *et al*. and Wang *et al*., seem to underestimate these transport costs by a factor of 3–4.

4.3. *Fossil Energy Inputs to Ethanol*

Because transportation is but a small fraction of the total energy outlay in ethanol production, there is little disagreement in the various estimates of the total energy used to produce ethanol from corn, which are all close to 15 MJ/L EtOH, (see Table 18). This is easily seen when the total lengths of the bars in Figure 15 are compared.[9]

4.4. *Energy Credits*

Major disagreements surface when it comes to energy credits used by the different authors to offset the high energy cost of ethanol production. The idea is to somehow use the market or energy value of gluten meal and gluten feed (see Table 1), both by-products of wet milled corn, to offset the fossil energy used to produce ethanol. Gluten meal is a more valuable by-product, but it is 4 times less abundant than gluten feed. The key assumptions made by the different authors are as follows:

- Wang *et al*. (1997) assume an energy credit of 30% of all energy inputs into ethanol production.
- Shapouri *et al*. (2002) assume an energy credit of 5.9 MJ/L of ethanol, justifying it as the replacement value of soybean meal with corn gluten feed and meal.
- Pimentel (2003, 2004a) assumes an energy credit of 1.9 MJ/L of ethanol, justifying it as the replacement value of distiller's dried grain in *dry* milling, which is similar in composition to soybean meal (it contains 30% protein, 8% fat). Pimentel also argues that gluten feed does not replace soybean meal; in addition soybean plants fix nitrogen, and corn does not, so the replacement is really difficult to justify.
- I give ethanol **zero energy credit**, and want the ethanol plants to bear the transportation and disposal costs of gluten feed and meal, as well as all other solid and liquid waste from ethanol production. Some of the environmental restoration costs will be included in the discussion of the carbon and water cycles in ethanol production from corn. In Section 3.12, I have already argued that all of the ethanol processing leftovers should be returned to the field to replenish soil humus and microelements.

4.5. *Overall Energy Balance of the Corn-Ethanol Process*

With the energy credits or without, ethanol production from corn is a fossil energy loosing proposition, even if the energy costs of environmental damage are neglected (see Figures 16 and 17). In addition, the net energy[10] gained from corn production is *small* (see Figure 18); several times lower than those of perennial grasses and sugarcane (Rogner, 2000). As I have already demonstrated, corn grain is not the sun's gift to the producers of corn ethanol, but it is one of the fossil energy inputs. The calorific value of corn grain is therefore shown in Figure 16 to demonstrate that a large fraction of the energy inputs into ethanol production is dissipated on fermentation, distillation, and farming. The horizontal lines in the middle of each bar in Figure 16 denote the corrected ethanol yield, *cf.* Section 4.1, given the corn yields shown in Figure 14.

Remark 3. It seems that the high net energy yields of corn production—up to 200 GJ/ha-crop—reported in the literature (*e.g*., Rogner, 2000), are unrealistic, and result from an incomplete thermodynamic analysis of industrial corn production.

PART II: SUSTAINABILITY AND RENEWABILITY

1. Introduction

The following type of reasoning (Sheehan *et al*., 2004) is not uncommon in environmental literature:

> . . . Sustainability is fundamentally an ethical issue, the technological context . . . is not adequate to fully assess the sustainability of ethanol or any other fuel choices. . . . The stakeholders[11] established a list of indicators that they felt should be used to measure the

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[9] For comparison, a recent feasibility study for a new ethanol plant (International, 2001) projects 13.08 MJ/L EtOH in methane, and 1.675 MJ/L EtOH in electricity, for the total of 14.8 MJ/L EtOH, excluding transport and commute costs. This study contains numerous mistakes. For example, the efficiency of grain conversion into ethanol is overestimated, and the amount of feed water is significantly underestimated.

[10] The energy of dry corn grain minus the fossil energy inputs per hectare and per crop.

[11] A group of farmers, environmentalists, automakers, grain processors, and government researchers.

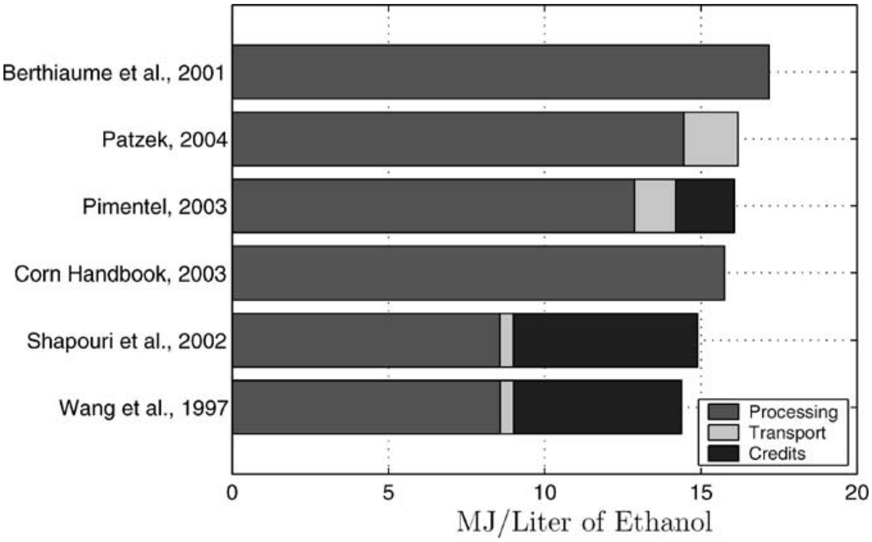

FIG. 15. The average fossil energy inputs to ethanol production in a wet milling plant. The length of each bar is the total energy outlay to produce 1 liter of EtOH, and the black (rightmost) parts denote the size of energy credits assumed by the different authors.

> relative sustainability of switching from gasoline to [corn] stover-derived ethanol to fuel our cars.[12] (page 118)

More broadly, an informal check of Amazon.com, performed on August 16, 2003, revealed 4,454 book titles containing the word "sustain⋆." In particular, there were 573 book titles with "sustain⋆" and "⋆culture."[13] The phrase *sustainable development* is firmly rooted in our consciousness. Therefore, one must ask the following question: Is sustainable *anything* possible in nature? In the economy? Also, how *sustained* are the processes deemed by some as "sustainable"?

Human nature, being what it is, destines us to choose a "truly great but brief, not a long and dull, career" (Georgescu-Roegen, 1971, p. 304) on the earth. After our eventual demise, the earth will be home to other less ambitious and impatient species. The name of the game, therefore, is to make the human presence on the earth as happy as possible, albeit not too short.[14] These two tasks require careful thought and delicate balance of human actions. No country has demonstrated an adequate implementation of either. In fact the opposite may be true. As the entropy on the earth increases, the actions of governments and societies resemble more and more episodic spasms, with ever less forethought and deliberation. The current hot button issues: the Hydrogen Economy, Ethanol from Corn, and the War on Terror are good examples.

2. Disclaimer

The next eight sections of this article are punctuated with verbatim quotations from, and my digestion of the most important book I have read in decades: *The Entropy and the Economic Progress* by Nicholas Georgescu-Roegen (1906–1994), who was a great 20th century thinker, economist, mathematician, historian, and philosopher. The impact of this book on my thinking has been profound.

3. Preliminaries

In science we divide actuality into two slices: one representing the *partial process* determined by our interest, and the second, its *environment* (see Figure 19). These two parts are separated by an *analytic*[15] *boundary*. The boundary has two attributes. The first separates the process from the environment at any time (we can call this attribute the *interface*, or the *frontier*), and the second defines the *duration* of the process.[16] Often the terms *process* and *environment* are used interchangeably with *system* and *surroundings*. We may not describe a process by what happens inside or outside of it, but only by what crosses its boundary. Anything of interest crossing the boundary from the environment into the process is an *input*, and anything crossing the boundary in the opposite direction is an *output*. Solar energy is a typical example of only an input for any terrestrial process. The various materials abbreviated as "waste" are examples of only outputs.

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[12] Therefore, any fuel or technology can be declared as "sustainable," whenever there exists a group of people who feel good about it, and say that it is!

[13] The author's favorite: *Permaculture: Principles and Pathways Beyond Sustainability* by David Holmgren, published by Holmgren Design Services (July 2003).

[14] Preaching alone will not do. People will never choose less fulfilling life styles without coercion. This is why communism, or any other totalitarian "ism," can never work; they strive to convert the thinking individuals into slaves or working animals. Says Percy Williams Bridgman (1955), p. 114, italics added: "The *individual* is the unit in terms of which all our social concepts ultimately find their meanings."

[15] The word *analytic* means well-defined mathematically in space and/or time.

[16] The process is not defined outside its time interval.

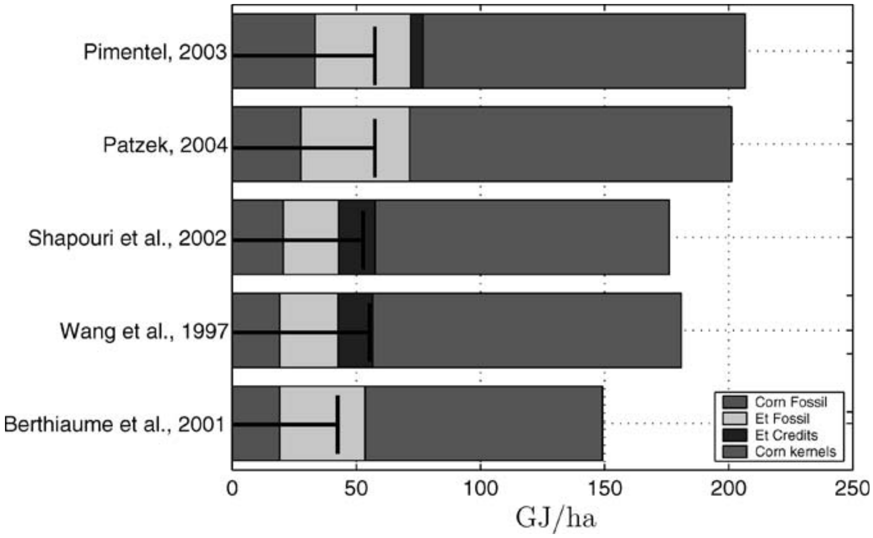

FIG. 16. The overall energy balance of ethanol production. The two or three leftmost parts of each bar represent the specific fossil energy used in corn farming and ethanol production. The fossil energy inputs into ethanol production are the sum of the light gray part and the dark energy credit part for some authors. The rightmost part is the calorific value of corn grain harvested from 1 hectare. The total lengths of the horizontal bars represent all energy inputs into ethanol production. The horizontal lines with the vertical anchors represent the calorific value of ethanol obtained from one hectare of corn. Note that the total energy inputs into ethanol production are equivalent to over 4 metric tons of gasoline per hectare. The ethanol's calorific value is equal to 1 metric ton of gasoline.

4. Laws of Thermodynamics

The three empirical laws of *Classical Thermodynamics*[17] were originated by Joule, Clausius, Thomson, Planck, and Nernst, and are often formulated as follows:

First Law or the Energy Conservation Law (Joule, Clausius, and Thomson)

- Energy can neither be created or destroyed;
- The energy of the universe remains constant; or
- You cannot win.

Second Law or the Entropy Law (Clausius)

- Without the compensating changes elsewhere, heat can flow only from a hotter to a colder body; or
- With passing chronological time, the entropy of the universe tends toward a maximum; or
- You cannot break even.

Third Law (Nernst and Planck)

- The entropy of any condensed substance, *i.e.*, liquid or solid, has at zero absolute temperature the value zero; or
- Zero absolute temperature cannot be reached; or
- You have to stay in the game.

The story of *Classical Thermodynamics* is rather simple if we ignore the fine print. Energy comes in two qualities: (1) *free* or *available*, and (2) *bound* or *dissipated*. Free energy can be transformed into mechanical work.[18] Like heat, free energy dissipates itself, without any loss, into bound energy. The material universe, therefore, changes spontaneously in such a way that free energy is degraded. The final outcome is a state where all energy is dissipated—the *Heat Death* as it was called in the earliest thermodynamics.[19]

For some technical reasons, which need not bother us now, *entropy* was defined by the formula:

$$\Delta S = \delta Q / T \qquad [9]$$

where ΔS is the entropy *increment*, δQ is the *quantity* of heat transferred from a hotter to a colder body, and T is the absolute temperature at which the transfer is made. The entropy increments are always determined in the direction of *Time*,[20] from the *earlier* to the *later* moment in Time. So, if chronological Time τ_2 is later than another Time τ_1, then the entropy of the universe (or another closed system) is

$$S(\tau_2) > S(\tau_1) \qquad [10]$$

The *Entropy Law* is the simplest (and thus far the only) law known to science, by which the existence of true *happening* in

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[17] Started in 1824 with a memoir, *Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance*, on the efficiency of steam engine by a French engineer, Sadi Carnot (1943).

[18] Initially *free heat* was defined as the heat that can be exchanged between a hotter body and a colder one, and that can move a turbine in power station. If the hotter body, *i.e.*, a steam boiler, remains unchanged, and the colder body, *i.e.*, the environment, warms up, the amount of free heat goes down and the power station produces less electricity, as happened in Europe during the record-breaking summer heat wave of 2003.

[19] Bridgman disagrees (1955), p. 265.

[20] Time is a notion of extraordinary complexity. The author uses the historical or chronological *Time*, as opposed to the mechanical clock *time*.

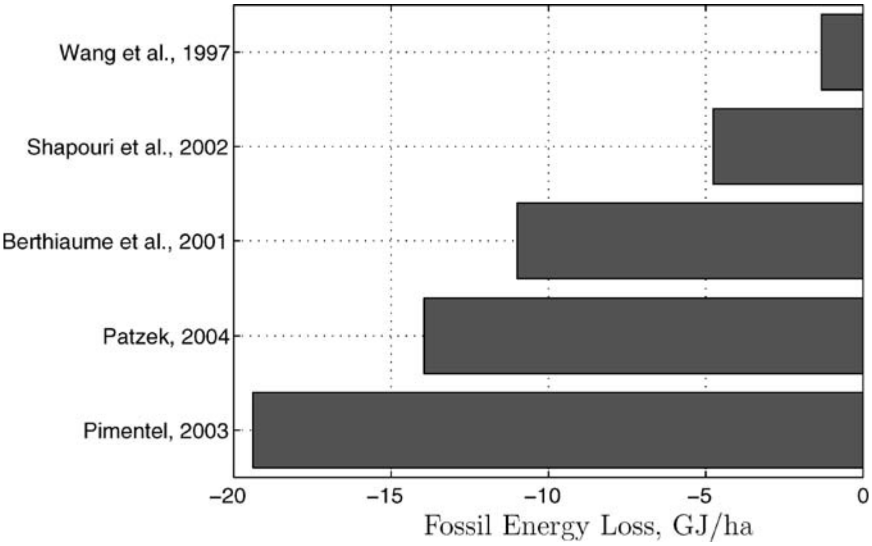

FIG. 17. Fossil energy loss in corn ethanol production. Note that the dubious energy credits described in Section 4.4 do not eliminate the use of fossil fuels in the first place, but present alternative useful outcomes of this use.

nature is recognized. The Entropy Law defines the boundaries of what *cannot* happen, but does not prescribe entirely what *can*. This loophole resulted in life. All life[21] feeds on an environment of low-to-moderate entropy (highly organized ecosystems,[22] such as shallow sea water, a river or lake, a jungle, *etc*.), and is extinguished when the entropy of the environment becomes too high (the degraded environment of sterile desert or chemically polluted water).

5. Thermodynamics and Economics

Classical thermodynamics and *economics*[23] are thoroughly bonded. In fact, thermodynamics has been mostly a physical theory of economic value from its inception by Carnot. Just as physical life, our whole economic life *feeds on low entropy*, for example, on grain, lumber, steel, copper, aluminum, cloth, and computers, all of which are highly organized structures. A slab of electrolytic aluminum is worth much more than the dispersed molecules of aluminum oxide, diffused so much as to be of no use to us.

In 1860 or so, William Stanley Jevons described the phenomenon of resource degradation and dilution as follows: "The expression exhaustion of our coal mines," states the subject in the briefest form, but is sure to convey erroneous notions to those who do not reflect upon the long series of changes in our industrial condition which must result from the gradual deepening of our coal mines and the increased price of fuel. Many persons perhaps entertain a vague notion that some day our coal seams will be found emptied to the bottom, and swept clean like a coal-cellar. Our fires and furnaces, they think, will then be suddenly extinguished, and cold and darkness will be left to reign over a depopulated country. It is almost needless to say, however, that our mines are literally inexhaustible. We *cannot get* to the bottom of them; and though we may some day have to pay dear for fuel, it will never be *positively* wanting."[24] Today we may substitute "crude oil" or "natural gas" for "coal," and Jevons' statement will be as true.[25]

In particular, thermodynamics explains to us (while economics usually does not[26]) why *land* has economic *value*, as opposed to *price*. Even though land cannot be consumed, it derives its economic value from two physical facts: (1) land allows humans to catch the most vital form of low entropy—sunlight—and (2) the earth stopped making land in large quantities. Other physical and chemical characteristics of fertile land[27] are *scarce* in a different sense: (1) the amount of low entropy in the soil is finite and it decreases[28] *continuously* and *irrevocably*, and (2) a given amount of low entropy can be used *only once*.

A different example of irrevocably lost low entropy is given by mining copper ore and transforming it into pure metallic

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[21] Not only biological life, but also social life. Consider the following comment made by Joseph Samaha in the daily *Al Safir* of Beirut about the desperately dissipative, high-entropy political situation in the Middle East: "Let us expel every mediator. Let us banish every international organization. Let the situation collapse. Let electricity and water be cut off. Let the pumping of oil stop. Let theft prevail. Let the universities and schools close down. Let businesses go bankrupt. Let civilian life break down" (New York Times, August 21, 2003, page A13).

[22] *eco*—From late Latin *oeco-* household, from Greek *oik-*, *oiko-*, from *oikos* house habitat or environment, *eco*system (Webster, 1993).

[23] A social science concerned chiefly with description and analysis of the production, distribution, and consumption of goods and services; from Greek *oikonomica*—skilled in the management of a household (Webster, 1993).

[24] (Jevons, 1866), *Preface*, pp. vi–vii, author's italics.

[25] In fact, it is more difficult to extract crude oil than coal. After an oilfield has been exploited, 1/2 to 2/3 of the oil present initially in the rock interstices is left there forever.

[26] With the notable exception of Georgescu-Roegen (1971).

[27] Natural soil fertilizers, soil-bonding humus, interstitial water, *etc*.

[28] Unless the soil is a part of an ecosystem that recycles all mass, see Section 10.

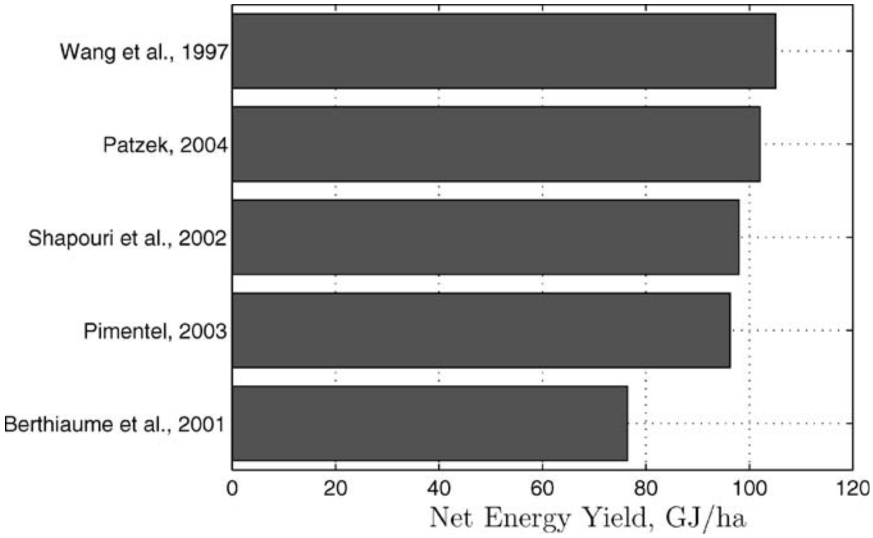

FIG. 18. The net energy yield in industrial corn production is small, ~80–100 GJ/ha-crop.

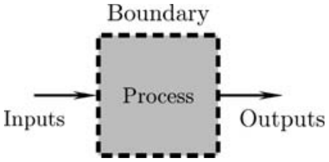

FIG. 19. The *boundary* separates the process from the environment at any time (it is the *interface*), and it defines the *duration* of the process. A process *may not* be describe by what happens inside or outside of it, but only by what crosses its boundary.

copper. A sheet of manufactured copper metal is made of: (1) copper ore, (2) other raw and processing materials, (3) electricity from fossil fuels, and (4) mechanical work. All these factors ultimately resolve into an orderly structure of primary materials (*e.g.*, highly concentrated copper atoms in the ore, fuel, electricity), that is to *environmental low entropy* and nothing else. The free energy used in production to deliver mechanical work, or to heat the ore, is *irrevocably lost*.

We cannot *bootleg* any entropy[29] by means of an ingenious process or device. Just like a Maxwell demon,[30] we have merely sorted the copper atoms from all others, but in order to achieve this end-result we have irrevocably used up a greater amount of low entropy than the difference between the entropy of the copper metal and that of the copper ore. In view of Figure 20, it would be a great mistake to compare just the latter two entropies and exclaim: "Lo! Man has created low entropy from high!" (Georgescu-Roegen, 1971). This claim, in effect, is made by all those who say that copper can be manufactured *sustainably*. The copper scrap recycling programs are successful, only because scrap copper (and aluminum) consumes less free energy than any other way of reconstituting metallic copper.[31] Nevertheless, insofar as fossil energy is used, by recycling we only postpone the inevitable exhaustion of low entropy in the environment.

6. Economic Activity

Economists have a tendency to view the economic process as a *closed system*, while ignoring the *continuous inflow* of low entropy from the environment.[32] From a physical point of view, the economic process is entropic; it neither consumes nor creates mass or energy, but only transforms low entropy to high. To make things worse, the entropy generation process in the environment is spontaneous, and goes on by itself without human intervention.

The material production process, in contrast, depends on the intervention of humans, who, like the Maxwell demon, sort and direct environmental entropy according to the process rules.[33] This sorting activity is not a part of natural environmental processes and creates high entropy, that is, waste, at a (much) faster rate than the biological life processes. *From a purely material point of view, the economic process always transforms low*

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[29] In the 1930s, the young physicists became so confused by statistical thermodynamics that a famous thermodynamicist, Percy Williams Bridgman (1955), wrote an essay on the impossibility of constructing a machine that "shall violate the second law of thermodynamics on a scale large enough to be commercially profitable" (pp. 236–268).

[30] J. Clerk Maxwell (2001) imagined a tiny demon posted near a microscopic swinging door separating two gases A, and B of equal temperature. The demon is instructed to open and close the door "so as to pass only the swifter molecules from A to B, and only the slower molecules form B to A." Clearly this demon can make the gas in B hotter and in A cooler. Therefore, Maxwell's demon creates low entropy—or does he?

[31] According to Stefan Gössling, entropy generation per ton of copper produced from ore is 52 MJ/K, and only 12 MJ/K for copper produced from scrap. See the caption of Figure 17 for reference.

[32] Georgescu-Rogen, (1971), Chapters IX and X.

[33] When watching an SUV commercial, a monstrous truck is often seen carelessly damaging a low-entropy fragile ecosystem, a pristine meadow, river bed, or an alpine mountain slope. Thus the SUV commercials are a good metaphor for the interactions of the present-day economics with the environment.

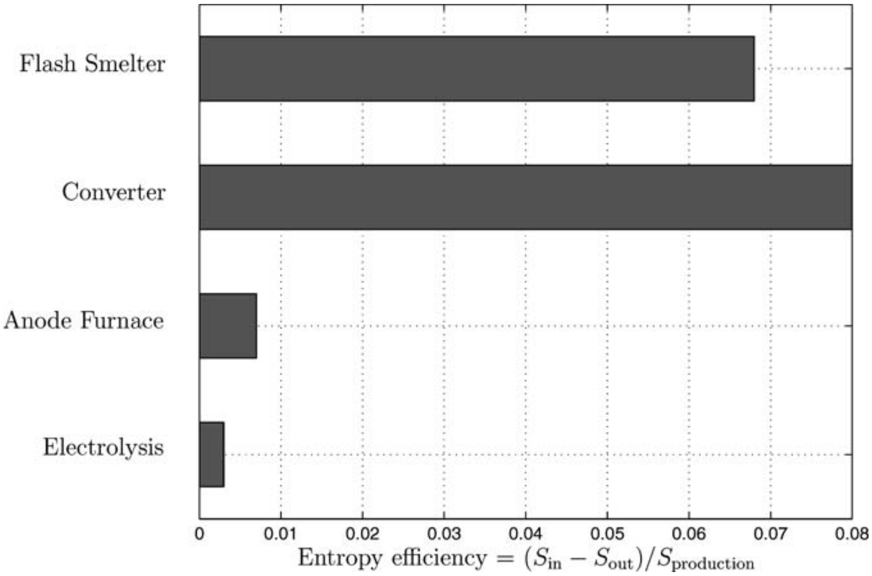

FIG. 20. The Second Law efficiency of copper production is incredibly small. The steps in sorting the copper atoms are: Ore Concentration 2% → 30% Cu (not shown); Smelter 30% → 63% Cu; Converter 63% → 99.1% Cu; Anode furnace 99.1% → 99.55% Cu; and Electrolysis 99.55% → 99.99% Cu. Source: Stefan Gössling, *Entropy Production as a Measure for Resource Use*, University of Hamburg, 2001.

entropy into waste. So what could be the justification for economic activity? As described by Georgescu-Roegen, the true output of an economic process is not merely waste, but the *enjoyment of life*. It is not a coincidence that the very country, which on July 4, 1776 declared: "We hold these truths to be self-evident, that all men are created equal, that they are endowed by their Creator with certain unalienable Rights, that among these are Life, Liberty and the *pursuit of Happiness*," uses over twice as much free energy per capita than any other country on the earth (see Figures 21–23). In general, abundant free energy equals enjoyment of life. The converse statement is as true in real life as it is in Logic (see Figure 24).

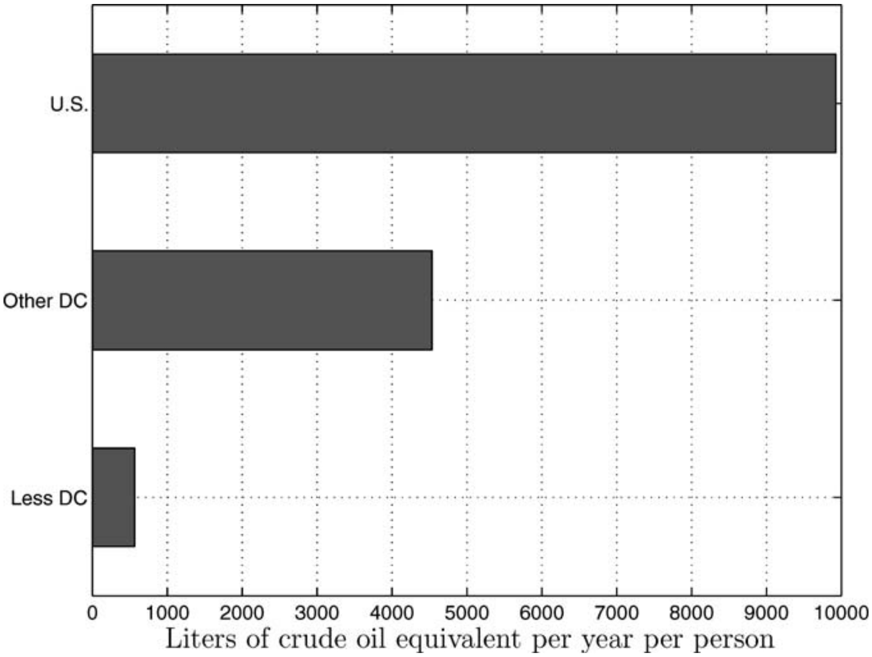

FIG. 21. The 2001 per capita energy consumption in the United States other Developed Countries (DC), and the less Developed Countries. Source: The U.S. DOE Energy Information Agency.

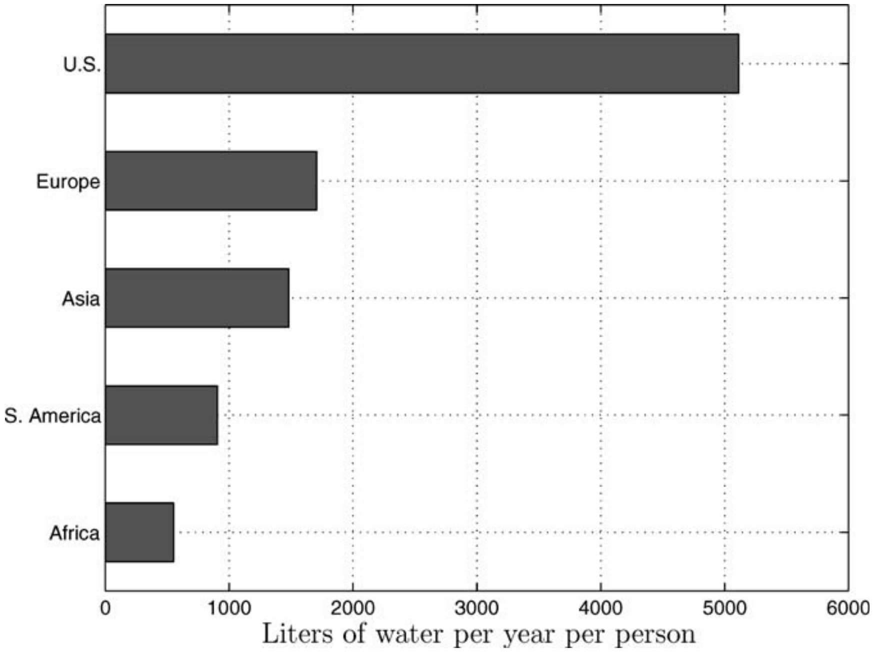

FIG. 22. The 1990 per capita total (personal + industrial) water consumption in the United States and elsewhere. Source: Water Quality Association, 151 Naperville Road Lisle, IL 60532-1088, USA.

7. Agriculture

The following statement is made surprisingly often: "Properly used, [the plants on the earth] can by their reproductive powers supply us indefinitely with the food, the wood, and the other natural products we require."[34] Even though the intensity of sunlight that reaches the earth has not changed appreciably over the human scale of Time, the apparent dominance of solar energy in agricultural production should not obscure the importance of the *entropic soil degradation* by continuous cultivation. Soil degradation can be severe over a human life span. Even the earliest farmers knew that manuring a soil does not remove its degradation, and to farm always meant to mine, in part, the soil. Clean water is necessary for agriculture. Water is inevitably polluted by agricultural waste; therefore, water too is mined.

It would be a mistake to believe that the practice of fertilizing soil can defeat the Entropy Law and transform food production into an everlasting process. Life feeds not only on sunlight but also on the low entropy of an *ecosystem*.[35]

With time, draft animals, oxen, buffalo, and horse, were replaced by machines. A tractor is made of iron, other metals, oil and coal, and it feeds on oil. The natural manure fertilizer from farm animals was replaced by the chemical fertilizers manufactured from methane, coal, oil, iron, copper, and the earth minerals. The importance of this switch should be self-evident: the main source of low entropy feeding agriculture has been switched from the practically *infinite* solar energy to the very *finite stock of minerals* in the earth's crust. Of course, this switch limits how long and how many people can be fed by the earth. It is no longer the practically unlimited stock of the energy in the sun that limits our survival, but the meager stock of natural minerals mined from the earth crust. If M is the *accessible fraction*[36] of this stock, and r is the average rate of its use, then $M = rt$, where t is the corresponding duration of human civilization that depends on the crustal minerals. Depending on the mineral, and its rate of use, this time can be estimated as several tens of years (high quality crude oil), through many hundreds of years (coal), to thousands of years (uranium); so much for sustainable development.

8. Industrial Production

Every car or appliance produced today means fewer human lives in the future. Every styrofoam cup, cell phone, or TV set in a landfill now means fewer resources and happy humans later. In industry, just as in agriculture, the price of technological progress has been a shift from the abundant source of low entropy—the sun—to the earth's mineral resources. Any time these resources are wasted, we shorten the survival time of humanity. Confronted in the distant future with exhaustion of mineral resources, mankind will be tempted to retrace its steps; however, in view of the Entropy Law, it is impossible. Human evolution is *irrevocable* and *cannot be retraced*.

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[34] Cépéde *et al.*, 1964), p. 309.

[35] A process that cycles living organisms. Only the solar energy and waste heat flow across the ecosystem boundary, everything else is recycled, *cf.* Section 10.

[36] This fraction may be very small. For example, the vast majority of carbon on the earth is bound in carbonate rock. No one in their right mind would dream of extracting this carbon. See also footnote 25.

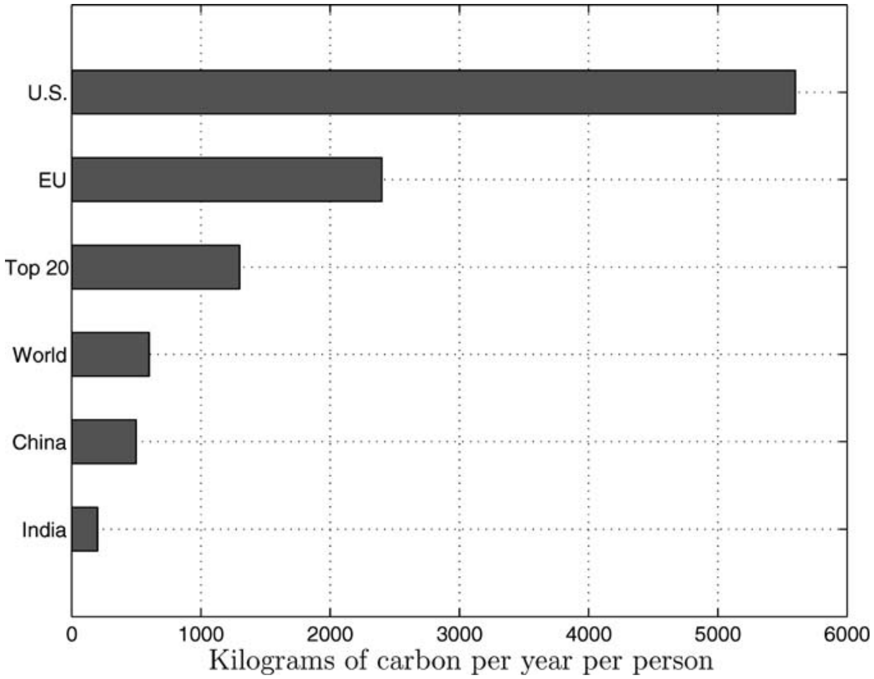

FIG. 23. The 1999 per capita carbon emission estimates in the United States and elsewhere. Source: World Resources Institute, U.S. EIA.

Because of the Entropy Law, the large-scale industrial production of fossil fuels (*e.g*., ethanol) from the industrial plants *manufactured* (Kimbrell, 2003) by modern agriculture, will only hasten the depletion of mineral resources and the eventual demise of our civilization.

9. Waste

The ever-increasing rate of economic activity generates ever more chemical waste. For the earth as a whole, this waste cannot be disposed of.[37] Unless we use more free energy to process it, toxic waste once produced is here to stay. This free energy can only be used once, and will always diminish our future standard of living. Waste cleanup, collection, and recycling have begun to interfere with our life and pockets,[38] and are no longer hidden from our industrial civilization. The ever-accumulating garbage and the toxic by-products of agriculture and industry are the living proof of the Entropy Law in action.

The process of concentrating copper atoms, whose entropy efficiency is shown in Figure 20, is analogous to the process of fishing out the contaminant molecules dispersed in a huge volume of water and rock. The entropy efficiency of any contaminant cleanup process must be lower than that of the copper production process.

10. Sustainability

The opposite of as yet undefined *sustainability* is *irreversibility*, and I define it first after Max Karl Ernst Ludwig Planck (1858–1947):

Definition 3. (Irreversibility): A process is *irreversible* if it can in *no* way be reversed; all other processes are *reversible*. It is impossible, even with the assistance of all agents in nature, to restore everywhere the exact initial state when the irreversible process has once taken place (Planck, 1926).

Corollary 1. *From this definition, a linear process that converts the low entropy of fossil fuels into waste is irreversible and cannot be sustainable.*

In a linear process (see Figures 25 and 26), a finite stock of fossil fuels is rapidly depleted and burned to serve as a collective heat source for all heat engines employed by our civilization (see Figure 28a). In addition, the atmosphere, which acts as a heat sink, becomes polluted by chemical waste from combustion (chemical entropy), as well as by waste heat (thermal entropy). The earth can only export thermal entropy through its atmosphere (see Appendix A). In addition to the atmosphere, the earth, which is a part of "the system" in Appendix B, also accumulates chemical entropy. As a result, the linear fossil fuel process accumulates chemical entropy in the earth and the

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[37] Therefore hiding waste by injecting it into the oceans, aquifers, or burying it in shallow graves—landfills—will always come back to haunt us.

[38] *NYT*, August 20, 2003: "Crews have completed the removal of more than 12 metric tons of weapons-grade plutonium from the Rocky Flats (CO) nuclear weapons site as part of a $7 billion cleanup effort that is expected to be finished in 2006, 12 *years ahead of schedule*. The plant manufactured plutonium triggers for 40 years until it was closed in 1989 for safety violations. The plutonium has been shipped to South Carolina; lower-grade nuclear waste will be sent to New Mexico. The 6,000-acre Rocky Flats site is expected to become a wildlife refuge." In other words, the cost of picking and sorting the plutonium waste is $583/g, compared with $11/g to buy gold.

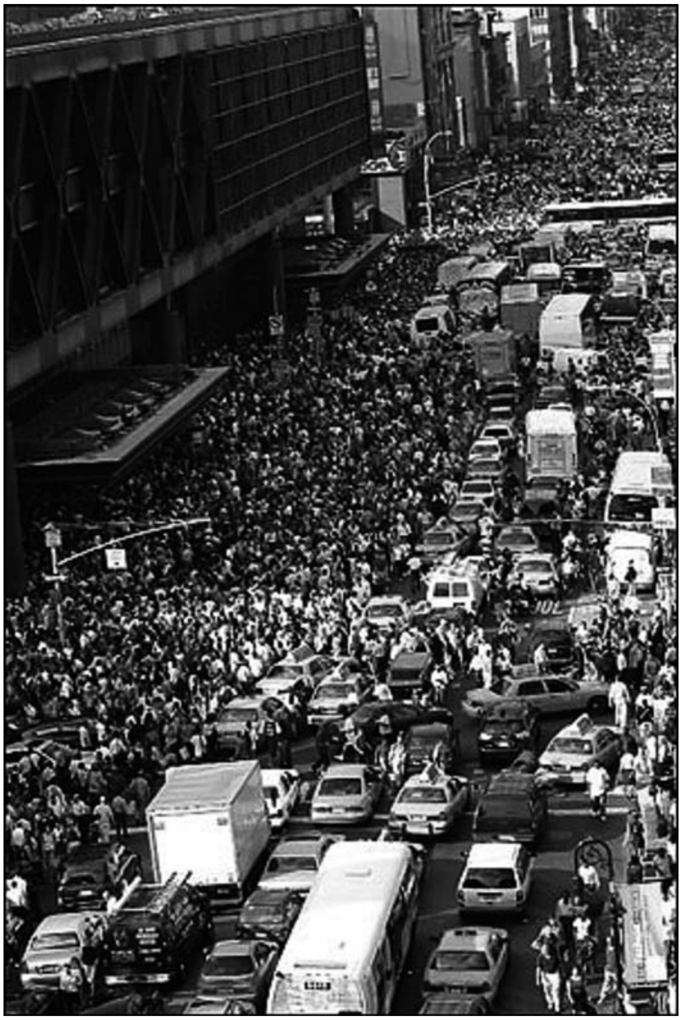

FIG. 24. After the power blackout, people poured onto 8th Avenue, outside the Port Authority, unable to leave the city. *The New York Times*, August 14, 2003.

atmosphere, and irreversibly degrades our planet on a time scale of our civilization, measured in hundreds of years.

In contrast, a *cyclic* ecosystem can be sustainable (see Figure 27). A natural cycle uses the sun as its source of energy and low entropy, and it expels only waste heat into the atmosphere and, ultimately, into the universe (see Figure 28b). Most importantly, *all materials* involved in an ecosystem are *recycled*, and when the natural cycle is completed, only waste heat, or thermal entropy, is generated.

In order to discuss the existence and constraints on *sustainability*, I need first to define it.

Definition 4. (Sustainability): A *cyclic* process is *sustainable* if and only if (1) It is capable of being *sustained*, that is, maintained without interruption, weakening, or loss of quality "forever," and (2) the environment on which this process feeds and to which it expels its waste is also sustained "forever."

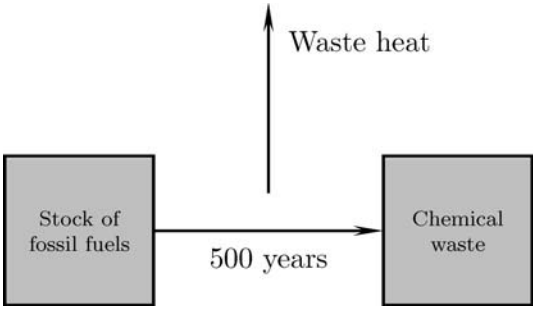

FIG. 25. A linear process of converting a stock of fossil fuels into waste matter and heat cannot be sustainable. The waste heat is exported to the universe, but the chemical waste accumulates. To replenish some of the fossil fuel stock, it will take another 50–400 million years of photosynthesis, burial, and entrapment.

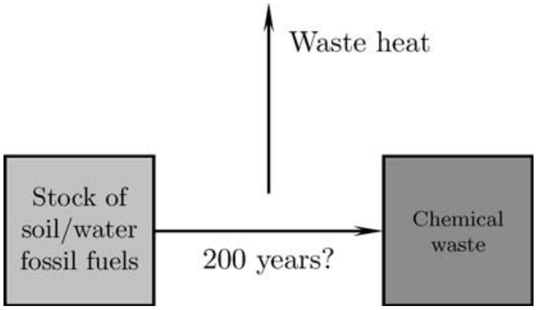

FIG. 26. Current industrial agriculture is another example of a linear process, which by definition cannot be sustainable.

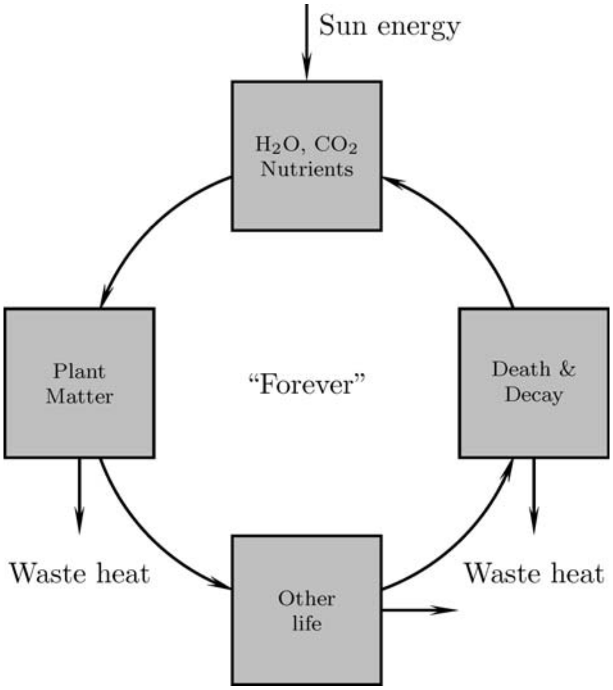

FIG. 27. An ecosystem transforms the sun energy (low thermal entropy) into waste heat (high thermal entropy). The waste heat is continuously exported to the universe. *Everything* else is completely reused or recycled.

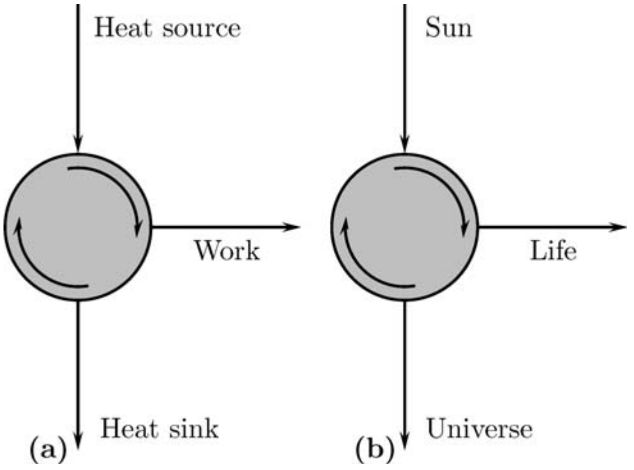

FIG. 28. Thermodynamic cycles: (a) A heat engine, and (b) An ecosystem.

Corollary 2. *A cyclic process, which is also "sustainable," must not reject chemicals into the environment, that is, its net mass production must be "close" to zero "forever."*

Corollary 3. ***A sustainable cyclic process** must not reject heat into the environment at a rate that is too high for the earth to export this heat to the universe; otherwise, the environment properties will change.*

10.1. The Earth is an Open System to Heat Flow

Attributes (1)–(2) of a sustainable cyclic process would be a *thermodynamic contradiction* if the earth were approximately a closed system with respect to infrared radiation (heat). These two attributes would then make a sustainable process a *perpetual machine of the second kind*. Luckily for us, the earth can be treated as an open system with respect to visible and infrared light, and a sustainable cyclic process may generate thermal entropy at a rate per unit area of the earth surface (*specific entropy rate* or *flux*) which is no more than the average flux of entropy export from the earth to the universe, j_S^E, calculated from Eq. (33) in Appendix A, minus the specific rate of entropy generation in the atmosphere due to export of the solar energy, calculated from Eq. (38) in Appendix A.

To quantify sustainability, I first assert that a cyclic process always converts all forms of entropy to thermal entropy. Thermal entropy is the ultimate waste from all "sustainable" cyclic processes on the earth, and it should be used for comparisons. Second, per unit area of the earth, we know that (1) the *always positive* specific rate of thermal entropy generation due to everything happening on the earth is $\sigma > 0$, (2) the rate of increase of the specific thermal entropy of the atmosphere due to all these happenings is $\sigma_a > 0$, and (3) the specific rate of thermal entropy generation due to the energy transport from the earth to the universe is $\sigma_t > 0$. Then, for cyclic processes, *strong sustainability* can be defined mathematically (see Appendix B), as

$$\sigma + \sigma_a \leq j_S^E - \sigma_t \tag{11}$$

at every point on the earth, and at all times.

Over an arbitrary time interval $[\tau_1, \tau_2]$, we can write the global condition of sustainability of all cyclic processes on the earth as (Eq. (54) in Appendix B)

$$\underbrace{[S_a(\tau_2) - S_a(\tau_1)]}_{\text{Increase of atmospheric entropy}} + \underbrace{[S(\tau_2) - S(\tau_1)]}_{\text{Increase of earth entropy}}$$
$$-S^E(\tau_1, \tau_2) + S_t(\tau_1, \tau_2) \leq 0 \tag{12}$$

where $S^E(\tau_1, \tau_2)$ is the total thermal entropy exported by the earth over the time interval $[\tau_1, \tau_2]$, and S_t is the corresponding thermal entropy generation in the atmosphere due to the solar energy export.

10.2. Conclusions

The immediate observations from this discussion are:

- To the extent that humans use 80–90% of fossil and nuclear energy to run the heat engines that power the global economy, our civilization is 80–90% unsustainable.
- If the atmosphere dissipates more energy due to the increased greenhouse gas loading by human (and natural) activities (σ_t increases), there will be less room for all other human activities to remain sustainable. Stahl (1996) estimates, Table 1, the specific entropy generation rate in the atmosphere to be $\sigma_t = 0.2$ W/K-m^2. So only 1 W/K-m^2 of thermal entropy generation is left to all human and other natural activities (see Appendix A).
- Only energy generation directly from the sun, sun-driven wind, and water can be sustainable.
- Burning or extracting large quantities of wood or green matter requires chemical fertilization and cannot be sustainable to the extent that growing plants mine low entropy from the soil; see Section 7.
- Industrial agriculture can never be sustainable because it relies on the irreversible burning and chemical transformations of fossil fuels; see Section 7.

PART III: SUSTAINABILITY OF CORN-ETHANOL CYCLE

1. Introduction

As pointed out in Part II, our standard of life is maintained by the exploitation of natural resources that have accumulated in the earth over millions of years. A natural resource whose chemical composition *differs most* from the dead states of the elements comprising it is *most valuable*.

This part is devoted to the life-cycle analysis of industrial corn and the ethanol biofuel produced from it. In my analysis, I will move along the trail charted in the brilliant, albeit incomplete, paper by three Canadian scientists, Richard Berthiaume, Christian Bouchard, and Marc A. Rosen (Berthiaume *et al.*, 2001). There will be, however, important differences. I define the industrial corn-ethanol system differently, include more inputs (which are more carefully estimated), and do not require the carbon and water cycles to close.

2. Available Free Energy

For example, relative to a *datum environment* ($T_0 = 25°\text{C}$, $p_0 = 1$ atm), the quality of heat rejected by a process depends on temperature:

$$\begin{aligned}\text{1J of heat at } 500°\text{C} &= 0.614 \text{ J of work}\\ \text{1J of heat at } 50°\text{C} &= 0.077 \text{ J of work}\end{aligned} \qquad [13]$$

Gibbs, Guoy, Stodola, and Keenan's available free energy (see Appendix B), is known in chemical and engineering thermodynamics as *exergy*, and is denoted with the symbol B. The concept of exergy and its cumulative consumption in an industrial process has been significantly advanced by the distinguished Polish thermodynamicist Jan Szargut, a professor at the Chemical Engineering Department of my *Alma Mater*, the Silesian Technical University, Gliwice, Poland. His monograph, published in English with David R. Morris and Frank R. Steward in 1988 (Szargut *et al.*, 1988) was based on two decades of development and industrial applications of life-cycle analysis. Today, this monograph is still the most comprehensive source of exergy concepts, data, and examples.

2.1. *Introduction to Exergy*

An easy to understand definition of exergy was proposed by Ludwig Riekert (1975).

Definition 5. Exergy, B, is equal to the shaft work or electrical energy necessary to produce a material in its specified state from materials common in the environment in a reversible way, heat being exchanged with the environment at constant temperature T_0.

We distinguish the *potential* exergy, B_p, *kinetic* exergy, B_k, *physical* exergy B_{ph}, and *chemical* exergy, B_{ch}:

- **Physical exergy**, B_{ph} is the work obtainable by a reversible physical process from its initial state (T, P) to the environment state (T_0, p_0).
- **Chemical exergy**, B_{ch}, is the work obtained by taking a substance at the pressure and temperature of the environment to the state of thermodynamic equilibrium with the datum levels of components of the environment.
- **Thermal exergy**, B_{th}, is the sum of physical and chemical exergies:

$$B_{\text{th}} = B_{\text{ph}} + B_{\text{ch}} \qquad [14]$$

2.2. *Change of* B$_{\text{th}}$ *between Two States*

Consider an ideal (reversible) flow machine (see Figure 29). An exergy carrier with enthalpy H_1, and entropy S_1 enters the machine. After physical and/or chemical changes, the effluent has enthalpy H_2, and entropy S_2. Heat is transferred between the environment and the working fluid at the ambient temperature T_0. The first and second law of thermodynamics are simply:

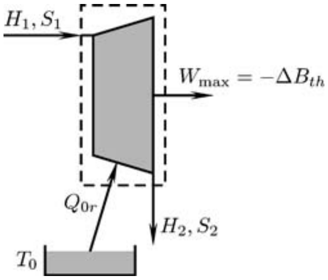

FIG. 29. Exergy balance in an isothermal, ideal flow machine. The maximum possible shaft work from this machine is equal to the negative change of thermal exergy.

$$\begin{aligned}W_{\max} &= B_{\text{th}_1} - B_{\text{th}_2} = H_1 - H_2 + Q_{0r} && \text{(I Law)}\\ S_2 - S_1 &- \frac{Q_{0r}}{T_0} = 0 && \text{(II Law)} \quad [15]\\ B_{\text{th}_1} - B_{\text{th}_2} &= -\Delta B_{\text{th}} = H_1 - H_2 \\ &\quad - T_0(S_1 - S_2) && \text{(I + II Law)}\end{aligned}$$

Physical exergy can be calculated immediately from Eq. (15)

$$B_{\text{ph}} = H - H_0 - T_0(S - S_0) = H_{\text{ph}} - T_0 S_{\text{ph}} \qquad [16]$$

2.3. *An Industrial Flow Process*

Consider now an industrial steady-state flow process, which can occur in a heat engine, corn field, or ethanol plant (see Figure 30). The input to this irreversible process is an exergy carrier with the enthalpy H_1, and entropy S_1. The process is also supplied with the quantity of heat Q_1 from the source having temperature $T_1 > T_0$. The process effluent has enthalpy H_2, and entropy S_2. The rejected amount of heat Q_0 is transferred to the environment. The useful outcome of the process can be mechanical work W_u or a chemical product having parameters H_u and S_u. The effect of irreversibility is studied by comparing the industrial process with a reversible process with the same inflow and outflow parameters, and the same amount of driving heat. The only difference between these two processes is the amount

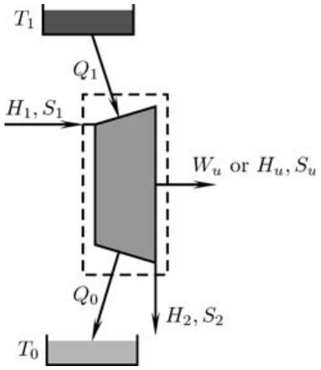

FIG. 30. Exergy balance in ideal (reversible) and real (irreversible) non-isothermal industrial process.

of heat rejected to the environment. For the reversible process this heat is Q_{0r}, and for the irreversible one, it is Q_0.

The first and second law balances for the two processes are:

$$\begin{aligned} H_u &= H_1 - H_2 + Q_1 - Q_0 \quad \text{Real process} \\ H_{ur} &= H_1 - H_2 + Q_1 - Q_{0r} \quad \text{Reversible process} \\ H_{ur} - H_u &= Q_0 - Q_{0r} \end{aligned} \tag{17}$$

The increased useful effect of the reversible process causes the amount of rejected heat to be smaller than that in the industrial process, $Q_{0r} > Q_0$. The sum of all entropy increases in the industrial process is

$$\sum \Delta S = -\frac{Q_1}{T_1} + S_2 - S_1 + \frac{Q_0}{T_0} + S_u > 0 \tag{18}$$

while that in the reversible process is

$$\sum \Delta S_r = -\frac{Q_1}{T_1} + S_2 - S_1 + \frac{Q_{0r}}{T_0} + S_{ur} \equiv 0 \tag{19}$$

From Eqs. (18) and (19) it follows that

$$Q_0 - Q_{0r} = T_0\left(\sum \Delta S + S_{ur} - S_u\right) \tag{20}$$

and we obtain

$$\underbrace{(H_{ur} - T_0 S_{ur})}_{B_{\text{th,r}}} - \underbrace{(H_u - T_0 S_u)}_{B_{\text{th}}} \equiv \delta B = T_0 \sum \Delta S \tag{21}$$

The left hand–side of Eq. (21) represents the difference of the useful thermal exergy in the reversible and industrial process, δB. It therefore represents the *exergy loss* due to the irreversibility of the industrial process under consideration. We have recovered, again, the famous Guoy-Stodola law, also derived in Appendix B.

2.4. *Cumulative Exergy Consumption (CExC)*

All steps of a production process leading from natural resources taken from the environment to the final product result in *exergy losses* or exergy *consumption*.

Definition 6. (CExC): The cumulative exergy consumption (CExC) is the sum of the exergy of all natural resources in all the steps of a production process.

The problem of cumulative *energy* consumption (CEnC), discussed in Part I, is better known, but calculation of CExC is more informative because it accounts for the exergy of non-energetic raw materials (soil, water, air, minerals) extracted from the environment.

3. The Ideal and Real Corn-Ethanol Cycle

Ideally (see Figure 31), the corn-ethanol system and cycle consist of three parts: (1) Sustainable corn farming, (2) Sustainable ethanol production, and (3) Ethanol combustion to produce useful work.

The cycle is driven *only* by solar energy, and all its chemical by-products are *fully* recycled. Only the low quality heat is rejected by the ideal corn-ethanol cycle into the environment, and this heat is exported through the atmosphere into the universe. All carbon dioxide is recycled, and so is all water. This low-rate ideal cycle *cannot* deliver the massive quantities of ethanol fuel from (bi)-annual corn crops (see Figure 32).

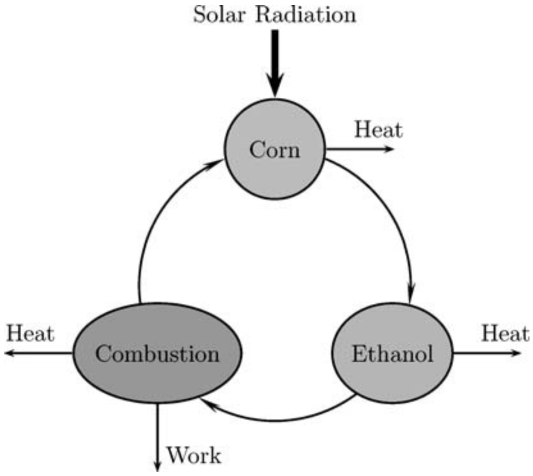

FIG. 31. The ideal corn-ethanol cycle.

Remark 4. Between 1866 and 1939 (NASS, 2004b), the average yield of corn in the U.S. hovered around 26 ± 3 bushels per acre, or 1600 kg/ha, 1/5 of the average yield today. I will assume that 1600 kg/ha is the *almost* sustained corn yield using manuring, composting, crop rotation, and other not quite sustainable field practices. Note that between 1906 and 1937, the average corn yield declined, most likely due to the progressing soil deterioration,[39] *cf.* Section 7.

Corollary 4. *From Remark 4 it follows that without the fossil fuel-derived fertilizers, the corn produced today in the United States would require at least 140 million hectares, more than the entire cropland area in the United States. There would not be enough animals to manure the fields, and low entropy in the soil would be exhausted within some 30 years. The same conclusion follows (perhaps with a different time scale) for any other industrial source of biomass. In short, no biofuel derived from plants is sustainable.*

Instead of relying on the current solar energy, we use the ancient solar energy in the form of fossil fuels to *accelerate* the

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[39] Pimentel (2004c) observes: “Between 1900 and 1938, the early [U.S.] farmers were probably mining the soil of nutrients and soil erosion was quite severe. At that time, most farmers kept livestock and were applying manure to the land. Most did not apply the manure until spring, when more than half of the nitrogen had escaped into the atmosphere. Most of the corn was grown in rotation. If the corn were grown after a legume crop, some nitrogen would be available to the corn crop. Although manure was being applied, it probably was applied in the neighborhood of only 5 tonnes of stored manure per hectare, and thus would have only about 12 to 15 kg/ha of nitrogen. For a corn yield of 1600 kg/ha the manure application only would provide a minimum amount of nitrogen.”

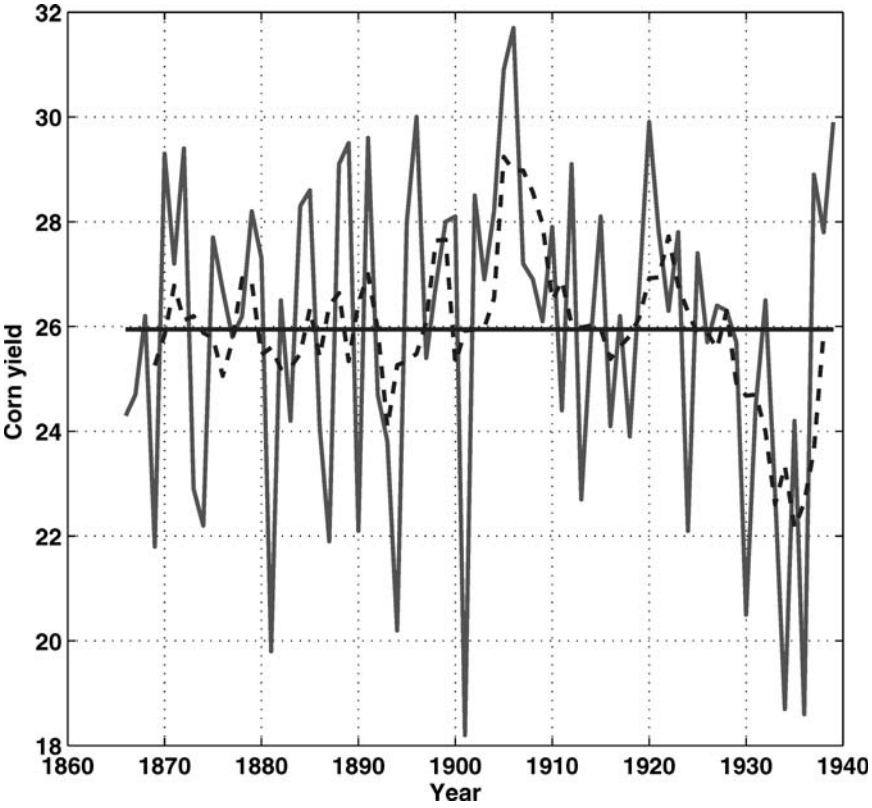

FIG. 32. Between 1866 and 1939, the average yield of corn in the United States was 26 ± 3 bushels/acre, or 1600 kg of moist corn grain per hectare. The broken line is the 5-year moving central average of annual reports. Between 1906 and 1937, the average yield declined in general due to soil mining. Source: USDA (NASS, 2004b).

ideal corn-ethanol cycle (see Figure 33). With the massive infusion of crude oil, natural gas, coal, and their products, as well as fertilizers, pesticides, and herbicides, we greatly increase the corn yield and the rate of ethanol production, but we also produce massive amounts of chemical waste. In addition, we deplete soil by removing too much plant matter from the fields, and deplete groundwater whenever there is not enough rain. The industrial corn-ethanol cycle relies on the linear processes of mining fossil fuels, soil, water, and air, and in view of Part II, it *cannot* be sustainable. All published statements to the contrary (*e.g.*, Wang *et al.*, 1997; Shapouri *et al.*, 2002; Deluga *et al.*, 2004; Sheehan *et al.*, 2004, and many others), are scientifically indefensible. In the following, I will quantify just how unsustainable the industrial corn-ethanol cycle is.

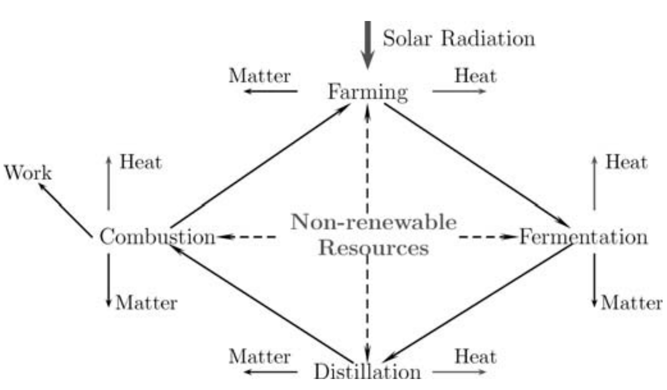

FIG. 33. The industrial corn-ethanol cycle. The nonrenewable resources (NRRs) at the center of the cycle are: crude oil, methane, coal, electricity from fossil fuels, earth minerals, soil nutrients, groundwater, and so on.

4. System Boundary

As required by thermodynamics (see Figure 31), I define the *system* as the topsoil of the corn fields, the corn plants, the corn-processing ethanol plants, and the ethanol-burning combustion engines. The system *inputs* are the manufactured hybrid corn seeds, solar energy, fossil fuels, field chemicals, earth minerals (muriate of potash, phosphates, calcinated lime, *etc.*), electricity, machines, air (oxygen and carbon dioxide), and the atmospheric, surface and subsurface water. The system *outputs* are heat, oxygen O_2, carbon dioxide CO_2, carbon monoxide CO, gaseous ammonia NH_3, nitrogen oxides NO_x, sulfur oxides SO_x, methane CH_4, water as liquid and vapor, and a multitude of organic and inorganic water, soil, and air contaminants.

5. The Carbon Cycle

The simplified carbon cycle *inside* the industrial corn-ethanol cycle is depicted in Figure 34. Consistently with the discussion in Part I, I require that all organic carbon be returned from the

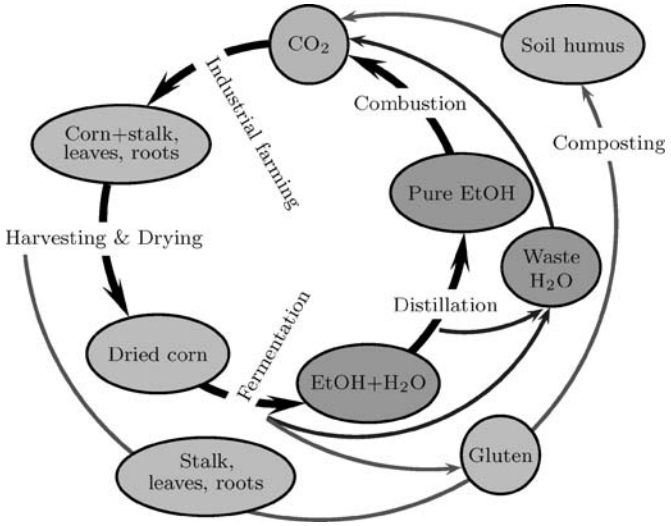

FIG. 34. The internal carbon cycle in the industrial corn-ethanol cycle can be closed only by recycling most of the corn-plant and corn-grain components.

TABLE 19

Specific CO_2 emissions

NRR	Emission	Units
Electricity	0.322	kg CO_2/kWh
Coal	0.089	kg CO_2/MJ
Gasoline	0.067	kg CO_2/MJ
Diesel	0.069	kg CO_2/MJ
LPG	0.059	kg CO_2/MJ
Methane	0.050	kg CO_2/MJ
Lime	0.785	kg CO_2/kg CaO
Nirrogen[a]	2.70	kg CO_2/kg N

Sources: Energy Information Administration (EIA, 2002), *Emissions of Greenhouse Gases in the United States 2001*, Table B1. [a]G. Kongshaug (1999).

ethanol plants to the fields. Therefore, the *internal* carbon cycle is *closed*. The corn plants bind CO_2 from the air, which is then released back into the atmosphere by burning the ethanol fuel produced by the cycle, and by decomposing the stalk, roots, and leaves of corn plants, as well as all those parts of corn grain that were not used to produce the ethanol.

Remark 5. Most of the biomass must be returned to the field[40] to preserve topsoil. This requirement puts severe restrictions of the various schemes of converting biomass (rice straw, corn straw, tree parts, whole plants, *etc*.) to biofuels.

5.1. Net CO_2 Emissions

As shown in Figure 33, our corn field–ethanol plant–combustion engine system uses fossil fuels as inputs, and outputs *their* combustion products into the environment. Therefore the industrial corn-ethanol cycle generates extra CO_2 and other greenhouse gases, which will all be translated into equivalent CO_2 for simplicity.

The question now is as follows: Does the industrial corn-ethanol cycle generate more equivalent CO_2 from its fossil fuel inputs than the gaseous emissions from replacing the cycle's ethanol with gasoline, methane, or diesel fuel? To make this comparison fair, I will account for the cumulative exergy consumption in production of the fossil fuels by adding another 15% to their calorific values, in agreement with Szargut *et al*. (1988).

By asking and answering this question, I seek to dispel common misconceptions about the industrially manufactured biofuels, best summarized by the following quotation:

> About 70 million barrels[41] of ethanol are included in annual U.S. gasoline consumption after 1992. Because ethanol is a biofuel, the carbon it contains should not be counted as an emission. Hence, carbon from ethanol is *deducted* from transportation gasoline consumption.[42]

EIA is right, but then the CO_2 emissions associated with the consumption of non-renewable resources in the industrial ethanol-corn cycle should be *added* to the transportation gasoline consumption. The question now is: What is the net balance?

To answer this question, I will use the EIA and the European Fertilizer Manufactures' Association (EFMA) data on the specific carbon dioxide emissions from the fossil fuel inputs into the industrial corn-ethanol cycle (see Table 19). These specific emissions, in kg of CO_2 per MJ in a fossil fuel, will be multiplied by the respective energy input fluxes in MJ ha^{-1} $crop^{-1}$, established in Part I. Electricity is treated differently, and its specific CO_2 emissions account for the average U.S. efficiency of conversion of thermal energy into electricity.

To convert the NO_x emissions from the industrial corn-ethanol cycle to the equivalent CO_2 emissions, I will follow the guidelines of EIA (2002), the Intergovernmental Panel on Climate Change (IPCC, 1997), and EFMA (Biermann *et al*., 1999):

- 1.25% of applied N fertilizer escapes into the air as N_2O.
- 30% of applied N escapes from the field, and 2.5% of that quantity is converted to N_2O in surface water.
- 10% of applied N escapes as NH_3 into the air, and 1% of that becomes N_2O.
- Nitrous oxide is 300 times more potent as a greenhouse gas (GHG) than CO_2.
- An average ammonia plant emits 0.03 kg N_2O/kg N in nitric acid, which is used to make ammonium nitrate.

The equivalent CO_2 emissions from the corn fields are then ~950 kg/ha. The equivalent CO_2 emissions from the production

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[40] Not necessarily the same field.

[41] About 11 giga liters.

[42] The U.S. Energy Information Agency (EIA) (2002), Appendix A, p. A3, author's italics.

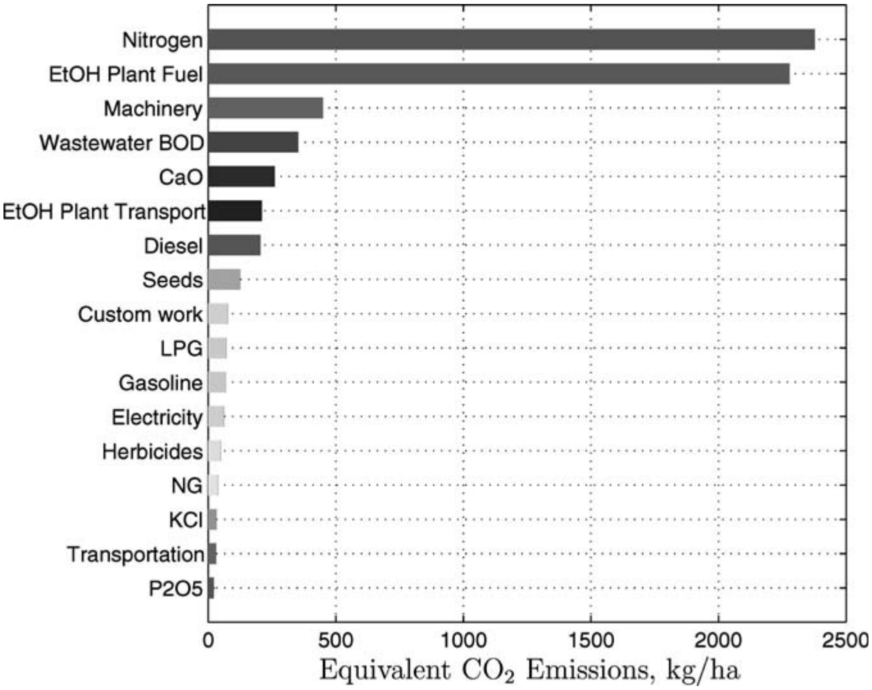

FIG. 35. Equivalent CO_2 emissions from each major nonrenewable resource consumed by the industrial Corn-EtOH cycle.

of ammonium nitrate are $\sim 150 \times 0.03 \times 300 \times 63/80 = \sim 1000$ kg/ha.[43]

The CO_2 emissions resulting from electricity use in the removal of Biological Oxygen Demand (BOD) in wastewater from ethanol plants, *cf.* Section 6, are also included.

5.2. *Conclusions*

The results of my calculations, shown in Figures 35 and 36, lead to the following conclusions:

1. According to my estimates, 1 ha of industrial corn-for-ethanol generates 6700 kg of CO_2 equivalent from the fossil fuel inputs.
2. If the amount of gasoline with the energy content of 115% of 2170 kg EtOH/ha obtained on average from corn were burned, it would generate 5100 kg of CO_2.
3. The net CO_2 emissions are then $6700 - 5100 \approx 1600$ kg/ha *above* those of gasoline.
4. Today, the industrial corn-ethanol cycle generates on 4.9 million hectares about 7.9 million metric tons of CO_2/year *over and above* the energy-equivalent gasoline.
5. To satisfy 10% of U.S. fuel consumption, the additional CO_2 emissions will be about 65 million metric tons per year.

6. Water Cycle

The water cycle can be idealized by bringing all necessary water to an imaginary "water tank" at the top of Figure 37. The water is then dispensed from this tank as rain, irrigation water, and ethanol plant feed water. Water is used by the corn plants, but it also evaporates from the fields, runs off as contaminated surface water, and seeps back into the groundwater, contaminating the underlying aquifers as well. Additional water is evaporated during drying of the harvested corn in NG/LPG driers.

To estimate the average water requirement by corn plants, I will use Pimentel's (2003) average estimate of $\sim$100 cm of water per crop.[44] This translates into 10×10^6 L/ha-crop. About 15% of the water demand (USDA, 1998), 8.1×10^5 L/ha-crop, comes from pumping groundwater and surface water to irrigate corn. For comparison, the average water requirement by corn in Nebraska is 53–71 cm, and roughly 50% of corn acreage is irrigated there (Benham, 1998). Nebraska sits on top of the most prolific part of the giant High Plains aquifer (USGS 2003; Rosenberg *et al.*, 1999). Water mining from the High Plains aquifer continues in Texas, Kansas, Oklahoma, New Mexico, and Colorado, whereas the water levels in Nebraska and Wyoming have stabilized or increased (see USGS (2003) and the references therein).

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[43] This last number may be disputed to the extent that ammonium nitrate is not used as fertilizer.

[44] The rule of thumb is that corn needs 1000–1800 kilograms of water per kilogram of grain produced. This rule translates into 86–150 cm of water requirement, see, *e.g.*, http://www.jica.go.jp/zenglish/publication/network/net_vol18/-02.html

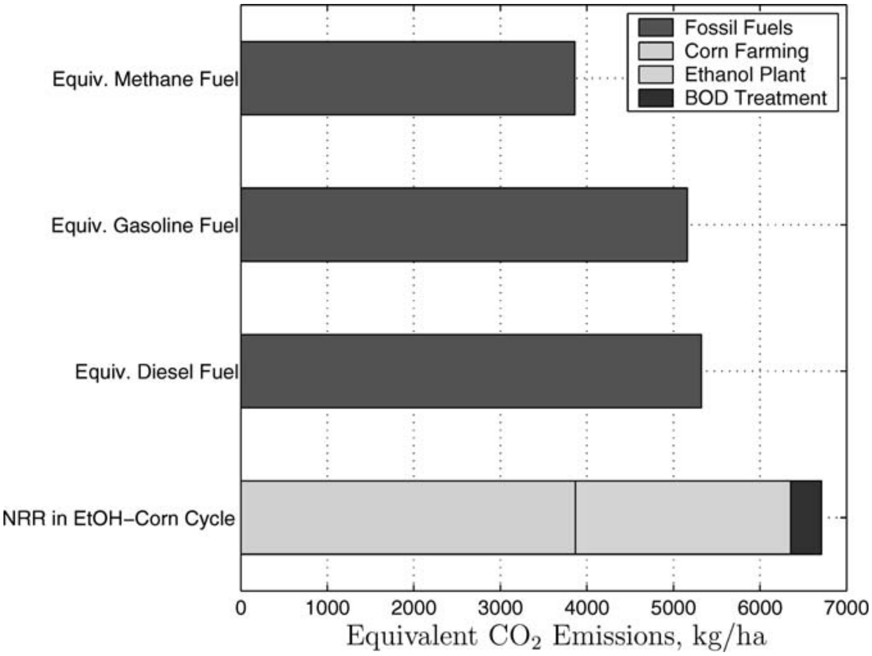

FIG. 36. The total equivalent CO_2 emissions from the consumption of nonrenewable resources by the industrial corn-ethanol cycle. The CO_2 emissions from the energy-equivalent amounts of methane, gasoline, and diesel fuel were increased by 15% to account for their recovery, transport, and refinement.

To estimate the water inputs into a wet-milling ethanol plant I will use the data published in the *Corn Chemistry and Technology Handbook* (White and Johnson, 2003) and by Pimentel (2003). According to White and Johnson 2003), one needs the following amounts of process water per 1 liter of ethanol:

- 10–12 liters in corn fractionation (p. 450).
- 20–25 liters in glucose fermentation (p. 697).
- The total amount is 30–37 liters of clean process water per 1 liter of ethanol, or 38–46 liters of water per kilogram of ethanol.

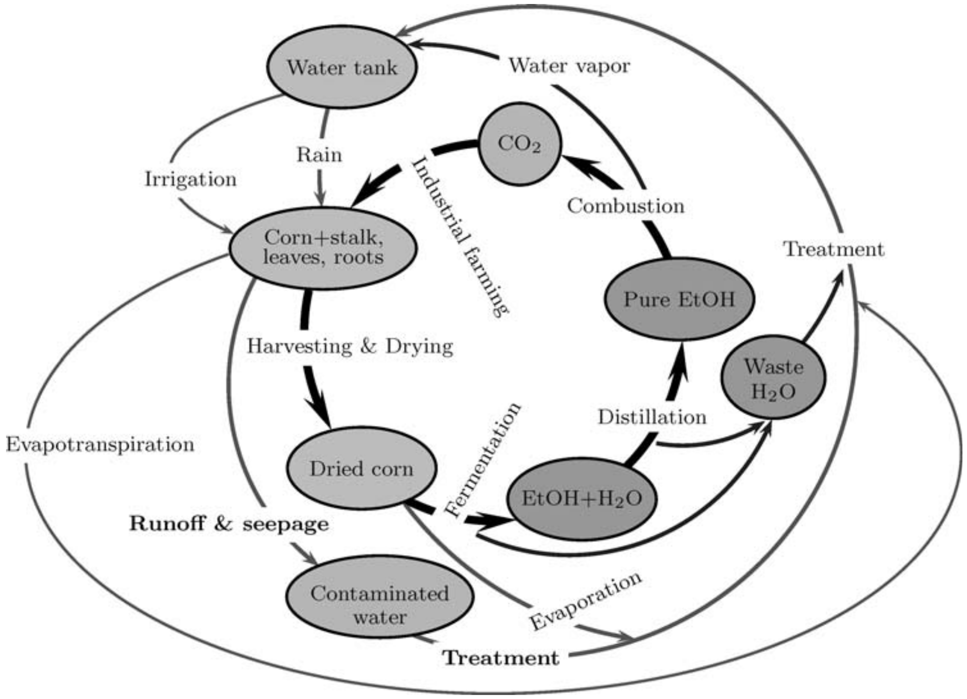

FIG. 37. The water cycle in corn-ethanol production. Compared with the water requirement by corn plants, the feed water requirement of an ethanol-producing plant is small, and the link between the tank and the fermentation stage was not drawn.

- The average 5-day biochemical oxygen demand (BOD) of waste water is 1000–2000 mg/L.

According to Pimentel (2003), 159 liters of water are needed to produce 1 liter of 95% ethanol, which translates to 190 liters of water per kg of 100% ethanol. Twelve liters of waste-water are generated per 1 liter of ethanol from the separation of industrial beer with 8 percent of ethanol by volume. The wastewater BOD is 18000–37000 mg/L, 10–20 times higher than the previous estimate. This estimate makes sense because the beer wastewater contains dead yeast and unreacted glucose. After mixing with cleaner process water, the overall BOD must go down. Berthiaume *et al.* (2001) erroneously used, 160 L of waste-water per L of EtOH, with the BOD of 20000 mg/L.

For the time being, I will go along with 46 L water/kg EtOH with the BOD[45] of 2000 mg/L. Thus, a wet milling ethanol plant needs on average

$$46\frac{\text{L}}{\text{kg EtOH}} \times 2170\frac{\text{kg EtOH}}{\text{ha-crop}} = 0.1 \times 10^6\frac{\text{L}}{\text{ha-crop}}, \qquad [22]$$

of water, and it generates 200 kg of BOD/ha-crop. This amount of process water is 100 times smaller than the amount of water needed to grow corn in the field.

Remark 6. The industrial corn-ethanol cycle needs about 10 × 10^6 liters of water per hectare and per crop. This amount of water must be deposited in the tank. Depending on the weather and location, some or most of this water may have to come from mining an aquifer or surface water.

Since the volume of process water passing through the ethanol plant is two orders of magnitude smaller than that passing through the field, and all of the process water is readily accessible in holding tanks, ponds, and so on, problems with cleaning it up are *insignificant* when compared with the field runoff water.

Remark 7. Industrial agriculture uses a huge land area, and it mines and contaminates huge amounts of soil, water, and air. The environmental damage it causes is much more widespread and more difficult to reign in than that from the highly concentrated industrial sources. In addition, industrial agriculture invades and destroys large ecosystems. In other words, 21st-century industrial agriculture poses a more acute threat to life on the earth than the 19th-century smoke stacks ever did.[46]

TABLE 20
The specific chemical exergies of compounds participating in the ideal corn-glucose-EtOH cycle. Source: Szargut *et al.* (1988), Tables 1 and 2 in Appendix

Component	Standard Chemical Exergy MJ/kmol
$C_6H_{12}O_6$(s)	2928.8
C_2H_5OH(l)	1363.9
CO_2(g)	19.87
O_2(g)	3.97
H_2O(l)	0.00
H_2(g)	236.1

7. Exergy Analysis of the Ideal Corn-Ethanol Cycle

7.1. *Chemistry of the CO_2-Glucose-EtOH Cycle*

The ideal CO_2-Glucose-EtOH cycle consists of three steps:

Step 1. Photosynthesis of glucose from atmospheric CO_2:

$$6CO_2 + 6H_2O + \text{Solar radiation} \rightarrow C_6H_{12}O_6 + 6O_2 + \text{Heat} \qquad [23]$$

Step 2. Production of ethanol from glucose:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 2C_2H_5OH + 2CO_2 + 6O_2 + \text{Heat} \qquad [24]$$

Step 3. Combustion of ethanol:

$$2C_2H_5OH + 2CO_2 + 6O_2 \rightarrow 4CO_2 + 2CO_2 + 6H_2O + \text{Heat} \qquad [25]$$

The compounds that appear on both sides of the chemical reactions in Steps 2 and 3 do not participate in these reactions, but appear to close the cycle. The chemical exergies of all compounds are listed in Table 20. The chemical exergies of the products of each step of the cycle are listed in Table 21, and the exergy flow is depicted in Figure 38.

7.1.1. The maximum cycle output per unit mass of corn. To calculate the maximum possible energy output from the ideal

TABLE 21
The calculated chemical exergies of the products of steps in Eqs. (23–25)

Step	Product exergy after step MJ/kmol $C_6H_{12}O_6$
1	2952.6
2	2791.4
3	119.2
Net	2833

Net chemical exergy per kg of glucose = 15.74 MJ/kg. Exergy of matter after Step 1 per kg of glucose = 16.4 MJ/kg = 3920 kcal/kg. Cycle efficiency = 96%.

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[45] A Google search yields BOD values between 600 and 9200 mg/L in the wastewater streams from wet- and dry-milling ethanol plants that use different biomass feeds.

[46] For an in-depth analysis of the deadly industrial agriculture, see Kimbrell (2002).

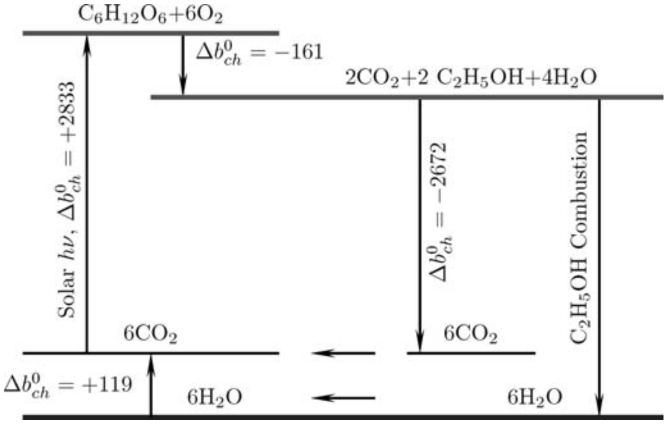

FIG. 38. Exergy diagram of the ideal CO_2-Glucose-EtOH cycle.

CO_2-Glucose-EtOH cycle, I made the following assumptions:

- Dry corn is 66% glucose (100% hydrolyzed starch) by mass.
- Starch is converted into ~100% ethanol with 0% losses.
- Corn delivered to an ethanol plant is 15% water.
- The net chemical exergy of an ideal ethanol cycle per kg of moist corn grain is

$$15.74\frac{\text{MJ}}{\text{kg glucose}} \times 0.66\frac{\text{kg glucose}}{\text{kg dry corn}} \times 0.85\frac{\text{kg dry corn}}{\text{kg wet corn}} = 8.83\frac{\text{MJ}}{\text{kg wet corn}} \quad [26]$$

- At 8600 kg of moist corn per hectare,[47] the chemical exergy from an **industrial** ethanol cycle is

$$8.83\frac{\text{MJ}}{\text{kg wet corn}} \times 8600\frac{\text{kg wet corn}}{\text{ha}} = \mathbf{75.9}\ \text{GJ/ha} \quad [27]$$

- With 88% conversion efficiency of starch into 100% ethanol, the chemical exergy is

$$75.9\ \text{GJ/ha} \times 0.88 = \mathbf{66.8}\ \text{GJ/ha} \quad [28]$$

Remark 8. The output of the industrial CO_2-Glucose-EtOH cycle is the chemical exergy of ethanol equal to 66.8 GJ/ha-crop. This exergy can be transformed into useful work (*e.g.*, shaft work or electricity) by different devices.

For example, the efficiency of an excellent internal combustion engine is 35% (usually it is 20%)

$$W_u = 66.8 \times 0.35 = 23\ \text{GJ/ha} \quad [29]$$

For fuel cell/electric motor vehicles the efficiency of conversion of chemical exergy to shaft work is higher. Suppose that we could reform ethanol to hydrogen, and use a fuel cell with 60% efficiency (Deluga *et al.*, 2004)

$$W_u = 66.8 \times 0.60 = 40\ \text{GJ/ha} \quad [30]$$

to obtain electricity, and shaft work.

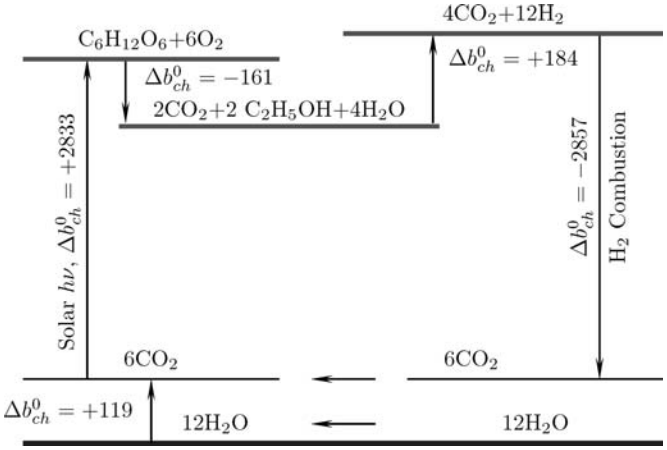

FIG. 39. Exergy diagram of the ideal CO_2-Glucose-EtOH-H_2 cycle.

8. Exergy Analysis of the Modified Ideal Corn-Ethanol Cycle

Now let us look at the useful exergy production in the modified ideal corn-ethanol-hydrogen cycle discussed by Deluga *et al.* (2004). This cycle is essentially the same as the cycle described in Eqs. (23–25). The only difference is in Step 3, which is moderately endothermic, and lowers the cycle efficiency by one percent (see Figure 39). The chemical exergies of the products of each step of the modified cycle are listed in Table 22.

Step 3, reforming ethanol to hydrogen, is a catalytic variant of water-shift reaction:

Steps 3a, b. Ethanol oxidation to CO, and then CO_2:

$$\begin{aligned} 2C_2H_5OH + 2H_2O &\rightarrow 4CO + 8H_2 \quad \mathbf{3a} \\ 4CO + 4H_2O &\rightarrow 4CO_2 + 4H_2 \quad \mathbf{3b} \end{aligned} \quad [31]$$

TABLE 22
The calculated chemical exergies of the products of steps 1–3 of the ideal corn-ethanol-hydrogen cycle

Step	Product exergy after step MJ/kmol $C_6H_{12}O_6$
1	2952.6
2	2791.4
3	2976.2
4	119.2
Net	2809.8

Net chemical exergy per kg of glucose = 15.61 MJ/kg.
Cycle efficiency = 95%.

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[47] See Remark 4. Without synthetic fertilizers, 1500 kg/ha-crop of corn would have to be used as the average yield.

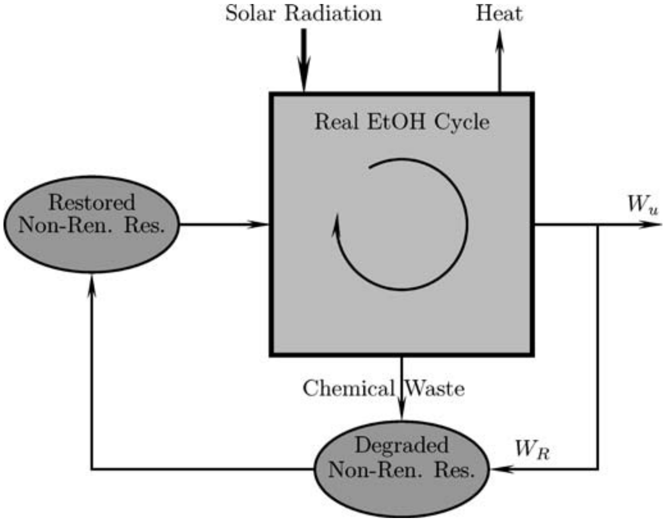

FIG. 40. A part, W_R, of the useful work, W_u, from the industrial corn-ethanol cycle is diverted to "undo" mining of the environment by this cycle. If $W_u > W_R$, there is net benefit from the ethanol biofuel, otherwise its use should be stopped.

Note that Deluga *et al.* (2004) use a somewhat different stoichiometry with $10H_2$ and $10H_2O$, but this difference is insignificant.

Remark 9. The ideal CO_2-Glucose-Ethanol-H_2 cycle discussed in Deluga *et al.* (2004) produces practically the same amount of useful chemical exergy as the ideal CO_2-Glucose-Ethanol cycle. Therefore, all conclusions pertinent to the latter hold for the former.

9. Resource Consumption and Waste Generation in the Industrial Corn-Ethanol Cycle

Now I will focus my attention on the industrial corn-ethanol cycle depicted in Figure 33. In contrast to the sun-driven ideal cycle, the industrial cycle relies heavily on fossil energy. Therefore, a part W_R of the useful work W_u, must be diverted to restore the non-renewable resources depleted by the cycle (see Figure 40). As long as the useful work exceeds the restoration work, $W_u > W_R$, the industrial corn-ethanol cycle is beneficial; otherwise it is indefensible.

Remark 10. The depletion of concentrated natural resources is *irrevocable, cf.* Part II. Without causing changes in the environment, we cannot remanufacture the depleted amounts of oil, methane, and coal in a reversible process, and put these fuels back into their deposits. Therefore, the reversible restoration work calculation provides the *lowest estimate* of the degree to which the irreversible industrial corn-ethanol cycle is also unsustainable.

From Definition 6, it follows directly that the *minimum* restoration work is equal to the sum of the cumulative exergy consumption (CExC) by all the processes that convert natural resources into inputs of the industrial corn-ethanol cycle. The specific CExC for each such input is listed in Table 23. For example, the CExC by the production of ammonium nitrate starts from natural gas in the subsurface and nitrogen in the atmosphere, and continues by summing up all the intermediate steps. Even though the chemical exergy of ammonium nitrate is only 10.51 MJ/kgN, the cumulative exergy consumption to produce it is almost 10 times larger. The CExC by electricity generation is based on the average exergy efficiency of ten large modern power stations in the United States (Gill, 1984; Termuehlen and Emsperger, 2003).

Remark 11. Currently, the fossil fuels are mined from very concentrated deposits and upgraded in very large and efficient plants. Therefore, their CExCs are relatively small. As the rich crude oil and natural gas deposits are depleted, in part to fuel extravagant and politically driven projects such as corn-ethanol in the United States, the CExC by gasoline, diesel fuel, and clean

TABLE 23
CExC of major non-renewable resources used in the industrial corn-ethanol cycle. Sources: Table 5.2 in Szargut *et al.* (1988), and calculations by the author

NRR	Exergy	CExC	Units	Comments
Ammonium Nitrate	10.51	99.6	MJ/kgN	30-years-old technology
Phosphate	0.1	10.1	MJ/kg P_2O_5	H_2SO_4 CExC
KCl	0.26	6.09	MJ/kg KCl	Sylvinite ore, 1:1 K:Na
Lime	1.96	10	MJ/kg CaO	Calcinated limestone
Herbicides	261	300	MJ/kg	1.15 exergy
Seeds	104	119	MJ/kg	1.15 exergy
Electricity	3.6	11.83	MJ/kWh	Plant eff. of 34.6%
Diesel	44.4	53.2	MJ/kg	Typical value
Gasoline	48.3	57.5	MJ/kg	Mean value
Natural Gas	50.7	57.9	MJ/kg	Typical value
LPG	48.8	61.6	MJ/kg	Authothermic cracking
Steel	7.1	45.9	MJ/kg	Process ore, blast furnace

natural gas will increase dramatically. I will address this looming problem elsewhere.

The total CExC for each input is the product of the specific value in Table 23 (in MJ/kg) multiplied by the flux (in kg/ha-crop) estimated in Part I. The CExC by cleanup of the water contaminated in the industrial ethanol cycle was not yet considered, and will be discussed now.

9.1. Cleanup of BOD in Ethanol Plant Waste-Water

The CExC by the cleanup of ethanol plant waste-water is the product of the total biological oxygen demand (BOD) in the waste-water stream in kg O_2/ha-crop, and the specific CExC by BOD removal in MJ/kg O_2. As discussed in Section 6, the total BOD is

$$\begin{aligned} \text{BOD} &= 46\frac{\text{L water}}{\text{kg EtOH}} \times 0.002\frac{\text{kg O}_2}{\text{L water}} \times 2170\frac{\text{kg EtOH}}{\text{ha-crop}} \\ &= 200\frac{\text{kg O}_2}{\text{ha-crop}} \end{aligned} \qquad [32]$$

After Berthiaume *et al*. (2001), I will base the specific CExC of BOD on a survey of energy consumption in municipal waste-water treatment facilities in the Canadian province of Quebéc. According to Blais *et al*. (1995), an average electricity consumption of 4.13 kWh per kg of BOD removal was observed there.

I have used these estimates in the CO_2 emission calculations shown in Figures 35 and 36.

9.2. Cleanup of Contaminated Field Runoff Water

Analysis of the cumulative exergy consumption in the cleanup of contaminated agricultural water that

- Seeps into the aquifers, causing, for example the omnipresent nitrate contamination of groundwater in the Corn Belt (Patzek *et al*., 2004), and
- Runs off to streams, rivers, into the Mississippi River, and to the Gulf of Mexico, generating a large anoxic zone there, is the subject of future research and will not be discussed here.

The Second Law of thermodynamics puts a high price on concentrating and removing dilute contamination, especially from the subsurface. Therefore, the restoration work of cleaning up the field runoff water will be *several orders* of magnitude larger than that of the ethanol plant runoff water.

Better fertilization practices (Worrell *et al*., 1995) and artificial wetlands (Horne, 1991, 1994; Horne and Gregg, 1993; Horne *et al*., 1994) around the corn fields could significantly help in containing and removing the pervasive contamination these fields generate.

9.3. Restoration Work

Now we are ready to estimate the restoration work of the non-renewable resources mined by the industrial corn-ethanol cycle. The results for each major input are shown in Figure 41. The three main sources of exergy consumption are ethanol plant fuel, nitrogen fertilizer, and the removal of biological oxygen demand in the ethanol plant wastewater. Note that I have not

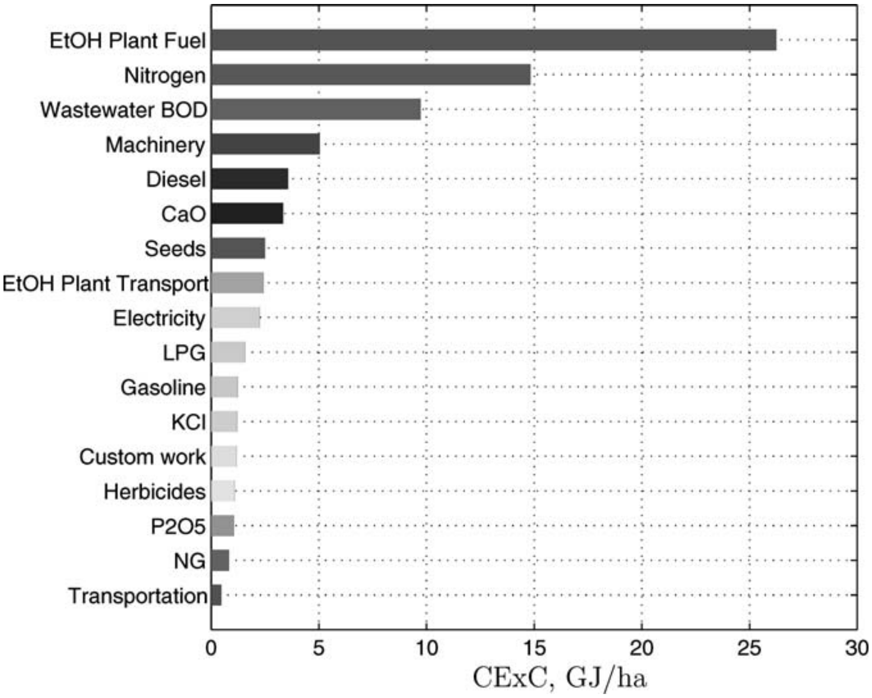

FIG. 41. The specific cumulative exergy consumption (CExC) by each major nonrenewable resource input to the industrial corn-ethanol cycle.

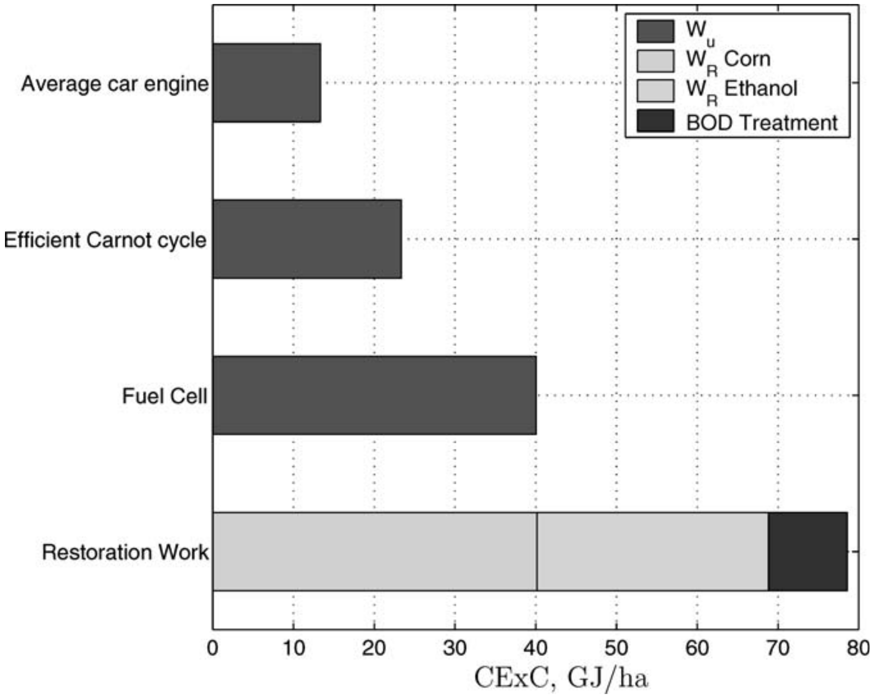

FIG. 42. The minimum cumulative exergy consumption by the industrial corn-ethanol cycle and its maximum useful work, W_u. For comparison, the cycle's ethanol is burned in an average car engine, an efficient Carnot engine, and in an ideal fuel cell. This comparison demonstrates that the industrial corn-ethanol cycle is unsustainable by a factor of 100–600%. It seems no adjustment of process parameters will change this terrible situation.

yet included the potentially huge restoration work of the High Plains aquifer (which underlies many of the Corn Belt states), other aquifers, the numerous streams and rivers which drain the field waste-water, the Mississippi River, and the Gulf of Mexico at the Mississippi River mouth.

The bottom-line comparison is shown in Figure 42. Here I compare the as yet incomplete cumulative exergy consumption by the industrial corn-ethanol cycle with the cycle's maximum useful work performed by three different machines. This comparison reveals that the corn-ethanol cycle consumes 100–600% more exergy than it replaces.

The lowest deficiency of the cycle, by a factor of 100%, is realized by employing a 60%-efficient, ideal fuel cell to power a car. Such a cell is 2–3 orders more expensive than a car engine, 10 times less reliable, and may never be mass-produced (Keith and Farrell, 2003; Dresselhaus *et al*., 2003; Bossel *et al*., 2003; Davis *et al*., 2002). A 35%-efficient Carnot engine produces 3 times less useful work than the restoration work, and today's average car engine produces 6 times less work.

Remark 12. No matter how efficient the engine is that transforms the industrial corn-ethanol cycle's output into shaft work, the cycle remains utterly unsustainable and unattractive as a source of fossil fuel.

10. Conclusions

- Excluding the restoration work of decontaminating aquifers, rivers, and the Gulf of Mexico, the *minimum* cumulative exergy consumption in restoring the environment polluted and depleted by the industrial corn-ethanol cycle is over 6 times higher than the *maximum* shaft work of a car engine burning the cycle's ethanol.
- This unfavorable ratio decreases to ∼3, when an efficient Carnot engine is used to burn the ethanol, and to 2 when a hydrogen fuel cell is used.
- The industrial corn cycle is not renewable, and is *unsustainable* by a wide margin (at least 100–600%).
- No process changes can make this cycle more viable.
- The annual corn-ethanol biofuel production is a human assault on geologic processes and the geologic time scale, and it can *never* work.
- The *limiting factors*, nutrient-rich humus and water that carries the dissolved nutrients to plant roots are augmented by chemicals obtained in the linear irreversible fossil fuel–based processes.
- Over the last fifty years, corn yield has grown five-fold, mostly because of the steep increase in fertilization rate of corn fields.
- Sunlight is *not* a limiting factor, and could be used to great benefit if we were in less of a hurry, *cf.* Appendix C.

PART IV: OTHER PROBLEMS WITH CORN-ETHANOL

1. Introduction

The results obtained in Parts I and III can now be used to estimate the annual subsidies of the U.S. corn-ethanol biofuel. These subsidies fall into two categories: (1) the monetary subsidies by the U.S. federal government and state governments to corn and ethanol producers, and (2) the non-monetary contributions of the U.S. population and environment polluted and mined by the industrial corn-ethanol cycle.

The first type of subsidy is easy to estimate:

- The U.S. pays its corn farmers \$10 billion a year in subsidies[48] (18% of corn acreage in now devoted to ethanol).
- The federal excise taxes per gallon of fuel:[49] \$0.184 for gasoline and \$0.132 for EtOH-10 (10 vol% ethanol).
- Relative to gasoline, the federal tax breaks per 1 gallon of ethanol are

$$10 \times (\$0.184 - \$0.132) = \$0.52$$

- The state excise taxes per gallon of fuel vary widely and their volume-weighted average is difficult to estimate:
  - Gasoline \$0.075 in Georgia, up to \$0.36 in Connecticut
  - EtOH-10 \$0 in Arizona, up to \$0.2535 in West Virginia
  - Minnesota offers a \$0.20 tax subsidy on EtOH-10. The state's 13 ethanol plants have received up to \$3 million a year.[50]
- I will assume that the average state subsidy is only \$0.10/gallon of ethanol. It is likely that the state subsidies of corn growers, ethanol producers, and EtOH-10 excise tax breaks are several times higher than my estimate.

The second type of subsidy can only be estimated by comparing the maximum useful output of the corn-ethanol cycle with the minimum restoration work necessary to undo the cycle's negative impact on the environment.

2. First-Law View of Corn-Ethanol Production in 2004

In February 2004, the U.S. ethanol industry set an all-time monthly production record of 212,000 barrels per day (b/d) (12.3 GL/year), according to data released by the U.S. Energy Information Administration (EIA), the Renewable Fuels Association (RFA) reported. The previous all-time record was 211,000 b/d in the previous month. Production was up 25 percent compared to last February when 169,000 b/d (9.8 GL/year) of ethanol were produced.

"U.S. ethanol producers are doing everything they can to add much needed volume and octane to the U.S. gasoline market, thereby helping to hold down gasoline prices," said RFA president Bob Dinneen. The ethanol industry is expected to produce more than 3.3 billion gallons in 2004, up from 2.81 billion gallons in 2003. Currently, 75 ethanol plants have the capacity to produce more than 3.2 billion gallons annually. *Thirteen* additional plants under construction will add 500 million gallons of annual production capacity, RFA said.

TABLE 24

The First Law summary of U.S. corn-ethanol production in 2004

12.28 GL/yr	of ethanol produced in the U.S.
9.21 GL GE/yr	as ethanol produced in the U.S.
9.25 GL GE/yr	burned to produce this ethanol
1.2%	of U.S. automobile fuel from ethanol
4.9 million hectares	of U.S. land growing corn for ethanol
17.7%	of all U.S. corn is farmed for ethanol
40.4 million hectares	for 10% U.S. automobile fuel energy
\$1.69 billion/yr	in federal subsidies for ethanol
\$0.32 billion/yr	in average state subsidies for ethanol
\$1.77 billion/yr	in corn-for-ethanol price subsidies
\$3.78 billion/yr	in total ethanol subsidies

GL = Giga Liter = 10^9 L; GE = Gasoline Equivalent.

The highlights of the annualized U.S. corn-ethanol production based on the February 2004 data are listed in Table 24. Note that the 12.3 GL/yr of corn-ethanol replace only 9.2 GL/yr of gasoline equivalent (GE), and require 9.3 GL/yr of GE to produce. Corn-ethanol brings *no* energy savings and *no* lessening of the U.S. energy dependency on foreign crude oil, natural gas, and liquified petroleum gas. The opposite happens; we import more methane, LPG, and crude oil. We then burn these fuels to produce corn-ethanol and, finally, we burn the ethanol in our cars, causing extensive environmental damage at each stage of the industrial corn-ethanol cycle. Also note that the ethanol and corn tax-subsidies projected for 2004 will be 12 times higher than the total political contributions of Agribusiness over the last 14 years.[51]

3. Second-Law View of Corn-Ethanol Production in 2004

Second Law exergy analysis brings into the picture the significant contribution of the environment to corporate profits. Depending on which thermodynamic device transforms the chemical exergy of corn-ethanol into useful work, the difference between the minimum restoration work and the maximum useful work by the cycle will vary. This difference in GJ/ha can be translated roughly into \$/ha, and into the cumulative environmental cost of the industrial corn-ethanol cycle. The hidden cost of mining the environment by the industrial corn-ethanol

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[48] Corn subsidies, OXFAM.

[49] Excise Taxes, Reuters, Washington, November 15, 2003.

[50] Cat Lazaroff—ENS, October 3, 2002.

[51] According to the Center for Responsive Politics, http://www.opensecrets.org/industries/indus.asp?Ind=A, between 1990 and mid-2004, Agribusiness paid \$320,901,260 to elected officials, 31% to Democrats and 69% to Republicans. The peak donations occurred in the 2000 and 2002 election cycles, exceeding 59 and 54 million dollars, respectively.

TABLE 25
The Second Law summary of the U.S. corn-ethanol production in 2004

\$1.84 billion/yr	Subsidy by the environment with 20% efficient car engine
\$1.56 billion/yr	Subsidy by the environment with 35% efficient car engine
\$1.09 billion/yr	Subsidy by the environment with 60% efficient car engine
\$15.07 billion/yr	10% of U.S. fuel consumption with 20% efficient car engine
\$12.75 billion/yr	10% of U.S. fuel consumption with 35% efficient car engine
\$8.90 billion/yr	10% of U.S. fuel consumption with 60% efficient car engine

cycle is real, but rarely mentioned. According to RFA president Bob Dinneen, ethanol displaces imported crude oil. Therefore, to arrive at an estimate of corn-ethanol's environmental costs, I assume that the total exergy deficit will be "paid" with the imported crude oil, whose price in the first half of 2004 was close to \$35/barrel. I also assume that 1 barrel of oil is 136 kg of 35° API oil, with the specific energy content of 45 MJ/kg. The results are listed in Table 25.

In 2004, the environment will contribute an estimated 2 billion dollars per year by being continuously and irrevocably damaged and depleted. This huge gift to the corporate coffers from the U.S. rural population, soil, water, air, plants, and wildlife is as real as the federal tax subsidies. The 60%-efficient fuel cell car does not exist now, and may never exist. But even if in the next 20 years we were to replace all existing cars with efficient fuel cell cars, the environment's contribution would still be \$1 billion per year. If 10% of fuel consumption in the United States were supplied by corn-ethanol, the annual contribution from the environment would be \$15 billion.

Again, my current estimate should be viewed as the *lowest* bound on the environmental costs for two reasons: (1) The true restoration work is irreversible and significantly larger than the reversible restoration work, and (2) I have not yet calculated the minimum reversible work of restoring surface and ground water, and soil contaminated by the corn field runoff water.

All the subsidies to corn growers, ethanol producers, and distributors are compared in Figure 43.

4. Public Health Problems

The stated goal of adding ethanol from corn to gasoline was to help in cleaning the air we breathe and lessen the U.S. dependence on foreign oil. The opposite is achieved. Air becomes more polluted, and as much oil and more methane are burned as without the corn-ethanol. At the same time, additional health hazards are created by the agricultural chemicals, fertilizers, insecticides, and herbicides, and by the waste-water streams.

For example, in 2002, 12 Minnesota ethanol plants agreed to spend \$2 million per plant, pay penalties of \$29,000–\$39,000,

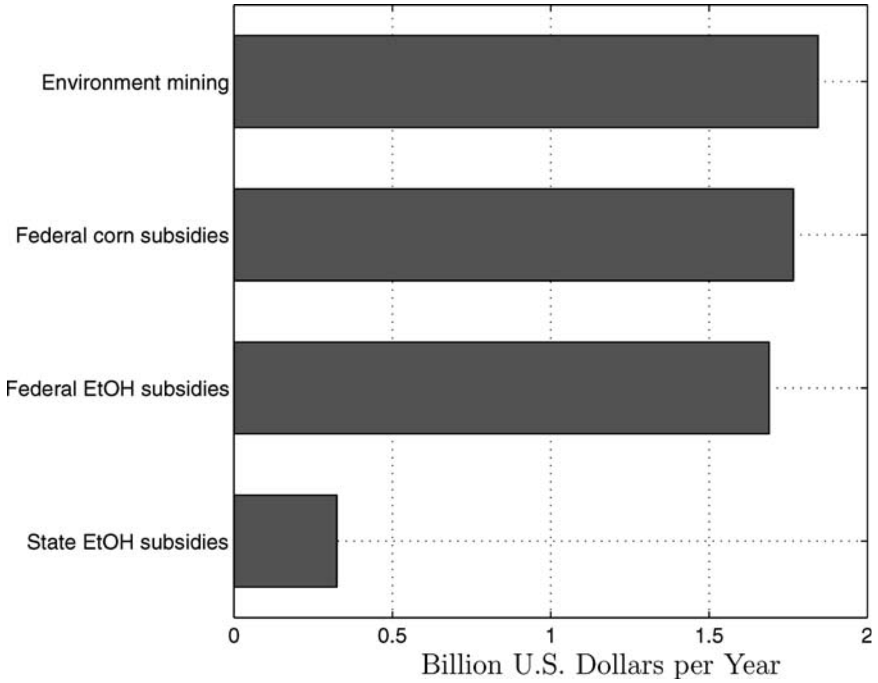

FIG. 43. The U.S. environment and taxpayers subsidize corn growers and ethanol producers. The U.S. rural population, soil, water, air, plants, fish, and wildlife pay the most.

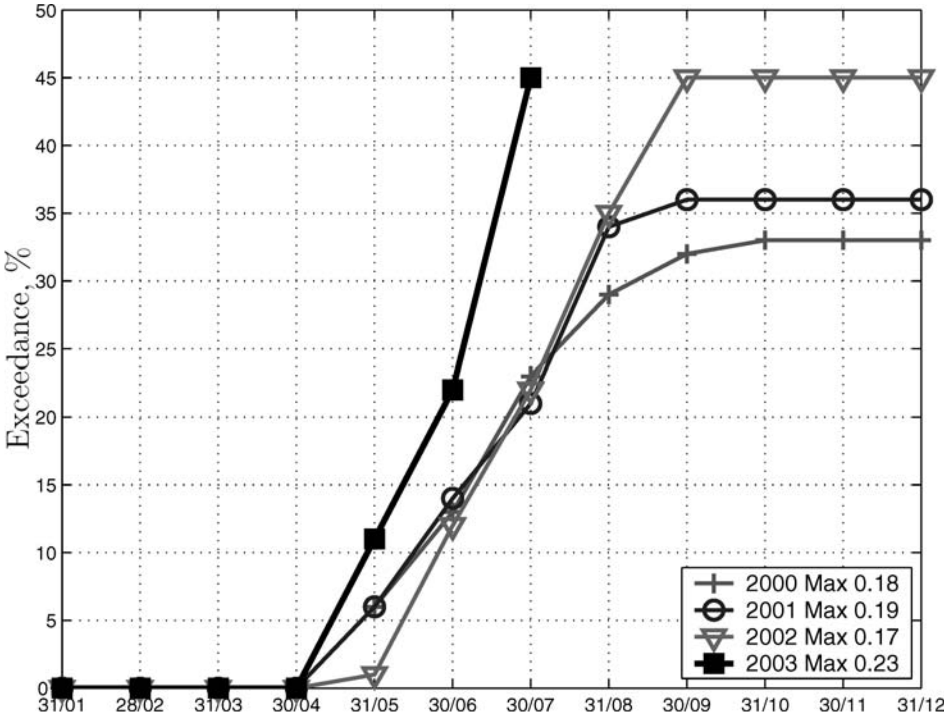

FIG. 44. The cumulative one-hour exceedances of maximum legal ozone level in Southern California. Source: Cal Hodge, President of A 2nd Opinion, Inc.

and limit the following air emissions:[52]

- Volatile organic compounds by 2400–4000 tons per year,
- Carbon monoxide emissions by 2000 tons per year,
- Nitrogen oxides emissions by 180 tons per year,
- Particulate matter by 450 tons per year,
- Other hazardous air pollutants by 250 tons per year.

Ethanol-in-gasoline seriously pollutes the air (Hodge, 2002). The reactivity of the combined exhaust and evaporative emissions using the ethanol-blended reformulated gasoline is estimated to be about 17% larger than those using the MTBE-blended reformulated gasoline (NRC, 1999). Ethanol does reduce the carbon monoxide emissions, but increases those of nitrogen oxides (NO_x), acetaldehyde, and peroxy-acetyl-nitrate (PAN) (Rice *et al*., 1999). The negative effects of using gasoline-ethanol blends are clearly seen in Southern California, where ozone levels in the air exceeded the one-hour legal limits more often (see Figure 44). By 2003, over 70% of gasoline produced in Southern California was blended with ethanol.

PART V: CONCLUSIONS

The purpose of this article was to prove beyond any reasonable doubt that the industrial corn-ethanol cycle accelerates the *irrevocable* depletion of natural resources: fossil fuels, minerals, top soil, surface and subsurface water, and air, while creating widespread environmental damage throughout the continental United States. My arguments relied entirely on the First and Second Law of thermodynamics, and on the Law of Mass Conservation.

I have tried to avoid political questions, but at some point one should ask how it was possible for a poor agri-industrial technology to grow so explosively in the last four years? The only plausible answer lies in politics. The recent growth of ethanol production could occur only because of the massive transfer of money from the collective pocket of the U.S. taxpayers to the transnational agricultural cartel, represented most notably by Archer Daniel Midlands Co., Cargill Inc., Monsanto Co., and A. E. Stanley Manufacturing Co. This flow of billions of dollars from the pockets of the many to the pockets of the few was accomplished by federal subsidies of corn producers, and the federal and state tax subsidies of ethanol producers. It was spearheaded by many powerful, and I would like to think, thoroughly misinformed politicians.

More ominously, as a country, we have diverted our collective attention from the most important issue of this century: energy conservation and increased reliance on the *only* renewable source of energy, the sun, and its weak derivative, the wind (see Appendix C). Instead, we have somewhat *accelerated* the rate of depletion of the precious natural gas and crude oil deposits in exchange for the significantly more widespread pollution of water, soil, and air over roughly 1/2 of the area of the United States, the incremental carbon dioxide emissions, the substandard ethanol fuel, and the continuous drain of taxpayers' money.

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[52] Cat Lazaroff—ENS, October 3, 2002.

To make things worse, the scientific community in the United States seems to be preoccupied with promulgating empty illusions of a future global energy bliss brought about by the new and sexy, but inherently unsustainable technologies. The ethanol biofuel for hydrogen (Deluga *et al.*, 2004), the fossil fuel-based "hydrogen economy" (Devis *et al.*, 2002; Bossel *et al.*, 2003; Dresselhaus *et al.*, 2003; Keith and Farrell, 2003; Tromp *et al.*, 2003; DOE, 2003), the subsurface carbon dioxide sequestration (Celia, 2002), and so on, come to mind. I suggest that we—the scientists—should instead be advocating the simpler and less expensive, but painful, real solutions of the overwhelming energy problems facing the world. These solutions must involve far more energy conservation in every aspect of the U.S. economy, and the significantly increased reliance on the sun.

The philosophical, ethical, and political arguments ought to be developed further, but I will leave this task to the others, see for example, the transcript of an excellent speech by Nicholas E. Hollis, *Ethics and Agribusiness—In Search of the New Food Security*, given in Newcastle-on-Tyne, United Kingdom, March 15, 2004. Here I will only reiterate the following:

1. The industrial corn-ethanol cycle brings *no* energy savings and *no* lessening of the U.S. energy dependency on foreign crude oil, natural gas, and liquified petroleum gas. The opposite happens: (a) we import somewhat more methane, LPG, and crude oil; (b) we burn these fossil fuels to produce corn and ethanol; and (c) we burn the corn ethanol in car engines. All three steps of this cycle increase the extent of environmental damage beyond that caused by burning the same fossil fuels directly in the cars.
2. The industrial corn-ethanol cycle generates more carbon-dioxide equivalents than would be generated by the energy-equivalent quantity of gasoline or diesel fuel penalized by 15% to account for the cumulative use of free energy in their production. Currently these incremental emissions are about 8 million tons of equivalent CO_2 per year.
3. The taxpayers' subsidies of the industrial corn-ethanol cycle are estimated at \$3.8 billion in 2004. The parallel subsidies by the U.S. environment are estimated at \$1.8 billion in 2004. The latter estimate will increase manifold when the restoration costs of aquifers, streams and rivers, and the Gulf of Mexico are also included.
4. The rate of sequestration of the unlimited solar energy as organic plant matter is controlled by the availability of water in soil and the minerals dissolved in this water. For the reasons explained in this article, water and soil nutrients are finite, easily degradable, and must be replenished by decomposing all corn plant leftovers, including the by-products of ethanol production.
5. The mass balance of starch in dry corn grain sets the theoretical efficiency of conversion of corn to ethanol to 0.337 kg EtOH/kg dry grain (0.423 L EtOH/kg dry grain), or to 2.85 gallons EtOH/dry bushel = 2.42 gallons EtOH/equivalent bushel of corn with 15% moisture. Therefore, the USDA estimate of the conversion efficiency, 2.66 gallons EtOH/bushel, must be applied to *dry* corn, and not to corn with 15% of moisture.
6. In general, the USDA estimate of 2.66 gallons EtOH/bushel has been multiplied by the moist corn grain yield; this is *incorrect* and leads to an overestimation of the corn-ethanol yield.
7. If used correctly, the USDA estimate is 93% of the theoretical efficiency of corn conversion into ethanol. I have used an 88% efficiency.
8. *All* considered analyses of the fossil energy inputs into the industrial corn-ethanol cycle (Wang *et al.*, 1997; Shapouri *et al.*, 2002; Pimentel, 2003; Berthiaume *et al.*, 2001; Patzek *et al.*, 2004) have been corrected and/or amended. All the changes to these inputs have been detailed in Part I.
9. With the corrected estimates of the fossil fuel inputs to corn farming and ethanol production, presented in Part I, *all* published estimates predict that production of corn-ethanol is a fossil energy-loosing proposition (see Figure 16).
10. In view of Conclusion 4, the robust ~30% energy credits for ethanol production used in Wang *et al.* (1997) and Shapouri *et al.* (2002) are indefensible. In Part II, the Second Law analysis of the industrial corn-ethanol cycle reaffirms this conclusion.
11. The mere energy balance of the industrial corn-ethanol cycle does not take into account the cumulative consumption of the non-fossil environmental resources: soil, water, air, and minerals, and provides an incomplete picture of this cycle.
12. Because all the published First Law balances of the industrial corn-ethanol cycle are by definition incomplete, their comparison has led to different interpretations, and endless acrimonious debate (see *e.g.*, Patzek *et al.*, 2004), which served little useful purpose. Worse yet, this debate has diverted our collective attention from the real problems with corn-ethanol and provided cover for the ethanol lobby.
13. Only when the Second Law of thermodynamics and the concept of available free energy, or *exergy*, are introduced (Parts II and III, Appendix A and B), a definitive analysis of the industrial corn-ethanol cycle is possible.
14. In the Second Law analysis, the *environment* is defined as anything but the top soil of the corn field, the corn plants, the ethanol-producing plants, and the devices that process the ethanol (internal combustion engines and fuel cells). The environment, therefore, is the sun, water, air, nutrients, crude oil, methane, coal, electricity, field chemicals, roads, trucks, and so on, and the cold universe to which the heat generated by the cycle's ethanol is rejected. Thus, the environment defined here *cannot* be dismissed summarily as the raving of a green lunatic.

15. From the definitions of *irreversibility* and *sustainability* (Part II, Appendix A and B), it follows clearly that the industrial corn-ethanol cycle, which relies heavily on mining the environment, is irrevocable and unsustainable. The common references to the cycle sustainability (see, *e.g.*, Deluga *et al.*, 2004), are scientifically indefensible.
16. In view of Conclusion 4, the recently advertised ethanol production from "agricultural waste," that is from plant leaves, stems, and roots is even more unsustainable.
17. Because the industrial corn-ethanol cycle is irrevocable, the precious natural resources wasted by it disappear forever from the earth, and diminish the well-being of future generations.
18. The free energy available on the earth (exergy) is consumed by the industrial corn-ethanol cycle. The cumulative net consumption of the exergy is a good quantitative indicator of the degree of unsustainability of this cycle.
19. The maximum useful free energy generated by the industrial cycle, 67 GJ/ha as corn-ethanol, produces useful shaft work, electricity, or both.
20. When an average car engine (20% efficiency) burns corn-ethanol, it produces 13.4 GJ/ha of useful work. A very efficient car engine (35% efficiency) produces 23 GJ/ha of useful work. An ideal fuel cell/electric motor car with 60% efficiency, produces 40 GJ/ha of useful work.
21. The *maximum* useful work from the industrial corn-ethanol cycle has been compared with the *minimum* reversible work required to undo the environmental damage caused by this cycle. Of course, this environmental damage cannot be undone in reality, and the minimum reversible restoration work is only a *tool* used to quantify the damage.
22. The cumulative exergy consumption in performing the minimum reversible work of "undoing" the industrial corn-ethanol cycle, exceeds by a factor 6, 3 and 2, respectively, the maximum useful work from a 20% efficient car engine, 35% efficient car engine, and 60% efficient fuel cell car.
23. No process change can improve the very unfavorable ratio of benefits from the industrial corn-ethanol cycle to its environmental costs, and I have not yet included the exponentially growing costs of restoring surface and ground water, and soil contaminated by the fertilizer-, pesticide-, and insecticide-rich runoff from the corn fields.
24. More attention should be devoted to harvesting the only renewable source of energy on the earth: sunlight. An inefficient solar cell that continuously operates at moderate latitude produces ∼100 times more electricity than a corn-ethanol–burning fuel cell (see Appendix C). Somewhat better, more durable, and cheaper solar cells that are distributed world-wide would dramatically

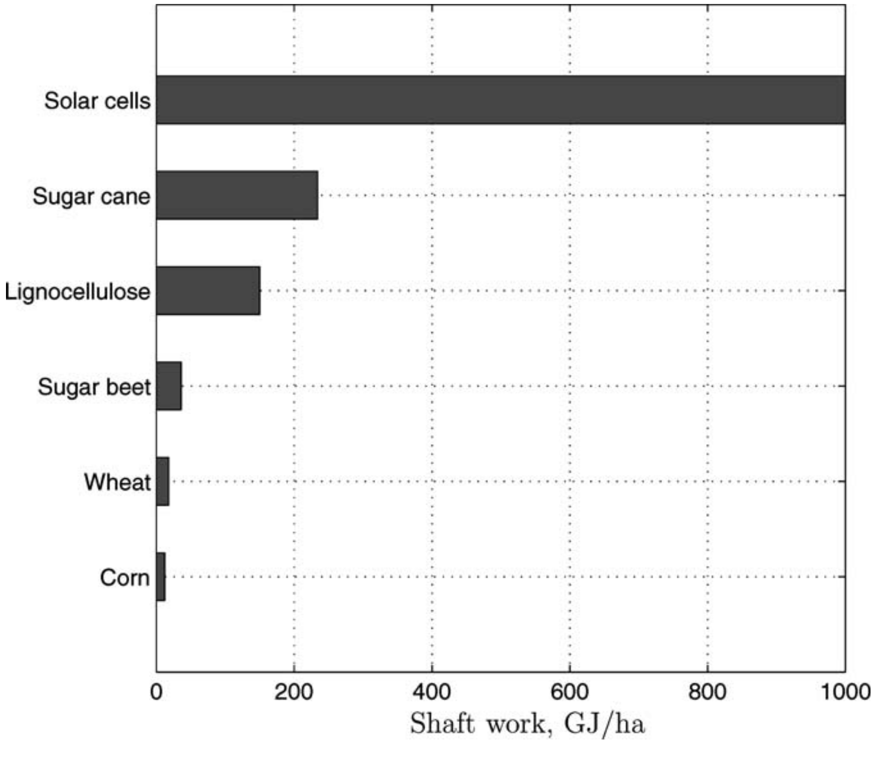

FIG. 45. Shaft work obtained in 120 days from the solar cells on 1 ha dwarfs that from the ethanol produced from all major biofuels. The *maximum* ethanol biofuel energy yields are from Table 7, p. 28, in Hamelinck' Ph.D. thesis (2004). The conversion efficiency from ethanol to electrical shaft work is an optimistic 0.6. The *minimum* solar cell yield follows the assumptions in this appendix. Note that annually the solar cells produce ∼100 times more electricity than corn ethanol.

increase the chances of long-term survival of our civilization.

25. One hectare of solar cells placed anywhere can free 100 hectares of fertile agricultural land from industrial corn, and allow for the low-intensity, diversified, and almost sustainable agriculture.

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APPENDIX A: EXAMPLES OF ENTROPY PRODUCTION AND DISPOSAL

The Rate of Entropy Export by the Earth

In the simplest model, the earth is in thermal equilibrium; continuously heated by the sun's radiation, and cooled by the infrared radiation into the universe.

The *solar constant* is the power collected at the top of the earth atmosphere by a unit area (1 m^2) perpendicular to the light path. This power is remarkably constant (see *e.g.*, Hickey *et al.*, 1980), and equal to $\dot{q} = 1370$ Watts[53] per square meter (W/m^2). The projection of the sun-lit earth hemisphere in the direction perpendicular to the sun light is πr_e^2, where $r_e = 6371$ km is the mean volumetric earth radius, or 1/2 of the hemisphere area, and 1/4 of the earth surface area ($A_e \approx 510 \times 10^6$ km^2).

The Planck temperature of the sun's radiation is $T_s \approx 5700$ K, and the Planck temperature at which the earth radiates its heat is $T_e \approx 254$ K.[54] The earth reflects about 30% of the sun radiation, so its surface is reached by only 0.7 of the solar energy. Therefore, the time-averaged flux of entropy exported by the earth into the universe is

$$j_S^E = \frac{\Delta \dot{S}}{4\pi r_e^2} = \frac{4}{3} 0.7 \dot{q} \frac{1}{4} \left(\frac{1}{T_e} - \frac{1}{T_s} \right) = 1.20 \text{ W/K} - \text{m}^2 \qquad [33]$$

where the factor 4/3 comes from the Stefan-Boltzmann law.[55] This estimate agrees very well with the $j_S^E = 1.2$ W/K-m^2 reported by Prof. Arne Stahl (1996).

The Simplest Climate Model

The earth is in thermal equilibrium:

Rate of energy input from the sun = Rate of energy radiation by the earth

$$\dot{E}_{\text{in}} = \dot{E}_{\text{out}} = P = \text{const} \qquad [34]$$

Similarly to Frondel, Oertel and Rübbelke (2002), I assume that the earth's atmosphere is a heat-transporting[56] gas layer. The surface temperature of the earth is T_0 and the Planck temperature of its radiation is T_e. The stationary heat flow through the atmosphere occurs at a constant rate:

$$P = kA_e(T_0 - T_e) \qquad [35]$$

where A_e is the surface area of the earth. In this simple model, the steady-state rate of energy export from the earth depends on the mean temperature difference between the earth surface and the uppermost atmosphere. The overall heat transfer coefficient, k, depends on how effectively the atmosphere transports heat. With the increasing concentration of heat absorbers (the greenhouse gases) this coefficient decreases, and the earth temperature must go up.

At steady state, the Second Law of thermodynamics requires the entropy flow rate to satisfy the following equation:

$$P = T_0 \dot{S}_0 = T_e \dot{S}_e \qquad [36]$$

where $\dot{S}_0$ is the rate of entropy change near the earth surface, and $\dot{S}_e$ is the rate of entropy change at the outer layers of the atmosphere. Therefore, the net rate of entropy generation in the atmosphere due to energy transport is

$$\dot{S}_t = P \left(\frac{1}{T_e} - \frac{1}{T_0} \right) > 0 \qquad [37]$$

Because both P and T_e are constant, it follows that as the temperature of the earth surface increases, so does the rate of entropy generation in the atmosphere. This *positive feedback* effect, or *domino effect*, will intensify the impact of human entropy production on the earth climate. The rate of entropy generation in the atmosphere per unit surface area of the earth defines the specific atmospheric entropy generation rate:

$$\sigma_t = \frac{\dot{S}_t}{A_e} \qquad [38]$$

With the numbers used in Eq. (33), this specific rate is equal to 0.11 W/K-m^2, not bad for such a simplistic model. For comparison, Stahl (1996) reports 0.2 W/K-m^2.

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[53] 1 Watt = 1 Joule/second.

[54] The actual temperature of the earth surface is about 34 K higher due to the greenhouse effect. Therefore there is entropy generation in the atmosphere; see the next section.

[55] See Szargut *et al.*'s one-of-a-kind monograph (1988), page 72, Eq. (2.53).

[56] Heat transport through the atmosphere proceeds through turbulent convection and mixing, water evaporation and condensation, thermal conduction, and radiation.

Entropy Generated by a Human

A sedentary human needs about 2400 kcal per day in food to live and work a little. This food consumption translates roughly into an average sustained power of $\dot{Q} = 100$ W, that is, one man = one 100 W bulb shining infrared light for 24 hours a day. This power is dissipated through work, thermal convection, radiation, excrements, and so on, and appears as heat at the ambient temperature $T_0 = 273 + 15 = 288$ K. Thus the entropy generation rate is

$$\dot{S} = \frac{\dot{Q}}{T_0} = 0.35 \text{ W/K} \qquad [39]$$

per person. At 3500 kcal per day, a quantity more representative of the U.S. feeding habits, the rate of entropy generation by one person is $\dot{S} = 0.5$ W/K, in agreement with Stahl (1996). This means, that if one crowds 2–3 people per square meter, they will generate more entropy than the earth can export.

Entropy Generated By Fossil Fuels

In the year 2000, the United States burned 83 quads (1 quad = 1 quadrillion or 10^{15} BTU[57]) in fossil energy and 2.9 quads in wood, alcohol, and so on. For simplicity, I will treat all this energy as the source of heat rejected[58] into the earth environment at the mean ambient temperature of $T_0 = 288$ K. The U.S. population was $N = 282$ million people in 2000. Therefore, in A.D. 2000, the per capita thermal entropy generation rate in the United States was

$$\dot{S} = \frac{\dot{Q}}{T_0 N} = \frac{(83 + 2.9) \times 10^{15} \times 1055/365/24/3600}{288 \times 282 \times 10^6}$$
$$= 36 \text{ W/K-person} \qquad [40]$$

My estimate of the per capita thermal entropy generation rate in the United States is somewhat higher than the 35 W/K-person calculated by Stahl (1996).

In the year 2000, the United States emitted about 1.65×10^{12} kg of carbon dioxide by burning fossil fuels (Marland *et al.*, 2004) (1/4 of the global carbon dioxide emissions). The standard molar entropy of carbon dioxide is 213.8 kJ/kmol-K. Therefore, the per capita U.S. rate of generation of chemical entropy of carbon dioxide in the atmosphere:

$$\dot{S}_{\text{chem}} = \frac{1.65 \times 10^{12} \times 213.8 \times 10^3}{44 \times 365 \times 24 \times 3600 \times 282 \times 10^6}$$
$$= 0.9 \text{ W/K-person} \qquad [41]$$

is much smaller than the corresponding thermal entropy rate in Eq. (40). Unfortunately, this chemical entropy cannot be exported to the universe, and thus accumulates on the earth.

The whole world produced 400 quads of energy in the year 2000, therefore the United States used roughly 1/4 of it. The per capita entropy rate for the whole world excluding the United States was 6 W/K-person, or 1/6 of the U.S. rate. This means that where it really counts, in entropy generation rate, the U.S. society is *six times as wasteful* as the world at large, including Europe and Japan.

The U.S. thermal entropy generation rate may also be expressed per unit surface area of the country (9,629,100 km^2), resulting in the specific anthropogenic entropy rate $\sigma + \sigma_a = 0.001$ W/K-m^2, or 0.1% of the net entropy flux exported from the earth. Of course, most of this entropy is generated on a small fraction of the U.S. land area. If all anthropogenic entropy were generated over 0.1% of the U.S. area,[59] roughly the area of Los Angeles, it would overwhelm the entropy export capacity of the earth. This calculation omits the entropy generation rate to "restore" the environment polluted chemically by the fossil fuel by-products. Nevertheless, the anthropogenic thermal entropy generation is still very small when compared with the capacity of the earth to export entropy. The chemical entropy, in contrast, continuously accumulates on the earth. Even the transport entropy in the atmosphere is generated at a specific rate 100–200 times higher than the mean generation rate of anthropogenic specific entropy in the United States. Note that in his interesting paper Rübbelke (1998) made a mistake (p. 198) by claiming that the U.S. population produced entropy at the rate of 35 W/K-m^2, not 35 W/K-person as calculated by Stahl (1996). The consequences of this mistake erroneously influenced his conclusions about sustainability.

What this calculation does not show is the fast and irreversible exhaustion of the meager stock of high-quality crustal materials (low entropy) that feed our civilization with the accompanying increase of chemical entropy.

APPENDIX B: AVAILABILITY AND IRREVERSIBILITY IN THERMAL SYSTEMS

Because the earth can export entropy by infrared radiation from the outer layers of the atmosphere, in this appendix I define any thermodynamic system on the earth as interacting with the atmosphere only. The atmosphere will be treated as being in stable dynamic equilibrium, and characterized by the constant absolute temperature T_0, volume V_a, and the hydrostatic pressure, $p_0 = 1$ atm, at sea level. By including within the system as much surface land area, surface water, groundwater, minerals, material, plants, machinery, and so on,[60] as affected by the process of interest, one is always able to construct the system that interacts with the atmosphere only. For simplicity, chemical entropy generated by the system is not considered here.

Gibbs[61] showed that for any process that can occur under these circumstances the quantity defined as

$$\Phi = E + p_0 V - T_0 S \qquad [42]$$

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[57] 1 BTU = 1055 Joules of energy.

[58] In reality, a portion of the fossil energy, probably 20–30%, generates work, resulting in less heat dumped into the environment. Therefore, this analysis provides the uppermost bound on the entropy generation rate.

[59] A physical impossibility!

[60] The entire globe, if necessary.

[61] Gibbs (1994), p. 40.

decreases

$$\Delta\Phi \le 0 \qquad [43]$$

where E is the total energy of the system, V its volume, S its entropy, and the increment of Φ, $\Delta\Phi$, is taken in the direction of increasing chronological Time.

The process of interest can only occur until the system pressure is uniformly hydrostatic and its uniform temperature is T_0. Therefore, the state from which no *spontaneous* change can occur is the state in which the system has the hydrostatic pressure (p_0 at sea level) and the atmospheric temperature T_0, and for which Φ has the smallest possible value, $\Phi_{\min}$. If only one state of the system results in this minimum value, the system is in *stable equilibrium*. Otherwise, if there are several states corresponding to the minimum value of $\Phi_{\min}$, the system is in *neutral equilibrium* of maximum stability.

Gibbs[62] referred to the difference

$$\Phi - \Phi_{\min}, \qquad [44]$$

where Φ corresponds to the state in question, as the "... available energy of the body (*our system*) and the medium (*our surroundings*)."

Joseph H. Keenan (1951) later showed that for the system undergoing change from an *earlier* state 1 to a *later* state 2, the amount of useful work W_u is

$$W_u \le \Phi_1 - \Phi_2 \le \Phi_1 - \Phi_{\min} \qquad [45]$$

Therefore, for any state 1, the maximum possible useful work done by the system is $\Phi_1 - \Phi_{\min}$. Keenan proposed to call this maximum value *availability*, Λ. It may be said[63] that for any system in the stable atmosphere

$$\Lambda \ge 0 \qquad [46]$$

and that for the most stable state of the system

$$\Lambda = 0 \qquad [47]$$

From Eq. (45) it also follows that

$$\begin{aligned} \Delta\Lambda &= \Delta\Phi \\ W_u \le W_{u,\max} &= \Phi_1 - \Phi_{\min} = -\Delta\Phi = -\Delta\Lambda \end{aligned} \qquad [48]$$

Keenan also quantified the *irreversibility*,[64] I, of a process executed by the system-atmosphere combination:

$$\begin{aligned} I &= W_{u,\max} - W_u \\ &= -\Delta\Phi - W_u \\ &= -\Delta\Lambda - W_u \end{aligned} \qquad [49]$$

and showed that

$$\begin{aligned} I &= T_0\Delta S + \Delta E_a + p_0\Delta V_a \\ &= T_0\Delta(S_a + S) \end{aligned} \qquad [50]$$

Of course, Keenan's irreversibility was discovered much earlier and independently by Gouy (1889) and Stodola (1898; 1927).[65] Regardless, the irreversibility of a process is equal to the increase of entropy of everything involved in the process multiplied by the temperature of the atmosphere.

One may use Eq. (50) in the differential form, and per unit area of the earth surface, by writing

$$\begin{aligned} \frac{1}{A_e}\frac{\mathrm{d}I}{\mathrm{d}t} &= T_0\left(\frac{1}{A_e}\frac{\mathrm{d}S_a}{\mathrm{d}t} + \frac{1}{A_e}\frac{\mathrm{d}S}{\mathrm{d}t}\right) \\ \sigma_I &= T_0(\sigma_a + \sigma) \end{aligned} \qquad [51]$$

where σ_I is the specific rate of irreversibility, σ_a is the specific rate of entropy increase in the atmosphere generated by the process, and σ is the specific rate of entropy increase of the system. Note that as the atmospheric temperature increases, so does the irreversibility of any process on the earth.

From Appendix A it follows that we can treat the atmosphere as an open system that exports entropy to the universe with the flux j_S^E calculated from Eq. (33). The energy transport through the atmosphere generates entropy at the specific rate of σ_t calculated from Eq. (38). Thus, we may rewrite Eq. (51) as

$$\sigma_I^{\text{net}}/T_0 = \underbrace{(\sigma_a + \sigma)}_{\substack{\text{Thermal entropy from} \\ \text{Earth processes}}} + \underbrace{(-j_S^E + \sigma_t)}_{\substack{\text{Thermal entropy from} \\ \text{Solar processes}}} \qquad [52]$$

Using Eq. (52), we can define sustainability as

$$\begin{aligned} &\sigma_I^{net} \le 0 \\ &\sigma_a + \sigma - j_S^E + \sigma_t \le 0 \\ &\text{For all places on the earth, and at all times} \end{aligned} \qquad [53]$$

For *sustainability*, Eq. (53) requires that the net rate of increase of entropy of everything at every place on the earth and for all times be less than or equal to zero! Note that the process and energy transport increase the entropy of the earth and the atmosphere, and low-temperature heat radiation decreases it.

Remark 13. As derived, Eq. (53) is quite deceiving. The anthropogenic part of the thermal entropy generation rates, $\sigma + \sigma_a$, can only be sustainable if this entropy is generated in cycles in which all process materials are completely recycled, and all chemical entropy is transformed into thermal entropy. If we rely on a finite stock of fossil energy, then even if the entropy generation rate in a process is much lower than the entropy export flux, the process is *never* sustainable. Therefore, sustainability can only be discussed in the context of *cyclic processes*.

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[62] Gibbs (1994) p. 53; author's comments in italics.

[63] Keenan. (1951), Eqs. (12) and (13).

[64] keenan, (1951), Eqs. (31)–(36).

[65] In particular, Volume II of Stodola (1927), pp. 1271–1330, brings a thorough discussion of *The Highest Possible Conversion into Work on the Basis of the Second Law of Thermodynamics.*

Over an arbitrary time interval $[\tau_1, \tau_2]$, we can write the global condition of *sustainability* of all cyclic processes on the earth as

$$\underbrace{[S_a(\tau_2) - S_a(\tau_1)]}_{\substack{\text{Increase of atmospheric entropy}\\ \text{from earth processes}}} + \underbrace{[S(\tau_2) - S(\tau_1)]}_{\text{Increase of earth entropy}} - S^E(\tau_1, \tau_2) + S_t(\tau_1, \tau_2) \le 0 \qquad [54]$$

For the entire earth, and arbitrary τ_1, τ_2

where $S^E(\tau_1, \tau_2) = j_S^E A_e(\tau_2 - \tau_1)$ is the total thermal entropy exported by the earth over the time interval $[\tau_1, \tau_2]$, and $S_t(\tau_1, \tau_2) = \sigma_t A_e(\tau_2 - \tau_1)$ is the corresponding thermal entropy generated in the atmosphere by the steady-state energy transport to the universe.

APPENDIX C: IS ECONOMIC SUSTAINABILITY POSSIBLE?

It has already been demonstrated that anything sustainable on the earth must involve a closed material loop (a cycle) that is driven by the sun. Solar energy is like a fine mist: it dribbles at a constant rate on every square inch of the earth's surface. We cannot increase its flow rate, it dries up overnight, and we cannot store it easily. So one may ask legitimately: is solar power enough to drive the world economy, and if so what constraints does it impose?

The time- and area-average solar energy flux in the U.S. is $\sim$200 W/m^2 at the earth surface. At more moderate latitudes this flux goes down to about 100–150 W/m^2, and in the tropics it can be as high as 300 W/m^2. Thirty percent of the earth's surface, 153×10^6 km^2, is land. Suppose that 1% of land mass on the earth were covered with solar cells that were 10% efficient, and received only 100 W/m^2 of solar energy. The total solar power converted by these cells to electricity would then be 1.5×10^4 gigawatts (1 GW = 10^9 W). Currently, the mean world power consumption is about 1.3×10^4 GW. Therefore, covering one percent of the earth's land with solar cells would deliver power equal to the mean world power consumption. For the United States, it would take closer to 3% of the land area, or 300,000 km^2 (the area of Poland) to replace the entire mean fossil and nuclear power.

There are problems, however, with these calculations:

1. With the necessary infrastructure, the surface area of the solar power plants would probably double or triple.
2. Large-scale manufacturing of solar cells does not exist.
3. Mass production of solar cells will generate associated chemical waste (high chemical entropy, which cannot be exported by the earth).
4. There are few big transmission lines in the hot barren areas of the world.
5. The peak power consumption in the world can be several times the mean power, and power is needed at night.
6. A significant portion of the world power (over 1/3 in the U.S.) is used by automobiles.
7. At 1 U.S. dollar per watt (1/7-1/5 of the current U.S. price), it would take 15 trillion dollars to replace most of the fossil and nuclear energy world-wide with solar cells. This amount would probably double if massive new transmission grids and the required transformers were to be built world-wide.

The first and the last item in this list suggest that decentralization of power generation is necessary. With small and micro power plants, one avoids access roads, big transformers, and long transmission lines. Covering large areas with solar cells is also impossible in the mountains and forests.

The second item requires an intensive research and development effort to weigh the solar cell efficiency and reliability versus the production costs, the use of exotic rare-earth elements, and the generation of chemical waste.

The fourth item dictates a dramatic adjustment of industrial activity: (1) Most factories would have to shut down before sunset. (2) For winter and nocturnal use, energy could be stored as hydrogen from solar-driven water electrolysis. (3) The industrial world would have to slow down, and reassess its social priorities, in sharp contrast to my introductory remarks in Part II.

Solar Cells vs. Biofuels. The superiority of solar cells over *any* biofuel can be illustrated as follows. The cumulative energy balance in Part I shows that the *unsustainable* industrial corn farming captures about 100 GJ/ha per crop that lasts, say, 120 days. The product, corn grain, is a fossil fuel that is later converted into another fossil fuel, ethanol, at a large expense of fossil energy. The ethanol yield is about 55 GJ/ha-crop, and the energy conversion efficiency of a fuel cell is 60%. Thus, corn can deliver $55 \times 0.60 = 33$ GJ/ha-crop as electricity. The fossil fuel inputs exceed the calorific value of the ethanol by about 2–20 GJ/ha-crop. In Part III, I showed that a fuel cell can deliver about 40 GJ/ha-crop as electricity from the industrial corn-ethanol cycle, but the restoration work is at least twice as large. My estimates are in line with those in the *United Nations Bioenergy Primer* (Kartha and Larson, 2000), Box 3-1, where it is estimated that 1 ha of eucalyptus trees could generate 21 GJ of electricity over 120 days by continuous wood burning.[66] During the same 120-day time interval, an inefficient solar cell that converts only 10% of only 100 W/m^2 will *sustainably* produce 1000 GJ/ha of electricity (see Figure 45). Of course, properly functioning solar cells collect sunlight all year long. Therefore, the solar cells described earlier can produce 3000 GJ/ha-yr of electricity, 100 times more than that generated by the corn ethanol-burning fuel cells. One hectare of solar cells placed anywhere can free 100 hectares of fertile agricultural land from industrial corn, and allow for the low-intensity, diversified, and almost sustainable agriculture. The socially and scientifically defensible choice is clear.[67]

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[66] The energy conversion to electricity is 22%, but no energy inputs into eucalyptus farming are given.

[67] Some, *e.g.*, Sheehan *et al.* (2004), argue that corn should be farmed continuously (with no crop rotation): the whole plants are harvested, the grain is processed for ethanol, and the rest is burned for energy. This energy supply scheme requires 2–10 times more field chemicals (see Part I), irreversibly depletes and damages the soil, and is even *more* unsustainable than a single corn crop (see Parts II and III).