

# Ethanol as an Alternative Fuel for Automobiles

## Using the First Law of Thermodynamics To Calculate the "Corn-Area-per-Car" Ratio

William J. Pietro

Department of Chemistry, York University, Toronto, ON M3J 1P3, Canada; [pietro@yorku.ca](mailto:pietro@yorku.ca)

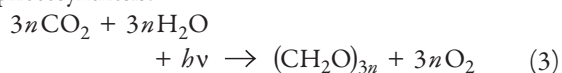
The notion of using ethanol as an alternative to gasoline in automobiles has received considerable attention in the past few years due primarily to carbon dioxide emission concerns. Indeed, a complete switch from all fossil fuels to ethanol should theoretically eliminate net carbon dioxide emission from automobiles. In North America, ethanol has been used as an additive to gasoline for decades mainly to increase the fuel's resistance to premature combustion during the engine's compression stroke. In South America, many cars are already running on E85, a by-volume mixture of 85% ethanol and 15% gasoline.

Ethanol is an attractive substitute for fossil fuels because of its potential for positive impact on greenhouse emissions and because it is generated biochemically through photosynthesis and fermentation and is therefore a completely renewable resource. Ethanol can be most effectively mass produced by the fermentation of starches or sugars (carbohydrates), products of photosynthesis in any of a number of plants such as sugar cane and corn. Although photosynthesis comprises a very complex sequence of biochemical reactions, its overall chemical equation, eq 2, is essentially the reverse of the combustion process for carbohydrate, eq 1:

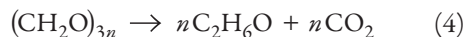


Photosynthesis is an energetically uphill process that uses the energy of sunlight. No other energy source is required to synthesize carbohydrate. Therefore, burning ethanol is literally equivalent to using solar energy. One can thus think of the plant as a solar energy converter, transforming the energy of sunlight into the potential energy stored in the chemical bonds of carbohydrate and ultimately ethanol. The overall chemical process from sun to car is illustrated below:

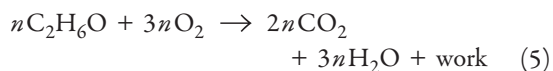
photosynthesis:



fermentation:



combustion:



Obviously, the ultimate quantity of work one will be able to derive from ethanol, or any fuel created by photosynthesis, is necessarily limited to the total photonic energy absorbed by the plant. This conclusion is a direct consequence of the first law of thermodynamics and is completely independent of what plant is used, how the ethanol is harvested, or how it is burned in the engine. Moreover, it does not even matter that ethanol is the fuel. The thermochemistry of the above cycle is straightforward, sunlight in–work out. Thus, undergraduate students can easily determine the thermodynamic feasibility of using ethanol, or any biofuel, to provide our current power requirements for automobiles. We demonstrate this through five considerations, each assigned to a team of students. This exercise has been performed with great enthusiasm by first-year chemistry students and non-science majors at this university and usually results in healthy chemistry-oriented debate on an issue of great current social importance.

### Consideration 1: Power of Sunlight

Corn grows between 30 and 45 degrees latitude. This arcs a region of the planet that includes almost all of North America (and, of course, a corresponding arc in the southern hemisphere). The average power density of sunlight reaching the surface of this region of the earth is  $240 \text{ W m}^{-2}$  (1). This is an overall average that includes the curvature of the planet, its rotation, and its yearly revolution around the sun. It does not consider weather and must therefore be regarded as a maximum average. Sunlight consists of wavelengths spanning infrared to ultraviolet; however, only the wavelength region between 400 nm and 700 nm is used by plants. This represents 43% of the solar power reaching the surface of the earth (1). Thus, the maximum power density of sunlight useful for photosynthesis is

$$(240 \text{ W m}^{-2}) 0.43 = 103 \text{ W m}^{-2}$$

Corn needs to be grown in rows to enable cross-fertilization for ear formation and therefore does not cover 100% of the available land. At best, farms can use about 80% land for the plant. Hence, the maximum solar power that can be used by the growing plants is

$$(103 \text{ W m}^{-2}) 0.80 = 82 \text{ W m}^{-2}$$

### Consideration 2: Efficiency of Photosynthesis

Photosynthesis is an extremely complex series of reactions. However, from a thermodynamic viewpoint, photosynthesis is simple—it requires eight photons to create one monomer unit of carbohydrate (2). In the visible region of 400 nm to 700 nm, the average energy of a photon is  $3.6 \times 10^{-19} \text{ J}$ . Eight moles of

photons will therefore contain  $1.7 \times 10^3$  kJ of energy. The  $\Delta G^\circ$  for reaction 2 is 528 kJ mol<sup>-1</sup> CO<sub>2</sub> (a nice exercise for students is to verify this using the well-known caloric food equivalent of combustion for carbohydrate of 4.2 kilocalories per gram). Thus,  $1.7 \times 10^3$  kJ of photonic energy is required to store 528 kJ of potential combustion energy in the bonds of carbohydrate. This means that photosynthesis has an overall thermodynamic efficiency of  $528 \text{ kJ} / 1.7 \times 10^3 \text{ kJ} = 0.31$ .

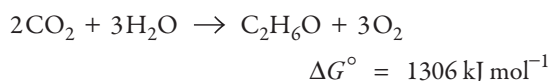
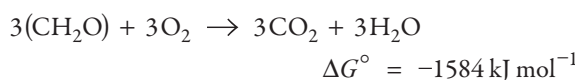
We must also consider the yearly duty cycle for photosynthesis. Carbohydrate is manufactured only while the plant is growing. This occurs at most 200 days out of the year (3). Hence, the plant's maximum duty cycle for the manufacture of carbohydrate is  $200/365 = 0.55$ .

### Consideration 3: Energy Requirements for Plant Life

Corn does not manufacture carbohydrates so we can make ethanol for our cars. Corn produces carbohydrate to fuel its own life processes. This occurs via the process of respiration. Therefore a substantial quantity of photosynthesized carbohydrate is metabolized by the plant to support its own life. In corn this value is about 70% (4). Hence, only about 30% of photosynthesized carbohydrate remains in the corn for us to convert to ethanol.

### Consideration 4: Thermochemistry of Fermentation

Just as corn does not enact photosynthesis for our convenience, microorganisms do not ferment carbohydrate so we can use the resulting ethanol for our cars. Microorganisms ferment carbohydrate to fuel their own life processes. The fermentation of carbohydrate to ethanol is energetically downhill. Thus, ethanol contains less combustion potential than does the starting material. That energy difference is what is used to support the life of the microorganism. Fermentation is a complex sequence of enzyme-catalyzed reactions; however, the overall process is represented by eq 4. Plant carbohydrates release 528 kilojoules per mole of monomer unit during combustion. Thus, the thermochemistry of fermentation follows by applying Hess's law to eqs 3 and 4:



Thus, the Gibbs energy of fermentation, eq 3, is -278 kJ per mole of ethanol produced. This represents the energy required by the microorganism to live. Thus, 18% of the original solar energy captured in the carbohydrate will be used by the microorganism during fermentation. This leaves 82% in the ethanol.

### Consideration 5: Power Requirements for Automobiles

The current worldwide consumption rate of gasoline is 750 billion kilograms per year (5), and there are 500 million vehicles in the world (6). One can therefore calculate the power

requirements for an average automobile,

$$\left( \frac{7.5 \times 10^{14} \text{ g C}_8\text{H}_{18}}{\text{year}} \right) \left( \frac{1 \text{ mol C}_8\text{H}_{18}}{114 \text{ g C}_8\text{H}_{18}} \right) \times \\ \left( \frac{5230 \text{ kJ}}{\text{mol C}_8\text{H}_{18}} \right) \left( \frac{1}{500 \times 10^6 \text{ car}} \right) = \frac{7.0 \times 10^7 \text{ kJ}}{\text{year car}}$$

where octane represents the gasoline and 5230 kJ is the heat of combustion. Thus, an average automobile dissipates power at  $7.0 \times 10^7 \text{ kJ y}^{-1}$ . This number is an average over 500 million vehicles. Obviously large trucks will operate at higher power, whereas motorcycles will dissipate less. This number also represents a yearly average. And this value is averaged over the world.

### Putting It Together

We now have enough information to estimate the "corn-area-per-car" ratio—the surface area of land required to grow enough corn to power an average vehicle. First, we convert the solar power density from watts m<sup>-2</sup> to kJ y<sup>-1</sup> m<sup>-2</sup>:

$$82 \text{ W m}^{-2} = \left( \frac{2.6 \times 10^6 \text{ kJ}}{\text{year m}^2} \right)$$

Next we multiply this total power density by the efficiency factors calculated in considerations 2–4:

$$\left( \frac{2.6 \times 10^6 \text{ kJ}}{\text{year m}^2} \right) (0.31)(0.55)(0.30)(0.82) = \frac{1.1 \times 10^5 \text{ kJ}}{\text{year m}^2}$$

Now we factor this into the power requirement calculated in consideration 5:

$$\frac{7.0 \times 10^7 \text{ kJ}}{\text{year car}} \times \frac{\text{year m}^2}{1.1 \times 10^5 \text{ kJ}} = \frac{640 \text{ m}^2}{\text{car}}$$

Simply put, an average vehicle will require a corn field of minimum area 640 m<sup>2</sup>—a square patch of land 25 m on an edge! Such an area occupies a grossly impractically large quantity of land, especially when compared to the size of the vehicle itself.

### Why the Situation Is Even Worse

This estimation is actually a best-case scenario because it does not consider several practical factors limiting the overall energy yield. First, the solar power density of 240 W m<sup>-2</sup> assumed every day to be a sunny day. Second, we assumed every photon reaching the plant is absorbed. This is certainly not the case. Moreover, the sun is not always overhead. Most of the day the sun illuminates the field at an angle, and therefore plants will cast shadows on each other. Also, the duty cycle calculated in consideration 2 is overestimated, as it is based on maximally optimized growing conditions for corn. Under typical conditions, corn grows for about 130 days from planting to harvest (3).

We also assumed that 100% of available (unmetabolized) carbohydrate in corn is used to make ethanol. This includes the celluloses and starches in the stems, leaves, roots, husks, and cobs. However in practice, only the kernels are utilized. In

consideration 4 we assumed that eq 4 proceeds with 100% yield. In practice, however, a rich variety of side products are formed depending on the microorganism employed, as any oenophile or beer aficionado will attest. At the time of this writing, the most efficient high-tech ethanol fermentation bugs known produce ethanol in about 91% of theoretical yield (7). Moreover, at present sugar is the only practical fermentation component, although much current research is directed towards efficient cellulose fermentation.

Another important factor we neglected is the energy required to isolate the ethanol from the fermentation mash. Obviously, one cannot use the raw product of fermentation directly. The ethanol needs to be distilled from the mixture and purified. Of course the use of biofuel is only potentially valuable if the energy required to grow, harvest, and process it is also alternate, and not fossil. It is a useful exercise for students to use the enthalpy of vaporization for ethanol to determine the minimum quantity of energy that needs to be cycled back into the fermentation mash to isolate the fuel, and what impact that will have on the corn-area-per-car ratio. In addition, ammonium nitrate fertilizer is currently prepared via the Haber process and requires energy to produce.

Finally, the calculations in consideration 5 assumed a gasoline consumption rate at the time of this writing. This number is currently increasing exponentially. Although this will not affect the calculation in consideration 5 since the total number of vehicles will increase proportionately, it will affect the overall quantity of land required to support the world's energy needs and will soon become a significant fraction of the planet's surface.

## Conclusion

Using only the first law of thermodynamics undergraduate chemistry students can readily determine the impracticality of employing corn ethanol as an alternative fuel for automobiles.

## Literature Cited

1. Muneer, T. *Solar Radiation and Daylight Models*; Butterworth-Heinemann: London, 2004.
2. Garrett, R. H.; Grisham, C. M. *Biochemistry*; Saunders College Publishing: Philadelphia, 1995; Chapter 22.
3. Neild, R. E.; Newman, J. E. *National Corn Handbook*; Purdue University: West Lafayette, IN, 2008.
4. (a) Poskuta, J. *Physiologia Plantarum* **1969**, *22*, 76–85. (b) Parkin, T. B.; Kaspar, T. C.; Senwo, Z.; Prueger, J. H.; Hatfield, J. C. *J. Hydrometeorology* **2005**, *6*, 812–824.
5. California Energy Commission Home Page. <http://www.eia.doe.gov/basics/quickoil.html> (accessed Dec 2007).
6. World Bank, 2002 World Development Indicators Report. [http://www.nationmaster.com/graph/tra\\_car-transportation-cars](http://www.nationmaster.com/graph/tra_car-transportation-cars) (accessed Dec 2008).
7. Verma, G.; Nigam, P.; Singh, D.; Chaudhary, K. *Bioresource Technology* **2000**, *72*, 261–266.

## Supporting JCE Online Material

<http://www.jce.divched.org/Journal/Issues/2009/May/abs579.html>

Abstract and keywords

Full text (PDF) with links to cited URLs