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A Statistical Analysis of the Theoretical Yield of Ethanol from Corn Starch

Tad W. Patzek[1,2]

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This paper analyzes the Illinois State Variety Test results for total and extractable starch content in 708 samples of 401 commercial varieties of corn. It is shown that the normally distributed extractable starch content has the mean of 66.2% and the standard deviation of 1.13%. The corresponding maximum theoretical yield of ethanol is 0.364 kg EtOH/kg dry corn, and the standard deviation is 0.007. In the ethanol industry units, this yield translates to 2.64 gal EtOH/nominal wet bushel, and the standard deviation is 0.05 gal/bu.
The U.S. ethanol industry consistently has inflated its ethanol yields by counting 5 volume percent of # 14 gasoline denaturant (8% of energy content) as ethanol. Also, imports from Brazil and higher alcohols seem to have been counted as U.S. ethanol. The usually accepted USDA estimate of mean ethanol yield in the U.S., 2.682 gal EtOH/bu, is one standard deviation above the rigorous *statistical estimate in this paper*.

KEY WORDS: Starch, extractable, total, statistics, Monte Carlo, distribution.

BACKGROUND

The purpose of this paper is to quantify the mean extractable starch in hybrid corn, and the mean stoichiometric (highest possible) yield of ethanol from this starch. My statistical calculations are based on the extensive database published annually for hybrid corn varieties in Illinois (Joos, 2005). I then compare my results with the ethanol industry's data and the USDA estimate of 2.682 gal EtOH/wet bushel (Shapouri, Duffield, and Wang, 2002).

CORN CHARACTERIZATION AND STARCH CONTENT

Based on the results of the Illinois State Variety Test in 2005 (Joos, 2005), the mean starch content of 778 samples of 401 commercial varieties of hybrid corn (see Table 1) was 71%, and the mean extractable starch[3] was 66%, the same as in (White and Johnson, 2003) and (Patzek, 2004; see Figure 1). As shown in Figure 2, extractable starch in Illinois follows almost perfectly the following normal distribution:

$$\mathrm{ES} = \frac{1}{\sqrt{2\pi} \times 1.13} \exp\left[-\frac{(\text{extractable starch} - 66.18)^2}{2 \times 1.13}\right] / 100 \tag{1}$$

[1]Department of Civil and Environmental Engineering, 425 Davis Hall, MC 1716, University of California, Berkeley, CA 94720.
[2]To whom correspondence should be addressed; e-mail: patzek@patzek.berkeley.edu.

[3] Measuring extractable starch is a tricky problem (Eckhoff and others, 1996; Paulsen and others, 2003). Corn starch measurements in the Illinois data set are performed using the Corn Refiners Association (CRA) method. The extractable starch is from a 100-g test by ECKHOFF (Eckhoff and others, 1996). PAULSEN (Paulsen and others, 2003) uses the 100-g extractable starch test as a reference method for the NIR prediction of extractable starch. Sources: DARIN JOOS and MARVIN PAULSEN, 360-B Ag Engr. Sciences Bldg, 1304 W. Pennsylvania Ave, Urbana, IL 61801, 217-333-7926. Private communication, Feb. 8, 2006.

Table 1. Hybrid Corn Varieties in the 2005 Illinois Database

Region or plant management	Yield & moisture location	Starch content[a]/extractable starch	# Samples/varieties
West Central	Monmouth, Perry, New Berlin	Urbana	143
South	Brownstown, Belleville Carbondale	Belleville	108
North	Mt Morris, DeKalb, Erie	DeKalb	154
East	Dwight, Goodfield, Urbana	Urbana	169
CFC[b] + RRC[c]	Urbana	Urbana	36 + 40
CFC + RRC	DeKalb	DeKalb	36 + 19
RRC	Bellevile	Belleville	20
CFC + RRC	Monmouth	Monmouth	34 + 19

[a] See Footnote 1.
[b] Corn following corn.
[c] Roundup-resistant corn.

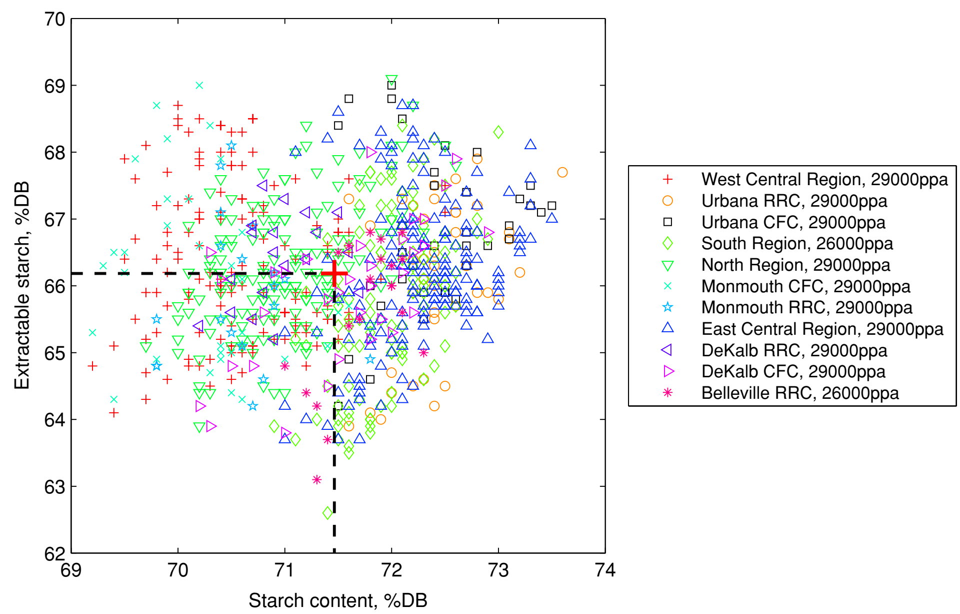

Figure 1. Source: 2005 Illinois State Variety Test (http://vt.cropsci.uiuc.edu/corn.html), accessed 12/01/05. Some 401 commercial hybrids were grown in four regions of Illinois (not all hybrids were grown in all regions). Starch content was predicted by NIR. Number of samples from 12 locations is 778. Mean starch content is 71.46 ± 0.92%. Mean extractable starch is 66.18 ± 1.13%. Acronyms are ppa = plants per acre, CFC = corn following corn, RRC = Roundup-resistant corn.

A measure of most interest to me is *fermentable starch.* Extractable starch measures what is available from a *wet milling process.* However, almost all new ethanol is produced in a dry grind process and more than extractable starch could be fermentable.

Remark 1. One could argue[4] that the *total*, not extractable, starch should be used to estimate the ultimate yield of corn ethanol in dry grind plants.[5] Also, the difference between the two starch contents may

[4] Apparently, FARRELL and others did not read this remark when they formulated their Response in Science (2006a, 2006b, 2006c): "... Nonetheless, much of his analysis (*i.e., this paper, TWP*) seems to be rigorous in detail but erroneous overall. For instance, extractable starch only applies to wet milling, which presently produces approximately 30% of U.S. ethanol. Almost all new ethanol plants are dry mills, for which total fermentable starch is a better measure of ethanol yield, and that yield at least 5% more ethanol per unit mass of corn than wet milling."

[5] MARVIN PAUL SCOTT, USDA-ARS, Private communication, Feb. 1, 2006.

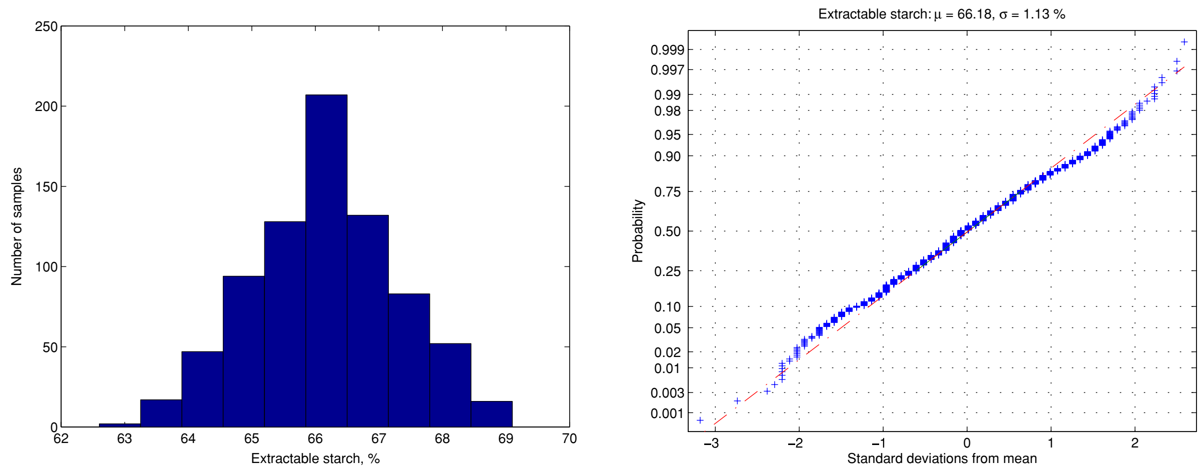

Figure 2. Histogram and normal distribution plot of extractable starch in 778 samples shown in Figure 1. Extractable starch is almost perfectly normally distributed.

depend on the measurement method. I will try to investigate this complex issue later.[6]

STARCH YIELD AND THEORETICAL ETHANOL YIELD

Now we are ready to obtain estimates of ethanol yield from the hybrid corn varieties tested in Illinois. To do so, Monte Carlo simulations have been run using the normal distribution in Equation (1). To obtain the net starch yield, the nominal grain losses (White and Johnson, 2003) caused by crushed grain, dirt, pebbles, etc., have been estimated as

$$\text{Loss} = \frac{1}{\sqrt{2\pi \times 0.7}} \exp\left[-\frac{(\text{Percent loss} - 3)^2}{2 \times 0.7}\right] / 100 \tag{2}$$

A single realization of the normal distribution (2) is shown in Figure 3.

To obtain a distribution of the net yield of extractable starch, the individual random variables (1) and (2) were treated as statistically independent and 2500 realizations were used.

[6] David Andress of EIA has observed that the corn starch analysis in this paper considers all corn samples, but ethanol plant operators attempt to purchase high extractable starch corn. This can be accomplished by segregation or the use of inexpensive testing procedures. The difference in extractable starch is on the order of several percent. I will investigate his observation if I pursue this subject further (Source: private comm., 22 Feb. 2006.)

Given the random extractable starch (ES) in Equation (1) and the corn losses in Equation (2), the maximum theoretical ethanol yield can be calculated as

$$\text{Theoretical.EtOH Yield} = (1 - \text{Loss}) \times \text{ES} \times \frac{180}{162} \times 0.51 \quad \frac{\text{kg EtOH}}{\text{kg dry corn}} \tag{3}$$

The Monte Carlo simulation results are shown in Figure 4. The mean stoichiometric ethanol yield is 0.364 kg EtOH/kg dry corn, and the standard deviation is 0.007. Note that the current statistical estimate

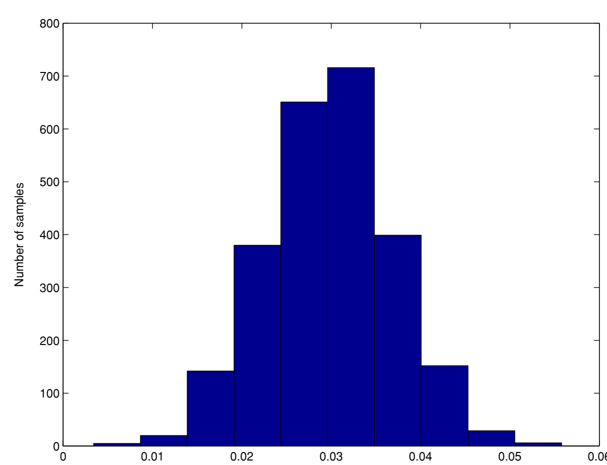

Figure 3. Histogram of nominal losses in #2 Yellow Corn (White and Johnson, 2003). Normal distribution mean is 3% and standard deviation is 0.7%.

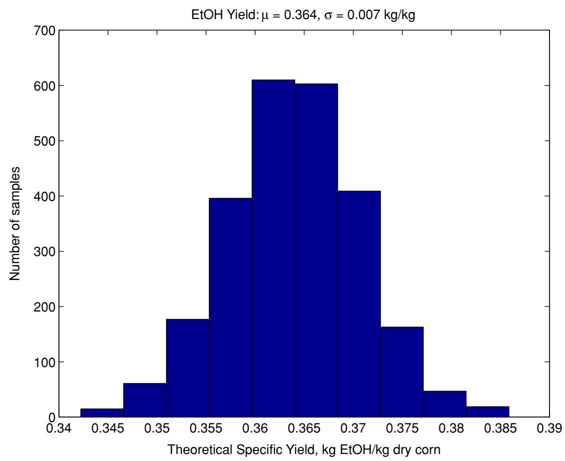

Figure 4. Theoretical stoichiometric yield of ethanol given extractable starch content in Figure 1 and nominal grain losses in Figure 3. Mean theoretical yield is 0.364 kg EtOH/kg of dry grain and standard deviation is 0.007 kg/kg.

of the theoretical yield of ethanol from absolutely dry corn grain is somewhat lower than the 0.374 kg EtOH/kg dry corn in (Patzek, 2004). According to Remark 1, the theoretical ethanol yield in dry grind plants may be higher.

The U.S. ethanol industry uses a confusing and imprecise system of units and it customarily exaggerates ethanol yields. For example, ethanol is measured by volume of unknown composition and corn grain is measured in bushels with unknown moisture content.

Remark 2. One gallon of ethanol reported by the industry contains 5% by volume of #14 gasoline denaturant, which is *not* ethanol, and, therefore, all ethanol yields are overestimated by at least 5%.

From Definition 1 in (Patzek, 2004) it follows that the *nominal* bushel of corn is 56 pounds of corn grain with 15% of moisture by mass. Depending on the source and age of corn grain, its moisture content will not be uniformly 15%. The moisture content in the Illinois hybrid corn varieties harvested in 2005 is shown in Figure 5. It follows a log-normal distribution

$$M = \frac{1}{\sqrt{2\pi \times 1.18}} \exp\left[-\frac{(\text{logarithm of moisture content} - 18.43)^2}{2 \times 1.18}\right] / 100 \quad (4)$$

with the mean of 18.4%, see Figure 5.

Remark 3. Moisture content in corn grain influences ethanol yield. In the situation illustrated in Figure 5, the theoretical ethanol yield will be lower by $\sim$3% on the average.

The rigorous Equation (3) is approximately converted to gallons of EtOH per nominal 15%-wet bushel by multiplying it by

$$\frac{56 \times 0.454 \times 0.85}{0.787 \times 3.785}. \quad (5)$$

The results are shown in Figure 6. The mean stoichiometric ethanol yield is 2.64 gal EtOH/nominal wet bushel, and the standard deviation is 0.05 gal/bu.

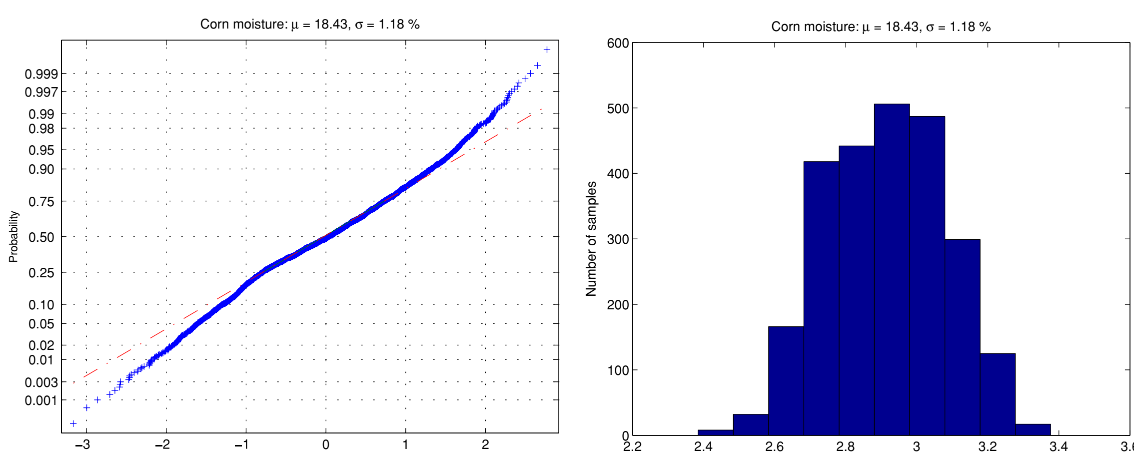

Figure 5. Histogram and normal distribution plot of logarithm of moisture content in 2500 corn samples in 2005 Illinois State Variety Test. Moisture content is almost log normally distributed. The Mean of 18.4% is significantly higher than nominal 15% used in most standard calculations of corn ethanol yields.

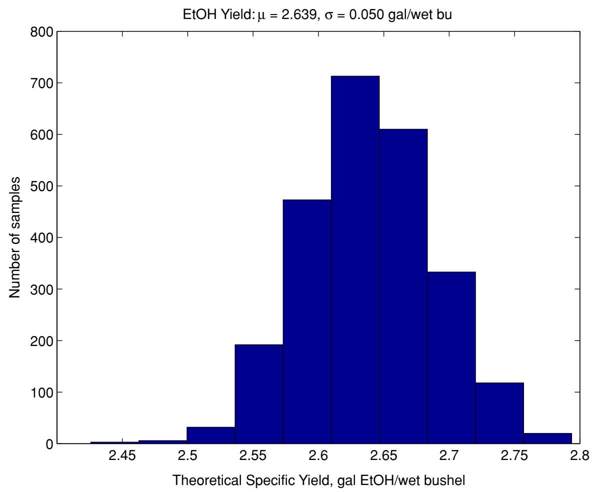

Figure 6. Theoretical stoichiometric yield of ethanol given extractable starch content in Figure 1 and nominal grain losses in Figure 3. Mean is 2.64 gal/wet bushel and standard deviation is 0.05 gal/wet/bushel.

The mean theoretically extractable starch in Figure 1 is 92.7% of the mean starch content in corn grain. This amount can be extracted only in the best refineries. Some of this starch and other components of the fermentation mash, corn oil, and germ are converted to other products (Dawes and Large, 1982), such as methyl, amyl, iso-amyl, isobutyl, *n*-propyl, 1,2,3-propanetriol (glycerol), and higher alcohols; ethers; acetic aldehyde and acid, other organic acids, etc. Some possible reaction paths are shown in Figure 7. The main byproducts are isopropyl and isobutyl alcohols. Other byproducts are formed in the deamination and decarboxylation reactions of amino acids in the mash, etc. In average refineries or poor fermentation batches, ethanol yield decreases by up to 10%. Any pentoses (5-carbon sugars) are also converted to furfural (furan-2-carbaldehyde), one of the best organic solvents. Furfural in an impure ethanol mixture will gradually dissolve almost any rubber or elastomeric seals or ducts in storage systems and car fuel systems.

Fermentation to ethanol is carried out by yeast. Fermentation to butanol (and decomposition to methane) is carried out by anaerobic bacteria. The outcome is critically dependent on the purity of either microorganism culture.

Remark 4. Corn mash must be thoroughly sterilized prior to addition of the appropriate microorganism culture to start the desired conversion. Quality of sterilization is even more important for cellulosic ethanol processes.

With time, a yeast fermentation process will be dominated by the most competitive bacteria. The longer the duration of the batch fermentation process is, the more equilibrium shifts towards higher alcohols, aldehydes, acids, or methane. Average duration of batch ethanol fermentation is 40-45 hours, but some factories use up to 72-h batches to achieve higher ethanol yields, while running substantial risk of having bad batches that must be recycled.[7]

Direct evidence of competing reaction pathways in a dry grind ethanol plant comes from the chemical analysis of gas emissions from plant equipment.[8] For example, in the Gopher Ethanol Plant, St. Paul, MN, (Anonymous, 2003), high-to-moderate concentrations of the following volatile organic substances (VOCs) occurred: Methane, methanol, ethanol, toluene, ethylbenzene, acetone, formaldehyde, acetaldehyde, acrolein, benzene, styrene, 1,3-butadiene, 1,3-pentadiene, 1-2-propadiene, 1-4-pentadiene, 1-decene, 1-dodecene, 1-heptene, 1-hexene, 1-methy1-2-cyclopropene, l-nonene, 1-octene, 1-undecene, 2-butanone, 2-butenal, 2-furancarboxaldehyde, 2-heptenal, 2-methyl-1-pentene, 2-methyl-2-propenal, 2-methyl-butanal, 2-methyl-furan, 2-methylpropenal, 2-pentyl-furan, 2-propen-1-ol, 2-propenal, 3-methyl-butanal, 6-heptenoic acid, benzaldehyde, furan, hexanal,

[7] This usually is done by dumping bad mash onto the surrounding land. As reported by PERRY BEEMAN of The Des Moines Register, 11 Sept 2005: “Iowa plants - which produce a third of the nation’s ethanol supply - have sent syrup, batches of bad ethanol and sewage into streams. As the pollutants decomposed, the waters lost oxygen, threatening fish. . . . Gieselman said inspectors discovered plant construction contractors were telling farmers the plants wouldn’t discharge into waterways. “They do,” Gieselman said. The state has forced many of the plants to install holding ponds so the pollutants decompose or settle out before the water flows into streams used by fishing enthusiasts, canoeists and thirsty livestock.”

[8] Under current rules, plants are classified as “major sources” of pollution and forced to go through the more-cumbersome approval process if they emit in excess of 100 tons per year of a particular pollutant, such as nitrogen oxide, dust, or volatile organic compounds such as formaldehyde. The EPA this week proposed to boost that cap to 250 tons per year. The agency said the higher cap is justified because that is the limit for grain-processing facilities that make alcohol along with a range of food products. The typical ethanol plant in Iowa puts out 300 to 350 total tons of pollutants per year, including nitrogen oxide, sulfur dioxide and various volatile organic compounds, according to the Iowa Department of Natural Resources. Source: The Des Moines Register, Des Moines, IA. 6 March 2006.

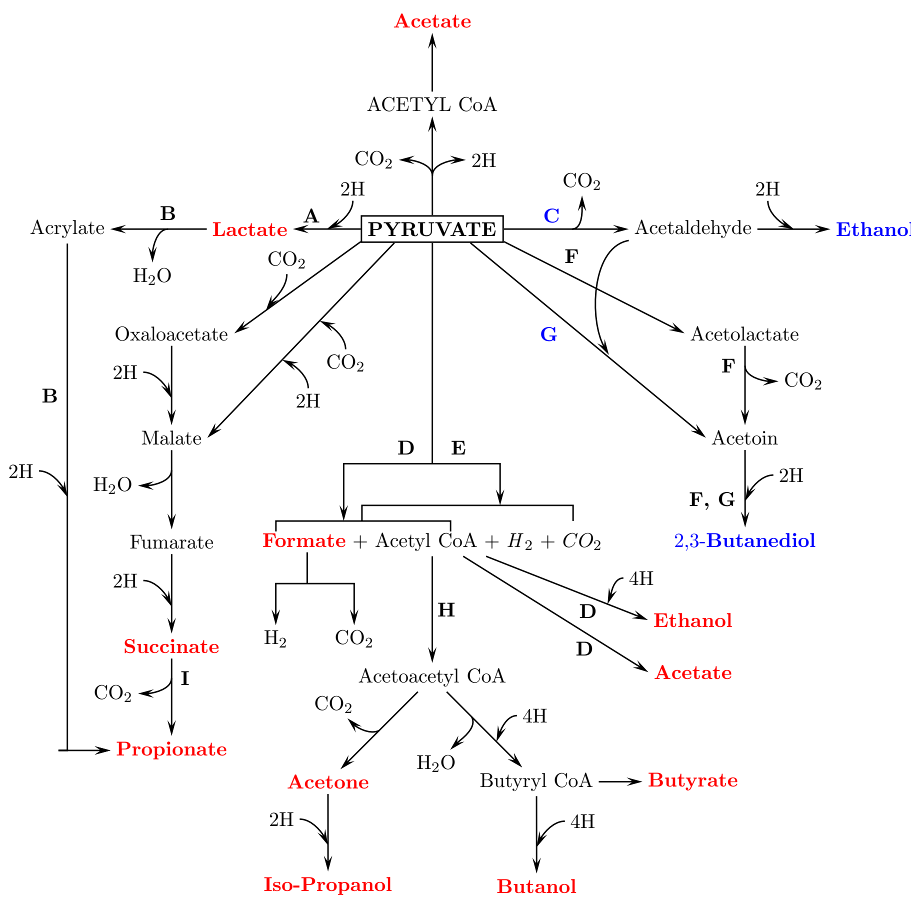

Figure 7. Pyruvate is first stage of decomposition of glucose in beer fermentation. Only pathways C and G are activated by yeast. All other pathways are activated by aerobic and or anaerobic bacteria. Some or most of these bacteria are present in fermentation mash. Adapted from (Dawes and Large, 1982).

nitro-methane, etc. Also liquid lactic acid, acetic acid, 2-furancarboxaldehyde, etc., were detected.

COMPARISON WITH ETHANOL INDUSTRY AVERAGE

The detailed calculation of theoretical ethanol yield in Illinois in 2005 is now compared with the annual ethanol industry's averages reported in 2000–2004 by the Renewable Fuels Association,[9] see Table 2.

Table 2. Overall Ethanol Yields Reported in Renewable Fuels Association's 2004 Ethanol Industry Outlook

Year	Billion Gallons	Million Bushels
2000	1.63	627
2001	1.77	681
2002	2.13	819
2003	2.81	1077
2004	3.41	1220

The national ethanol industry average of 2.6 gal/wet bushel, inflated at least 5% by volume, is 98% of the theoretical average for Illinois. This industry average includes dry and wet mill plants, some of which are 20 years old. The jump of 0.2 gal/bu in 2004 can be attributed to counting ethanol imports from Brazil[10] and ~2% of other distillation fractions, e.g.,

[9] As of 7 Feb. 2006, the data shown in Table 2 are available at http://www.ksgrains.com/ethanol/useth.html. The newly redesigned website of the Renewable Fuels Association, http://www.ethanolrfa.org. no longer posts the corn bushels used to produce ethanol. Therefore Table 2 could not be extended beyond 2004.

[10] Between 1 January and 1 November 2004, the U.S. ethanol imports from Brazil were 334.531,283 kg or ~0.142 billion

Table 3. 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

fuel alcohol,[11] as ethanol produced in the U.S. Figure 8 compares the various estimates from 2000 to 2004. In 2005, the industry stopped reporting corn bushels used to produce ethanol.

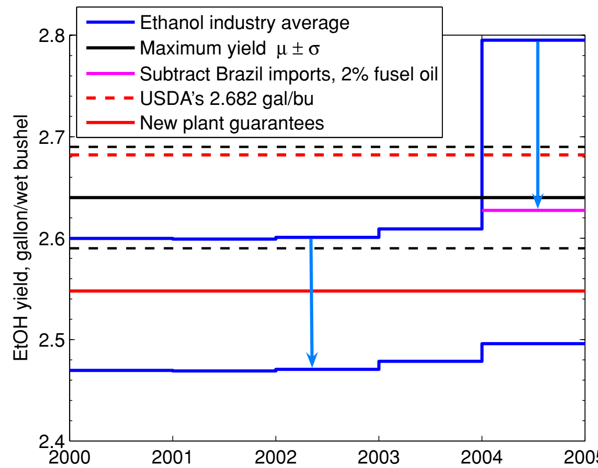

Figure 8. Self-reported ethanol industry yield for all plants has been close to 2.6 gal/wet bushel. Jump to 2.8 gal/wet bushel in 2004 seems to have been caused by counting 0.14 billion gallons (denatured) of ethanol imported from Brazil and additional 2% of fusel fraction as ethanol produced in U.S. Upper arrow denotes my correction. Ethanol yield data source: Renewable Fuels Association's 2004 Ethanol Industry Outlook http://www.ksgrains.com/ethanol/useth.html. Mean result of Illinois 2005 Variety Test in Figure 7 is shown as black line. Broken black lines denote ± one standard deviation from theoretical mean of 2.64 gal/bu. It follows that ethanol industry's U.S. average for all plants (blue line), new and 20-years old, is 98% of theoretical stoichiometric ethanol yield (black line), and above guaranteed ethanol yield in new most efficient plants (Morris, 2005), red line. Industry average therefore must be discounted by at least 5% (lower arrow).

CONCLUSIONS

Some 778 corn starch measurements and 2500 corn grain samples from the 2005 Illinois Corn Variety Test have been used to obtain the detailed statistical estimates of the mean extractable corn starch (66.18 ± 1.13%) and the mean theoretical ethanol yield (2.64 ± 0.05 gal EtOH/wet bushel). These results demonstrate that the extractable starch content estimate of 66% used in (Patzek, 2004) is correct, see Table 3. The ethanol industry's national average of 2.6 gal/wet bushel has been inflated by counting 5% by volume of gasoline as ethanol. Consequently, this average is too high, about 98% of the theoretical yield in Illinois, and it is above the more reasonable yield guarantees of 2.55 gal EtOH/wet bushel (Morris, 2005) in the new efficient plants. If the national average is discounted 5% by removing the volume of gasoline counted as ethanol, it becomes 2.46 gal/bushel, somewhat above my estimate of 2.30 gal/bushel in (Patzek, 2004), which also discounts heavy alcohols. After subtracting ethanol imports from Brazil, the average ethanol yield in 2004 was discounted by another 2% to bring it below the mean theoretical yield calculated here.

Remark 5. The USDA estimate of 2.682 gallons of 100% pure ethanol per nominal wet bushel of corn with 15% of moisture by weight has been accepted as the basis of net energy calculations in (Farrel and others, 2006a, 2006c). Based on the analysis here, this USDA estimate is incorrect.

In 2004, after the correction for #14 gasoline and fusel oil, corn ethanol satisfied less than 1.5% of U.S. motor gasoline consumption, because the 1 psi Reid Vapor Pressure (RVP) waiver for gasoline-EtOH blends was *not* repealed by states fighting increased air pollution.[12] In 2012, with the waiver

gallons of denatured ethanol per year. These Brazilian imports accounted for ∼5% of ethanol produced in the U.S. in 2004. Source: Balan$cLo_Exp_Imp_Etanol_Brasil_EUA_1981-2004-DATAGRO.xls. an Excel spreadsheet with the U.S. - Brazilian balance of ethanol trade between 1981 and 2004, sent to me by Mr. Juan M. Granados of Biotrade USA, Inc., 17 March 2006.

[11] ASTM D5798-99 Standard Specification for Fuel Ethanol for Automotive Spark-Ignition Engines allows for up to 2% by volume of higher aliphatic alcohols (C3-C8), see Table 3 in http://www.nrel.gov/does/fy02osti/30849.pdf.

[12] States no longer will have to add corn-based ethanol or MTBE to gasoline to fight pollution—a requirement that costs as much as 8 cents a gallon—under rules announced on 15 February 2006, by the Environmental Protection Agency. They eliminate a mandate from the 1990 Clean Air Act that gasoline used in metropolitan areas with the worst smog contain 2% oxygen by weight. The

upheld, ethanol will displace another 1% of U.S. motor gasoline consumption on an energy-equivalent basis. If the waiver is repealed, the lighter gasoline components will be removed in refineries to lower the RVP. The repeal of the waiver would reduce[13] ethanol displacement of conventional gasoline by 30 or 40%. Note that fossil energy use in corn ethanol production has not been accounted for in the given estimates.

REFERENCES

Anonymous, 2003, Public health assessment gopher state ethanol, City of St. Paul. Ramsey County, Minnesota: Report Under Cooperative Agreement with the Agency for Toxic Substances and Disease Registry, The Minnesota Department of Health, St. Paul, MN 55164-0975, www.health.state.mn.us/divs/eh/hazardous/sites/ramsey/gopher/pha.html.

Dawes, I., and Large, P. J., 1982, Biochemistry and bacterial growth: Chapt. Class 1 reactions: Supply of carbon skeletons: Blackwell, Oxford, p. 125–158.

Eckhoff, S. R., Singh, K., Zehr, B. E., Rausch, K. D., Fox, E. J., Mistry, A. K., Haken, A. E., Niu, Y. X., Zou, S. H., Buriak, P., Tumbleson, M. E., and Keeling, P. L., 1996, A 100 g laboratory corn wet milling procedure: Cereal Chemistry, vol. 73, no. 1, p. 54–57.

Farrell, A. E., Plevin, R. J., Turner, B. T., Jones, A. D., O'Hare, M., and Kammen, D. M., 2006a. Ethanol can contribute to energy and environmental goals: Science, vol. 311, no. 5760, p. 506–508.

Farrell, A. E., Plevin, R. J., Turner, B. T., Jones, A. D., O'Hare, M., and Kammen, D. M., 2006b, Science Letters - Response: Science, vol. 312, no. 5781, p. 1747–1748.

Farrell, A. E., Plevin, R. J., Turner, B. T., Jones, A. D., O'Hare, M., and Kammen, D. M., 2006c, Supporting Online Material: www.sciencemag.org/cgi/content/full/311/5760/506/DC1.

Joos, D., 2005, Variety Testing, Department of Crop Sciences, 2008 South Wright St., Urbana, IL 61801, http://vt.cropsci.uiuc.edu/corn.html.

Morris, D., 2005, The Carbohydrate Economy, Biofuels and the Net Energy Balance: Web report, www.ilsr.org, Institute for Local Self-Reliance, Washington, D.C., 24 p.

Patzek, T. W, 2004, Thermodynamics of the corn-ethanol biofuel cycle: Critical Reviews in Plant Sciences, vol. 23, no. 6, p. 519–567, An updated web version is at http://petroleum.berkeley.edu/papers/-patzek/CRPS416-Patzek-Web.pdf.

Paulsen, M. R., Mbuvi, S. W., Haken, A. E., and Ye, B.R., 2003, Extractable starch as a quality measurement of dried corn: Applied Engineering in Agriculture, vol. 19, no. 2, p. 211–217.

Shapouri, H., Duffield, J. A., and Wang, M., 2002, The energy balance of corn ethanol: An update: Agricultural Econ. Rep. No. 814, U.S. Department of Agriculture, Economic Research Service, Office of the Chief Economist, Office of Energy Policy and New Uses, Washington, D.C., 19 p.

White, P. J., and Johnson, L. A., eds., 2003, Corn chemistry and technology (2nd edn.): Am. Assoc. Cereal Chemists, St. Paul, Minnesota, 892 p.

law did not say which oxygenate must be used, but most refiners use either ethanol or methyl tertiary butyl ether, known as MTBE. Source: Associated Press, 15 Feb. 2006.

[13] (Source: *Potential Supply Impacts of Removal of 1-Pound RVP Waiver*, September 2002, Office of Oil and Gas of the EIA, Mary J. Hutzler (202-586-2222, mhutzler@eia.doe.gov). The EIA study was requested by Senator Jeff Bingaman, Chairman of the Senate Committee on Energy and Natural Resources).