Isobutanol

Glenn Johnston

September 26th, 2017 Scottsdale, AZ

Western Weights and Measures Association 60th Annual Technical Conference

Gevo's Current Business System

Gevo Production Facilities

Isobutanol Production – Side-by-Side with Ethanol

Isobutanol

Hydrocarbon Biorefinery

Isobutanol

Hydrocarbons

Core Near Term Markets

Drop-in Markets - Isobutanol

Specialty Chemicals & Solvents

Specialty Gasoline Blendstock (Marine/Off-Road)

Drop-in Markets - Hydrocarbons

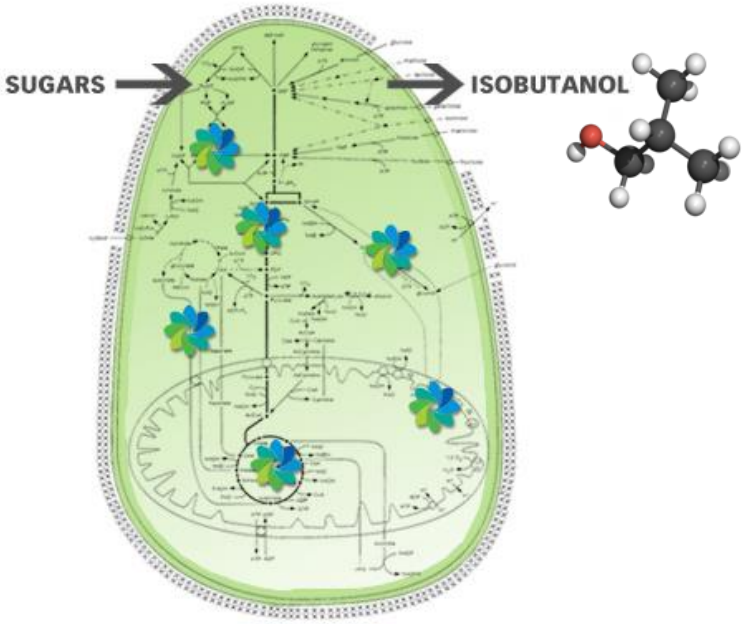
Jet Fuel

Isooctane (gasoline)

Production

Technology Based on Metabolic Engineering

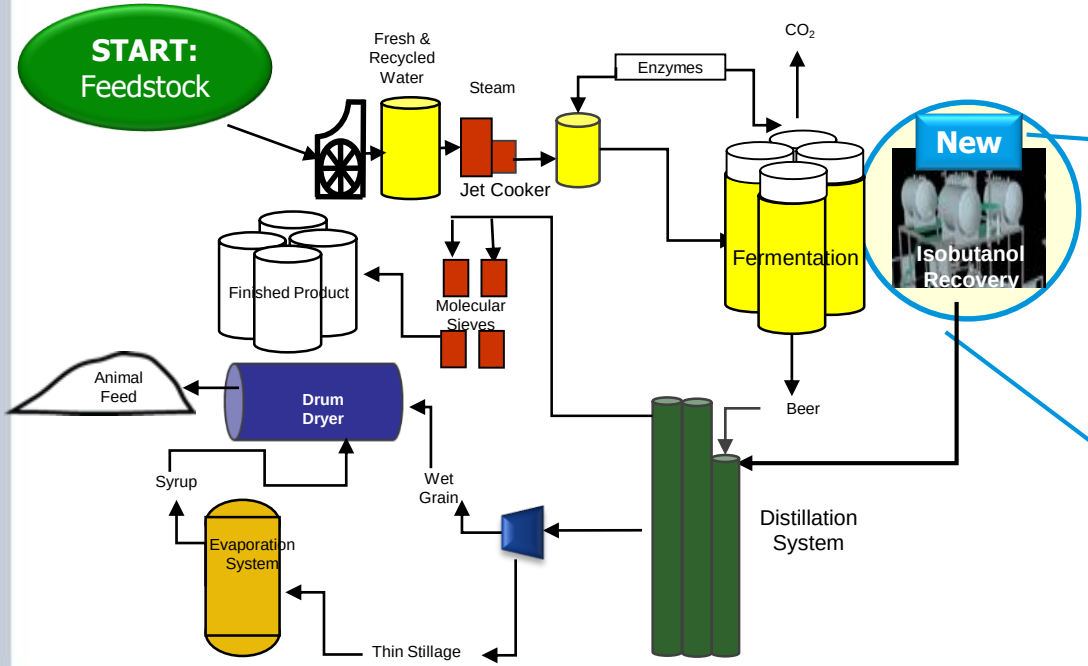
- Proprietary yeast biocatalyst converts sugars (carbohydrates) to isobutanol
- Combination of biotechnology and process technology leads to competitive position

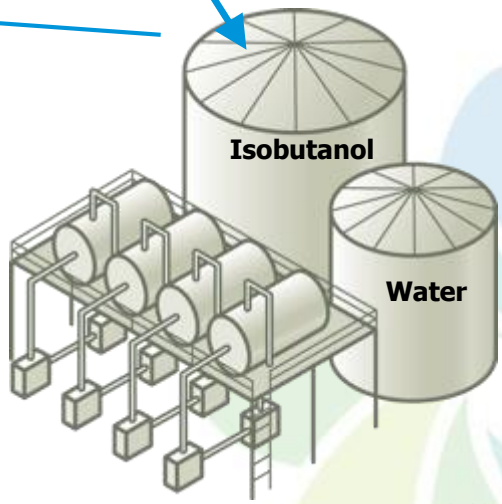


How We Produce Isobutanol (GIFT®)

- Our patented Gevo Integrated Fermentation Technology® (GIFT®) continually separates isobutanol during fermentation

Standard Fermentation Process





Commercial Isobutanol/Ethanol Plant in Luverne, MN

Agri-Energy

Statistics

- First commercial scale renewable isobutanol plant in the world
- Purchased in 2010 & 100% owned by Gevo
- World-scale chemicals plant

Commissioning timeline

Date	Event
September 2010	Purchased Luverne plant
Sep.-May 2013	Revamped plant and procedures to address contamination issues
May – Sep. 2013	Tested new systems and procedures Made minor system and hardware upgrades
May 2014 – Present	Running in side-by-side mode to better handle water and solids. Improves operability of plant, and simplifies IBA production. Approaching production rates of 75-100,000 gallons per month.

	gevo Luverne Facility	Typical Specialty Chemical Plant
Feedstock	Carbohydrates-based	Petroleum-based
Expected Production	100 MM lbs per year of Isobutanol/Ethanol 100 MM lbs per of year of animal feed	50-175 MM lbs per year(1)

(1) Derived from a sample of 10 operating specialty chemical plants producing chemicals such as Methyl Amines, Dimethyl Formamide, EPVC, Phenol Acetone, Formaldehyde, Polyamides and Methanol

Source: International Process Plants, EIA

Isobutanol Gasoline Blendstock

Oxygenate Properties

	Ethanol	Isobutanol
Chemical Formula	C_2H_6O	$C_4H_{10}O$
Blend Octane	110-120 Gasoline component dependent	103.5
Blend Vapor Pressure, psi	18-22	4.5-5.5
Boiling Point, °F	173	226
Specific Gravity @ 20°C	0.794	0.802
Water Solubility @ 20°C	100% Miscible	8.7%
Energy , % of gasoline	65-70	82
Viscosity @20°C, cSt	1.5	8.3

ASTM Specification Comparison

	Test Method	ASTM Limit	Denatured Ethanol (D4806)	Isobutanol (D7862)
API Gr @ 60°F	D1298	NA	46.4	44.0
KF H_20, vol%	E1064	1.0 (max)	0.969	0.114
Gums, mg/100mL	D381	5.0 (max)	<0.5	<0.5
Purity, vol%	**D5501** **D7862, Annex A1**	92.1 (min) 96.0 (min)	96.5	*98.0+
Vapor Pressure, psi Blend Vapor Pressure, psi	D5191	NA	2.87 18-22	0.47 4.5-5.5
Inorganic Chloride, mg/kg	D7328 / D7319	DNE=10 max ISOB=8 max	<0.1	<0.1
Sulfur, ppm	D7039	30 (max)	2.7	1.4
Total Sulfate, mg/kg	D7328 / D7319	4.0	0.1	0.7

Isobutanol Gasoline Blend Properties

	Gasoline	Ethanol	Isobutanol
RON	95	107.4	105.1
MON	85	88.2	89.3
RVP (psi)	7-15	19	5.2
Density 20C [kg/m3]	720-775	794	801
Boiling Point (C)	32.2	21.1	26.6
% Heating Value of Gasoline	100	66	84
Water Solubility	<0.1	Fully Miscible	<7.6
Oxygen (%w/w)	<2.7%	34.7	21.6

Blend Oxygen % Comparison

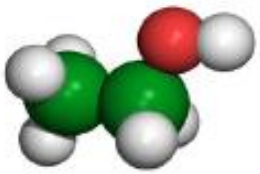
Wt % Oxygen	Ethanol % of Blend	Isobutanol % of Blend
2.7	5.7	12.5
3.5	10.0	16.1
5.2	15.0	24.0
Ethanol is 35 wt% oxygen and Isobutanol is 22 wt% oxygen		

US EPA Renewable Fuel Standard (RFS2)

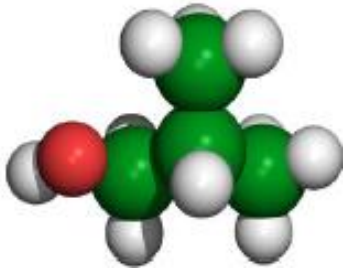
- Refinery can produce finished products, with a renewable content that helps them meet their RVO.
- "Blend Wall" issue is mitigated with increased RIN-gallon generation rate
- Non-closed loop engine manufacturers have more latitude to accept the gasoline produced

	Volume in Gasoline	Oxygen Content	RIN-gallons per 100 gallons finished product
E10	10.0%	3.5%	10.00
E15	15.0%	5.2%	15.00
Isobutanol (Substantially similar gasoline)	12.5%	2.7%	16.25
Isobutanol (Octamix or DuPont Waiver)	16.1%	3.5%	20.93
Isobutanol (Waiver to match E15 oxygen content)	24.3%	5.2%	31.39

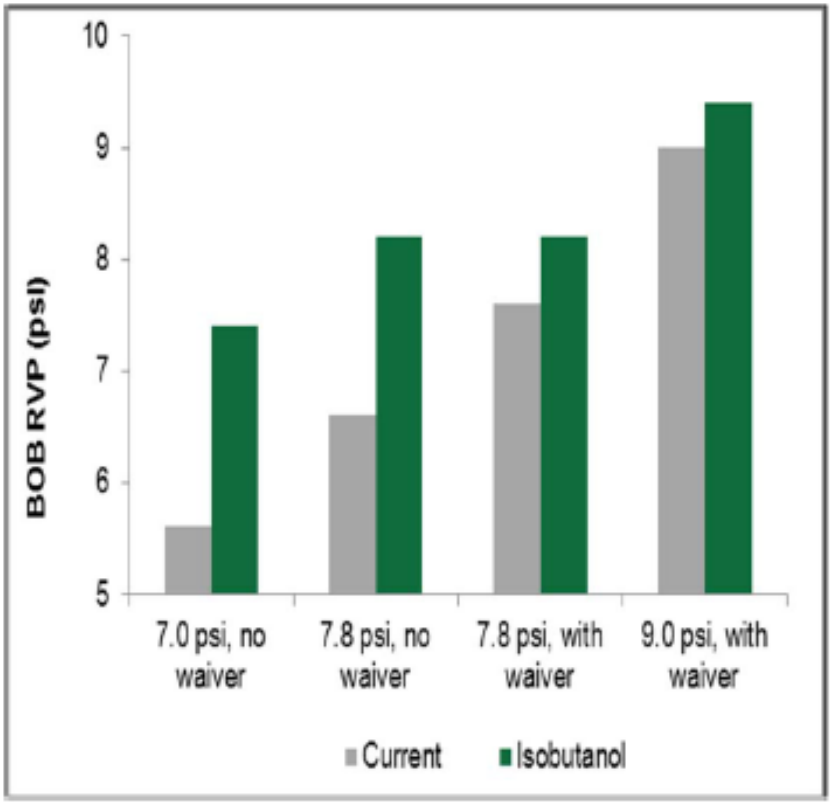
Ethanol Molecule
(34.8% oxygen)



Isobutanol Molecule
(21.6% oxygen)



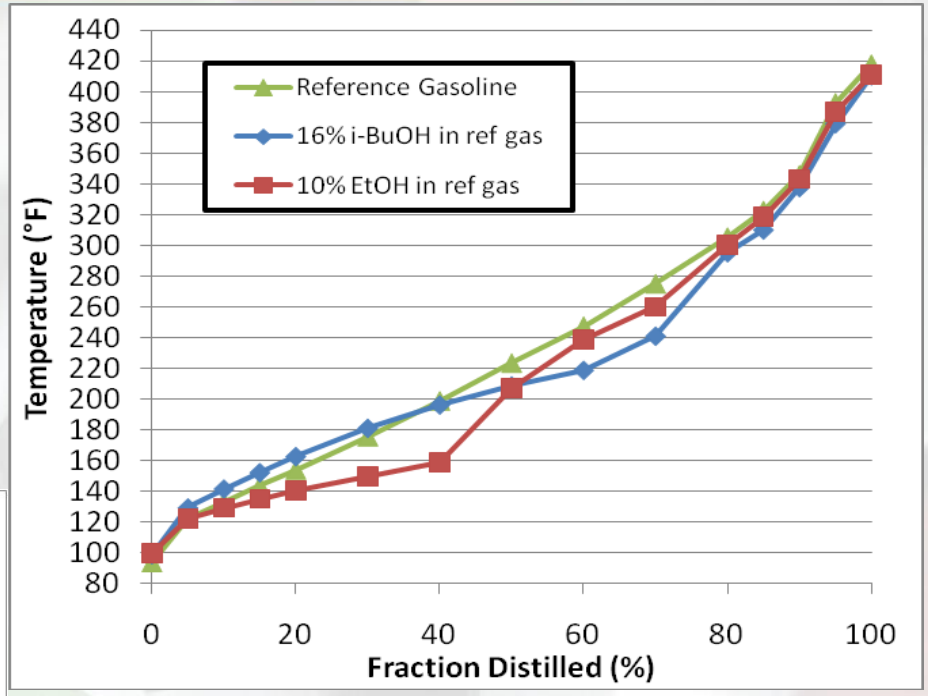
Low Blending Volatility

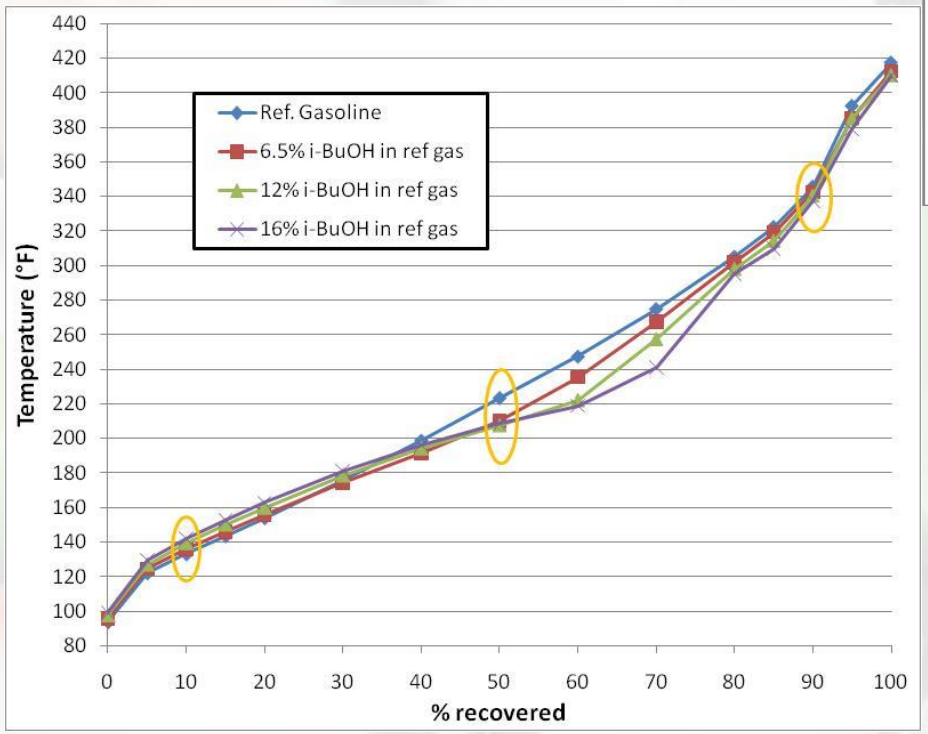


- Isobutanol benefits the blending of low cost feedstocks.
- Isobutanol's value to the refiner increases as RVP decreases
- Future gasoline volatility may be lowered do to the current 70 ppb ozone standard reduction from 75 ppb.
- Using isobutanol may mitigate expensive operations refinery upgrades

Gasoline Blendstock

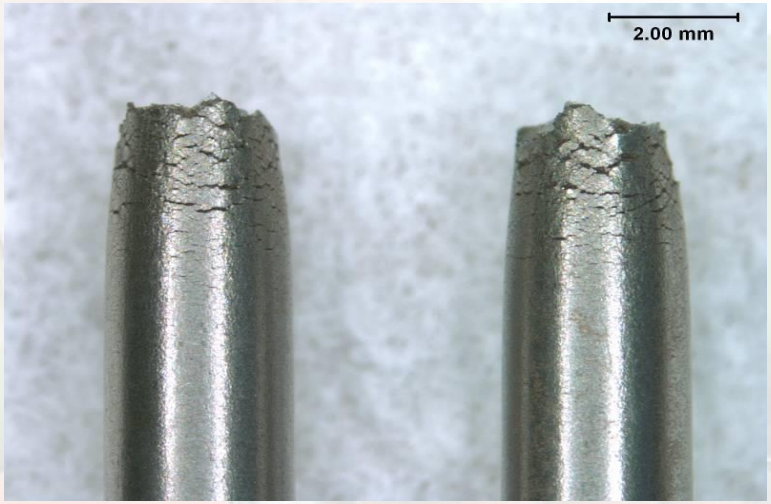
- Isobutanol due to its chemistry can be blended at refineries and shipped via current pipeline infrastructure.
- Isobutanol has low RVP, enabling refiners to blend incremental volumes of butanes and pentanes



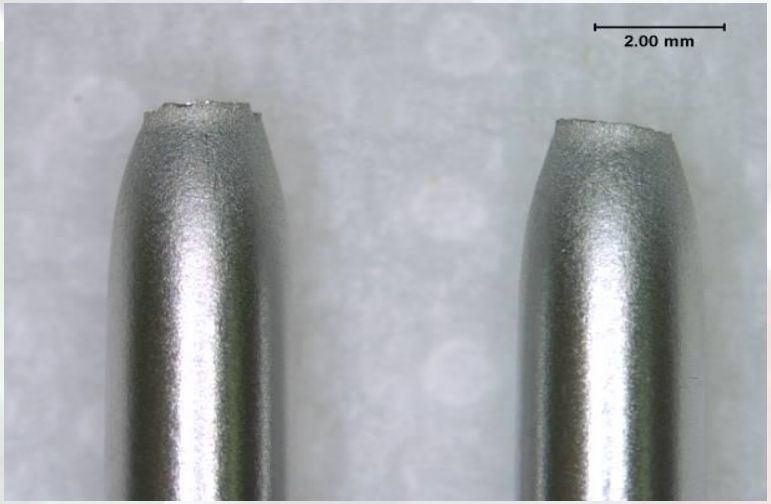


Corrosion

- SCC susceptibility was measured using the slow strain rate test (SSRT)
- No SCC was noted on the SSRT samples tested in isobutanol-gasoline blends at concentrations of 12.5%, 50% as well as in the pure isobutanol solution.
- Work completed by DET NORSKE VERITAS and paper given at NACE March 2011.



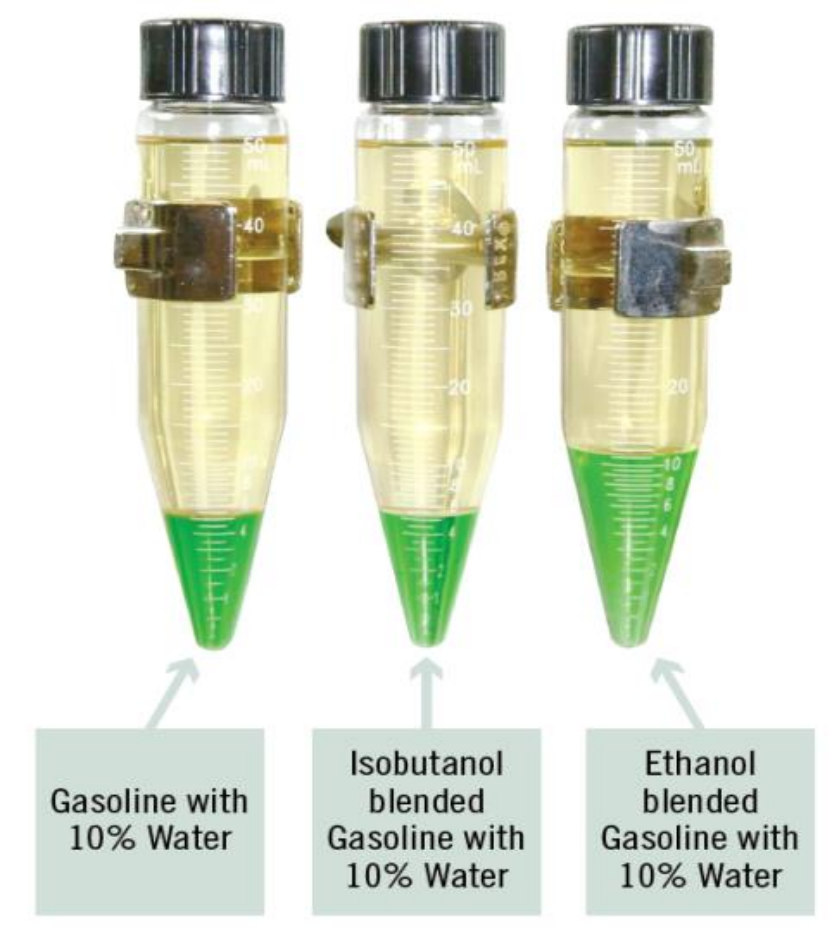
Example Stress Corrosion Cracking (SCC)



No Stress Corrosion Cracking (SCC) (12.5% Isobutanol)

Corrosion

- If you have water inclusion into your fuel system, soluble alcohol with water will separate into the water layer and potentially cause increased corrosion outside the hydrocarbon phase.
- Temperature has a great affect on corrosion – the higher the temperature the more corrosion.
- Corrosion inhibitors show impact (in some cases inhibition, in others acceleration)



Water Tolerance

- ETOH and H_20 are 100% miscible
- If you have water in your system the loss of ethanol from the hydrocarbon phase can lead to loss of Octane in the hydrocarbon phase.
- Loss of ETOH and Octane 3-4#s
- Isobutanol stays in hydrocarbon and does not lose octane.

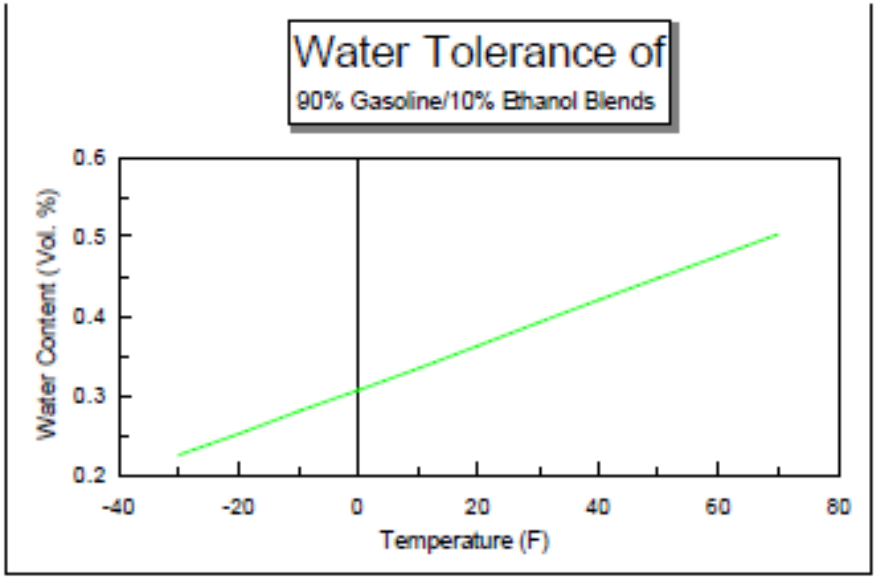
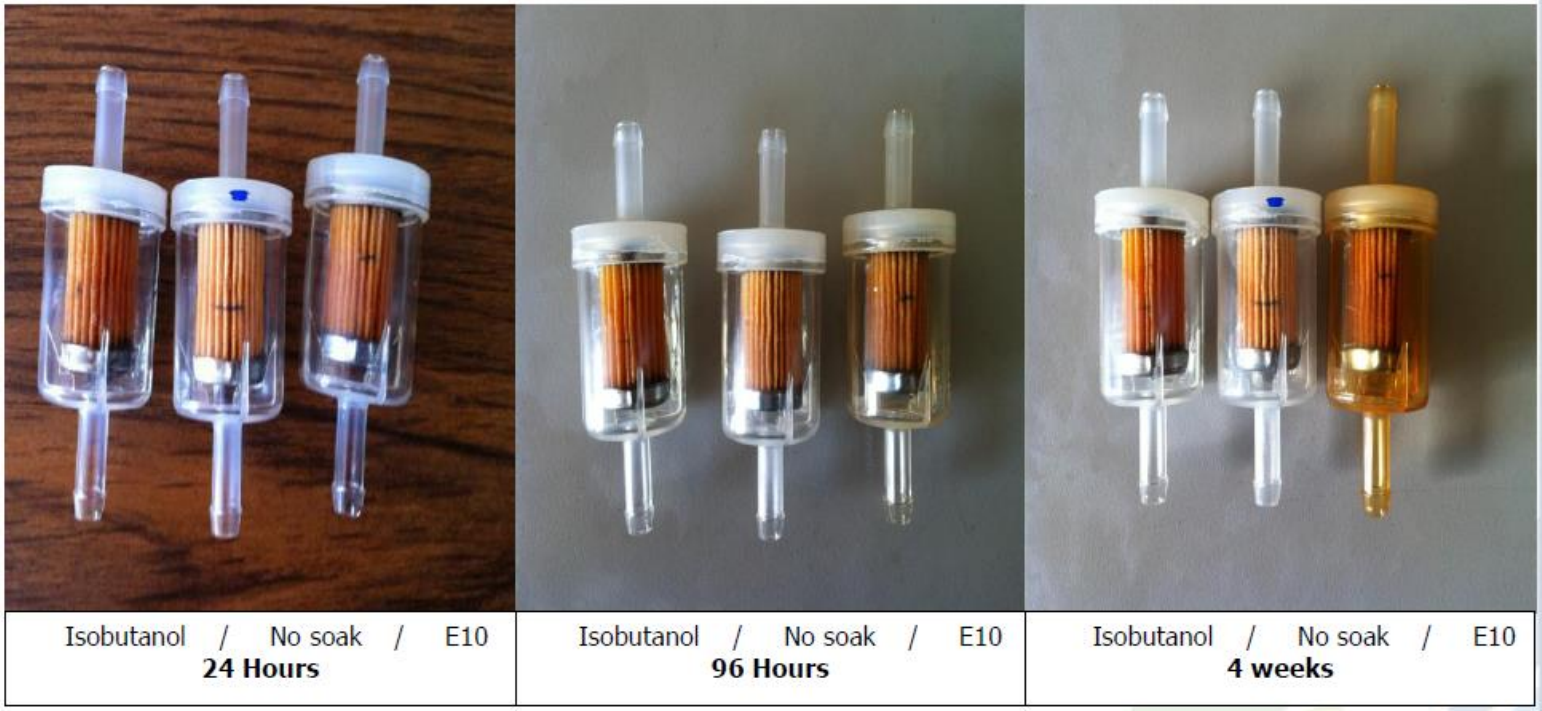


Figure 1

Briggs and Stratton Testing

- 30 unique intake component materials were tested



Isobutanol / No soak / E10 **24 Hours**	Isobutanol / No soak / E10 **96 Hours**	Isobutanol / No soak / E10 **4 weeks**

- Briggs & Stratton engines exhibited no issues while running on Isobutanol fuel blends. "No issues have been uncovered that would suggest the fuel could not be approved for use in our engines."

Cole-Parmer Chemical Compatibility Metals and Carbon Materials

Material	1-Butanol	Ethanol	Gasoline High Aromatic	Gasoline Unleaded	Isobutanol
304 Stainless Steel	A	A	A	A	A
316 Stainless Steel	A	A	A	A	A
Aluminum	B	B	D	A	B
Brass	A	A	N/A	N/A	N/A
Bronze	A	A	A	A	A
Carbon Graphite	A	A	A	A	A
Carbon Steel	B	B	N/A	B	B
Carpenter 20 Steel	A	A	A	A	A
Cast Iron	B	B	A	A	C
Copper	A	A	N/A	B	N/A
Hastelloy - Cr	A	A	A	A	A
Titanium	A	A	B	A	B

Ratings – Chemical Effect:

A – Excellent

B – Good – minor effect, slight corrosion or discoloration

C – Fair – moderate effect, not recommended for continuous use

D – Severe effect, not recommended for any use

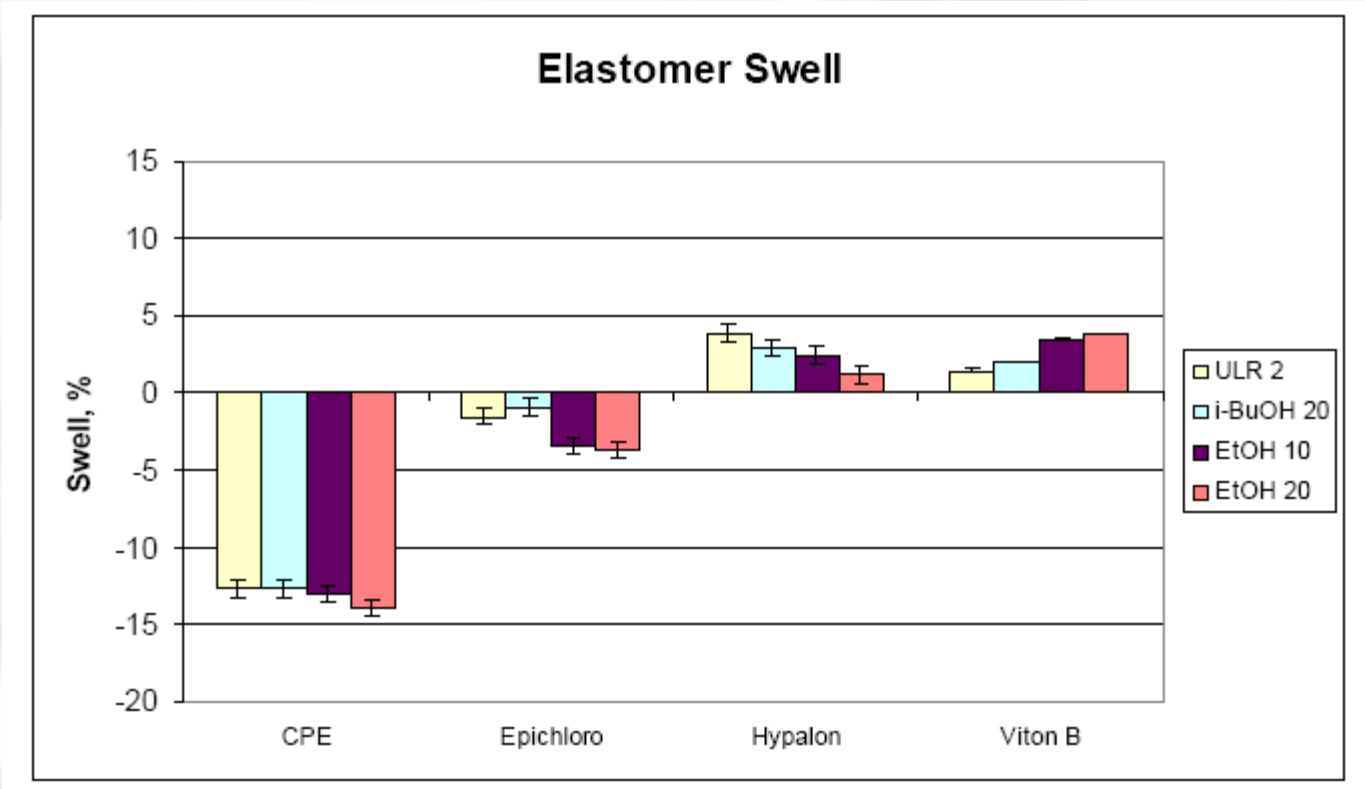
N/A – Information not available

Cole-Parmer Instrument Company
Vernon Hills, IL 60061
www.coleparmer.com

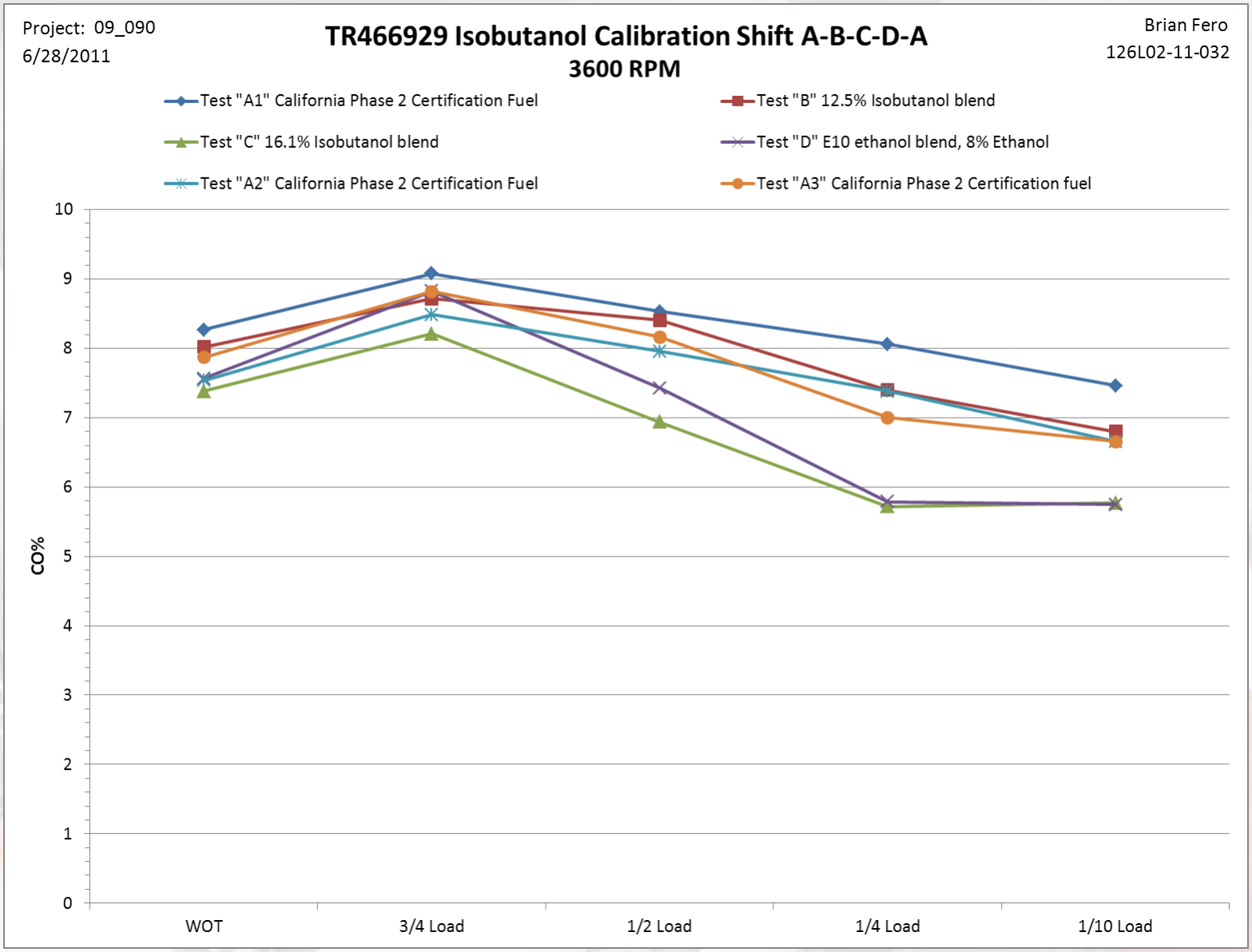
Materials Compatibility Literature

- Published by elastomer, pump, and engineering companies including:
  - Parker Hannifin Corporation
  - eFunda, Inc. – on-line engineering tools and databases
  - Cole-Parmer, Inc.
  - Others including Wilden Pump and Engineering Company, Cat Pumps, Precision Polymer Engineering, etc.
- Additional literature:
  - Parker O-Ring Handbook 2007 (most comprehensive review of elastomer issues)
  - Wilden Chemical Resistance Guide 2005
  - Cat Pumps Chemical Compatibility Guide
  - A Technical Guide to Elastomer Compounds and Chemical Compatiblity, Precison Polymer Engineering, Ltd. (a very comprehensive review of issues and a guide)
  - Fuel Quality Services Presentation on fuel compatibility with fuel storage and distribution equipment

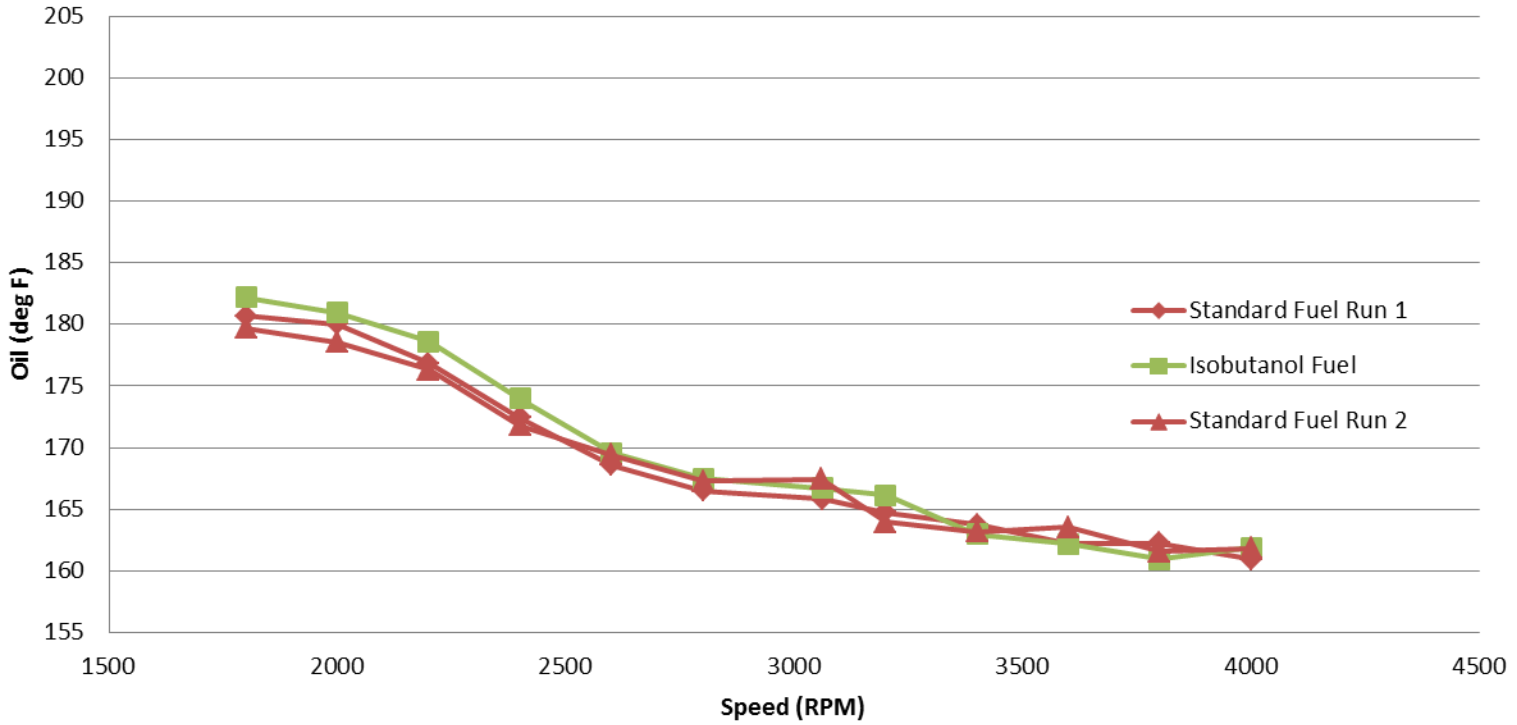
Elastomer Data



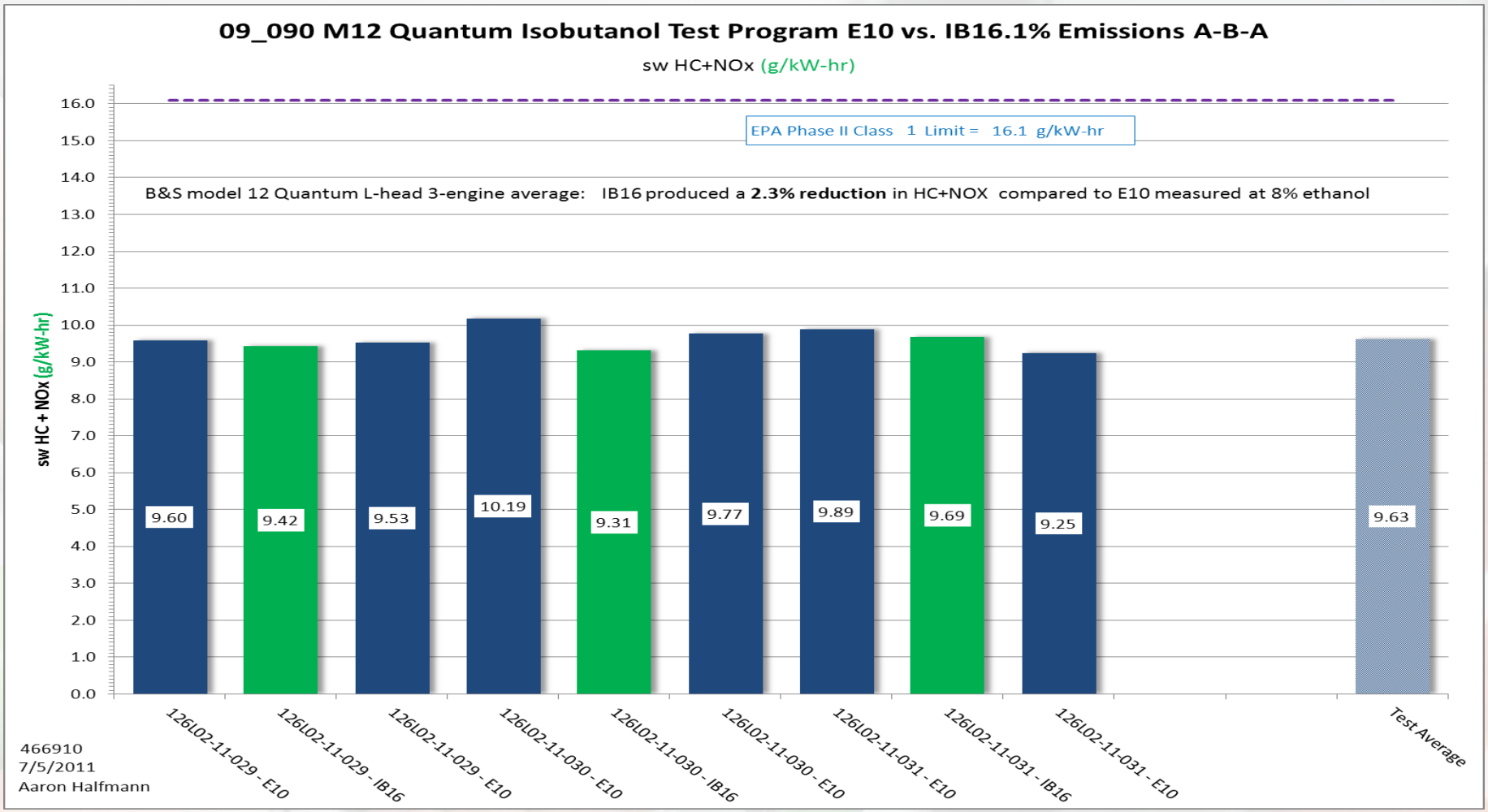
Small Engine Data – Emissions 2012



Small Engine Temperatures



Small Engine Emissions



Vehicle Testing Completed on Isobutanol

- Testing has been completed through various OEMs and Universities through out the globe.
- A reference list on testing was established to support the ASTM ballot. A small excerpt from the list is included below.
  - "Vehicle Emissions and Fuel Economy Effects of 16% Butanol and Various Ethanol Blended Fuels (E10, E20, and E85)", Melissa Schulz and Shaleen Clark - General Motors Powertrain, Journal of ASTM International, Vol. 8, No. 2 Paper ID JAI103068.
  - Baustian, J. and Wolf, L., "Cold-Start/Warm-Up Vehicle Performance and Driveability Index for Gasolines Containing Isobutanol," SAE Technical Paper 2012-01-1741, 2012, doi:10.4271/2012-01-1741.
  - Stansfield, P., Bisordi, A., OudeNijeweme, D., Williams, J. et al., "The Performance of a Modern Vehicle on a Variety of Alcohol-Gasoline Fuel Blends," *SAE Int. J. Fuels Lubr.* 5(2):813-822, 2012, doi:10.4271/2012-01-1272.
  - Bata, R., Elrod, A., and Lewandowskia, T., "Butanol as a Blending Agent with Gasoline for I. C. Engines," SAE Technical Paper 890434, 1989, doi:10.4271/890434.

Regulatory Status

40 CFR Part 79

- Gevo has registered its isobutanol as a fuel/fuel additive with US EPA under part 79.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OCT - 6 2010

OFFICE OF
AIR AND RADIATION

Gevo Inc.
Mr. Glenn Johnston
Vice President of Regulatory Affairs
345 Inverness Drive South
Building C, Suite 310
Englewood, CO 80112

Dear Mr. Johnston:

Pursuant to your September 15, 2010 notification, the following fuel additive has been registered per 40 CFR 79.23 (our internal identification number precedes the name):

252620001 Isobutanol

Note that per 40 CFR 79.21(f) you would be required to notify us in writing if certain information in your notification were to change. In addition, note, that with your notification, you have provided assurances that you will not represent, directly or indirectly, in any notice, circular, letter, or other written communication, or any written, oral or pictorial notice or other announcement in any publication or by radio or television, that registration constitutes endorsement, certification, or approval by any agency of the United States.

40 CFR Part 80

- Gevo has a completed pathway under the Renewable Fuel Standard and has completed the 3rd party engineering review and has booked RINs for renewable isobutanol on the EMTS system.
- Isobutanol due to its energy density receives 1.3 RINs per gallon.

ASTM D7862

-Created a Task Group at ASTM in D02.AO in spring of 2010

- Multiple teleconferences and face to face meetings to develop a ballot.
- First Ballot Spring 2012
  - Status - Withdrawn
- Second Ballot Fall 2012
  - Status – Withdrawn
- Third Ballot D02 Concurrent Spring 2013 (April 2013)
  - Status - Passed
  - Note – Negatives withdrawn based on follow on ballot.
- Fourth Ballot D02 Concurrent Spring 2013 (May 2013)
  - Status – Passed

Created/updated two ASTM analytical methods-

-D7319 Test Method for Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol by Direct Injection Suppressed Ion Chromatography.

-D7875 Test Method for Determination of Butanol and Acetone Content of Butanol for Blending with Gasoline by Gas Chromatography.

ASTM D7862

- Standard Specification for Butanol for Blending with Gasoline for Use as Automotive Spark-Ignition Engine Fuel
- Currently covers three isomers of butanol (isobutanol, n-butanol, and sec-butanol)

Designation: D7862 – 13

Standard Specification for Butanol for Blending with Gasoline for Use as Automotive Spark-Ignition Engine Fuel[1]

TABLE 1 Requirements

Property	Limit	Method
Butanol, volume %, min	96.0	Annex A1
1-butanol, volume %	Report	Annex A1
2-butanol, volume %	Report	Annex A1
2-methyl 1-propanol, volume %	Report	Annex A1
Methanol, volume % max	0.4	Annex A1
Water content, volume %, max	1.0	E203 or E1064
Acidity (as acetic acid CH_3COOH), mass % (mg/L), max	0.007 (56)	D1613
Inorganic Chloride, mg/kg (mg/L), max	8 (6)	D7319
Solvent-washed gum, mg/100 mL, max	5.0	D381
Sulfur, mg/kg, max	30.	D2622, D5453
Existant sulfate, mg/kg, max	4	D7319

RFG/Isobutanol and Complex Model

Back in 2011 the following wording was included in the Federal Register on the update to 40 CFR Part 80 "Regulation To Mitigate the Misfueling of Vehicles and Engines With Gasoline Containing Greater Than Ten Volume Percent Ethanol and Modifications to the Reformulated and Conventional Gasoline Programs; Final Rule" (Reference Federal Register / Vol. 76, No. 142 / Monday, July 25, 2011/Page 44430-44431)

We proposed modifying the Complex Model only for the increased level of oxygen associated with E15. Two commenters suggested that the modification not be limited only to ethanol but to all renewable fuels and fuel additives that supply oxygen up to the new 5.8 wt% level. We believe that this comment has merit, since the Complex Model treats the parameter of oxygen independently of the oxygenate which supplies it. In other words, the model was developed using fuel oxygen level as an input independent of which oxygenate contributed the oxygen. In addition, we believe that the increased use of any oxygenate in the range of 4.0 wt% to 5.8 wt% would have effects on VOC emissions that are similar directionally to those of increased ethanol use in that range. Thus, we agree with the commenters that it is not necessary to limit the higher levels of oxygen in fuel (i.e. above 4.0 up to 5.8 wt%) only to ethanol for purposes of modifications to the Complex Model. **We will therefore modify the regulations to allow the Complex Model to be run for fuels containing oxygen levels up to 5.8 wt% from any oxygenate.**

RFG/Isobutanol

- Per 40 CFR 80.69(a)(10) more than one type of oxygenate may be specified on the RBOB product transfer documentation (PDT).

- 6.4-10.0 psi RVP acceptable range at 40 CFR 80.45(f)(1)(i) is a requirement for reformulated gasoline (RFG)

RFG Clarification – US EPA

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
NATIONAL VEHICLE AND FUEL EMISSIONS LABORATORY
2565 PLYMOUTH ROAD
ANN ARBOR, MICHIGAN 48105-2498

June 30, 2016

OFFICE OF
AIR AND RADIATION

Mr. Glenn Johnston
Executive Vice President Regulatory Affairs
Gevo, Inc.
345 Iverness Drive South
Building C, Suite 310
Englewood, Colorado 80112

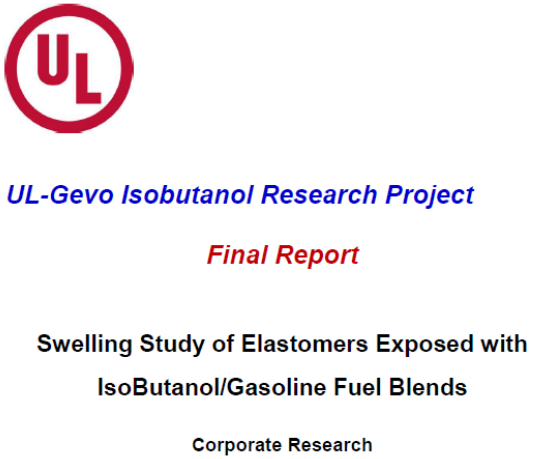
Dear Mr. Johnston,

Thank you for your inquiry and recent discussions with us concerning the use of isobutanol in reformulated gasoline (RFG). For an oxygenate blender to produce RFG by blending isobutanol with reformulated gasoline blend stock for oxygenate blending (RBOB), the refiner or importer of the RBOB must comply with the requirements of 40 CFR 80.69, including the requirement that the product transfer document (PTD) accompanying the RBOB state that the RBOB will become RFG upon the addition of isobutanol at a specified percentage of isobutanol.

The oxygenate blender must also comply with the requirements under section 211(f) of the Clean Air Act when it blends isobutanol into the RBOB to make the RFG. As relevant for isobutanol, the oxygenate blender may blend isobutanol to produce gasoline at up to 2.7 percent oxygen by weight. See "substantially similar" interpretive rule (73 FR 22277, April 25, 2008). Alternatively, the oxygenate blender may blend isobutanol to produce gasoline at up to 3.7 percent oxygen by weight under the "Octamix" waiver (77 FR 66074, November 1, 2012), as long as the oxygenate blender also complies with all other conditions of the waiver such as the need for a specified corrosion inhibitor.

UL Position of Isobutanol-Gasoline Blends

- 2012 Gevo commissioned on a study with UL
- A total of fifteen commercial elastomers were selected to investigate compatibility with isobutanol-gasoline fuel blends.
  - *Natural Rubber, Silicone Rubber,*
  - *Styrene-Butadiene Rubber (SBR), Neoprene,*
  - *Nitrile Butadiene Rubber, (NBR)-impregnated*
  - *Cork, Polyurethane, five individual NBR*
  - *compounds, Epichlorohydrin-impregnated Cork,*
  - *Fluorosilicone and two Fluorocarbons (Viton© A410C and Viton© B601C).*



- Isobutanol/Gasoline blends 16% will not require special investigation by UL if they have been listed for use with applicable UL standards including fuel dispensing equipment listed to UL 87A
- In anticipation of the changes to ASTM specifications UL initiated a technical review of isobutanol fuel and conducted extensive material testing using isobutanol. The findings indicated no adverse safety effects.

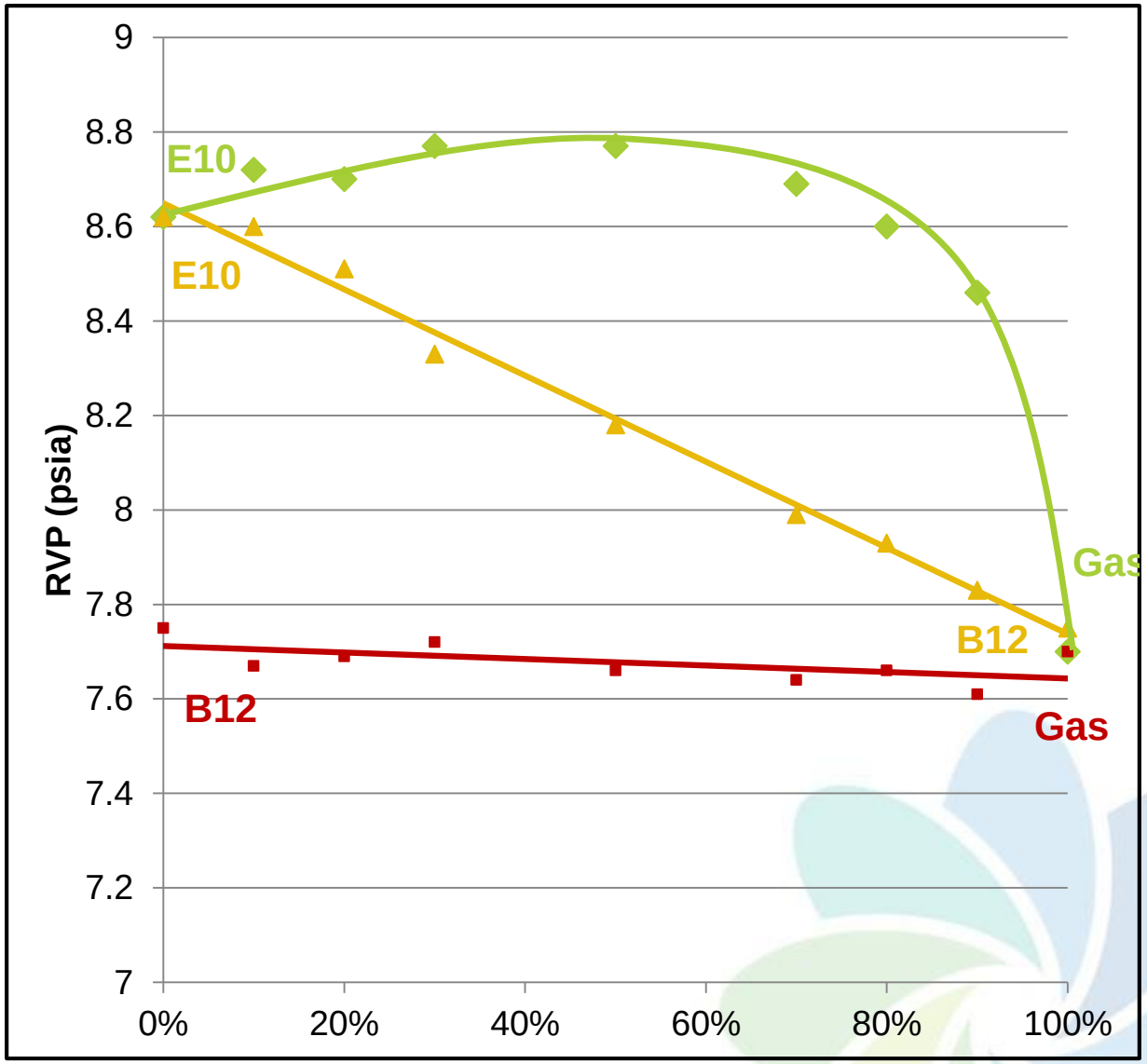
http://industries.ul.com/wpcontent/uploads/sites/2/2015/01/Isobutanol.pd

Co-Blending Fuels in a Market with E10 Waiver

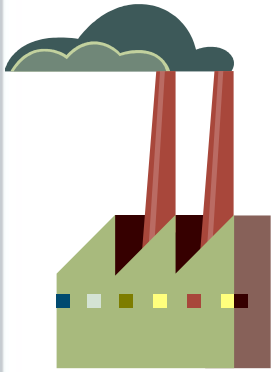
- Co-Blends of 3 base fuels
- E10 (target <8.8 psi)
- Gasoline (target <7.8 psi)
- iB12.5 (target <7.8 psi)

- Linear relationship for either fuel blended with isobutanol blend
- Very nonlinear relationship for E10 blended with gasoline

- Any co-mixing of E10 with any other fuel will likely be out of spec



Supply Chain Dynamics - 1 lb Wavier



Refiner

BOB, Clear

Ethanol
Or Isobutanol

E10 Part 79 Fuel
or B12.5 Part 79 Fuel

Service Station
Retail Outle

Federal Register June 14, 2013
Discussed allowing for commingling of compliant products at the retail facility level. – Currently not legal

US EPA tests RVP according to ASTM D5191

Pass RVP Spec

Yes

Legal Gasoline

No

Determine alcohol content
ASTM D5599 or D4815

EtOH 9-10%?

No

Unregistered Gasoline

Yes

Legal Gasoline

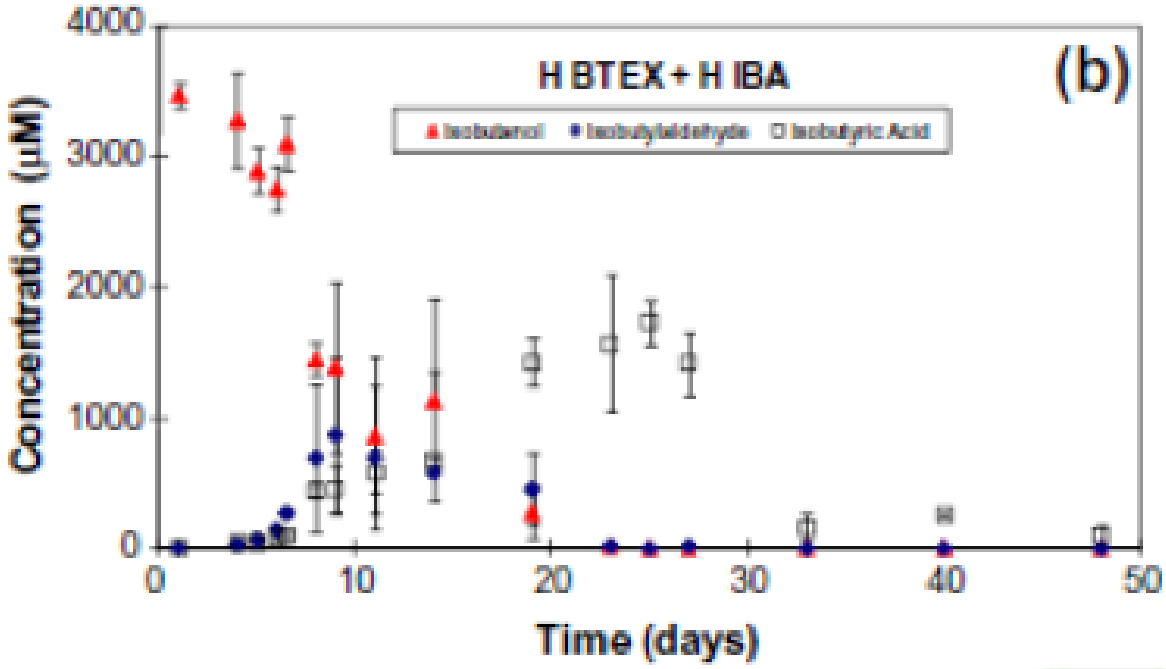
Other Property Data

Toxicology Information

- Biodegradation
  - Isobutanol is readily biodegradable under aerobic conditions. Multiple references also indicate Isobutanol's biodegradable under anaerobic conditions
- Food Usage
  - Is used as a flavouring agent in butter, cola, fruit, liquor, rum, and whisky.
  - Natural isobutanol is produced by the fermentation of carbohydrates. It is found in brandy, cider, gin, coffee, cherries, raspberries, blackberries, grapes, apples, hop oil, bread, and Cheddar cheese.
- Reference's
  - Journal of Chemical Technology and Biotechnology, Use of Anaerobic Hybrid Reactors for Treatment of Organic Solvents. 1996.
  - Biodegradability Prediction, Development of structure biodegradability relationships for estimating half-lives of organic contaminants in soil systems, 1996.

Biodegradation in Soil

- Isobutanol degrades relatively quickly under both aerobic and anaerobic conditions; metabolites also degrade quickly
- Reduced inhibition of BTEX degradation
- Published -Chemosphere (October 2010)



Odor thresholds

Odor Thresholds	Detect (ppm)	Recognize (ppm)
Conventional Gasoline	0.94	1.24
Butanol-10	0.66	0.86
Ethanol-10	0.34	0.50

Fire Safety

Product	Flashpoint	Autoignition Temp	Water Solubility	Explosive Limits (vol % in air) UEL/LEL
Isobutanol	28°C (82°F)	415°C (779°F)	Insoluble	1.7-10.9
Ethanol	12.8°C (55°F)	365°C (689°F)	Soluble	3.3-19
Gasoline	-40°C (-40°F)	246°C (475°F)	Insoluble	1.4-7.6

Marine Information

Marine Research Overview

18' Mako boat with 175 HP Evinrude GDI Outboard

24' SeaDoo Challenger boat with 215 HP Rotax engine

Volvo-Penta 5.7 Closed-loop catalyst – Almar Boat

1999 OMC Johnson Conventional Carbureted 2-stroke Intruder Boat

Indmar 6.0L Closed-loop catalyst – Malibu Ski Boat

150 HP Yamaha on Century Boat

Marine Test Fuels

Fuel grade ethanol and fuel grade isobutanol were blended with a base stock for oxygenate blending (BOB) to simulate a final test fuel representative of what would be available at a marine pump

Table 3. Fuel Specifications

			indolene EEE	E10	iB16
Density	ASTM D4052	kg/L	0.743	0.7397	0.7489
RVP	ASTM D5191	psi	9.1	8.81	7.97
Carbon	ASTM E191	wt%	86.31	82.916	83
Hydrogen	ASTM E191	wt%	13.34	13.094	12.998
Oxygen		wt%	0	3.99	4.002
H/C ratio	ASTM E191	mole/mole	1.841	1.895	1.879
O/C ratio		mole/mole	0	0.036	0.036
AFR_{ST}			14.571	13.856	13.832
RON	ASTM D2699		96.6	94.0	94.7
MON	ASTM D2699		88.7	85.4	83.8
LHV	ASTM D240	MJ/kg	43.01	39.75	39.54
LHV		MJ/L	31.96	29.40	29.61

Marine Biobutanol over 5 years of research

-Alternative Fuel Butanol: Preliminary Investigation on Performance and Emissions of a Marine Two-Stroke Direct Fuel Injection Engine

-Impact of Blending Gasoline with Isobutanol Compared to Ethanol on Efficiency, Performance and Emissions of a Recreational Marine 4-Stroke Engine

-Gaseous and Particulate Emissions Using Isobutanol-Extended Fuel in Recreational Marine Two-Stroke and Four-Stroke Engines

-In-Use Performance Testing of Butanol-Extended Fuel in Recreational Marine Engines and Vessels

-Effect of Fuel Contamination of Lubrication with Marine Engine Oil

-Isobutanol Testing Update – International Boat Builders Exposition 2014

-Effect of Fuel Weathering on RVP, Distillation and Oxygen Content of Ethanol and iso-Butanol Blends

-Compatibility Study for Plastic, Elastomeric, and Metallic Fueling Infrastructure Materials Exposed to Aggressive Formulations of Isobutanol-Blended Gasoline

-Butanol Mercury Marine CRADA Report - US Coast Guard

-Butanol Honda CRADA Report - US Coast Guard

https://sites.google.com/site/marinebiobutanolfuel/research

Harbor Marina – Lake Pomme de Terre

- Discussed ahead of time with Missouri Weights and Measures
- Let them know when we introducing, name of marina, etc. before it was released.
- Sampling on the pump fuel was collected and tested.

Commercial Placement

Buc ee's Katy Store

- 108 nozzles of 87 octane with 12.5% IBA
- Store opened in August 2017

Thank you

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