

Market Specifications and Methods for Fuel Ethanol

SYMPOSIUM ON BIOFUELS

**Measurements and Standards to Facilitate
the Transition to a Global Commodity**

**US National Institute of Standards and Technology (NIST)
Brazil's National Institute of Metrology (INMETRO)**

June 26-29, 2007

**José Felix Silva Junior
UNICA/IETHA**

Complex X Simple

Composition Cleaning tissue alcohol-free for Face and Hands

- Water, parfum
- PPG-1-Peg-9 Lauryl Glycol Ether
- Coceth-7
- Peg-40 Hydrogenated Castor Oil
- Imidazolidinyl Urea
- Methylisothiazolinone
- Methylchloroisothiazolinone

Composition of Ethanol For Fuel

- Etanol (92,6 to 99,7%)
- Propanol, isopropanol, butanol, isobutanol, isoamyl (650 mg/L)
- Chloride (<1 mg/kg)
- Sulfate (< 4 mg/kg)
- Conductivity (< 500 uS/m)

Anhydrous is better than some ACS Chemicals

SPECIFICATION

Ethanol Specification

The specification or “statement of needs” has to be clear, concise and logical in functional and performance terms.

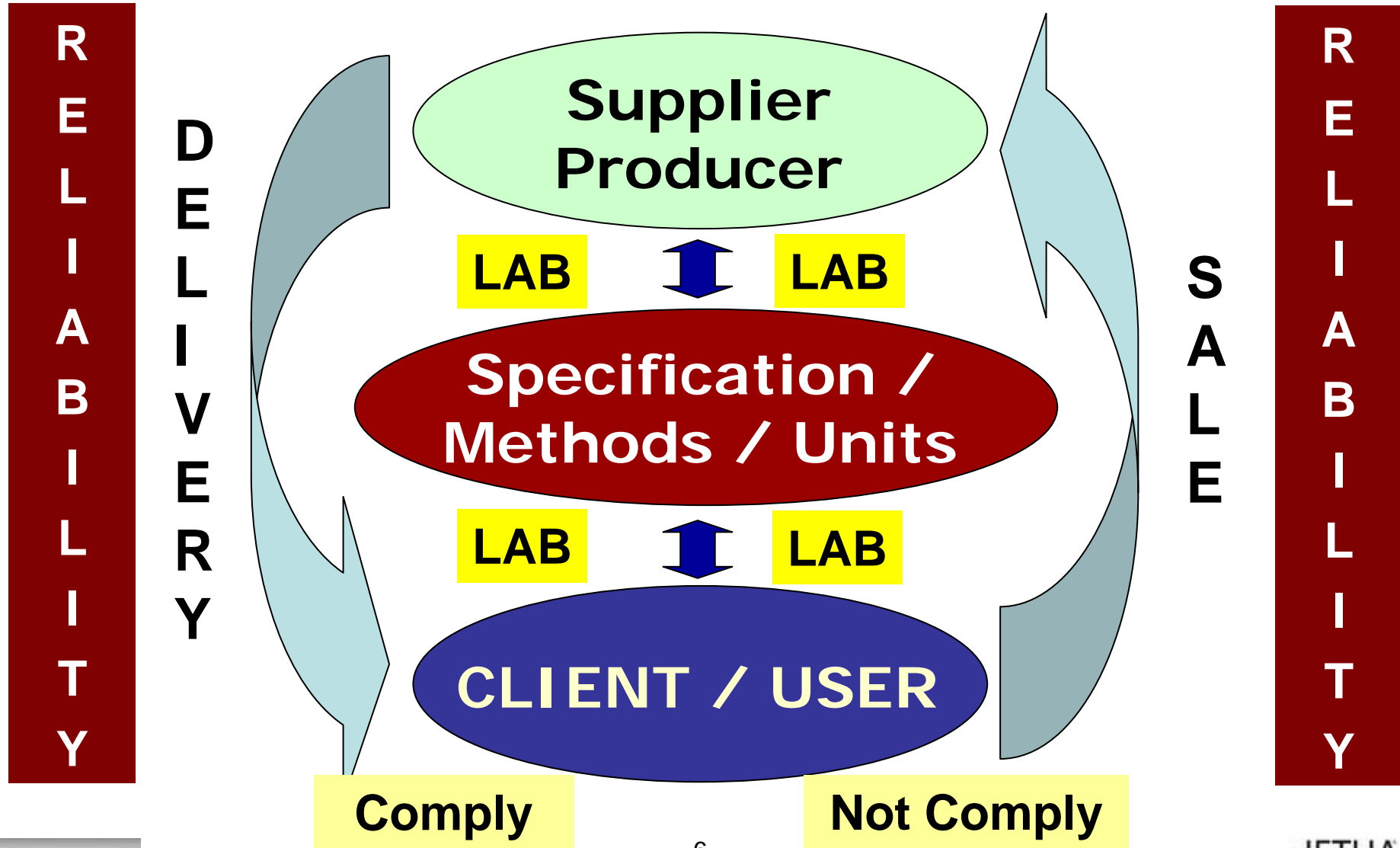
It is necessary to know the needs of the client (buyer/user), but at the same time offer an economically viable product.

Ethanol Specification

The product should be evaluated against defined and sound methods of analysis and units, and be **understandable** by all people involved in the operation.

The definition and implementation of a specification and quality system is a complex task that has to involve **skilled** people from all the **supplier-user chain**.

Relationship – Trader - Supplier



Quality Assurance - Reliability

Process Control at the factory



Factory Lab

Quality Control at the Factory Tanks



Factory Lab

3rd party Lab

Quality Control at the Port Tanks

Trucks, railway cars



3rd party Lab

Quality Control at the Ship – Port of Origin



3rd party Lab

Quality Control at the Ship – Port of Destination

3rd party Lab

Types of Anhydrous Ethanol

- **Denatured Anhydrous Ethanol**

Ethanol which has been rendered toxic or otherwise undrinkable, and in some cases dyed.

- **Undenatured Anhydrous Ethanol**

Pure ethanol without any chemical additive.

- **Ethanol from oil or gas**

- **Ethanol from biomass - fermentation**

Specifications for Fuel Anhydrous Ethanol

Anhydrous Ethanol Specification					
Characteristics	Unit		Brazil	ASTM	Europe
Density (20°C)	kg/m ³	max.	791.5	-	
Alcoholic strength @ 20°C	%m/m	min.	99.3*	-	98,7**
Alcoholic strength @ 20°C	%v/v	min.	99.6	92.1**	
Water	%v/v (%m/m)	max.	(0.7)	1,0	(0.3)
Total Acidity - max.	mg/L (%m/m)	max.	30	56 (0.007)	56 (0.007)
Electrical Conductivity	uS/m	max.	500	-	
pHe	-		-	6.5 a 9.0	?
Copper	mg/kg	max.	0.07	0.1	0.1
Chloride	mg/kg (mg/L)	max.	-	40 (32)	(20)
Solvent-washed gum	mg/100 mL	max.	-	5.0	
Aspect	-		Clear	Clear	Clear
Methanol	%v/v (%m/m)	max.	-	0.5	(1.0)
C3-C5 max.	%m/m	max.	-	-	2.0
Denaturant content	%v/v		-	1.96 a 5.0	
Sulfur	mg/kg	max.	-	30	10
Sulfate	mg/kg	max.	-	4	
Phosphorus	mg/L	max.	-	-	0.5
Non-volatil material	mg/L	max.	-	-	100

* Densimetry

** Gas chromatography

ASTM International - D4806-06c Europe - Draft prEN 15376 (March 2006)

98,7 - Ethanol + Higher Saturated alcohols.

More Specification (1)

PROPERTIES	SPECIFICATION / UNITS	METHOD
Alcohol Strength	minimum 99.4% weight	ASTM D5501
- Ethanol	minimum 98.4 %wt	
- Methanol	Maximum 0.6 % wt	
water content	0.6% weight max	ASTM D1744
Higher alcohols	max 200g/hl (= max 0.25% weight)	ASTM D5501
Acidity as acetic acid	max 100 ppm	ASTM D1613
Chlorure	max 10 ppm	IMPCA-002
Esters	max 50 g/hl (= max 0.06% weight)	CEE.L.130
Aldehydes	max 50 g/hl (= max 0.06% weight)	CEE.L.130
Sulfur	max 10 ppm (= max 0.001 % weight)	ASTMD-3961
Cyclohexane	max 20 ppm (= max 0.002 % weight)	ASTM D3054
Benzene	max 10 ppm (= max 0.001 % weight)	ASTM D4534
Iron	Max 1 ppm	
pHe	< 7.5	
Suspended matters	Free	
Non volatiles	Max 50 ppm	

Client Specification and Certificate

Analysis	Specification	Methodology	Unit	Results
Ethanol	99,5 Min	ASTM D 5501	Vol %	99,4 *L
Methanol	0,5 Max	GLC	Vol %	0,0069
Solvent - washed gum	5,0 Max	ASTM D-381	mg/100mL	1
Water	1,0 Max	ASTM E 203	Vol %	0,554
Chloride Content	32 Max	ASTM D-512	mg/L	< 1
Copper content	0,10 Max	ASTM D 1688	mg/kg	< 0,05
Acidity (Acetic acid)	0,007 Max	ASTM D 1613	Wt %	0,0011
pH	6,5 to 9,0	ASTM D 6423	--	6,5
Sulphur	10 Max	ASTM D 3120	ppm	3
Sulphates	4 Max	Turbidimetric	ppm	< 1
Appearance	Clear	Visual	--	Clear

Specification for Anhydrous Ethanol

Comments

“Technical Translation” is needed

- ✓ Units in volume and mass – for ethanol is a big difference, around $\pm 20\%$ from volume to mass and vice-versa.
- ✓ Expressions in %, mg/L, mg/100mL, hectolitres, ppm(?), ppm mass(?).
- ✓ Many methods for the same parameters.

Are those Characteristics Necessary?

Characteristics seems to be unnecessary for the use of ethanol as a fuel mixture.

- **pHe (in 99,7% v/v)**
- **Methanol (0.5% v/v)**
- **C3-C5 alcohols (2.0% v/v)**
- **Phosphorus (0,5 mg/kg)**
- **Basic Nitrogen (1 mg/kg)**
- **Sulfur (50, 10, 2 ,1 mg/kg)**

What is the relevance? – Papers, research works.

Anhydrous Ethanol - pHe

pH measurement

- pH is measured to relate it with corrosion.
- Corrosion due to ethanol is insignificant.
- “Steel underground storage tanks have been tested and found to be compatible with ethanol and methanol fuel blends”.

Compatibility of Steel with Oxygenated Fuels.
Wayne B. Geyer. Steel Tank Institute. 16th Annual
ILTA Conference, JUNE 10-11, 1996.

Anhydrous Ethanol - pHe

- **What is the meaning?**
- **Is the measurement stable and reproducible?**
- **Is the electrode available for all?**

In Brazil, pH is not specified for anhydrous ethanol 25%, but only for hydrated fuel ethanol for flexfuel and alcohols cars.

No corrosion problems in the gasohol running cars

Corrosion

- **All the tanks for anhydrous and hydrated ethanol in Brazil are made of carbon steel.**
- **The life span is more than 20 years.**
- **There is no information of leakage or loss of ethanol.**
- **No special care is necessary.**

Anhydrous Ethanol – Organic Compounds

- **What is the negative influence of methanol (0.5% v/v) and C3-C5 (2.0% v/v) in fuel ethanol?**
- **Again in Brazil they are not specified, even for the hydrated ethanol used straight in the flexfuel and alcohol cars.**
- **No problem is related by the automakers.**

Anhydrous Ethanol – Organic Compounds

“The presence of aldehydes, esters and other alcohols in hydrated ethanol, with content 4, 13 and 20 times higher than the emission standard, did not caused any significant difference in the content of the same components in the exhaust gas.”

Influence on the car emission of the content of aldehydes, ester, higher alcohols and gasoline in fuel hydrated ethanol. Laerte Graner e Maurício C. Carmona. Volkswagen Emission Laboratory.

Amount of Components in the Fuel mixture (mg)

Characteristics	E5			E85		
	5L/100L			85L/100L		
	Brazil	ASTM	Europe	Brazil	ASTM	Europe
%Ethanol	5	5	5	85	85	85
Water (Karl Fischer)	250	500	150	4.250	8.500	2.040
Total Acidity - max.	1,5	2,8	2,8	26	48	48
Copper	0,003	0,004	0,004	0,05	0,07	0,07
Chloride		1,6	1,0		21,5	13,4
Solvent-washed gum		2,5			42,5	
Methanol		250	500		4.250	8.500
C3-C5 max.			1.000			17.000
Sulfur		1,2	0,4		20	6,7
Sulfate		0,2			2,7	
Phosphorus			0,03			0,43
Non-volatile material			5,0			85
Total (mg)	252	758	1.659	4.276	12.885	27.693

Possible Roadmap – Brussels (Feb/2007)

*Possible areas of convergence:
US, EU, Brazil specification*

- Acidity
- Copper
- Chloride
- Methanol
- Sulphur
- Aspect
- % Alcohol

*Possible areas of divergence:
US, EU, Brazil specification*

- Water
- Denaturant
- Sulfates
- Phosphorous
- Density
- pHe
- Electrical conductivity
- Gum/Non Volatile content

This Roadmap was not intensively discussed

Undenatured Anhydrous Ethanol

Proposed Specification for Discussion

Characteristics	Unit			Test Method
Density @ 20°C	kg/m ³	max.	790.8	NBR 5992 / ASTM D4052
Alcoholic strength @ 20°C	%m/m	min.	99,5*	NBR 5992 / ASTM D4052
Alcoholic strength @ 20°C	%v/v	min.	99,7*	NBR 5992 / ASTM D4052
Water	%m/m	max.	0.5	ASTM E203 / E1064
Total Acidity - max	mg/L	max.	30	NBR 9866 / ASTM D1613-06
Electrical Conductivity	uS/m	max.	500	NBR 10547
Chloride	mg/kg	max.	1	NBR 10894, ASTM D7319-07, ASTM D7328-07e1
Aspect			Clear	Visual
Sulfur	mg/kg	max.	10	ASTM D2622, D3120, D5453, D6428
Sulfate	mg/kg	max.	4	NBR 10894, ASTM D7319-07, D7328-07e1

Test Methods and units have to be homogeneous and validated

Quality of Undenatured Anhydrous Fuel Ethanol

Average Results of 99 Samples and 28 Distilleries São Paulo Region

Characteristics	Unit	Lower	Average	Higher
Total Acidity	mg/L	4.8	10.8	29.6
Chloride	mg/kg	< 0.1	0.2	0.3
Copper	mg/kg	< 0.01	0.07	0.07
Conductivity	uS/m	9	69	346
pH CTC		2.7	6,8	7,9
pH Mill Lab		1.4	5.9	7,9
Sodium	mg/kg	< 0.1	0.4	1.2
Sulfate	mg/kg	< 0.2	1.0	8,1
Methanol	mg/L	6,2	36,3	99,1
C3-C5	mg/L	33.7	649.8	2551.8

METHODS

Standards Tests for Anhydrous Fuel Ethanol

Characteristics	Brazil	ASTM	Europe
Density (20°C)	NBR 5992 / ASTM D 4052	-	-
Alcoholic strength @ 20°C	NBR 5992 / ASTM D 4052	-	-
Ethanol %	ASTM D 4052	ASTM D 5501	EC/2870/2000 Method B
Water (Karl Fischer)	-	ASTM E 203	prEN 15489
Total Acidity - max.	NBR 9866 / ASTM D 1613-06	ASTM D 1613-06	prEN 15491
Electrical Conductivity	NBR 10547	-	-
pHe	-	ASTM D 6423	?
Copper	NBR 10893	ASTM D 1688A	prEN 15488
Chloride	-	ASTM D 7319-07, D 7328-07e1	prEN 15484 / 15492
Solvent-washed gum	-	ASTM D 381	-
Aspect	Visual	Visual	Visual
Methanol	-	ASTM D 5501	EC/2870/2000, EN 1601 / EN 13132
C3-C5 max.	-	-	EC/2870/2000 EN 1601 / EN 13132
Sulphur	-	ASTM D 2622, D 3120, D 5453, D 6468	prEN 15485 / 15486
Sulfate	-	ASTM D 7319-07, D 7328-07e1	-
Phosphorus	-	-	prEN 15487
Non-volatile material	-	-	EC/2870/2000, method II

ASTM - American Society of Testing Materials
 NBR - Associação Brasileira de Normas Técnicas

EC - European Community
 EN - European Norms / prEN - Draft method

Methods for Anhydrous Fuel Ethanol

Comments

- ✓ **Methods developed for other matrix is used for ethanol. Who tested them?**
- ✓ **Methods for denatured ethanol are asked for undenatured one – unnecessary.**
- ✓ **Tables for density are different – IUPAC, OIML, in air, in vacuum.**

Methods for Anhydrous Fuel Ethanol

Comments

- ✓ **There are no results from validation and comparison of methods, to know the differences in results (as far as I know).**
- ✓ **Uncertainty are not know.**
- ✓ **Repeatability and reproducibility are not know for all methods.**

Simple Measurements

- It can be performed in almost any laboratory without special equipment and well-trained technicians.
- Low cost to implement and maintain.
- Easy calibration.
- Easy validation.
- Used easily to control of the process and product.

Complex Measurement

- It can be performed in well-equipped laboratory with special equipment and trained technicians.
- High cost to implement and maintain.
- Special calibration.
- Equipment used only to measure the quality of the ethanol, without any other use for the process.
- Difficult validation

Work Being Done

- Revision of the Brazilian Standards Methods – **ABNT (Brazilian Assoc. of Technical Standards)**
- Production of Certified Reference Material (CRM) for pH and conductivity, water and other characteristics in anhydrous ethanol. **INMETRO**
- Proficiency test with sugar/ethanol mills – **Sugar Cane Technology Center (CTC)**.
- Protocol to develop standards for ethanol. **INMETRO – NIST – UNICA – IETHA**

WHAT WE SHOULD DO AND GO FOR IT

**Collaborate to set International
Standards for the Quality of Fuel
Ethanol.**

Specifications and Methods

- ➡ Define what characteristics is necessary for ethanol to be used as a fuel mixture. **Rational**
- ➡ Define specifications for undenatured ethanol and fuel mixture. **Simplification**
- ➡ Define method, units and acceptable limits for each parameter, considering the type of ethanol. **Matrix consideration**

Specifications and Methods

- For each complex or instrumental methods, find a simple one, to be performed at the industry, even with a low accuracy, but comparable between them. **Process control**
- Validate the methodology for the ethanol matrix. **Metrology**
- Provide interlab tests to know the repeatability and reproducibility of the methods. **Reliability**

Quality Program for Ethanol

- ➡ Encourage and sponsor studies and researches for new methods and in the production of a certified reference material. **R & D**
- ➡ Qualify laboratories to analyse ethanol with reliability. **Accreditation**

Thank you

José Felix Silva Junior
UNICA / IETHA

jfelix@unica.com.br

Jose.felix@ietha.org

Who is responsible by the specification?

Brazil

Internal Market

- Fuel ethanol (anhydrous and hydrated) – ANP
- Industrial hydrated Ethanol – Clients

Other countries

- Fuel Ethanol – ASTM, NYBOT, Europe, Government, Stakeholders, etc.
- Industrial hydrated Ethanol – Clients

Distribution of some components

Sulfate (mg/kg)

<i>Class</i>	<i>Freq.</i>	<i>%</i>	<i>% Cum.</i>
1	88	88,9	88,9
2	4	4,0	92,9
3	2	2,0	94,9
4	1	1,0	96,0
> 4	4	4,0	100,0
99			

Methanol (mg/L)

<i>Class</i>	<i>Freq.</i>	<i>%</i>	<i>% Cum.</i>
20	18	18,2	18,2
40	51	51,5	69,7
60	25	25,3	94,9
80	1	1,0	96,0
100	4	4,0	100,0
99			

C3-C5 (mg/L)

<i>Class</i>	<i>Freq.</i>	<i>%</i>	<i>% Cum.</i>
200	4	4,0	4,0
400	17	17,2	21,2
600	34	34,3	55,6
800	27	27,3	82,8
1000	5	5,1	87,9
> 1000	12	12,1	100,0
99			

Collaborate to Set International Fuel Quality Standards

In order to develop a significant international biofuel market, fuel quality standards need to be agreed upon and enforced on the international level. This is necessary for **consumer confidence** and will gain increased importance as **international trade** in biofuels expands. Automakers need assurances of **consistent fuel** characteristics so they can honor vehicle warrant

- BIOFUELS FOR TRANSPORTATION GLOBAL POTENTIAL AND IMPLICATIONS FOR SUSTAINABLE AGRICULTURE AND ENERGY IN THE 21st CENTURY
- Prepared by Worldwatch Institute for the German Federal Ministry of Food, Agriculture and Consumer Protection

Laboratory Analytical Efficiency

	Sample A33			Sample A34		
	Alcoholic Strength	Acidity	Conduc tivity	Alcoholic Strength	Acidity	Conduc tivity
	%m/m	mg/L	uS/m	%m/m	mg/L	uS/m
Average	99.6	7.0	96	99.4	6.8	64
Number of Laboratories - 69						
Results	Labs %			Labs%		
Good	92	72	85	83	74	89
Questionable	4	8	5	1	4	3
Unsatisfactory	4	20	10	16	22	8

- **Simple and complex**
- **Statement of needs - specification**
- **Sales relationship – reliability**
- **Types of anhydrous ethanol**
- **Specifications: Brazil – ASTM – Europe, other specifications, comments and proposed one**
- **Methods**