Testing Evolution

Expanding Analytical Needs in Corn Processing

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LONE STAR DAIRY PRODUCTS

DAIRY

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SEP Committee

Quick survey

Show of hands

Who are the dry millers in the room?

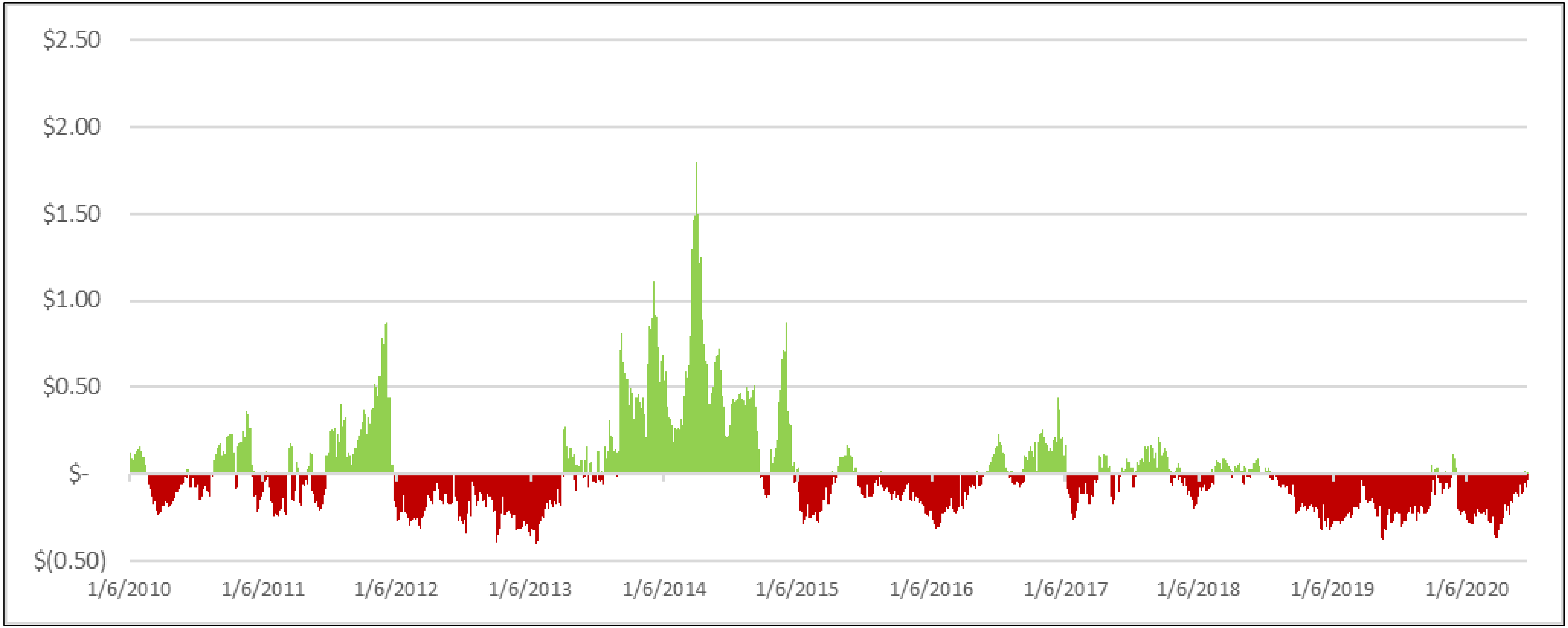
How about the wet mills?

Anybody with both?

Basic dry mill economics

Motivated to enhance & stabilize profitability

Estimated margin per gallon from a university profitability model



Diversification

Dry mills are diversifying, in order to stabilize and improve profitability:

- **Corn oil**
- **Specialty, non-fuel ethanol products**
- **High-protein feed**
- **High-fiber stream**
- **Sweeteners**

"Bolt-on" process technologies

Examples include:

To put it another way…

The evolving biorefinery is starting to look more and more like a wet mill every day!

Wet milling basics

Characteristics

- LARGE!
- VERY capital intensive to build
- They tend to be the older plants in the industry
- Characterized in part by the front-end process of STEEPING the corn before milling

∴ capable of mechanically separating the physical components of the corn kernel into discrete materials for further processing into a catalogue of value-added ingredients

Are wet mills dinosaurs?

Accessible products, component by component

From STARCH

- ***Modified starches:***

Dextrin
Acid-treated starch
Alkaline-treated starch
Bleached starch
Oxidized starch
Starches, enzyme-treated
Monostarch phosphate
Distarch phosphate
Phosphated distarch phosphate
Acetylated distarch phosphate
Starch acetate
Acetylated distarch adipate
Hydroxypropyl starch
Hydroxypropyl distarch phosphate
Hydroxypropyl distarch glycerol
Starch sodium octenyl succinate
Acetylated oxidized starch

List from Codex Alimentarius

From STARCH

- ***Unmodified ("common") starch***
- ***Resistant starch***
- ***Starting material for sweeteners***

Dextrose	High fructose corn syrups (42 and 55)
Crystalline dextrose	Hydrogenated starch hydrolysate
Corn syrups (30-80 DE)	Sorbitol
Maltose	Mannitol
Maltodextrin	Maltitol
Crystalline fructose	Erythritol

From STARCH

- *Ethanol ranging from fuel to GNS*
- *Carbon dioxide*
- *Feedstock for any number of fermentations, producing useful ingredients ranging from organic acids to amino acids to vitamins, and beyond*

From the GERM

- *Germ*
- *Germ meal*
- *Defatted germ meal*
- *Corn oil (any of RBDW)*

From the FIBER

- ***Corn gluten feed***
- ***Feedstock for cellulosic fuels production***

From the GLUTEN

- ***Corn gluten meal***

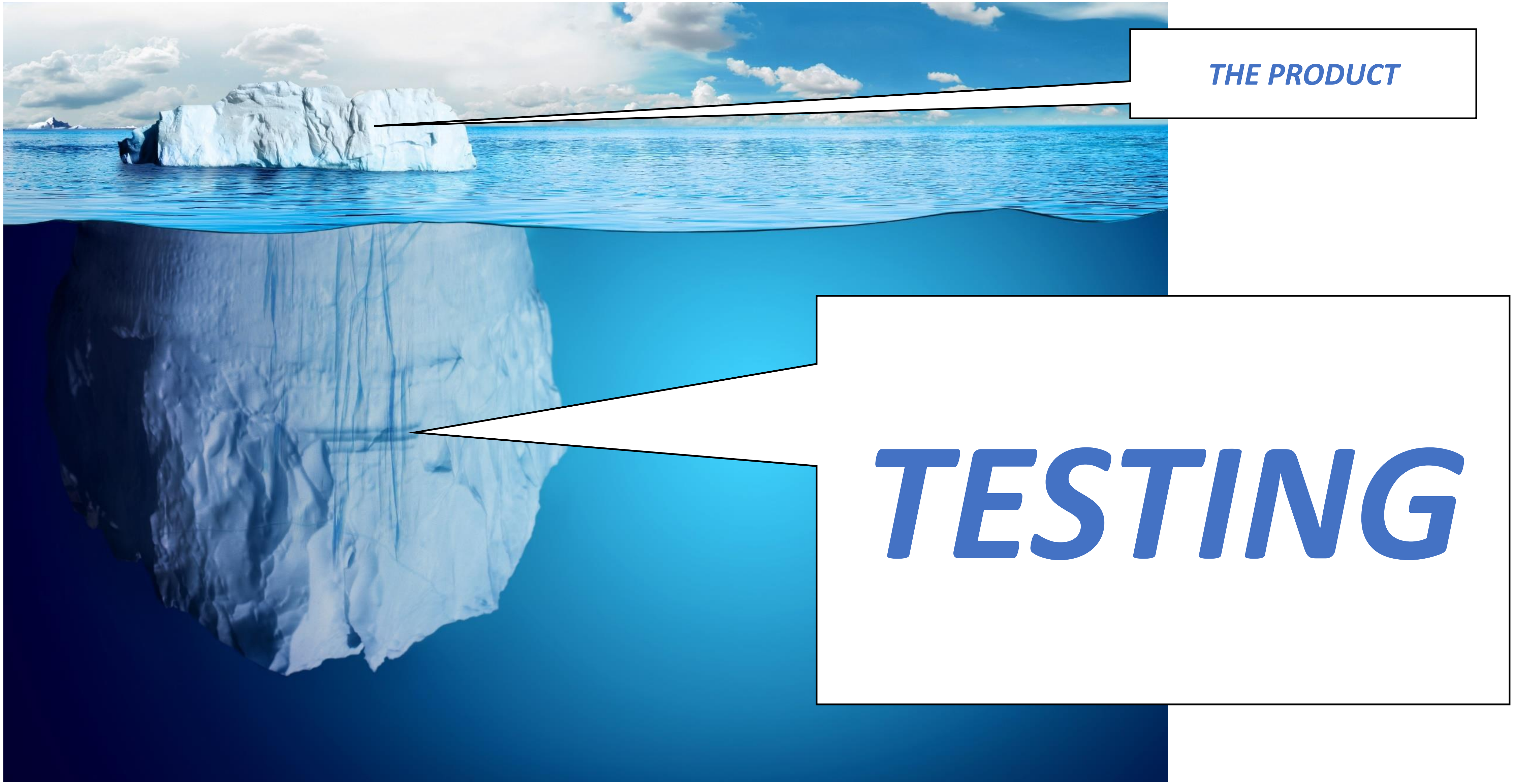
To put it another way…

That's more than 40 products, some of which are themselves the jumping-off point for some other product or process!

To put it another way…

And they all require TESTING!

It’s all about what lurks beneath the surface



Testing authorities relevant to wet mill testing

Diverse products and their broad range of end-use applications mean that MANY agencies and industry consortia are defining quality parameters and testing methods, including:

- Association of Official Analytical Chemists (AOAC)
- ASTM International
- American Oil Chemists' Society (AOCS)
- Corn Refiners Association (CRA)
- Association of American Feed Control Officials (AAFCO)
- Food Chemicals Codex (FCC)
- International Society of Beverage Technologists (ISBT)
- United States Pharmacopeia – National Formulary (USP-NF)
- International Pharmaceutical Excipients Consortium (IPEC)
- American Chemical Society (ACS)

One source of methods: CRA

ACETA.01	Acetaldehyde	7	12/19/2006
ACETA.02	Acetaldehyde and Isovaleraldehyde	6	10/9/2009
ACETY.01	Acetyl	3	3/30/1993
ACIDI.01	Acidity	3	4/15/2010
ACIDI.02	Acidity, Paste	2	10/8/2009
AFLAT.01	Aflatoxins (Presumptive)	3	12/8/2006
AMYLO.01	Amylose (Blue Value)	4	3/10/1997
ARSEN.01	Arsenic	6	4/15/2010
ASHXX.01	Ash	5	10/9/2009
BAUME.01	Baumé	9	10/24//1994
BORAX.01	Borax	2	3/1/1995
BULKD.01	Bulk Density	3	4/9/1998
CALCI.01	Calcium (EGTA Titrimetric)	5	4/15/2010
CARBO.01	Carboxyl	3	3/31/1992
CHLOR.01	Chloride (Potassium Chromate)	2	3/28/2006
CHLOR.02	Chloride (Potentiometric)	3	4/15/2010
COLDT.01	Cold Test	3	3/31/1992

Corn Refiners Association (www.corn.org)

CRA continued

COLDT.01	Cold Test	3	3/31/1992
COLOR.01	Color (Spectrophotometric)	5	11/9/2010
COLOR.02	Color (Spectrophotometric)after heat	2	4/28/1987
COLOR.03	Color (%T @ 390 nm)	2	2/27/1996
COLOR.04	Color (%T @ 390 nm)after heat	2	2/27/1996
COLOR.05	Color, Tristimulus	4	4/15/2010
DEXTR.01	Dextrose, Enzamatic	4	10/24/1994
DEXTR.02	Dextose Equivalent	4	4/15/2010
EXTER.01	External Filth and Internal Insect Infestation in Corn	5	2/27/1996
EXTRA.01	Extraneous Materials (Sugars)	3	3/31/1992
EXTRA.02	Extraneous Materials(Lactic)	3	9/8/2006
FATCR.01	Fat , Crude, (Oil)(Hexane Extractables)	3	10/8/2009
FATTO.01	Fat, Total (Oil)	6	11/9/2010
FIBER.01	Fiber, Crude	4	4/15/2011
FREEF.01	Free Fatty Acids	2	10/9/2009
HYDRO.01	Hydroxyalkoxyl	6	5/19/1995

CRA continued…

HYDRO.02	Hydroxyethyl Substitution Level	5	6/30/1998
IODIN.01	Iodine Affinity	6	3/5/2004
IODIN.02	Iodine Number (Wijs Method)	5	4/11/1994
IRONX.01	Iron (Colorimetric)	5	4/15/2010
LACTI.01	Lactic Acid	7	3/10/1997
LEADX.01	Lead	6	4/15/2010
LEADX.02	Lead (Graphite Furnace AAS)	8	6/3/1998
METAL.01	Metals, Heavy, H2S ppt	4	11/9/2010
METAL.02	Metals, Trace (Flame Atomic Absorption Spectroscopy)	4	12/22/2006
MOIST.01	Moisture (Azeotropic Distillation)	8	11/9/2010
MOIST.02	Moisture (Karl Fischer)	8	11/9/2010
MOIST.03	Moisture (Karl Fischer, Buffered)	6	9/8/2006
MOIST.04	Moisture (Oven)	7	11/9/2010
MOIST.05	Moisture in Sweet Feed	2	4/9/1998
NITRO.01	Nitrogen, Ammonia	4	3/5/2004
ODORA.01	Odor and Flavor	3	10/21/1986

CRA continued……

PHXXX.01	pH (Paste)	3	4/15/2010
PHXXX.02	pH (Slurry	4	4/15/2010
PHOSP.01	Phosphorus	10	11/9/2010
PROPY.01	Propylene Oxide	2	12/8/2006
PROTE.01	Protein, Kjeldahl	6	11/9/2010
PROTE.02	Protein, Nitrogen (Chemiluminescence)	5	3/30/1993
PROTE.03	Protein, Nitrogen (Combustion)		
READI.01	Readily Carbonizable Substances, Colorimetric	3	9/8/2006
READI.02	Readily Carbonizable Substances, Spectrophotometric	4	9/8/2006
REFRA.01	Refractive Index	3	10/9/2009
SACCH.01	Saccharides (Gas Liquid Chromatography)	7	10/17/1989
SACCH.02	Saccharides, Minor (Gas Liquid Chromatography)	4	3/1/1995
SACCH.03	Saccharides(Liquid Chromatography)	5	4/1/2009
SACCH.04	Saccharides,Minor (Liquid Chromatography)	4	4/1/2009
SOLUB.01	Soluble Polystyrene Sulfonate (Quinine Haze Test)	2	10/7/1996

CRA continued………

SOLUB.02	Solubles	4	11/9/2010
SPECI.01	Specific Rotation	3	4/15//2010
STARC.01	Starch (Polarimetry)	4	4/15/2010
STARC.02	Starch, Apparent	2	10/9/2009
STARC.03	Starch Identification (Microscopy)	8	6/20/1991
SUGAR.01	Sugars, Fermentable, GC	5	4/28/2001
SUGAR.02	Sugars, Reducing (Schoorl Method)	6	4/15/2010
SUGAR.03	Sugars, Total	5	2/27/1996
SULFA.01	Sulfates	2	10/23/2001
SULFU.01	Sulfur Dioxide (Iodometric)	4	11/9/2010
SULFU.02	Sulfur Dioxide, Monier Williams	6	4/15/2010
VISCO.01	Viscosity, Brabender	3	4/11/1994
VISCO.02	Viscosity, Inherent (One Point)	5	4/2/2003
VISCO.03	Viscosity,Small Sample Brookfield (SSB)	3	4/9/1998
WAXYA.01	Waxy and Nonwaxy (Corn)	3	4/1/2009
WAXYA.02	Waxy and Nonwaxy (Starch)	3	4/1/2009
XANTH.01	Xanthophylls	6	10/9/2009

Mixed bag

It’s great that many useful methods are documented and available…
…but some of them haven’t been reviewed / updated since 1986.

Another source: AOAC

Typical "vintage" AOAC method, circa 1963.

28.1.29

AOAC Official Method 962.12
Acidity (Titratable) of Wines

First Action 1962
Final Action 1963

American Society of Enologists–AOAC Method

Remove CO_2, if present, by either of following methods: (*1*) Place ca 25 mL test portion in small Erlenmeyer and connect to water aspirator. Agitate 1 min under vacuum. (*2*) Place ca 25 mL test portion in small Erlenmeyer, heat to incipient boiling and hold 30 s, swirl, and cool.

Add 1 mL phenolphthalein indicator solution to 200 mL hot, boiled water in 500 mL wide-mouth Erlenmeyer. Neutralize to distinct pink. Add 5.00 mL degassed test portion and titrate with 0.1M (or 0.0667M) standardized NaOH to same end point, using well-illuminated white background.

Calculate g tartaric acid/100 mL wine = mL NaOH × molarity × 0.075 × 100/5. If 0.0667M alkali is used, g tartaric acid/100 mL = mL NaOH/10.

To calculate as g malic/100 mL wine, multiply by 0.893. To calculate as g citric/100 mL wine, multiply by 0.933.

References: *Am. J. Enol. Viticult.* **13,** 40(1962).
JAOAC **46,** 293(1963).

More AOAC

Even better, this is a 1920 vintage.

28.1.04

AOAC Official Method 920.57
Alcohol in Wines
By Volume from Specific Gravity
First Action 1920
Final Action

Measure 100 mL wine into 300–500 mL distillation flask, noting temperature, and add 50 mL H_2O. Attach flask to vertical condenser by means of bent tube, distil almost 100 mL, and dilute to 100 mL at same temperature. (Foaming, which sometimes occurs, especially with young wines, may be prevented by adding a small amount of antifoam material.) For wines that contain an abnormal amount of CH_3COOH, neutralize exactly with 1M NaOH solution [calculated from acidity, 962.12 (*see* 28.1.29)] before proceeding with distillation (unnecessary for wines of normal taste and odor). Proceed as in 945.06C (*see* 26.1.06), at room temperature if desired, and obtain corresponding % alcohol by volume from **913.02** (*see* Appendix C).

So what, now what?

The good news

Many of the fundamental testing techniques, whether physical, traditional wet chemistry, or instrument-based, are already familiar to the fuel ethanol laboratory.

As you might expect

Depending on the product(s) you pursue, you will have new skills, materials, and instruments to obtain and master.

A noteworthy new skill

One last thought

Raise your hand if in the last couple of years:

- ***Your facility had changes in department-level leadership?***
- ***In top management?***
- ***You added a new process / product?***
- ***You gained customer(s) in a new industry?***
- ***You changed your facility's regulatory registration(s) and/or permits?***
- ***You implemented new testing?***
- ***You implemented a Quality or Food Safety Management System?***

Some observations

The industry is experiencing:

- ***Management turnover***
- ***Ownership changes***
- ***Decline in "old-school" wet milling expertise***
- ***Decline in "old-school" GNS distillation expertise***

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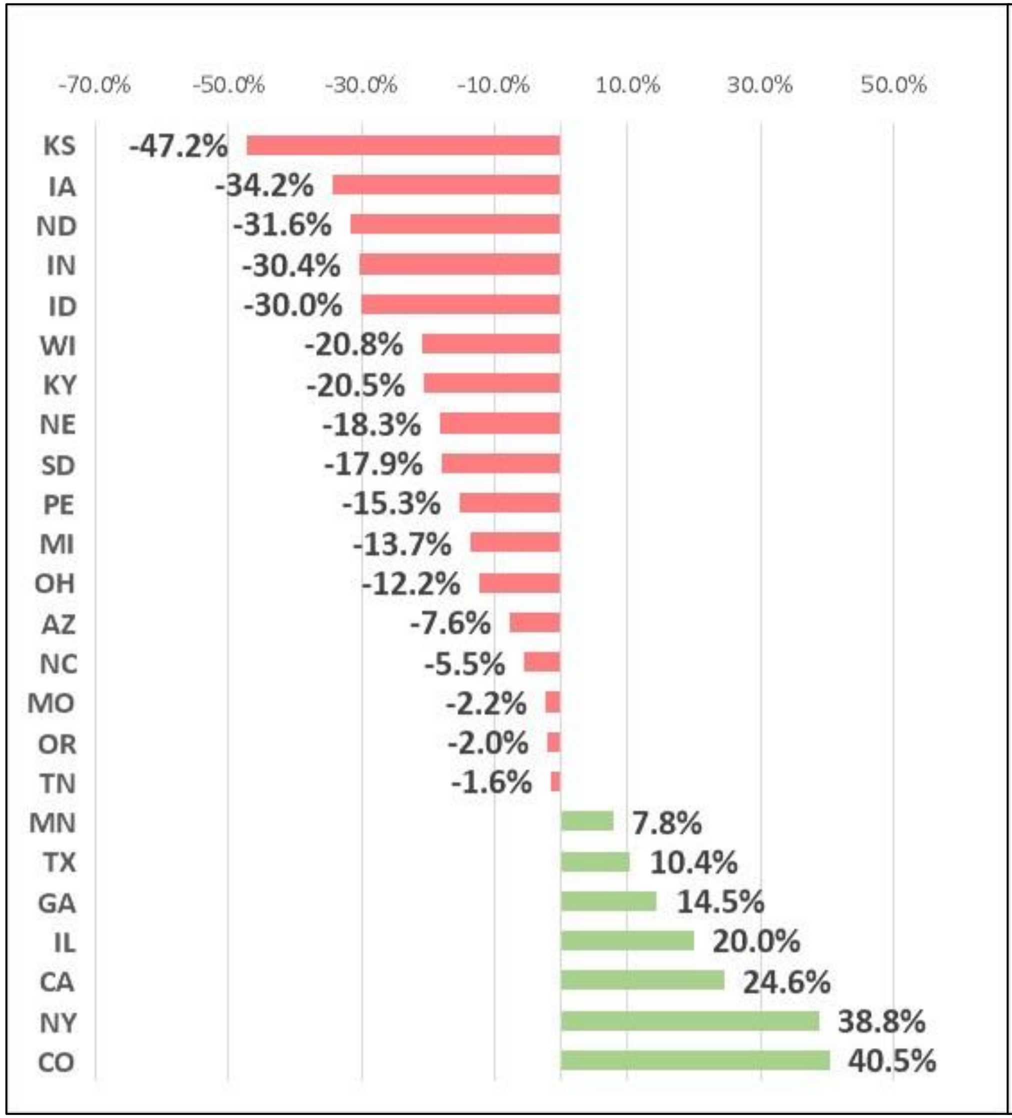
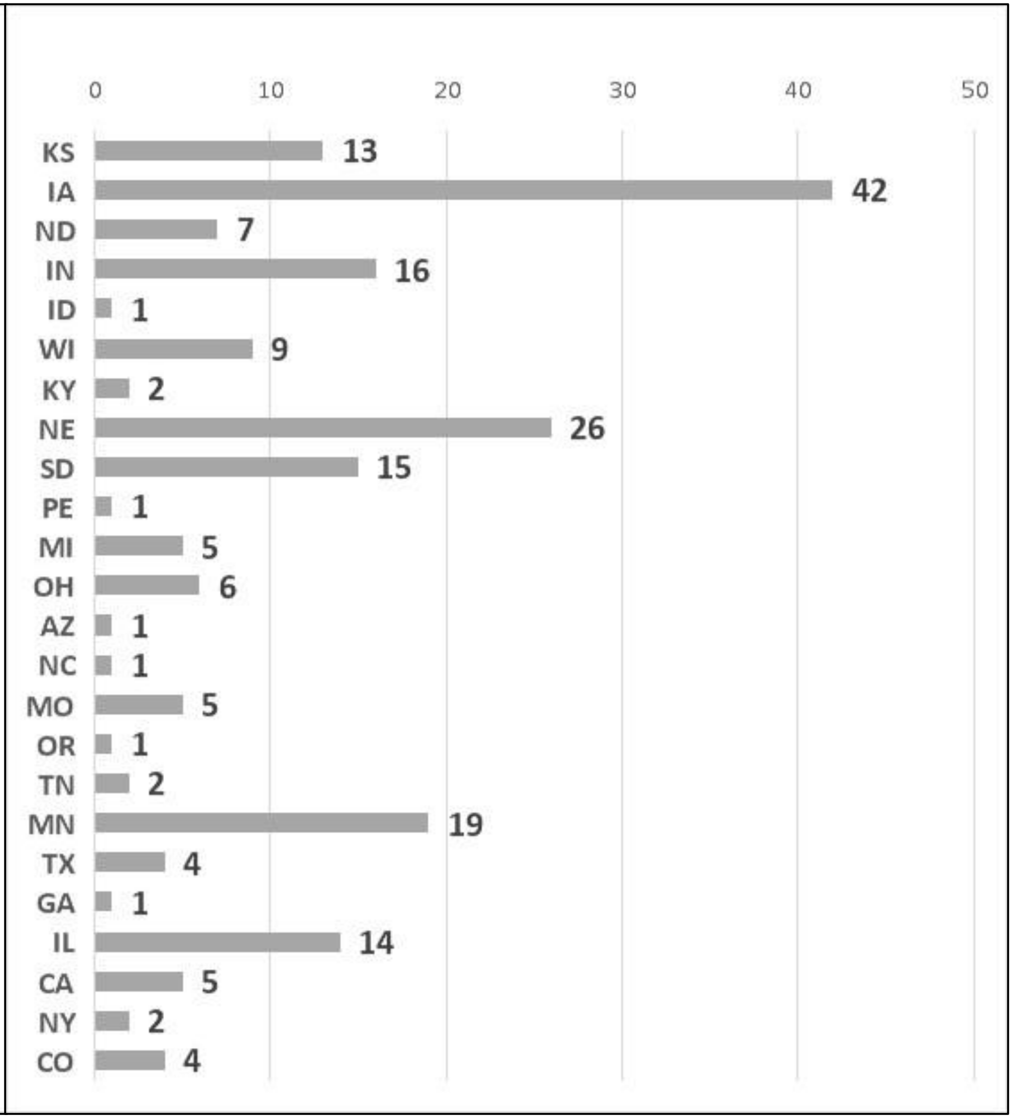
College graduate retention





The left-hand chart shows rate of college graduate retention (or loss) by state.

The right-hand chart shows the number of ethanol plants each state.

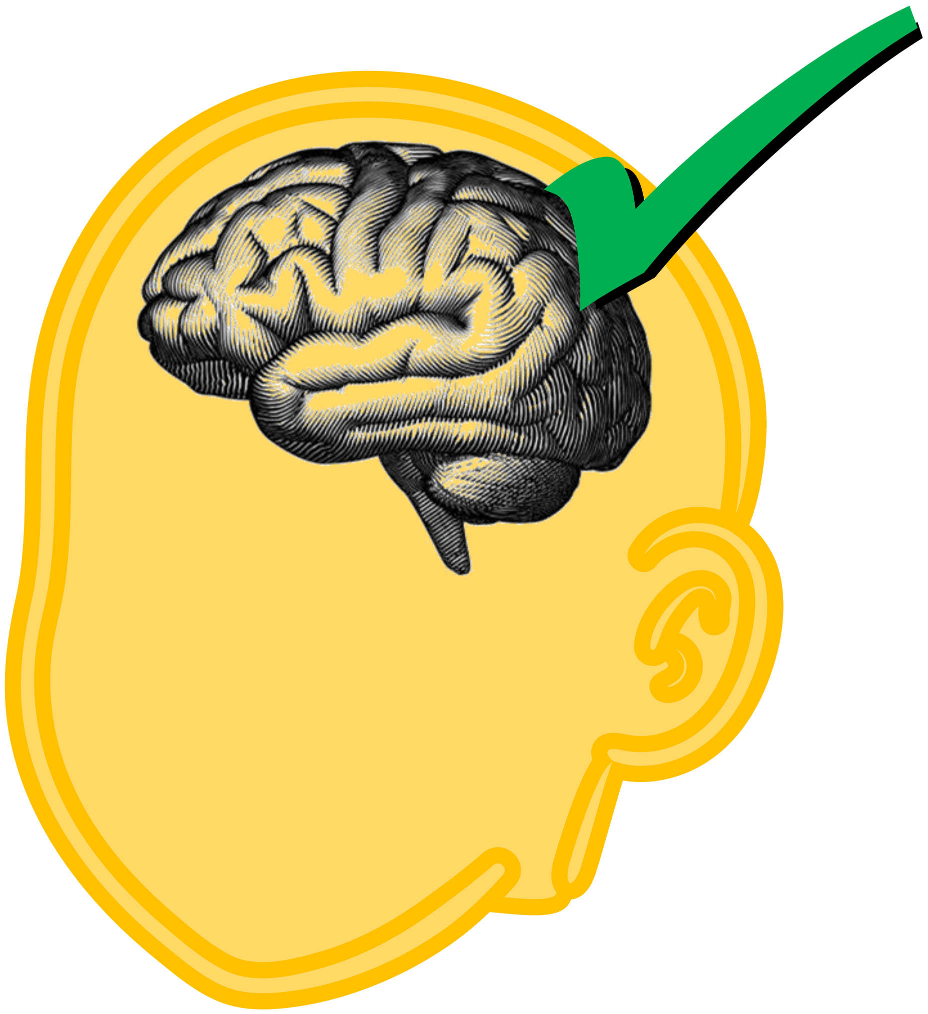
(Only states with ethanol plants are listed.)

Newton Enterprises, Inc. analysis of raw data from the Renewable Fuels Association (plants by state) and *The Washington* Post (college graduate statistics)

Need to grow industry skills

Industry challenges:

- ***Product diversification requires a "bigger brain"***
- ***Look into those future methods and plan for new instruments, new tests, new skills today***
- ***Get ahead of the learning curve!***



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