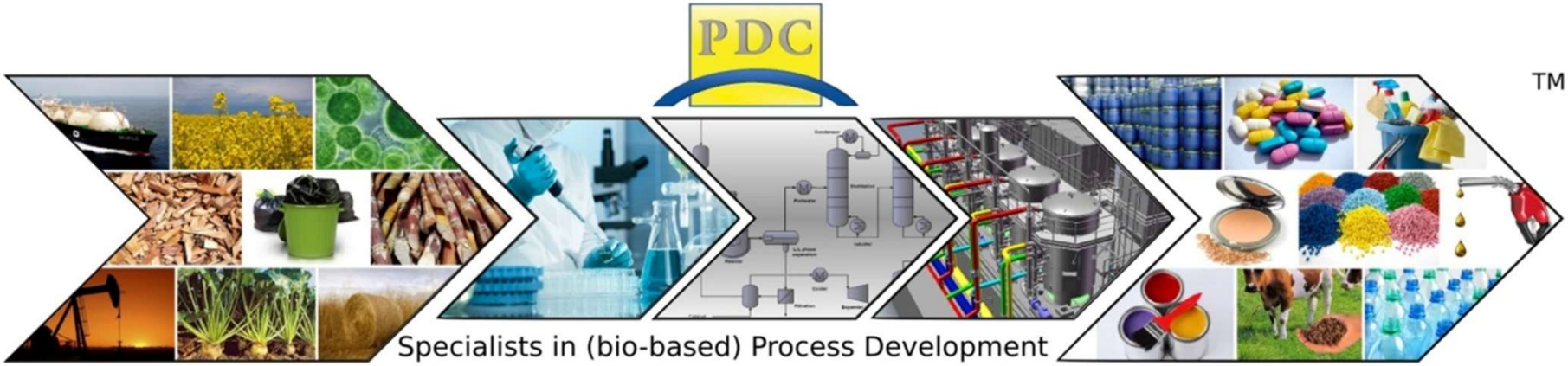
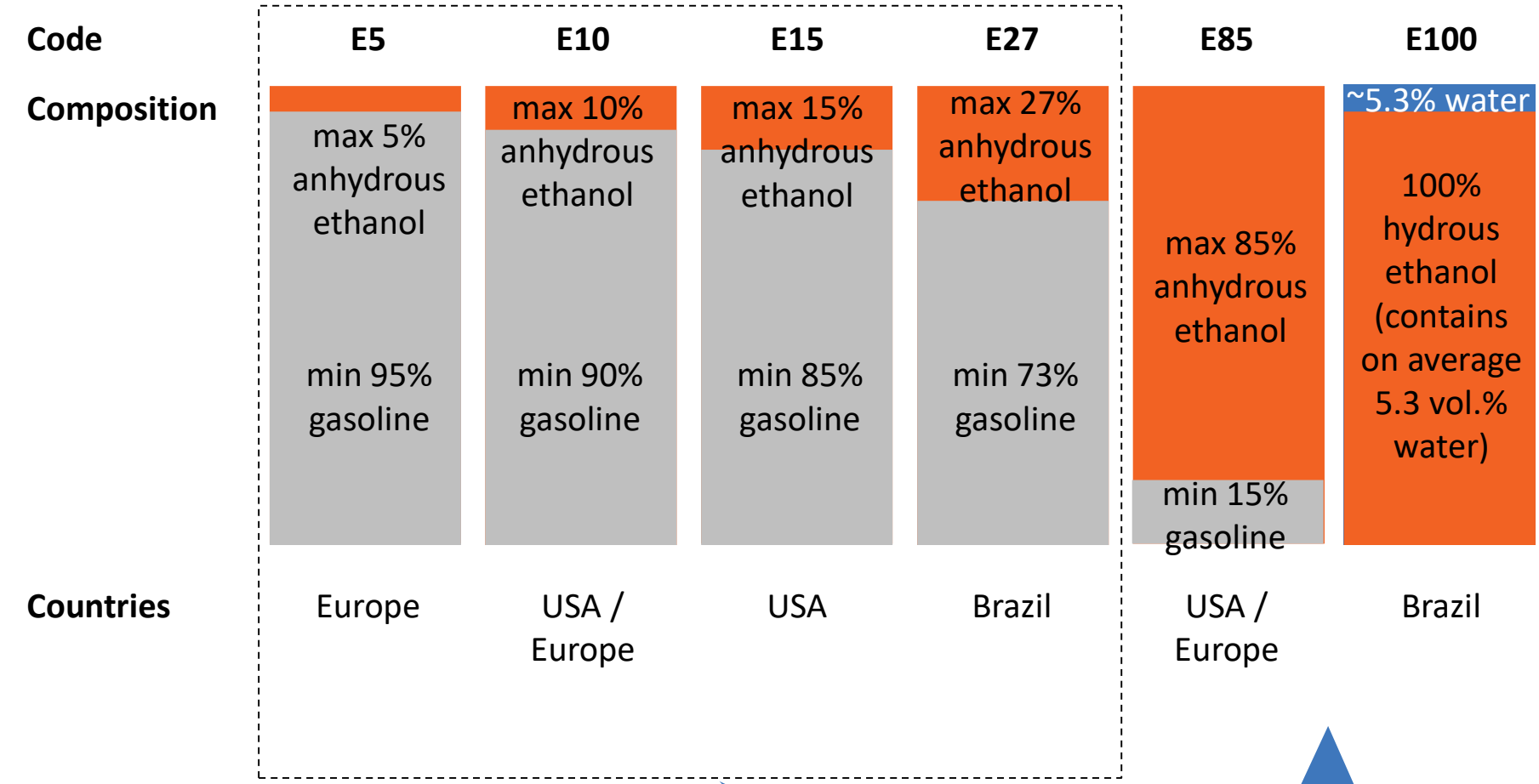


Hydrous versus Anhydrous Ethanol in Gasoline

May 2021

By: Hans Keuken, CEO

Composition of ethanol containing fuels



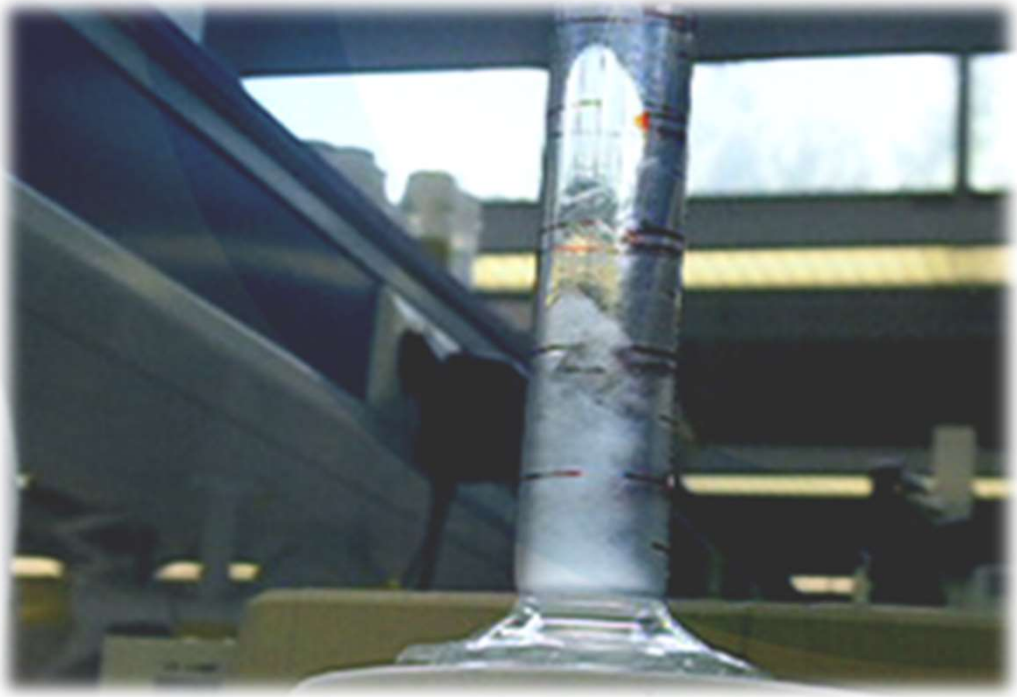
Hydrous & anhydrous ethanol

- Hydrous ethanol can be distilled up to 3.5 volume% water (limit = azeotrope)
- Anhydrous ethanol is further dehydrated to contain less water typically < 1%
- Dehydration units require additional capital & operating cost (energy)
- Brazilian prices in US$/ltr. can be found at www.cepea.esalq.usp.br/english/ethanol/?id_page=243

  Hydrous ethanol is cheaper
- Ethanol and especially hydrous ethanol are strong and cheaper octane enhancers than MTBE

Conventional wisdom in blending

- Gasoline and water do not mix (2-liquid-phase system).
- One expects simply water to create corrosion.
- Ethanol has to be free of water to be blended in gasoline.
- Blends of dry ethanol with gasoline will pick-up water, e.g. from air humidity, logistical systems.



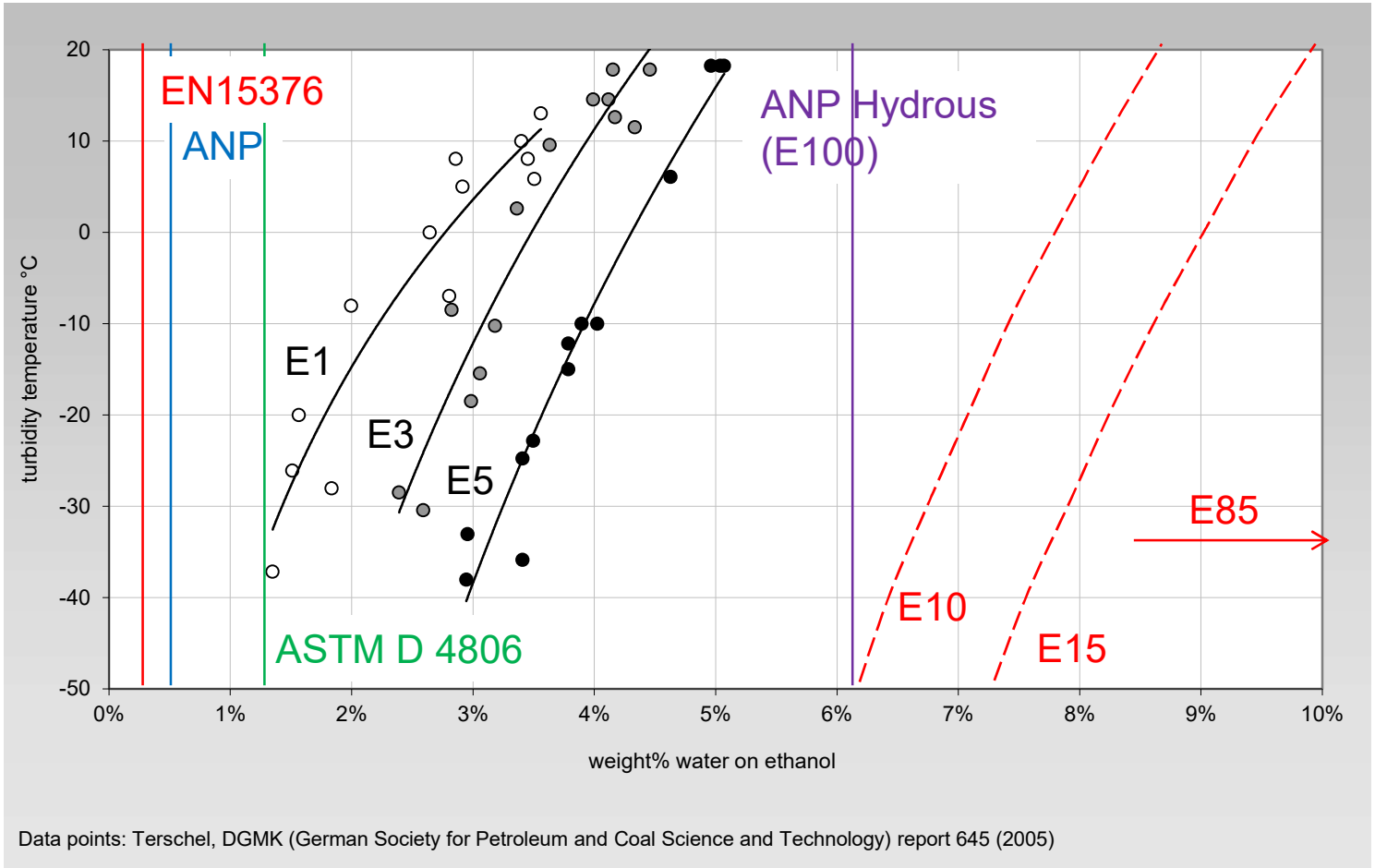
Shell confirmation hydrous ethanol for E10+ in EU

Shell Research - Amsterdam Sept. 2006

- **Straight gasoline: haziness observed at -5ºC**
- **Straight gasoline + 5% hydrous Ethanol (hE5): haziness observed at -34ºC**
- **10, 15 and 20% hydrous Ethanol: haziness could not be detected at -60ºC**

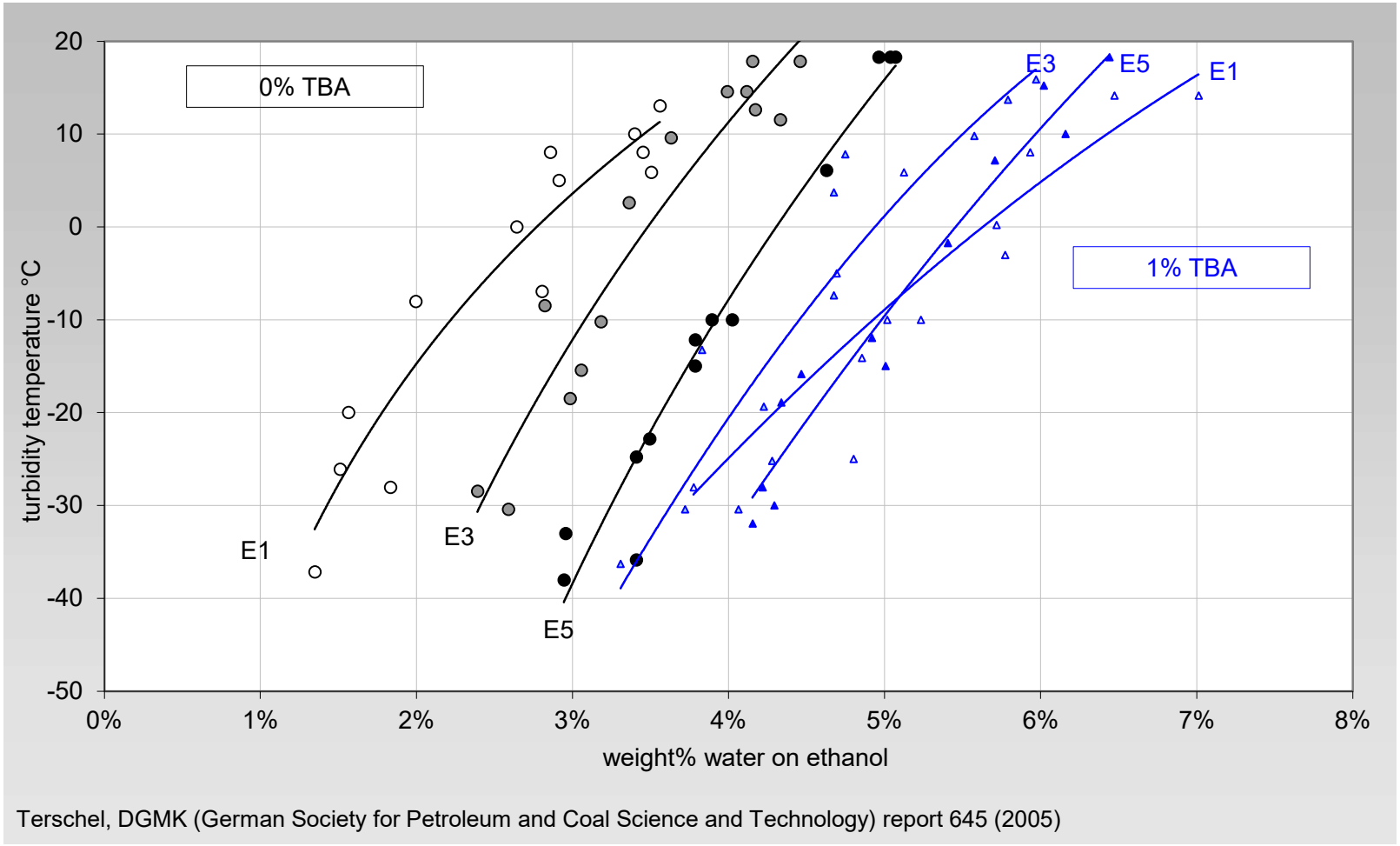
Phase separation is not observed in any of the above blends!

Phase Stability Ethanol Blends in EU



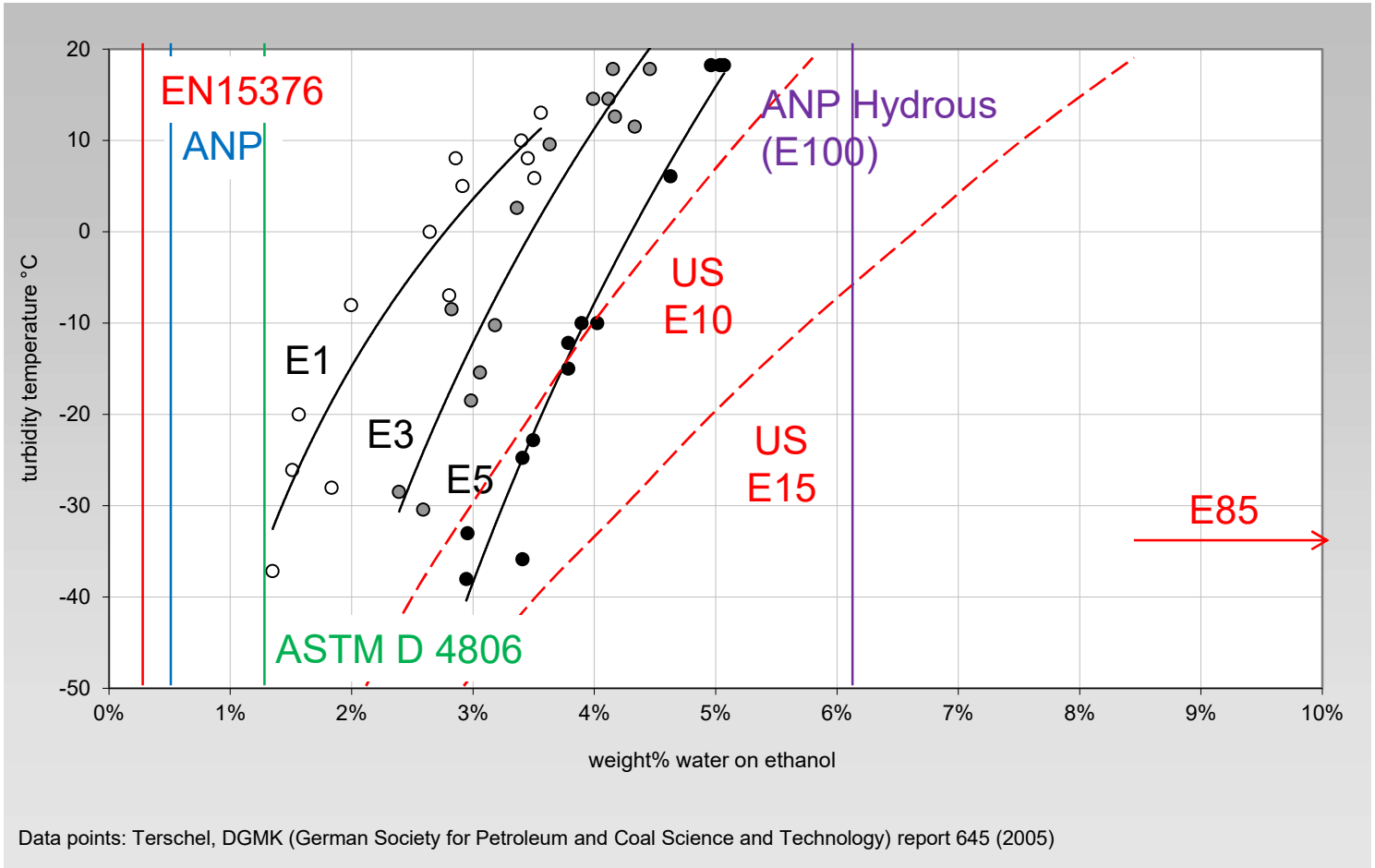
Data points: Terschel, DGMK (German Society for Petroleum and Coal Science and Technology) report 645 (2005)

Effect of 1% TBA (C4 alcohol)



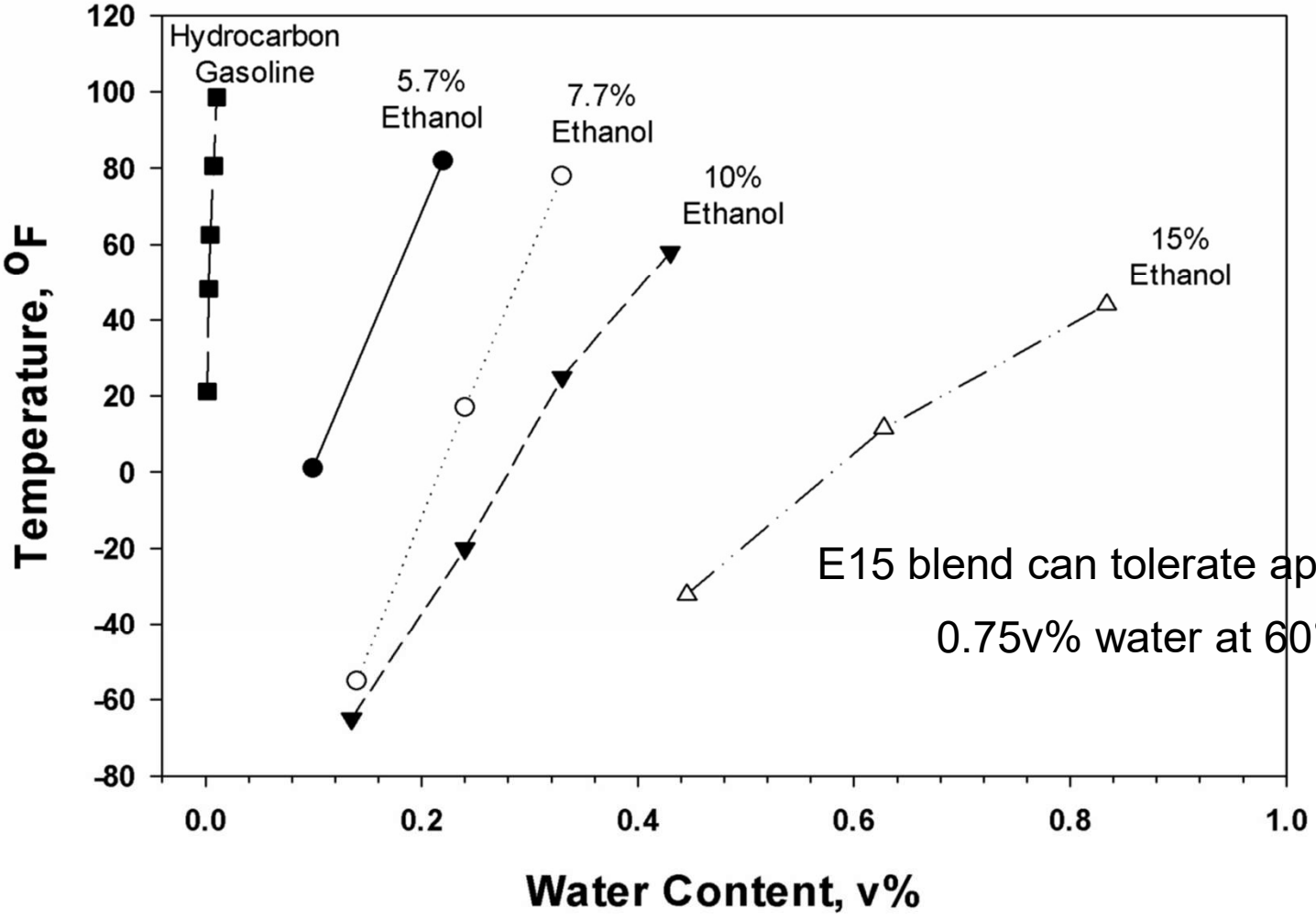
Terschel, DGMK (German Society for Petroleum and Coal Science and Technology) report 645 (2005)

Phase Stability Ethanol Blends European E1-E5 versus US E10 and US E15 based on RFA 2012 data



Data points: Terschel, DGMK (German Society for Petroleum and Coal Science and Technology) report 645 (2005)

A lower aromatic content results in a lower water tolerance



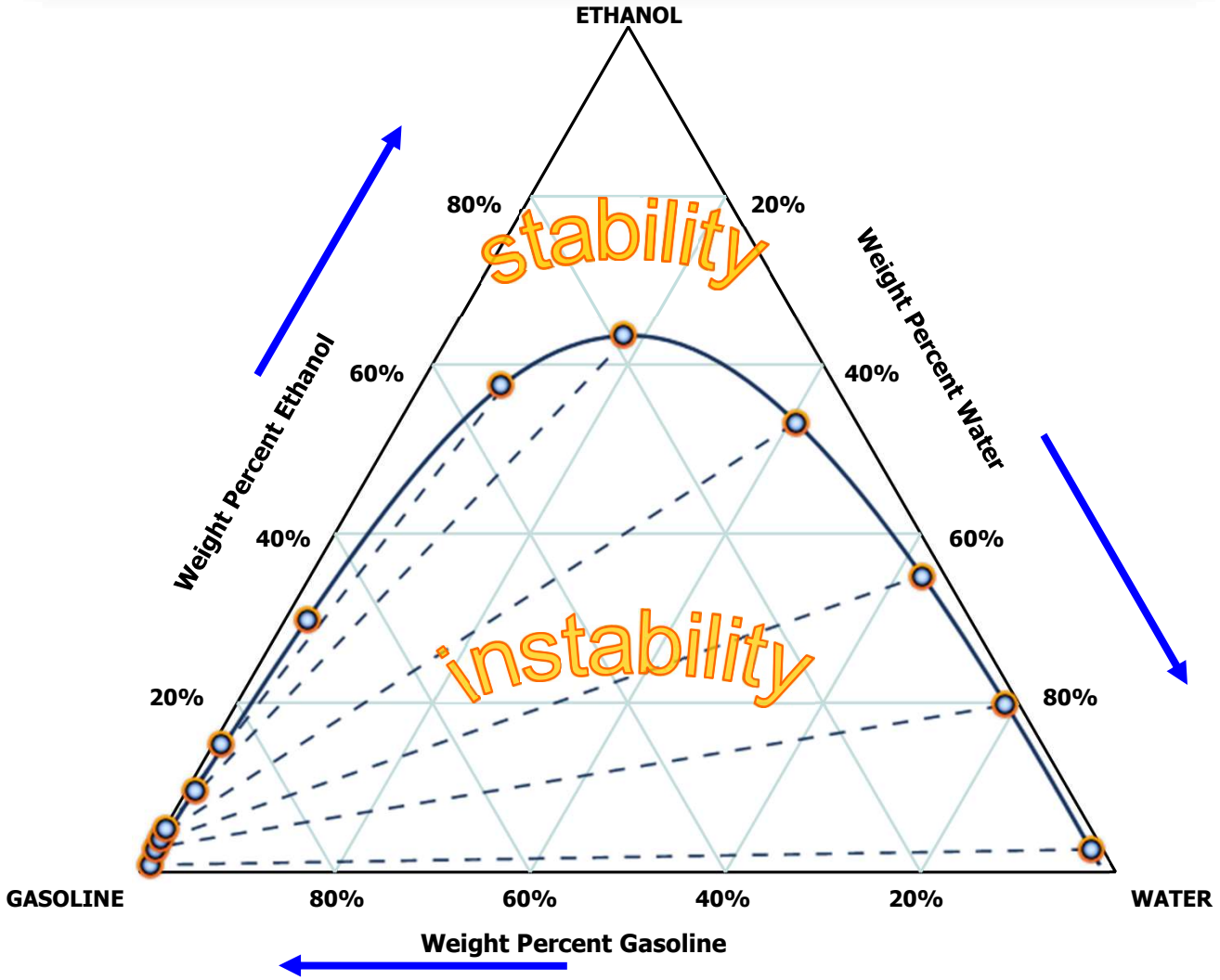
E15 blend can tolerate approximately 0.75v% water at 60°F

Wet Corrosion Tests by Sasol

- **Sasol's "wet corrosion" tests (ASTM D665) of E2 and E10 on aluminum parts.**
  - Wet corrosion is corrosion in the presence of water
- **Sasol found:**
  - **The E0 and E2 blends were corrosive during the wet corrosion test.**
  - These fuels required additisation in order to prevent wet corrosion.
  - **The E10 blends were not corrosive in the wet corrosion test.**

Presented at the XVIII International Symposium on Alcohol Fuels
(Delhi – India ISAF 2010)

Ternary Diagram & Phase Separation



Conductivity E10's adding salt water

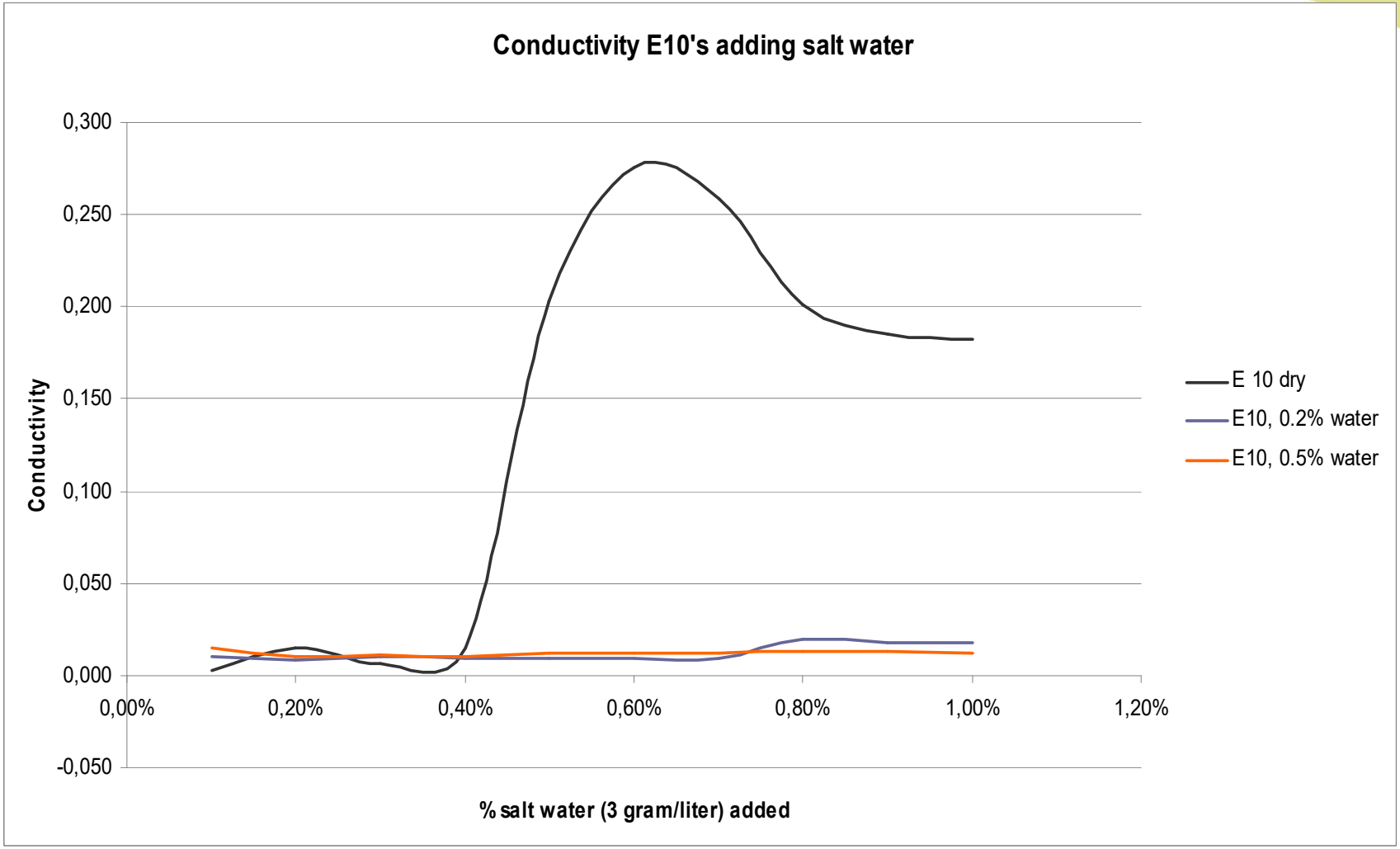
Salt Water	E10, dry	E10, 0.2% water	E10, 0.5% water
0,10%	0,003	0,010	0,015
0,20%	0,015	0,008	0,010
0,30%	0,006	0,010	0,011
0,40%	0,015	0,009	0,010
0,50%	0,203	0,009	0,012
0,60%	0,276	0,009	0,012
0,70%	0,259	0,009	0,012
0,80%	0,201	0,020	0,013
0,90%	0,185	0,018	0,013
1,00%	0,182	0,018	0,012

Test by SGS to see if more hydrous E10 picks up more salts?

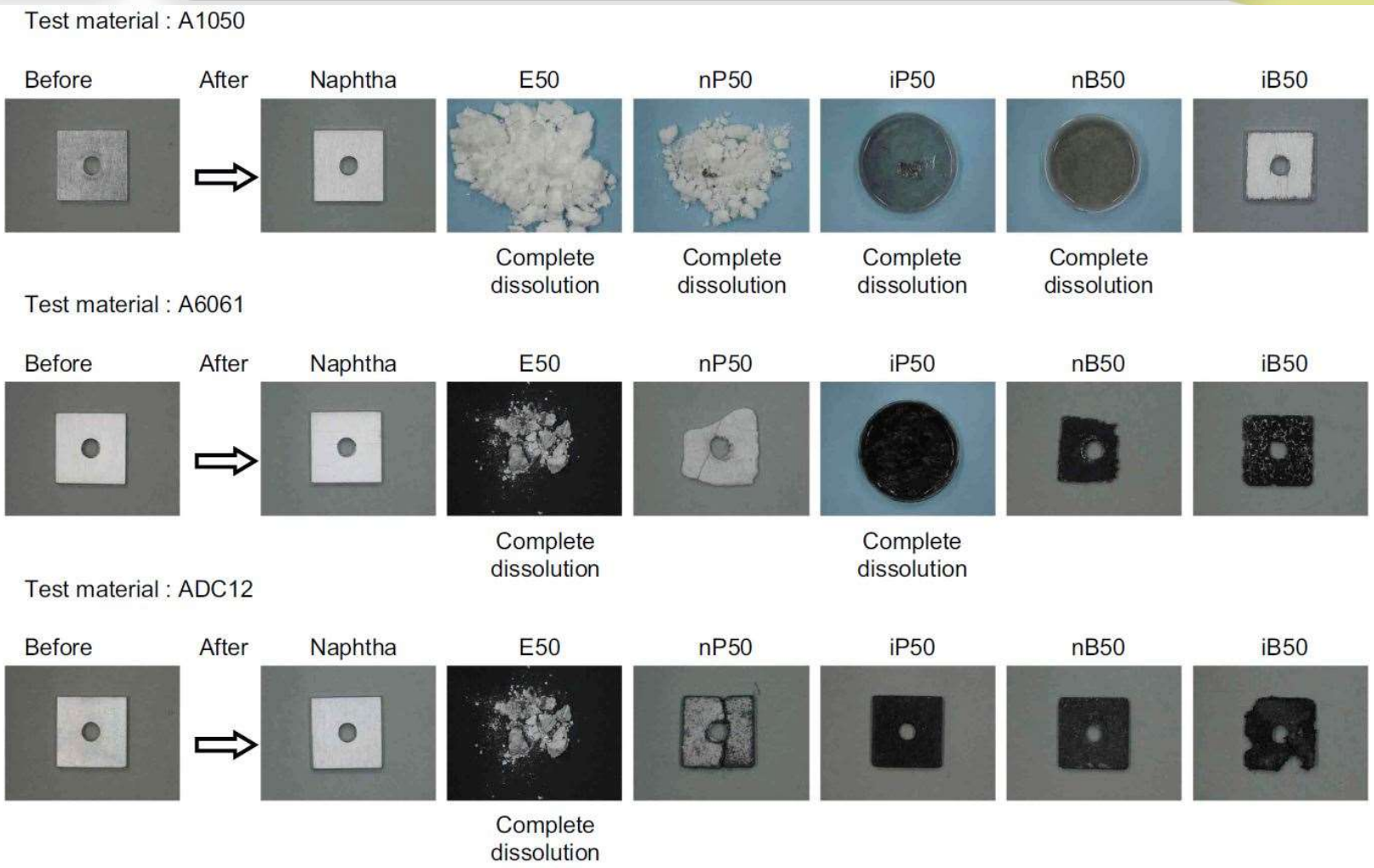
salt drops out

free water

Conductivity E10's adding salt water



Dry Corrosion Research Japan (JARI)



Appendix 3.1 Photographs of the immersion test results using a single alcohol fuel.
(Alcohol content : 50%, Water content : 150ppm).

Dry Corrosion Research Japan (JARI)

Material in fuel system	Type	Gasoline 100%	E50 with 150 ppm water (overall) *	E50 with 500 ppm water (overall) *	E50 with 2000 ppm water (overall) *	E50 with 10.000 ppm water (1%, overall) *
Aluminum	A1050	OK	complete dissolution	complete dissolution	complete dissolution	OK
Aluminum	A6061	OK	complete dissolution	complete dissolution	OK	OK
Aluminum	ADC12	OK	reduction in mass	reduction in mass	OK	OK
Steel		change in surface	OK	OK	OK	change in surface
Copper		change in surface	change in surface	change in surface	change in surface	change in surface
Nickel		OK	OK	OK	OK	OK
Zinc		OK	change in surface	change in surface	OK	change in surface
Tin		OK	change in surface	change in surface	change in surface	OK

Legend:

OK	*No change observed*
change in surface	*change in color for instance, but no reduction in mass*

* *1 vol% overall water in E50 means a concentration of 2 vol% water in the added ethanol*

Alcoholate corrosion of aluminum

TECHNISCHE UNIVERSITÄT DARMSTADT

- Refers to the chemical corrosion of metals in the presence of fuel alcohol containing fuel blends
- Alcohols can react with aluminium alloys, lead and magnesium with the formation of alkoxide or alcoholate corrosion products

$$3C_2H_5OH + Al \rightarrow (C_2H_5O)_3Al + 3/2H_2 \quad (1)$$

$$(C_2H_5O)_3Al + 3H_2O \rightarrow Al(OH)_3 + 3C_2H_5OH \quad (2)$$

$$(C_2H_5O)_3Al \rightarrow Al_2O_3 + 6C_2H_4 + 3H_2O \quad (3)$$

(1) alcoxides (alcoholate) get hydrolyzed (2) or decomposed (3)

Damaging process may progress rapidly and is accompanied by an increase in pressure due to hydrogen formation

Alcoholate corrosion of Al

Alcoholate (dry) corrosion of aluminum

Technical temperature threshold

Influence of water-content

TECHNISCHE UNIVERSITÄT DARMSTADT

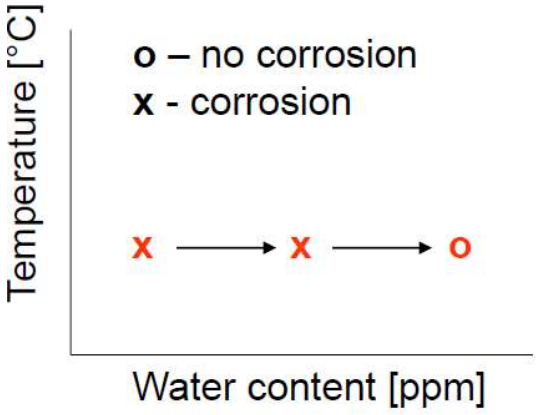
Starting temperature:

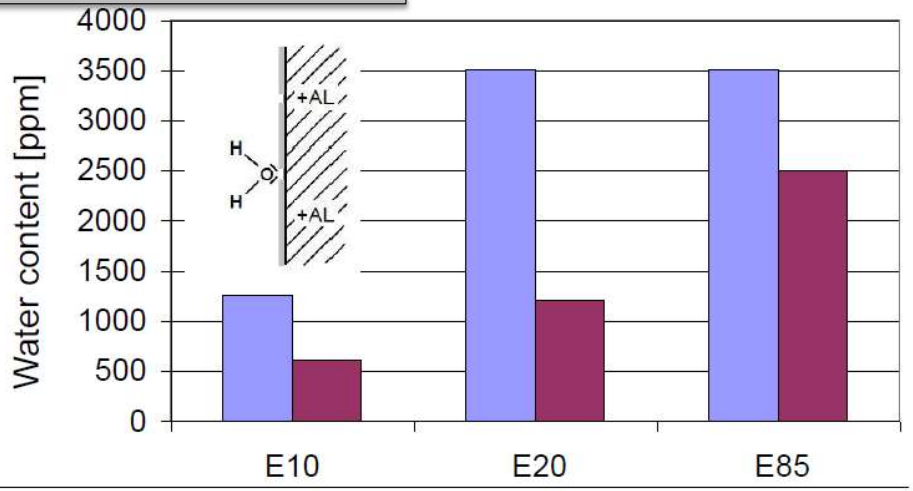
10 °C above the highest temperature level with **assured** alcoholate corrosion ➔ water addition, until no alcoholate corrosion occurs at this temperature level.

Starting temperature:

Al99,5	AlSi9Cu3
E10: 130°C	E10: 120°C
E20: 130°C	E20: 110°C
E85: 120°C	E85: 100°C

⇨ **Inhibition of alcoholate corrosion by water additions is possible, but….**





Dry corrosion E5, E10, E15 and E20

Accomplishments and Progress – Task 3

- Aluminum 1100 exhibited corrosion rates that increased with dry ethanol concentration
  - similar trends for other aluminum alloys and fluid temperatures
  - increasing %ethanol decreases reaction incubation time

Water as inhibitor in E100

Accomplishments and Progress – Task 3

- Temperature and water concentration significantly impacts aluminum corrosion in E100

Temperature (°C)	Water Content						
	≤ 50 ppm	≤200 ppm	≤ 0.1%	≤ 0.5%	≤ 1%	≤ 5%	≤ 10%
20	No	No	No	No	No	No	No
40	No	No	No	No	No	No	No
60							
80	Yes	Yes	No	No	No	No	No
100							
120	Yes	Yes	Yes	No	No	No	No
140							
160	Yes	Yes	Yes	Yes	Yes	No	No
180							
200	Yes	Yes	Yes	Yes	Yes	No	No

* YES = corrosion occurred in ≤ 24 h

Evaluation time ≤ 24 hrs

Effect of water on alcoholate corrosion

A little water works as fluoride in toothpaste and avoids corrosion

Hydrous ethanol standard (NTA 8115) for E10+ blending

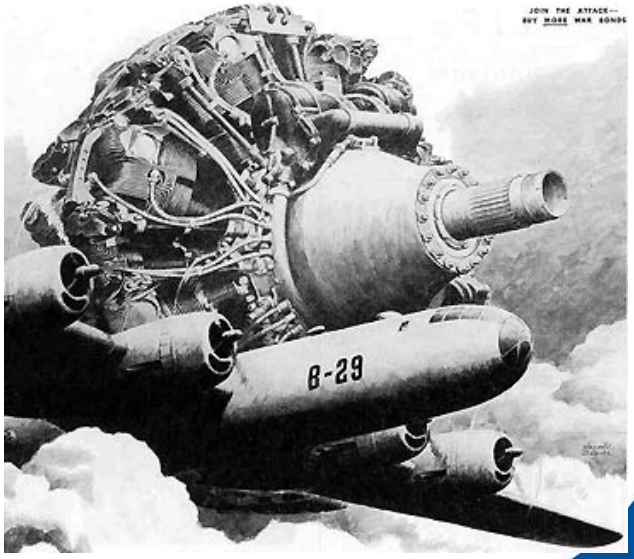
Property	Unit	Limits		Test method [a]
		Minimum	Maximum	(See Clause 2. Normative references)
Ethanol content	% (*m/m*)	93,0		EN 15721
Methanol content	% (*m/m*)		0,5	EN 15721
Water content [b]	% (*m/m*)	at 2,52%	6,1	EN 15489 EN 15692
pH [c]		6,0	8,0	EN 15490 ASTM D 6423 NBR 10891
Total acidity (expressed as acetic acid) [d]	mg/l		40 or 30 [d]	ASTM D 1613 EN 15492 NBR 9866
Electrical conductivity [e]	µS/cm		3,5	EN 15938 ASTM D 1125
Appearance		Clear and bright		Visual inspection [f]
Inorganic chloride content	mg/kg		1,0	EN 15492
Sulfate content	mg/kg		4,0	EN 15492
Phosphorus content [g]	mg/kg		0,2	EN 15487 EN 15837
Involatile material content [h]	mg/100ml		5	EN 15691 NBR 8644

"Water Injection"
70 years proven technology!

2010

1983

1940's



Energy efficiency in a modern down sized turbo charged Volvo S60 T4F (Flex Fuel Vehicle)

Tests results by the European Commission

Emission tests of hydrous versus anhydrous to quantify the effect of a higher water content in ethanol containing gasoline.

E10 - hE10

E15 - hE15

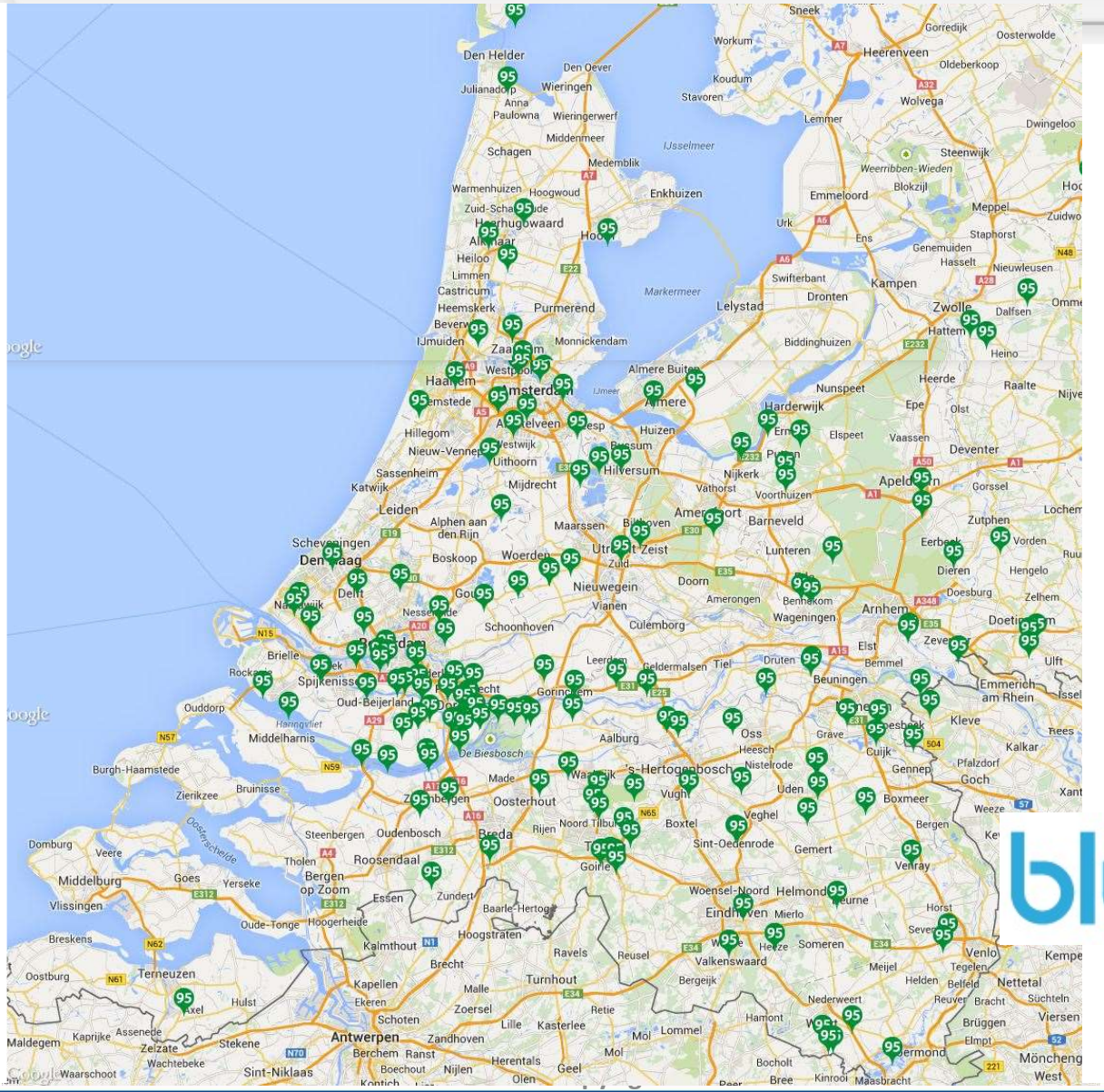
E70 - hE70

E85 - hE85

"The results suggest that there are no marked differences on the regulated and unregulated emissions when hydrous ethanol blends are used instead of anhydrous ethanol blends."

Netherlands in 2008
hE15 opening by Minister Cramer

Currently 181 gas stations selling hydrous E15



6.5 years experience

Approximately:

5000 tankings/day

and

100,000 cars

blueone

General conclusions

- A more hydrous E15, E20, etc. (cheaper premium gasoline to produce) is an interesting business case for the several countries.
- The patented higher water content provides additional octane, additional corrosion protection of aluminum alloys, additional resistance to pick up corrosive salts and additional cooling of the cylinder inlet providing a higher thermodynamic efficiency.
- We are looking for partners to make this happen.